# Additive-Controlled Synthesis of Hume-Rothery Inspired Intermetallic Clusters for Catalytic Application 

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"Do. Or do not. There is no try!"

Yoda

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#### Abstract

This project focused on the investigation of Hume-Rothery inspired cluster synthesis controlled by the addition of additives. Since alkynes bind well to TM(0) compounds and are themselves a model substrate for catalytic applications, e.g. semi-hydrogenation of acetylene, they were used as the appropriate additive to control cluster size and distribution of intermetallic TM/E compounds ( $\mathrm{TM}=\mathrm{Ni}$, $\mathrm{Pd}, \mathrm{Pt} ; \mathrm{E}=\mathrm{Al}, \mathrm{Ga})$. The reaction progress was systematically studied by varying the temperature, additive concentration, additive itself and metal ratios, and monitored using in-situ NMR spectroscopy and LIFDI mass spectrometry. In the second part, selected compounds were evaluated for their applicability in semi-hydrogenation reactions.

The studies showed a strong dependency of the additive concentration on TM-E cluster formation. In the case of $\mathrm{Ni} / \mathrm{Ga}$, $\mathrm{Ni} / \mathrm{Al}$ as well as $\mathrm{Pt} / \mathrm{Ga}$ and $\mathrm{Pt} / \mathrm{Al}$, cluster growth was controlled by varying the additive concentration. While a high additive concentration caused small TM-E clusters with a high additive amount attached to the metal core, low concentrations resulted either in the formation of large clusters as in case of Ni/Ga or Ni/Al or in no reaction as in case of Pt/Ga. Furthermore, the variation of the respective metal content is directly affected the metal ratio in the cluster especially when $\mathrm{AlCp}^{*}$ was used. Therefore, the higher the concentration of AICp* in comparison to Ni, the lower was the TM:AI ratio in the resulting compound. However, this mostly resulted in the formation of homoleptic $\left[\mathrm{TM}\left(\mathrm{AICp}^{*}\right)_{4}\right](\mathrm{TM}=\mathrm{Ni}, \mathrm{Pt})$ which is expected to be kinetically inert. In case of $\mathrm{GaCp}^{*}$, such a dependency was not detected. Additionally, TM/E systems were also revealed to be very sensitive to different temperatures. In this regard, high temperatures led to cluster growth reactions while low temperatures favored the formation of smaller clusters. Moreover, the addition of an alkyne prevented $\mathrm{Cp}^{*}$ transfer reactions from the ligand metal, e.g. GaCp*, to the transitions metal as previously observed for Ni/Ga systems. Due to the binding of the additive to the open coordination sites of the catalytically active transition metal center, catalytic inertness of the system was avoided which would be observed if TM$\mathrm{Cp}^{*}$ is obtained. Further, this thesis enabled additive controlled intermetallic cluster synthesis obtained via ligand substitution, cluster growth or cluster degradation. This was demonstrated by a combinatorial approach that detects reactive intermediates in cluster libraries and thus overcoming the difficulties associated with the elaborate isolation and crystallization of intermetallic compounds. Size-focused solutions were achieved from cluster mixtures by appropriate addition of precursors which were not done yet for cluster mixtures. Structurally valid suggestions were identified by combining experimental and theoretical methods and verified by comparison with compounds already known in the literature.

In the last part of this thesis, suitable Ni/Al and Ni/Ga compounds were investigated for their catalytic applicability. While Ni/Ga clusters mostly decompose after complete hydrogenation of the alkynes and alkenes, Ni/Al compounds were found to be potential candidates for semi-hydrogenation processes as they have been shown to be intact after the catalytic cycle.


## Zusammenfassung

Dieses Projekt befasste sich mit der Untersuchung von Hume-Rothery inspirierten Clustersynthesen, die durch die Zugabe von Additiven gesteuert werden kann. Da Alkine gut an TM(0)-Verbindungen binden und selbst ein Modellsubstrat für katalytische Anwendungen, z. B. die Halbhydrierung von Acetylen, darstellen, wurde es als entsprechendes Additiv verwendet, um sowohl die Clustergröße als auch die -verteilung von intermetallischen $\mathrm{TM} / \mathrm{E}$-Verbindungen ( $\mathrm{TM}=\mathrm{Ni}, \mathrm{Pd}, \mathrm{Pt} ; \mathrm{E}=\mathrm{Al}, \mathrm{Ga}$ ) zu steuern. Der Reaktionsverlauf wurde systematisch durch Variation der Temperatur, der Additivkonzentration, des Additivs selbst und des Metallverhältnisses untersucht und mit Hilfe von in-situ NMR-Spektroskopie und LIFDI-Massenspektrometrie überwacht. Im zweiten Teil wurden ausgewählte Verbindungen auf ihre Eignung für Semi-Hydrierungsreaktionen getestet.

Die Untersuchungen zeigten eine starke Abhängigkeit der TM-E-Clusterbildung von der Additivkonzentration. Im Falle von Ni/Ga, Ni/Al sowie Pt/Ga und Pt/Al konnte das Clusterwachstum durch Variation der Additivkonzentration gesteuert werden. Während hohe Additivkonzentrationen zu kleinen TM-E-Clustern mit hoher Additivmenge am Metallkern führten, resultierten niedrige Konzentrationen entweder in der Bildung großer Cluster wie im Falle von Ni/Ga oder Ni/Al oder in keiner Reaktion wie im Falle von Pt/Ga. Darüber hinaus beeinflusste die Variation des jeweiligen Metallgehalts direkt das Metallverhältnis im Cluster, insbesondere wenn AICp* verwendet wurde. Je höher die Konzentration von AICp* im Vergleich zu Nickel, desto geringer war das TM:Al-Verhältnis in der resultierenden Verbindung. Dies führte jedoch meist zur Bildung von homoleptischem [TM( $\left.\mathrm{AlCp}^{*}\right)_{4}$ ] ( $\mathrm{TM}=\mathrm{Ni}, \mathrm{Pt}$ ), das kinetisch inert sein sollte. Im Falle von $\mathrm{GaCp}^{*}$ wurde eine solche Abhängigkeit vom Metallverhältnis nicht festgestellt. Die TM/E-Systeme erwiesen sich zudem als sehr empfindlich gegenüber unterschiedlichen Temperaturen. Hohe Temperaturen führten dabei zu einer Clusterwachstumsreaktion, während niedrige Temperaturen die Bildung kleinerer Cluster begünstigt. Darüber hinaus verhinderte die Zugabe eines Alkins die $\mathrm{Cp}^{*}$-Transferreaktion vom Ligandmetall, z.B. $\mathrm{GaCp}^{*}$, zum Übergangsmetall, wie sie für das Ni/Ga-System beobachtet wurde. Aufgrund der Bindung des Additivs an die offenen Koordinationsstellen des katalytisch aktiven Übergangsmetallzentrums, wird eine katalytische Inertheit des Systems, welche durch die $\mathrm{Cp}^{*}$-TM Bindung ausgelöst werden würde, verhindert. Diese Arbeit ermöglichte eine Additiv-gesteuerte intermetallische Clustersynthese, die durch Ligandensubstitution, Clusterwachstum oder Clusterabbau erreicht wird. Dies wurde durch einen kombinatorischen Ansatz demonstriert, der reaktive Zwischenstufen in Clusterbibliotheken detektiert und damit die Schwierigkeiten überwindet, die mit der aufwändigen Isolierung und Kristallisation von intermetallischen Clustern verbunden sind. Durch geeignete Zugabe von Präkursoren konnten größenfokussierte Lösungen aus Clustermischungen gewonnen werden. Darüber hinaus wurden strukturell gültige Vorschläge durch die Kombination experimenteller und theoretischer Methoden und durch den Vergleich mit bereits in der Literatur bekannten Verbindungen identifiziert.

Im letzten Teil dieser Arbeit wurden geeignete Ni/Al- und Ni/Ga-Verbindungen auf ihre katalytische Anwendbarkeit hin untersucht. Während sich Ni/Ga-Cluster nach der vollständigen Hydrierung der Alkine und Alkene meist zersetzen, erwiesen sich Ni/Al-Verbindungen als potenzielle Kandidaten für Halbhydrierungsprozesse, da sie nach dem katalytischen Zyklus erwiesenermaßen intakt sind.

## List of Abbreviations

| Cdt | Cyclododecatriene |
| :---: | :---: |
| Coa | Cyclooctane |
| Cod | 1,5-Cyclooctadiene |
| Coe | Cyclooctene |
| Cp* | 1,2,3,4,5-Pentamethylcyclopentadienyl |
| DFT | Density Functional Theory |
| Dpa | diphenylacetylene |
| Dраз | hexaphenylbenzene |
| dvds | 1,1,3,3-Tetramethyl-1,3-divinyldisiloxane |
| EXAFS | Extended X-ray absorption fine structure |
| Hex | 3-hexyne |
| HMBC | Heteronuclear Multiple Bond Correlation |
| HSQC | Heteronuclear Single Quantum Coherence |
| HT | High temperature |
| IR | Infrared spectroscopy |
| LIFDI | Liquid injection field desorption ionization |
| LT | Low temperature |
| MS | Mass spectrometry |
| NEXAFS | Near-edge X -ray absorption fine structure |
| $\mathrm{Ni}_{2}$ (dvds) ${ }_{3}$ | $\left[\left(\mathrm{Ni}\left(\mathrm{n}-\mathrm{CH}_{2}=\mathrm{CHSiMe} 2\right)_{2} \mathrm{O}\right)_{2}\left(\mu-\left(\mathrm{n}-\mathrm{CH}_{2}=\mathrm{CHSiMe}_{2}\right)_{2}\right)\right]$ |
| NMR | Nuclear magnetic resonance |
| NPs | Nanoparticles |
| SC-XRD | Single crystal X-ray diffraction |
| STM | surface tunneling microscopy |
| TDDFT | Time dependent DFT |
| Tebd | tetraethylbutadiene |
| TM | Transition metal |
| Tmeda | Tetramethyl ethylenediamine |
| Tol-d8 | Deuterated toluene |
| Tpbd | tetraphenylbutadiene |
| UHC | Unsaturated hydrocarbons |
| UHV | Ultra-high vacuum |
| UV-Vis | Ultraviolett-visible |
| Ve | Valence electrons |
| VT | Variable temperature |
| XANES | X-ray absorption near-edge structure |
| XPS | X-Ray photoelectron spectroscopy |

## Table of Content

Acknowledgment ..... i
Abstract ..... iii
Zusammenfassung ..... iv
List of Abbreviations ..... V
Table of Content ..... vi

1. Introduction. ..... 1
2. Theoretical Background ..... 4
2.1. Bimetallic Nanoparticles: Control of Size and Metal Distribution ..... 4
2.2. (Inter)metallic Compounds: How to Control Cluster Size, Metal Composition and Metal Distribution ..... 7
2.3. Reactive Sites and Bond Activation applying Intermetalloid Compounds ..... 12
2.4. Ligand Protected Hume-Rothery Inspired Intermetallic Compounds as Molecular Models for Catalytic Application ..... 16
3. Motivation And Research Goal ..... 21
4. Results and Discussion ..... 24
4.1. Synthesis and Reactivity of Ni-E containing clusters ..... 24
4.1.1. Reactivity studies on $\mathrm{Ni} / \mathrm{Ga}$ as a versatile system influenced by temperature, additive concentration and metal-ratio ..... 24
4.1.2. NiAl cluster synthesis: Selection of precursor as an important building block ..... 49
4.1.3. Comparison and Conclusion of $\mathrm{Ni} / \mathrm{E}$ cluster synthesis ..... 65
4.2. Synthesis and Reactivity studies of $\mathrm{Pd} / \mathrm{E}$ containing compounds ..... 66
4.2.1. $\quad\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ as temperature sensitive precursor for $\mathrm{Pd} / \mathrm{E}$ compounds ..... 66
4.2.2. Definite cluster structures as building blocks for further cluster growth or cluster reactivity: Alkyne addition to $\left[\mathrm{PdAl}_{4}\right]$ or $\left[\mathrm{PdGa}_{4}\right]$ ..... 70
4.2.3. Conclusion Pd-Chemistry ..... 74
4.3. Synthetic access to Pt-E complexes ..... 75
4.3.1. Pt-Ga clusters obtained from $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right]$ ..... 75
4.3.2. Influence of diphenylacetylene as additive on Pt-Al cluster formation ..... 80
4.3.3. Conclusion: $\mathrm{Pt} / \mathrm{E}$ cluster synthesis ..... 83
4.4. Synthesis of TM/Zn compounds ..... 84
4.4.1. Synthesis of $\mathrm{Ni} / \mathrm{Zn}$ and $\mathrm{Ni} / \mathrm{Ga} / \mathrm{Zn}$ compounds ..... 84
4.4.2. $\mathrm{TM}-\mathrm{Zn}$ complexes from $\left[\mathrm{TM}(\operatorname{cod})_{2}\right]$ with $\mathrm{Zn}_{2} \mathrm{Cp}^{*} 2(\mathrm{TM}=\mathrm{Ni}, \mathrm{Pt})$ ..... 91
4.4.3. Conclusion: TM-Zn cluster synthesis ..... 94
4.5. Semi-hydrogenation experiments with $\mathrm{Ni} / \mathrm{Ga}$ and $\mathrm{Ni} / \mathrm{Al}$ clusters ..... 95
4.5.1. Reaction of Ni/Ga compounds with hydrogen ..... 95
4.5.2. Reaction of $\mathrm{Ni} / \mathrm{Al}$ compounds with hydrogen ..... 97
5. Conclusion ..... 100
6. Experimental ..... 102
6.1. General Materials and Methods ..... 102
6.2. Experimental part: Synthesis of new compounds ..... 105
6.3. Reactivity part: Overview of the studies on parameter contro ..... 108
6.3.1. Additional experimental data for $\mathrm{Ni} / \mathrm{Ga}$ system ..... 108
6.3.2. Additional experimental data for $\mathrm{Ni} / \mathrm{Al}$ system ..... 121
6.3.3. Additional data for Pd-Ga compounds ..... 133
6.3.4. Additional data for Pt-E compounds ..... 136
6.3.5. Additional data for TM-Zn compounds ..... 139
6.3.6. Experimental for semi-hydrogenation experiments ..... 143
7. References ..... 144
8. Appendix ..... 149
8.1. Supplementary information of the experimental part ..... 149
8.2. Supplementary information of the computational part ..... 167
8.3. Table of Figures ..... 184
8.4. List of Tables ..... 191
8.5. List of Schemes ..... 194
8.6. List of Publications ..... 196
8.7. Reprint Permissions ..... 197
9. Eidesstattliche Erklärung ..... 241

## 1. Introduction

The global production of plastics is continuously increasing from 502 billion USD (2016) to 593 billion USD (2021) and is expected to further grow by 3.7 \% until 2030. ${ }^{1}$ One of the most important materials in the global production of plastics are polyethylene (PE), polypropylene (PP) and polyurethane (PU) while the European demand reports PE, PP and polyvinylchloride (PVC) as the most produced materials in plastics (Figure 1). ${ }^{2}$ Their applications range from packaging, building and construction sector, electronics and electrics to automotive industry or consumer goods (Figure 1). With over 25.0 \%, polyethylene accounts for the largest share and is mostly applied in the packaging sector. ${ }^{2}$


Figure 1: Distribution of the European fossil-based plastics demand in 2018/2019 (left) and European fossil-based plastics demand by application in 2018 / 2019 (right). ${ }^{2}$

Such polyethylene is manufactured by polymerization of ethylene. The applied conditions in this process which leads to PE play an important role and influence different binding motifs and related properties. Using high pressure (1000-3000 bar) at max. $300^{\circ} \mathrm{C}$ for PE synthesis results in low-density polyethylene (LDPE) which features a highly branched polymer. ${ }^{3}$ It is synthesized via a radical polymerization with bond scission of oxygen being the initial step. ${ }^{4}$ In contrast, high-density polyethylene (HDPE) is produced at lower pressure (10-80 bar) and lower temperatures $\left(70-300{ }^{\circ} \mathrm{C}\right)$ resulting in a linear polymer. The gas phase or liquid phase synthesis of HDPE requires a catalyst such as Titanium-based Ziegler-Natta or Chromium-based Philips catalyst allowing for more benign conditions. ${ }^{3-5}$ Addition of a co-monomer, e.g. $n$-butene, $n$-hexene or $n$-octene, during the process lead to the synthesis of linear low-density polyethylene (LLDPE).
The starting material for the polymerization is ethylene which can be obtained by e.g. steam cracking of petroleum feedstock. ${ }^{6}$ The separation of light-chain hydrocarbons (ethylene, propylene, butadiene) observed in the feedstock relies on highly-energy consuming cryogenic distillation. ${ }^{7}$ Although the ethylene extracted is rather pure, it still contains approximately $1 \%$ acetylene, which must be removed prior to polymerization to prevent catalyst poisoning. ${ }^{8}$ Therefore, a catalytic process is required that selectively converts acetylene to ethylene in the presence of excess ethylene without conversion of the olefin. In industrial scale, this so-called semi-hydrogenation is performed by a heterogeneous catalyst, e.g. PdAg supported on alumina. ${ }^{9}$ Considering a $\operatorname{Pd}(111)$ surface, the first step is the adsorption of gaseous acetylene on the catalysts surface, followed by the hydrogenation of the alkyne revealing ethylene on the metal's surface as proposed by Studt et al. (Figure 2, left). ${ }^{10}$ The formed ethylene may then either react to ethane via further hydrogenation or desorb from the surface. To avoid
over-hydrogenation to ethane, the energetic barrier for the next hydrogenation step needs to be higher than the desorption of the olefin yielding the desired ethylene. By introduction of a second metal, prominently silver, the selectivity towards ethylene is increased as an effect of electronical and geometrical parameters. The adsorbent, here acetylene, still binds to the catalytically active metal (Pd) whose electronic properties are influenced by the second metal and therefore, on the binding to the adsorbent. It has to be pointed out, that the adsorbent does not directly interact with the second metal, Ag. ${ }^{10}$ In contrast to Studt's suggestion, however, Spanjers et al. proposed an increased conversion of acetylene to ethylene due to the suppression of oligomerization reactions when using a second metal. ${ }^{11}$ Further, the higher the content of the second metal, the higher is the selectivity to ethylene due to hampered competing oligomerization reaction. ${ }^{12}$


Figure 2: Left: Energy diagram of the hydrogenation process of acetylene on a Pd (black) or PdAg (red) surface calculated from Studt et al.. Right: Diagram of the conversion of acetylene dependent on the metal ratios with respect to the observed ethane concentration from F. Studt, F. Abild-Pedersen, T. Bligaard, R. Z. Sørensen, C. H. Christensen, J. K. Nørskov, Science 2008, 320, 1320-1322 ${ }^{10}$, reprinted with permission from AAAS. Copyright in 2008.

As alternatives for the established $\mathrm{Pd} / \mathrm{Ag}$ or Pd systems, recent investigations point to Hume-Rothery intermetallic phases as cost-efficient catalysts. With this regard, $\mathrm{PdGa}^{13-14}, \mathrm{FeAl}^{15}, \mathrm{NiZn}^{11,16}$ and $\mathrm{NiGa}^{17}$ were investigated in terms of selectivity and metal ratios as potential semi-hydrogenation catalysts. Figure 2 (right) illustrates the dependency of selectivity for the conversion of acetylene on the metal ratio. ${ }^{10}$ As an example, when using solely Ni as semi-hydrogenation catalyst, the selectivity for ethylene is rather low since the ethane concentration is increasing already with an acetylene conversion of about $40 \%$. The addition of a second metal significantly increases the selectivity towards ethylene which can be determined by a lower ethane concentration, even over 90\% acetylene conversion. Comparable trends in selectivity applying bimetallic catalyst systems have been also observed for $\mathrm{Pd} / \mathrm{Ag}$ (Figure 2, right). DFT calculations performed with various metal combinations and ratios revealed $\mathrm{NiZn}_{3}$ as the best compromise regarding metal costs, selectivity and turnover number ${ }^{10}$ while experimental data showed $\mathrm{Ni}_{5} \mathrm{Zn}_{21}$, instead, as selective catalyst in case of a NiZn intermetallic system ${ }^{11}$. In summary, both experimental as well as theoretical data indicate Hume-Rothery intermetallic systems, especially NiZn with high Zn content, are particularly suitable as a selective catalyst for semi-hydrogenation.
In particular, the experimentally and theoretically well-studied intermetallic $\mathrm{Pd} / \mathrm{Ga}$ system resembles a model system which allows for investigations as potential catalyst for the semi-hydrogenation of
acetylene. Different synthetic procedures are applied to obtain such intermetallic systems having an impact on the selectivity due to metal distribution. While doping of bulk materials (Pd), which gains intermetallic catalyst's surfaces, increases activity but lowers selectivity to ethylene due to surface defects, nanostructured intermetallic compounds (Ga-Pd) have both advantages exhibiting high activity as well as high selectivity. ${ }^{18}$

Investigations of a catalytically active PdGa surface ( $\mathrm{Pd}_{2} \mathrm{Ga}$ or PdGa ) indicates a Pd-center which is coordinated by gallium acting as a geometric spacer. This phenomenon is known as active-site isolation concept where the active metal is surrounded by a second metal. ${ }^{19}$ Theoretical calculations supports this assumption of isolated Pd atoms as reactive center with a Ga rich environment. ${ }^{20}$ In contrast to previous findings, the acetylene, thus, is strongly attached on the top of one Pd atom or between two Ga atoms whereas the vinyl (half-hydrogenated acetylene) indicates bridging position between the Pd and Ga. However, the semi-hydrogenated ethylene then fully binds to the palladium center. ${ }^{13}$ Further, Ga causes the reduction of the adsorption energy of the alkene resulting in a weak Pd-ethylene bond and thus, releasing of the desired ethylene is favored instead of further hydrogenation. ${ }^{21}$
In summary, the introduction of a second metal such as $\mathrm{Ga}, \mathrm{Al}, \mathrm{Zn}$ or Ag in a catalytic reaction does not only influence the system due to geometrical effects, e.g. as spacer, but acting actively while bonding molecules during the hydrogenation process and having impact on the bonding energy between the desired molecule and the transition metal. This results in a higher selectivity in the semi-hydrogenation when applying intermetallic catalysts instead of monometallic compounds. In order to investigate such reactions and the role of intermetallic catalysts, in particular the influence on the binding of the substrate, the effect of the second metal and the associated reaction mechanism, elaborate methods as surface tunneling microscopy (STM) or X-Ray photoelectron spectroscopy (XPS) under ultra-high vacuum (UHV) are required. ${ }^{22}$ Applying nanoparticles or nanoclusters, such system can be investigated due to decreased complexity. However, the control of particle size and distribution of such nanoparticles or nanocatalysts resembling the heterogeneous surface is rather complex and will be specified in the following. ${ }^{23}$

## 2. Theoretical Background

### 2.1. Bimetallic Nanoparticles: Control of Size and Metal Distribution

Monometallic or bimetallic nanoparticles (NPs), consisting of one or two metals, are obtained either by top-down or bottom-up synthesis. The top-down method is applied to convert bulk materials to metallic nanoparticles. Several top-down approaches have been developed in the recent years to synthesize mono- or bimetallic nanoparticles which enhance catalytic properties caused by a higher surface area. However, milling and etching, usually applied for top-down approaches, revealed structural defects on the surface which decreased the selectivity of the material. ${ }^{24-25}$ On the other hand, the bottom-up procedure implies the synthesis of nanoparticles via colloidal synthesis, sol-gel processing, chemical reduction and precipitation, and atomic layer deposition. Using this synthetic pathway, the defects on the catalyst's surface are better controllable as well as the particle size and distribution. ${ }^{23,26}$

In particular, monometallic NPs are mostly synthesized by chemical reduction which produces metals in the zero-valent state due to the addition of a reducing agent and are stabilized by a stabilizing agent. ${ }^{27}$ Additionally, the synthesis of bimetallic NPs are usually prepared in a wet-chemical approach involving the simultaneous reduction of two metals. ${ }^{27}$ This procedure offers the control of metal distribution and nanoparticle size dependent on the applied synthesis method and the respective conditions. ${ }^{23,} 28$ Depending on the starting material and on the synthesis conditions, different metal arrangements in the nanoparticles or nanocrystals can be obtained (see Figure 3) which are attributed to different cross section types: core-shell (A), cluster-in-cluster (B), layered (C) and randomly distributed (D) metal alloys, and multi-shell alloys (E). ${ }^{27-30}$


Figure 3: Cross sections of nanoparticle showing different types of metal distribution: core-shell (A), cluster-in-cluster (B), intermetallic alloy with ordered metal atoms (C), intermetallic alloy with randomly distributed metal atoms (D), multi-shell alloy (E).

While bimetallic NPs are usually obtained by simultaneous reduction of both metals, the nanoparticles featuring a core-shell structure (A) are prepared by successive reduction of a second metal which is deposited on an already existing monometallic nanoparticle of another metal. ${ }^{31}$ At the core-shell type, the catalytically active metal is exposed on the surface of the core making this type economically more efficient and enhances catalytically properties due to stronger interaction of the substrate with the catalytically active metal compared to monometallic NPs. ${ }^{23}$ The cluster-in-cluster typed nanomaterial (B) reveals only a few $\mathrm{M}_{\mathrm{a}}-\mathrm{M}_{\mathrm{b}}$ bonds of the different metals which are located on the interface between the two clusters. This subcluster segregated nanoalloy is in principle possible, but specific examples are rather scarce. ${ }^{28}$ The intermetallic alloy with ordered (C) or randomly distributed metal atoms (D), instead, exhibit many metal-metal bonds due to increased amount of layer interfaces. The fifth possible metal
arrangement of nanoparticles is the multi-shell mixing pattern (E). This type which is also known as onion-type structure shows a core consisting of a metal $A$ and/or metal $B$, an intermediate shell of metal A and an outer shell of metal B. ${ }^{28,30}$

Accordingly, the degree of mixing or ordering in the respective alloys are highly depending on relative bond strength of metal $A$ and $B$, the surface energy of the bulk elements (metal with lowest surface energy prefers surface position), the relative atomic sizes, the charge transfer (high deviation of electronegativity favors metal mixing), the bond strength to surface ligands as well as specific electronic or magnetic properties of the respective metal. ${ }^{28}$

Although the conditions and metal's properties can modify the distribution of both metals in the alloy, the applied method should also be adjusted to fulfil the following requirements, if used for catalytic application: the reactive sites on the alloy's surface have to be accessible to reactants (i), the stabilizer should not affect the reactive sites by poisoning (ii) and the bimetallic material have to be stable under the respective catalytic conditions (iii). ${ }^{30}$

## Size Control of NPs



Figure 4: Different steps of nanoparticle synthesis: Reduction, nucleation and growth to obtain nanostructured metal colloids. ${ }^{32-34}$

Depending on the choice of precursor, reducing agent, stabilizer and reaction conditions, the particle size of such nanomaterials can be well controlled. ${ }^{33}$ In principle, the stepwise formation of nanomaterials is divided in three sections: reduction, nucleation, growth and agglomeration as published from Turkevich et al. (see Figure 4). ${ }^{35}$ At first, the metal precursor consisting of $\mathrm{M}^{+}$and X - is chemically reduced forming the zero-valent and highly reactive metal atom. The nucleation is defined as a process in which a new particle of a new phase is formed. This could occur due to collision of two or more metal ions, metal atoms or small already formed clusters. ${ }^{33}$ This process step is a complex interplay of redox potentials (metal salt compared to reducing agent) and reaction conditions as well as rate of addition, temperature and stirring rate. ${ }^{34}$ The following growth process describes the deposition of an additional material on the particle surface enabling size control. ${ }^{35}$ The separation of the nucleation and growth is of upmost importance as it results in a broad particle size distribution if both steps are overlapping. ${ }^{34}$ Therefore, short nucleation times are highly desirable to achieve monodispersed particle formation as induced by fast addition of the reducing agent. ${ }^{34}$ Furthermore, the growth process is dependent on the respective surface energy of the metal which must not be higher than the entropy loss, otherwise uncontrolled growth of the particle will occur leading to a broadening of particle size distribution. The obtained nanostructured colloidal metals are then protected by stabilizing agents which prevents the particles from agglomeration. ${ }^{33}$

## Additives as Stabilizing Agents

The use of additives or surfactants as stabilizers in nanoparticle synthesis can drastically influence the catalytic properties of the nanoparticle while preventing the nanoparticles from agglomeration. ${ }^{36-37}$ Already traces of additives could enhance the catalytic activation and the respective selectivity due to electronic and steric effects on the nanoparticles. ${ }^{38-40}$ In terms of selectivity, the application of additives hampers over-hydrogenation especially when using alkynes for semi-hydrogenation reactions as the hydrogens are more separated on the metal's surface and thus, are less accessible for overhydrogenation. ${ }^{23}$ Based on its nature, the additive can stabilize the metallic compound by influencing either sterically or electrostatically. ${ }^{23,41-42}$ While polymers, dendrimers or ligands are described as steric stabilizers, surfactants in micelles or ionic liquids resemble electrostatic additives. ${ }^{23}$ Both prevent the nanoparticles from agglomeration and precipitation in solution. Similar to tetra(octyl)ammonium chloride for Pd-NPs ${ }^{43}$, electrostatic stabilizers feature a characteristic double layered structure around the metal particle which consists of an anionic and cationic layer. Dependent on the repulsive forces, these stabilizer class could also hamper catalytic activity due to strong shielding of the NPs. Polymeric stabilization (e.g.), which is identified as steric stabilizer, is based on their weak bonding on the surface of the nanoparticle instead of less strong binding to the metal surface. ${ }^{29}$ One of the most reported polymeric stabilizers are poly( $N$-vinyl-2-pyrrolidone) (PVP) and poly(vinylalcohol) (PVA).40, 44-46 Furthermore, ligands as an example for steric protection are intrinsically stabilizers itself and traditionally combined with organometallic compounds or precursors. Typical ligand stabilizers are amines, sulfides, phosphines, $N$-heterocyclic carbenes (NHCs) as well as ionic ligands. ${ }^{29}$ The presence of the ligand on the NP's surface protects the formed nanomaterial while maintaining reactive sites due to sub-stoichiometric amount of the ligands compared to metal. ${ }^{47}$ Nevertheless, there are examples where the stabilizer can poison the catalyst's surface, especially observed with sulfides. Due to the strong bond between the RS group and the electrophilic nanocluster surface, the catalytically vacant sites on the metal are decreased. ${ }^{42,48} \operatorname{In}$ 1981, G. Schmid introduced the first phosphine-stabilized Au55-nanocluster, Au55 $\left[\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3}\right]_{12} \mathrm{Cl}_{6}$, that are well defined in structure and shape. ${ }^{49}$ From that on, many examples using phosphines as well as amines as steric stabilizers for e.g. Pd, Ni and Co NPs have been reported. ${ }^{50-53}$ However, these stabilizing agents do not appear to be the most appropriate ones since the colloids often agglomerate due to lower binding to the metal NPs leading to the formation of superstructures. A well-studied ligand class for stabilizing NPs are $N$-heterocyclic carbenes (NHCs). ${ }^{23,54-61}$ Mostly used in organometallic chemistry, they already demonstrated their wide range of applications. Additionally, based on their functionalization possibilities, they have more recently been applied in materials synthesis. ${ }^{55}$ NHCs have not only been used in Au-NPs, but also in the stabilization of more reactive metals as Pd , Ru and Ir. ${ }^{56-57,59-62}$ Due to the various applications depending on the ligand residues attached to the nitrogen atoms, the steric shielding of NHC ligands can be precisely adjusted leading to the desired effect.

Although, investigation of nanoparticles is a good opportunity to comprehend reaction mechanisms and bonding affinity, it requires elaborate analytical methods as high-energy X-ray spectroscopy (XAS, EXAFS, NEXAFS, XANES, XPS), energy-disperse X-ray microanalysis (EDX), magnetic measurements, ion spectroscopy/scattering, partly under ultra-high vacuum, only to name a few. ${ }^{28}$

## 2.2. (Inter)metallic Compounds: How to Control Cluster Size, Metal Composition and Metal Distribution

## Cluster Size Control as a Function of Ligand Amount

Therefore, complexity of such materials is decreased when using nanoclusters or molecularly defined cluster instead of NPs. ${ }^{63}$ The line between molecular clusters and nanoclusters is rather blurred. Nanoclusters usually exhibit a large number of metals, which could be also applied for bigger molecular clusters. However, control of size and distribution of nanoclusters are rather difficult implementing high temperatures, e.g. thermal annealing, due to high kinetic barriers as a result of low atomic mobility. ${ }^{63}$ The following will focus on potential parameters or conditions to control molecularly defined cluster sizes and metal distribution. Gold clusters represent a well-studied class in terms of cluster size (ranging from Au $u_{2}$ until Aus5 and higher), cluster shape and ligand protection, which is mostly surrounded by thiolates, phosphines or NHC ligands. ${ }^{64-67}$ Furthermore, NHCs and phosphines have already been intensively investigated for cluster control of Fe-S clusters (Figure 5). ${ }^{68}$


Figure 5: Synthesis of NHC and phosphine stabilized Iron-Sulfur clusters. ${ }^{68}$ Adapted reprinted with permissions from L. Deng, R. H. Holm, J. Am. Chem. Soc. 2008, 130, 9878-9886. Copyright 2008, American Chemical Society.

There, the cluster size and shape are highly dependent on the order of the addition of sulfur-component and the NHC ligand which could be added either simultaneous or sequential. The clusters are synthesized starting from a soluble $\mathrm{Fe}^{\prime \prime}$-source and $\left(\mathrm{Me}_{3} \mathrm{Si}\right)_{2} \mathrm{~S}$ as the sulfur source. The reactions which only contains the sulfur-component in the beginning of the reaction resulted in the formation of phosphine-containing tetracubic $\left[\mathrm{Fe}_{16} \mathrm{~S}_{16}\right]\left(\mathrm{PiPr}_{3}\right)_{8}$ or arm-chair shaped $\left[\mathrm{Fe}_{7} \mathrm{~S}_{6}\right]\left(\mathrm{PEt}_{3}\right) \mathrm{Cl}_{2}$ dependent on
the used phosphine. Further addition of NHC ligand, $\left({ }^{( } \operatorname{Pr}\right)_{2}(\mathrm{NHC})(\mathrm{Me})_{2}$, led to a substitution reaction and revealed the formation of dicubic $\left[\mathrm{Fe}_{8} \mathrm{~S}_{8}\right](\mathrm{NHC})_{6}$ which could also be obtained directly from $\left[\mathrm{Fe}\left(\mathrm{PiPr}_{3}\right)_{2} \mathrm{Cl}_{2}\right]$ due to simultaneous addition of the sulfur and NHC component. Further, increase of the NHC concentration led to cluster degradation resulting in monocubic $\left[\mathrm{Fe}_{4} \mathrm{~S}_{4}\right](\mathrm{NHC})_{4}$.
Similar cluster degradation of metal clusters was also described for Co-S and Mn-Te clusters. Analog to $\mathrm{Fe}-\mathrm{S}$, the $\mathrm{Co}-\mathrm{S}$ cubic clusters were prepared from $\mathrm{Co}{ }^{11}$ with a phosphine and a sulfur source. ${ }^{69}$ Addition of respective amount of NHC resulted in the desired mono- or dicubic Co-S clusters. Cubane typed $\left[\mathrm{Mn}_{4} \mathrm{Te}_{4}\right](\mathrm{NHC})_{4}$ synthesis was described as a ligand exchange reaction from the phosphine-analog. ${ }^{70}$ Decreasing the NHC amount, related to Mn, the cluster size is increasing to dicubic [Mn $\left.{ }_{8} \mathrm{Te}_{8}\right](\mathrm{NHC})_{6}$ as described for $\mathrm{Fe}-\mathrm{S}$ cubanes where the Fe-S cubes were decreasing with higher amounts of NHC ligand.

## Synthesis of $\mathrm{Pt} / \mathrm{E}$ or Pd/E clusters: Control of clusters size and metal composition dependent on conditions

In contrast to TM-S or TM-NHC clusters, the size of Hume-Rothery inspired intermetallic clusters, which are often stabilized by ECp* ligands, strongly depends on the precursor, ligand-constitution, concentration and conditions, especially temperature and solvent. While the reaction of $\left[\mathrm{Pt}\left(\mathrm{C}_{2} \mathrm{H}_{4}\right)_{3}\right]$ with $\mathrm{GaCp}{ }^{*}$ yielded dinuclear $\left[\mathrm{Pt}_{2}\left(\mathrm{GaCp}^{*}\right) 5\right],{ }^{71}$ the mononuclear compound, $\left[\mathrm{Pt}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ was obtained from $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ as precursor. ${ }^{72}$ Further addition of Pt -precursor to $\left[\mathrm{Pt}(\mathrm{GaCp})_{4}\right]$ also revealed the quantitative formation of dinuclear $\left[\mathrm{Pt}_{2}\left(\mathrm{GaCp}^{*}\right)_{5}\right]$ which increased the Pt-content in the cluster in comparison to $\mathrm{Ga} .{ }^{72}$ Both syntheses are based on ligand substitution reactions and dissociation/association mechanisms.



Figure 6: Schematic representation of the synthesis of different Pd-Ga compounds as published by Fischer et al. in 2002 and 2005. ${ }^{72-73}$

Similar behavior was observed for Palladium-ECp* clusters. In contrast to Pt-Ga, these intermetallic compounds are highly sensitive to temperature as well as precursor choice (Figure 6). Reaction of $\left[\mathrm{Pd}(\right.$ tmeda $\left.)(\mathrm{Me})_{2}\right]$ (tmeda $=$ tetramethyl-ethylenediamine) was reacted with $\mathrm{GaCp}{ }^{*}$ (5 eq.) at $-80^{\circ} \mathrm{C}$ yielding the mononuclear $\left[\mathrm{Pd}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ (Figure 6). ${ }^{72}$ In contrast to the Pt-syntheses, the formation of
$\left[\mathrm{Pd}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ involves redox processes (reduction of $\mathrm{Pd}^{\prime \prime}$, oxidation of $\mathrm{Ga}^{\prime}$ ) as well as ligand substitution reactions. Contrary to the mononuclear Pd-compound, the synthesis of higher nuclear clusters as $\left[\mathrm{Pd}_{2}\left(\mathrm{GaCp}^{*}\right)_{5}\right]$ and $\left[\mathrm{Pd}_{3}\left(\mathrm{GaCp}^{*}\right)_{8}\right]$ were obtained solely based on ligand substitution from $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ (dvds = divinyl tetramethyl disiloxane) dependent on the temperature and solvent (Figure 6). Performing the reaction in toluene at room temperature, the reaction revealed linear shaped $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{8}\right]\left(\mathrm{Cp}^{*}\right)_{8}$ as the favored product, while the synthesis of $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ requires lower temperatures $\left(-30^{\circ} \mathrm{C}\right)$ and $n$-hexane as solvent. ${ }^{73}$ Performing the reaction with $\operatorname{InCp} *$ instead of $\mathrm{GaCp}^{*},\left[\mathrm{Pd}_{3}\left(\operatorname{InCp}{ }^{*}\right)_{8}\right]$ was obtained from $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ which exhibits the same structural motif of three linear arranged Pd -centers as the Gaanalog. Nevertheless, the reaction conducted with $\operatorname{AICp}{ }^{*}$ did not result in $\left[\mathrm{Pd}_{3}\left(\mathrm{AICp}^{*}\right)_{8}\right]$, but in the formation of $\left[\mathrm{Pd}_{3}\left(\mathrm{AICp}^{*}\right)_{6}\right]$. This $\mathrm{Pd}-\mathrm{Al}$ compound features a trigonal $\mathrm{Pd}_{3}$-core structure with three different binding modes of the $\mathrm{AlCp}^{*}$ : $\mathrm{Pd}_{2}$-edge-bridging, $\mathrm{Pd}_{3}$-face-bridging and terminal. While $\left[\mathrm{Pd}_{3} \mathrm{E}_{8}\right]\left(\mathrm{Cp}^{*}\right)_{8}(\mathrm{E}=\mathrm{In}, \mathrm{Ga})$ offers a linear arrangement of all three Pd atoms which are bridged by two ECp*, each, and two terminal bound ECp* to two Pd atoms, they reveal a fluxional process in solution while forming a similar structural motif as observed for $\left[\mathrm{Pd}_{3} \mathrm{Al}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6} .{ }^{73}$

## $\mathrm{Cu} / \mathrm{Zn}$ and $\mathrm{Cu} / \mathrm{Al}$ clusters achieved via redox processes

In contrast to $\mathrm{Pd}-\mathrm{E} / \mathrm{Pt}-\mathrm{E}$, the synthesis of $\mathrm{Cu}-\mathrm{Zn}$ clusters is more complex as it involves redox reactions. Therefore, the reaction of $\left[\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}\right]$ with $\left[\mathrm{CpCu}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)\right]$ do not only yield desired [Cu4Zn4] $\left(\mathrm{Cp}^{*} 4\right)\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{4}$, but also $\mathrm{ZnCp}^{*}{ }_{2}$ and $\mathrm{ZnCp}^{*} \mathrm{Cp}$ as side-products which hints to the oxidation of $\mathrm{Zn}(\mathrm{I})$ to $\mathrm{Zn}(\mathrm{II})$ while reducing $\mathrm{CpCu}(\mathrm{I})$ to $\mathrm{Cu}(0) .{ }^{74}$ The stabilization of the $\mathrm{Cu}_{4}$ tetrahedron by isonitrile ligands is a crucial step during synthesis as the reaction with CuCl as the precursor led to the formation of embryonic brass, $\left[\mathrm{CuZn}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{3}{ }^{75-76}$ The structure of the latter can be seen as the side-on coordination of a $\mathrm{Cp} \mathrm{Zn}_{\mathrm{n}} \mathrm{ZnCp}$ * fragment to a CuCp * core due to oxidative addition to the electron deficient $\mathrm{Cu}(\mathrm{I})$ center forming a $3 \mathrm{c}-2 \mathrm{e}$ bond. ${ }^{77}$ The isoelectronic $\left[\mathrm{Zn}_{3}\left(\mathrm{Cp}^{*}\right)_{3}\right]^{+}$was obtained from reaction of $\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ with $\mathrm{ZnCp}^{*}{ }_{2}$ and $\left[\mathrm{H}\left(\mathrm{Et}_{2} \mathrm{O}\right)_{2}\right]\left[\mathrm{BAr}_{4}\right]$ in THF at $-78{ }^{\circ} \mathrm{C}$. The molecular structure of this compound features the same structural motif of a $\mathrm{M}_{3}$ core stabilized by three $\mathrm{Cp}^{*}$ moieties. ${ }^{75-76}\left[\mathrm{CuZn}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ was also obtained as the major product from $\mathrm{Cu}(\mathrm{OAc})$ with $\mathrm{Zn}_{2} \mathrm{Cp}^{*} 2$ at room temperature. ${ }^{78}$ In addition, $\left[\mathrm{Cu}_{3} \mathrm{Zn}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ was identified as minor side-product due to intensive manual crystal picking after fractionated crystallization. The isoelectronic Zn -analog, $\left[\mathrm{Cu}_{2} \mathrm{Zn} 5\right]\left(\mathrm{Cp}^{*}\right) 5^{+}$was synthesized from reaction of $\left[\mathrm{CuZn}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ with a $\mathrm{ZnZnCp}{ }^{*}$-transfer reagent, $\left[\mathrm{Cp}{ }^{*} \mathrm{ZnZn}\left(\mathrm{Et}_{2} \mathrm{O}\right)_{3}\right]\left[\mathrm{BAr}_{4}\right]$, at room temperature. ${ }^{78}$ Both $M_{7}$ compounds exhibit a bipyramidal structure with a $\mathrm{M}_{3}$ core either consisting of $\mathrm{Cu}_{3}$ or $\mathrm{Cu}_{2} \mathrm{Zn}$ triangular metal core (Figure 7). This nicely demonstrates the proposed properties of $\mathrm{CuZn}_{2}$ as a building block for higher nuclear cluster. Although, a disproportionation reaction of $\mathrm{Zn}(\mathrm{I})$ to $\mathrm{Zn}(0)$ and $\mathrm{Zn}(\mathrm{II})$ was indicated by the detection of $\mathrm{Zn}(\mathrm{OAc})_{2}$ and $\mathrm{ZnCp}^{*}{ }_{2}$ as side-products, the ongoing redox reactions and ligand exchange mechanisms of this reaction were not completely understood, yet.
Depending on the precursor choice and on the respective reaction conditions, higher nuclear $\mathrm{Cu}-\mathrm{Zn}$ cluster with either Zn -rich or Cu-rich metal cores could be also achieved. Thus, zinc-rich $\left[\mathrm{CuZn}_{10}\right]\left(\mathrm{Cp}^{*}\right)_{7}=\left[\mathrm{Cu}\left(\mathrm{ZnZnCp}^{*}\right)_{3}\left(\mathrm{ZnCp}^{*}\right)_{4}\right]$ was synthesized from temperature-sensitive [iDippCuH] (iDipp $=1,3$-bis(2,6-diisopropylphenyl)-1H-imidazol-2-ylidene) and $\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ whereas copper-rich $\left[\mathrm{Cu}_{10} \mathrm{Zn}_{2}\right](\mathrm{Mes})_{6}\left(\mathrm{Cp}^{*}\right)_{2}$ was obtained from reaction of $[\mathrm{Cu}]^{\prime}(\mathrm{Mes})_{5}\left(\mathrm{Mes}=\right.$ mesityl) with $\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ at
elevated temperatures. ${ }^{79}$ The former reaction demonstrates the importance of the precursor choice as $\left[\mathrm{CuZn}{ }_{10}\right]\left(\mathrm{Cp}^{*}\right)_{7}$ cannot be synthesized from $\left[\mathrm{Cu} \mathrm{H}_{6}\right](\mathrm{H})_{6}\left(\mathrm{PPh}_{3}\right)_{6}$ due to $\mathrm{Cp}^{*}$ transfer reaction. ${ }^{79}$ Summarizing, $\mathrm{Cu}-\mathrm{Zn}$ cluster synthesis is highly sensitive to the choice of precursor, temperature and stabilizing agents, e.g. CNtBu or $\left[\mathrm{BAr}^{\mathrm{F}} 4\right]$, as it performs ligand exchange as well as redox reactions.

$\left[\mathrm{CuZn}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{3}$

$\left[\mathrm{Cu}_{2} \mathrm{Zn}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}{ }^{+}$

$\left[\mathrm{Cu}_{3} \mathrm{Zn}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{5}$

Figure 7: Molecular structures of $\left[C u Z n_{2}\right]\left(C p^{*}\right)_{3}$ (left), $\left[C u_{2} Z n_{5}\right]\left(C p^{*}\right)_{5}{ }^{*}$ (middle) and $\left[C u_{3} Z n_{4}\right]\left(C p^{*}\right)_{5}$ (right) as determined by SC- XRD. ${ }^{75-76,78}$ Color code: Cu, orange; Zn, light blue; C, grey. H atoms are omitted for clarity. Cp* rings are depicted in wireframes.

Due to the different binding possibilities of $\mathrm{AlCp}^{*}$, as demonstrated in the case of $\left[\mathrm{Pd}_{3} \mathrm{Al} 6\right]\left(\mathrm{Cp}^{*}\right) 6$, it is versatile applicable as a ligand and thus, offers diverse cluster formation in combination with Cu precursors, often accompanied by redox processes and $\mathrm{Al}(\mathrm{I})$ disproportionation. Reaction of $[\mathrm{Cu}]\left[(\mathrm{H})_{6}\left(\mathrm{PPh}_{3}\right)_{6}\right.$ with $\mathrm{AlCp}^{*}$ at $70^{\circ} \mathrm{C}$ leads to the intermetallic $\left[\mathrm{Cu}_{6} \mathrm{Al}_{6}\right]\left(\mathrm{Cp}^{*}\right) 6(\mathrm{H})_{4}$ cluster. ${ }^{80}$ The molecular structure as determined by SC-XRD features a dicapped Cu tetrahedron resulting in a $\mathrm{Cu}_{6}$ core which is stabilized by an $\left(\mathrm{AlCp}^{*}\right)_{6}$ octahedron. Due to the four hydrides bound on the cluster surface, which could not be localized by XRD, it is reactive towards different unsaturated substrates. Nevertheless, only the reaction of $\left[\mathrm{Cu}_{6} \mathrm{Al}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}(\mathrm{H})_{4}$ with benzonitrile allowed the structural characterization with SC-XRD while other products could not be crystallized. ${ }^{80}$


Figure 8: Schematic representation of different synthetic pathways for Cu-Al clusters including cluster degradation from $\left[C u_{4} A I_{4}\right]\left(C p^{*}\right)_{5}(\mathrm{Mes})$ to embryonic $\left[\mathrm{Cu}_{2} A I_{1}\right]\left(C p^{*}\right)_{3}$, thermal cluster growth from $\left[C u_{4} A I_{4}\right]$ or chemical cluster growth from $\left[\mathrm{Cu}_{2} \mathrm{Al}_{1}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ to obtain $\left[(\mathrm{H}) \mathrm{Cu}_{77} \mathrm{Al}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$. Organic residues are omitted for clarity. Color code: Cu, red; Al, blue. ${ }^{81}$ Reprinted with permission from M. Schütz, C. Gemel, M. Muhr, C. Jandl, S. Kahlal, J.-Y. Saillard, R. A. Fischer, Chem. Sci. 2021, 12, 6588-6599. Copyright 2021, by the Royal Society of Chemistry. Permission conveyed through Copyright Clearance Center, Inc..

In accordance with $\mathrm{Cu}-\mathrm{Zn}$, our group was able to isolate the embryonic CuAl cluster $\left[\mathrm{Cu}_{2} \mathrm{Al}_{1}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ and [Cu4Al4](Cp*) ${ }_{5}(\mathrm{Mes}) .{ }^{81}$ While [Cu4Al4] is obtained from the reaction of [Cu5](Mes) ${ }_{5}$ with $\mathrm{AlCp}^{*}$ after one hour at $75^{\circ} \mathrm{C},\left[\mathrm{Cu}_{2} \mathrm{Al}_{1}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ is observed through chemically induced cluster degradation from [Cu4Al4](Cp*) ${ }_{5}(\mathrm{Mes})$ (Figure 8). In order to enhance cluster degradation and selectively forming [Cu2 $\mathrm{Al}_{1}$ ], 3 -hexyne was added as additive to stabilize $\mathrm{Cu}(\mathrm{I})$ centers during the degradation process which is underpinned by the consumption of four equivalents of 3-hexyne as well as by the detection of $\left[\mathrm{Cu}_{2} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{Mes})(\text { hex })_{2}$ by means of LIFDI MS. It is assumed that the 3 -hexyne moieties are stabilizing the $\mathrm{Cu}(\mathrm{I})$ centers in the cluster through coordination. Besides cluster degradation cluster growth reaction of this system was also obtained within this work which could be either thermally or chemically induced. Chemically induced cluster growth is observed starting from $\left[\mathrm{Cu}_{2} \mathrm{Al}_{1}\right]\left(\mathrm{Cp}^{*}\right)_{3}$, whereas thermally induced cluster growth is derived from $\left[\mathrm{Cu} \mathrm{HAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{Mes})$. Both approaches result in the formation of a complex cluster mixture consisting of $\left[\mathrm{Cu} \mathrm{Al}_{\mathrm{I}}\right]\left(\mathrm{Cp}^{*}\right) 6,\left[\mathrm{HCu}_{7} \mathrm{Al}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ and $\left[\mathrm{Cu}_{8} \mathrm{Al}_{6}\right]\left(\mathrm{Cp}^{*}\right) 6 .{ }^{.81}$

It can be concluded, that the synthesis of intermetallic clusters can be influenced by several components. Whereas Pd-Ga and Pt-Ga complexes are sensitive towards temperature and ligand concentration mostly applying ligand substitution but also redox reactions, the formation of $\mathrm{Cu}-\mathrm{Zn}$ and Cu -Al clusters strongly depends on the redox potential of both metals, but cluster core size is also influenced especially due to addition of stabilizing agents ( $\left[\mathrm{BAr}_{4}\right]^{\prime}$ ) or to chemical or thermal cluster degradation or growth.

### 2.3. Reactive Sites and Bond Activation applying Intermetalloid Compounds

## Reactive Sites due to Ligand Substitution Reactions

Due to the four hydrides on the cluster shell, $\left[\mathrm{Cu}_{6} \mathrm{Al}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}(\mathrm{H})_{4}$ is expected to be highly reactive to unsaturated functional groups as alkynes or nitriles. Although the cluster showed diverse reactivity towards different substrates, only the reaction with excess of benzonitrile enabled characterization by means of XRD, as previously described. The resulting molecular structure of $\left[\mathrm{Cu}_{6} \mathrm{Al}_{6}\right]\left(\mathrm{Cp}{ }^{*}\right)_{6}(\mathrm{~N}=\mathrm{CHPh})$ revealed the migration of one hydride to the nitrilic carbon. In addition, the nitrilic nitrogen is determined to bridge the Cu - Al bond which is also expected for heterogeneous surfaces as in case of $\mathrm{Fe}_{3} \mathrm{Al}_{14}$ or PdGa. ${ }^{13,15}$


Scheme 1: Schematic representation of the performed substitution reactions of $\left[T M_{2}\left(E C p^{*}\right)_{5}\right]$ with $T M=P d, P t .{ }^{73}$

Besides the surface reactivity as observed in [Cu6 $\left.{ }_{6} \mathrm{~A}_{6}\right]$, the intrinsic reactivity of already formed clusters was also explored in the recent years. Most of the mononuclear [TM(ECp*)4] were described as kinetically inert due to the saturated 18ve complex formation and the steric demand of the $C p^{*}$ shell which could act as a protecting shield. ${ }^{82}$ In contrast, the dinuclear and trinuclear complexes showed high reactivity for substitution reactions with various ligands such as $\mathrm{CO}, \mathrm{CN}{ }^{*} B u, \mathrm{PR}_{3}, \mathrm{AlCp}^{*}$, which is exemplarily shown in Scheme 1 for $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5},\left[\mathrm{Pt}{ }_{2} \mathrm{Ga} 5\right]\left(\mathrm{Cp}^{*}\right) 5$ and $[\mathrm{PtPdGa} 5]\left(\mathrm{Cp}^{*}\right) 5^{73}$ As predicted from theoretical calculations ${ }^{83}, \mathrm{GaCp}^{*}$ show high tendency for $\mathrm{GaCp}^{*} \rightarrow \mathrm{AlCp}^{*}$ substitution reactions. Thus, the reaction of $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ with $\mathrm{AlCp}{ }^{*}$ resulted in fully-exchanged $\mathrm{GaCp}^{*}$ forming $\left[\mathrm{Pd}_{2} \mathrm{Al}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$, whereas the Pt -analog was only able to substitute three $\mathrm{GaCp}^{*}$ moieties leading to $\left[\mathrm{Pt}_{2}\left(\mathrm{AlCp}^{*}\right)_{3}\left(\mathrm{GaCp}^{*}\right)_{2}\right]$. The molecular structure of the latter shows the exchange in the bridged positions
preferred by AICp* due to higher $\sigma$-donor properties of Al compared to Ga , while the terminal positions are still occupied by GaCp*. In contrast, using CO or $\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}$ as the substitution reagent, the terminal bound $\mathrm{GaCp}^{*}$ is preferentially substituted yielding $\left[\mathrm{Pt}_{2}(\mathrm{GaCp})_{3}(\mathrm{CO})_{2}\right.$, when $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ is reacted with CO , and $\left[\mathrm{Pt}_{2}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{2}\right]$ when $\mathrm{CN}^{\mathrm{t} B u}$ is added. Similar behavior was observed for phosphines: Addition of $\mathrm{PR}_{3}$ to $\left[\mathrm{TM}_{2}\left(\mathrm{GaCp}^{*}\right)_{5}\right](\mathrm{TM}=\mathrm{Pd}, \mathrm{Pt})$ led to the exchange of terminal bound GaCp* while maintaining the overall cluster structure. The exchange by $\mathrm{CO}, \mathrm{CN}^{\star} \mathrm{Bu}$ and $\mathrm{PR}_{3}$ in the terminal position is a result of their $\pi$-acceptor properties. As the exchange of bridging ligands do not result in cluster degradation leading to monomeric structures, the authors proposed a dissociative mechanism (Scheme 2). Thereby, one bridging E ligand is breaking up the structure of three bridging ligands while forming two terminal ligands on one metal center and one metal center only bears one terminal ligand and two bridging. The highly reactive TM-center is then open for further coordination by the substitution ligand which is followed by the dissociation of the ligand $E$.


Scheme 2: Proposed mechanisms for ligand exchanged reactions based on fluxional processes. $M=P d$, Pt. ${ }^{73}$ Reprinted with permissions from T. Steinke, C. Gemel, M. Winter, R. A. Fischer, Chem. Eur. J. 2005, 11, 1636-1646. Copyright 2005, John Wiley and Sons.

In accordance with $\left[\mathrm{TM}_{2}\left(\mathrm{GaCp}^{*}\right)_{5}\right]$, such ligand substitution studies were also performed on trinuclear clusters. In particular, the reaction of $\left[\mathrm{Pd}_{3}(\operatorname{InCp})_{8}\right]$ with $\mathrm{PPh}_{3}$ resulted in $\left[\mathrm{Pd}_{3}\left(\mathrm{InCp}^{*}\right)_{3}\left(\mathrm{PPh}_{3}\right)_{3}\right]$ with three bridging $\operatorname{InCp}$ * (two are $\mathrm{Pd}_{3}$-face-bridging and one is $\mathrm{Pd}_{2}$-edge-bridging) and three terminally bound $\mathrm{PPh}_{3}$ ligands (see Figure 9). As previously mentioned, it is proposed that the linear $\mathrm{Pd}_{3}$-arrangement is broken up in solution forming a $\mathrm{Pd}_{3}$ triangular $\left[\mathrm{Pd}_{3}\left(\operatorname{InCp}^{*}\right)_{6}\right]$ compound while releasing two $\operatorname{lnCp}{ }^{*}$ ligands. ${ }^{73}$ As a consequence, the reaction with $\mathrm{PPh}_{3}$ is exchanging the terminally bound $\mathrm{InCp}{ }^{*}$ of solution $\mathrm{Pd}_{3} \mathrm{In}_{6}$. The resulting structure of $\left[\mathrm{Pd}_{3}\left(\operatorname{InCp}^{*}\right)_{3}\left(\mathrm{PPh}_{3}\right)_{3}\right]$ is indicated in Figure 9.


Figure 9: Schematic representation of the reaction between $\left[\mathrm{Pd}_{3}\left(\operatorname{InCp}{ }^{*}\right)_{8}\right]$ with $\mathrm{PPh}_{3}$ yielding $\left[\mathrm{Pd}_{3}(\operatorname{InCp})_{3}\left(\mathrm{PPh}_{3}\right)_{3}\right]^{73}$

## Bond Activations on Intermetallic Compounds

Besides the formation of reactive sites due to substitution reaction, it is also possible to gain reactive clusters based on bond activations. Thus, $\mathrm{C}-\mathrm{H}$ and $\mathrm{Si}-\mathrm{H}$ bond activation was observed for $\mathrm{Ni}-\mathrm{Al}$ and Ru-Ga clusters. In case of Ni-Al, the $\mathrm{Si}-\mathrm{H}$ and $\mathrm{C}-\mathrm{H}$ bond activation were obtained during the synthesis of $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{4}\right]$ from $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]$ which turned out to be depending on the solvent (Figure 10). ${ }^{82}$ As the homoleptic $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right) 4\right]$ is prepared in hexane, similar reactions were performed in triethylsilane or benzene and revealed the formation of $\mathrm{Si}-\mathrm{H}$ activated $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$ or $\mathrm{C}-\mathrm{H}$ activated $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}(\mathrm{H})\left(\operatorname{AlCp}^{*}(\mathrm{Ph})\right]\right.$, respectively. It is proposed that the bond activations take place on the open coordination site of an unsaturated $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}\right]$ intermediate which is formed during reaction of $\left[\mathrm{Ni}(\mathrm{Cod})_{2}\right]$ and $\mathrm{AlCp}^{*}$. The assumption is supported by the conversion of $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$ in benzene yielding $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}(\mathrm{H})\left(\mathrm{AlCp}^{*}(\mathrm{Ph})\right)\right]$ while triethylsilane is released. Further reaction with $\mathrm{PPh}_{3}$ or $\mathrm{GaCp}^{*}$ resulted in $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}\left(\mathrm{PPh}_{3}\right)\right]$ and $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}\left(\mathrm{GaCp}^{*}\right)\right]$ which could be seen as stabilized $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}\right]$-centers. ${ }^{82}$


Figure 10: Schematic representation of the reaction between $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ and AlCp * in different solvents resulting in $\mathrm{C}-\mathrm{H}$ and $\mathrm{Si}-\mathrm{H}$ bond activated products. ${ }^{82}$ Reprinted with permissions from T. Steinke, C. Gemel, M. Cokoja, M. Winter, R. A. Fischer, Angew. Chem. Int. Ed. 2004, 43, 2299-2302. Copyright 2004, John Wiley and Sons.

Similar Si-H and C-H bond activations were recently explored on Ru-Ga clusters. ${ }^{84}$ Reaction of [ $\left.\mathrm{Ru}(\operatorname{cod})(\mathrm{MeAlly})_{2}\right]$ with $\mathrm{GaCp}^{*}$ in triethylsilane under hydrogenolytic conditions (3 bar, $\mathrm{H}_{2}$ ) resulted in $\mathrm{Si}-\mathrm{H}$ activated $\left[\mathrm{Ru}\left(\mathrm{GaCp}^{*}\right)_{3}(\mathrm{H})_{3}\left(\mathrm{SiEt}_{3}\right)\right]$. DFT calculations predicted an umbrella shaped H -bonding around the Ru center without any hydrogen interactions. Nevertheless, performing the reaction under analog conditions in toluene, the mass spectrometric analysis revealed the formation of $\mathrm{C}-\mathrm{H}$ activated $\left[\mathrm{Ru}\left(\mathrm{GaCp}^{*}\right)_{3}(\mathrm{H})_{3}\left(\mathrm{C}_{7} \mathrm{H}_{7}\right)\right]$. With the help of DFT, a toluene-activation on the electron-deficient $\left[\mathrm{Ru}\left(\mathrm{GaCp}^{*}\right)_{2}(\mathrm{H})_{2}\right]$ intermediate is predicted which was not yet verified. ${ }^{84}$ However, in 2008, our group presented a similar prediction for the synthesis of dinuclear $\left[\mathrm{Ru}_{2}(\mathrm{Ga})\left(\mathrm{GaCp}^{*}\right)_{7}(\mathrm{H})_{3}\right] .{ }^{85}$ The formation of $\mathrm{Ru}_{2} \mathrm{Ga}_{7}$ was proposed to involve $\mathrm{GaCp}^{*}$ dissociation/association and require intermediates as $\left[\mathrm{Ru}\left(\mathrm{GaCp}^{*}\right)_{4}(\mathrm{H})(\mathrm{Ga})\right]$ and $\left[\mathrm{Ru}\left(\mathrm{GaCp}^{*}\right)_{4}(\mathrm{H})_{2}\right]$. Nevertheless, the latter was not isolated so far, but the phosphine analog $\left[\mathrm{Ru}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{PCy}_{3}\right)_{2}(\mathrm{H})_{2}\right]$ could be determined by SC-XRD. ${ }^{86}$

## Reactive Sites Formation due to Potential Ligand Dissociation

Due to the high dissociation potential of phosphines on $\mathrm{Ni}(0)$ centers ${ }^{87-89}$, complexes of the formula $\left[\mathrm{Ni}\left(\mathrm{ECp}^{*}\right)_{n}\left(\mathrm{PR}_{3}\right)_{4-n}\right]$ were predicted to be possible candidates for generating open coordination sites. ${ }^{90}$ Therefore, a series of $\left[\mathrm{Ni}\left(\mathrm{ECp}^{*}\right)_{n}\left(\mathrm{PR}_{3}\right)_{4-n}\right]$ with $\mathrm{E}=\mathrm{Al}, \mathrm{Ga}$ and $\mathrm{R}=\mathrm{Me}, \mathrm{Et}$, Ph was synthesized and partly investigated regarding their dissociation behavior. ${ }^{90-91}$ In contrast to the homoleptic $\left[\mathrm{Ni}\left(\mathrm{PR}_{3}\right)_{4}\right]$ which shows high dissociation potential in solution, the dissociation of phosphine was determined to be strongly affected by the coordination of ECp*. With the help of EDA-NOCV, which enables the prediction of bond strengths, it was proposed that the Ni-P bond strength is gradually increasing upon ECp* coordination and thus, results in gradual decrease of Ni-P bond distances. Additionally, the performed UV-vis spectra at variable temperatures did not reveal ligand dissociation from the metal center and therefore, no generation of open coordination sites was observed from Ni-phosphine compounds. 90

## Potential Reactive Sites due to Steric Overcrowding on the Metal Center

Follow up on this publication, our group extended their studies to Zn -containing species of the formula $\left[\mathrm{Ni}\left(\mathrm{ZnCp}^{*}\right)_{n}(\mathrm{ZnMe})_{n}\left(\mathrm{PR}_{3}\right)_{4-n}\right]$ due to higher steric demand of $\mathrm{Zn}_{2} \mathrm{R}^{\prime} 2$ in contrast to $\mathrm{ECp}{ }^{*} .{ }^{91-92}$ In case of $\mathrm{PEt}_{3}$, we were able to synthesize the whole series originating from respective $\left[\mathrm{Ni}\left(\mathrm{ECp}^{*}\right)_{n}\left(\mathrm{PR}_{3}\right) 4-n\right]$ due to $\mathrm{E} / \mathrm{Zn}$ exchange reactions which enables steric overcrowding on the metal center (see Scheme 3).92-93 In particular, $E p^{*}$ containing TM-complexes undergo $\mathrm{E} / \mathrm{Zn}$ and $\mathrm{Cp}^{*} / \mathrm{Me}$ exchange reactions upon treatment with $\mathrm{ZnMe}_{2}{ }^{94-96}$


Scheme 3: Synthesis of full E/Zn exchanged compounds of the formula $\left[\mathrm{Ni}\left(\mathrm{ZnCp}^{*}\right)_{n}(Z n M e)_{n}\left(P E t_{3}\right)_{4-n}\right](n=1-3)$ originating from $\left[\mathrm{Ni}\left(E C p^{*}\right)_{n}\left(\mathrm{PEt}_{3}\right)_{4-n}\right]$ precursors. Partial exchange was observed due to the synthesis of $\left[\mathrm{Ni}\left(\mathrm{GaCp}{ }^{*}\right)\left(Z n C p^{*}\right)\left(\mathrm{ZnMe}^{2}\right)\left(\mathrm{PEt}_{3}\right)_{2}\right]^{92}$ Reprinted with permission from P. Heiß, J. Hornung, X. Zhou, C. Jandl, A. Pöthig, C. Gemel, R. A. Fischer, Inorg. Chem. 2020, 59, 514-522. Copyright 2020, American Chemical Society.

Due to the neighborhood of Ga and Zn in the periodic table, they exhibit comparable atomic values and electronegativities. If $\mathrm{GaCp}^{*}$ is considered as two electron-donor ligand, it is exchanged by two ZnR ligands which are acting as one electron donor ligand each. The strong reducing power of $\mathrm{Ga}^{1}$ enables
the reduction of $\mathrm{Zn}^{\prime \prime}$ in $\mathrm{ZnMe}_{2}$ to $\mathrm{Zn}^{\prime} \mathrm{R}$ ligands while $\mathrm{Ga}^{1}$ is concomitantly oxidized to $\mathrm{Ga}^{111} .{ }^{96}$ Therefore, addition of $\mathrm{ZnMe}_{2}$ to $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ resulted in fully exchanged $\left.\left[\mathrm{Ni}(\mathrm{ZnCp})_{4}\right)_{4}(\mathrm{ZnMe})_{4}\right] .{ }^{96}$ As half of the Zn ligands are bearing Cp * instead of $\mathrm{Me}, \mathrm{Cp}$ * transfer reactions from Ga to Zn must have occurred during the synthesis. In this step, the methyl groups are simultaneously transferred to Ga forming $\mathrm{GaMe}_{2} \mathrm{Cp}^{*}$ and $\mathrm{GaMe}_{3}$ as side-products of such reactions.

Although, the synthesis of $\left[\mathrm{Ni}\left(\mathrm{ZnCp}^{*}\right)_{n}(\mathrm{ZnMe})_{n}\left(\mathrm{PEt}_{3}\right)_{4-n}\right]$ provided a complete range of $\mathrm{Ni}-\mathrm{Zn}$ compounds with a highly sterically shielded Ni-center, the performed UV-vis studies of such compounds did not show an increase of phosphine dissociation based on steric overcrowding compared to $\mathrm{Ni}-\mathrm{E}$ compounds. ${ }^{92}$ As a consequence, no free coordination sites are generated on the active metal which could enable high reactivity or further cluster growth.

### 2.4. Ligand Protected Hume-Rothery Inspired Intermetallic Compounds as Molecular Models for Catalytic Application

As shown by previous chapters, well-defined bimetallic/intermetallic compounds with atomic precision enable control of size, metal composition and metal distribution. Additionally, they enhance investigation of structural parameter and bonding situation by easy accessible analytical techniques as SC-XRD, IR and NMR spectroscopy as well as mass spectrometry. Therefore, intermetallic compounds were applied in fundamental research for e.g. semi-hydrogenation of acetylene, methanol synthesis or methanol steam reforming, and electrocatalytic processes (OER, HRR). ${ }^{19}$ The systematic investigation of such reactions and their requirements led to catalytically relevant materials with outstanding properties. ${ }^{63}$ In addition, application of molecular mimics facilitates characterization under operando conditions offering in-situ monitoring of active species. Atom precise clusters, potentially being intermetallic, can serve as molecular models that mimic the catalyst's surface with its active centers while reducing complexity of identification. ${ }^{80,97}$

## Molecular models linking solid-state with molecularly defined compounds

As $\mathrm{Pd} / \mathrm{Ga}, \mathrm{Ni} / \mathrm{Zn}$ and $\mathrm{Fe} / \mathrm{Al}$ intermetallic compounds show outstanding catalytic properties, especially for semihydrogenation ${ }^{10,18}$, the synthesis of Hume-Rothery inspired compounds which consist of different metal combinations including late transition metals combined with $\mathrm{Al}, \mathrm{Ga}$, In and Zn are of high interest. Theoretical calculations of such molecular models including Hume-Rothery inspired clusters have been published from Fischer et al. in 2019.97 They investigated the structural and electronic properties of $\left[\mathrm{Ni}(E R)_{n}\left(\mathrm{C}_{2} \mathrm{H}_{x}\right)_{4-n}\right]\left(x=2,4 ; R=M e, C p^{*}\right)$, theoretically, depending on different metals $E$ which could be either Al , Ga or Zn . The optimized structures containing Ga as $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{\mathrm{n}}\left(\mathrm{C}_{2} \mathrm{H}_{x}\right)_{4-n}\right]$ ( $x=2$, acetylene; $x=4$, ethylene) showed classical side-on coordination of acetylene or ethylene as expected. While the ethylene species of Al and Zn resulted in similar structural motifs of side-on coordinated ethylene on the Ni-center, some of the acetylene species behaved different. The structural optimization of $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{1}\left(\mathrm{C}_{2} \mathrm{H}_{2}\right)_{3}\right],\left[\mathrm{Ni}\left(\mathrm{AlCp}{ }^{*}\right)_{2}\left(\mathrm{C}_{2} \mathrm{H}_{2}\right)_{2}\right]$ and $\left[\mathrm{Ni}(\mathrm{ZnR})_{4}\left(\mathrm{C}_{2} \mathrm{H}_{2}\right)_{2}\right]$ proposed the acetylene to coordinate different to the metal center as in Ni-Ga case. In particular, $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{1}\left(\mathrm{C}_{2} \mathrm{H}_{2}\right)_{3}\right]$ revealed the
dimerization of two acetylene moieties while forming a metallacycle with AI, which coordinates via the obtained double bonds to the nickel center. The third acetylene is still side-on bound to Nickel. In case of $\left.\left[\mathrm{Ni}(\mathrm{AlCp})_{2}\right)_{2}\left(\mathrm{C}_{2} \mathrm{H}_{2}\right)_{2}\right]$, one acetylene is bridging two $\mathrm{AICp}{ }^{*}$ residues while coordinating to nickel via the triple bond whereas the other acetylene is side-on coordinated solely to nickel. This TM-E bridging position of acetylene was previously predicted for $\mathrm{PdGa}_{2}$ heterogeneous surfaces as published from Passerone and Prinz et al. ${ }^{13}$ Additionally, for $\left[\mathrm{Ni}(\mathrm{ZnR})_{4}\left(\mathrm{C}_{2} \mathrm{H}_{2}\right)_{2}\right]$, the acetylene was proposed to bind in a bridging position while coordinating to the nickel center. For all the other $\mathrm{Ni}-\mathrm{Al}$ or $\mathrm{Ni}-\mathrm{Zn}$ compounds within the formula, $\left[\mathrm{Ni}(\mathrm{ER})_{n}\left(\mathrm{C}_{2} \mathrm{H}_{2}\right)_{4-n}\right]$, the acetylene was predicted to coordinate in a side-on fashion to the transition metal center. ${ }^{97}$ Although these theoretical calculations nicely proposed Ni-ethylene and Ni -acetylene bonding in dependence to the second metal, experimental data of such molecular compounds are still missing.

One of the recent experimentally obtained examples for a heterogeneous surface modelling is the isolation of molecular cut-out of $\gamma$-brass, $\left[\mathrm{Cu}_{4} \mathrm{Zn}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}\left(\mathrm{CN}^{t} \mathrm{Bu}_{4}\right)_{4}$ which is obtained by reaction of $\left[\mathrm{CpCu}\left(\mathrm{CN}^{\dagger} \mathrm{Bu}\right)\right]$ with $\mathrm{Zn}_{2} \mathrm{Cp}^{*} 2$ in toluene at room temperature. ${ }^{74}$ The molecular structure reveals two inverted tetrahedra, where the $\mathrm{Cu}_{4}$ tetrahedron forms the inner sphere and the $\mathrm{Zn}_{4}$ tetrahedron is displaying the outer sphere (Figure 11, right). In comparison to $y$-brass, similar structural motif was found in the respective $\gamma$-phase, $\mathrm{Cu}_{5} \mathrm{Zn}_{8}$, although the inner and outer tetrahedral arrangement of Cu and Zn atoms are inverted. Besides $\mathrm{Cu}_{4} \mathrm{Zn}_{4}$, $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{4}\left(\mathrm{Cp}^{*}\right)_{4}$ also exhibits two inverted $\mathrm{M}_{4}$ tetrahedra which could be obtained by reaction of $\left[\left\{\mathrm{Pd}\left(\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}\right)_{2}\right\}_{3}\right]$ either with $\mathrm{GaCp}^{*}$ or with $\left[\mathrm{Pd}_{3}\left(\mathrm{CN}^{\mathrm{tBu}}\right)_{3}\left(\mathrm{GaCp}^{*}\right)_{4}\right] .{ }^{98}$ Whereas Fischer et al. described the structural motif as $\mathrm{Pd}_{4} \mathrm{Ga}_{4} 4$-fold capped tetrahedron, it could also be seen as two inverted tetrahedra and thus, as a brass-like Pd-analog. In contrast to $\mathrm{Cu}_{4} \mathrm{Zn}_{4}$, there was no significant outer and inner sphere that could be assigned. ${ }^{98}$


Figure 11: Left: Molecular structure of $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{CN}^{*} \mathrm{Bu}\right)_{4}\left(\mathrm{Cp}^{*}\right)_{4}$ and the core structure (middle left) showing two interconnected tetrahedra. Pd, red; Ga, blue; N, yellow. ${ }^{98}$ Right: Molecular structure of $\left[\mathrm{Cu}_{4} \mathrm{Zn}_{4}\right]\left(\mathrm{CN} \mathrm{N}^{t} \mathrm{Bu}\right)_{4}\left(\mathrm{Cp}^{*}\right)_{4}{ }^{74}$ and the respective core structure ${ }^{78}$ showing two inverted tetrahedra with $\mathrm{Zn}_{4}$ forming the outer sphere and $\mathrm{Cu}_{4}$ the inner spherical tetrahedron. Cu , dark red; Zn , green; N, yellow. Left and middle left: Adapted reprinted with permissions from M. Molon, K. Dilchert, C. Gemel, R. W. Seidel, J. Schaumann, R. A. Fischer, Inorg. Chem. 2013, 52, 14275-14283. Copyright 2013, American Chemical Society. Middle right. Adapted reprinted with permissions from K. Freitag, C. Gemel, P. Jerabek, I. M. Oppel, R. W. Seidel, G. Frenking, H. Banh, K. Dilchert, R. A. Fischer, Angew. Chem. Int. Ed. 2015, 54, 4370-4374. Copyright in 2015, John Wiley and Sons. Right: Adapted reprinted with permissions from K. Freitag, H. Banh, C. Gemel, R. W. Seidel, S. Kahlal, J.-Y. Saillard, R. A. Fischer, Chem. Commun., 2014, 50, 8681-8684. Copyright 2014, Royal Society of Chemistry; Permission conveyed through Copyright Clearance Center, Inc.

Further, Fischer et al. were able to isolate embryonic brass, [ $\left.\mathrm{CuZn} n_{2} \mathrm{Cp}_{3}{ }_{3}\right]$ by reaction of $\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ with in-situ synthesized CuCp* and [ZnCp*]. ${ }^{75-76}$ The obtained compound can be seen as smallest possible building block for brass-like Cu-Zn structures. Indeed, this [CuZn ${ }_{2}$ ] compound enabled the synthesis of
larger clusters yielding $\left[\mathrm{Cu}_{2} \mathrm{Zn}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}{ }^{+}$upon reaction with $\left[\mathrm{Zn}_{2}\right]\left(\mathrm{Cp}^{*}\right)\left(\mathrm{Et}_{2} \mathrm{O}\right)_{3^{+}}$revealing a $[\mathrm{CuZn} 2]$ triangle which is face-capped by two $\mathrm{ZnZnCp} *$ units. ${ }^{78}$ The neutral Cu -analog, $\left[\mathrm{Cu}_{3} \mathrm{Zn}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{5}$, showing a $\mathrm{Cu}_{3}$ triangle as cluster core, was observed as by-product while $\left.[\mathrm{CuZn}]_{2}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ is formed as major product. In fact, it has been shown that both, $\mathrm{Cu}_{4} \mathrm{Zn}_{4}$ as molecular brass and $\mathrm{CuZn}_{2}$ as embryonic brass, can serve as molecular mimics for complex systems such as brass. This represents a case study of complex surfaces using model systems on a molecular level that can be investigated by easily accessible methods such as NMR and IR spectroscopy as well as SC-XRD combined with DFT calculations.

## Electronic situation in TM-ECp* compounds

In contrast to solid-state materials, molecularly defined intermetallic clusters have to be stabilized either in a matrix ${ }^{99-100}$ or in the gas phase ${ }^{101}$ when dealing with naked clusters or in a ligand shell when involving ligand-stabilized clusters. Besides the already mentioned and well-known ligands as phosphines or NHCs, there are also clusters described in literature that exhibit ECp* as ligand instead of well-known $\mathrm{CO}, \mathrm{PR}_{3}$ and NHC. Due to the isolobal principle, ER ligands as $E C p^{*}(E=G a, A I, \mathrm{In})$ bears a lone pair on the metal center which are comparable to common CO, NHC or $\mathrm{PR}_{3}$ (Scheme 4). ${ }^{102-103}$ This lone pair can donate electrons from the $\sigma$-HOMO orbital in the d-orbital of a transition metal revealing an electron rich metal center which offers interesting electronic properties. ${ }^{102}$


Scheme 4: Isolobal principle applied for $\mathrm{CO}, \mathrm{NHC}, \mathrm{PR}_{3}$ and $E C p^{*}$ ligands.

The first ER-ligand stabilized TM complex which was structurally characterized by X-ray diffraction was $\left[\mathrm{Fe}(\mathrm{CO})_{4}\left(\mathrm{AlCp}^{*}\right)\right] .{ }^{104}$ The electronic situation in this complex was described as a typical donor-acceptor complex involving $\sigma$-donating and $\pi$-backdonating properties of ligand and metal. Nevertheless, the analysis of the bonding situation has been controversially discussed in literature. The electronic situation applying the Dewar-Chatt-Duncanson model, which was first published for TM-CO complexes by M. Dewar, is of high acceptance. ${ }^{105}$ As depicted in Scheme 5, the $\sigma$-orbital including the lone pair of the ER ligand donates electrons to the empty $\sigma$-orbital of the transition metal resulting in $\sigma$-donation. The $\pi$-backdonation from the TM orbitals to the orbitals of $E$ are dependent on the residue on $E$. Therefore, the empty $\pi$-orbital of $E$ either receives electron density from the occupied $\pi$-orbitals of the transition metal or from the substituent $R$ bound to $E$ (Scheme 5a).

a)


b) • (1)E—R
$\mathrm{q}(+) \mathrm{TM} \quad \mathrm{q}(-)$

Scheme 5: Electronic situation in ER-ligands applying the Dewar-Chatt-Duncanson donor-acceptor-model. Adapted reprinted with permission from G. Frenking, K. Wichmann, N. Fröhlich, C. Loschen, M. Lein, J. Frunzke, V. c. M. Rayón, Coord. Chem. Rev. 2003, 238-239, 55-82. Copyright 2003, Elsevier.

Besides the orbital interaction, the electrostatic contributions in such compounds have to be considered. The population analysis of a TM-ER complex showed E as a highly positively charged metal while TM is negatively charged resulting in an ionic bond character. ${ }^{106-107}$ These values, however, are misleading as the dominant charge attraction takes place between the negative lone pair of ER and the positive TM nucleus (Scheme 5b). In summary, the electronic situation of TM-ER compounds can be described by an interplay of electrostatic as well as orbital interactions while revealing $\sigma$-donation as the major contribution (>80\%) to covalent bonding instead of $\pi$-backdonation. ${ }^{83}$

Depending on the residue R of the ER ligands, the $\pi$-backdonating properties of $\mathrm{TM} \rightarrow \mathrm{E}$ are influenced. As an example, the sterically demanding ligands $\mathrm{Cp}^{*}$ and Cp were shown to have high $\pi$-donor properties, which led to a rather weak $\pi$-backdonation of $\mathrm{TM} \rightarrow \mathrm{E} .{ }^{108} \mathrm{In}$ addition, $\mathrm{C}\left(\mathrm{SiMe}_{3}\right)_{3}, \mathrm{Si}\left({ }^{( } \mathrm{Bu}\right)_{3}$ and $\mathrm{Si}\left(\mathrm{SiMe}_{3}\right)_{3}$ were also described as suitable ligands to stabilize the oxidation state +1 of the group 13 metal. ${ }^{109-116}$ The unusual oxidation state of +1 of group 13 metals offered high potential for TM-ER complexes in organometallic chemistry leading to the synthesis of several $\left[T M_{a}(E R) b\right]$-compounds. ${ }^{72, ~ 80,}$ ${ }^{117-124}$ As previously mentioned, the first characterized ECp* containing TM complex was $\left[\mathrm{Fe}(\mathrm{CO})_{4}\left(\mathrm{AlCp}^{*}\right)\right]$ (see Figure 12) ${ }^{104}$ which is obtained from reaction of $\mathrm{K}_{2}\left[\mathrm{Fe}(\mathrm{CO})_{4}\right]$ with $\mathrm{Cp}^{*} \mathrm{AlCl}_{2}$ in toluene in low yields. The structure reveals four terminal bound CO ligands and one terminal bound AICp* residue. DFT calculations of the electronic situation of $\left[\mathrm{CpAl}-\mathrm{Fe}(\mathrm{CO})_{4}\right]$ clearly indicated a donoracceptor complex with AICp being the donor due to the lone pair of the aluminum.


Figure 12: Molecular structure of $\left[\mathrm{Cp}^{*} \mathrm{Al}-\mathrm{Fe}(\mathrm{CO})_{4}\right]$ as determined by $S C-X R D$. $H$ atoms are omitted for clarity. Color code: Fe, orange; O, red; Al, yellow; C, grey. ${ }^{104}$

Additionally, depending on the reaction conditions and on the nature of ER, mononuclear, dinuclear or polynuclear clusters could be obtained with different ER binding modes as previously described for PdAl compounds. In mononuclear clusters of the [TM(ER)4], as [TM(ECp $\left.\left.{ }^{*}\right) 4\right](\mathrm{TM}=\mathrm{Ni}, \mathrm{Pd}, \mathrm{Pt})^{72,117,125}$, $\left[\mathrm{TM}\left(\mathrm{ECp}^{*}\right)_{5}\right]$ with $\mathrm{TM}=\mathrm{Fe}, \mathrm{Ru}^{124}$, or $\left[\mathrm{TM}\left(E C p^{*}\right)_{6}\right]$ with $\mathrm{TM}=\mathrm{Mo}^{126}, \mathrm{ER}$ is usually terminal bound to the transition metal center. Additionally, in higher nuclear clusters ER ligands offer diverse bonding modes as terminal, edge- or face-bridging. Mononuclear clusters are obtained based on ligand substitution of labile precursor ligands by ER. As an example, $\left[\mathrm{Ni}\left(E \mathrm{Ep}^{*}\right)_{4}\right]$ was synthesized from $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]$ with stoichiometric amount of $E C p^{*}\left(E=A 1^{182}, G a^{177}\right)$ whereas the Pt and Pd analog were received from $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ or $\left[\mathrm{Pd}(\mathrm{tmeda})(\mathrm{Me})_{2}\right]^{72}$ Homoleptic polynuclear complexes of $\mathrm{Ni}, \mathrm{Pd}$ or Pt could be either achieved by addition of TM-source to the monomeric compound as observed for $\left[\mathrm{Pt}_{2}\left(\mathrm{GaCp}^{*}\right)_{5}\right]$ which was synthesized from $\left.\left[\mathrm{Pt}(\mathrm{GaCp})^{*}\right)\right]$ or due to excess of ECp to the respective TM-sources. ${ }^{73}$ Further increase of transition metal content in such clusters leads to polynuclear compound that resembles the link between molecular and solid-state chemistry as already described for $\mathrm{Cu}_{4} \mathrm{Zn}_{4}$ and $\mathrm{Pd}_{4} \mathrm{Ga}_{4}$ as molecular cut-out of $\gamma$-brass which can be investigated by common analytical methods in contrast to highly sophisticated analytics as in case for solid-state materials.

## 3. Motivation And Research Goal

Catalytically relevant reactions using heterogeneous catalysts e.g. semi-hydrogenation of alkynes, $\mathrm{CO}_{2}$ to methanol synthesis, electrocatalysis performing hydrogen evolution reaction (HER) or oxygen reduction reaction (ORR), etc., are usually investigated applying highly sophisticated methods partly under harsh conditions. ${ }^{19,}$, 127-128 Top-down synthesized bulk materials are often used for basic understanding of reaction processes. However, deeper insights are difficult to obtain since doped bulk material does not correctly resemble the catalyst's surface and its reactivity, due to defects on the catalyst's surface caused by the synthesis. ${ }^{18}$ The investigation of such reactions and its accompanying mechanism are not only essential for basic understanding, but also useful for planning and optimization to make production most efficiently. ${ }^{129}$ Although, investigation of nanoparticles is a good opportunity to comprehend the reaction mechanisms and bonding affinity, it requires highly sophisticated analytical methods such as high-energy X-ray spectroscopy (XAS, EXAFS, NEXAFS, XANES, XPS), energy-disperse X-ray microanalysis (EDX), magnetic measurements, ion spectroscopy/scattering, partly under ultra-high vacuum, only to name a few. ${ }^{28}$
Therefore, ligand-stabilized intermetallic compounds are evaluated as potential candidate resembling the catalyst's surface on a molecularly defined level. ${ }^{80, ~ 82, ~ 130-131 ~ S u c h ~ H u m e-R o t h e r y ~ i n s p i r e d ~ c l u s t e r s ~}$ can be viewed as molecular cut-outs of the active catalyst for example as molecular brass in case of $\mathrm{Cu}_{4} \mathrm{Zn}_{4}$ (see Figure 13). Hereby, a key advantage is that accurate structural information can be obtained through a large pool of analytical techniques for molecular compounds as SC-XRD, NMR, IR spectroscopy, mass spectrometry etc. ${ }^{74}$


Figure 13: Left: Molecular structure of $\left[\mathrm{Cu}_{4} \mathrm{Zn}_{4}\right]\left(C N^{t} B u\right)_{4}\left(\mathrm{Cp}^{*}\right)_{4}$ as molecular model for $\gamma$-brass. The same structural motif of the two interpenetrated polyhedra of $\left[\mathrm{Cu}_{4} \mathrm{Zn}_{4}\right]$ cluster core is also found in solid-state structure of $y$-brass $\mathrm{Cu}_{10} \mathrm{Zn}_{16}$ (right) where a tetrahedral $\mathrm{Zn}_{4}$ is surrounded by tetrahedral $\mathrm{Cu}_{4}$ being inverse to ligand protected $\left[\mathrm{Cu}_{4} \mathrm{Zn} n_{4}\right](\mathrm{L})_{8}{ }^{74} \mathrm{Color}$ code: Cu , red; Zn , green. (Adapted) reprinted with permission from K. Freitag, H. Banh, C. Gemel, R. W. Seidel, S. Kahlal, J.-Y. Saillard, R. A. Fischer, Chem. Commun. 2014, 50, 8681-8684. Copyright 2014, Royal Society of Chemistry; permission conveyed through Copyright Clearance Center, Inc.

Recently, the group of R. A. Fischer started to investigate the behavior of such intermetallic compounds towards different substrates, e.g. PhCN, PhH, $\mathrm{PhMe}, \mathrm{Et}_{3} \mathrm{SiH}$, alkynes or alkenes. ${ }^{80,82, ~ 97, ~ 130-131}$ However, the isolation of such single clusters proved to be possible in only few cases. ${ }^{80,82}$ Therefore, they started to investigate possible intermetallic clusters in mixtures and recently presented a showcase of such a "non-classical" reactivity study by testing the reaction of CO or $\mathrm{H}_{2}$ with a mixture of clusters $\left[\mathrm{Ni}_{\mathrm{a}} \mathrm{Gab}_{\mathrm{b}}\right]\left(\mathrm{Cp}^{*}\right)_{\mathrm{c}}(\mathrm{a}=6,7, \mathrm{~b}=6-8, \mathrm{c}=6) .{ }^{132}$

In addition, treatment of a $\mathrm{Cu} / \mathrm{Zn}$ cluster library of 23 compounds with $\mathrm{CO}_{2}$ resulted in $\left[\mathrm{Cu}_{5} \mathrm{Zn}_{5}\right](\mathrm{L})_{6}\left(\mathrm{CO}_{2}\right)_{2}$ and $\left[\mathrm{Cu}_{8} \mathrm{Zn}_{3}\right](\mathrm{L})_{7}\left(\mathrm{CO}_{2}\right)(\mathrm{L}=\mathrm{Cp} *$, Mes $)$ with $\mathrm{CO}_{2}$ binding to the cluster shell. ${ }^{133}$ In particular, $\mathrm{CO}_{2}$ remains unaffected and does not decompose to CO and O which could be evidenced by labeled MS analysis and FT-IR spectroscopy. Further conversion of this cluster mixture with dihydrogen reveals $\mathrm{Cu} / \mathrm{Zn}$ to be reactive due to the formation of formate-containing $\left[\mathrm{Cu}_{11} \mathrm{Zn}_{6}\right](\mathrm{L})_{8}\left(\mathrm{CO}_{2}\right)_{2}\left(\mathrm{HCO}_{2}\right)$ as confirmed by combining NMR and IR spectroscopic methdos with mass analysis. ${ }^{133}$ This approach applying different analytical techniques without compound isolation could further help to understand reaction mechanisms during catalytic processes.
In addition, in 2018, Fischer et al. published a theoretical study of the interaction of $\left[\mathrm{Ni}_{\mathrm{a}} \mathrm{E}_{b}\right](\mathrm{L})_{b}(\mathrm{E}=\mathrm{Zn}$, $\mathrm{Al}, \mathrm{Ga} ; \mathrm{L}=\mathrm{Cp} *, \mathrm{Me}$ ) with alkynes or alkenes as a surface model of the semi-hydrogenation reaction. ${ }^{97}$ The calculations predicted a chemisorption-like activation of $\mathrm{C}_{2} \mathrm{H}_{2}$ with TM-E bridging coordination in case of $\mathrm{Ni} / \mathrm{Al}$ and $\mathrm{Ni} / \mathrm{Zn}$. In contrast, the corresponding $\mathrm{Ni} / \mathrm{Ga}$ compounds exhibit regular side-on coordination to the central Ni atom without interaction of acetylene and Gallium. However, at the time of this study, the methodology to experimentally confirm these calculations was not yet as advanced as it is today. By using a combinatorial approach in combination with different analytical techniques as described above, it is now of great interest to support these theoretical predictions with experimental data. Such compounds could be experimentally achieved either by post-synthetic modification as reductive elimination or dissociation/substitution, or by early-stage incorporation using ligandexchange/substitution reaction. ${ }^{134}$ In particular, early-stage incorporation describes the introduction of a substrate in an early stage of the reaction prior to cluster formation, while the post-synthetic modification deals with the substrate-bonding after the cluster exhibits a definite composition. Since phosphines are known to dissociate readily from Ni centers, ${ }^{87-89}$ the first attempt was to synthesize all-hydrocarbon ligated Ni/E center via substitution of phosphine ligands by alkynes as the substrate. Therefore, $\left[\mathrm{Ni}\left(E \mathrm{Ep}^{*}\right)_{n}\left(\mathrm{PR}_{3}\right)_{4-n}\right](\mathrm{E}=\mathrm{Al}, \mathrm{Ga} ; \mathrm{R}=\mathrm{Me}, \mathrm{Et}, \mathrm{Ph})$ could be synthesized by addition of stoichiometric amounts of $E C p^{*}$ and $\mathrm{PR}_{3}$ to $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]^{90}$ The $\mathrm{Ni} / \mathrm{Zn}$ compounds of the formula $\left[\mathrm{Ni}\left(\mathrm{ZnCp}^{*}\right)_{n}(\mathrm{ZnMe})_{n}\left(\mathrm{PR}_{3}\right)_{4-n}\right]^{92}$, ${ }^{135}$ were obtained due to stepwise $\mathrm{E} / \mathrm{Zn}$ exchange from $\left[\mathrm{Ni}\left(\mathrm{ECp}^{*}\right)_{n}\left(\mathrm{PR}_{3}\right)_{4-n}\right]$ as described by Molon et al. ${ }^{94}$ In contrast to the expectations, phosphine dissociation in $\mathrm{Ni} / \mathrm{E}$ complexes is suppressed with increasing number of E -ligands due to $\mathrm{Ni}-\mathrm{P}$ bond strengthening. ${ }^{90}$, 92

In this thesis, different approaches for control of size or metal composition of $\mathrm{Ni} / \mathrm{E}, \mathrm{Pd} / \mathrm{E}$ and $\mathrm{Pt} / \mathrm{E}$ compounds will be investigated. These studies try to unravel the following research questions:
(I) Is it possible to control cluster growth, size or metal composition and distribution by using additives in cluster synthesis due to a combinatorial approach?
(II) What are possible precursors for TM-clusters interacting with the substrate?
(III) How can computations help to give insight in clusters formed in mixture, e.g. via combination with standard analytical techniques?
(I) A combinatorial approach describes the synthetic study of a pool of molecules (library) that are investigated in mixtures without the necessity of isolation. This access allows the potential identification of new reactions or reactive intermediates in organometallic chemistry which could not be isolated so
far and potentially leads to new ways of thinking. As additives have a wide range of applications, e.g. in (nano)cluster or nanoparticle synthesis controlling size, shape or metal distribution ${ }^{50,136-138}$, this will be extended to cluster chemistry or synthesis where the use of additives is less common. Therefore, this dissertation investigates the influence of additives on cluster formation and growth depending on metal combinations $\mathrm{Ni} / \mathrm{E}$ with E being $\mathrm{Al}, \mathrm{Ga}$ or Zn by addition of different amounts, additives and conditions. After the synthesis of cluster libraries, experiments for in-situ size-focusing, as known for nanoparticles, are performed while varying the conditions and adding additional amount of additive.
(II) Since this work focuses on group 10 metals, different TM-precursor for Ni, Pd and Pt are tested for their reactivity towards alkynes. Alkynes can themselves serve as model substrates for semi-hydrogenation reactions, but also as additives to possibly control cluster size and distributions as known for nanoparticles. ${ }^{36,50,136-139} \mathrm{In}$ addition to mononuclear precursors as [TM(cod)2] (TM = Ni, Pt), polynuclear precursor with a definite clusters structure, e.g. $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{7}\right]$ or $\left[\mathrm{Pd}_{2}\left(\mathrm{dvds}_{3}\right)_{3}\right]$, will be the scope of this study. The reactions are optimized by investigating the influence of stoichiometry, metal ratio (TM/E) and typical parameters as temperature, time and solvent. In this context, a new tool for size-focused clusters will be explored and monitored using in-situ NMR spectroscopy and Liquid Injection Field Desorption Ionization (LIFDI) mass spectrometry.
(III) Since the discovery of cluster ensembles as for $\left[\mathrm{NiaEb}_{\mathrm{b}}\right]\left(\mathrm{Cp}^{*}\right) 6^{81,132}$ and $\left[\mathrm{CucAl}_{c}\right]\left(\mathrm{Cp}^{*}\right) 6^{81}$ and their demonstration of the limitations of standard analytical techniques, it is of utmost importance to establish a new tool that combines different analytical methods with theoretical methodologies. In this approach possible structures are calculated theoretically on the basis of already known compounds and compared to the obtained experimental data in order to get a valid structural suggestion. This new methodolgy, which can also be applied in-situ, could replace the previously indispensable isolation of organometallic clusters and their sometimes complex structure elucidation. Besides investigating reactive sites that may bind catalytically relevant substrates at the cluster surface such as acetylene, $\mathrm{CO}_{2}$ or other so far unknown relevant compounds, it is of great importance to understand cluster growth reactions which are the link between molecular models and solid-state catalysis.

## 4. Results And Discussion

### 4.1. Synthesis and Reactivity of Ni-E containing clusters

Since alkynes bind well to $\mathrm{Ni}(0)$, various internal and highly symmetric (to avoid polymerization) alkynes such as 3-hexyne (hex), 4-octyne, diphenylacetylene (dpa) are used as additives in order to investigate their influence on various metals and cluster growth via a combinatorial approach. Additionally, the impact of physical parameters as temperature or concentration will be analyzed in-situ using LiquidInjection Field Desorption Ionization mass spectrometric (LIFDI-MS) analysis and Nuclear Magnetic Resonance spectroscopy (NMR). The experimental data will be accompanied by theoretical calculation (DFT).

Note: Parts of this chapter have been published in Chemical Communications in 2022 (P. Heiß, J. Hornung, C. Gemel, R. A. Fischer, Chem. Commun. 2022, 58, 4332-4335). ${ }^{140}$

### 4.1.1. Reactivity studies on $\mathrm{Ni} / \mathrm{Ga}$ as a versatile system influenced by temperature, additive concentration and metal-ratio


$\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}(\mathbf{1})$

$\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}(3)$

$\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}(\mathbf{2})$

$\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4}(4)$

$\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})_{2}\left(\mathbf{1}_{\mathrm{dpa}}\right)$

$\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}(\mathbf{5})$

Figure 14: Overview of the Ni-Ga clusters discussed in this chapter. It has to be noted, these are all calculated structures with ORCA4.0 or ORCA5.0.

### 4.1.1.1. Reactivity studies of 3-hexyne on in-situ formed Ni-Ga compounds



Scheme 6: Overview of the reactions including [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}^{*}$ and 3-hexyne discussed in this chapter. The reactions were investigated depending on additive or temperature control.

Addition of 3-hexyne to a solution of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ in nonpolar solvents as toluene, hexane or cyclohexane forms in-situ the burgundy red adduct complex $\left[\mathrm{Ni}_{2}(\operatorname{cod})_{2}(\right.$ hex $\left.)\right]$ within seconds as already published by Muetterties et al. ${ }^{141}$ Isolation of this compounds failed, so far, since 3-hexyne is a volatile residue and the reaction is reversible due to equilibria processes. Therefore, $\left[\mathrm{Ni}_{2}(\operatorname{cod})_{2}(\right.$ hex $\left.)\right]$ was freshly prepared before treatment with ECp*. In the following section, the reactivity of Ni-Ga clusters towards different alkynes as 3-hexyne and dpa were tested while varying the temperature (room temperature, $60^{\circ} \mathrm{C}$, $90^{\circ} \mathrm{C}$ ) as well as concentration. 3-hexyne and GaCp* were added as 1 m or 0.5 m stock solution either in toluene or hexane.
Reaction of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$, 3-hexyne and $\mathrm{GaCp}^{*}$ in a ratio of $1: 0.5: 1$ at room temperature selectively resulted in the formation of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}(\mathbf{1})$ as confirmed by LIFDI-MS measurements. Neither the variation of the additive concentration nor the GaCp* amount revealed any changes at room temperature (see Experimental Figure 68). It should be noted that the mass spectra obtained by LIFDI MS consisted of further signals that were assigned to parts of the cluster due to instrumentally induced fragmentation. Therefore, the LIFDI mass spectrum of analytically pure 1 showed signals for 1-GaCp* at $\mathrm{m} / \mathrm{z}$ 1012.0188, 1 -GaCp*-hex at $\mathrm{m} / \mathrm{z} 929.9385,1-\mathrm{GaCp}^{*}-2 h e x$ at $\mathrm{m} / \mathrm{z} 845.8494,1-2 G a C p^{*}$ at $\mathrm{m} / \mathrm{z} 807.9739$ and for $1-2 G a C p^{*}$-hex at $\mathrm{m} / \mathrm{z} 721.8676$ besides the product signal at 1218.0633 (calc. $1218.0633 \mathrm{~m} / \mathrm{z}$ ). To confirm instrumentally induced fragmented ion peaks and exclude any further products, collision induced fragmentation can be varied as described by M. Schütz in his dissertation. ${ }^{133}$ RF voltages of CE10.0 are required as the lowest collision energy for detection with this setup (passing the HCD cell) and are used in all experiments unless otherwise stated. A gradual increase of the collision energy (CE) from CE10.0 until 40.0 enabled the identification as product, intermediate or fragment (Figure 15). While the peaks for fragments were only increasing and product peaks were solely decreasing during the increase of the collision energy, intermediate signals are first increasing, but also decreasing. Thus, the signal related to 1 was validated as product signal, while the other peaks were unambiguously assigned as intermediates or fragments.


Figure 15: LIFDI mass spectra of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}(1,1218.0627 \mathrm{~m} / \mathrm{z})$ at different collision energies of the HCD cell (Orbitrap system from Thermo Fisher) enables unambiguous identification of product, intermediate or fragment signals. Following signals/intermediates or fragments were assigned to 1 ( $1218.0633 \mathrm{~m} / \mathrm{z}$, calc. $1218.0633 \mathrm{~m} / \mathrm{z}$ ), 1-GaCp* ( $\mathrm{m} / \mathrm{z}$ 1012.0188), 1-GaCp*-hex at $m / z$ 929.9385, 1-GaCp*-2hex at $m / z$ 845.8494, 1-2GaCp* at $m / z 807.9739$ and for 1-2GaCp*-hex at $\mathrm{m} / \mathrm{z} 721.8676$. RF voltages of CE10.0 are required as the lowest collision energy for detection with this setup and are used in all experiments unless otherwise stated. ${ }^{140}$

Labelling experiments under equal conditions which include $\mathrm{GaCp}{ }^{* E t}$ instead of $\mathrm{GaCp}^{*}$ (one methyl group of the $\mathrm{Cp}^{*}$ ring is exchanged by an ethyl moiety) enable the determination of exact amount of $\mathrm{Cp}^{*}$ groups by shifting of $14 \mathrm{~m} / \mathrm{z}$ each (see Appendix, Figure 68 (7)). Since this spectrum showed a signal shift of $56 \mathrm{~m} / \mathrm{z}$ to $1274 \mathrm{~m} / \mathrm{z}$, it confirms the assumption of $4 \mathrm{Cp}^{*}$ groups $(4 \times 14=56)$.
Considering the fragmentation behavior of $\mathbf{1}$ (loss of $\mathrm{GaCp}^{*}$ and 3 -hexyne) and the labelling experiments, it was possible to identify one sum formula which matches all requirements. Due to fragmentation induced by the instrument, the fragmentation behavior could offer structural information if it is assumed that intermediates or fragments originates from the product. As the spectrum only indicates the cleavage of $\mathrm{GaCp}^{*}$ (in a ratio of 1:1) and 3 -hexyne and the sum formulas include Ga and $\mathrm{Cp}^{*}$ in a ratio of $1: 1$, one can assume that the product still contains intact GaCp w without any $\mathrm{Cp}^{*}$ transfer
 be helpful to add 4-octyne instead of 3 -hexyne to identify the alkyne amount but this was not necessary in this case.
For further verification of the sum formula, it was possible to measure a LIFDI mass spectrum of $\mathbf{1}$ on a JEOL AccuTOF GCx instrument equipped with a LIFDI ion source at the University of Heidelberg without any fragmentation behavior (see Appendix, Figure 101). Although the conclusions drawn from this spectrum were very insightful, the effort was very high including stability tests, driving hours only to name a few and the resolution of the instrument was very low compared to the Orbitrap system. Moreover, the mass spectrometer required high concentrated solution instead of a few milligrams as in
case of the Orbitrap system, whereby it will not be practicable as a standard analytical technique or for standard validation.

## Temperature controlled reactions



Figure 16: LIFDI mass spectra of the reaction [Ni(cod) ${ }_{2}$ ] (1eq.) and $\mathrm{GaCp}^{*}$ (1eq.) at $90^{\circ} \mathrm{C}$ after 6 h in toluene showing the influence of additive on cluster formation: Black trace: with 3-hexyne ( 0.5 eq.) as additive, red: without any additive. Additive containing reaction led to Ni-rich clusters as $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6} \quad(1637.7517 \mathrm{~m} / \mathrm{z} ; \quad \mathrm{F}), \quad\left[\mathrm{Ni}_{8} \mathrm{Ga}_{6}\right]\left(C p^{*}\right)_{6}-2 \mathrm{H} \quad(1693.6507 \mathrm{~m} / \mathrm{z}$, G) and $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}(h e x)(1719.8331 \mathrm{~m} / \mathrm{z})$ while the reaction without any additive favors Ga-enriched clusters as $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ (1649.7700 m/z) and [ $\left.\mathrm{Ni}_{7} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}-2 \mathrm{H}(1706.6904 \mathrm{~m} / \mathrm{z})$. Further signals assigned: $\mathrm{A}:\left[\mathrm{NiGa}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(468.0185 \mathrm{~m} / \mathrm{z})$ for reaction without additive, $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})(468.1774 \mathrm{~m} / \mathrm{z})$ for reaction with additive; $B: \quad\left[\mathrm{Ni}_{6} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4} \quad(1169.7576 \mathrm{~m} / \mathrm{z}) \quad \mathrm{C}$ : $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}-2 \mathrm{H} \quad(1333.8977 \mathrm{~m} / \mathrm{z}) ; \quad \mathrm{D}: \quad\left[\mathrm{Ni}_{5} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{hex}) \quad(1399.9414 \mathrm{~m} / \mathrm{z}) ; \quad E: \quad\left[\mathrm{Ni}_{5} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{hex})_{2}+2 \mathrm{H}$ (1484.8918 m/z). ${ }^{140}$

Increasing the temperature from r.t. to $60^{\circ} \mathrm{C}$ or $90^{\circ} \mathrm{C}$, the obtained LIFDI mass spectra of the reaction [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ] (1eq.), GaCp* (1eq.) and 3-hexyne ( 0.5 eq .) were completely different if compared to each other. While for the reactions at r.t. and $90^{\circ} \mathrm{C}$ a size-focused solution controlled by temperature was observed, the spectrum at $60^{\circ} \mathrm{C}$ was more complex containing more than 20 signals (Figure 17). As described above, the reaction at r.t. revealed the formation of $1(1218 \mathrm{~m} / \mathrm{z})$, while the reaction at $90^{\circ} \mathrm{C}$ showed signals at higher $\mathrm{m} / \mathrm{z}$ values which could be assigned to higher nuclear clusters as $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}-2 \mathrm{H} \quad(1333 \mathrm{~m} / \mathrm{z} ; ~ \mathrm{C}), \quad\left[\mathrm{Ni}_{5} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{hex})_{2}+2 \mathrm{H} \quad(1484 \mathrm{~m} / \mathrm{z} ; \quad \mathrm{E}), \quad\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ ( $1637 \mathrm{~m} / \mathrm{z}$; F) and $\left[\mathrm{Ni}_{8} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}-2 \mathrm{H}(1693 \mathrm{~m} / \mathrm{z} ; \mathrm{G})$. Interestingly, performing the same reaction (at $90^{\circ} \mathrm{C}$ ) without additive, only Ga-enriched clusters as $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}(1647 \mathrm{~m} / \mathrm{z})$ and $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ ( $1708 \mathrm{~m} / \mathrm{z}$ ) were observed (see Figure 16). Accordingly, the signal at $468 \mathrm{~m} / \mathrm{z}$ is related to $\left[\mathrm{NiGa} \mathrm{Na}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ in case of additive-free reaction while it is assigned to $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})$ when using additives. Noteworthy, these two compounds can be clearly distinguished due to its different isotopic pattern.


Figure 17: Left: LIFDI mass distribution of the reaction [Ni(cod) ${ }_{2}$ ] (1eq.), GaCp* (1eq.) and 3-hexyne (0.5eq.) after 5 h at $60^{\circ} \mathrm{C}$ showing a library of clusters in solution. ${ }^{140}$ Highlighted signals are assigned as products and are related to clusters given in the right table. Figure left is reprinted with permission from P. Heiß, J. Hornung, C. Gemel, R. A. Fischer, Chem. Commun. 2022, 58, 4332-4335. Copyright 2022, Royal Society of Chemistry; permission conveyed through Copyright Clearance Center, Inc.

However, if the reaction temperature is decreased to $60^{\circ} \mathrm{C}$, the obtained mass spectrum appeared to be very complex (Figure 17). Considering instrumentally induced fragmentation, the complexity of the mass spectrum $\left(60^{\circ} \mathrm{C}\right)$ could be reduced to 9 different clusters that vary in their nuclearities from $\mathrm{M}_{8}$ to $\mathrm{M}_{13}$ of the formula $\left[\mathrm{Ni}_{\mathrm{a}} \mathrm{Gab}\right]\left(\mathrm{Cp}^{*}\right)_{c}(\text { hex })_{d}$, with $\mathrm{b}=\mathrm{c}$ if the cluster bears 3 -hexyne. Interestingly, when performing the reaction without additives it directly led to $M_{12} / M_{13}$ clusters $\left[\mathrm{Ni}_{a} \mathrm{Gab}_{\mathrm{b}}\right]\left(\mathrm{Cp}^{*}\right)_{6}(a=6,7 ; b=$ 6,$7 ; a+b=12,13$ ) (see Appendix). Similarly to the r.t. reaction, most of the clusters bearing 3 -hexyne have a Ga:Cp* ratio of 1 indicating an intact $\mathrm{GaCp}^{*}$ ligand which is in contrast to the $\mathrm{M}_{12} / \mathrm{M}_{13}$ clusters having a $\left(\mathrm{NiCp}^{*}\right)_{6}$ shell.
Summarizing the temperature dependent studies starting from $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right],\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}(\mathbf{1})$ could be seen as kinetically metastable cluster, which is initially formed and undergoes cluster growth reaction upon treatment at higher temperatures. Further, size and selectivity could be controlled during cluster synthesis due to different temperatures. Moderate (r.t.) and high temperatures ( $90^{\circ} \mathrm{C}$ ) led to size-focused reaction solutions revealing "smaller" NiGa clusters $\left(\mathrm{M}_{8}\right)$ at lower temperatures while high temperatures formed higher nuclear clusters with up to 14 metals. However, a large Ni/Ga cluster library was obtained when reacting at $60^{\circ} \mathrm{C}$. Since the reaction without additives directly led to the formation of $\mathrm{M}_{13}$ clusters, it is possible to trap intermediates of such cluster growth reactions due to addition of alkyne which allows a deeper insight in reaction mechanisms to understand cluster growth. In particular, the $\mathrm{M}_{13}$ clusters consists of a $\left(\mathrm{NiCp}^{*}\right)_{6}$ shell and a [ $\mathrm{Nix}_{x} \mathrm{Gay}_{y}$ ] core. In case of additive-containing reactions, it is proposed to hamper $\mathrm{Cp}^{*}$ transfer reactions by blocking the open-coordination site with the alkyne binding to the nickel center. The additive could further activate the transition metal center as supported by observing Ni-rich cluster in the reactions with additives which is potentially advantageous for catalytic applications (as nickel is the catalytically active metal).

Additive controlled reactions: Different equivalents of GaCp* and 3-hexyne


|  | Experimental | Cluster |
| :--- | :--- | :--- |
| A $^{1}$ | 945.98 | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{3}-2 \mathrm{H}$ |
| $\mathrm{B}^{2}$ | 1030.05 | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{4}$ |
| $\mathrm{C}^{3}$ | 1152.02 | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}$ |
| D | 1194.21 | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{6}$ |
| E | $\mathbf{1 2 3 4 . 0 9}$ | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}$ |
| F | $\mathbf{1 2 9 2 . 0 2}$ | $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}$ |
| G | 1579.86 | $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ |
| H | 1637.78 | $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ |
|  | $\mathbf{1 6 4 9 . 7 7}$ | $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}+\mathrm{H}$ |

${ }^{1}$ Fragment of D: -3hex; ${ }^{2}$ Fragment of D: -2hex; ${ }^{3}$ Fragment of D: -hex

Figure 18: Left: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ and $\mathrm{GaCp}^{*}$ with different equivalents 3-hexyne at $60{ }^{\circ} \mathrm{C}$ in toluene. Right: Overview of assigned clusters in the spectra left. Sum formulas assigned as products are given in bold.

Besides varying the temperature, the influence of different equivalents of the additive on the cluster formation was studied. Performing the reaction of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}^{*}$ and 3-hexyne at room temperature, 1 was formed as the most favored product regardless of the additive and GaCp* amount. Neither a gradual increase from 1 to 5 equivalents of $\mathrm{GaCp}^{*}$ while maintaining Ni:hex ratio to 1:0.5, nor increasing the additive amount from 0.5 to 2.5 equivalents while maintaining the Ni:Ga ratio to 1 had an impact on the formation of $\mathrm{Ni}-\mathrm{Ga}$ clusters and only revealed 1 as the kinetically favored product at room temperature. Nevertheless, conducting these studies (variation of 3-hexyne amount) under elevated temperatures, the changes in the mass spectra can be seen in Figure 18. Noteworthy, when looking at the obtained mass spectra, the trend of cluster formation is clearly indicated. Low concentrations of additive ( 0.5 and 1.0 eq.; black and red trace) led to a large cluster library including higher nuclear cluster as $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6},\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6},\left[\mathrm{Ni}_{6} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ and $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}$, while in contrast high additive concentrations up to 6 eq. of 3-hexyne, related to Ni , resulted in smaller clusters as $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})_{6}$ and $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]_{\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}}$ with high 3 -hexyne content, but low Ga amount (blue and green trace). Particularly, when looking at the signal $E$ in the figure above, which was assigned to $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}$, it was a prominent peak at lower additive amounts while it is gradually decreased when increasing the additive amount. Contrary behavior was obtained for the signal D which was related to $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})_{6}$ : it is almost undetectable at low additive concentrations but is the main peak at high concentrations. However, such behavior is not surprising, when considering the Ni-Hex ratio. While signal $E$ in Figure 18 features a hex-Ni ratio of 0.8 , it is increased to 1.2 at signal $D$ which is equal to high 3-hexyne amount. Besides signals $A, B$ and $C$ which are attributed to fragment peaks, signal D assigned as $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{6}$, was preferentially formed with high additive amount. In conclusion,
medium-sized clusters are obtained due to additive control. While high additive amounts favored cluster with $\mathrm{M}_{7}-\mathrm{M}_{13}$, lower additive concentrations preferred the formation of bigger $\mathrm{Ni}-\mathrm{Ga}$ clusters.

Performing similar reactions at $90^{\circ} \mathrm{C}$, the same trend is observed. While the reaction with 0.5 eq. 3-hexyne mostly formed $\left[\mathrm{Ni}_{8} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}-2 \mathrm{H}(1693 \mathrm{~m} / \mathrm{z})$ and $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}(1637 \mathrm{~m} / \mathrm{z})$, the reaction with 1 eq. hex led to hexyne-containing $\mathrm{M}_{10}$ clusters as $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{hex})_{2}(1484 \mathrm{~m} / \mathrm{z})$ and [ $\mathrm{Ni}_{6} \mathrm{Ga}_{4}$ ] $\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}(1333 \mathrm{~m} / \mathrm{z})$ (see Appendix Figure 70). Thus, the above-mentioned assumption of additive controlled cluster formation is supported. Moreover, a general trend is observed: the higher the 3-hexyne concentration, the smaller are the obtained clusters while increasing the additive amount in the respective cluster core.

### 4.1.1.2. Diphenylacetylene as electron-rich, sterically demanding and solid additive controlling Ni -Ga cluster formation



Scheme 7: Overview of the herein reported products obtained during the reaction of [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ], GaCp* and dpa dependent on the metal amount (variation of GaCp*, left) and additive concentration (right).

Noteworthy, since 3-hexyne has its boiling point at $82^{\circ} \mathrm{C}$, further increase of temperature is therefore not reasonable and possible. By using another heavier alkyne, in this case diphenylacetylenes (dpa), this limitation can be extended. Additionally, the influence of electronic and steric effects of different alkynes on cluster formation can be investigated. In accordance with 3-hexyne, the influence of dpa on $\mathrm{Ni}-\mathrm{Ga}$ cluster formation was studied varying concentration and temperature. The reactions were monitored by in-situ LIFDI-MS measurements and additionally analyzed by NMR spectroscopy in parts of the reactions. Being poorly soluble in hexane, the reactions including dpa are performed in toluene unless otherwise stated.
Addition of 0.5 eq. dpa to dissolved $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ (1 eq.) in toluene led to the formation of $\left[\mathrm{Ni}_{2}\right](\mathrm{cod})_{2}(\mathrm{dpa})$ within a few minutes as also described for 3-hexyne. Nonetheless, this experiment could already show that dpa is less reactive and requires longer reaction times than 3-hexyne, which forms [ $\left.\left.\mathrm{Ni}_{2}\right]^{(c o d}\right)_{2}$ (hex)
within a few seconds. After the formation of $\left[\mathrm{Ni}_{2}\right](\mathrm{cod})_{2}(\mathrm{dpa})$, which was visually determined by the dark red color (usually after $2-3$ minutes), the respective quantities of GaCp* were added as 0.5 M or 1 m solution in toluene and reacted at room temperature. The GaCp* amounts varied from $0.5,1,2,3$ and 4 eq. related to nickel (Figure 19). Interestingly, with a Ni-Ga stoichiometry of 2 ( 0.5 eq . GaCp*), clusters could be obtained at higher m/z values: $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})_{2}\left(1410 \mathrm{~m} / \mathrm{z}, \mathrm{H} ; \mathbf{1}_{\mathrm{dpa}}\right),\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ ( $1384 \mathrm{~m} / \mathrm{z}, \mathrm{G} ; 3$ ) and $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right](\mathrm{Cp})_{2}(\mathrm{dpa})_{4}(1356 \mathrm{~m} / \mathrm{z}, \mathrm{F} ; 4)$. Considering both dpa and $\mathrm{GaCp}^{*}$ as ligands, each of the obtained clusters feature a $\mathrm{Ni}_{4}$ core carrying six ligands comprising dpa and GaCp*, only varying in their ratio to each other. It is proposed that $\mathrm{GaCp}^{*}$ as well as dpa have similar bonding energies of $\mathrm{Ni}-\mathrm{L}$ and are, as a consequence, competing ligands which results in a mixture of clusters with different $\mathrm{GaCp}^{*}$ :dpa ratios. Further, the spectrum revealed the formation of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}$
 [ $\mathrm{Ni}_{4} \mathrm{Ga}_{2}$ ] $\left.\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{2}(999 \mathrm{~m} / \mathrm{z}, \mathrm{B})$. While B and D appeared to be fragments, $C$ and $E$ were presumably related a product peak as they vary in intensities with various GaCp* amount. Since signal A assigned as $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})$ is varying randomly, it is assumed to be induced by collision of fragmented ions.


Figure 19: Left: LIFDI mass spectra of the reaction [Ni(cod)2] (1 eq.) with dpa ( $0.5 \mathrm{eq}$. .) and different equivalents of $\mathrm{GaCp}^{*}$ in toluene at room temperature. Right: Cluster assignment of obtained compounds. Sum formulas related to products are given in bold.

The gradual increase of $\mathrm{GaCp}^{*}$ from 0.5 eq. to max. 4 eq. caused the clusters $\mathrm{C}(1025 \mathrm{~m} / \mathrm{z})$ and E $(1204 \mathrm{~m} / \mathrm{z})$, related to $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{1}$ and $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]^{3}\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}$, to be formed preferentially. Higher nuclear clusters as observed for low Ga-concentrations were nearly not detectable. Considering the sum formulas of both clusters, they did not vary in the $\mathrm{GaCp}^{*}$ but in the dpa amount included in the clusters, potentially as a result of stronger Ni -Ga bonding. Indeed, GaCp * donates electron density from the free electron pair to Ni requiring strong $\sigma$-donation and $\pi$-backdonation in contrast to dpa which has $\pi$-donating/accepting character resulting in a stronger Ni-dpa bond compared to Ni-Ga. Thus, it is assumed that dpa-rich NiGa clusters can only be formed with dpa-excess.

Gradually raising the dpa-concentration from $0.5,2,4$ and 8 eq. at room temperature while maintaining the $1: 1 \mathrm{Ni}$ :Ga ratio resulted in less dependency on additive concentration (Appendix, Figure 71). While 0.5 eq. dpa led to the formation of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}(1204 \mathrm{~m} / \mathrm{z})$ and its fragment (-dpa; $\left.1025 \mathrm{~m} / \mathrm{z}\right)$ as described above (Figure 19, red trace), the use of an excess of dpa (above 2 eq.) only formed Ni -organyls at small $\mathrm{m} / \mathrm{z}$ values that did not exhibit bound $\mathrm{GaCp}^{*}$. The $\mathrm{Ni}-\mathrm{dpa}$ compound [ $\mathrm{Ni}_{3}$ ] $(\mathrm{dpa})_{2}(\mathrm{cod})_{2}$ at $748 \mathrm{~m} / \mathrm{z}$ and its fragment (-cod; $640 \mathrm{~m} / \mathrm{z}$ ) was one of the products identified expected to be the kinetically preferred compound and possibly serve as a building block for higher Ni-Ga cluster compounds.
However, increasing the temperature to $60^{\circ} \mathrm{C}$, the reaction progress is different compared to room temperature reaction. Similar to r.t., low dpa concentration ( 0.5 eq .) led to the formation of already mentioned $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}(1204 \mathrm{~m} / \mathrm{z})$, but also to higher m/z values at 1384 and $1553 \mathrm{~m} / \mathrm{z}$ assigned to $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ and $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})_{1}$, respectively (see Appendix, Figure 72). Increasing the additive amount to 1 and 2 eq., the most preferred product is identified as $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}(1534 \mathrm{~m} / \mathrm{z}$; 5). In contrast, further increase to 4 eq. (equivalent to excess dpa) resulted in similar behavior as at room temperature reaction: only Ni-organyls, containing $\mathrm{Ni}, \mathrm{Cp}^{*}$ and dpa, were identified. When the temperature was increased to $90^{\circ} \mathrm{C}$, two major signals which are identified as products and two minor signals were detected: [ $\mathrm{Ni}_{6} \mathrm{Ga}_{5}$ ] $\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})_{1}$ at $1553 \mathrm{~m} / \mathrm{z}$ and a mixture consisting of $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ and $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ at 1637 and $1647 \mathrm{~m} / \mathrm{z}$ were obtained as major peaks while a mixture of $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}(\mathrm{dpa})_{1}$ at $1815 \mathrm{~m} / \mathrm{z}$ and $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}(\mathrm{dpa})_{1}$ at $1825 \mathrm{~m} / \mathrm{z}$ were only detected as small peaks, although it is possible that the mixture at $1637 / 1647 \mathrm{~m} / \mathrm{z}$ is a result of dpacleavage during ionization.
In conclusion, higher temperature improved the formation of Ni-Ga-dpa compounds while enhancing the additive-activation. Nonetheless, an excess of dpa inhibited the formation of Ni-Ga compounds due to the occupation of the vacant coordination sites at the nickel center and stronger Ni-alkyne bonding compared to Ni-Ga. Additionally, a reaction between $\mathrm{GaCp}^{*}$ and dpa was suspected, since Cp *-Ni-L compounds were observed, where GaCp* must serve as a $\mathrm{Cp}^{*}$-supplier. In comparison to 3-hexyne, dpa is a stronger $\pi$-acceptor while 3-hexyne is a stronger $\pi$-donor induced by +l -effect of the alkyl groups. Thus, dpa-containing Ni-Ga compounds consist of a cluster library of the same Ni-core which is limited by the $\sigma$-donor properties of $\mathrm{GaCp}^{*}$. In contrast, 3-hexyne, which is by itself a $\sigma$-donor, led to a specific cluster composition.

### 4.1.1.3. Reactivity of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ (1) towards $\mathrm{AICp}^{*}, \mathrm{PR}_{3}$ and diphenylacetylene



Scheme 8: Overview of herein discussed products of the reactivity test of 1 with $A^{*} C p^{*}, P R_{3}$ and dpa.

The following chapter focuses on the reactivity of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}(\mathbf{1})$ which could possibly enhance the vacuo stability of the core structure and thus, improve crystallization. Further, still reactive centers could be revealed linking molecular with solid state chemistry. Therefore, $\mathbf{1}$ was converted with different amounts of $\mathrm{AlCp}^{*}$ and $\mathrm{PR}_{3}(\mathrm{R}=\mathrm{Et}, \mathrm{Ph})$ being isolobal to $\mathrm{GaCp}^{*}$ as well as dpa to possibly exchange the vacuo sensitive 3 -hexyne ligand by a stronger binding alkyne.

## Reactivity of 1 towards AICp*

In order to avoid cluster agglomeration resulting in $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right) 6$ and $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right) 6$ at high temperatures (up to $90^{\circ} \mathrm{C}$ ), the reaction including $\mathrm{AICp}{ }^{*}$ was conducted at $40^{\circ} \mathrm{C}$ as AICp * is insoluble and not reactive at room temperature. 1 eq . of $\mathrm{AlCp}^{*}$, related to Ni , was added to freshly prepared $\mathbf{1}$ in hexane. The mixture was heated for several hours at $40^{\circ} \mathrm{C}$ and in-situ monitored by LIFDI-MS measurements. Indeed, $\mathbf{1}$ is reactive towards $\mathrm{AlCp}^{*}$ forming $\left[\mathrm{NiGaAl}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(615.1554 \mathrm{~m} / \mathrm{z})$ as major product after one and two days, respectively. After one day, the signal resulting from $\mathbf{1}(1218 \mathrm{~m} / \mathrm{z})$ has fully disappeared and aluminum-containing compounds as $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{1} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})$ and $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{1} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}^{*}\right)(\text { hex })_{2}$ were obtained (see Figure 20). In contrast to the reactions only including $\mathrm{GaCp}^{*}$, the interpretation of the peaks originating from the reactions with both $\mathrm{AlCp}^{*}$ and $\mathrm{GaCp}^{*}$ is more complex: two 3-hexyne moieties ( $164 \mathrm{~m} / \mathrm{z}$ ) have similar molecular masses than AICp* ( $162 \mathrm{~m} / \mathrm{z}$ ) and the latter usually releases $\mathrm{Cp}^{*}$ during instrumental ionization. Further, some product signals overlapped with fragment peaks originating from 1. Thus, the assignment of the following compounds must be handled with carefulness.


Figure 20: Exchange reaction of 1 with AICp* monitored by in-situ LIFDI MS measurements. Left: LIFDI mass spectrum of the reaction of 1 with 1 eq. AlCp* (related to Ni) in hexane after one day at $40^{\circ} \mathrm{C}$. Right: Table of experimentally observed $\mathrm{m} / \mathrm{z}$ values and assigned clusters.

Nevertheless, this experiment showed the reactivity of $\mathbf{1}$ towards $\mathrm{AlCp}^{*}$ by substitution of $\mathrm{GaCp}^{*}$. Since the reaction resulted in both Al and Ga containing complexes, it appeared that an excess of $\mathrm{AlCp}^{*}$ is required. However, this could lead to cluster degradation and thus, to the formation of inert $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{4}\right]$. In addition, the formation of $\left[\mathrm{NiGaAl}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ was observed as evidenced by single crystal X-ray diffraction and MS measurements ( $615 \mathrm{~m} / \mathrm{z}$, $\left.\left[\mathrm{NiGaAl}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\right)$. It is proposed that $\left[\mathrm{NiGaAl}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ is a result of unreacted $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]$ and can be seen as a stabilized and reactive $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}\right]$ fragment as proposed from Steinke et al. ${ }^{82}$ An excess of AICp* seems to be required to react off the remaining $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]$, which is left unreacted during the in-situ synthesis of $\mathbf{1}$.
In summary, it is possible to substitute $\mathrm{GaCp}^{*}$ with AlCp * ligands in Ni-E clusters or compounds under mild conditions. Such ligand substitution reactions have already been published by Fischer et al. in 2005 for $\left.\left[\mathrm{TM}_{2}\left(\mathrm{GaCp}^{*}\right)\right)_{5}\right]^{73}$ In this work, they performed ligand exchange reactions in the homoleptic $\left.\left[\mathrm{TM}_{2}(\mathrm{GaCp})^{*}\right)_{5}\right]$ complexes with $\mathrm{M}=\mathrm{Pd}, \mathrm{Pt}$, leading to the substitution of the two terminal and/or the three bridging $\mathrm{GaCp}^{*}$ as mentioned in the introduction. While in the case of Pd only the bridging positions were exchanged, in the case of the Pt analogue it was possible to substitute all five positions with AICp*. Therefore, such substitution reactions could provide additional information about binding modes in the corresponding compound. However, the assignment of the obtained clusters remains complex and requires a combination of different analytical methods followed by labeling experiments.

## Reactivity of 1 towards $\mathrm{PEt}_{3}$ and $\mathrm{PPh}_{3}$

As known from previous studies, ECp * ligands can either bind terminal or bridging while phosphines favor terminal positions due to their $\sigma$-donor properties. ${ }^{73}$ Further, phosphines can be applied as additives in nanoparticle synthesis to control particle size. ${ }^{50}$ Thus, the reactivity of $\mathbf{1}$ could potentially lead to further cluster growth reactions, but also reveal some bonding information. In order to use electronically as well as sterically different phosphines, either PEt 3 or $\mathrm{PPh}_{3}$ was added to a freshly prepared solution of $\mathbf{1}$ in toluene- $d_{8}$ or toluene. To avoid cluster growth reactions induced by temperature, the reactions were conducted at room temperature. The reaction progress was monitored by in-situ LIFDI MS and ${ }^{1} \mathrm{H} /{ }^{31} \mathrm{P}$ NMR spectroscopic measurements.

1 was used as synthesized without any workup and $\mathrm{PEt}_{3}$ was added via a syringe to the NMR tube using glovebox technique. Already after two hours at r.t., the signals in the respective mass spectrum related to 1 has disappeared while phosphine containing signals appeared. Besides the typical Ni-phosphine signals $\left[\mathrm{Ni}\left(\mathrm{PEt}_{3}\right)_{3}\right]$ and $\left[\mathrm{Ni}\left(\mathrm{PEt}_{3}\right)_{2}\right]$ at $412.2065 \mathrm{~m} / \mathrm{z}$ (calc. $412.2088 \mathrm{~m} / \mathrm{z}$ ) and $294.1163 \mathrm{~m} / \mathrm{z}$ (calc. $294.1176 \mathrm{~m} / \mathrm{z})$, also $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{PEt}_{3}\right)(\text { hex })_{2}(1044.1614 \mathrm{~m} / \mathrm{z}$; calc. $1044.1606 \mathrm{~m} / \mathrm{z}$ ) was obtained which can be seen as a one-substitution product of 1 . Due to the better ionizability, homoleptic Ni-P signals appear to be the most favored product. Especially in this context, LIFDI MS must not be considered as a quantitative method. Therefore, ${ }^{31} \mathrm{P}$ NMR measurements were conducted to identify the amount of possible products and potentially assign literature known compounds. The ${ }^{31} \mathrm{P}$ NMR spectrum, depicted in Figure 21, revealed signals for $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{1}\left(\mathrm{PEt}_{3}\right)_{3}\right]$ ( 16.6 ppm ) as the major product and $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{PEt}_{3}\right)_{2}\right]$ ( 31.3 ppm ) as well as a small broad peak for free $\mathrm{PEt}_{3}(-19.8 \mathrm{ppm})$ as already published by Fischer et al. ${ }^{90}$ These findings are in accordance with the signals originating from the MS.


Figure 21: Enlarged ${ }^{31} P$ NMR spectrum of the reaction $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(C p^{*}\right)_{4}(h e x)_{2}$ with 3 eq. $P E t_{3}$ showing free $P E t_{3}(-19.98 \mathrm{ppm})$, $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right](16.5 \mathrm{ppm})$ and $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}\left(P E t_{3}\right)_{2}\right](31.3 \mathrm{ppm})$ as literature known compounds.

Besides the literature known compounds, small signals at 26.3, 25.1 and 24.9 ppm were detected at the ${ }^{31}$ P NMR spectrum hinting to new Ni-P compounds. Additionally, the ${ }^{1} \mathrm{H}$ NMR spectrum showed new signals at 2.90 ppm (hex), $1.96 \mathrm{ppm}\left(\mathrm{GaCp}^{*}\right)$ and 1.52 ppm (hex or $\mathrm{PEt}_{3}$ ), beside the already assigned known compounds, which can be attributed to $\left[\mathrm{Ni}_{2}\left(\mathrm{GaCp}^{*}\right)_{3}(\mathrm{~L})_{2}\right]$ with L being 3-hexyne or $\mathrm{PEt}_{3}$. Precise signal assignment and integration was not possible as most of the peaks overlap with each other. Both, ${ }^{31} \mathrm{P}$ and ${ }^{1} \mathrm{H}$ NMR spectra as well as the MS measurements led to the assumption of mononuclear Ni-P compounds as the major product when treating 1 with $\mathrm{PEt}_{3}$. Nevertheless, 1 is reactive towards $\mathrm{PEt}_{3}$ forming $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{PEt}_{3}\right)(\text { hex })_{2}$ in small quantities. Reaction of 1 at lower temperature could provide the before-mentioned $\mathrm{Ni}_{4}$ compound as major product while affecting the formation of the mononuclear $\mathrm{Ni}-\mathrm{P}$ complexes as the thermodynamically favored product. Further, $\mathrm{PEt}_{3}$ is able to deconstruct the $\mathrm{Ni}_{4}-$ framework of 1 at r.t., which means that lower temperature lowers the activity of $\mathrm{PEt}_{3}$ and thus, potentially hampers $\mathrm{Ni}-\mathrm{Ni}$ bond breaking.

As an electronically different and sterically more demanding phosphine, $\mathrm{PPh}_{3}$ is further tested towards the reactivity of 1 . Thus, 3 eq. of $\mathrm{PPh}_{3}$ were added to freshly prepared 1 in toluene- $\mathrm{d}_{8}$ or toluene and in-situ monitored by LIFDI MS and NMR spectroscopic measurements. Dissolved 1 was used without any further workup. After 2.5 h at room temperature, the signal related to 1 at $1218 \mathrm{~m} / \mathrm{z}$ has already
disappeared while signals at $614.1051 \mathrm{~m} / \mathrm{z}$ (not yet identified) and $582.1160 \mathrm{~m} / \mathrm{z}$ assigned to $\left[\mathrm{Ni}\left(\mathrm{PPh}_{3}\right)_{2}\right.$ ] (calc. $582.1172 \mathrm{~m} / \mathrm{z}$ ) were rising. Besides mononuclear Ni-compounds also phosphine analog of $\mathbf{1}$ is observed where one $\mathrm{GaCp}^{*}$ is substituted by one $\mathrm{PPh}_{3}$ ligand resulting in $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{PPh}_{3}\right)(\text { hex })_{2}$ ( $1274.1140 \mathrm{~m} / \mathrm{z}$; calc. $1274.1132 \mathrm{~m} / \mathrm{z}$ ). As $\mathrm{PPh}_{3}$ favors a terminally bound position on Ni centers, mononuclear and small complexes are preferred as the kinetically favored product formed under cluster deconstruction. ${ }^{31} \mathrm{P}$ NMR spectroscopic studies supported these findings due to the observation of major signals referring to $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{PPh}_{3}\right)_{2}\right](40.4 \mathrm{ppm})$ and free $\mathrm{PPh}_{3}(-5.3 \mathrm{ppm})$. Besides the known compounds, further signals at 39.4 ppm and 32.7 ppm were detected in the ${ }^{31} \mathrm{P}$ NMR spectrum (see Figure 22), in which the obtained compound should, when comparing with literature data, have similar electronically environment as $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{PPh}_{3}\right)_{2}\right]\left(40.6 \mathrm{ppm}^{91}\right)$ or $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{PEtt}_{3}\right)_{2}\right]\left(31.3 \mathrm{ppm}^{90}\right)$.


Figure 22: Enlarged ${ }^{31} P$ NMR spectrum of the reaction $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}$ with 2.5 eq. $\mathrm{PPh}_{3}$ showing free $P P h_{3}(-5.3 \mathrm{ppm})$ and $\left.\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}(P \mathrm{Ph})_{3}\right)_{2}\right](40.5 \mathrm{ppm})$ as literature known compounds.

It is proposed that $\mathrm{PPh}_{3}$ is terminal bound to a Ni-center which is surrounded by GaCp*. The ratio of $\mathrm{GaCp} *: \mathrm{PPh}_{3}$ is estimated to be $1: 1$ (close to 30 ppm in ${ }^{31} \mathrm{P} \mathrm{NMR}$ ) or $3: 1$ (predicted in the range of 40 ppm in ${ }^{31} \mathrm{P} N M R$ ). These values are referred to mononuclear, literature known Ni-P complexes of the formula $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{n}\left(\mathrm{PEt}_{3}\right)_{4-n}\right](\mathrm{n}=1-3) .{ }^{90}$ Additionally, the ${ }^{1} \mathrm{H}$ NMR spectrum revealed signals related to free cod (5.54, 2.21 ppm ), free 3-hexyne ( $2.01,1.01 \mathrm{ppm}$ ) and $\mathrm{Cp}{ }^{*} \mathrm{H}$. Although, no signals for 1 or free GaCp* were detected, new signals for $C p^{*}$ in the range typically for $G a C p^{*}$ were observed: 1.91, 1.90 and 1.82 ppm with the ratio 2:2:1. Considering $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{PPh}_{3}\right)(\mathrm{hex})_{2}$, it is possible that GaCp * has two different environments in the complex with two $\mathrm{GaCp}^{*}$ being identical and one $\mathrm{GaCp}^{*}$ being different. Further, a second $\mathrm{Ni}-\mathrm{Ga}-\mathrm{PPh}_{3}$ compound has been formed in $50 \%$ yield related to $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{PPh}_{3}\right)(\text { hex })_{2}$ since the signals of the ${ }^{1} \mathrm{H}$ as well as the ${ }^{31} \mathrm{P}$ were close to $1: 1$ besides the mononuclear compounds.
In conclusion, similar to $\mathrm{PEt}_{3}, \mathrm{PPh}_{3}$ was able to substitute $\mathrm{GaCp}^{*}$ in 1. However, $\mathrm{PPh}_{3}$ only exchanged one GaCp* while $\mathrm{PEt}_{3}$ was able to substitute two GaCp * moieties. With a cone angle of $145^{\circ}, \mathrm{PPh}_{3}$ is more sterically demanding than $\mathrm{PEt}_{3}$ which exhibits a cone angle of $132^{\circ} .{ }^{89}$ Such behavior has also been observed for mononuclear compounds of the formula $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{n}\left(\mathrm{PR}_{3}\right)_{4-n}\right](\mathrm{R}=\mathrm{Ph}, \mathrm{Et} ; \mathrm{n}=1-3) .90-$ ${ }^{91}$ It was only possible to synthesize the whole range of compounds with $\mathrm{n}=1-3$ in case of $\mathrm{PEt}_{3}$, while the formation of other compounds than $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{PPh}_{3}\right)_{2}\right]$ has never been observed for $\mathrm{PPh}_{3}$ due to steric effects. Besides that, also electronic properties of $\mathrm{PR}_{3}$ influenced the cluster stability. As mentioned before, $\mathrm{PEt}_{3}$ substituted two GaCp* ligands while $\mathrm{PPh}_{3}$ only exchanged one ligand. As the
stronger $\sigma$-/ $\pi$-donor ligand, $\mathrm{PEt}_{3}$ was able to stabilize the cluster core. In contrast, due to the phenyl moieties, $\mathrm{PPh}_{3}$ is a better $\pi$-acceptor ligand. Since $\mathrm{PR}_{3}$ ligands are usually terminal bound to Ni-clusters, the reaction of 1 with $\mathrm{PR}_{3}$ revealed unsaturated Ni-centers which reassembled under cluster degradation and caused $\mathrm{Ni}_{1}$-complexes.
Summarizing, $\mathrm{PR}_{3}$ can be used to substitute GaCp * ligands in clusters as previously observed for smaller compounds as $\left[\mathrm{M}_{2}\left(\mathrm{GaCp}^{*}\right)_{5}\right](\mathrm{M}=\mathrm{Pd}, \mathrm{Pt})$. Only one or two GaCp * ligands were exchanged, due to steric effects. Further, $\mathrm{PR}_{3}$ was able to act as a second additive as known for nanoparticles. Due to the ability to substitute ECp* ligands, $\mathrm{PR}_{3}$ can be used in cluster synthesis to control cluster size and distribution of the metals enriching Ni and reduce the Ga compound in Ni-Ga clusters, respectively.

## Reactivity of 1 towards diphenylacetylene

1 could not be crystallized, yet, possibly due to high 3-hexyne volatility, less bonding energy to Ni and temperature sensitivity. Exchanging the 3-hexyne moieties by a stronger binding alkyne as dpa could improve crystallization and lead to stable crystals. 1 was in-situ synthesized and further used without any workup procedure. 1 eq. of dpa was added and the reaction progress was monitored in-situ using mass spectrometric measurements. After two days, the mass spectrum showed two intense signals at $1438 \mathrm{~m} / \mathrm{z}$ and $1178 \mathrm{~m} / \mathrm{z}$ which were assigned to $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})(\mathrm{dpa})_{4}$ and its fragment $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{3}$ as the major products (Figure 23). Simultaneously, the disappearance of the signal for 1 allows to assert its conversion. In addition, signals for the fully hexyne-exchanged product $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}(1178 \mathrm{~m} / \mathrm{z})$ and dimerized dpa were found. In contrast to 1, the observed compounds contain more ligands than 1, if considering dpa and GaCp* as ligands, which imply the rearrangement of the cluster under treatment with dpa.


|  | Experimental <br> $[\mathrm{m} / \mathrm{z}]$ | Cluster |
| :--- | :--- | :--- |
| A | 607.1440 | $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{2}$ |
| B | 721.8720 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{1}-4 \mathrm{H}$ |
| C | 807.9782 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{2}$ |
| D | 929.9355 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{1}$ |
| E | 1178.0631 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{3}$ |
| F | $\mathbf{1 2 1 8 . 0 6 7 5}$ | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}(\mathbf{1})$ |
| $\mathbf{G}$ | $\mathbf{1 4 3 8 . 2 1 5 5}$ | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{1}(\mathrm{dpa})_{4}$ |
| $\mathbf{H}$ | $\mathbf{1 5 3 4 . 2 1 0 7}$ | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}$ |

Figure 23: LIFDI mass spectra of the reaction of 1 (black trace) with $1 \mathrm{eq} . \mathrm{dpa}$ (red trace) after two days at $40^{\circ} \mathrm{C}$ in toluene. The assignment of the signals is given in the table right.

As previously mentioned, dpa is the stronger ligand compared to 3-hexyne as well as GaCp*. Therefore, the substitution of 3 -hexyne as well as $\mathrm{GaCp}^{*}$ was expected in contrast to intended hex $\rightarrow$ dpa exchange. As a result, introducing dpa in such clusters led to a unchanged Ni-core, but in a different Ni environment. In a catalytic context, the binding of the additive to the catalytically active metal enhances catalytic activity as the Ni-centers become more accessible upon reaction with dpa.

### 4.1.1.4. Reactivity of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right) 4\right]$ towards alkynes

The following chapter summarizes parts of the bachelor's thesis from Anna-Julia Herold supervised by this author. The idea and the concept for the performed experiments originated from this author.


Scheme 9: Overview of the herein discussed products which are formed during the reaction of [ $\mathrm{NiGa}_{4}$ ] $\left(\mathrm{Cp}^{*}\right)_{4}$ with 3-hexyne (left) or diphenylacetylene (dpa; right).

Contrary to the published assumption that $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right) 4\right]$ is kinetically inert ${ }^{82}$, it unexpected appeared to be reactive to both temperature and alkynes. Therefore, the reactivity was systematically studied by varying the temperature as well as the alkyne amount. The mixtures were analyzed by in-situ LIFDI-MS.

Reactivity of $\left[\mathrm{Ni}(\mathrm{GaCp})_{4}\right]$ towards 3-hexyne


|  | Experimental <br> $[\mathrm{m} / \mathrm{z}]$ | Cluster |
| :--- | :--- | :--- |
| A | 327.1606 | $[\mathrm{Ni}]\left(\mathrm{Cp}^{*}\right)_{2}-\mathrm{H}$ |
| B | 468.0182 | $\left[\mathrm{NiGa}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ |
| C | 1637.7740 | $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ |
| D | 1647.7824 | $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}-\mathrm{H}$ |
| E | 1691.6897 | $\left[\mathrm{Ni}_{8} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}-4 \mathrm{H}$ |
| F | 1705.7014 | $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}-3 \mathrm{H}$ |

Figure 24: LIFDI mass spectrum of $\left[\mathrm{Ni}\left(\mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}\right.$ after 4.5 hours at $60^{\circ} \mathrm{C}$ in toluene. The assignment of the signals is given in the table right.

The first part deals with the reactivity of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ and 3-hexyne in toluene or hexane at room temperature and $60^{\circ} \mathrm{C}$ with different equivalents of alkyne ( 4 and 6 eq.). Before starting with the reactivity towards alkynes, the stability of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ at different temperatures was tested. Already after dissolving $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right) 4\right]$ in toluene, a color change from orange to brown was recognized. Heating the mixture for several hours at $60^{\circ} \mathrm{C}$, the mass spectrum, depicted in Figure 24, showed the slow
formation of higher nuclear clusters as $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}(1647 \mathrm{~m} / \mathrm{z})$ and $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}(1637 \mathrm{~m} / \mathrm{z})$ from $\left[\mathrm{NiGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ which is indicated by the signal at $468 \mathrm{~m} / \mathrm{z}\left(\left[\mathrm{NiGa}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\right)$. As known from previous studies of our group ${ }^{132,142}$, the $\mathrm{M}_{13}$ clusters reveal an octahedral $\left(\mathrm{NiCp}^{*}\right)_{6}$ shell which stabilizes the $\mathrm{M}_{7}$ core either consisting of $\mathrm{NiGa}_{6}$ or $\mathrm{Ga}_{7}$. In this case, the $\mathrm{Cp}^{*}$ has to be transferred from Ga to Ni which is evidenced by the observation of $[\mathrm{Ni}]\left(\mathrm{Cp}^{*}\right)_{2}$ at $327 \mathrm{~m} / \mathrm{z}$ in the mass spectrum. Indeed, $[\mathrm{NiGa} 4]\left(\mathrm{Cp}^{*}\right)_{4}$ is itself temperature sensitive and forms higher nuclear clusters. However, due to the Cp * transfer, further reactions are hampered as the catalytically active Ni center is covered by a Cp* ligand shell.


Figure 25: Left: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{GaCp})_{4}\right]$ with 3-hexyne ( $\Delta$ eq. related to Ni) in toluene at room temperature after one day showing strong interaction. Right: Table of LIFDI MS signal assignment.

In order to avoid undesired $\mathrm{Cp}^{*}$ transfer while covering the Ni-center with an organic ligand or substrate that can be easily removed afterwards, cluster growth reactions starting from [NiGa4](Cp*)4 were performed in the presence of an alkyne. Already at room temperature, the reactions showed high sensitivity towards different equivalents of 3 -hexyne (Figure 25). The reaction with four equivalents 3-hexyne led to $\mathbf{1}$ as the most favored product ( $G$ ) after one day, besides its fragments and characteristically peaks at $468 / \mathrm{z}$ assigned to a mixture of $\left[\mathrm{NiGa}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ and $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ (hex). Notably, immediately after addition of 3-hexyne, the reaction mixture turned (dark) brown. This color change was confirmed by the detection of $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})(608 \mathrm{~m} / \mathrm{z})$ and $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})(814 \mathrm{~m} / \mathrm{z})$ while the signals for $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ has almost disappeared. The latter compound could either refer to $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}($ hex $)$ or $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{2}$, but, since only traces of the former could be detected at $1018 \mathrm{~m} / \mathrm{z}$, it is assumed that the signal at $814 \mathrm{~m} / \mathrm{z}$ is related to $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})$ while releasing $\mathrm{GaCp}^{*}$ during ionization. Already after one hour, the formation of $\mathbf{1}$ could be determined. It is assumed that $\mathbf{1}$ is formed using both [ $\mathrm{Ni}_{2} \mathrm{Ga}_{3}$ ] and [ $\mathrm{Ni}_{2} \mathrm{Ga}_{2}$ ] as building blocks in a cluster growth reaction. In fact, 3-hexyne undergoes an "activation" of [ $\mathrm{NiGa}_{4}$ ] forming higher nuclear clusters as 1. Increasing the alkyne amount, the cluster growth reaction is much faster revealing $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{4}(1234 \mathrm{~m} / \mathrm{z}, \mathrm{H})$ and its fragment $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{3}-2 \mathrm{H}(947 \mathrm{~m} / \mathrm{z}, \mathrm{F})$ as the most favored products.


|  | Experimental <br> $[\mathrm{m} / \mathrm{z}]$ | Cluster |
| :--- | :--- | :--- |
| A* | 468.0197 | $\left[\mathrm{NiGa}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ |
|  | 468.1822 | $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}($ hex $)$ |
| B | 678.9546 | $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{1}$ |
| C | 761.0322 | $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{2}$ |
| D | 1036.1617 | $\left[\mathrm{Ni}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}$ |
| E | 1234.0905 | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}$ |
| F | 1777.9207 | $\left[\mathrm{Ni}_{8} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}($ hex $)$ |

*mixture of two signals: first, $\mathrm{NiGa}_{2}$ is higher which decreases during reaction progress.

Figure 26: Left: Reaction progress monitored by LIFDI MS of $\left[\mathrm{Ni}(\mathrm{GaCp})_{4}\right]_{\text {w }}$ with 4 eq. 3-hexyne (related to Ni) at $60^{\circ} \mathrm{C}$ in toluene. Right: Cluster assignment of obtained compounds. Sum formulas related to products are given in bold.

In contrast to the room temperature reaction, the reaction at $60^{\circ} \mathrm{C}$ showed a different behavior. Small NiGa compounds as $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}($ hex $)(678 \mathrm{~m} / \mathrm{z})$ and $\left[\mathrm{Ni}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{3}(1036 \mathrm{~m} / \mathrm{z})$ were observed in the reaction with 4 eq. 3-hexyne, related to Ni , besides $\left[\mathrm{NiGa}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(468 \mathrm{~m} / \mathrm{z})$ which can be seen as fragment of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$. During the reaction progress, this fragment peak at $468 \mathrm{~m} / \mathrm{z}$ became smaller which can be considered equivalent to the conversion of $\left[\mathrm{NiGa}_{4}\right]\left(\mathrm{Cp}^{*}\right) 4$ (Figure 26). Simultaneously, the peaks at $761 \mathrm{~m} / \mathrm{z}, 1035 \mathrm{~m} / \mathrm{z}$ and $1234 \mathrm{~m} / \mathrm{z}$ were rising which were assigned to $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})_{2}$, $\left[\mathrm{Ni}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}$ and $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}$ while 1 could only be observed in small traces after one hour. In accordance with these findings, $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]_{\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{4} \text { has been also observed in the reaction }}$ with 6 eq. 3-hexyne at room temperature as the thermodynamically favored product. It can be excluded that $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ (hex), which was detected as the major product at the beginning of the reaction, originated from $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{2}$ as a fragment since the ratio of these two peaks was varying during the reaction progress. However, both compounds, $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ (hex) and $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{2}$ represent fragment peaks as one $\mathrm{Cp}^{*}$ per molecule was cleaved off during ionization. Increasing the 3 -hexyne amount from 4 to 6 equivalents, $\left[\mathrm{Ni}_{3} \mathrm{Ga}_{3}\right]_{\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{3}(1036 \mathrm{~m} / \mathrm{z}) \text { was only detected at the }}$ beginning of the reaction (after two hours) and decreased as the reaction proceeded. $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}(1234 \mathrm{~m} / \mathrm{z})$ was only observed in small traces over the whole reaction monitored while $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]_{\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})_{1}(678 \mathrm{~m} / \mathrm{z})}$ resembled the most favored product being thermodynamically favored (see Appendix, Figure 74).

Interestingly, comparing both reactions, at room temperature and $60^{\circ} \mathrm{C}$, the formation of higher nuclear clusters was different. While the room temperature reaction favored the formation of 1, built from $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ (hex) and $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ (hex), the reaction at $60^{\circ} \mathrm{C}$ prefered clusters as $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{2},\left[\mathrm{Ni}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}$ and $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}$. Therefore, $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}($ hex $)$ and 1 can be seen as kinetically favored products while $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]^{\left(\mathrm{Cp}^{*}\right)}{ }_{2}(\mathrm{hex})_{2},\left[\mathrm{Ni}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}$ and
$\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}$ seemed to be thermodynamic products. These findings are also in accordance with the reaction progress starting from $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]$ with $\mathrm{GaCp}^{*}$ and 3 -hexyne where $\mathbf{1}$ was obtained at room temperature resembling kinetic control and $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]_{\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{4} \text { was formed upon heating as controlled }}$ by thermodynamic parameters.

Reactivity of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ towards diphenylacetylene


Figure 27: Left: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}\left(\mathrm{GaCp}{ }^{*}\right)_{4}\right]$ with dpa ( $\Delta$ eq.) at room temperature after one day (1 eq.) and three days (4 eq.). Right: Table includes cluster assignment of the obtained compounds. Compounds related to products are given in bold.

The second part of this chapter deals with the reactivity of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ and dpa ( 1 and 4 eq .) in toluene at room temperature. The reaction carried out showed high reactivity towards dpa within a few days (Figure 27). In the first reaction period (less than one day), the reaction with 1 eq. of dpa showed moderate reactivity while observing trimeric dpa ( $534 \mathrm{~m} / \mathrm{z}$, hexaphenyl benzene), $\left[\mathrm{Ni}\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{2}\right.$ ] $(549 \mathrm{~m} / \mathrm{z})$ and $\left[\mathrm{Ni}_{2}\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})\right](564 \mathrm{~m} / \mathrm{z})$ besides $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}\right](468 \mathrm{~m} / \mathrm{z})$ serving as indicator for remaining starting material. However, after one day this signal for the starting material has completely disappeared while a signal at $1534 \mathrm{~m} / \mathrm{z}$ assigned to $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}$ (Figure 27, F, black trace) was arising. Further signals at 1356, 1384 and $1467 \mathrm{~m} / \mathrm{z}$ were observed which were related to $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4},\left[\mathrm{Nii}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ and $\left[\mathrm{Ni}_{5 \mathrm{Ga}}^{4}\right.$ ] $\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})_{2}$. It cannot be said with certainty whether $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4}$ resulted from fragmentation of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}$ or if both are independent product signals and thus, no fragments. Increasing the dpa concentration to four equivalents, the reaction revealed the preferred formation of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4}(1356 \mathrm{~m} / \mathrm{z})$ and $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}(1384 \mathrm{~m} / \mathrm{z})$. As previously mentioned, the increase of the additive amount resulted in the decrease of overall cluster which has also been observed for the corresponding [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ] experiments.
In summary, $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right) 4\right]$ showed high reactivity towards alkynes in contrast to previous publications. As $\mathrm{Cp}^{*}$ and Ga were always assigned in a ratio 1:1 in all observed clusters, the addition of alkynes as additives suppressed the $\mathrm{Cp}^{*}$ transfer reaction from Ga to Ni. Furthermore, the additives being either 3 -hexyne or dpa were able to control cluster growth or degradation by varying the concentration or temperature.

### 4.1.1.5. From sum formula to structural suggestion: Combining NMR, MS and DFT

Single crystals of 1 suitable for X-ray diffraction (XRD) were obtained by storing a concentrated reaction solution at $-30^{\circ} \mathrm{C}$ in hexane or toluene. However, due to temperature sensitivity and decomposition upon removal of the crystal from the reaction solution, which also means loss of excess 3-hexyne around the crystal, the crystal structure could not be determined by SC-XRD. Neither picking under inert Ar atmosphere nor cooling improved the lifetime of the crystal. In addition, $\mathbf{1}$ underwent further reaction to $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ and $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ during long storage times. Therefore, a combination of different analytical techniques as NMR spectroscopy and mass spectrometry accompanied by DFT calculation was required to propose a valid structural suggestion.

Considering the mass spectrum of 1 and its fragmentation behavior, conclusions about the ligand can be drawn if it is assumed that fragments originate from the periphery of the molecule. As Fischer et al. previously published, $\mathrm{Cp}^{*}$ transfer from Ga to Ni was observed when reacting [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ] or [ $\mathrm{Ni}_{2}(\mathrm{dvds})_{3}$ ] with $\mathrm{GaCp}^{*}$ which decreased the reactivity of the respective $\mathrm{Ni} / \mathrm{Ga}$ compound and thus, being less relevant for catalytic applications. ${ }^{132,134,142-143}$ A more detailed analysis of the fragmentation behavior of 1 can potentially provide important information about the structure of this cluster. The fragmentation of 1 induced by LIFDI MS only revealed GaCp*- and hexyne-cleavage during ionization and no loss of $\mathrm{NiCp}{ }^{*}$ or $\mathrm{Ni}\left(\mathrm{Cp}^{*}\right)_{2}$ which was typically observed for $\mathrm{Cp}^{*}$ bound to Ni as in case of $\left[\mathrm{Ni}_{6} \mathrm{Gaa}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ and [ $\mathrm{Ni}_{7} \mathrm{Ga}_{6}$ ]((%5Cleft.%5Cmathrm%7BCp%7D%5E%7B*%7D%5Cright)_{6}\). Further, the sum formulas contain $\mathrm{Ga}: \mathrm{Cp}^{*}$ in a ratio of $1: 1$. These observation led to the conclusion that $\mathrm{Cp}^{*}$ is solely bound to Ga and not to Ni. In-situ ${ }^{13} \mathrm{C}$ NMR spectroscopy accompanied with 2D NMR spectroscopic measurements confirmed this suggestion. The ${ }^{13} \mathrm{C}$ NMR studies showed a peak at 113.6 ppm which is in the characteristic range of $\mathrm{GaCp}^{*}$ (Lit. values: 112.9-114.5 ppm) ${ }^{90-92,143-}$ ${ }^{144}$ rather than $\mathrm{NiCp}^{*}$ (Lit. values: 97.9-98.8 ppm) ${ }^{143,145}$. Additionally, this signal correlated to 1.97 ppm in the respective ${ }^{1} \mathrm{H}$ NMR spectrum as determined by 2D NMR spectroscopy $\left({ }^{1} \mathrm{H} /{ }^{13} \mathrm{C}\right.$ NMR; HMBC). Moreover, the NMR studies provided information about the geometry of 1. Variable temperature NMR studies revealed three signals in the respective range with an integral ratio of 2:1:1 detected at $-80^{\circ} \mathrm{C}$ which was assigned to GaCp*. All these ${ }^{13} \mathrm{C}$ shifts correlated to one Cp * shift in the ${ }^{1} \mathrm{H}$ NMR spectrum leading to the assumption of two isomers, one with four equivalent $\mathrm{GaCp}^{*}$ moieties and one with two chemically inequivalent $\mathrm{GaC}{ }^{*}$ ligands with an integral ratio of $1: 1$ (at $-80^{\circ} \mathrm{C}$ ).
DFT calculations (BP86-D3/def2-tzvpp) for two different GaCp* ligands resulted in one local minimum for a cluster following the composition $\left[\mathrm{Ni}_{4}\left(\mathrm{GaCp}^{*}\right)_{4}(\mathrm{hex})_{2}\right]$ which is in accordance with the NMR results (Figure 28A). The structure features a square planar $\mathrm{Ni}_{4}$ core with two $\mathrm{Ni}_{4}$-face-bridging $\mathrm{GaCp}^{*}$ moieties. The $\mathrm{Ni}_{2}$-edges are coordinated by two 3-hexyne and two GaCp* moieties which are trans bridging the Ni -edges. Since the NMR spectrum, ${ }^{1} \mathrm{H}$ as well as ${ }^{13} \mathrm{C}$, showed only one signal at room temperature, it can be assumed that the Cp * or GaCp * ligands undergo fluxional processes that are hampered at lower temperatures.


A
Square-planar $\mathrm{Ni}_{4}$ core
$2 \mathrm{Ni}_{2}$-edge-bridging GaCp*
$2 \mathrm{Ni}_{4}$-face-bridging GaCp*
$2 \mathrm{Ni}_{2}$ edge-bridging 3-hexyne (trans)


B
Tetrahedral $\mathrm{Ni}_{4}$ core $4 \mathrm{Ni}_{2}$-edge-bridging GaCp*
$2 \mathrm{Ni}_{2}$ edge-bridging 3-hexyne (trans)


C

Square-planar $\mathrm{Ni}_{4}$ core $4 \mathrm{Ni}_{2}$-edge-bridging GaCp*
$2 \mathrm{Ni}_{2}$ edge-bridging 3-hexyne


D

Square-planar $\mathrm{Ni}_{4}$ core 4 terminal GaCp*
2 Ni-face-bridging 3-hexyne (trans)


E

Square-planar $\mathrm{Ni}_{4}$ core
$4 \mathrm{Ni}_{2}$-edge-bridging GaCp* 2 Ni-face-bridging 3-hexyne (trans)

Figure 28: Five possible geometries for $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(h e x)_{2}$. $A$, B and $C$ resulted in local minima calculated by ORCA4.0 (BP86-D3/def2-tzvpp) while $D$ and E could not be optimized to a minimum. Color code: Ni, green; Ga, blue; C, grey. Hydrogen atoms are omitted and Cp* rings are depicted in wireframe for clarity. C was previously suggested by J. Hornung ${ }^{134}$.

For the second isomer obtained in the NMR spectrum, it is proposed to have four equivalent GaCp* moieties. Thus, different possible structures have been tried to optimize to a local minimum. Two geometries reached convergency featuring two $\mathrm{Ni}_{2}$-edge-bridging 3 -hexyne as well as four $\mathrm{Ni}_{2}$-edgebridging $\mathrm{GaCp}^{*}$. These two geometries only differed in their arrangement of the $\mathrm{Ni}_{4}$-core being either tetrahedrally (Figure 28B) or square-planar arranged (Figure 28C). The other two possible geometries are conceivable, but do not result in a local minimum in this arrangement. Instead, the geometry optimization of $D$ aimed to bridging GaCp* positions and a Ni-arrangement more reminiscient of B with a tetrahedral $\mathrm{Ni}_{4}$-core. In addition, a Cp* transfer from Ga to nickel can be observed in D, which has already been excluded by NMR spectroscopy. Similar behavior could be observed with the geometry optimization of E which also exhibited bridging GaCp*, but transferred two $\mathrm{Cp}^{*}$ from Ga to Ni .

Similar structures for $\left[\mathrm{TM}_{4} \mathrm{Ga}_{4}\right]$ than the proposed geometries $A$ and $B$ were previously obtained for $\left[\mathrm{Pd}_{4}\left(\mathrm{GaCp}^{*}\right)_{4}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{4}\right]$ which also featured two different structures due to different precursors (Figure 29). ${ }^{98}$


Figure 29: Metal arrangement of possible $\mathrm{Ni}_{4} \mathrm{Ga}_{4}$ clusters compared with already published $\mathrm{Pd}_{4} \mathrm{Ga}_{4}$ clusters. Left: square planar $\mathrm{Ni}_{4}$-core with two $\mathrm{Ni}_{2}$-edge-bridging $\mathrm{GaCp}^{*}$ and two $\mathrm{Ni}_{4}$-face-bridging GaCp*. The same structure motif was obtained for $\left[\mathrm{Pd}_{4}\left(\mathrm{GaCp}^{*}\right)_{4}\left(\mathrm{CN}^{*} \mathrm{Bu}\right)_{4}\right]$ from $\left[\left\{\mathrm{Pd}\left(\mathrm{CN}^{*} \mathrm{Bu}\right)_{2}\right\}_{3}\right]^{98}$ (middle left). Middle right: Tetrahedrally arranged $\mathrm{Ni}_{4}$ core with four $\mathrm{Ni}_{2}$-edgebridging $\mathrm{GaCp}^{*}$ ligands. Right: Metal arrangement of $\left[\mathrm{Pd}_{4}\left(\mathrm{GaCp}{ }^{*}\right)_{4}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{4}\right]$ originating from $\left[\mathrm{Pd}_{3}\left(\mathrm{GaCp}^{*}\right)_{4}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{3}\right]^{98}$ featuring a $\mathrm{Pd}_{4}$ tetrahedra with four $\mathrm{Pd}_{4}$-face-bridging GaCp* ligands. Color code: Ni, green; Ga, blue; Pd, red.

While the reaction originating from $\left[\left\{\mathrm{Pd}\left(\mathrm{CNHBu}_{2}\right)_{3}\right\}_{3}\right]$ resulted in a square-planar Pd 4 -core with two $\mathrm{Pd}_{2}$-edge-bridging and two $\mathrm{Pd}_{4}$-face-bridging $\mathrm{GaCp}^{*}$, the reaction starting from $\left[\mathrm{Pd}_{3}\left(\mathrm{GaCp}^{*}\right)_{4}\left(\mathrm{CN}^{*} \mathrm{Bu}\right)_{3}\right]$ revealed a Pd4-tetrahedra with four $\mathrm{Pd}_{3}$-face-bridging $\mathrm{GaCp}^{*}$. In contrast to the proposed structure B which featured only edge-bridging ligands, the Pd-analog exhibited only face-bridging Ga-ligands. This is only possible due to additional $\sigma$-donor ligands (CN'Bu) which stabilize the metal-core. In case of [ $\mathrm{Ni}_{4} \mathrm{Ga}_{4}$ ], the additional ligand is acetylene being a $\pi$-donor ligand which prefers bridging positions. $G a C p^{*}$ interact as $\sigma$-donor ligand featuring a 3 -center-2-electron bond ( $3 \mathrm{c}-2 \mathrm{e}$ ) which increases the electron to metal ratio compared to tetrahedral $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{4}\right]$ which exhibited less electron on the metal having a 4 -center-2-electron bond.

### 4.1.1.6. Structure suggestions for $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{4,}\left[\mathrm{Ni}_{4} \mathrm{Ga}_{n}\right]\left(\mathrm{Cp}^{*}\right)_{\mathrm{n}}(\mathrm{dpa})_{6-\mathrm{n}}$ ( $\mathrm{n}=2-4$ ) and $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}$

## Structure suggestion for $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}$ compared to $\left[\mathrm{Pd}_{3}(\mathrm{AICp})_{6}\right]$

Following the above-established procedure to evaluate valid structure suggestions, also calculations for $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}$ were performed. As acetylene is known to bind either face-bridging or edgebridging, only positions for those possibilities were included. In Figure 30 a possible structure for $\left.\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}\right]$ is depicted. The geometry optimization revealed a distorted pyramidal $\mathrm{Ni}_{5}$ core with three $\mathrm{Ni}_{3}$-face-bridging and one $\mathrm{Ni}_{2}$-edge-bridging 3-hexyne ligands. The $\mathrm{GaCp}^{*}$ moieties are bound in three different fashions: once terminal, once $\mathrm{Ni}_{2}$-edge-bridging and once $\mathrm{Ni}_{3}$-face-bridging.


Figure 30: Left: Structure suggestion for $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(h e x)_{4}$ as calculated by ORCA4.0 (BP86-D3/def2-tzvpp). Right: Crystal structure of $\left[\mathrm{Pd}_{3} A l_{6}\right]\left(C p^{*}\right)_{6}$ as determined by SC-XRD from Fischer et al. ${ }^{73}$. Color code: Ni, green; Ga, blue; Pd, red; Al, yellow, C, grey. H atoms are omitted for clarity. Cp* and ethyl moieties are depicted in wireframe.

The $\mathrm{Pd}_{3}$ core of $\left[\mathrm{Pd}_{3}\left(\mathrm{AICp}^{*}\right)_{6}\right]$ is stabilized only by AICp * ligands which bind either $\mathrm{Pd}_{2}$-edge-bridging or terminal. If two of the four $\mathrm{Pd}_{2}$-edge-bridging are considered as core-member, the cluster exhibits a distorted pyramidal $\mathrm{Pd}_{3} \mathrm{Al}_{2}$ core with two $\mathrm{Pd}_{2}$-edge-bridging and two terminally bound $\mathrm{AlCp}^{*}$ ligands. In contrast to $\left[\mathrm{Pd}_{3} \mathrm{Al}_{6}\right]$, [ $\mathrm{Ni}_{5} \mathrm{Ga}_{3}$ ] additionally featured TM-face-bridging ligands. These 3 -hexyne ligands stabilize the Ni atoms which are located on the respective Al-core positions. The second terminally bound $\mathrm{AICp} *$ in $\left[\mathrm{Pd}_{3} \mathrm{Al}_{6}\right]$ is exchanged by edge-bridging GaCp * which provides electrons to two Ni-atoms instead of one if terminally bound, since 3-hexyne is only bound bridging and thus, donates less electrons to one Ni -atom while forming 3-center-2-electron or 4-center-2-electron bonds.

## Structure suggestion for $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{\mathrm{n}}\right]\left(\mathrm{Cp}^{*}\right)_{n}(\mathrm{dpa})_{6-\mathrm{n}}(\mathrm{n}=2-4)$



Square planar $\mathrm{Ni}_{4}$ core



$\mathrm{Ni}_{4}$ tetrahedron
Figure 31: Structure suggestions for $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{n}\right]\left(\mathrm{Cp}^{*}\right)_{n}(\mathrm{dpa})_{6-n}(n=2-4)$ as calculated by ORCA5.0 (BP86-D3/def2-tzvpp). Top: square-planar $\mathrm{Ni}_{4}$ core structures; bottom: Tetrahedrally arranged $\mathrm{Ni}_{4}$-core structures. Left: [ $\mathrm{Ni}_{4} \mathrm{Ga}_{4}$ ] $\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})_{2}$; middle: $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$; right: $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4}$. H atoms are omitted for clarity. Phenyl- and Cp*-rings are depicted in wireframe. Color code: Ni, green; Ga, blue; C, grey.

Reaction of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$, dpa and $\mathrm{GaCp}^{*}$ in the ratio $1: 0.5: 0.5$ at room temperature led to a product mixture consisting of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})_{2}\left(\mathbf{1}_{\mathrm{dpa}}\right),\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}(\mathbf{3})$ and $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4}(\mathbf{4})$ all having six ligands being either dpa or $\mathrm{GaCp}^{*}$. Based on the previous findings for the structure of $\mathbf{1}$, the geometries of these compounds can be proposed assuming hex $\rightarrow$ dpa exchange. Similar to $\mathbf{1}$, all of these compounds could either possess a tetrahedrally arranged $\mathrm{Ni}_{4}$ core (Figure 31, bottom) or a square planar Ni4-core with two Ni4-face-bridging GaCp* featuring an octahedrally arranged Ni4 ${ }^{\text {Gaz }}$ core (Figure 28, top). In particular, [ $\left.\mathrm{Ni}_{4} \mathrm{Ga} 4\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})_{2}$ showed similar bonding of the alkyne compared to $\mathbf{1}$ having either two $\mathrm{Ni}_{2}$-edge-bridging and two $\mathrm{Ni}_{4}$-face-bridging $\mathrm{GaCp}^{*}$ with two $\mathrm{Ni}_{2}$-edge-bridging dpa units, in case of square-planar $\mathrm{Ni}_{4}$, or four $\mathrm{Ni}_{2}$-edge-bridging $\mathrm{GaCp}^{*}$ with two $\mathrm{Ni}_{2}$-edge-bridging dpa when considering tetrahedrally arranged $\mathrm{Ni}_{4}$ core. In contrast to $\mathbf{1}$ and $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})_{2}$, $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ revealed one edge-bridging $\mathrm{GaCp}^{*}$ exchanged by a dpa unit resulting in three Ni -edge-bridging dpa and one Niz-edge-bridging $\mathrm{GaCp}^{*}$ besides the core atoms in octahedrally arranged $\mathrm{Ni}_{4} \mathrm{Ga}_{2}$. In case of tetrahedrally arranged $\mathrm{Ni}_{4}$-core structure in $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}{ }^{*}\right)_{3}(\mathrm{dpa})_{3}$, the structure exhibited six Niz-edge-bridging ligands, specifically three GaCp* and three dpa. The geometry optimization of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4}$ showed the substitution of both Ni -edge-bridging $\mathrm{GaCp}^{*}$ by dpa
leading to four equivalent $\mathrm{Ni}_{2}$-edge-bridging dpa-units while maintaining the octahedral $\mathrm{M}_{6}$ cluster core with square planar $\mathrm{Ni}_{4}$. Considering a $\mathrm{Ni}_{4}$ tetrahedron for $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4}$-structure suggestions, the optimized geometry possessed four $\mathrm{Ni}_{2}$-edge-bridging dpa and two $\mathrm{Ni}_{2}$-edge-bridging GaCp * ligands. Further ligand substitution ( $\mathrm{GaCp}^{*} \rightarrow$ dpa) is not possible, since the $\sigma$-donor properties of the Ga-ligands are important to stabilize the $\mathrm{Ni}_{4}$ core. In case of a $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]$ octahedron, the exchange of one $\mathrm{Ni}_{4}$-facebridging $\mathrm{GaCp}^{*}$ by dpa would result in an electron deficit on the Ni -center since the $\sigma$-donor is exchanged by a $\pi$-acceptor, possibly causing cluster growth. In contrast, using 3-hexyne as the alkyne, it should be thinkable to substitute the $\mathrm{Ni}_{4}$-face-bridging $\mathrm{GaCp}^{*}$ as 3-hexyne having ethyl moieties and thus, being the better electron-donor-ligand compared to dpa. However, also in this case, the $\sigma$-donor character of $\mathrm{GaCp}^{*}$ is important to stabilize the Ni framework.

## Structure suggestion for $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}$ : Comparison with $\left[\mathrm{Ni}_{4}(\mathrm{CNtBu})_{7}\right],\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{4}(\mathrm{dpa})_{3}\right]$ and $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{CNtBu})_{7}$



Figure 32: Comparison of different $\mathrm{Ni}_{4}$ compounds. Left: Structure suggestion for the herein reported $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}$ calculated with ORCA5.0 (BP86-D3/def2-tzvpp); middle left: molecular structure of [ $\left.\mathrm{Ni}_{4}\left(\mathrm{CN}{ }^{t} \mathrm{Bu}\right)_{7}\right]$ determined by $S C-X R D^{146}$; middle right: molecular structure of $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{4}(\mathrm{dpa})_{3}\right]$ as determined by $\mathrm{SC}-X R D^{147}$; right: molecular structure of $\left[\mathrm{Ni}_{4}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{4}\right]$ as determined by $S C-X R D^{98}$. Middle left and middle right are reprinted with permission from M. G. Thomas, W. R. Pretzer, B. F. Beier, F. J. Hirsekorn, E. L. Muetterties, J. Am. Chem. Soc. 1977, 99, 743-748 and E. L. Muetterties, E. Band, A. Kokorin, W. R. Pretzer, M. G. Thomas, Inorg. Chem. 1980, 19, 1552-1560. Copyright 1977 (middle left) and 1980 (middle right), American Chemical Society.

Reaction of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$, dpa and $\mathrm{GaCp}^{*}$ at $60^{\circ} \mathrm{C}$ in the ratio $1: 1: 1$ led to $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}(5)$ as the major and thermodynamically favored product. Several crystallization attempts to obtain single crystal suitable for X-ray analysis failed so far. Thus, a structural suggestion for $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}$ was calculated on the BP86-D3/def2-tzvpp level of theory (Figure 32, left) and was based on previous findings for $\mathrm{Ni}_{4}$-compounds (see chapter 4.1.1.5.).
The optimized structure revealed a distorted $\mathrm{Ni}_{4}$ tetrahedron with two terminally bound GaCp * ligands and five $\mathrm{Ni}_{2}$-edge-bridging dpa moieties. All $\mathrm{Ni}-\mathrm{Ni}$ axes featured bridging dpa except one $\mathrm{Ni}-\mathrm{Ni}$ axis both Ni -atoms having terminally bound $\mathrm{GaCp}{ }^{*}$. The $\mathrm{C}=\mathrm{C}$ triple bond of $\mathrm{Ni}_{2}$-edge-bridging dpa is $90^{\circ}$ bent to the Ni-Ni bond which offered a strong $\sigma$-interaction of both carbon atoms to both adjacent Ni-metals. This caused a C-C bond elongation from 1.20 to 1.29-1.35 Å which was also previously described from Muetterties and coworkers. ${ }^{141}$
Since $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}$ only consists of a $\mathrm{Ni}_{4}$ core, it could be better described as $\left[\mathrm{Ni} \mathrm{i}_{4}\right]\left(\mathrm{GaCp}^{*}\right)_{2}(\mathrm{dpa})_{5}$ bearing seven ligands. In contrast to other already published $\mathrm{Ni}_{4}$ clusters as $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{7}\right]$, $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{\mathrm{t} B u}\right)_{4}(\mathrm{dpa})_{3}\right]$ and $\left[\mathrm{Ni}_{4}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{4}\right]$ (see Figure 32$),\left[\mathrm{Ni}_{4}\right]\left(\mathrm{GaCp}^{*}\right)_{2}(\mathrm{dpa})_{5}$ only featured edge-
bridging dpa while $\mathrm{GaCp}^{*}$ is terminally bound. Previous studies of $\left[\mathrm{Ni}_{4}\left(\mathrm{CN} \mathrm{CNu}_{7}\right)_{7}\right.$ with dpa or $\mathrm{GaCp}^{*}$ resulted in the formation of either $\left[\mathrm{Ni}_{4}\left(\mathrm{CNHBu}_{4}\right)_{4}(\mathrm{dpa})_{3}\right]$ in case of $\mathrm{dpa}^{147}$ or $\left[\mathrm{Ni}_{4}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{CN}^{*} \mathrm{Bu}\right)_{4}\right]$ when using $\mathrm{GaCp}^{* 98}$. Both compounds consisted of face-bridging ligands either dpa or $\mathrm{GaCp}^{*}$ while the isonitriles were terminally bound to the Ni-core atoms. Compared to $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}$, the basic structure of the nickel atoms in $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{CNtBu})_{4}$ was rather similar, as they both have a distorted tetrahedron with elongated Ni-Ni distances. The interatomic Ni-Ni distances in $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}$
 Ni -Ni distances of 2.41-2.84 $\AA$ as published from Fischer and coworkers in 2013. ${ }^{98}$ The observed distances were significantly longer than for $\left[\mathrm{Ni}_{4}\left(\mathrm{CNBL}^{\prime} \mathrm{Bu}\right)_{7}\right]$ with $2.34 \AA$. In accordance, $\left[\mathrm{Ni}_{4}\left(\mathrm{CNNBL}^{\prime} \mathrm{Bu}_{4}(\mathrm{dpa})_{3}\right]\right.$ also featured a distorted $\mathrm{Ni}_{4}$ tetrahedron with partially elongated $\mathrm{Ni}-\mathrm{Ni}$ distances. The compound consisted of two different types of Ni atoms: one $\mathrm{Ni}_{\mathrm{a}}$ atom with three adjacent face-bridging dpa moieties and three Nib atoms with two face-bridging dpa ligands. The averaged bond distance of Nia-Nib was measured to be 2.37 A which is comparable to $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{\prime} \mathrm{Bu}_{\mathrm{H}}\right)_{7}\right]$ while the $\mathrm{Nib}_{\mathrm{i}}-\mathrm{Nit}_{\text {b }}$ bond was elongated to a bond distance of 2.69 Å. ${ }^{147}$
The longer Ni -Ni bond distances as observed in $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}$ are potentially caused by sterically more demanding ligands as $\mathrm{GaCp}^{*}$ compared to terminally bound and more flexible CNtBu in $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{7}\right]$. There, the sterically demanding tert-butyl moiety is more far away from the metal core causing less influence on Ni-Ni bond interaction and thus, on interatomic interactions and distances.

### 4.1.2. NiAl cluster synthesis: Selection of precursor as an important building block

The following image shows an overview of the structures included in this chapter.

[ NiAl$]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})(6)$ SC-XRD

[ NiAl$]\left(\mathrm{Cp}^{*}\right)($ tebd $)($ hex $)(7)$
DFT

[ NiAl$]\left(\mathrm{Cp}^{*}\right)($ tpbd $)(\mathrm{dpa})(8)$ $S C-X R D$

$\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}(9)$ DFT

$\left[\mathrm{Ni}_{2} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})(10)$ DFT

$\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}(11)$
DFT

$\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CNBBu}_{\text {SC-XRD }}{ }_{4}\left(\mathbf{1 2 \cdot C N}{ }^{\mathrm{t} B u}\right)\right.$

Figure 33: Overview of the herein discussed structures of Ni-Al compounds. The structures were either determined by SC-XRD or proposed with ORCA4.0 or ORCA5.0.

### 4.1.2.1. [ $\left.\mathrm{Ni}(\operatorname{cod})_{2}\right]$ as Ni -source of all-hydrocarbon $\mathrm{Ni} /$ Al-clusters



Scheme 10: Overview of the herein discussed products which are formed during the reaction [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right]$ with AlCp * and either 3-hexyne (left) or diphenylacetylene (dpa; right). Additionally, the Ni-Al ratio was varied (bottom).

When thinking of a suitable Ni-source for Ni/Al clusters, [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right]$ plays a crucial role due to its easy substitutable and flexible cod ligands. Solely addition of $\mathrm{AlCp}^{*}$ to $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ led to formation of [ $\left.\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{4}\right]$ or $\mathrm{C}-\mathrm{H} / \mathrm{C}-\mathrm{Si}$ activated Ni/Al compounds depending on the solvent. ${ }^{82}$ Using an alkyne as a second reagent, the formation of all Al-coordinated Ni-compounds as $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{4}\right]$ and $\left[\mathrm{Ni}_{2}\left(\mathrm{AlCp}^{*}\right)_{5}\right]$ is affected while forming clusters of the formula $\left[\mathrm{Ni}_{\mathrm{a}} \mathrm{Alb}\right]\left(\mathrm{Cp}^{*}\right)_{b}(\mathrm{~L})_{c}(\mathrm{~L}=$ alkyne $)$. In order to investigate the reactivity of the $\mathrm{Ni} / \mathrm{Al}$ system depending on the additive, the additive concentration and temperature were systematically studied by in-situ mass spectrometry. Further, the impact of the Ni/Al metal ratio and different alkynes as 3 -hexyne and diphenyl acetylene (dpa) were analyzed.

## Additive controlled reactions: Variation of 3-hexyne amount

Being unreactive at room temperature, the reactions with AICp * were performed at 60 and $90^{\circ} \mathrm{C}$ to investigate the temperature dependency of the NiAl cluster formation. First, the reactions carried out at $60^{\circ} \mathrm{C}$ with different 3 -hexyne concentrations were discussed (Figure 34). The reaction with one equivalent of 3 -hexyne resulted in a mixture of different species. Due to similar molecular masses of two hexyne moieties ( $164 \mathrm{~m} / \mathrm{z}$ ) with AICp* ( $162 \mathrm{~m} / \mathrm{z}$ ), some signals could overlap with two or three different species making the interpretation of such mass spectra more complex. As an example, for the signal at
 carefully comparing the molecular masses and their isotopic pattern, the former could be identified as the main signal. In some cases, however, two possible molecules could be detected which overlaps in their isotopic patterns. Thus, the mixture of the reaction with low additive concentration (1 eq.) revealed the formation of $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}$ (9) $(908 \mathrm{~m} / \mathrm{z})$, $\left.\left[\mathrm{Ni}_{2} \mathrm{Al} 4\right]\left(\mathrm{Cp}^{*}\right)_{4}\right](766 \mathrm{~m} / \mathrm{z}) /\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{2}$
$(764 \mathrm{~m} / \mathrm{z})$ and $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{cod})(h e x)_{2}(6)(492 \mathrm{~m} / \mathrm{z})$ whereby the former could only be detected in traces. In contrast, the reaction with higher additive concentration (2 and 4 eq., red/blue trace) resulted in the formation of $6(492 \mathrm{~m} / \mathrm{z})$ being preferred at high additive concentrations (Figure 34). Substitution reaction to exchange the still bound cod-ligand was achieved by addition of additive in excess (8 eq.) at $60^{\circ} \mathrm{C}$ while forming the highly desired all-hydrocarbon coordinated NiAl compound, $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{hex})_{3}$ (7) (466 m/z). Comparing the Ni-hex ratio for the different reactions at $60^{\circ} \mathrm{C}$, a general trend could be recognized. The higher the concentration of the additive, the lower is the Ni/hex ratio while forming lower nuclear clusters.


Figure 34: Left: LIFDI mass spectra of the reaction [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ] (1eq.), AICp* (1eq.) and 3-hexyne ( $\Delta$ eq.) after 6 h at $60^{\circ} \mathrm{C}$ in toluene/hexane. Right: Cluster assignment of observed signals. Compounds related to a product peak are given in bold.

## Temperature controlled reactions

In the following, the influence of temperature on the formation of NiAl clusters at different additive concentrations was investigated (Figure 35). Therefore, the reaction temperature was increased to $90^{\circ} \mathrm{C}$ and the 3-hexyne amount was varied using one, two, four and eight equivalents of 3-hexyne related to Ni . The reaction with one equivalent conducted at $90^{\circ} \mathrm{C}$ while maintaining Ni:Al ratio at 1 , resulted in the formation of $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]_{\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{3}(9)(908 \mathrm{~m} / \mathrm{z}) \text { as major product. While the reaction with }}$ 1 eq. additive at $60^{\circ} \mathrm{C}$ only revealed traces of 9 , it is the main product when performing the reaction at $90^{\circ} \mathrm{C}$. Due to instrumentally induced fragmentation also its accompanying fragmentation products $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{2}(908-h e x ; ~ 826 \mathrm{~m} / \mathrm{z})$ and $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}($ hex $)(908-2 h e x ; 742 \mathrm{~m} / \mathrm{z})$ were observed. Increasing the additive concentration to 2, 4 and 8 eq., the reaction mainly resulted in the formation of bimetallic [ NiAl ] compounds as $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{cod})(\mathrm{hex})_{2}(492 \mathrm{~m} / \mathrm{z})$ and $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{hex})_{3}(466 \mathrm{~m} / \mathrm{z})$ consisting of a low Ni/hex ratio. Noteworthy, the reaction with a high amount of additive led to the lowest
$\mathrm{Ni} /$ hex ratio while forming smallest possible $\left[\mathrm{NiAl]}\left(\mathrm{Cp}^{*}\right)(\text { hex })_{3}\right.$ as also observed for the reaction at $60^{\circ} \mathrm{C}$ with excess 3-hexyne.
Similar to the reaction at $60^{\circ} \mathrm{C}$, smaller NiAl compounds were preferred when using high amount of additive, while higher nuclear NiAl clusters as $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right] \mathrm{L}_{x}$ were achieved at a low additive concentration. The additive amount directly influenced the cluster growth reaction by capping the open coordination sites of the nickel and hampering bonding to other substrates or compounds. Therefore, no formation of unreactive $\left[\mathrm{Ni}(\mathrm{AlCp})_{4}\right)_{4}$ were observed neither at 60 nor at $90^{\circ} \mathrm{C}$ when using additives. To confirm these suggestion, the reactions were carried out under same conditions without the additive resulting in the homoleptic $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right) 4\right]$.


|  | Experimental <br> $[\mathrm{m} / \mathrm{z}]$ | Cluster |
| :--- | :--- | :--- |
| A | 312.0957 | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tol $)$ |
| B | 384.1894 | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\text { hex })_{2}$ |
| C | 466.2682 | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\text { hex })_{3}$ |
| D | 492.2844 | $\left[{\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\text { cod })(\text { hex })_{2}}\right.$ |
| E | 742.1636 | $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}($ hex $)$ |
| F | 826.2496 | $\left[\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{2}\right.$ |
| G | 908.3374 | $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}$ |

Figure 35: Left: LIFDI mass spectra of the reaction [Ni(cod) ${ }_{2}$ ] (1eq.), AICp* (1eq.) and 3-hexyne ( $\Delta$ eq.) after 6.5 h at $90^{\circ} \mathrm{C}$ in toluene/hexane. Right: Signal assignment of obtained compounds. Clusters related to product peaks are given in bold.

## Reactions controlled by the metal ratios

In addition, further experiments including variation of the aluminum amount (1, 2 and 4 eq.) while maintaining the Ni-hex ratio ( $1: 1$ and 1:4) were performed to investigate the influence of Ni/Al ratio on the cluster nuclearity and cluster growth. Using one equivalent of additive while varying the aluminum content ( 1,2 and 4 eq.), a high impact of the aluminum on cluster formation was observed. Increasing the aluminum equivalents from one to four, the cluster nuclearity was decreasing while concomitant increasing the aluminum amount in the cluster. In particular, in the reaction with one equivalent aluminum (using leq. additive) clusters as $\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}($ hex $)(684 \mathrm{~m} / \mathrm{z}), 9(908 \mathrm{~m} / \mathrm{z})$ and $\left[\mathrm{Ni}_{2} \mathrm{Al}_{5}\right]_{\left(\mathrm{Cp}^{*}\right)_{5}}$ ( $927 \mathrm{~m} / \mathrm{z}$ ) were observed. As the Ni:Al ratio was decreasing, which is equal to increasing Al amount, the reaction was shifted favoring undesired $[\mathrm{NiA} 14]\left(\mathrm{Cp}^{*}\right)_{4+} \mathrm{H}(707 \mathrm{~m} / \mathrm{z})$. In contrast, the reaction with a high additive concentration ( 4 eq .) was only slightly influenced by the Ni:Al ratio, with the homoleptic $\left.\left[\mathrm{NiAl}_{4}\right]\left(\mathrm{Cp}^{*}\right) 4\right]+\mathrm{H}(707 \mathrm{~m} / \mathrm{z})$ emerging as the thermodynamically preferred product (Figure 36). It is interesting and contrary to chemical intuition that high concentrations of the additive favor non-additive
clusters while low additive concentrations prefer hexyne-containing NiAl compounds when using the same NiAl ratio. This could be explained by a faster or stronger activation of the nickel center when higher additive concentrations were used and thus, a faster formation of the thermodynamically preferred compound. Increasing the reaction temperature to $90^{\circ} \mathrm{C}$, only the homoleptic $\left[\mathrm{NiAl}_{4}\right]\left(\mathrm{Cp}^{*} 4\right)$ was detected regardless of the concentrations.


Figure 36: LIFDI mass spectra of the reaction [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right]$ (1 eq.), AICp* ( $\triangle$ eq.) and 3-hexyne after 6 h at $60^{\circ} \mathrm{C}$ in toluene/hexane. Left: 1 eq. 3-hexyne, right: 4 eq. 3-hexyne.

## Additive controlled reactions: Variation of dpa amount

Since 3-hexyne has its boiling point at $81^{\circ} \mathrm{C}^{148}$ and $\mathrm{AICp}{ }^{*}$ is not reactive at room temperature, the limits of the reactions are unambiguous. Additional experiments using diphenylacetylene (dpa) as the additive was tested for its applicability, reactivity and influence on Ni/Al clusters formation. Varying the dpa concentration in the reaction of $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]$ ( 1 eq .) and $\mathrm{AICp}{ }^{*}$ ( 1 eq .) at $60^{\circ} \mathrm{C}$, a similar behavior of NiAlcluster formation using dpa instead of hex was observed. In the reaction with 1 eq . dpa, the mass spectrum revealed the formation of $\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}(11)(958 \mathrm{~m} / \mathrm{z})$ (Figure 37). Besides the product signal, its fragmentation product $\left[\mathrm{Ni}_{2} \mathrm{Al}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})(618 \mathrm{~m} / \mathrm{z})$ was observed which is formed upon dpa and AICp* cleavage. Increasing the additive concentration to 2 or 4 eq., the reduced formation of this $\mathrm{M}_{5}$ compound can be observed while $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}$ (8) (754 m/z) and $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{cod})(\mathrm{dpa})_{2}$ ( $684 \mathrm{~m} / \mathrm{z}$ ) and their fragment $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{2}(577 \mathrm{~m} / \mathrm{z})$ are preferentially formed. Further increase of the additive amount to 8 eq. resulted in cluster degradation which is supported by the detection of [ $\left.\mathrm{Ni}\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{2}\right]$ at $549 \mathrm{~m} / \mathrm{z}$.
In summary, dpa showed similar behavior and impact during NiAl cluster formation as hexyne. The higher the concentration of the additive, the smaller are the formed clusters. While the reaction with low additive amount favored $\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}(11)(958 \mathrm{~m} / \mathrm{z})$ having a $\mathrm{M}_{5}$ cluster core, the reaction with high additive amount preferred the formation of bimetallic $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}(8)(754 \mathrm{~m} / \mathrm{z})$ only consisting
of two metals. The higher the additive concentration, the more favored is the formation of all-dpa containing 8. However, dpa-containing reaction mixtures only revealed the formation of $\mathrm{M}_{5}$ clusters as the biggest observed compound under these conditions, while hex led to $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]$ (9) consisting of six metals in the core. This effect can be argued by steric effects as dpa is a more sterically demanding ligand compared to 3-hexyne. Due to the phenyl moieties, dpa is less flexible and requires more space in the cluster shell. Additionally, with two ethyl moieties adjacent to the acetylene bond, 3-hexyne is a better electron donor compared to dpa being a better $\pi$-acceptor which influences the ability for stabilizing the cluster core. Conclusively, the formation of NiAl cluster can be controlled by the choice of additive as well as the additive concentration.


|  | Experimental <br> $[\mathrm{m} / \mathrm{z}]$ | Cluster |
| :--- | :--- | :--- |
| A | 576.1880 | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{2}$ |
| B | 618.1411 | $\left[\mathrm{Ni}_{2} \mathrm{Al} \mathrm{I}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})$ |
| C | 668.2505 | $\left[\mathrm{NiAl}^{2}\right](\mathrm{Cp})(\mathrm{cod})(\mathrm{dpa})_{2}$ |
| D | 754.2657 | $\left[\mathrm{NiAl}^{2}\right]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}$ |
| E | 958.3152 | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}$ |

Figure 37: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ (1 eq.), $A I C p^{*}(1 \mathrm{eq}$.$\left.) and dpa ( \Delta \mathrm{eq}.\right)$ after 6 h at $60^{\circ} \mathrm{C}$ in toluene/hexane.

## Excursus: Interpretation of sum formulas

The reactions with alkyne excess resulted in the formation of $[\mathrm{NiAl}](\mathrm{Cp} *)(\mathrm{L})_{3}$ with $\mathrm{L}=$ hex or dpa. However, no information about the bonding could be concluded from the sum formulas. Thus, when working with reactions including alkyne excess, it should be considered that alkynes are known for cyclometallation and transmetallation reactions on metal centers. ${ }^{149}$ This has been also suggested by theoretical calculations indicating dimerization of alkynes on Ni/Al-centers. ${ }^{97}$ This means, that the AICp* is trapped by dimerized alkyne forming a five-membered metallacycle while simultaneously oxidizing the Al from +1 to +3 . Upon formation of the metallacycle (aluminacyclopentadiene), the metallacycle then binds via the dimerized alkyne to the transition metal, in this case nickel. Considering the beforementioned $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{L})_{3}$, such metallacycle was also obtained for $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}$ as determined by SC-XRD and can therefore also be denoted as $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tpbd})(\mathrm{dpa})$ with tpbd $=$ tetraphenylbutadiene. The characterization of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}$ via single crystal X-ray diffraction (SC-XRD) supported the formation of a metallacycle. A detailed structural description is given in a separate chapter.

### 4.1.2.2. Reactivity studies on $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})$

Since $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]$ is known for substitution reactions due to its easy exchangeable cod ligands, the reactivity of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\operatorname{cod})(6)($ tebd $=$ tetraethylbutadiene) was tested as it still bears such cod ligand on the nickel center. To exchange the cod ligand, the reactivity towards alkynes (3-hexyne, dpa), $E C p^{*}(E=A I, G a)$ and $\mathrm{PPh}_{3}$ was tested at different temperatures and concentrations and the reaction progress was monitored using LIFDI MS measurements.

## Reactivity of 6 with alkynes

In the following, the approach to substitute the cod by an alkyne will be discussed. It was only possible to substitute the cod ligand at elevated temperatures and with excess of the alkyne. In case of 3-hexyne, the cod ligand could be released when using excess of 3 -hexyne ( 8 eq .) at $60^{\circ} \mathrm{C}$ yielding desired $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)($ hex $)(7)$ while two equivalents at room temperature did not show any reactivity while observing only 6. In contrast, applying the same conditions in the reaction with dpa ( 8 eq., $60^{\circ} \mathrm{C}$ ), it was not possible to exchange the cod. In that case, only the precursor or other unidentified [ $\mathrm{Ni}_{1}$ ] compounds were obtained which could not be referred to products resulting from substitution reactions. However, increasing the temperature and decreasing the dpa concentration led to the desired product (Figure 38). Hence, $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{dpa})(8)$ could be obtained as the major product after one day at $90^{\circ} \mathrm{C}$ when using 2 eq. dpa. In summary, the cod ligand of 6 can be substituted by alkynes resulting in all-alkyne coordinated $\mathrm{Ni}-\mathrm{Al}$ clusters of the formula $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{L})$ with L being either 3 -hexyne or dpa.


|  | Experimental <br> $[\mathrm{m} / \mathrm{z}]$ | Cluster |
| :--- | :--- | :--- |
| A | 312.0946 | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tol $)$ |
| B | 384.1895 | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\text { hex })_{2}$ |
| C | $\mathbf{5 6 2 . 2 6 6 7}$ | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\text { hex })_{2}(\mathrm{dpa})$ |

Figure 38: LIFDI mass spectrum of the reaction of [NiAl](Cp*)(tebd)(cod) with 2 eq. dpa at $90^{\circ} \mathrm{C}$ after one day in hexane. MS samples were measured in a solvent mixture (toluene/hexane).

## Reactivity of 6 with $E C p^{*}(E=A I, G a)$

Secondly, in order to increase the content of main group metals in Ni-Al compounds, it was also investigated whether it is possible to replace the cod ligand by further addition of $E C p^{*}(E=A I, G a)$. In case of AICp*, the choice of solvent plays a crucial role as it can activate benzene ${ }^{82}$ and thus, toluene activation is expected. Therefore, hexane was used as solvent, but solvent mixtures consisting of hexane and toluene were applied for MS. Reaction of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})$ with $\mathrm{AlCp}^{*}(1$ and 2 eq.) at
$60^{\circ} \mathrm{C}$ revealed the homoleptic $[\mathrm{NiAl} 4]\left(\mathrm{Cp}^{*}\right) 4(+\mathrm{H})(707 \mathrm{~m} / \mathrm{z})$ as the major compound regardless of the used equivalents. Besides the product signals, the mass spectra also exhibit signals for the precursor which vary in intensity depending on the AICp* amount used. The higher the aluminum content in the reaction, the more is the formation of $\left[\mathrm{NiAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ favored. Interestingly, Performing the same reaction in toluene (same conditions), the mass spectrum revealed the formation of four different compounds while forming $\left[\mathrm{NiAl}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}($ tol $)$ as intermediate: $\left[\mathrm{NiAl}_{4}\right]\left[\mathrm{Cp}^{*}\right)_{3}(\mathrm{tol})(663 \mathrm{~m} / \mathrm{z}),\left[\mathrm{NiAl}_{4}\right]\left[\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{cod}^{2}\right)\left(\mathrm{H}_{2}\right)$ ( $681 \mathrm{~m} / \mathrm{z}$ ), an unidentified $\left[\mathrm{Ni}_{1} \mathrm{~A} \mathrm{~A}_{x}\right]$ compound ( $699 \mathrm{~m} / \mathrm{z}$ ) and $\left[\mathrm{NiA} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4} \mathrm{H}(707 \mathrm{~m} / \mathrm{z})$. All of the identified compounds exhibited a distinct [ $\mathrm{NiAl}_{4}$ ] core structure, presumably arranged tetrahedrally. The compound related to $681 \mathrm{~m} / \mathrm{z}$ is assumed to bind coe (cyclooctene) instead of cod, in which one double bond is hydrated while only one double bond is still linked to the transition metal. As $\mathrm{Cp}^{*}$ is typically cleaved off in $\mathrm{AlCp}^{*}$-containing Ni compounds, $[\mathrm{NiAl} 4]\left(\mathrm{Cp}^{*}\right)_{3}($ tol $)$ can be seen as toluene-analog to already known benzene-activated $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right) 3(\mathrm{H})\left(\mathrm{AlCp}{ }^{*} \mathrm{Ph}\right)\right]^{82}$. In contrast to $\mathrm{AlCp}^{*}$, the reactions with $\mathrm{GaCp}^{*}$ only revealed the detection of the precursor regardless of the concentration (1, 2 and 8 eq.) or temperature (room temperature, $60^{\circ} \mathrm{C}, 90^{\circ} \mathrm{C}$ ).

## Reactivity of 6 with $\mathrm{PPh}_{3}$

Due to the isolobal principle to $E \mathrm{Ep}^{*}$ and being a common reagent with transition metals in cross coupling reactions, the reactivity of [ NiAl$]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})(6)$ to phosphines was tested. $\mathrm{PPh}_{3}$ was added to a reaction solution of 6 at different temperatures ( 60 and $90^{\circ} \mathrm{C}$ ) and concentrations ( 2 and 4 eq .). The reaction progress was monitored by NMR spectroscopy and LIFDI MS. Although the reaction with 2 eq. at $90^{\circ} \mathrm{C}$ (high T ) and 4 eq . at $60^{\circ} \mathrm{C}$ (high eq.) did not lead to NiAl- $\mathrm{PPh}_{3}$ compounds (only starting material was detected), the reaction with low $\mathrm{PPh}_{3}$ amount at $60^{\circ} \mathrm{C}$ seemed to be reactive. The mass spectrum of the reaction with 2 eq. $\mathrm{PPh}_{3}$ after one day showed the disappearance of the signal related to 6 while a few new signals were detected. Since many smaller signals overlap with their isotopic pattern, the spectrum was only interpreted on the significant large peaks. Thus, the spectrum revealed two major products at $744 \mathrm{~m} / \mathrm{z}$ assigned to $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)\left(\mathrm{PPh}_{3}\right)_{2}$ and $776 \mathrm{~m} / \mathrm{z}$ which could not be identified so far. As phosphines are known for their dissociation behavior in solution ${ }^{87-88}$, the signal could refer to the formation of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)\left(\mathrm{PPh}_{3}\right)_{3}$ as suggested which, however, could not be detected possibly due to fragmentation during ionization. In summary, it is possible to exchange the cod ligand in 6 by phosphines, however, the alkyne ligand, namely tebd, was also substituted accompanied by a rearrangement of the cluster core.
In conclusion, 6 is reactive to other substrates as alkynes, $\mathrm{AlCp}^{*}$ and $\mathrm{PPh}_{3}$. While the reactions with alkynes resulted in the expected substitution reaction under formation of [ NiAl$]\left(\mathrm{Cp}^{*}\right)(\mathrm{tebd})(\mathrm{L})(\mathrm{L}=$ hex, dpa), $\mathrm{AlCp}^{*}$ and $\mathrm{PPh}_{3}$ revealed the formation of $\left[\mathrm{NiA}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ and $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)\left(\mathrm{PPh}_{3}\right)_{2}$, respectively. Contrary to expectations, $\mathrm{GaCp}^{*}$ did not show any tendency for ligand exchange reactions.

### 4.1.2.3. Synthesis and Characterization of [NiAl](Cp*)(tebd)(cod), [ NiAl$]\left(\mathrm{Cp}^{*}\right)($ tebd $)($ hex $)$ and $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tpbd)(dpa)



Scheme 11: Overview of the isolated compounds starting from Ni(cod) ${ }_{2}$. As 3-hexyne (3-hex) or diphenyl acetylene (dpa) are dimerized in the molecular structure they are named as tebd (tetraethylbudadiene) or tpbd (tetraphenylbutadiene).

In the following, the syntheses and characterizations of the compounds 6, $\mathbf{7}$ and $\mathbf{8}$ are discussed individually as shown in Scheme 11.

Addition of four equivalents of 3-hexyne (hex) to a solution of [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ] ( 1 eq .) in hexane formed in-situ burgundy red $\left[\mathrm{Ni}_{2}(\mathrm{cod})_{2} h e x\right]$, which was not isolable so far. ${ }^{141}$ Subsequent treatment with AICp* (1 eq.) and heating to $60^{\circ} \mathrm{C}$ for 3.5 hours resulted in the formation of a dark brown solution from which yellow crystals of 6 were obtained (Scheme 11). Since the 3 -hexyne moieties are dimerized in the complex, it is further named as tetraethylbutadiene (tebd). The ${ }^{1} \mathrm{H}$ NMR spectrum of 6 shows typical signals for the cod ( 4.38 and 3.80 ppm for $\mathrm{CH} ; 2.37,2.17,2.10$ and 1.92 ppm for $\mathrm{CH}_{2}$ ), the $\mathrm{AlCp}^{*}(1.98 \mathrm{ppm}$ ) and the tebd ligand ( $2.10,2.04$ and 1.77 ppm for $\mathrm{CH}_{2} ; 1.25$ and 1.17 ppm for $\mathrm{CH}_{3}$ ) which is in accordance with the ${ }^{13} \mathrm{C}$ NMR spectrum.
From that, $\mathbf{7}$ was obtained by further addition of an excess 3 -hexyne ( 8 eq.) to 6 and heating to $60^{\circ} \mathrm{C}$ for three hours. Additionally, $\mathbf{7}$ could be synthesized from the reaction of [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right]$ ( 1 eq .), $\mathrm{AlCp}^{*}$ ( 1 eq .) and 3 -hexyne ( 8 eq.) at $90^{\circ} \mathrm{C}$ for six hours. Due to the weakly bound and very volatile 3 -hexyne residue on the central nickel atom, $\mathbf{7}$ is not stable in vacuo and could therefore not be isolated. In-situ NMR studies, however, showed signals of side-on coordinated 3 -hexyne, as well as slightly shifted butadiene signal (compared to 6) besides the signals for one AICp* ligand ( 1.99 ppm ) and free cod ( 5.50 and $2.10 \mathrm{ppm})$. The NMR shifts of the ${ }^{13} \mathrm{C}$ NMR spectrum are in accordance with the ${ }^{1} \mathrm{H}$ NMR spectrum. Single crystals of 6 suitable for X-ray analysis were obtained by storing the reaction solution at $-30^{\circ} \mathrm{C}$ overnight. 6 crystallizes in the monoclinic spacegroup $P 2_{1} / c$. The molecular structure features a coordinated cod unit and a metallacycle formed during the reaction between the $\mathrm{AlCp}^{*}$ and two 3 -hexynes. The metallacycle then exhibits a tetraethylbutadiene moiety that binds via the double bonds to the Ni-center while bridging the Ni-Al bond. A similar structure has already been published by Krüger et al. ${ }^{150}$ However, the reactions with DPA performed by Krüger et al. already started from a butadiene derivative and an $\mathrm{Al}(\mathrm{III})$ compound giving the metallacycle beforehand. Compared to these studies, the $\mathrm{C}-\mathrm{C}$ coupling of acetylene was obtained during the reaction induced by a Ni/Al intermediate. Therefore, the aluminum was oxidized in-situ forming the metallacycle. The single crystal structure reveals a Ni-Al
distance of $2.67 \AA$ which is longer than for common Ni-Al complexes ( $2.18-2.21 \AA)^{90-91,151}$ assuming only weak Ni-Al interactions. Noticeably, the metallacycle deviates from planarity by $15.5^{\circ}$ with the AI atom out of the plane and is bent away from nickel (see Figure 39, middle). This distortion is measured with a dihedral angle between the plane $\mathrm{C}_{\text {tebd }}-\mathrm{Al}-\mathrm{C}_{\text {tebd }}$ (grey plane) and the plane between the four tebdring atoms (red plane). By comparing the deviation of 6 and 7, it should be recognized that distortion from planarity decreases when the steric demand of the ligand on the transition metal center also decreases (Table 1). In case of 7 the dihedral angle, thus, was calculated to be "only" $9.2^{\circ}$. Therefore, it can be concluded that the latter complex has a stronger Ni-Al interaction due to less demanding residues on the nickel center which is also supported by a shorter Ni-Al distance (2.48 $\AA$ ).

$[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})$
(6)


[NiAl](Cp*)(tpbd)(dpa)
(8)

Figure 39: Left: Molecular structure of $\left[\operatorname{Ni}\left(A / C p^{*}\right)(t e b d)(c o d)\right]$ (6) determined by single crystal X-ray diffraction.. Middle: Measured dihedral angle between the plane $C_{\text {tebd }}-A l-C_{\text {tebd }}$ (grey) and the plane of the four ring-C's (red) of the metallacycle. Right: Molecular structure of $\left[N i\left(A / C p^{*}\right)(t p b d)(d p a)\right]$ (8) determined by single crystal x-ray diffraction. Hydrogen atoms are omitted for clarity and cod and Cp* ring are depicted in wireframe Color code: green, Ni; orange, Al; grey, C.

Table 1: Selected interatomic distances or angles of 6, 7, $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tpbd})(\mathrm{cod})$ and 8. Abbreviations: tebd: tetraethylbutadiene; tpbd: tetraphenylbutadiene.

|  | [ NiAl](Cp*)(tebd)(cod) exp. (calc.) | [NiAl](Cp*)(tebd)(hex) (calc.) | [ NiAl$]\left(\mathrm{Cp}^{*}\right)($ tpbd)(cod) (calc.) | [NiAl](Cp*)(tpbd)(dpa) exp. (calc.) |
| :---: | :---: | :---: | :---: | :---: |
| Ni-Al distance | 2.67 Å (2.65 $\AA$ ) | 2.48 Å | 2.69 Å | $2.54 \AA$ ( 2.47 Å) |
| Al-Cp* ${ }_{\text {centroid }}$ distance | 1.93 Å (1.93 $\AA$ ) | 1.91 Å | 1.91 Å | 1.87 A (1.87 $\AA$ ) |
| $\mathrm{Ni}-\mathrm{C}_{\text {tebd }} / \mathrm{Ni}-\mathrm{C}_{\text {tpbd }}$ distance | 1.95 Å (1.96 $\AA$ ) | 1.98 Å | 1.97 Å | 2.00 Å (2.00 $\AA$ ) |
| Al-tebd/Al-tpbd angle | $15.5^{\circ}\left(15.3^{\circ}\right)$ | $9.19^{\circ}$ | $15.4{ }^{\circ}$ | $11.8^{\circ}\left(10.2^{\circ}\right)$ |

$[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tpbd})(\mathrm{dpa})(8 ; \operatorname{tpbd}=$ tetraphenylbutadiene) was synthesized accordingly to 7. Therefore, [ $\mathrm{Ni}(\operatorname{cod})_{2}$ ] (1 eq.) and $\mathrm{AICp}^{*}$ (1 eq.) was reacted with excess dpa (8 eq.) at $90^{\circ} \mathrm{C}$ for six hours to give a dark red reaction solution. Similar to 7, 8 is vacuo-sensitive only allowing short exposure to reduced pressure. NMR spectroscopic analysis revealed typical signals for the phenyl rings in the aromatic range with one signal at 7.76 ppm which corresponds to $\mathrm{o}-\mathrm{H}$ of the PhAcetylene (side-on coordinated) being significant for 8. The AICp*-ligand showed a signal at 1.65 ppm which is upfield shifted due to the aromatic residues on the metallacycle forming a large conjugated $\pi$-system. Such shifting of AlCp * ligands in ${ }^{1} \mathrm{H}$ NMR spectroscopy has been previously observed for $\left[\mathrm{Ni}\left(\mathrm{AICp}{ }^{*}\right)_{2}\left(\mathrm{PPh}_{3}\right)_{2}\right](1.79 \mathrm{ppm})^{91,152}$.

Single crystals suitable for X-ray analysis were obtained by diffusion crystallization (hexane/toluene) of the reaction mixture at $-30^{\circ} \mathrm{C}$ within two weeks. 8 crystallizes in the monoclinic spacegroup Pn with two independent and complete molecules and one co-crystallized dpa unit in an asymmetric unit. As for 6, the molecular structure of 8 consists of a metallacycle including dimerized dpa (tpbd) and AICp* which binds via the tetraphenylbutadiene (tpbd) double bonds to the central nickel (Figure 39, right). In accordance with 6, the cod unit is substituted by side-on coordinated dpa. Such binding modes in Ni-AlUHC complexes (UHC = unsaturated hydrocarbons) was previously proposed by theoretical calculations conducted by Hornung et al. revealing a dimerized alkyne and one side-on coordinated alkyne to the transition metal. ${ }^{97}$ As also observed for 6, the metallacycle is slightly distorted with a deviation of $11.8^{\circ}$. In addition, the $\mathrm{Ni}-\mathrm{Al}$ bond ( $2.54 \AA$ ) is also elongated compared to common $\mathrm{Ni}-\mathrm{Al}$ complexes assuming a weak $\mathrm{Ni}-\mathrm{Al}$ interaction. Compared to calculated $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tpbd})(\mathrm{cod})$ which is the dpa analog of 6 , the deviation decreases from $15.4^{\circ}$ to $11.8^{\circ}$ when exchanging cod by dpa while simultaneously the Ni-Al bond is shortened from $2.69 \AA$ to $2.54 \AA$ when the cod is substituted by a third dpa ligand.

### 4.1.2.4. Structural suggestions of $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{3},\left[\mathrm{Ni}_{2} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}{ }^{*}\right)_{4}(\mathrm{dpa})$ and $\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}$ as proposed by DFT calculations

In contrast to the reactions with 3-hexyne which revealed higher nuclear clusters as $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{3}$ (9) besides small complexes as 6 and 7, the reactions with dpa only exhibited dinuclear clusters as $\left[\mathrm{Ni}_{2} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})(10)$ and $\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}$ (11) or $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}$ (8) consisting of max. two nickel atoms.


Figure 40: Calculated structure of $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}$ (left) using ORCA5.0 (BP86-D3/def2-tzvpp) and crystal structure of $\left[\mathrm{Pd}_{3} \mathrm{Al}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}{ }^{73}$ (right) showing the same structural motif in the metal core as [ $\left.\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]$. Color code: yellow: Al; green: Ni; blue: Pd .
$\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]^{\prime}\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}(9)$ could be determined in the reaction of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{AlCp}^{*}$ and 3-hexyne in a ratio of $1: 1: 1$ after 6 h at $90^{\circ} \mathrm{C}$. Due to the instability in vacuo, 9 has not been isolated, yet. Although the geometry optimization was started from a trigonal bipyramidal core structure, the optimized structure pointed to a structure similar to the already known $\left[\mathrm{Pd}_{3}\left(\mathrm{AlCp}^{*}\right)_{6}\right]^{73}$ consisting of a distorted pyramid with three Ni and two Al in the cluster core (Figure 40). As the sum formula revealed three Al ligands, the
remaining AICp*, bridges a Ni-Ni bond which is formed via a Ni from the square base with the Ni on top of the pyramid. Further, the 3-hexyne moieties are bound in two different fashions, but always attached to nickel: twice as terminal ligands (side-on) and once as Ni-Ni bridging ligand. Compared to the structure of $\left[\mathrm{Pd}_{3} \mathrm{Al}_{6}\right]$, three AICp * are substituted by 3 -hexyne ligands revealing similar bonding motifs. As depicted in Figure 40 left, the one $\mathrm{Ni}_{2}$-edge-bridging 3-hexyne ligand is slightly distorted. During optimization, the $\mathrm{H}_{\mathrm{ch}}$ atom of the ethyl group came closer to the adjacent Ni atom assuming a $\mathrm{C}-\mathrm{H}$ activation that can further lead to dimerization or isomerization reactions.

$\left[\mathrm{Ni}_{2} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})(10)$
DFT

$\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}(\mathbf{1 1})$
DFT

Figure 41: Calculated structures of $\left[\mathrm{Ni}_{2} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}{ }^{*}\right)_{4}\left(\right.$ dpa ) (left) and $\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]_{\left(C p^{*}\right)_{3}(\text { dpa })_{2} \text { (right) using BP86-D3/def2-tzvpp level of }}$ theory. Color code: yellow: Al; green: Ni. Cp* rings are depicted in wireframe. H atoms are omitted for clarity.

In contrast to the reactions with 3-hexyne, the reactions involving dpa led to smaller Ni-Al clusters as $\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}$ (11) and $\left[\mathrm{Ni}_{2} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})$ (10). Until now, no crystallographic data could be obtained. However, applying theoretical calculations compared to similar literature known clusters, the geometry as well as bonding of the alkyne can be predicted. Reactivity tests on similar compounds of the formula $\left[\mathrm{TM}_{2}\left(E C p^{*}\right)_{5}\right](\mathrm{TM}=\mathrm{Pt}, \mathrm{Pd})$ indicated that AlCp * prefers the bridging position and the terminally bound ECp* can be easily substituted by $\mathrm{CO}, \mathrm{PR}_{3}$ or $\mathrm{CN}^{+} \mathrm{Bu}$ while preserving the entire cluster core. ${ }^{73}$ Similar to $\left[\mathrm{Ni}_{2} \mathrm{Al}_{5}\right]\left(\mathrm{Cp}^{*}\right) 5^{134}$, both obtained compounds reveal a $\mathrm{Ni}_{2}$ core with three bridging AICp* ligands (Figure 41). Compared to [ $\mathrm{Ni}_{2} \mathrm{Al}_{5}$ ], the two additional terminally bound AICp * ligands are further substituted by one or two dpa moieties, respectively, as proposed from the reactivity test with other transition metals, which are then side-on coordinated to Ni and slightly distorted.

In comparison, compounds with smaller metal cores as [ NiAl$]$ and a high alkyne amount in the complex as $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{L})_{3}(\mathrm{~L}=3$-hexyne, dpa$)$ favored dimerization of the alkynes while higher nuclear clusters as $\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]$ or $\left[\mathrm{Ni}_{2} \mathrm{Al}_{4}\right]$ with less alkyne ligands still have alkynes attached via the triple bond. In can be concluded that the bigger the clusters get, the more far away are the alkynes bound to the nickel hampering dimerization reactions of the alkyne. Further, lower sterically demanding alkynes as 3-hexyne can be more easily activated by the transition metal ( Ni ) than the bulkier dpa due to better accessibility. Therefore, dpa is less dimerized in higher nuclear NiAl clusters compared to 3-hexyne as indicated by potential C-H activation of 3 -hexyne in case of 9 . In addition, the dimerization of the additive revealed further cluster growth which potentially releases an open coordination side on the transition metal.

### 4.1.2.5. $\quad\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{4}\right]$ and $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$ as potential NiAl-source for allhydrocarbon Ni/Al-clusters

Since $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ has shown to be reactive towards alkynes also the Al -analog, $\left[\mathrm{Ni}\left(\mathrm{AlCp}{ }^{*}\right)_{4}\right]$, was tested for its reactivity towards alkynes and its potential for cluster growth forming higher nuclear NiAl clusters. In previous studies it was found that the $\mathrm{Ni} / \mathrm{Al}$ system is strongly depending on the solvent and its used substrates. While the reaction of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ with $\mathrm{AICp} *$ in hexane resulted in $\left[\mathrm{Ni}\left(\mathrm{AlCp}{ }^{*}\right) 4\right]$, it formed $\mathrm{C}-\mathrm{H}$ or $\mathrm{Si}-\mathrm{H}$ activated NiAl complexes via the unsaturated intermediate $\left[\mathrm{Ni}(\mathrm{AICp})_{3}\right]$ when using benzene or triethylsilane instead of hexane as solvent. ${ }^{82}$ When reacting $\left[\mathrm{Ni}(\mathrm{AICp})_{4}\right]$ either with 3-hexyne or dpa, only the typical signals for the homoleptic NiAl-complex was observed via MS (this was verified by measuring isolated $\left.\left[\mathrm{Ni}\left(\mathrm{AICp}^{*}\right)_{4}\right]\right)$. However, performing the reactions with $\left[\mathrm{Ni}\left(\mathrm{AlCp}{ }^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$ as precursor in the presence of additional $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ and dpa, the dinuclear complex $\left[\mathrm{Ni}_{2}\left(\mathrm{AICp}^{*}\right)_{4}\right]$ was favored (Figure 42). Since this would be an unsaturated complex having 16 valence electrons (ve) per nickel, the signal could either refer to $\left[\mathrm{Ni}_{2}\left(\mathrm{AlCp}^{*}\right)_{4}(\mathrm{dpa})\right]$ or $\left[\mathrm{Ni}_{2}\left(\mathrm{AICp}{ }^{*}\right)_{5}\right]^{134}$ while releasing dpa or AICp* during ionization. The mass spectrum exhibited the formation of the former cluster by detecting the corresponding signal at $945 \mathrm{~m} / \mathrm{z}$ in small traces. Noteworthy, without any additional [ $\left.\mathrm{Ni}(\operatorname{cod})_{2}\right]$, only the mononuclear $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{4}\right]$ was formed from $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right) 3(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$ upon reaction with dpa at $60^{\circ} \mathrm{C}$. Therefore, it can be concluded that in case of already existing cluster structures, an additional Ni source plays an important role. The compound $\left[\mathrm{Ni}_{2}(\mathrm{cod})_{2}(\mathrm{dpa})\right]$ which is in-situ formed by reaction of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ with dpa, served as an additional Ni -source in the formation of higher nuclear clusters due to the already existing dinuclear $\mathrm{Ni}_{2}$-core. Further, it is itself an unsaturated complex with 16 ve per nickel and thus, enhances the reactivity of the saturated $\left[\mathrm{NiAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ intrinsically as $\left[\mathrm{Ni}_{2}(\operatorname{cod})_{2}(\mathrm{dpa})\right]$ behaves as a Lewis acid and AICp* acts as a Lewis base.


Figure 42: LIFDI mass spectrum of the reaction $\left[\mathrm{Ni}(\mathrm{AlCp})_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$ with DPA (black) and DPA/Ni(cod) $)_{2}$ mixture (red) after $1 d$ at $60^{\circ} \mathrm{C}$ in cyclohexane.

### 4.1.2.6. $\quad\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{7}\right]$ as TM -source with a tetrahedral $\mathrm{Ni}_{4}$ cluster core



Scheme 12: Overview of the herein discussed products obtained from the reactions of [ $\left.\mathrm{Ni}_{4}\left(\mathrm{CN}^{*} \mathrm{Bu}\right)_{7}\right]$ with AlCp * and 3-hexyne (left) or diphenylacetylene (dpa; right).

Instead of mononuclear Ni/Al precursors, also the tetranuclear $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{* B u}\right)\right]^{153}$ cluster has to be considered as potential Ni source for cluster formation or growth. Having a tetrahedral Ni-core with three face-bridging and four terminal binding isonitriles, it already exhibits a definite cluster core structure. As previously reported, the three face-bridging ligands can be easily substituted by acetylenes resulting in $\left[\mathrm{Ni}_{4}(\mathrm{CNtBu})_{4}(\mathrm{RC}=\mathrm{CR})_{3}\right]{ }^{154}$ Therefore, $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{1 \mathrm{Bu}}\right) 7\right.$ ] was reacted with AlCp * and different acetylenes as dpa or hex (Figure 43). With 3 -hexyne as the additive, the reaction was initially directed to isonitrile- and Ni-rich $\quad\left[\mathrm{Nis}_{5} \mathrm{Al}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{CNHBu}_{6 / 7}\right.$ and $\quad\left[\mathrm{Ni}_{4} \mathrm{Al}_{2}\right]_{\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{CNB}^{*} \mathrm{Bu}\right)_{5} \text { and progressed to smaller }}$ $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]_{\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{4} \mathrm{Bu}\right)_{2 / 3} \text { as the thermodynamically favored product during the reaction. In contrast, the }}$ reaction with dpa as the alkyne led directly to the latter $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]$ cluster after only one hour. Over the reaction time, however, it still seemed to be reactive towards the additive, forming dpa-containing clusters as $\left[\mathrm{Ni}_{4} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{CNtBu})_{4}(\mathrm{dpa})$ and $\left[\mathrm{Ni}_{3} \mathrm{Al}_{2}\right]_{\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{CNtBu})_{4}(\mathrm{dpa})_{0 / 1} \text { initially and, after longer }}$ reaction times to smaller clusters $\left[\mathrm{Ni}_{2} \mathrm{Al}_{2}\right]_{\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{CNtBu})_{3}(\mathrm{dpa}) \text { and }\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{CNtBu})_{2} \text {. Noteworthy, }}^{\text {. }}$ performing the reaction without acetylene, $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{*} \mathrm{Bu}_{3}\right)_{3}(\mathbf{1 2 )}$ could be also obtained as major product after 6 h at $60^{\circ} \mathrm{C}$. The reaction progress could be compared to that including 3 -hexyne where the formation of $\mathbf{1 2}$ was also preferred after six hours.



|  | Exp. <br> $[\mathrm{m} / \mathrm{z}]$ | 3-Hexyne- assignment |
| :--- | :--- | :--- |
| A | 828.2415 | $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{2}$ |
| B | $\mathbf{9 1 1 . 3 1 4 0}$ | $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{3}$ |
| C $^{*}$ | 973.2956 | $\left[\mathrm{Ni}_{4} \mathrm{Al}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{5}$ |
| D | 1116.3075 | $\left[\mathrm{Ni}_{5} \mathrm{Al} \mathrm{I}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{6}$ |
| E | $\mathbf{1 1 9 9 . 3 7 9 0}$ | $\left[\mathrm{Ni}_{5} \mathrm{Al}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{7}$ |

${ }^{*}$ After 1 h : Mixture of $2 / 3\left[\mathrm{Ni}_{4} \mathrm{Al}\right]\left(\mathrm{Cp}^{*}\right)\left(\mathrm{CN}^{\prime} \mathrm{Bu}\right)_{4}(\mathrm{hex})_{3}(974.1723 \mathrm{~m} / \mathrm{z})$ and $1 / 3\left[\mathrm{Ni}_{4} \mathrm{Al}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{CN}^{\mathrm{H}} \mathrm{Bu}\right)_{5}(973.2956 \mathrm{~m} / \mathrm{z})$. The former is decreasing over time.

|  | $\begin{aligned} & \text { Exp. } \\ & {[\mathrm{m} / \mathrm{z}]} \end{aligned}$ | Dpa- assignment |
| :---: | :---: | :---: |
| A | 817.2536 | $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}\right)_{2}(\mathrm{dpa})_{3}$ |
| B* | 828.2400 | $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{2}$ |
|  | 832.2948 | $\left[\mathrm{Ni}_{3} \mathrm{Al}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}\right)_{4}$ |
| C | 867.3619 | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{2}\right]\left(\mathrm{Cp}{ }^{*}\right)_{2}\left(\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}\right)_{3}($ dpa $)$ |
| D | 911.3143 | $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}{ }^{*}\right)_{3}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{3}$ |
| E | 1010.3707 | $\left[\mathrm{Ni}_{3} \mathrm{Al}_{2}\right]\left(\mathrm{Cp}{ }^{*}\right)_{2}\left(\mathrm{CN}^{\text {t }} \mathrm{Bu}\right)_{4}(\mathrm{dpa})$ |
| F | 1230.4028 | [ $\left.\left.\mathrm{Ni}_{4} \mathrm{Al}_{3}\right]^{(C p}{ }^{*}\right)_{3}\left(\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}\right)_{4}($ dpa $)$ |

Figure 43: Time dependent LIFDI mass spectra of the reactions $\left[\mathrm{Ni}_{4}\left(C N^{*} B u\right)_{7}\right]$ with 4 eq . $\mathrm{AlCp}^{*}$ and 4 eq. acetylene at $60{ }^{\circ} \mathrm{C}$. Left. 3-hexyne, right: dpa. Clusters given in bold are referred to product peaks.

While the reaction with 3-hexyne indicated cluster synthesis without direct influence of the alkyne, since it acted only as an initiator or support (no hexyne-containing clusters were detected), the reaction with dpa resulted in dpa-containing $\mathrm{Ni} / \mathrm{Al}$ clusters suggesting a direct impact of the additive in binding to the Ni center and thus on cluster formation or structure. In addition, the clusters obtained in the reaction with dpa have a lower Ni-Al ratio, but have higher nucleation in the metal core compared to hexcontaining reactions. In contrast to 3-hexyne, dpa still stabilizes an $M_{4}$ cluster core with direct bonding of the dpa to the cluster core as initially intended.
It should be noted that $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{t} \mathrm{Bu}_{4}\right)_{7}\right]$ is known from our group experiences to be unstable in vacuo and forms dimeric $\left[\mathrm{Ni}_{8}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{12}\right]$ under reduced pressure. It is therefore not certain whether the formed species were produced only during instrumental evacuation or by the reaction itself. Therefore, NMR spectroscopic studies were carried out to support the formation of 12 . The ${ }^{1} \mathrm{H}$ NMR showed broad signals at 2.15 ppm and 1.42 ppm in toluene- $\mathrm{d}_{8}$ with a ratio of $45: 36$ which could be assigned to AlCp * and $\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}$ moieties in a ratio of $3: 4$ and not as expected $3: 3$. Accordingly, the ${ }^{13} \mathrm{C}$ NMR spectrum showed signals at $112.9,55.0,31.8 \mathrm{ppm}$ and 11.1 ppm which are related to $\mathrm{AlCp}^{*}\left(112.9\right.$ ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ ), 11.1 $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)$ ) and $\mathrm{CN}^{t} \mathrm{Bu}$ (55.0 ( $\mathrm{CNCMe}_{3}$ ), 31.8 ( $\mathrm{CNCMe}_{3}$ ). These values are in accordance with already known $\left[\mathrm{Ni}_{4}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{CN}^{\dagger} \mathrm{Bu}\right)_{7}\right] .{ }^{98}$


Figure 44: Left: Molecular structure of $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}{ }^{*} \mathrm{Bu}\right)_{4}$ (12) determined by single crystal x-ray diffraction. Hydrogen atoms are omitted for clarity. Color code: green, Ni; orange, Al; light blue, N; grey, C. Right: Core structure of 12 showing a trigonal bipyramid consisting of a $\mathrm{Ni}_{3}$ triangle which is face-capped by two Al atoms. Further one Al atom is bridging the Ni-Ni bond.

Single crystals of $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{4}\left(\mathbf{1 2} \cdot \mathbf{C N}^{t} \mathrm{Bu}\right)$ were obtained by storing a concentrated solution in toluene at $-30^{\circ} \mathrm{C}$. It crystallizes in the triclinic space group $P 1$ with two whole molecules in the asymmetric unit. The cluster core exhibits a trigonal bipyramidal structure consisting of a $\mathrm{Ni}_{3}$ triangle capped with two AICp* units. Two nickels have terminally bound CNtBu moieties while one nickel binds two isonitriles. Additionally, one AICp * is bridging the $\mathrm{Ni}-\mathrm{Ni}$ bond where both Ni only binds one isonitrile ligand. 12 revealed the same structural motif of the clusters core as $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{3}\right](\mathrm{Cp})_{3}(\mathrm{PMe})_{3}{ }^{120,152}$ and $\left[\mathrm{Pd}_{3} \mathrm{In}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{PPh}_{3}\right)_{3}{ }^{73}$. In contrast to these already published clusters, one Nickel in 12 bears two isonitriles while in the known compounds only one terminal ligand was attached to each transition metal. In summary, $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{3}$ (12) is formed in the presence of an additive with dpa being the faster modulator to obtain 12 than 3-hexyne. In addition, dpa has a direct influence on the growth or synthesis of the cluster binding and activating the transition metal, while 3-hexyne acts independently as it is not part of the cluster core/structure itself. Since $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}\right)_{4}\left(\mathbf{1 2} \cdot \mathbf{C N}^{\mathrm{t} B u}\right)$ seemed to be reactive towards dpa, it reacted further with the alkyne to form smaller NiAl compounds. Knowing this, 12 was treated with dpa after formation which was confirmed by in-situ detection of $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{+B u}\right)_{3}$. Indeed, it was reactive towards the acetylene showing arising signals at $921 \mathrm{~m} / \mathrm{z}$, $1090 \mathrm{~m} / \mathrm{z}$ and $1550 \mathrm{~m} / \mathrm{z}$ which were assigned to $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)\left(\mathrm{CN}^{t B u}\right)_{2}(\mathrm{dpa})_{3}(921 \mathrm{~m} / \mathrm{z})$ and $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{+B u}\right)_{3}(\mathrm{dpa})(1090 \mathrm{~m} / \mathrm{z})$, respectively. For $1550 \mathrm{~m} / \mathrm{z}$ there are several possibilities which could not yet be assigned with high certainty, but they all point to higher nuclear Ni-rich clusters as $\left[\mathrm{Ni}_{6} \mathrm{Al}_{2}\right]$ or $\left[\mathrm{Ni}_{5} \mathrm{Al}_{\mathrm{x}}\right]$ with x being 1,3 or 5 .

In conclusion, starting from a definite cluster core structure, higher nuclear Ni -Al clusters are possible to synthesize. The choice of additive reveals a new tool to control the cluster synthesis especially size and distribution. While 3-hexyne is a more independently acting additive, dpa is stronger binding to the transition metal. In contrast to 3-hexyne, dpa can be applied at higher temperature, while 3-hexyne is only useful below $80^{\circ} \mathrm{C}$ due to its boiling point. Since dpa is almost insoluble in hexane at room temperature, it can mainly be used only at higher temperatures or when using toluene. Conclusively, both dpa and 3-hexyne are suitable additives and modulators, respectively, in cluster growth reactions, which should be used according to requirements.

### 4.1.3. Comparison and Conclusion of $\mathrm{Ni} / \mathrm{E}$ cluster synthesis

Since additives are widely used in the synthesis of nanoparticles or -clusters to control size and distribution ${ }^{50,136-139}$, the applicability of such modulators to the atomic-scale synthesis of clusters has been evaluated. In this chapter, the reactivity of various Ni-precursors as $\left.\left[\mathrm{Ni}(\operatorname{cod})_{2}\right],\left[\mathrm{Ni}(\mathrm{ECp})^{*}\right)_{4}\right]$, $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$ and $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{\dagger} \mathrm{Bu}_{3}\right)_{7}\right]$ and their ability for cluster growth and cluster formation was investigated depending on the addition of alkynes as additives. While the reaction of $\left[\mathrm{Ni}(\mathrm{Cod})_{2}\right]$ with $\mathrm{GaCp}^{*}$ led to the selective formation of $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ and $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ as the thermodynamically favored product, the reaction including additives allowed for kinetic control, trapping intermediate compounds such as $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}$ and $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{4}$ on the way to mentioned $\mathrm{M}_{13}$ clusters. The $\mathrm{Cp}^{*}$ transfer from Ga to the catalytically active Ni as observed in the formation of [ $\mathrm{Ni}_{7} \mathrm{Ga}_{6}$ ] or [ $\mathrm{Ni}_{6} \mathrm{Ga}_{7}$ ] was thereby hampered by the affinity of alkynes to $\mathrm{Ni}^{0}$ centers and thus, by the occupation of the open coordination sites on the nickel center which was confirmed by the observation of GaCp* instead of NiCp * or related compounds.
It was shown that the Ni/Ga system is strongly temperature dependent leading to the formation of higher nuclear clusters as $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa}),\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ and $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}$ as well as $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}$ at higher temperatures, whereas $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ was selectively obtained at lower temperatures. In contrast, the investigation of $\mathrm{Ni} / \mathrm{Al}$ cluster formation indicated a strong dependency on the additive concentration. While low additive concentrations led to higher nuclear clusters as $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}$ with a low hex/Ni ratio, increasing the concentration reduced the metal content in $\mathrm{Ni} / \mathrm{Al}$ compounds causing the formation of $[\mathrm{NiAl}](\mathrm{Cp} *)($ tebd $)(\mathrm{L})$ (with $\mathrm{L}=$ cod, hex) and $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tpbd})(\mathrm{dpa})$ with an alkyne/Ni ratio of max. 3. In summary, reactions involving $\mathrm{Ni}^{0}$ and $\mathrm{GaCp}^{*}$ could form higher nuclear clusters with up to 11 metals controlled by temperature while $\mathrm{Cp}^{*}$ transfer reactions are hindered. In contrast, $\mathrm{Ni} / \mathrm{Al}$ reactions originating from $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ resulted in clusters with maximum $\mathrm{M}_{6}$ core. However, if these cluster growth reactions were performed with a pre-existing definite core structure, higher nuclear Ni-rich clusters with up to $\mathrm{M}_{7}$ cores such as $\left[\mathrm{Ni}_{5} \mathrm{Al}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{CN}{ }^{\mathrm{B}} \mathrm{Bu}\right)_{7}$ and $\left[\mathrm{Ni}_{4} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{4}(\mathrm{dpa})$ were also obtained.

Additionally, the chapter dealt with the identification of reactive intermediates and the structure determination of such intermetallic clusters which are usually determined by means of SC-XRD. Applying a combinatorial, coordination modulated approach to study the cluster mixtures in-situ, in this case with NMR spectroscopy and LIFDI mass spectrometry, allows reactive intermediates to be identified and further reacted which is not possible with isolated compounds to this extend. This approach enabled size-focused compounds or solutions to be obtained from cluster mixtures by adjusting the temperature or additive and precursor concentration.
With a new methodological approach which combines analytical methods, such as NMR spectroscopy and MS, with theoretical calculations, it was feasible to propose valid structures for the obtained Ni/Ga and $\mathrm{Ni} / \mathrm{Al}$ compounds. By comparison to compounds that are already known from literature, the structural suggestion could be supported.

### 4.2. Synthesis and Reactivity studies of $\mathrm{Pd} / \mathrm{E}$ containing compounds

### 4.2.1. $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ as temperature sensitive precursor for $\mathrm{Pd} / \mathrm{E}$ compounds



Scheme 13: Overview of the herein discussed products obtained from the reactions of $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ with GaCp * dependent on the temperature (left) and with dpa as additive dependent on temperature (right).

## Reaction with $\mathrm{GaCp}^{*}$ at different temperatures

As $\left[\mathrm{Ni}_{2}(\mathrm{dvds})_{3}\right]$ (dvds $=1,3$-divinyl-tetramethyldisiloxane) was previously be shown to have a very flexible dvds ligand while forming Ni-Ga compounds upon treatment with $\mathrm{GaCp}^{* 132,143,}\left[\mathrm{Pd} 2(\mathrm{dvds})_{3}\right]$ was investigated for its potential to form higher nuclear Pd-Ga compounds and their dependency on additive addition. Therefore, $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ was reacted with $\mathrm{GaCp}^{*}$ in a Pd:Ga ratio of 1 at different temperatures $\left(-30^{\circ} \mathrm{C}\right.$, room temperature) and monitored via LIFDI mass spectrometry and NMR spectroscopy. As a previous publication reported a temperature sensitive $\mathrm{Pd} / \mathrm{Ga}$ system ${ }^{155}$, the reaction was first conducted at $-30^{\circ} \mathrm{C}$. The LIFDI mass spectra revealed a very selective reaction within a few minutes, while forming $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dvds})(1190 \mathrm{~m} / \mathrm{z})$ and its fragmentation product (-dvds, $\left.1003 \mathrm{~m} / \mathrm{z}\right)$ (Figure 45) which has been also observed in nanoparticle synthesis ${ }^{156-157}$. It has to be stated clearly, that these experiments were carried out independently and simultaneously to this published work and differ in their aim. While the authors of the publication targeted the synthesis of catalytically relevant nanoparticles from organometallic compounds, these studies were focused on the synthesis of intermediate metal mixtures embedded in a ligand shell. The influence of additives on those intermetallic compounds and their respective synthesis were investigated while the authors aimed catalytic applications.


Figure 45: LIFDI mass spectra of the reaction $\left[\mathrm{Pd}_{2}(d v d s)_{3}\right]$ with GaCp* (2 eq.) in toluene (black trace) or toluene- $\mathrm{d}_{8}$ (red trace) or with $\mathrm{GaCp}{ }^{* E t}$ (blue trace) after one day at $-30^{\circ} \mathrm{C}$. Cluster assignments are given on the right.

The mass spectrum conducted after 30 minutes points to a Ga:Cp* ratio less than one which is in contrast to the previous finding for Ni where Ga and Cp* was always obtained in a ratio of 1 as described above. Notably, as known from our group, Pd-E compounds often releases $C p^{*}$ or ECp* during ionization. Therefore, the reaction was also conducted with a Cp* derivative where one methyl moiety is exchanged by an ethyl group. This then results in a mass shift of $14 \mathrm{~m} / \mathrm{z}$ per $\mathrm{Cp}^{*}$ to determine the exact $C p^{*}$ amount. As the mass spectrum of the $C p^{* E t}$ reaction revealed a $m / z$ shift of 42 , it can be concluded that the complex bears three $C p^{*}$ ligands ( $3 \times 14=42$ ). Furthermore, careful comparison of the calculated with the isotopic pattern, $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dvds})$ was identified as product. However, previous findings revealed the formation of $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}{ }^{* P h}\right)_{4}(\mathrm{dvds})$ when performing the reaction with $\mathrm{GaCp}{ }^{* P h}$ with a Ga:Cp*Ph ratio of 1 . Thus, the formation of $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right) 4(\mathrm{dvds})$ is assumed but has not yet been confirmed as the mass spectrum only revealed the compound with loss of Cp*. Low temperature NMR studies could be conducted to determine the ratio of $\mathrm{Cp}^{*}$ to dvds and thus, support the assumption. Several attempts to crystallize $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dvds})$ from a concentrated solution or by diffusion crystallization failed so far.


Figure 46: LIFDI mass spectra of the reaction $\left[\mathrm{Pd}_{2}(d v d s)_{3}\right]$ with GaCp* (2 eq.) in toluene (black trace) or toluene- $d_{8}$ (red trace) or with $\mathrm{GaCp}^{* E t}$ (blue trace) after one day at room temperature. Cluster assignments are given on the right.

Gradual increase of the reaction solution from $-30^{\circ} \mathrm{C}$ to room temperature led to the formation of $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dvds})$ from $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dvds})$ as part of a cluster growth reaction (see Appendix, Figure 90). Such cluster growth reactions due to temperature increase was also observed for the synthesis $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ yielding $\left[\mathrm{Pd}_{3} \mathrm{Gaa}\right]\left(\mathrm{Cp}^{*}\right)_{8}$ at room temperature. ${ }^{73}$ Besides the product peak at $1500 \mathrm{~m} / \mathrm{z}$ referring to [Pd4Ga5], the mass spectrum also showed signals at $1406 \mathrm{~m} / \mathrm{z}$ and $1190 \mathrm{~m} / \mathrm{z}$ which refer to $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{tol})$ and $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ (dvds) as confirmed by reactions with $\mathrm{GaCp}^{* E t}$ instead of $\mathrm{GaCp}^{*}$ or toluene-ds instead of toluene (Figure 46). As it seems, that toluene can exchange the flexible dvds ligand, HCD cell experiments were conducted. Stepwise increase of the energy in the collision chamber of the MS instrument enabled the assignment of product, intermediate and fragment as also previously described in the Ni -Ga chapter. The toluene-containing molecule B was therefore identified as an intermediate which is formed during ionization while the other two compounds A and C could be established as product peaks. In accordance to already mentioned $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dvds})$, $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dvds})$ is also assumed to undergo $\mathrm{Cp}^{*}$ cleavage during ionization. Due to the high solubility in organic solvent, it was not possible to obtain single crystals suitable for X -ray analysis. Further increase of the reaction temperature to $60^{\circ} \mathrm{C}$ resulted in the formation of $\left[\mathrm{Pd}_{4} \mathrm{Gaa}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dvds})$ at first, but after one day, the reaction ended in $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ as the thermodynamically favored product which was confirmed by the detection of $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ at $1102 \mathrm{~m} / \mathrm{z}$. As described by Fischer et al. ${ }^{155}$, $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dvds})$ and $\left[\mathrm{Pd}_{4} \mathrm{Gaa}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dvds})$ can be seen as isolable intermediate compounds in the formation of $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$. Further, $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dvds})$ is the first observed Ga-rich Pd cluster with a $\mathrm{Pd}_{4}$ core which could be a perfect candidate for substitution reactions as it still contains a flexible dvds ligand attached.

## Reaction of $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ with GaCp * and alkynes at different temperatures

In the following, the influence of alkynes as additives during the synthesis of Pd-Ga clusters is discussed. The reaction with $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ with $\mathrm{GaCp}^{*}$ and 3-hexyne at room temperature immediately resulted in a black precipitate and a clear solution. LIFDI mass spectra did not reveal any cluster formation while only small signals referring either to mononuclear metal-organyls or organic residues, which could not be identified so far. Performing the reaction with dpa instead at lower temperature, dpa-containing compounds were observed. Similar to the reaction without additives, the dpa-containing reactions mostly resulted in $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dvds})$ at $-30^{\circ} \mathrm{C}$ and $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right) 4(\mathrm{dvds})$ at room temperature as discussed above. Thus, the overall cluster formation and especially the cluster core is not strongly influenced by the additive, so far. Nonetheless, the reaction with additional 2 eq. of dpa at $-30^{\circ} \mathrm{C}$ while maintaining the $\mathrm{Pd}-\mathrm{Ga}$ ratio did result in $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dvds})(\mathrm{dpa})(1162 \mathrm{~m} / \mathrm{z})$ and $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})+2 \mathrm{H}$ $(1076 \mathrm{~m} / \mathrm{z})$ besides the major signal for $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dvds})$ as evidenced by LIFDI MS (Figure 47).


|  | Experimental <br> $[\mathrm{m} / \mathrm{z}]$ | Cluster assignment |
| :--- | :--- | :--- |
| A | 1076.8809 | $\left.\left[\mathrm{Pd}_{2} \mathrm{Ga}_{4}\right](\mathrm{Cp})_{3}\right)_{3}(\mathrm{dpa})+2 \mathrm{H}$ |
| B | 1102.9032 | $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right](\mathrm{Cp})_{4}$ |
| C | 1162.8982 | $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{3}\right](\mathrm{Cp})_{2}$ (dvds)(dpa) |
| D | 1190.8577 | $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right](\mathrm{Cp})_{3}(\mathrm{dvds})$ |

Figure 47: LIFDI mass spectra of the reaction $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ and $\mathrm{GaCp} *$ (2 eq.) at $-30^{\circ} \mathrm{C}$ (black trace) or at $60^{\circ} \mathrm{C}$ (blue trace) and additional with dpa (2 eq.) at $-30^{\circ} \mathrm{C}$ (red trace) or at $60^{\circ} \mathrm{C}$ (green trace). The spectra were recorded after one or two days in toluene. Observed peaks are assigned in the table on the right.

Increasing the reaction temperature from $-30^{\circ} \mathrm{C}$ to $+60^{\circ} \mathrm{C}$, the reaction formed $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ as the major product (Figure 47, green trace), which can be seen equal to the formation of $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right) 5$. Besides that also a signal for $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dvds})$ at $1190 \mathrm{~m} / \mathrm{z}$ was observed which was only obtained in traces without dpa. As previously published, $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dvds})$ resembles an intermediate compound on the way to $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$. Considering the dpa-containing reaction, the conversion of [ $\left.\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]$ to kinetically inert $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ is slower when adding an additive. As no dpa-containing compounds were observed at that temperature, the additive has only indirect influence on cluster formation while slowing down the reaction rate to the thermodynamically favored product. However, the
addition of additives in Pd-Ga clusters synthesis enabled the observation of new compounds while slowing down the reaction rate. Therefore, additives can be applied to trap intermediate compounds. Structurally, $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})$ resembles the already described $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ if one terminally bound GaCp* is exchanged with dpa. It features a $\mathrm{Pd}_{2}$ center which is bridged by three $\mathrm{GaCp}^{*}$ ligands. The complex is additionally stabilized by two terminally bound ligands, $\mathrm{GaCp}^{*}$ and side-on coordinated dpa. The structure of $\left[{P d_{3} G a_{3}}^{d}\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dvds})_{2}(\mathrm{dpa})\right.$ is proposed to be structurally related to $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{* P h}\right)_{4}(\mathrm{dvds})^{155},\left[\mathrm{Pd}_{3} \mathrm{Al}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}{ }^{73}$ and $\left[\mathrm{Pd}_{3} \mathrm{In}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{PPh}_{3}\right)_{3}{ }^{73}$ when dvds is seen as a twocoordinating ligand. In particular, all three known compounds exhibit a $\mathrm{Pd}_{3}$ triangular core structure with three bridging ECp* ligands. Compared to $\left[\mathrm{Pd}_{3} \mathrm{Al}_{6}\right]$, the dvds ligand binds to two Pd-centers, as also observed for $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{\star \mathrm{Ph}}\right)_{4}(\mathrm{dvds})$, instead of two terminally bound $\mathrm{AlCp}{ }^{*}$. The dpa unit is supposed to coordinate side-on to one Pd core atom instead of terminally bound ECp*.
In summary, dpa can influence the synthesis of Pd-Ga compounds while slowing down the formation to catalytically inert and thermodynamically favored $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$. As intermediate compounds, the formation of $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dvds})$, $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dvds})(\mathrm{dpa})$ and $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})$ were detected which give hints to the formation mechanism of $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$. In particular, the Pd-Ga system formed first mediate and afterwards higher nuclear compounds, which is then converted to $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ while releasing Pd-metal in a cluster degradation reaction. Furthermore, as previously described for $\left[\mathrm{Pd}_{3} \mathrm{In}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}{ }^{73}$, the terminally bound $\mathrm{ECp}{ }^{*}$ can be exchanged by stronger binding ligands. Thus, one GaCp* unit of $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dvds})$, which is assumed to bind terminally, was substituted by dpa, resulting in $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dvds})(\mathrm{dpa})$. This exchange reaction enabled the structural suggestion of a $\mathrm{Pd}_{3}$ triangle bridged by three GaCp * ligands as only one $\mathrm{GaCp}^{*}$ was substituted by a dpa ligand.

### 4.2.2. Definite cluster structures as building blocks for further cluster growth or cluster reactivity: Alkyne addition to $\left[\mathrm{PdAl}_{4}\right]$ or $\left[\mathrm{PdGa}_{4}\right]$

The following chapter summarizes parts of the master's thesis from Alexandra A. Heidecker supervised by the author of this dissertation.

### 4.2.2.1. Reactivity of $\left[\mathrm{PdGa}_{4}\right]$ with alkynes



Scheme 14: Overview of the herein discussed products obtained from the reaction of $\left[P d G a_{4}\right]\left(C p^{*}\right)_{4}$ with either 3-hexyne or dpa resulting in the formation of dinuclear $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ regardless of the additive.

In contrast to previously published results, $\left.\left[\mathrm{Ni}(\mathrm{GaCp})^{*}\right)_{4}\right]$ showed high reactivity towards alkynes revealing a new route for cluster growth reactions. Therefore, the reactivity of $[\mathrm{PdGa} 4]\left(\mathrm{Cp}^{*}\right) 4$ was tested
towards different equivalents of 3-hexyne at different temperature while the reaction progress was monitored using LIFDI MS and NMR spectroscopy. As Pd-Ga compounds are known from own experiences to perform $\mathrm{Cp}^{*}$ cleavage during ionization, a reference mass spectrum of the starting material was recorded. As expected, the mass spectrum showed signals which refer to $[\mathrm{PdGa} 4]\left(\mathrm{Cp}^{*}\right)_{3}$ ( $790 \mathrm{~m} / \mathrm{z}$ ) and $\left[\mathrm{PdGa}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(586 \mathrm{~m} / \mathrm{z})$ (see Appendix, Figure 124). Further, it revealed the formation of $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}\left(1233 \mathrm{~m} / \mathrm{z}\right.$ and $\left.\left[\mathrm{M}-\mathrm{Cp}^{*}\right]^{+}: 1103 \mathrm{~m} / \mathrm{z}\right)$ during ionization which can be excluded as a sideproduct by NMR spectroscopy as it was only obtained in traces (6 \%).
Reaction of $\left[\mathrm{PdGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ with 1,2 or 4 eq. of 3 -hexyne at room temperature did not result in any changes in the mass spectrum which displayed the typical signals for $[\mathrm{PdGa} 4]\left(\mathrm{Cp}^{*}\right) 4$ as described above. This is in agreement with the recorded ${ }^{1} \mathrm{H}$ NMR spectrum which, nevertheless, showed a slight shift of the typical signals presumably as a result of 3-hexyne presence. Therefore, both the temperature as well as the additive amount was increased to improve the reactivity. Adding an excess of 3-hexyne (100 eq.) to a solution of $\left[\mathrm{PdGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$, the spectrum was changing within one hour (see Figure 48). The characteristic signals for the starting material disappeared with the reaction progress, whereas signals for the dinuclear compound, $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$, were detected. After three days, $\left[\mathrm{PdGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ was completely converted to $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$. However, hexyne-containing signals could not be obtained.


|  | Experimental <br> $[\mathrm{m} / \mathrm{z}]$ | Cluster assignment |
| :--- | :--- | :--- |
| A | 586.9018 | $\left[\mathrm{PdGa}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ |
| B | 790.9415 | $\left[\mathrm{PdGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ |
| C | 896.8426 | $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ |
| D | $\mathbf{9 2 6 . 0 5 9 7}$ | $\left[\mathrm{PdGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ |
| E | $\mathbf{1 1 0 2 . 8 8 5 9}$ | $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ |

Figure 48: Time dependent LIFDI mass spectra of the reaction $\left[P d G a_{4}\right]\left(C p^{*}\right)_{4}$ with excess 3-hexyne at room temperature in toluene/benzene- $d_{6}$.

Increasing the temperature while using excess of 3-hexyne, the formation of $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ was faster observing the respective peak at $1102 \mathrm{~m} / \mathrm{z}$ and the full disappearance of $[\mathrm{PdGa} 4]\left(\mathrm{Cp}^{*}\right)_{4}$ after twelve hours at $60^{\circ} \mathrm{C}$ and already after one hour at $90^{\circ} \mathrm{C}$. Thus, $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right](\mathrm{Cp})_{5}$ can be seen as the thermodynamically favored product which was also proposed in the previous chapter.
Performing the reaction with 2 eq. dpa instead of 3 -hexyne at $60^{\circ} \mathrm{C}$, signals for $[\mathrm{PdGa} 4]\left(\mathrm{Cp}^{*}\right)_{4}$ were only observed in traces after five hours while peaks referring to $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ were the major products (see

Experimental, Figure 92). In fact, the addition of dpa influenced the reaction rate with the thermodynamically preferred product being formed faster compared to 3-hexyne. Further, both additives affected the cluster growth reaction which was also controlled and influenced by temperature. In both cases, $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ was formed from $\left[\mathrm{PdGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ as building block when applying additives. However, keeping $\left[\mathrm{PdGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ in solution for several hours at the respective temperatures did not lead to the formation of $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$, but rather to decomposition, which could be determined by the release of $\mathrm{Cp}^{*} \mathrm{H}$ by NMR. For the trinuclear compound $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{8}\right]\left(\mathrm{Cp}^{*}\right)_{8}$, it was proposed that it forms $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ in solution which must be accompanied by the dissociation of two $\mathrm{GaCp}^{*}$ in solution. ${ }^{73}$ Accordingly, in case of $\left[\mathrm{PdGa}_{4}\right]\left(\mathrm{Cp}^{*}\right) 4$, it is also possible that one or two $\mathrm{GaCp}^{*}$ dissociate from the Pdcenter in solution induced from alkynes leading to the formation of highly unsaturated [PdGa2] ${ }^{\left(\mathrm{Cp}^{*}\right)_{2}}$ and [PdGa3](Cp*)2 intermediates, thus, favoring the formation of dinuclear compounds. This is also consistent with the unusual changes in the ratio of suggested fragments compared to product or starting material (see peaks $A, B$, and $D$ ).

### 4.2.2.2. Reactivity of $\left[\mathrm{PdAl}_{4}\right]$ with 3-hexyne



Scheme 15: Overview of the herein discussed products obtained during the reaction of $\left[\mathrm{PdAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ with 3-hexyne.
[PdGa4] $\left(\mathrm{Cp}^{*}\right)_{4}$ favored the selective formation of dinuclear compounds as $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ while the dinuclear Ni-analog was not obtained from $\left[\mathrm{NiGa}_{4}\right]\left(\mathrm{Cp}^{*}\right) 4$, but higher nuclear compounds as $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ and $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}$. In contrast, $\left[\mathrm{NiAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ did not show any reactivity for cluster growth reactions. Thus, $\left[\mathrm{PdAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ was investigated as a potential candidate for cluster growth. In this context, the influence of alkynes on the dissociation behavior of $\left[\mathrm{PdAl} l_{4}\right]\left(\mathrm{Cp}^{*}\right){ }_{4}$ and the associated cluster growth reaction were studied with different concentrations of the additive and at different temperatures and monitored using LIFDI MS and NMR spectroscopy.
In accordance to $\mathrm{Pd} / \mathrm{Ga}$, a reference mass spectrum of $\left[\mathrm{PdAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ was recorded showing signals at $754 \mathrm{~m} / \mathrm{z}\left([\mathrm{M}]^{+}\right)$and $592 \mathrm{~m} / \mathrm{z}\left(\left[\mathrm{M}-\mathrm{AlCp}^{*}\right]^{+}\right)$and a small peak for the dinuclear $\left[\mathrm{Pd}_{2} \mathrm{Al}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ at $1024 \mathrm{~m} / \mathrm{z}$ (see Figure 49, black trace). The reactivity of $\left[\mathrm{PdAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ in the presence of 3 -hexyne as the additive was similar to $\left[\mathrm{PdGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)$. No significant changes in the mass spectrum were observed at room temperature with low concentrations (1, 2 or 4 eq.) of 3-hexyne. Increasing the amount of the additive to an excess of 100 eq., the reaction showed the formation of the dinuclear compound $\left[\mathrm{Pd}_{2} \mathrm{Al}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ ( $1024 \mathrm{~m} / \mathrm{z}$ ). Compared to PdGa, the formation of the dinuclear compound in Pd-Al is less favored as the starting material was still present after three days at room temperature and after 12 hours at $60^{\circ} \mathrm{C}$ in
high yields (see Appendix). Performing the reaction at $90^{\circ} \mathrm{C}$, however, the mass spectrum revealed the formation of higher nuclear compounds within five hours (Figure 49) which can be assigned to $\left[\mathrm{Pd}_{4} \mathrm{Al}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{7}(1559 \mathrm{~m} / \mathrm{z})$ and its fragments. Notably, as mentioned before, the assignment of AlCp*and 3-hexyne-containing reaction mixtures is complex and requires highly accurate evaluation as it only differs in $2 \mathrm{~m} / \mathrm{z}$. In this case, nevertheless, hexyne units are unlikely to attach to Pd-Al compounds as the reactions were performed above the boiling point of 3-hexyne.


Figure 49: Time-dependent LIFDI mass spectra of the reaction $\left[\mathrm{PdAl}_{4}\right]\left(\mathrm{Cp}{ }^{*}\right)_{4}$ with 100 -fold excess 3 -hexyne at $90{ }^{\circ} \mathrm{C}$ in toluene/benzene- $d_{6}$. Clusters assigned to products are given in bold.

Due to the different binding modes of $\mathrm{AlCp}^{*}$, which can be both terminally or bridging, the structure of the observed compound $\left[\mathrm{Pd}_{4} \mathrm{Al}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{7}$ can be modeled by comparison to already known $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{\dagger} \mathrm{Bu}\right)_{7}\right]$ (Figure 50). Both exhibit four core metals which are surrounded by seven ligands. Thus, the proposed structure features a $\mathrm{Pd}_{4}$-tetrahedron which is stabilized by three $\mathrm{Pd}_{2}$-edge-bridging and four terminal bound AICp* moieties.


Figure 50: Molecular structure of $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{*} \mathrm{Bu}\right)_{7}\right]$ determined by $\mathrm{SC}-\mathrm{XRD}{ }^{146}$ (left) and structural suggestion for $\left[\mathrm{Pd}_{4}\left(\mathrm{AlCp}^{*}\right)_{]}\right]$as proposed by ORCA5.0 (BP86-D3/def2-tzvpp).

It has to be stated clearly that this is the first time observing a homoleptic $\mathrm{M}_{11}$ compound of a Pd-Al system obtained in a cluster growth reaction. Such behavior has so far only been observed for Ni-Ga clusters.

### 4.2.3. Conclusion Pd-Chemistry

The influence of additives (3-hexyne, dpa) and temperature on the Pd-E cluster formation was tested either during synthesis or by addition to a definite cluster structure as $\left[\mathrm{PdE}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{E}=\mathrm{Al}, \mathrm{Ga})$. It was shown that $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ as precursor is highly sensitive to temperature only allowed addition of ECp* at low temperatures. Therefore, these studies were only carried out with GaCp*, as AICp* is not reactive below $40^{\circ} \mathrm{C}$. While the reaction at $-30^{\circ} \mathrm{C}$ resulted in $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dvds})$, the reaction performed at room temperature led to a cluster growth reaction yielding $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dvds})$ or $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})$ in the presence of dpa. Further increase of the temperature revealed the formation of the thermodynamically favored $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ as previously reported. ${ }^{73}$ The clusters $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]$ and $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{5}\right]$ can be seen as intermediate compounds on the way to $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]$. These intermediates can be trapped by the appropriate choice of temperature or by the addition of an additive. Based on these findings, it is assumed that $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]$ is formed by cluster growth and subsequently cluster degradation caused by excess $\mathrm{GaCp}^{*}$ in solution.
Starting from a definite cluster structure, such as $\left[\mathrm{PdGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ or $\left[\mathrm{PdAl}_{4}\right]\left(\mathrm{Cp}^{*}\right) 4$, the compound initially showed no reactivity towards additives. Only excess of additives led to the formation of dinuclear compounds as $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ or $\left[\mathrm{Pd}_{2} \mathrm{Al}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$. As previously reported for $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{8}\right]\left(\mathrm{Cp}^{*}\right)_{8}$ which showed the formation of $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ in solution by dissociation of $\mathrm{GaCp}^{*}$, the formation of $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ is proposed to be formed as a result of $\mathrm{GaCp}{ }^{*}$ dissociation from $\left[\mathrm{PdGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$. Thus, highly reactive and unsaturated intermediates as $\left[\mathrm{PdGa}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ and $\left[\mathrm{PdGa} a_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ are formed in solution which then recombine to form the dinuclear compounds as evidenced by mass spectrometry. In case of Pd-AI, the reaction starting from $\left[\mathrm{PdAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ with an excess of the additive resulted in $\left[\mathrm{Pd}_{2} \mathrm{Al}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ first, and at higher temperature in $\left[\mathrm{Pd}_{4} \mathrm{Al}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{7}$ which is the first high tetranuclear $\mathrm{Pd}-\mathrm{Al}$ compound. It is hypothesized that the formation of $\left[\mathrm{Pd}_{4} \mathrm{Al}_{7}\right]$ is the result of the recombination of two intermediates, specifically $\left[\mathrm{Pd}_{2} \mathrm{Al}_{4}\right]$ and $\left[\mathrm{Pd}_{2} \mathrm{Al}_{3}\right]$, which are formed by AlCp * dissociation. Considering that GaCp * is known for its dissociation behavior in solution as demonstrated in the case of [PdGa4], such cluster growth is also expected for [ $\mathrm{Pd}_{2} \mathrm{Ga}_{5}$ ], possibly when high temperatures, such as $120^{\circ} \mathrm{C}$, are applied and dpa is used as an additive.
In conclusion, in this chapter, the cluster growth behavior of $\mathrm{Pd}-\mathrm{Ga}$ or $\mathrm{Pd}-\mathrm{Al}$ compounds depending on the temperature and additive concentration has been studied. While Pd-Ga ended up at the thermodynamically stable $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]$ in the presence of excess of additive, the formation of the first tetranuclear $\left[\mathrm{Pd}_{4} \mathrm{Al}_{7}\right]$ was observed in the case of $\mathrm{Pd}-\mathrm{Al}$.

### 4.3. Synthetic access to Pt-E complexes

The following chapter summarizes parts of the Bachelor's thesis from Patricia Aufricht supervised by the author of this dissertation. The idea and the concept for the performed experiments originated from the author of this thesis.

In the following, the synthesis and reactivity of Pt-E clusters are systematically investigated depending on different parameters. For this purpose, $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right]$ was reacted with $E C p^{*}$ and alkynes as the additive as illustrated in Scheme 16. The temperature (RT, $60^{\circ} \mathrm{C}, 90^{\circ} \mathrm{C}$ ) and the additive itself as well as the concentration of ECp* and additive were varied and monitored in-situ by means of NMR spectroscopy and LIFDI mass spectrometry.


Scheme 16: Reaction of $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ with different ECp* and additives as performed in this thesis.

### 4.3.1. Pt -Ga clusters obtained from $\left[\mathrm{Pt}(\mathrm{Cod})_{2}\right]$



Scheme 17: Overview of the herein discussed products obtained during the reaction of $\left[P t(c o d)_{2}\right]$, GaCp* and either 3-hexyne (left) or dpa (right) dependent on additive or temperature control.

## Reaction of $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right]$ with $\mathrm{GaCp}^{*}$ and 3-hexyne

In accordance with $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right],\left[\mathrm{Pt}(\operatorname{cod})_{2}\right]$ was chosen as the platinum-precursor due to its flexible and easy substitutable ligands. Both 3-hexyne and GaCp* were handled as 1 M solutions in toluene, with 3-hexyne added prior to $\mathrm{GaCp}^{*}$. The reaction was performed with 1 eq . $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right], 1 \mathrm{eq}$. $\mathrm{GaCp}^{*}$ and different concentrations 3 -hexyne ( 1 and 4 eq.) at room temperature. Compared to Ni , it was highly
sophisticated to obtain any useful spectrum as it mostly offered a bad signal-to-noise ratio when using the same concentrations as for Ni. Therefore, higher concentrations related to Pt were used to obtain useful mass spectra.


|  | Experimental <br> $[\mathrm{m} / \mathrm{z}]$ | Cluster assignment |
| :--- | :--- | :--- |
| A | 1229.0539 | $\left[\mathrm{Pt}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{2}$ |
| B | $\mathbf{1 3 1 0 . 1 3 2 3}$ | $\left[\mathrm{Pt}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{3}$ |
| C | 1433.0999 | $\left[\mathrm{Pt}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{2}$ |

Figure 51: Left: Time dependent LIFDI mass spectra of the reaction [Pt(cod) ${ }_{2}$ ] (1 eq.), GaCp* (1 eq.) and 3-hexyne (1 eq.) in toluene at room temperature. Right: Cluster assignment of observed peaks. Signals which are related to product signals are given in bold.

While the reaction with high additive amount only revealed signals below $600 \mathrm{~m} / \mathrm{z}$ which refer to organic residues, the reaction with 1 eq. of 3-hexyne showed the formation of $\left[\mathrm{Pt}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})_{3}(1310.13 \mathrm{~m} / \mathrm{z})$ and its fragment $\left[\mathrm{Pt}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{2}\left(1229.05 \mathrm{~m} / \mathrm{z}\right.$, [M-hex] $\left.{ }^{+}\right)$already after two hours (Figure 51). After six hours, a similar cluster, $\left[\mathrm{Pt}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{2}(1433.10 \mathrm{~m} / \mathrm{z})$, was obtained accompanied by the
 increase of $505 \mathrm{~m} / \mathrm{z}$ as the major product was recognized which could not yet be unambiguously assigned but is attributed to an organic residue based on the isotopic pattern. After one day, the Pt-Ga clusters are completely decomposed as only organic isotopic patterns could be detected. For platinumbased clusters, Cp *-cleavage induced by instrumental fragmentation was also observed which has already been described for Pd-compounds in the previous chapter. It is assumed that the described Pt -Ga clusters are kinetic products which are not stable in solution for a longer period of time which decomposes within one day while releasing organic residues. Keeping the reaction solution at $-80^{\circ} \mathrm{C}$ should slow down decomposition and enable longer storing without further reaction which has not been yet verified.
If instrumentally induced $\mathrm{Cp}^{*}$ cleavage is considered, the obtained clusters $\left[\mathrm{Pt}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})_{3}$ and $\left[\mathrm{Pt}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{2}$ can be seen as structurally analog for already known $\left[\mathrm{Pd}_{3}\left(\mathrm{InCp}^{*}\right)_{3}(\mathrm{PPh})_{3}\right]$ and $\left[\mathrm{Pd}_{3} \mathrm{Al}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ as published by the group of $R$. A. Fischer. ${ }^{73}$ As depicted in Figure 52, the crystal structure of $\left[\mathrm{Pd}_{3}(\operatorname{InCp})_{3}(\mathrm{PPh})_{3}\right]$ features a $\mathrm{Pd}_{3}$-triangle which is face-capped by two $\operatorname{InCp}{ }^{*}$ ligands revealing a trigonal-bipyramidal $\mathrm{Pd}_{3} \mathrm{In}_{2}$-core. The third $\operatorname{InCp}{ }^{*}$ moiety is $\mathrm{Pd}_{2}$-edge-bridging, while one phosphine is terminally bound to one Pd atom each.


Figure 52: Crystal structure of $\left[\mathrm{Pd}_{3}(\operatorname{InCp})_{3}\left(P P h_{3}\right)_{3}\right]$ as determined by SC-XRD from Fischer et al. ${ }^{73}$ resembling a structural analog of $\left[\mathrm{Pt}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(h e x)_{3}$. H atoms are omitted for clarity. Phenyl rings are depicted in wireframe. Color code: Pd, red; In, light yellow; $P$, light blue; $C$, grey.

Considering now Pt to be analog to Pd and Ga to be analog to In (to some extent), the obtained complex $\left[\mathrm{Pt}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}$ is expected to have a trigonal bipyramidal $\mathrm{Pt}_{3} \mathrm{Ga}_{2}$ core structure with one additional $\mathrm{Pd}_{2}$-edge-bridging $\mathrm{GaCp}^{*}$. In addition, both, phosphine and 3-hexyne, can be considered as twoelectron donor ligands, which suggests a side-on coordination of 3 -hexyne to one Pd metal per ligand. The same is applicable for [ $\mathrm{Pt}_{3} \mathrm{Ga}_{4}$ ] where only one 3 -hexyne ligand is exchanged by $\mathrm{GaCp}^{*}$ which can either bind terminally or $\mathrm{Pd}_{2}$-edge-bridging. In that case, the trigonal bipyramidal core structure is maintained.

## Reaction of $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right]$ with $\mathrm{GaCp}^{*}$ and dpa

As a second additive, the influence of dpa during Pt-Ga synthesis was investigated while varying different parameters as temperature (r.t., $60^{\circ} \mathrm{C}, 90^{\circ} \mathrm{C}$ ) and additive concentration ( $1 \mathrm{eq} ., 4 \mathrm{eq}$.). Performing the reaction of $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ ( 1 eq .) with $\mathrm{GaCp}^{*}$ ( 1 eq .) and dpa ( 1 eq .) in toluene at room temperature, the mass spectrum showed the selective formation of $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})(1252 \mathrm{~m} / \mathrm{z})$ within two hours. Further reaction at room temperature resulted in $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{2}(1157 \mathrm{~m} / \mathrm{z})$ after six hours (see Figure 53), besides the signal for $\left[\mathrm{Pt}_{2} \mathrm{Ga} 4\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})$, which can be either seen as product itself or as fragment of $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}$ due to $\mathrm{GaCp}^{*}$ cleavage which unfortunately could not even be detected in traces in the respective mass spectrum. If $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{2}$ is assumed as product, it is possible to exhibit a Pt 2 center which is bridged by a tpbd-unit as also observed for $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tpbd})(\mathrm{dpa})$ or $\left[\mathrm{Ni}_{3}\right](\mathrm{Cp})_{2}(\mathrm{tpbd})(\mathrm{dpa})^{158}$. The $\mathrm{Pt}_{2}$ complex has to be further stabilized by terminally bound $\mathrm{GaCp}^{*}$ where one $\mathrm{GaCp}^{*}$ is attached to one Pd -atom. Nevertheless, it could also be obtained due to dpa cleavage and thus results from $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{3}$.


Figure 53: Left: LIFDI mass spectra of the reaction $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ (1 eq.) with $\mathrm{GaCp}^{*}(1 \mathrm{eq}$. ) and dpa ( $\Delta$ eq.) at room temperature after six hours in toluene. Right: Cluster assignment related to the obtained signals.

Increasing the additive concentration to four equivalents while maintaining the Pt-Ga ratio, the signal at $1157 \mathrm{~m} / \mathrm{z}$ assigned to $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{2}\right]$ is obtained as major product while the signal for $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})$ at $1253 \mathrm{~m} / \mathrm{z}$ could not be observed. Increasing the reaction temperature to 60 or $90^{\circ} \mathrm{C}$, the mass spectrum revealed the formation of $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})$ at $1253 \mathrm{~m} / \mathrm{z}$, initially (Appendix, Figure 93). After six hours at $60^{\circ} \mathrm{C}$, two additional signals at $1626 \mathrm{~m} / \mathrm{z}$ and $1652 \mathrm{~m} / \mathrm{z}$ could be detected in traces which were assigned to $\left[\mathrm{Pt}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}$ and $\left[\mathrm{Pt}_{3} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})$ being structurally related to the above described hexyne species. However, the increase in temperature also caused the preferred formation of organic residues which is a result of cluster decomposition and is preferred over time. Consequently, although Pt-Ga cluster syntheses can be controlled by addition of additives and their concentrations, they are also showed high temperature-sensitivity and less stability at high temperatures for a long time. As the formation of $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{2}$ was favored at higher temperatures and higher concentrations, it resembles the thermodynamically preferred product. The metal content in the obtained clusters is decreasing, while the dpa-Pt ratio is increasing with higher additive amount from 0.5 in $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})$ to 1 in $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{2}$. These findings are comparable to the experiences in Ni -Al cluster syntheses where smaller clusters were preferred at higher additive concentrations due to the binding affinity of the alkynes to transition metals.

## Structural suggestion for $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})$

For $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})$, a similar structure to previously published $\left[\mathrm{Pt}_{2}\left(\mathrm{ECp}^{*}\right)_{a}(\mathrm{~L})_{c}\right]$ compounds, as $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}{ }^{71}$ and $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}\left(\mathrm{PPh}_{3}\right)^{73}$, is expected (see Figure 54). Both known compounds feature a $\mathrm{Pt}_{2}$ core bridged by three $\mu_{2}$-coordinated GaCp *. The remaining two ligands are each terminally bound to one Pt atom. Since all $\left[\mathrm{TM}_{2} \mathrm{~L}_{5}\right](\mathrm{TM}=\mathrm{Ni}, \mathrm{Pd}, \mathrm{Pt})$ shows similar structural motifs with a $\mathrm{TM}_{2}$ center bridged by three ligands, this is also suggested for $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right){ }_{4}(\mathrm{dpa})$. It is further proposed that $G a C p^{*}$ is favored in the bridging position compared to dpa, while the dpa is expected to bind side-on to one Pt atom.




Figure 54: Left: Proposed structure for $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})$; Structure of $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}\left(\mathrm{PPh}_{3}\right)($ middle $)$ and $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{right})$ as published from Fischer et al. ${ }^{71,73}$

These findings are also in agreement with the NMR spectra. As the NMR spectra were recorded in-situ, full assignment of the signals was not possible. Though, the ${ }^{1} \mathrm{H}$ NMR spectrum showed typical signals for cod at 2.21 and 5.54 ppm and $\mathrm{Cp}^{*} \mathrm{H}$ at 0.99 , 1.72, 1.79 and 2.47 ppm besides the residual proton signal of the solvent toluene- $\mathrm{d}_{8}$. Further, it exhibited a signal at 1.88 ppm which is in the characteristic range for bound ECp*71, 73 and correlates to 10.9 ppm and 113.3 ppm in the ${ }^{13} \mathrm{C}$ NMR spectrum when performing 2D NMR measurements $\left({ }^{1} \mathrm{H} /{ }^{13} \mathrm{C}\right.$ HSQC/ HMBC$)$. It can be excluded that the signal is related to non-coordinated GaCp* which would have its signal at 1.93 ppm . As the spectrum only revealed the signal for one $\mathrm{GaCp}^{*}$, but the structure suggests two signals in a ratio $3: 1$, it is assumed that terminal and bridging GaCp* are exchanging on the NMR time scale due to fluxional processes. This could be resolved by low temperature NMR measurements which were not done yet. In the range of the aromatic signals, there were many overlapping peaks detected which could not be fully assigned. However, it was possible to identify two significant signals: 7.78 ppm (dd) and $7.46 \mathrm{ppm}(\mathrm{m})$. The latter could be assigned to free dpa when comparing to the 2D NMR spectra and previously obtained data (see chapter 4.1.2.3.). The former signal at 7.78 ppm revealed an integral of four H atoms when comparing to 60 H atoms of the GaCp* which is referred to $o-H$ atom of the dpa-phenyl-rings. This duplet of duplet correlates to the signal at 130.9 ppm in the ${ }^{13} \mathrm{C}$ NMR spectrum. These values could be carefully compared to the data obtained for $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tpbd})(\mathrm{dpa})$ that exhibited the duplet of duplet of the $0-\mathrm{H}$ and $o-C$ atoms at 7.76 ppm and 130.0 ppm , respectively. Due to the low resolutions in HMBC and the low concentration, it was not possible to assign further signals related to dpa. Nevertheless, it is suggested that the dpa is side-on coordinated to the platinum which is supported by the obtained NMR shift as well as the ratio of the $\mathrm{Cp}^{*}$ compared to the $o-\mathrm{H}$ atom of the dpa. For further assignment and proof of the suggestion, an isolation of the compound accompanied with SC-XRD measurement or a workup procedure to separate unreacted dpa is necessary.

### 4.3.2. Influence of diphenylacetylene as additive on Pt-Al cluster formation



Scheme 18: Overview of the herein discussed products obtained during the reaction of [ $\mathrm{Pt}(\mathrm{cod})_{2}$ ], AlCp* and dpa depending on the additive concentration (left) or on the metal ratio (right).

As additives and temperature showed a high impact on the formation of Pt-Ga clusters and complexes, it is of utmost importance to systematically investigate their influence on Pt-Al cluster synthesis. Therefore, $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right], \mathrm{AlCp} *$ and dpa was reacted at different temperatures and ratios, and monitored in-situ by LIFDI MS and NMR spectroscopy. At first, the dpa concentration is varied while using 1 eq. $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ and 1 eq. AICp*. Due to the insolubility of $\mathrm{AlCp}^{*}$ at room temperature, those experiments were only performed at elevated temperatures. The reactions with low additive concentrations ( 0.5 and 1.0 eq.) did not result in any cluster formation as only $\mathrm{m} / \mathrm{z}$ values below 300 were detected which could not be referred to Pt-organyls. Nevertheless, the increase of the additive amount to 4 eq. enabled the formation of $[\mathrm{PtAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}(891 \mathrm{~m} / \mathrm{z})$ within two hours which can be seen as Pt-analog of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}$ as discussed in chapter 4.1.2.3. The mass spectrum depicted in Figure 55, black trace, further showed the fragment peak at $713 \mathrm{~m} / \mathrm{z}$ which is obtained due to dpa-cleavage. Although the formation of $[\mathrm{PtAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}$ was indicated in the reaction with dpa, it could only be detected in traces. Interestingly, Pt did not form a complex similar to $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})$ as in case of Ni during the synthesis of $[\mathrm{PtAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})$. However, after five hours at $60^{\circ} \mathrm{C}$, the formed PtAl complex has been completely disappeared as evidenced by LIFDI MS. It can be concluded that this Pt-AI complex is not stable in solution or at elevated temperature for an extended period of time. Performing the reaction with the same ratios at $90^{\circ} \mathrm{C},[\mathrm{PtAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}$ and its fragment peak was only detected as small signals while organic residues ( $<300 \mathrm{~m} / \mathrm{z}$ ) resembled the major products. This could be caused by either decomposition of the compound itself or the precursor at high temperatures, inhibiting the reaction even before it could start.


|  | Experimental $[\mathrm{m} / \mathrm{z}]$ | Cluster assignment |
| :---: | :---: | :---: |
| A | 682.2664 | $\left[\mathrm{PtAl}_{3}\right](\mathrm{Cp} *)_{3}+\mathrm{H}$ |
| B | 708.2397 | $\left[\mathrm{PtAl}_{4}\right](\mathrm{Cp} *)_{3}$ |
| C | 713.2145 | [PtAl](Cp*)(dpa) ${ }_{2}$ |
| D | 844.3623 | $\left[\mathrm{PtAl}_{4}\right]\left(\mathrm{Cp}{ }^{*}\right)_{4}+\mathrm{H}$ |
| E | 891.2952 | [PtAI](Cp*)(dpa) ${ }_{3}$ |
| F* | 1048.4085 | [ ](Cp*)  ${ }_{4}$ (dpa) |

Figure 55: Left: LIFDI mass spectra of the reaction $\left[P t(c o d)_{2}\right]$ (1 eq.) with dpa (4 eq.) and $A I C p^{*}\left(\Delta\right.$ eq.) at $60{ }^{\circ} \mathrm{C}$ after two hours in toluene. Right: Cluster assignment of the obtained signals. Peaks which could be assigned as product are given in bold.

As the reaction with 4 eq. dpa and 1 eq. $A I C p^{*}$ selectively yielded $[\mathrm{PtAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}$ (13) (Figure 55, black trace), the impact of the Al content on cluster formation and potential cluster growth was also investigated. Therefore, the reaction was further carried out using $1 \mathrm{eq} .\left[\operatorname{Pt}(\operatorname{cod})_{2}\right], 4$ eq. dpa and 4 eq . AICp* since lower additive concentration did not show the expected results with 1 eq . AICp* as mentioned before. The mass spectrum recorded after two hours showed the selective formation of catalytically inert $\left[\mathrm{PtAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(844 \mathrm{~m} / \mathrm{z})$ accompanied by its fragments $\left[\mathrm{PtAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(708 \mathrm{~m} / \mathrm{z})$ and $\left[\mathrm{PtAl}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(682 \mathrm{~m} / \mathrm{z})$, but no dpa-containing compounds were detected (Figure 55, red trace).
Consequently, dpa as additive enabled the synthesis of small Pt-Al complexes while stabilizing the metal core as a ligand. However, if the used Al content is too high, only the homoleptic compound $[\mathrm{PtAl} 4](\mathrm{Cp})_{4}$ is preferentially formed.

## Structural suggestion for [PtAl](Cp*)(dpa)3 (13)

As previously mentioned, the obtained mononuclear complex $[\mathrm{PtAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}$ (13) could be seen as Pt-analog of the above described $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}=[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tpbd})(\mathrm{dpa})(8)$. In order to confirm this hypothesis, 1D and 2D NMR studies were conducted and compared to the Ni-analog. The ${ }^{1} \mathrm{H}$ NMR spectrum revealed signals at 1.65 ppm related to bound AICp * as metallacycle and at 2.21 ppm and 5.54 ppm for cod in addition to solvent residual signals. Further, it showed many signals in the aromatic range which partly overlaps with either impurities or solvent. Unreacted dpa was determined at 7.46 and 7.00 ppm . All other signals referred to 13 which were assigned in comparison with 8 as mentioned in the Ni-Al chapter. The signal assignment was divided in three different phenyl-moieties which are depicted in Figure 56. The signals at $7.93(o), 7.29(m)$ and $7.17 \mathrm{ppm}(p)$ belong to the phenyl rings bound to side-on coordinated acetylene (red). For the tpbd-metallacylcle, signals at 7.22 (o), 6.69 ( $m$ ) and $6.55 \mathrm{ppm}(p)$ were related to backbone phenyl-rings (light blue) while the peaks at 7.32 (o), 6.94 $(m)$ and $6.85 \mathrm{ppm}(p)$ referred to the phenyl rings adjacent to the aluminum (dark blue). With the help of ${ }^{1} \mathrm{H} /{ }^{13} \mathrm{C}$ HSQC and HMBC the respective ${ }^{13} \mathrm{C}$ signals were assigned. Therefore, the signals at $128.8\left(\mathrm{C}^{1}\right)$, $133.5\left(\mathrm{C}^{2}\right), 130.9\left(\mathrm{C}^{3}\right), 129.1\left(\mathrm{C}^{4}\right)$ and $128.9 \mathrm{ppm}\left(\mathrm{C}^{5}\right)$ relate to side-on coordinated dpa, while the peaks
at $132.3\left(C^{6}\right), 146.0\left(C^{7}\right), 131.6\left(C^{8}\right), 128.0\left(C^{9}\right)$ and $124.5 \mathrm{ppm}\left(C^{10}\right)$ were assigned to carbon and phenyl adjacent to aluminum and $126.6\left(\mathrm{C}^{11}\right), 136.1\left(\mathrm{C}^{12}\right)$, $132.3\left(\mathrm{C}^{13}\right)$, $127.8\left(\mathrm{C}^{13}\right)$ and $127.3 \mathrm{ppm}\left(\mathrm{C}^{14}\right)$ to carbon and phenyl rings on the backbone of the metallacycle, respectively. Compared to $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}$ which is structurally similar to $[\mathrm{PtAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}$, the NMR shifts of the characteristic signals for $\mathrm{AICp}^{*}$ and the o-H of side-on coordinated dpa were in a similar range. While the NMR spectrum of the Ni-compound exhibited signals at 1.65 ppm for AICp* and 7.76 ppm for $\mathrm{o}-\mathrm{CH}$ of the acetylene, the Pt-analog shows peaks at 1.65 ppm for $\mathrm{AlCp}^{*}$ and 7.93 ppm for $\mathrm{O}-\mathrm{CH}$ of the acetylene. Based on the findings from the NMR and MS studies accompanied with theoretical calculations, it can be concluded that $[\mathrm{PtAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}$ forms a metallcycle consisting of a tetraphenylbutadiene unit as obtained for the Ni-analog as well as side-on coordinated acetylene as depicted in Figure 56 left.


Figure 56: Left: Structural suggestion of $[P t A I]\left(C p^{*}\right)(t p b d)(d p a)$ as proposed by theoretical calculations (BP86-D3/def2-tzvpp). Color code: light blue, Pt; yellow, Al; grey, C. Phenyl and Cp* rings are partly depicted in wireframe. H-atoms are omitted for clarity. Right: ${ }^{1} \mathrm{H}^{1} \mathrm{H}$ COSY NMR spectrum of $[P t A I]\left(C p^{*}\right)(t p b d)(d p a)$ with signal assignment.

### 4.3.3. Conclusion: $\mathrm{Pt} /$ E cluster synthesis

This chapter dealt with the investigation of Pt-Ga and Pt-Al clusters depending on the additive concentration and temperature. The reaction of $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right]$ with $\mathrm{GaCp}^{*}$ and 3 -hexyne revealed the formation of $\left[\mathrm{Pt}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{3}$ which can be seen as structural analog of already known $\left[\mathrm{Pt}_{3} \mathrm{In}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{PPh}_{3}\right)_{3}$. In contrast, the reaction including dpa as the additive led to the formation of the dinuclear compound $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})$ which is an analog compound of the [ $\mathrm{TM}_{2} \mathrm{~L}_{5}$ ] class. However, those compounds are highly sensitive to temperature and are not stable in solution at room temperature (or higher) as it decomposed over a longer period of time as determined by LIFDI MS. Performing the reaction with $\mathrm{AICp}^{*}$ instead of $\mathrm{GaCp}^{*}$, the mass spectra only revealed the formation of mononuclear compounds as $\left[\mathrm{PtAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ and $[\mathrm{PtAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}$ depending on the $\mathrm{AlCp}{ }^{*}$ amount. Nevertheless, these compounds were only obtained at $60^{\circ} \mathrm{C}$ in high yields while the reactions with higher temperatures only resulted in the detection of organic residues and low yields of desired Pt - Al compounds.

Similar to the findings of Ni-E cluster synthesis, $\mathrm{Pt}-\mathrm{Ga}$ and $\mathrm{Pt}-\mathrm{Al}$ could be distinguished by the different binding modes of the acetylenes depending on the metal $E$ as well as the ability to form higher nuclear clusters. While the Pt-Al system favored the formation of mononuclear clusters as also observed for $\mathrm{Ni}-\mathrm{Al}, \mathrm{Pt}-\mathrm{Ga}$ cluster syntheses could be controlled either by the choice of additive forming tri- and dinuclear clusters or by temperature. Furthermore, the acetylene in Pt-Ga system preferred the most possible distance and did not show any interaction of two alkynes or with the second ligand, ECp*. In contrast, the Pt-Al system showed the dimerization and trimerization of dpa while forming a metallacycle with AICp* in case of dimerized dpa as indicated by NMR spectroscopy.

In accordance with $\mathrm{Ni}-\mathrm{Ga}$ and $\mathrm{Ni}-\mathrm{Al}$, it was possible to propose a valid structure for the obtained $[\mathrm{PtAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{3}$ using the combination of different analytical methods. This exhibits a metallacycle consisting of AICp* and dimerized dpa, resulting in a butadiene unit, as well as a side-on coordinated dpa unit. This additional example underpins the conceptual idea of in-situ characterization of either intermediates or highly sensitive compounds towards vacuo or advanced work-up procedures.

### 4.4. Synthesis of $T M / Z n$ compounds

As TM/Zn offer high catalytic activity with outstanding selectivity, ${ }^{10}$ the synthesis of TM-Zn compounds ( $\mathrm{TM}=\mathrm{Ni}, \mathrm{Pt}$ ) was studied partly depending on the addition of additives. Such TM-Zn cluster or complexes can be either obtained using $\mathrm{ZnMe}_{2}$ or $\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$. While $\mathrm{ZnMe}_{2}$ undergoes $\mathrm{Ga} / \mathrm{Zn}$ exchange reactions where one GaCp* is substituted by two Zn -ligands, namely ZnMe and ZnCp * as one electron
 $\left[\mathrm{TM}\left(\mathrm{ZnZnCp}{ }^{*}\right)_{n}\right]$ or $\left[\mathrm{TM}\left(\mathrm{ZnCp}{ }^{*}\right)_{\mathrm{m}}\right]$ complexes via substitution.

### 4.4.1. Synthesis of $\mathrm{Ni} / \mathrm{Zn}$ and $\mathrm{Ni} / \mathrm{Ga} / \mathrm{Zn}$ compounds

### 4.4.1.1. Reaction of $\left[\mathrm{NiGa}_{4}\right]\left(\mathrm{Cp}^{*}\right) 4$ with $\mathrm{ZnMe}_{2}$ and 3-hexyne

The following chapter summarizes parts of the Bachelor's thesis from Anna-Julia Herold supervised by the author of this dissertation. The idea and the concept for the performed experiments originated from the author of this thesis.


Scheme 19: Overview of the herein discussed products obtained during the reaction of $\left[\mathrm{NiGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ and $\mathrm{ZnMe} \mathrm{Z}_{2}$ depending on the metal ratio (left) and with 3-hexyne as additive depending on the additive concentration and temperature (right).

## Synthesis of $\mathrm{Ni} / \mathbf{G a} / \mathbf{Z n}$-complexes via $\mathbf{G a} / \mathbf{Z n}$ exchange

Note: As the LIFDI MS with a Thermo Fisher Exactive Plus Orbitrap analyzer was not installed at the date of the experiments performed, the following mass spectra were recorded on a Waters Micromass LCT TOF mass spectrometer equipped with a LIFDI ion source (LIFDI 700) from Linden CMS GmbH. As a consequence, the mass spectra could differ by max. $1.5 \mathrm{~m} / \mathrm{z}$ due to insufficient calibration and the resolution of the obtained spectra is lower compared to the Orbitrap system.

As previously mentioned, $\mathrm{Ni}-\mathrm{Zn}$ compounds can be obtained by a redox reaction substituting Ga with Zn ligands. The replacement of one $\mathrm{GaCp}^{*}$ ligand with two Zn ligands ( $\mathrm{ZnCp}^{*}, \mathrm{ZnMe}$ ) increases the steric demand on the transition metal center and thus, influencing potential reactivity.

Therefore, $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ was suspended in toluene and different equivalents $\mathrm{ZnMe}_{2}$ was added as a 1 m solution in toluene at different temperatures. The reactions were monitored using in-situ LIFDI MS. The experiments were conducted at low temperatures to avoid the formation of $\left.\left[\mathrm{Ni}(\mathrm{ZnCp})_{4}\right)_{4}(\mathrm{ZnMe})_{4}\right]$ which is usually synthesized at $80^{\circ} \mathrm{C} . .^{96}$


Figure 57: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ with $\Delta \mathrm{eq} . \mathrm{ZnMe}{ }_{2}$ after one hour at $-30^{\circ} \mathrm{C}$ in toluene.

The reactions at $-30^{\circ} \mathrm{C}$ were conducted with 2, 4, 8 and 11 eq . ZnMe . Although the reaction performed with 2 eq. was expected to exchange one GaCp*, the spectrum only revealed the signal at $878.17 \mathrm{~m} / \mathrm{z}$ which is related to $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$. However, performing the reaction with higher concentrations of $\mathrm{ZnMe}_{2}$, the mass spectra showed the formation of $\mathrm{Ni}-\mathrm{Zn}-\mathrm{Ga}$ containing compounds of the formula $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4-n}\left(\mathrm{ZnCp}^{*}\right)_{n}(\mathrm{ZnMe})_{n}\right]$ (Figure 57). Using more than two equivalents $\mathrm{ZnMe}_{2}$, the mass spectrum revealed $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})\right](952 \mathrm{~m} / \mathrm{z})$ as the preferred product. Increasing the $\mathrm{ZnMe}_{2}$ amount to an excess ( 11 eq .) also the Zn -rich species $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)\left(\mathrm{ZnCp}^{*}\right)_{2}(\mathrm{ZnMe})_{2}\right](1104 \mathrm{~m} / \mathrm{z})$ and its fragment $\left(-\mathrm{Cp}^{*} ; 969 \mathrm{~m} / \mathrm{z}\right)$ were observed besides $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})\right]$. Noteworthy, the formation of fullyzinc coordinated $\left[\mathrm{Ni}\left(\mathrm{ZnCp}^{*}\right)_{4}(\mathrm{ZnMe})_{4}\right]$, which is favored with excess $\mathrm{ZnMe}_{2}$, was suppressed due to low temperatures.
As it is assumed that $\mathrm{Ga} / \mathrm{Zn}$ exchange is partly influenced by temperature, the reactions were also performed at $0^{\circ} \mathrm{C}$. Similar to the reaction performed at $-30^{\circ} \mathrm{C}$, the reaction with $2 \mathrm{eq} . \mathrm{ZnMe} \mathrm{Z}_{2}$ showed moderate reactivity towards $\mathrm{ZnMe}_{2}$ as it still revealed the starting material as one of the two major signals. Besides the signal of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right) 4\right]$ at $878 \mathrm{~m} / \mathrm{z}$, the spectrum also indicated the formation of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})\right]$ at $952 \mathrm{~m} / \mathrm{z}$ after one hour (Figure 58). The increase in $\mathrm{ZnMe}_{2}$-amount resulted in the full conversion of the starting material, but not as expected in the selective formation of all three valid trimetallic NiGaZn compounds. While the reaction with 4 and 8 eq . $\mathrm{ZnMe}_{2}$ led to the selective formation of Ga -rich $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})\right]$, where one $\mathrm{GaCp}^{*}$ is exchanged, only excess
of $\mathrm{ZnMe}_{2}$, resulted in the desired zinc-rich compound $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)\left(\mathrm{ZnCp}^{*}\right)_{3}(\mathrm{ZnMe})_{3}\right](1104 \mathrm{~m} / \mathrm{z})$ where three GaCp* ligands are exchanged by six ZnR -ligands. However, when an excess of ZnMe 2 and $0^{\circ} \mathrm{C}$ was applied, the mass spectrum additionally revealed fully exchanged $\left[\mathrm{Ni}\left(\mathrm{ZnCp}{ }^{*}\right)_{4}(\mathrm{ZnMe})_{4}\right]$ at $1181 \mathrm{~m} / \mathrm{z}$. Surprisingly, $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{ZnCp}^{*}\right)_{2}(\mathrm{ZnMe})_{2}\right]$ could only be detected in traces which was expected as the most stable product as it should feature higher symmetry compared to other NiZnGa compounds. Nevertheless, the preferred formation of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{ZnCp}{ }^{*}\right)(\mathrm{ZnMe})\right]$ could be argued by the lower steric demand of five ligands on the central metal compared to zinc-rich compounds as $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)(\mathrm{ZnCp})_{3}(\mathrm{ZnMe})_{3}\right]$ with seven ligands.


|  | Experimental <br> $[\mathrm{m} / \mathrm{z}]$ | Cluster assignment |
| :--- | :--- | :--- |
| A | 818.62 | $\mathrm{C}-\mathrm{Cp}^{*}$ |
| B | $\mathbf{8 7 7 . 6 7}$ | $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ |
| C | 952.74 | $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})\right]$ |
| D | 969.65 | $\mathrm{G}-\mathrm{Cp}^{*}$ |
| E | $\mathbf{1 0 3 1 . 5 1}$ | $\left[\mathrm{Ni}^{\left.\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{ZnCp}^{*}\right)_{2}(\mathrm{ZnMe})_{2}\right]}\right.$ |
| F | 1047.39 | $\mathrm{H}-\mathrm{Cp}^{*}$ |
| G | $\mathbf{1 1 0 4 . 4 7}$ | $\left.\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{(Z n C p *}\right)_{3}(\mathrm{ZnMe})_{3}\right]$ |
| H | $\mathbf{1 1 8 1 . 0 8}$ | $\left[\mathrm{Ni}\left(\mathrm{ZnCp}^{*}\right)_{4}(\mathrm{ZnMe})_{4}\right]$ |

Figure 58: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ with $\triangle \mathrm{eq} . \mathrm{ZnMe}_{2}$ after one/two hour at $0{ }^{\circ} \mathrm{C}$ in toluene

## Reactivity of $\mathrm{Ni} / \mathrm{Ga} / \mathrm{Zn}$-complexes towards 3-hexyne

In order to perform NiGaZn-cluster formation or conversion depending on 3-hexyne without any interaction with residual $\mathrm{ZnMe}_{2}$ or $\mathrm{GaCp}^{*}$, the above-mentioned reactions were dried under vacuo before treatment with 3-hexyne.
Starting from a $\left[\mathrm{NiGa}_{1} \mathrm{Zn}_{6}\right]=\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)\left(\mathrm{ZnCp}^{*}\right)_{3}(\mathrm{ZnMe})_{3}\right]$ enriched solution (Figure 58, green) and adding 4 eq. 3-hexyne related to Ni at room temperature, the mass spectrum, recorded after 3 h , showed the formation of undesired $\left[\mathrm{NiZn}_{8}\right](1181 \mathrm{~m} / \mathrm{z})$ and tetramerized 3-hexyne ( $330 \mathrm{~m} / \mathrm{z}$ ) besides the starting material. However, starting from a mixture which consists of $\left[\mathrm{NiGa}_{4}\right]=\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ and $\left[\mathrm{NiGa}_{3} \mathrm{Zn}_{2}\right]=$ $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})\right]$ (Figure 58, black) and adding 4 eq. 3-hexyne at $60^{\circ} \mathrm{C}$, the mass spectrum revealed highly symmetric $\left[\mathrm{NiGa}_{2} \mathrm{Zn}_{4}\right]=\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{ZnCp}^{*}\right)_{2}(\mathrm{ZnMe})_{2}\right](1030 \mathrm{~m} / \mathrm{z})$ as the preferred product where two $\mathrm{GaCp}^{*}$ moieties are exchanged by four ZnR ligands. The spectrum further exhibits signals which could be assigned to $\left[\mathrm{NiGa}_{3} \mathrm{Zn}_{2}\right]$, $\left[\mathrm{NiGa}_{1} \mathrm{Zn}_{6}\right]$ and $[\mathrm{NiZn} 8$ ] as byproducts (see Appendix, Figure 95). The stepwise conversion of $\left[\mathrm{NiGa}_{3} \mathrm{Zn}_{2}\right]$ to $\left[\mathrm{NiGa}_{2} \mathrm{Zn}_{4}\right]$ could be also observed when starting
from a $\left[\mathrm{NiGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ solution and small amount [ $\mathrm{NiGa}_{3} \mathrm{Zn}_{2}$ ] (Figure 57, black). This mixture was parallel reacted with two different concentrations of 3 -hexyne at $60^{\circ} \mathrm{C}$ in toluene: 4 eq. and 8 eq. The mass spectra recorded after one day revealed the stepwise synthesis of $\left[\mathrm{NiGa}_{2} \mathrm{Zn}_{4}\right]$ from $\left[\mathrm{NiGa}_{3} \mathrm{Zn}_{2}\right]$ induced by 3 -hexyne as the additive. The latter was formed during the reaction from [ $\mathrm{NiGa}_{4}$ ] which was used as the major starting component in the reaction mixture (see Figure 59).


|  | Experimental <br> $[\mathrm{m} / \mathrm{z}]$ | Cluster assignment |
| :--- | :--- | :--- |
| A | 878.15 | $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ |
| B | 894.51 | $\mathrm{D}-\mathrm{Cp}^{*}$ |
| C | 953.58 | $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})\right]$ |
| D | 1029.27 | $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{ZnCp}^{*}\right)_{2}(\mathrm{ZnMe})_{2}\right]$ |
| E | 1105.12 | $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)(\mathrm{ZnCp})_{3}(\mathrm{ZnMe})_{3}\right]$ |
| F | 1183.12 | $\left[\mathrm{Ni}(\mathrm{ZnCp})_{4}(\mathrm{ZnMe})_{4}\right]$ |

Figure 59: LIFDI mass spectra of the reaction $\left[\mathrm{NiGa}_{4}\right]\left(C p^{*}\right)_{4}$ and $\left[\mathrm{NiGa}_{3} \mathrm{Zn}_{2}\right]\left(C p^{*}\right)_{4}(\mathrm{Me})$ (black trace) with 4 eq . (red) or 8 eq . 3-hexyne after one day at $60^{\circ} \mathrm{C}$ in toluene.

However, no hexyne-containing species or cluster growth could be observed using stoichiometric amounts of alkyne. Thus, the experiments were also performed at room temperature and $60^{\circ} \mathrm{C}$ using 3 -hexyne as solvent to gain excess of 3 -hexyne. The reaction with 4 eq. of $\mathrm{ZnMe} \mathrm{e}_{2}$ at $0^{\circ} \mathrm{C}$ (Figure 58 , red) was used as starting material as it formed almost selectively $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{ZnCp}{ }^{*}\right)(\mathrm{ZnMe})\right]$. After the removal of all volatiles, 0.5 mL of 3 -hexyne were added to the solid. Besides the detection of two small peaks which refer to [ $\mathrm{NiGa}_{2} \mathrm{Zn}_{4}$ ] and a fragment of [ $\mathrm{NiZn}_{8}$ ], the reaction conducted at room temperature did not show significant changes as [ $\mathrm{NiGa}_{3} \mathrm{Zn}_{2}$ ] is still the highest peak after one day. Nevertheless, if the reaction was carried out at elevated temperatures $\left(60^{\circ} \mathrm{C}\right)$, there were significant changes recognized in the mass spectrum. Although [ $\mathrm{NiGa}_{3} \mathrm{Zn}_{2}$ ] was still the highest signal, the reaction was less selective and formed hexyne-containing $\mathrm{Ni} / \mathrm{Ga} / \mathrm{Zn}$ species, besides already identified $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4-n}\left(\mathrm{ZnCp}^{*}\right)_{n}(\mathrm{ZnMe}) \mathrm{n}\right]$. As the molecular masses for ZnMe and 3 -hexyne as well as for $\mathrm{GaCp}^{*}$ and $\mathrm{ZnCp}^{*}$ only differ by 3 and $5 \mathrm{~m} / \mathrm{z}$, respectively, and the calibration of the TOF instrument is rather difficult and less precise compared to the Orbitrap system, the identification of the peaks was rather complex. Due to careful comparison of different opportunities, it was possible to identify three possible compounds for the respective signals (Figure 60). For the identification of a valid sum formula, the four highest peaks of each pattern were compared to the experimental ones. As the signals for already assigned compounds differed by max. $1.5 \mathrm{~m} / \mathrm{z}$, the exact masses were not taken into consideration if it
was below the experienced deviation. For the signal obtained at $1017.29 \mathrm{~m} / \mathrm{z}$, there were three clusters figured out: $\left[\mathrm{Ni}_{2}\left(\mathrm{GaCp}^{*}\right)_{2}(\mathrm{ZnMe})(\text { hex })_{5}\right],\left[\mathrm{Ni}_{3}\left(\mathrm{ZnCp}^{*}\right)_{3}(\mathrm{ZnMe})_{3}\right]$ and $\left[\mathrm{Ni}_{5}\left(\mathrm{ZnCp}^{*}\right)_{2}(\mathrm{ZnMe})_{2}(\mathrm{hex})_{2}\right]$. By comparing the highest peaks and their ratio to each other as well as the pattern width, the first compound was determined as possible product as all criteria fitted the best to the experimental pattern. However, as ZnMe is a one electron donor ligand, the compound would reveal an unusual number of electrons on the nickel center. Further, the signal observed at $1170.96 \mathrm{~m} / \mathrm{z}$ could possibly be assigned to clusters as $\left[\mathrm{Ni}_{4}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})(\text { hex })_{3}\right], \quad\left[\mathrm{Ni}_{4}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})_{2}(\text { hex })_{2}\right] \quad$ and $\left[\mathrm{Ni}_{6}\left(\mathrm{GaCp}^{*}\right)_{2}(\mathrm{ZnMe})(\text { hex })_{4}\right]$. As this pattern overlapped with the pattern of $\left[\mathrm{Ni}\left(\mathrm{ZnCp}{ }^{*}\right)_{4}(\mathrm{ZnMe})_{4}\right]$ at $1181 \mathrm{~m} / \mathrm{z}$, it was rather difficult to identify possible candidates. Due to the strong overlap of the right half of the pattern with the peak at 1181 , only the three highest peaks and the left side of the experimental spectrum could be compared with the calculated ones. If the two second highest peaks of the respective possibilities were compared with the obtained spectrum, the first proposed cluster could be excluded as the second highest peak is too high if overlap of the signals was considered. As the two remaining possibilities did not significantly differ by their isotopic pattern, chemical intuition was now required. Considering $\left[\mathrm{Ni}_{6}\left(\mathrm{GaCp}^{*}\right)_{2}(\mathrm{ZnMe})(\mathrm{hex})_{4}\right]$, the $\mathrm{Ni}_{6}$ core might be stabilized by $2 \mathrm{GaCp}^{*}$ and one ZnMe ligands besides the 3-hexyne ligands which are weakly bound to Ni as it is side-on coordinated. In contrast, $\left[\mathrm{Ni}_{4}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})_{2}(\mathrm{hex})_{2}\right]$ reveals two $\mathrm{GaCp}^{*}, \mathrm{ZnCp}^{*}$ and two ZnMe ligands besides the hexyne units. However, both compounds require stabilization from 3-hexyne ligands and are not strongly stabilized by ER-ligands as GaCp*, ZnCp* and ZnMe. Therefore, no conclusion can be established and both clusters remain potential candidates for the signal at $1170 \mathrm{~m} / \mathrm{z}$.


Figure 60: Top: LIFDI mass spectrum of the reaction $\left[\mathrm{Ni}(\mathrm{GaCp})_{3}\left(\mathrm{ZnCp}{ }^{*}\right)(\mathrm{ZnMe})\right]$ with 3-hexyne as solvent after one day at $60^{\circ} \mathrm{C}$. Peaks are assigned as follows: A: [Ni(GaCp*) $\left.{ }^{*}\right](877.59 \mathrm{~m} / \mathrm{z})$; B: [ $\left.\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{ZnCp}{ }^{*}\right)(\mathrm{ZnMe})\right](953.77 \mathrm{~m} / \mathrm{z})$; C: see below left $(1017.29 \mathrm{~m} / \mathrm{z}) ; \mathrm{D}: \quad\left[\mathrm{Ni}(\mathrm{GaCp})_{2}(\mathrm{ZnCp})_{2}(\mathrm{ZnMe})_{2}\right] \quad(1032.31 \mathrm{~m} / \mathrm{z}) ; \quad \mathrm{E}: \quad \mathrm{H}-\mathrm{Cp}^{*} \quad(1047.29 \mathrm{~m} / \mathrm{z}) ; \quad \mathrm{F}: \quad\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)\left(\mathrm{ZnCp}{ }^{*}\right)_{3}(\mathrm{ZnMe})_{3}\right]$ (1105.19 m/z); G: see below, middle (1170.96 m/z); H: [Ni(ZnCp*) $\left.)_{4}(Z n M e)_{4}\right](1181.00 \mathrm{~m} / \mathrm{z})$; J: see below, right (1246.81 m/z).

As the third new signal, the peak at $1246.81 \mathrm{~m} / \mathrm{z}$ was identified which could be related either to [ $\mathrm{Ni}_{6}\left(\mathrm{GaCp}^{*}\right)\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})(\mathrm{hex}) 5$ ],

$$
\left[\mathrm{Ni}_{6}\left(\mathrm{GaCp}^{*}\right)\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})_{2}(\text { hex })_{4}\right]
$$

$\left[\mathrm{Ni}_{4}\left(\mathrm{GaCp}^{*}\right)\left(\mathrm{ZnCp}^{*}\right)_{2}(\mathrm{ZnMe})_{2}(\text { hex })_{3}\right]$. Similar to the first example, the three highest peaks of the patterns as well as their relative intensities were of high interest. Comparing the two highest peaks of the latter two clusters, the intensities of the two highest peaks in the pattern are similar. Considering the experimentally obtained spectrum, the pattern revealed two signals which differ in their intensity. In case of $\left[\mathrm{Nis}_{( }\left(\mathrm{GaCp}^{*}\right)\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})(\mathrm{hex}) 5\right]$, these two peaks of the calculated pattern were consistent with the experimental ones. Further, the third and fourth peaks were also in accordance with the detected spectrum, while the both other possibilities also differed in these intensities from the measured ones. Thus, $\left[\mathrm{Ni}_{6}\left(\mathrm{GaCp}^{*}\right)\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})(\right.$ hex $)$ 5$]$ was identified as potential cluster with high certainty. However, in order to identify the signals unambiguously, the respective mass spectrum have to be measured on a mass spectrometer with high resolution, e.g. Orbitrap, and additionally compared with an NMR spectrum.

In conclusion, it was possible to synthesize Ni-Ga-Zn containing clusters at low temperatures. Their reactivity and dependency towards 3 -hexyne as the alkyne model substrate was investigated which enabled control of Ga:Zn stoichiometry. Due to temperature control, the synthesis without 3-hexyne either resulted in $\left[\mathrm{NiGa}_{3} \mathrm{Zn}_{2}\right]$ or in $\left[\mathrm{NiGa} \mathbf{Z n}_{6}\right.$ ]. However, using 3 -hexyne in excess, the reaction led to the preferred formation of [ $\mathrm{NiGa}_{2} \mathrm{Zn}_{4}$ ]. Addition of 3 -hexyne as solvent to [ $\mathrm{NiGa}_{3} \mathrm{Zn}_{2}$ ], it was possible to obtain compounds of higher nuclearity as $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{2} \mathrm{Zn}\right]$ or $\left[\mathrm{Ni}_{6} \mathrm{GaZn}_{2}\right]$ which are additionally stabilized by hexyne-ligands.

### 4.4.1.2. Reaction of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ with $\mathrm{ZnMe}_{2}$

Addition of 10 eq . $\mathrm{ZnMe} 2_{2}$ to a freshly prepared solution of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ at room temperature selectively led to the formation of $1170 \mathrm{~m} / \mathrm{z}$. However, even in this case the assignment was very difficult, as the signals were partly superimposed with fragments of small by-products. Comparing the obtained isotopic pattern of $1171.0782 \mathrm{~m} / \mathrm{z}$ with the suggestions in Figure 60 , none of the suggestions did perfectly fit the experimentally obtained pattern. With the help of the program "Mass spectra evaluation" written by C . Gemel, $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{1} \mathrm{Zn}_{1}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{5}+4 \mathrm{H}$ was figured out as the best fit of the isotopic pattern with a calculated $\mathrm{m} / \mathrm{z}$ of 1171.1143 . As $\mathrm{GaCp}^{*}$ and $\mathrm{ZnCp}^{*}$ only differ by $5 \mathrm{~m} / \mathrm{z}$ and the suggestion required four additional H -atoms, $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})_{5}-\mathrm{H}$ is also thinkable with a $\mathrm{m} / \mathrm{z}$ value of 1171.0735 . The second valid suggestion for $1171 \mathrm{~m} / \mathrm{z}$ is $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2} \mathrm{Zn}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{Me})(\text { hex })_{3}+\mathrm{H}$. Here, however, the second highest peak of the measured pattern differs from the calculated one (Figure 61). Careful comparison of the calculated patterns for both compounds revealed $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})_{5}-\mathrm{H}$ as the pattern with the best fit. Interestingly, this compound did not bind any Zn -compounds as it potentially interacts with excess 3 -hexyne. In addition, $\mathrm{GaCp}^{*}$ which was cleaved off from $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]$ should also show interaction with either $\mathrm{ZnMe}_{2}$ forming $\mathrm{Ga}^{\prime \prime \prime} \mathrm{Me}_{2} \mathrm{Cp}^{*}$ or with 3-hexyne as the Ni:Ga ratio is shifted to nickel. To further study the nature of $1171 \mathrm{~m} / \mathrm{z}$, NMR spectroscopic measurements as well as SC-XRD measurements are required. Only the combination of both techniques would offer a valid structural suggestion as Ga and Zn are difficult to differentiate by SC-XRD while the NMR would reveal the binding of the organic residue as Me or $\mathrm{Cp}^{*}$.


Figure 61: Left: LIFDI mass spectrum of the reaction of 1 with 10 eq. $\mathrm{ZnMe}_{2}$ after one day at room temperature. Right: Calculated pattern for $\left[\mathrm{Ni}_{4}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})(\mathrm{hex})_{3}\right]+\mathrm{H}(1171.0608 \mathrm{~m} / \mathrm{z})$ and $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{2}\right]_{\left(\mathrm{Cp}^{*}\right)_{2}(h e x)_{5}-\mathrm{H}(\mathrm{m} / \mathrm{z} 1171.0735) \text { vs. measured }}$ $\mathrm{m} / \mathrm{z} 1171.0782$.

### 4.4.2. $\mathrm{TM}-\mathrm{Zn}$ complexes from $\left[\mathrm{TM}(\operatorname{cod})_{2}\right]$ with $\mathrm{Zn}_{2} \mathrm{Cp}^{*} 2(\mathrm{TM}=\mathrm{Ni}, \mathrm{Pt})$

## $\mathrm{Ni}-\mathrm{Zn}$ compounds from $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and alkynes



Scheme 20: Overview of the herein discussed products obtained during the reaction of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ with $\mathrm{Zn}_{2} \mathrm{Cp}_{2}{ }_{2}$ and alkynes (3-hexyne and dpa). The product were obtained regardless of temperature and alkyne.

As $\mathrm{Zn}_{2} \mathrm{Cp}^{*} 2$ was previously shown to be an interesting $\mathrm{Zn}^{1}$-source for $\mathrm{TM}-\mathrm{Zn}$ compounds, especially for Cu-Zn-clusters ${ }^{74-75,79}$, $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ was reacted with two equivalents $\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}(\mathrm{Ni}: \mathrm{Zn} 1: 4)$ at $80^{\circ} \mathrm{C}$. In accordance with the publication from Fischer et al. ${ }^{145}$, the mass spectrum recorded after 5.5 hours revealed signals which were assigned to $\left[\left(\mathrm{Cp}^{*}\right) \mathrm{Ni}\left(\mathrm{ZnCp}^{*}\right)_{3}\right](794 \mathrm{~m} / \mathrm{z})$ and its fragments either releasing Cp * or ZnCp *. However, performing the reaction with alkynes as additive, the mass spectrum conducted after six hours showed the selective formation of $\left[\mathrm{Ni}_{2} \mathrm{Zn}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ (alkyne) regardless of alkyne or Zn concentration and temperature ( 60 or $90^{\circ} \mathrm{C}$ ) (see Appendix, Figure 96 and Figure 97). Only the undesired formation of $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ (alkyne) and $\left[\mathrm{Ni}\left(\mathrm{Cp}^{*}\right)_{2}\right]$ was affected by the amount of alkyne as well as Zn which were decreasing with increasing amount of Zn or additive. Further, in case of 3-hexyne, the formation of a 3-hexyne-tetramer was observed at $328 \mathrm{~m} / \mathrm{z}$ while dpa did not show such oligomerization reactions. In contrast to 3-hexyne, dpa revealed to be highly reactive towards the Ni-Zn reaction mixture: the mass spectrum showed only a signal referring to $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})$ after six hours at $90^{\circ} \mathrm{C}$ and the complete disappearance of $\left[\mathrm{Ni}_{2} \mathrm{Zn}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})$ while simultaneously the reaction vial exhibited a metallic precipitate potentially caused by metallic Zn . In case of 3-hexyne, such metallic residue was only obtained when an excess $\mathrm{Zn}_{2} \mathrm{Cp}^{*} 2$ related to 3-hexyne was used.


|  | Experimental <br> $[\mathrm{m} / \mathrm{z}]$ | Cluster assignment |
| :--- | :--- | :--- |
| A | $\mathbf{3 2 8 . 1 7 0 2}$ | $[\mathrm{Ni}]\left(\mathrm{Cp}^{*}\right)_{2}$ |
| B | 384.0897 | Not yet identified |
| C | $\mathbf{4 6 8 . 1 8 3 0}$ | $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}($ hex $)$ |
| D | $\mathbf{7 3 5 . 1 5 1 7}$ | $\left[\mathrm{Ni}_{2} \mathrm{Zn}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{3}($ hex $)$ |

Figure 62: LIFDI mass spectrum of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ with $1.9 \mathrm{eq} . \mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and 1.9 eq . 3-hexyne recorded after 6 hours at $90^{\circ} \mathrm{C}$ in toluene. Peak assignment is given in the table on the right.

It is conceivable that Ni and Zn form a tetrahedron, with two $\mathrm{Cp}^{*}$ ligands binding to the zinc atoms each and the two Ni atoms are stabilized by $\mathrm{Cp}^{*}$ and side-on coordinated alkyne, respectively. Further, it is possible that Ni , Ni and $\mathrm{Zn}_{2}$ forms a triangle if both Zinc atoms are considered as a $\mathrm{Zn}_{2}$-unit. The binding of the organic residue should be similar to the suggestion before. Nevertheless, this has to be confirmed by SC-XRD analysis and IR spectroscopic measurements.

## $\mathrm{Pt}-\mathrm{Zn}$ compounds from $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right], \mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and alkynes



Scheme 21: Overview of the herein discussed products obtained during the reaction of $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right]$ with $\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and dpa dependent on the temperature.

The reactions with $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right], \mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and alkyne were conducted in accordance with $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$. As the Ni-reaction did not show significant differences when using 3-hexyne or dpa, the following discussed reactions were only carried out with dpa as the alkyne due to its better handling as a solid. Thus, the reaction with 1 eq. [Pt(cod)2], 1 eq. $\mathrm{Zn}_{2} \mathrm{Cp}^{*}$ (Pt:Zn ratio 1:2) and 1 eq. dpa were performed at different temperatures (r.t., 60 and $90^{\circ} \mathrm{C}$ ) in toluene and monitored using LIFDI MS. The mass spectrum revealed the formation of $\left[\mathrm{Cp}{ }^{*} \mathrm{Pt}(\mathrm{ZnCp})_{3}\right]$ at $932 \mathrm{~m} / \mathrm{z}$ accompanied with its respective fragments at $797 \mathrm{~m} / \mathrm{z}(-$ $\left.C p^{*}\right)$ and $662 \mathrm{~m} / \mathrm{z}\left(-2 C p^{*}\right)$ as the most intense peaks (see Figure 63). Further, $\left[\operatorname{Pt}\left(\mathrm{Cp}^{*}\right)_{2}\right](464 \mathrm{~m} / \mathrm{z})$ was observed as one of the major products which, however, could also be caused by ionization. As the reaction mixture included $\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ as reactant, $\mathrm{Pt}-\mathrm{Zn}$ containing species were expected. Nevertheless, compounds that exhibit $\mathrm{Pt}, \mathrm{Zn}$ and dpa was determined only in traces: $\left[\mathrm{Pt}_{3} \mathrm{Zn}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{dpa}_{2}\right)(\mathrm{cod})$ ( $1385 \mathrm{~m} / \mathrm{z}$ ) and its related fragment peaks at $1184 \mathrm{~m} / \mathrm{z}\left(-\mathrm{ZnCp}^{*}\right)$ and $1141 \mathrm{~m} / \mathrm{z}(-\mathrm{Zn}-\mathrm{dpa})$. Noteworthy, here, the Zn -content in these compounds was less than Pt -amount as it was mostly consumed by the formation of $\left[\mathrm{Cp}^{*} \mathrm{Pt}\left(\mathrm{ZnCp}^{*}\right)_{3}\right]$. One additional major signal was determined at $815 \mathrm{~m} / \mathrm{z}$ which could be referred to a $\mathrm{Zn}_{3}\left(\mathrm{Cp}^{*}\right) 3$-compound which was confirmed by reactions including either ${ }^{68} \mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ or $\mathrm{Zn}_{2} \mathrm{Cp}^{* E \mathrm{t}_{2}}$ where one methyl moiety of the $\mathrm{Cp}^{*}$ was exchanged by an ethyl group. Nevertheless, this compound could not be completely identified.


Figure 63: LIFDI mass spectra of the reaction $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ with $1 \mathrm{eq} . \mathrm{Zn}_{2} \mathrm{Cp}_{2}^{*}$ and 1 eq . dpa at different temperatures in toluene. The spectrum was recorded after five hours. Peak assignment are given in the table on the right.

For the identified $\left[\mathrm{Pt}_{3} \mathrm{Zn}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{2}(\mathrm{cod})$, a structure similar to that depicted in Figure 64 is assumed which is proposed according to $\left.\left[\mathrm{Pd}_{3} \mathrm{In}_{3}\right](\mathrm{Cp})_{3}\right)_{3}(\mathrm{PPh})_{3} .^{73}$ As previously described, this compound exhibits a $\mathrm{Pd}_{3}$ triangular center which is stabilized by two $\mathrm{Pd}_{3}$-face-bridging and one $\mathrm{Pd}_{2}$-edge-bridging $\mathrm{InCp}^{*}$ as well as three terminal bound $\mathrm{PPh}_{3}$ units. Accordingly, the proposed Pt-compound is therefore expected to feature a $\mathrm{Pt}_{3}$ triangular metal core which is stabilized by $\mathrm{ZnCp}^{*}, \mathrm{Cp}^{*}$ and cod as they are preferring terminal positions. As a result, two Pt -centers are oxidized to $\mathrm{Pt}^{1}$ while one Pt remains $\mathrm{Pt}^{0}$ that binds cod. Further, the proposed structure shows two $\mathrm{Pt}_{3}$-face-capping dpa units revealing a $\mathrm{Pt}_{3}(\mathrm{dpa})_{2}$ trigonal bipyramid. To validate the proposed structure, further analytical methods have to be applied as NMR and IR spectroscopy as well as SC-XRD measurements.


Figure 64: Structural suggestion of $\left[\mathrm{Pt}_{3} \mathrm{Zn}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{2}(\mathrm{cod})$ revealing a $\mathrm{Pd}_{3}$ triangular metal core with two face-capping dpa units.

### 4.4.3. Conclusion: TM-Zn cluster synthesis

In conclusion, the synthesis of $\mathrm{Ni}-\mathrm{Zn}$ and $\mathrm{Pt}-\mathrm{Zn}$ clusters or compounds was discussed depending on the starting material which was either $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right],\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}$ or $\left[\mathrm{TM}(\operatorname{cod})_{2}\right](\mathrm{TM}=\mathrm{Ni}, \mathrm{Pt})$. If $\mathrm{ECp}{ }^{*}$ was already included in the starting material, $\mathrm{ZnMe}_{2}$ was used as Zn source while $\mathrm{Zn}_{2} \mathrm{Cp}^{*} 2$ was added when starting from $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]$ and $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right]$, respectively.

Addition of different stoichiometric amounts of $\mathrm{ZnMe}_{2}$ to [ $\mathrm{NiGa}_{4}$ ] resulted in the formation of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4-n}\left(\mathrm{ZnCp}^{*}\right)_{n}(\mathrm{ZnMe})_{n}\right]$ depending on the $\mathrm{Ga}-\mathrm{Zn}$ stoichiometry and temperature. Additionally, the influence of 3-hexyne as the additive on the formation of $\mathrm{Ni}-\mathrm{Ga}-\mathrm{Zn}$ compounds was studied, with $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{ZnCp}^{*}\right)_{2}(\mathrm{ZnMe})_{4}\right]$ being preferentially formed in the presence of additives. However, performing the reaction in 3-hexyne as solvent resulted in $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{2} \mathrm{Zn}_{1}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{Me})_{1}(\mathrm{hex})_{5}$, $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{5}$ and $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{1} \mathrm{Zn}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{Me})(\text { hex })_{5}$ as products which all exhibit a high number of hexyne ligands stabilizing the cluster core. Notably, the last two compounds differed only by one exchanged GaCp* ligand with ZnCp * and ZnMe , but amount of Ni and 3-hexyne remained the same. Interestingly, adding $\mathrm{ZnMe}_{2}$ to a freshly prepared solution of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right) 4$ (hex) ${ }_{2}$, the mass spectrum also revealed the formation of $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{5}$ which is, in this case, selective.

The addition of $\mathrm{Zn}_{2} \mathrm{Cp}^{*}$ and alkyne to a solution of $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]$ showed the selective synthesis of $\left[\mathrm{Ni}_{2} \mathrm{Zn}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{~L})(\mathrm{L}=$ hex, dpa) regardless of temperature or equivalents. Only the formation of undesired side-product as $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{~L})$ is influenced as it is preferred at higher amount of Zn and 3-hexyne. Since the addition of alkyne to $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ immediately resulted in $\left[\mathrm{Ni}_{2}\right](\mathrm{cod})_{2}$ (alkyne), it was assumed that the alkyne first activates the Ni center which could then further react with $\mathrm{Zn}{ }^{1}$. Due to the existence of metallic precipitate detected in the reaction tube, it was assumed that at least one Cp* binds to a nickel center formed by oxidation of $\mathrm{Ni}^{0}$ to $\mathrm{Ni}^{1}$ and the simultaneous reduction of $\mathrm{Zn}^{1}$ to $\mathrm{Zn}^{0}$.

Conducting the reaction starting from $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right]$ with $\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and dpa, a similar reaction behavior was expected. However, the mass spectrum only revealed the formation of already known $\left[\mathrm{Cp}{ }^{*} \operatorname{Pt}\left(\mathrm{ZnCp}{ }^{*}\right)_{3}\right]^{145}$ as the most favored product. Besides the signals referring to the preferred product, also small signals which were related to $\left[\mathrm{Pt}_{3} \mathrm{Zn}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{2}(\mathrm{cod})$ and some fragmentation peaks could be detected. Compared to nickel, the formation of $\left[\mathrm{Pt}_{2}\right](\mathrm{cod})_{2}$ (alkyne) was not observed, neither in the mass spectrum nor visually by a color change. As a consequence, the Pt atoms are not activated by alkynes as in the case of nickel, and thus, the reactive Pt centers analog to Ni are not formed.

### 4.5. Semi-hydrogenation experiments with $\mathrm{Ni} / \mathrm{Ga}$ and $\mathrm{Ni} / \mathrm{Al}$ clusters

In the following chapter, selected NiGa and NiAl compounds are tested for their applicability to semi-hydrogenation reactions.

### 4.5.1. Reaction of $\mathrm{Ni} / \mathrm{Ga}$ compounds with hydrogen

Reaction of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}{ }^{*}\right)_{4}(\text { hex })_{2}$ (1) with 1 bar $\mathrm{H}_{2}$

1 was synthesized as described above. After stirring of the reaction solution for 3.5 h at room temperature, the reaction mixture was shortly exposed to vacuo to remove cod and excess 3-hexyne. The oily residue was resolved in 2 mL toluene- $\mathrm{d}_{8}$ and divided in four equal parts. Following experiments were conducted: Reference (a), 1 bar $\mathrm{H}_{2}$ (b), 1 bar $\mathrm{H}_{2}$ and exc. 3-hexyne (c). Besides the signals for 1, the NMR reference spectrum showed peaks which were assigned to $\left[\mathrm{Ni}_{2}(\operatorname{cod})_{2}(\right.$ hex $\left.)\right]$ at 5.25 and 2.06 ppm for cod as well as 2.60 and 1.17 ppm for 3 -hexyne. The reaction only including $\mathrm{H}_{2}$ showed similar behavior in reaction solution at the beginning compared to 1 over time, but also revealed hydrogenation of $\operatorname{cod},\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]$ and $\left[\mathrm{Ni}_{2}(\operatorname{cod})_{2}(h e x)\right]$ while releasing cyclooctane and hexane. The signals for $\mathbf{1}$ have almost disappeared after one day which is potentially caused by decomposition of the cluster or by hydrogenation of the ligands.
The reaction which contains $\mathrm{H}_{2}$ and excess 3-hexyne revealed high reactivity for 3-hexyne conversion. As depicted in Figure 65, after one day, 1 was mostly consumed while releasing cis-/trans-hexene as well as fully hydrogenated hexane besides the hydrogenation products of cod. In addition, the signals for 3-hexyne have also completely disappeared due to (semi)-hydrogenation of the excess 3-hexyne. However, it cannot be definitely stated whether the decomposition of 1, leading to metallic residue that may catalyze the hydrogenation process, or the adsorption/desorption of hexyne on the cluster surface occurred first. Comparing the reaction which includes only $\mathrm{H}_{2}$ with that including hydrogen and 3-hexyne, a higher selectivity to semi-hydrogenated products was determined. While the reaction with hydrogen, only resulted in fully hydrogenated compounds as cyclooctane (coa) or hexane, the reaction with additional 3-hexyne led to partial-hydrogenated products as cyclooctene (coe) or cis-/trans-hexene besides the fully hydrogenated compounds. If the protection of the cluster core is assumed to be ensured by the excess of 3-hexyne and thus, decomposition is hampered at the beginning of the reaction, the semi-hydrogenation of the 3-hexyne substrate is enabled by acetylene-adsorption and ethylenedesorption on the cluster core.


Figure 65: Time-dependent ${ }^{1} \mathrm{H}$ NMR spectra of the reaction of 1 with 1 bar $\mathrm{H}_{2}$ and excess 3-hexyne. Color code: orange all components referring to a derivative of cod or cod-containing species, light blue: species that originates from 3-hexyne, grey: starting material. Abbreviations: cod: 1,5-cyclooctadiene; coe: cyclooctene; coa: cyclooctane; tol-d $d_{8}$ : deuterated toluene.

## Reaction of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}(3)$ with 1 bar $\mathrm{H}_{2}$

3 was synthesized from [ $\mathrm{Ni}(\operatorname{cod})_{2}$ ] ( 1.9 eq .), $\mathrm{GaCp}^{*}$ ( 1.9 eq .) and dpa ( 1.0 eq .) in toluene-d8. The reaction was finished after one day at room temperature which was evidenced by LIFDI MS measurements only revealing a signal at $1204 \mathrm{~m} / \mathrm{z}$ as the major signal which refer to the product with dpa-cleavage. The assumption of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ was confirmed by ${ }^{1} \mathrm{H}$ NMR spectroscopic measurements showing signals at $7.38,7.18$ and 7.02 ppm for the dpa-ligands while the $\mathrm{GaCp}^{*}$ moieties were determined at 1.92 ppm . The signals are in the corresponding ratio resulting in a dpa:GaCp* ratio of 3:3.

After the synthesis, the hydrogenation experiments were conducted by addition of $1 \mathrm{bar} \mathrm{H}_{2}$ to an evacuated NMR-tube. The reaction was monitored by in-situ NMR spectroscopic as well as LIFDI MS measurements. After one day at room temperature, the ${ }^{1} \mathrm{H}$ NMR spectrum showed the conversion of free dpa while forming diphenylethylene (dpe; stilbene) and diphenylethane (bibenzyl; bb) which were identified by their characteristic signals at 6.44 (s) and 2.72 ppm and are in accordance to literature known values ${ }^{159-160}$ (see Appendix, Figure 126). The ${ }^{1} \mathrm{H}$ NMR spectrum did not result in dimerized or trimerized dpa, respectively. In contrast to $\mathbf{1},\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]^{2}\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ was only consumed to some extent, but still showed its respective signals after one day. However, the signal for $\mathrm{GaCp}^{*}$ decreased to a different ratio than the dpa signal which led to the assumption of a cluster-reorganization or -deconstruction while transferring the $\mathrm{Cp}^{*}$ to nickel.
The mass spectrum recorded after one day did not show significant changes in the respective signals when compared to the reference spectrum, but the ratio between the different compounds varied (see Appendix, Figure 127). The reference as well as the spectrum from the $\mathrm{H}_{2}$ reaction showed a decrease of the peak assigned to the starting material. Noteworthy, both spectra revealed [ $\mathrm{Ni}_{2}(\operatorname{cod})_{2}(\mathrm{dpa})$ ] $(511 \mathrm{~m} / \mathrm{z}),\left[\mathrm{Niz}\left(\mathrm{Cp}^{*}\right)(\mathrm{cod})(\mathrm{dpa})\right](537 \mathrm{~m} / \mathrm{z})$ and $\left[\mathrm{Ni}_{2}\left(\mathrm{Cp}^{*}\right) 2(\mathrm{dpa})\right]$ as major products within one day which was not yet confirmed by NMR spectroscopy. The formation of Ni-cod compounds is nevertheless possible, since signals that are in the range for Ni -alkenes were obtained in addition to the signal for cyclooctane ( 1.52 ppm ).

## Reaction of $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})$ with 1 bar $\mathrm{H}_{2}$

 toluene-d8. The reaction was finished after one day at $60^{\circ} \mathrm{C}$ which was evidenced by LIFDI MS measurements only revealing a signal at $1553 \mathrm{~m} / \mathrm{z}$ as the major signal. The respective ${ }^{1} \mathrm{H}$ NMR spectrum showed two singlets at 1.93 ppm and 1.64 ppm in the typical range for $\mathrm{Cp}^{*}$ moieties and two duplets at 8.10 ppm and 7.30 ppm which are both in the range for $\mathrm{o}-\mathrm{H}$ atoms of dpa. All other signals either refer to cod-containing species or to dpa which overlaps in the aromatic range. Comparing the intensities of the mentioned signals, only 8.10 and 1.93 ppm featured an integral ratio of $4: 75 \mathrm{H}$ atoms which is equal to a dpa:Cp* ratio of $1: 5$ as expected for $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}{ }^{*}\right)_{5}(\mathrm{dpa})_{1}$. Nevertheless, since the signals of the aromatic range were partly overlapping, this has to be confirmed by a NMR spectrum of the isolated or purified compound.
After the in-situ synthesis of $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})_{1}$, the NMR tube was pressurized with 1 bar $\mathrm{H}_{2}$. The reaction was monitored by in-situ NMR spectroscopic as well as LIFDI MS measurements. After 1.5 h at room temperature, the ${ }^{1} \mathrm{H}$ NMR spectrum showed the decrease of the signals 1.93 and 8.10 ppm which are assigned to the starting material and could be seen as the conversion of $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}{ }^{*}\right)_{5}(\mathrm{dpa})$ (see Appendix, Figure 128). No significant change of the signal for stilbene could be observed as it is also observed in the reference spectrum. However, after one day, the formation of bibenzyl could be detected. In addition, signals for coe are increasing, but no peak for coa is observed. This in fact means, that this reaction mixture did not only influence the (semi-)hydrogenation of dpa but also the partial hydrogenation of cod. The mass spectrum, however, showed the formation of $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ and [ $\mathrm{Ni}_{7} \mathrm{Ga}_{6}$ ] $\left(\mathrm{Cp}^{*}\right)_{6}$ at $1647 \mathrm{~m} / \mathrm{z}$ and $1637 \mathrm{~m} / \mathrm{z}$ upon decreasing of $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})$ at $1553 \mathrm{~m} / \mathrm{z}$ (see Appendix, Figure 129). Since this conversion was not detected in the reference spectrum, which still showed the starting material at $1553 \mathrm{~m} / \mathrm{z}$, this is potentially caused by dpa-hydrogenation and thus, releasing the cluster. Due to the resulting open-coordination site on the $\mathrm{Ni}_{6}$ cluster core of $\left[\mathrm{Ni}_{6} \mathrm{Ga} 5\right]\left(\mathrm{Cp}^{*}\right)_{5}$, Cp * transfer from Ga to Ni could take place to form both $\mathrm{M}_{13}$ clusters as these are the thermodynamically favored products.

### 4.5.2. Reaction of $\mathrm{Ni} / \mathrm{Al}$ compounds with hydrogen

After suitable Ni-Ga clusters have been investigated for the semi-hydrogenation of alkynes, in the following section $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})$ and $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)($ hex $)$ are tested for their reactivity towards hydrogen and semi-hydrogenation.

## Reaction of [NiAl](Cp*)(tebd)(cod) (6) with 1 bar $\mathrm{H}_{2}$

6 was synthesized from [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ] ( 1 eq .), $\mathrm{AlCp}^{*}$ (1 eq.) and 3-hexyne (4 eq.) in hexane at $60^{\circ} \mathrm{C}$ as described above. $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})(0.021 \mathrm{mmol})$ was dissolved in 0.34 mL in toluene-d8 and 3-hexyne ( $0.16 \mathrm{mmol}, 7.7$ eq.) was added as a 1 M solution in toluene-d8. Subsequently, the NMR tube was pressurized with 1 bar $\mathrm{H}_{2}$ at room temperature.

The NMR spectra, depicted in Figure 64, showed the conversion of the starting material while forming $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)$ (tebd)(hex) which is supported by the decrease of the signals at $4.40 \mathrm{ppm}(\mathrm{m})$ and 3.40 ppm (dt) and the increase of the characteristic multiplet at 2.80 ppm indicating the formation of 7 . Already after five hours at room temperature, the spectrum revealed the selective conversion of cis-hexene as evidenced by the signals at 0.91 ppm (dt) and $5.34 \mathrm{ppm}(\mathrm{m})$. After five days, 3 -hexyne was completely reacted to hexane without any semi-hydrogenated products as cis-/trans-hexene while cod showed conversion to coe, but not to coa.

In conclusion, the NMR spectra revealed the conversion of 6, 3-hexyne and cod while forming the respective alkenes/alkanes and 7, catalyzed by the Ni/Al cluster. In contrast to Ni/Ga, the Ni/Al clusters were able to selectively (semi-)hydrogenate alkynes and alkenes depending on the temperature while remaining intact after the catalytic cycle. If the temperature would be reduced to $0^{\circ} \mathrm{C}$, the trapping of the semi-hydrogenated products would be possible and full hydrogenation could be inhibited.


Figure 66: Hydrogen experiment of [NiAl](Cp*)(tebd)(cod) (A) with 8 eq. 3-hexyne and 1 bar $H_{2}$. Abbreviations: A, $[\mathrm{NiAl}]\left(C p^{*}\right)(t e b d)(c o d) ; \boldsymbol{B},[\mathrm{NiAl}]\left(C p^{*}\right)(t e b d)(h e x)$; coa, cyclooctane; coe, cyclooctene; cod, 1,5-cyclooctadiene; tol-d ${ }_{8}$, deuterated toluene.

## Reaction of [ NiAl$]\left(\mathrm{Cp}^{*}\right)($ tebd $)($ hex $)(7)$ with 1 bar $\mathrm{H}_{2}$

7 was synthesized from $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})$ and 8 eq. 3 -hexyne in toluene- d 8 at $90^{\circ} \mathrm{C}$ as describe above. The reaction mixture was allowed to cool to room temperature and subsequently, the NMR tube was pressurized with 1 bar $\mathrm{H}_{2}$ at room temperature. It has to be noted that the mixture still contained the starting material and 3 -hexyne when exposed to $\mathrm{H}_{2}$.
While the NMR spectrum recorded after one hour did not show significant changes, only indicating the formation of cis-hexene, it revealed the selective conversion of 3-hexyne to cis-hexene after one day at room temperature. Due to stronger alkyne binding on the transition metal compared to alkenes, which is in this case 3-hexyne instead of cod, the conversion of alkynes to alkenes were slower and therefore, more selective. In contrast to 6, $\mathbf{7}$ underwent semi-hydrogenation preferring cis-alkene while the formation of hexane was only detected in traces.


Figure 67: Hydrogen experiment of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(t e b d)(h e x)(B)$ with 8 eq. 3-hexyne and 1 bar $\mathrm{H}_{2}$ at room temperature. Abbreviations: $\boldsymbol{A},[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(t e b d)(c o d) ; \boldsymbol{B},[\mathrm{NiAl}]\left(C p^{*}\right)(t e b d)(h e x) ;$ coa, cyclooctane; coe, cyclooctene; cod, 1,5-cyclooctadiene; tol- $d_{8}$, deuterated toluene.

## Conclusion

## 5. Conclusion

This work dealt with a new approach to identify reactive intermediates instead of complex and timeconsuming isolation of organometallic compounds. Further, this strategy enabled size-focusing of complex reaction mixtures by temperature or additive control, which has never been applied for cluster chemistry before. In addition, further reaction of such mixtures allowed the in-situ identification of reactive intermediates. However, isolation of such reactive compounds was not possible in some cases as the ligands are not stable when exposed to vacuo or in solution for a longer time. By combining different analytical techniques, namely LIFDI MS and NMR spectroscopy, structural suggestions of in-situ obtained compounds could be provided and verified by theoretical calculations. This thesis was divided in three main parts: additive controlled clusters synthesis leading to cluster growth or cluster degradation (I) combined with the evaluation of metal precursors (II) and the identification of valid structures by combining theoretical and experimental data (III).

Additive controlled TM-E cluster synthesis. The formation of $\mathrm{Ni} / \mathrm{E}$ clusters and compounds influenced by different parameters was the main part of this thesis. The synthesis of Ni/Ga and Ni/Al compounds showed to be highly depending on the metal-precursor, the additive, the additive concentration, temperature (NiGa) and metal-ratio (NiAl). The reaction of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}^{*}$ and 3 -hexyne led to the formation of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}$ (1) and $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{4}$ (2) which can be considered as intermediate compound for higher nuclear clusters as $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ and $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ which are preferred at elevated temperatures. In this work, $\mathrm{Cp}^{*}$ transfer reactions from Ga to Ni , which were observed during the formation of the latter two $\mathrm{M}_{13}$ compounds, could be hampered due to coordination of the alkyne on vacant sites on the Ni-center. Further, the Ni-Ga system was shown to be strongly temperature dependent. Thereby, size-focused solutions could be obtained at low temperatures, whereas cluster growth reactions, were observed at high temperatures. While the Ni-Ga system offered a large variety of clusters depending on the conditions, the synthesis of Ni/Al compounds seemed to be more selective. In this context, the formation of higher nuclear Ni-Al clusters preferred lower additive concentrations, whereas high concentrations of additives hampers cluster growth reactions, leading to smaller Ni-Al complexes. Due to the proximity of the alkynes, smaller Ni-Al complexes preferentially form metallacycles consisting of $\mathrm{AICp}^{*}$ and dimerized hexyne.

The investigation of Pd-Ga clusters synthesis revealed to be highly sensitive to temperatures and must be handled at low temperatures to prevent nanoparticle synthesis. Depending on the temperature, the formation of $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{5}\right](\mathrm{L})_{\times}$and $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right](\mathrm{L})_{\times}$was observed which were attributed to intermediates during the synthesis of the kinetically inert $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$. For Pd-Al, the formation of $\left[\mathrm{Pd}_{4} \mathrm{Al}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{7}$ was obtained from $\left[\mathrm{PdAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ as a recombination of two highly reactive intermediate compounds which are potentially formed due to ligand dissociation in the presence of additives in excess.
Moreover, the Pt-E system showed an additive-dependency which preferred different metal core sizes depending on the additive. While hexyne as additive favored trinuclear Pt-Ga cluster, the sterically more demanding dpa preferred the formation of dinuclear $\mathrm{Pt}-\mathrm{Ga}$ compounds. In contrast, Pt-Al clusters showed high sensitivity towards the Pt-Al metal ratio and preferred to form $\left[\mathrm{PtAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ at high Alconcentrations. However, Pt-E compounds were found to be very temperature-sensitive and unstable
in solution. Furthermore, structural considerations showed that no interactions could be assumed between the alkynes themselves or with $\mathrm{GaCp}^{*}$ in the case of Pt Ga , while alkynes were dimerized in Pt Al compounds and formed a metallacycle with AICp*, as also obtained for Ni-AI.
Further, it was possible to synthesize TM-Zn compounds either from pre-existing TM-E clusters via E/Zn exchange or by addition of $\mathrm{Zn}_{2} \mathrm{Cp}^{*} 2$ to a TM-precursor. In case of $\mathrm{Ni}-\mathrm{Zn}$, the introduction of Zn -ligands into a definite cluster structure led to higher nuclear, Ni - and additive-rich clusters as $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{5}$. Moreover, the addition of a Zn source to a Ni-precursor as $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ formed only small Ni-Zn compounds. In contrast, the reaction of $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ with $\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and additives was shown to be unreactive to additives as only $\mathrm{Pt}-\mathrm{Zn}$ compounds were obtained which are already known.

Semi-hydrogenation reactions. Selected $\mathrm{Ni}-\mathrm{Ga}$ and $\mathrm{Ni}-\mathrm{Al}$ compounds were tested for their applicability as catalysts in semi-hydrogenation reactions. Thus, the Ni-Al compounds, $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}(\right.$ tebd $)(\mathrm{cod})$ (6) and $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)($ hex $)(7)$ were identified as suitable catalysts for (semi-)hydrogenation reactions since they were not consumed during the catalytic cycle. In contrast, NiGa compounds as $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}(\mathbf{1}),\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ (3) and $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})$ are completely decomposed after treatment under catalytic conditions. While Ni-Ga clusters showed the formation of both partly hydrogenated or semi-hydrogenated and fully hydrogenated products as cis/trans-hexene, hexane, cyclooctene and cyclooctane, the Ni-Al system revealed the conversion of 3-hexyne to hexene with the tendency to cis-hexene without the formation of fully-hydrogenated hexane at the beginning of the reactions. Optimization of the reaction conditions could provide a new catalyst system for semi-hydrogenation of alkynes.

Dependency on precursor choice. In this project, various transition metal precursors with different ligands as well as metal cores were studied, especially for $\mathrm{Ni} / \mathrm{E}$. While metal precursors as $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ and $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right]$ exhibited a high affinity for ligand substitution which resulted in the full exchange of the labile cod ligands and offered diverse reactivity depending on the metal E , the tetranuclear $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{\dagger} \mathrm{Bu}_{4}\right)_{7}\right]$ and dinuclear $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ did not lead to a complete exchange of the ligands. However, using a definite cluster structure as in the case of $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{\dagger} \mathrm{Bu}\right)_{7}\right]$ or $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$ cluster growth reactions are preferred enabling Ni-rich clusters as in case of the former precursor. This was also observed for $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ which resulted in high nuclear clusters as $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{5}\right](\mathrm{L})_{\mathrm{x}}$ and $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right](\mathrm{L})_{y}$.

Identification of structure suggestions. Structural identification of metal clusters by SC-XRD is a long practiced and established method in organometallic chemistry. However, this method is time-consuming and requires single crystals, which are sometimes difficult to obtain. A new approach to gain structural information overcomes those problems by combining in-situ analytical techniques with theoretical calculations, and enables the identification of reactive intermediates which cannot be isolated. Since 3-hexyne is a very volatile ligand, $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}$ could not be isolated so far. Based on literature-known compounds and the information obtained from NMR spectroscopy and LIFDI mass spectrometry, five proposed structures for this compound were calculated. Nevertheless, only three geometries resulted in a local minimum from geometry optimization. Careful comparison with literature known compounds allowed the identification of two possible compounds which either a tetrahedrally or a square planar $\mathrm{Ni}_{4}$ core. Further studies need to be conducted and extended to other systems to confirm this approach.

## 6. Experimental

### 6.1. General Materials and Methods

## Chemicals and Solvents

Unless otherwise noted, all chemicals and solvents were used as purchased from common suppliers as $A B C R$, ACROS and Sigma Aldrich. All reactions with air and moisture sensitive compounds were carried out under standard Schlenk techniques using Argon 4.6 from Westfalen or in a glove box UNIlab from M.Braun. The solvents toluene, hexane, tetrahydrofuran and diethylether were predried with a solvent purification system SPS-800 from M.Braun. All liquid chemicals and solvents were dried over $4 \AA$ molecular sieve before using. Deuterated solvents for NMR spectroscopy were received from Sigma Aldrich, dried over 4 Å molecular sieves and degassed using Freeze-Pump-Thaw. The final $\mathrm{H}_{2} \mathrm{O}$ content of all solvents was checked by Karl Fischer titration and was below 5 ppm.

## Literature known compounds:

The following compounds were synthesized accordingly to literature known procedures.

| $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]^{161}$ | $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]^{162}$ | $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]^{163}$ | $\left[\mathrm{Pd}(\mathrm{tmeda})(\mathrm{Me})_{2}\right]^{164}$ |
| :--- | :--- | :--- | :--- |
| $\left[\mathrm{Pd}(\text { tmeda })(\mathrm{Cl})_{2}\right]^{49}$ | $\mathrm{GaCp}{ }^{* 165}$ | $\mathrm{AlCp}^{* 166}$ | $\mathrm{Zn}_{2} \mathrm{Cp}^{*} 2^{167}$ |
| $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]^{117}$ | $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{4}\right]^{151}$ | $\left[\mathrm{Pd}\left(\mathrm{AlCp}^{*}\right)_{4}\right]^{151}$ | $\left[\mathrm{Pd}\left(\mathrm{GaCp}^{*}\right)_{4}\right]^{72}$ |
| $\left[\mathrm{Pd}_{2}\left(\mathrm{GaCp}^{*}\right)_{5}\right]^{73}$ | $\left[\mathrm{Pd}_{3}\left(\mathrm{GaCp}^{*}\right)_{8}\right]^{73}$ | $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]^{82}$ | $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{+1} \mathrm{Bu}\right)_{7}\right]^{153}$ |

## NMR-Spectroscopy

The NMR spectra were taken at a Bruker AV400 with the frequency of 400 MHz for ${ }^{1} \mathrm{H}, 101 \mathrm{MHz}$ for ${ }^{13} \mathrm{C}$ and 162 MHz for ${ }^{31} \mathrm{P}$ NMR or a Bruker AV500 with 500 MHz for ${ }^{1} \mathrm{H}$ and 126 MHz for ${ }^{13} \mathrm{C}$ NMR. The chemical shifts ( $\delta$ ) are given in ppm and referenced to the solvent residual signals with respect to tetramethylsilane. Abbreviations of the signal multiplicity observed in the NMR spectra are: s: singlet, d: duplet, t : triplet, p : pentet, sept: septet, dt: duplet of triplet, m : multiplet. The resulting spectra were analyzed with the software MestReNova (Version 14.1.1-24571).

Solvent residual signals:
Tol-d ${ }_{8} \delta(\mathrm{ppm})=2.08(\mathrm{p}), 6.98(\mathrm{~s}), 7.00(\mathrm{~s}), 7.09(\mathrm{~m})$ for ${ }^{1} \mathrm{H}$ NMR; $137.9(\mathrm{~s}), 129.2(\mathrm{t}), 128.3(\mathrm{t}), 125.5$ (t), 20.4 (sept) for ${ }^{13} \mathrm{C}$ NMR.
$\mathrm{C}_{6} \mathrm{D}_{6} \delta(\mathrm{ppm})=7.16$ (s) for ${ }^{1} \mathrm{H}$ NMR; 128.1 for ${ }^{13} \mathrm{C}$ NMR.
$\mathrm{C}_{6} \mathrm{D}_{12} \delta(\mathrm{ppm})=1.38(\mathrm{~s})$ for ${ }^{1} \mathrm{H}$ NMR; 26.4 for ${ }^{13} \mathrm{C}$ NMR.

## Experimental

## IR-Spectroscopy

Infrared spectra were measured on an Alpha FT-IR from Bruker equipped with an ATR device using a platinum diamond in a glovebox LABstarPro ECO from M.Braun. The interferometer measured in a range of 400 to $4000 \mathrm{~cm}^{-1}$. The compounds were measured as dried powder under inert atmosphere in a glovebox from M.Braun. In case of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}$ and $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\text { hex })_{3}$, the reaction mixture in hexane was dropwise added to the diamond and allowed to release the solvent on the top of the diamond.

## LIFDI-MS

Liquid injection field desorption ionization mass spectrometry (LIFDI-MS) data were measured on an Exactive Plus Orbitrap system by Thermo Fisher Scientific equipped with an ion source (LIFDI) or Waters Micromass LCT TOF mass spectrometer equipped with a LIFDI ion source (LIFDI 700). Both LIFDI ion sources were supplied by LINDEN CMS GmbH. The Orbitrap system is connected to a GS Glovebox due to a whole on the backwall enabling sample application under inert atmosphere. For further information of the construction, please read M. Muhr, P. Heiß, Dalton Trans. 2021, 50, 90319036. ${ }^{168}$ The samples were dissolved in either dry toluene or hexane and filtered over a syringe filter under an inert atmosphere.

## UV-Vis-Spectroscopy

The UV-Vis-spectra were recorded on a double beam Lambda 365 UV-Vis spectrophotometer from PerkinElmer. The compounds were dissolved in dry hexane with a concentration of $5 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1}$.

## SC-XRD-Spectroscopy

Data were collected on a single crystal x-ray diffractometer equipped with a CMOS detector (Bruker APEX III, к-CMOS), a TXS rotating anode with MoK ${ }_{\alpha}$ radiation ( $\lambda=0.71073 \AA$ ) and a Helios optic using the APEX3 software package. ${ }^{1}$ Measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on top of a kapton micro sampler and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarization effects, scan speed, and background using SAINT. ${ }^{2}$ Absorption correction, including odd and even ordered spherical harmonics was performed using SADABS. ${ }^{2}$ Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. The structures were solved using SHELXT with the aid of successive difference Fourier maps, and were refined against all data using SHELXL-2014 in conjunction with SHELXLE. ${ }^{3,4,5}$ Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a $\mathrm{C}-\mathrm{H}$ distance of $0.98 \AA$ and $\mathrm{U}_{\text {iso }(\mathrm{H})}=1.5 \cdot \mathrm{U}_{\text {eq(C) }}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic $\mathrm{C}-\mathrm{H}$ distances of $0.99 \AA$ and $0.95 \AA$, respectively, other $C-H$ distances of $1.00 \AA$, all with $U_{\text {iso }(H)}=1.2 \cdot U_{\text {eq(C) }}$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w\left(F_{0}{ }^{2}-F_{c}{ }^{2}\right)^{2}$ with the SHELXL weighting scheme. ${ }^{3}$ Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms
were taken from International Tables for Crystallography. ${ }^{6}$ A split layer refinement was used for disordered groups and additional SIMU, DELU, RIGU, ISOR, SAME and SADI restraints and EADP constraints were employed to ensure convergence within chemically reasonable limits, if necessary. Images of the crystal structures were generated with PLATON and Mercury. ${ }^{7,8}$

## References-SCXRD:

[1] APEX suite of crystallographic software, APEX 3, Version 2015-5.2, Bruker AXS Inc., Madison, Wisconsin, USA, 2015.
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## Elemental Analysis

Elemental analysis was performed either at the microanalytical laboratory at the Technical University Munich or at Mikroanalytisches Labor Kolbe at Fraunhofer Institut Oberhausen. The microanalytical laboratory at TU Munich uses an Euro EA Analyzer from HEKAtech for CHNS determination and a AA280FS fast sequential AAS spectrometer from Varian for AAS determination of metals. The laboratory in Oberhausen conducted the elemental analysis on a Vario-EL CHNS-Analyzer from Elementar and on a AAnalyst200 from PerkinElmer Inc. for AAS analysis. Samples were prepared in a glovebox to prevent contact with moisture and air.

## Computational Details

Structures of the calculated molecules were optimized using the ORCA4.0 ${ }^{169}$ software package and Becke's exchange functional ${ }^{170}$ with Perdew's correlation functional ${ }^{171}$ (BP86). Grimme's Dispersion correction including Becke-Johnson damping (D3BJ) ${ }^{172-173}$ was used. After preoptimization and analytical calculation of the Hessian using Ahlrich's def2-SVP basis set these structures were further optimized using the def2-TZVPP basis sets. ${ }^{174}$ The resolution of identity approximation (RI) was applied to speed up the calculations. ${ }^{175}$ Time-dependent density functional theory (TDDFT) calculations were performed to compute the UV-Vis spectra and included the lowest 50 eigenvalues.

## Experimental

### 6.2. Experimental part: Synthesis of new compounds

$\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}(1) .{ }^{140} \mathrm{Ni}(\text { cod })_{2}(50 \mathrm{mg}, 0.182 \mathrm{mmol}, 1.0$ eq.) and 3-hexyne ( $0.09 \mathrm{~mL}, 1 \mathrm{~m}$ solution in toluene, $0.180 \mathrm{mmol}, 0.5 \mathrm{eq}$ ) were dissolved in toluene giving a dark red solution within seconds. Subsequently, $\mathrm{GaCp}^{*}(0.18 \mathrm{~mL}, 0.180 \mathrm{mmol}, 1.0 \mathrm{eq}$.) was added as a 1 m solution in toluene and stirred for two hours at ambient temperature to obtain a brown solution. Note: Long exposure of 3 to vacuo led to an insoluble black precipitate. In solution, however, it is stable for several days when stored at $-30^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, 298 \mathrm{~K}$, toluene- $\mathrm{d}_{8}$ ): $\delta(\mathrm{ppm})=2.70\left(\mathrm{~s}, 8 \mathrm{H}, \mathrm{CH}_{2}\right.$, hex), $1.98(\mathrm{~s}, 60 \mathrm{H}$, $\mathrm{C}_{5} \mathrm{Me}_{5}$ ), $1.33\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{CH}_{3, \text { hex }}\right) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, 298 \mathrm{~K}$, toluene- $\mathrm{d}_{8}$ ): $\delta(\mathrm{ppm})=134.8\left(\mathrm{C} \equiv \mathrm{C}_{\text {Acetylene }}\right)$, 113.6 ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ ), 22.9 ( $\mathrm{CH}_{2, \text { Acetylene })} 16.6$ ( $\mathrm{CH}_{3, \text { Acetylene }), ~} 10.90\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)$. IR (ATR, neat, $\mathrm{cm}^{-1}$ ): 2959, 2906, $2864,2822,2725,1739,1670,1600,1510,1448,1375,1260,1240,1152,1063,1022,856,800,589$. HRMS (LIFDI, toluene): m/z calcd for $\mathrm{C}_{52} \mathrm{H}_{80} \mathrm{Ni}_{4} \mathrm{Ga}_{4}: 1218.0627$; found: 1218.0633.
[NiAl](Cp*)(tebd)(cod) (6). ${ }^{140} \mathrm{Ni}(\text { cod })_{2}(100 \mathrm{mg}, 0.364 \mathrm{mmol}, 1.0$ eq.) was suspended in 1 mL hexane and 3-hexyne ( $1.41 \mathrm{~mL}, 1.41 \mathrm{mmol}, 3.9 \mathrm{eq}$ ) was added as a 1 M solution in hexane to give a red solution within seconds. Afterwards, AICp* ( $60 \mathrm{mg}, 0.370 \mathrm{mmol}, 1.0 \mathrm{eq}$.) was added and the reaction mixture was stirred at $60^{\circ} \mathrm{C}$ for 3.5 h giving a greenish-brown solution. After slowly cooling to $-30^{\circ} \mathrm{C}$ overnight, yellow crystals could be obtained which were dried in vacuo after filtration (yield: $15 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, 293 \mathrm{~K}$, toluene- $\mathrm{d}_{8}$ ): $\delta(\mathrm{ppm})=4.43-4.33(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C}=\mathrm{CH}), 3.40\left(\mathrm{dt},{ }^{3} \mathrm{~J}=5.0 \mathrm{~Hz}, 2 \mathrm{H}\right.$, $\mathrm{C}=\mathrm{CH}$ ), 2.45 - 2.32 (m, 2H, CHCH2), $2.25-2.12$ ( $\mathrm{m}, 4 \mathrm{H}, \mathrm{CHCH}_{2}$ ), 2.12 - 2.08 ( $\mathrm{m}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{3}$ ), 2.08 $1.99\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.97\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 1.96-1.89\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CHCH}_{2}\right), 1.77\left(\mathrm{dq},{ }^{3} \mathrm{~J}=14.4,{ }^{3} \mathrm{~J}=\right.$ $7.4 \mathrm{~Hz}, 2 \mathrm{H}\left(\mathrm{m}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.25\left(\mathrm{t},{ }^{3} \mathrm{~J}=7.5 \mathrm{~Hz}, 6 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.17\left(\mathrm{t},{ }^{3} \mathrm{~J}=7.5 \mathrm{~Hz}, 6 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right)$. Note: The signal intensity of the multiplet at 2.25-2.10 ppm is higher than expected due to the overlap with the methyl group of the solvent (toluene). ${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, 293 \mathrm{~K}$, toluene- $\mathrm{d}_{8}$ ): $\delta(\mathrm{ppm})=129.5$ (AI$\left.C_{4}\right)$, $114.5\left(C_{5} \mathrm{Me}_{5}\right)$, $88.7\left(\mathrm{CHCH}_{2}\right), 79.6\left(\mathrm{CHCH}_{2}\right), 32.2\left(\mathrm{CHCH}_{2}\right), 31.3\left(\mathrm{CHCH}_{2}\right), 26.4\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right)$, $20.4\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right)$, $18.1\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right)$, $16.8\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 11.8\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)$. IR (ATR, neat, $\left.\mathbf{c m}^{-1}\right)$ : 2958, 2905, 2865, 2921, 2725, 1738, 1669, 1600, 1511, 1448, 1431, 1376, 1326, 1298, 1260, 1240, 1152, 1097, 1063, 1022, 855, 799, 727, 589. HRMS (LIFDI, toluene): m/z calcd for $\mathrm{C}_{30} \mathrm{H}_{47} \mathrm{NiAI}: 492.2847$; found: 492.2822. UV/Vis (n-hexane): $\lambda_{\max }=285,220 \mathrm{~nm}$.
[NiAl](Cp*)(tebd)(hex) (7). ${ }^{140}$ Procedure A: $6(52 \mathrm{mg}, 0.105 \mathrm{mmol}, 1.0 \mathrm{eq}$.) was suspended in 1.5 mL toluene and 3-hexyne ( $0.80 \mathrm{~mL}, 0.80 \mathrm{mmol}, 7.6 \mathrm{eq}$ ) was added as a 1 M solution in toluene. The reaction was stirred for 6 h at $90^{\circ} \mathrm{C}$ to give a dark red solution. Procedure B : $\mathrm{Ni}(c o d) 2(50 \mathrm{mg}$, $0.182 \mathrm{mmol}, 1.0$ eq.) and $\mathrm{AlCp}^{*}(29 \mathrm{mg}, 0.179 \mathrm{mmol}, 1.0$ eq.) were suspended in 3 mL hexane and 3-hexyne ( $1.54 \mathrm{~mL}, 1.54 \mathrm{mmol}, 8.6 \mathrm{eq}$ ) was added as a 1 m solution in toluene to give a red solution within seconds. The reaction was stirred for 6 h at $90^{\circ} \mathrm{C}$ to give a dark red solution. Note: Due the instability in vacuo and the high solubility in unpolar solvents, 7 could not be isolated. ${ }^{1} \mathrm{H} \mathbf{N M R}(400 \mathrm{MHz}$, $293 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{12}$ ): $\delta(\mathrm{ppm})=2.82-2.49\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2, \text { Acetylene }}\right), 2.23-2.10\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2, \text { butadiene }}\right)$, $2.04-2.01$ ( $\mathrm{m}, 4 \mathrm{H}, \mathrm{CH}_{2, \text { Acetylene }}$ ), $1.99\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right.$ ), $1.15\left(\mathrm{t},{ }^{3} \mathrm{~J}=7.4 \mathrm{~Hz}, 6 \mathrm{H}, \mathrm{CH}_{3, \text { Acetylene }}\right.$ ), 0.98 ( $\mathrm{dt},{ }^{3} \mathrm{~J}=7.5 \mathrm{~Hz}$, $12 \mathrm{H}, \mathrm{CH}_{3, \text { Acetylene })}{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, 293 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{12}$ ): $\delta(\mathrm{ppm})=132.2$ ( $\mathrm{C}=\mathrm{C}_{\text {Acetylene }}$ ), 122.7 ( $\left.\mathrm{C}=\mathrm{C}_{\text {butadiene }}\right)$,

## Experimental

113.9 ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ ), $27.0\left(\mathrm{CH}_{2, \text { butadiene }), ~} 21.8\left(\mathrm{CH}_{2, \text { Acetylene }), ~} 19.9\left(\mathrm{CH}_{2, \text { butadiene }}\right)\right.\right.$, $16.6\left(\mathrm{CH}_{3, \text { butadiene }}\right)$, 16.5 $\left(\mathrm{CH}_{3, \text { butadiene })}\right.$, $16.0\left(\mathrm{CH}_{3, \text { Acetylene })}\right.$, 10.6 ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ ). IR (ATR, neat, $\left.\mathrm{cm}^{-1}\right)$ : 2961, 2927, 2869, 1825, 1576, 1453, 1374, 1304, 1260, 1055, 1021, 804, 716, 678, 527, 508. HRMS (LIFDI, toluene/hexane): m/z calcd for $\mathrm{C}_{52} \mathrm{H}_{40} \mathrm{NiAl}: 466.2685$; found: 466.2684. UV/Vis ( $n$-hexane): $\lambda_{\max }=375,315,215 \mathrm{~nm}$.
[ NiAl ](Cp*)(tpbd)(dpa) (8). ${ }^{140} \mathrm{Ni}(c o d)_{2}(60 \mathrm{mg}, 0.218 \mathrm{mmol}, 1.0 \mathrm{eq}$.) and diphenylacetylene ( $310 \mathrm{mg}, 1.74 \mathrm{mmol}, 8.0 \mathrm{eq}$.) were suspended in 6 mL hexane to give a red solution after a few minutes. Subsequently, AICp* ( $36 \mathrm{mg}, 0.222 \mathrm{mmol}, 1.0 \mathrm{eq}$.) was added and the reaction mixture was stirred at $90^{\circ} \mathrm{C}$ for 6 h giving a red solution. After slowly cooling to room temperature, the obtained red precipitate was cannula filtered, washed with cold pentane $(3 \times 1.5 \mathrm{~mL})$ and shortly exposed to vacuo to obtain a red powder (yield: $64 \%$ ). Single crystals suitable for X-ray analysis was either obtained by diffusion crystallization (toluene/hexane) or by storing a concentrated solution in toluene at $-30^{\circ} \mathrm{C}$ within one week. Note: $\mathbf{8}$ is only stable with excess dpa. In addition, long exposure of $\mathbf{8}$ to vacuo led to a black precipitate which is insoluble in common solvents. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, 293 \mathrm{~K}$, benzene- $\mathrm{d}_{6}$ ): $\delta(\mathrm{ppm})=$ 7.76 ( $\mathrm{dt},{ }^{3} \mathrm{~J}=8.2 \mathrm{~Hz}, 4 \mathrm{H}, o-\mathrm{CH}_{\text {acetylene }}$ ), 7.33 ( $\mathrm{d},{ }^{3} \mathrm{~J}=7.0 \mathrm{~Hz}, 4 \mathrm{H}, o-\mathrm{CH} H_{\text {butadiene }}$ ), $7.29-7.25(\mathrm{~m}, 4 \mathrm{H}, 0-$ CH $H_{\text {butadiene }}$ ), $7.25-7.20\left(\mathrm{~m}, 4 \mathrm{H}, m-\mathrm{CH}_{\text {acetylene }}\right)$, $6.97-6.93$ ( $\mathrm{m}, 4 \mathrm{H}, m-\mathrm{CH}_{\text {butadiene }}$ ), $6.89-6.84$ ( $\mathrm{m}, 2 \mathrm{H}, p-$ CHoutadiene), $6.80-6.74\left(\mathrm{~m}, 4 \mathrm{H}, p-\mathrm{CH}_{\text {acetylene }}, m-\mathrm{CH}_{\text {butadiene }}\right.$ ), 6.63 ( $\mathrm{tt},{ }^{3} \mathrm{~J}=7.3 \mathrm{~Hz}, 2 \mathrm{H}, p-\mathrm{C} H_{\text {butadiene }}$ ), 1.65 (s, 15H, C5 Me5). ${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, 293 \mathrm{~K}$, benzene- $\mathrm{d}_{6}$ ): $\delta(\mathrm{ppm})=146.4$ ( $\mathrm{C}=\mathrm{C}_{\text {butadiene }}$ ), 141.0 ( $\mathrm{C}=\mathrm{C}_{\text {butadiene }}$ ), 138.6 $\mathrm{C}_{\text {Ph,butadiene }}$ ), 135.3 ( $\mathrm{C}_{\text {Ph,Aceytylene }}$ ), 134.2 ( $\mathrm{C}_{\text {F }} \mathrm{C}_{\text {Acetylene }}$ ), 131.5 (o- $\mathrm{C}_{\text {Ph,butadiene }}$ ), 131.1 (o-
 $m$-CPh,butadiene), 126.3 ( $p$ - CPh,butadiene ), 123.9 ( $p$ - CPph,butadiene), 115.2 ( $C_{5} \mathrm{Me}_{5}$ ), 10.3 ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ ). IR (ATR, neat, $\left.\mathrm{cm}^{-1}\right): 3058,2917,1812,1592,1485,1440,1400,1269,1175,1070,1026,911,758,690,646,562$, 509. HRMS (LIFDI, toluene): m/z calcd for $\mathrm{C}_{52} \mathrm{H}_{45} \mathrm{NiAl}$ : 754.2690; found: 754.2692. UV/Vis ( $n$-hexane): $\lambda_{\max }=215,280,330 \mathrm{~nm}$.
$\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}(9) .\left[\mathrm{Ni}_{2}(\operatorname{cod})_{2}(\right.$ hex $\left.)\right]$ was in-situ prepared in 3 mL hexane from $\mathrm{Ni}(\mathrm{cod})_{2}$ ] ( $50 \mathrm{mg}, 0.182 \mathrm{mmol}, 1.0 \mathrm{eq}$.) and 3-hexyne ( $0.18 \mathrm{~mL}, 1.0 \mathrm{M}$ in hexane, $0.18 \mathrm{mmol}, 1.0 \mathrm{eq}$.$) .$ Subsequently, AICp* ( $29 \mathrm{mg}, 0.179 \mathrm{mmol}, 1.0$ eq.) was added and diluted with 1 mL hexane. The red mixture was stirred for six hours at $90^{\circ} \mathrm{C}$. The mixture is shortly exposed to vacuo to obtain a reddishbrown oil. Note: As the NMR spectrum includes also by-products as 6, cod and $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]$, full assignment was not possible due to signal overlapping. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, 293 \mathrm{~K}$, benzene- $\mathrm{d}_{6}$ ): $\delta$ $(\mathrm{ppm})=2.02\left(\mathrm{~s}, 45 \mathrm{H}, \mathrm{AlCp}^{*}\right) .{ }^{13} \mathrm{C}$ NMR ( 101 MHz , 293 K , benzene- $\mathrm{d}_{6}$ ): $\delta(\mathrm{ppm})=113.9\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 12.6$ (C5 Mes). HRMS (LIFDI, toluene): [M] ${ }^{+}=908.3327 \mathrm{~m} / \mathrm{z}$ (calc. 908.3329), $[\mathrm{M}-\mathrm{hex}]^{+}=826.2522 \mathrm{~m} / \mathrm{z}$ (calc. 826.2547), $[\mathrm{M}-2 h e x-2 H]^{+}=742.1607 \mathrm{~m} / \mathrm{z}$ (calc. 742.1609).

## $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}\right)_{4}$ (12).

Procedure A: $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{7}\right](8.2 \mathrm{mg}, 0.010 \mathrm{mmol}, 1.0 \mathrm{eq}$.) and AICp* ( $6.6 \mathrm{mg}, 0.041 \mathrm{mmol}$, 4.1 eq.) were suspended in 1.5 mL hexane and subsequently, 3-hexyne was added $(0.08 \mathrm{~mL}, 0.5 \mathrm{M}$ in hexane, $0.04 \mathrm{mmol}, 4.0$ eq.) to obtain a reddish brown reaction mixture. After one hour at $60^{\circ} \mathrm{C}$, all

## Experimental

volatiles were removed. The oily residue was resolved in toluene (max. 1 mL ) and filtered. Storing the concentrated solution at $-30^{\circ} \mathrm{C}$ yield red crystals which are suitable for SC-XRD analysis.

Procedure B: [ $\left.\mathrm{Ni}_{4}\left(\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}\right)_{7}\right]\left(8.2 \mathrm{mg}, 0.010 \mathrm{mmol}, 1.0 \mathrm{eq}\right.$ ) and $\mathrm{AlCp}^{*}(6.6 \mathrm{mg}, 0.041 \mathrm{mmol}$, 4.1 eq.) were suspended in 1 mL hexane. The reaction mixture was stirred for six hours at $60^{\circ} \mathrm{C}$. The reaction progress is detectable by in-situ LIFDI MS.
${ }^{1} \mathrm{H}$ NMR ( 400 MHz , 293 K , toluene- $\mathrm{d}_{8}$ ): $\delta(\mathrm{ppm})=2.15\left(\mathrm{~s}, 45 \mathrm{H}, \mathrm{Cp}{ }^{*}\right), 1.42(\mathrm{~s}, 36 \mathrm{H}, \mathrm{CNtBu}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, 293 K , toluene- $\left.\mathrm{d}_{8}\right): \delta(\mathrm{ppm})=113.0\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)$, $55.0\left(\mathrm{CNC}\left(\mathrm{CH}_{3}\right)_{3}\right), 31.9\left(\mathrm{CNC}\left(\mathrm{CH}_{3}\right)_{3}\right), 11.1$ (C5Me5). HRMS (LIFDI, toluene): m/z calc. for $\mathrm{C}_{50} \mathrm{H}_{81} \mathrm{Al}_{3} \mathrm{~N}_{4} \mathrm{Ni}_{3}$ : 994.3922; found: [M-CN $\left.{ }^{+} \mathrm{Bu}\right]^{+}$: $911.3164 \mathrm{~m} / \mathrm{z}$ (calc. $911.3189 \mathrm{~m} / \mathrm{z}$ ).
[PtAl](Cp*)(tpbd)(dpa) (13). [Pt(cod) $\left.{ }_{2}\right] \quad(8.2 \mathrm{mg}, \quad 0.020 \mathrm{mmol}, 1.0 \mathrm{eq}),. \quad \mathrm{AlCp}{ }^{*}(3.3 \mathrm{mg}$, $0.020 \mathrm{mmol}, 1.0$ eq.) and diphenylacetylene ( $14.4 \mathrm{mg}, 0.080 \mathrm{mmol}, 4.0 \mathrm{eq}$. ) were suspended in 0.5 mL toluene or toluene- $d_{8}$ and stirred for two hours at $60^{\circ} \mathrm{C}$ to obtain 13 in a red solution. The reaction progress is detectable by in-situ LIFDI MS and NMR spectroscopy. ${ }^{1} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, 293 \mathrm{~K}$, toluene- $\mathrm{d}_{8}$ ): $\delta(\mathrm{ppm})=7.93$ ( $\mathrm{dt},{ }^{3} \mathrm{~J}=7.2 \mathrm{~Hz}, 4 \mathrm{H}, o-\mathrm{CH}^{3}$ acetylene), $7.35-7.31\left(\mathrm{~m}, 4 \mathrm{H}, o-\mathrm{CH}^{8}{ }_{\text {butadiene }}\right)$, $7.31-7.27\left(\mathrm{~m}, 4 \mathrm{H}, m-\mathrm{CH}^{4}\right.$ acetylene $), 7.22\left(\mathrm{dt},{ }^{3} \mathrm{~J}=6.8 \mathrm{~Hz} \mathrm{4H}, \quad 0-\mathrm{CH}^{13}\right.$ butadiene), $7.20-7.15(\mathrm{~m}, 2 \mathrm{H}$, $p-\mathrm{CH}^{5}$ acetylene $), 6.96-6.92\left(\mathrm{~m}, 4 \mathrm{H}, m-\mathrm{CH}^{9}\right.$ butadiene $), 6.88-6.84\left(\mathrm{~m}, 2 \mathrm{H}, p-\mathrm{CH}^{10}{ }_{\text {butadiene }}\right), 6.68\left(\mathrm{t},{ }^{3} \mathrm{~J}=7.7 \mathrm{~Hz}\right.$, $4 \mathrm{H}, m-\mathrm{CH}^{14}$ butadiene), $6.55\left(\mathrm{~m}, 2 \mathrm{H}, p-\mathrm{CH}^{15}\right.$ butadiene), $1.65\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, 293 \mathrm{~K}$, toluene- $\left.\mathrm{d}_{8}\right): \quad \delta(\mathrm{ppm})=146.0 \quad\left(\mathrm{C}^{7} \mathrm{Ph}\right.$, butadiene $), \quad 136.1 \quad\left(\mathrm{C}^{12}{ }_{\mathrm{Ph}, \text { butadiene }}\right), \quad 133.5 \quad\left(\mathrm{C}^{2} \mathrm{Pr}\right.$, Aceytylene $), \quad 132.3$
 $\mathrm{C}^{4} \mathrm{Ph}$, Acetylene $), 128.9$ ( $p-\mathrm{C}^{5} \mathrm{Ph}$, Acetylene $), 128.8\left(\mathrm{C}^{1} \equiv \mathrm{C}_{\text {Acetylene }}\right), 128.0$ ( $m-\mathrm{C}^{9}{ }^{\mathrm{P}} \mathrm{p}$, butadiene $), 127.8$ ( $m$ - $\mathrm{C}^{14} \mathrm{Pr}$, butadiene $)$,
 (LIFDI, toluene): $\left[\mathrm{M}^{+}=891.2952 \mathrm{~m} / \mathrm{z}\right.$ (calc. 891.2985), $[\mathrm{M}-\mathrm{dpa}]^{+}=713.2145 \mathrm{~m} / \mathrm{z}$ (calc. 713.2202 ).

### 6.3. Reactivity part: Overview of the studies on parameter control

### 6.3.1. Additional experimental data for $\mathrm{Ni} / \mathrm{Ga}$ system

General procedure for 3-hexyne: [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ] was dissolved in the respective solvent and 3-hexyne was added as a 1 m solution in toluene/hexane via a syringe to observe a burgundy red solution within seconds. Subsequently, GaCp* was added as a 1 M solution in toluene/hexane via a syringe which immediately cause color changed to brown. The reactions were stirred at the mentioned temperatures.

General procedure for dpa: [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ] was dissolved in toluene and dpa was added as a solid to observe a burgundy red solution within minutes (approx. 2-3 min). Subsequently, GaCp* was added as a 1 M solution in toluene/hexane via a syringe. The reactions were stirred at the mentioned temperatures.
[ $\left.\mathrm{Ni}(\mathbf{c o d})_{2}\right]$ : NiGa reactions with 3-hexyne at room temperature

Table 2: Overview of Ni-Ga-hex reactions performed at room temperature for several hours in toluene. The reactions were conducted with 5-20 mg of [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ].

| No. | [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ] [eq.] | 3-hexyne [eq.] | GaCp* [eq.] | t [h] |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 1 | 0.5 | 1 | 2 |
| 2 | 1 | 0.5 | 2 | 3 |
| 3 | 1 | 0.5 | 3 | 16 |
| 4 | 1 | 0.5 | 4 | 7 |
| 5 | 1 | 0.5 | 5 | 19 |
| 6 | 1 | 1 | 1 | 4 |
| 7* | 1 | 1 | 1* | 2 |
| 8 | 1 | 2.5 | 1 | 21 |



Figure 68: LIFDI mass spectra of the reaction [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}$ * and 3-hexyne at room temperature for several hours in toluene. The equivalents used are given in Table 2.

Table 3: Assignment of clusters obtained in the reactions of [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}^{*}$ and 3-hexyne at room temperature as listed in Table 2. $M / z$ values assigned to product peaks are given in bold.

| Experimental $[\mathrm{m} / \mathrm{z}]$ | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster | Fragment | Cp*Et reaction $(7)[\mathrm{m} / \mathrm{z}]$ |
| :--- | :--- | :--- | :--- | :--- |
| 468.02 | 468.0204 | $\left[\mathrm{NiGa}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ |  | 496.0519 |
| $468.18^{*}$ | 468.1837 | $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})$ |  | 496.2149 |
| 721.86 | 721.8685 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})-4 \mathrm{H}$ | $1218-2 \mathrm{GaCp}^{*}-\mathrm{hex}$ | 749.8974 |
| 807.97 | 807.9784 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})_{2}$ | $1218-2 \mathrm{GaCp}^{*}$ | 836.0040 |
| 845.84 | 845.8497 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}-2 \mathrm{H}$ | $1218-\mathrm{GaCp}^{*}-2 \mathrm{hex}$ | 887.8923 |
| 929.93 | 929.9431 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})$ | $1218-\mathrm{GaCp}^{*}-\mathrm{hex}$ | 971.9920 |
| 1012.00 | 1012.0213 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{2}$ | $1218-\mathrm{GaCp}^{*}$ | 1056.0674 |
| $\mathbf{1 2 1 8 . 0 6 3 3}$ | $\mathbf{1 2 1 8 . 0 6 3 3}$ | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ | Product | $\mathbf{1 2 7 4 . 1 2 4 6}$ |

Due to different calibration used in the different reactions, the experimental values vary with the third/fourth decimal places and are therefore only given with two decimal places just to summarize the obtained peaks.*Only obtained in reactions no. 2-5

## [ $\mathrm{Ni}(\operatorname{cod})_{2}$ ]: NiGa reactions with 3-hexyne at $60^{\circ} \mathrm{C}$

Table 4: Overview of Ni-Ga-hex reactions performed at $60^{\circ} \mathrm{C}$ for 4-6 hours in toluene. The reactions were conducted with 5-20 mg of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right.$ ].

| No. | [Ni(cod) ${ }_{2}$ [eq.] | 3-hexyne [eq.] | GaCp* [eq.] |
| :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | 0.5 | 1 |
| 2 | 1 | 1 | 1 |
| 3 | 1 | 2.5 | 1 |
| 4 | 1 | 2.5 | 2.5 |
| 5 | 1 | 6 | 1 |



Figure 69: LIFDI mass spectra of the reaction [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}^{*}$ and 3-hexyne at $60^{\circ} \mathrm{C}$, after 4-6h in toluene. Used equivalents are given in Table 4.

Table 5: Assignment of clusters obtained in the reactions of [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ], $\mathrm{GaCp}^{*}$ and 3-hexyne at $60^{\circ} \mathrm{C}$ as listed in Table 4. $\mathrm{m} / \mathrm{z}$ values assigned to product peaks are given in bold.

|  | Experimental [m/z] | Calculated [m/z] | Cluster | Fragment |
| :---: | :---: | :---: | :---: | :---: |
| A | 468.18 | 468.1837 | [ $\mathrm{Ni}_{2}$ ] $\left(\mathrm{Cp}^{*}\right)_{2}$ (hex) |  |
| B | 703.25 | 703.2635 | [ $\left.\mathrm{Ni}_{2} \mathrm{Ga}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})_{3}$ |  |
| C | 945.98 | 945.9760 | [ $\mathrm{Ni}_{5} \mathrm{Ga}_{2}$ ] $\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{3}-2 \mathrm{H}$ | G-3hex |
| D | 1030.05 | 1030.0702 | [ $\mathrm{Ni}_{5} \mathrm{Ga}_{2}$ ] $(\mathrm{Cp})_{2}(\text { (hex })_{4}$ | G-2hex |
| E | 1112.14 | 1112.1485 | [ ](Cp*)  ${ }_{2}(\mathrm{hex})_{5}$ | G-hex |
| F | 1152.02 | 1152.0349 | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}$ | J-hex |
| G | 1194.21 | 1194.2267 | [ ](Cp*)  ${ }_{2}(\mathrm{hex})_{6}$ |  |
| H* | 1218.0633 | 1218.0633 | [ $\mathrm{Ni}_{4} \mathrm{Ga}_{4}$ ] $\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}$ |  |
| J | 1234.09 | 1234.1132 | [ $\mathrm{Ni}_{5} \mathrm{Ga}_{3}$ ] $\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{4}$ |  |
| K | 1292.02 | 1292.0485 | [ $\left.\mathrm{Ni}_{6} \mathrm{Ga}_{3}\right]^{\left(C p^{*}\right)_{3}(\text { hex })_{4}}$ |  |
| L | 1333.91 | 1333.9144 | $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{4}\right](\mathrm{Cp})_{4}{ }_{4}(\mathrm{hex})_{2}-2 \mathrm{H}$ | N-hex |
| M | 1399.97 | 1399.9608 | [ $\mathrm{Ni}_{5} \mathrm{Ga}_{5}$ ] $\left(\mathrm{Cp}{ }^{*}\right)_{5}($ hex $)$ |  |
| N | 1415.98 | 1415.9933 | $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{3}-2 \mathrm{H}$ |  |
| 0* | 1457.88 | 1457.8958 | [ $\mathrm{Ni}_{6} \mathrm{Ga}_{5}$ ] $\left(\mathrm{Cp}{ }^{*}\right)_{5}$ (hex) |  |
| $\mathbf{P}^{*}$ | 1579.86 | 1579.8608 | [ ](Cp*)  ${ }_{6}$ |  |
| Q* | 1637.78 | 1637.7943 | [ $\mathrm{Ni}_{7} \mathrm{Ga}_{6}$ ] $\left(\mathrm{Cp}^{*}\right)_{6}$ |  |
| R* | 1649.77 | 1649.7960 | [ $\mathrm{i}_{6} \mathrm{Ga}_{7}$ ] $\left(\mathrm{Cp}{ }^{*}\right)_{6}+\mathrm{H}$ |  |

*H is only obtained in reaction 1 requiring low equivalents of 3-hexyne. O is only detected in reactions 1-4. P, Q and R are only observed in
reactions 1 and 2 .
Due to different calibration used in the different reactions, the experimental values vary with the third/fourth decimal places and are therefore only given with two decimal places just to average the obtained peaks.

## [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ]: NiGa reactions with 3-hexyne at $90^{\circ} \mathrm{C}$

Table 6: Overview of Ni-Ga-hex reactions performed at $90^{\circ} \mathrm{C}$ for 6 hours in toluene. The reactions were conducted with 10-30 mg of [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ].

| No. | $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right][$ eq. $]$ | 3-hexyne [eq.] | GaCp* ${ }^{\text {[eq.] }}$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | 0.5 | 0.5 |
| 2 | 1 | $\mathbf{1}$ | 1 |



Figure 70: LIFDI mass spectra obtained of the reaction [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp} *$ and 3 -hexyne at $90^{\circ} \mathrm{C}$, after 6 h in toluene. Used equivalents are given in Table 6.

Table 7: Assignment of clusters obtained in the reactions of [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ], $\mathrm{GaCp}^{*}$ and 3-hexyne at $90^{\circ} \mathrm{C}$ as listed in Table 4. M/z values assigned to product peaks are given in bold.

|  | Experimental [m/z] | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster | Fragment |
| :--- | :--- | :--- | :--- | :--- |
| A | 1169.78 | 1169.7769 | $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ | B-2hex |
| B | 1333.92 | 1333.9144 | $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}-2 \mathrm{H}$ |  |
| C | 1399.97 | 1399.9608 | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{hex})$ |  |
| D | 1483.92 | 1484.0552 | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{hex})_{2}+2 \mathrm{H}$ |  |
|  |  | 1483.9089 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{hex})$ |  |
| E | 1637.79 | 1637.7943 | $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ |  |
| F $^{*}$ | 1693.68 | 1693.7140 | $\left[\mathrm{Ni}_{8} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}-2 \mathrm{H}$ |  |
| G $^{*}$ | 1775.77 | 1775.7923 | $\left[\mathrm{Ni}_{8} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}(\mathrm{hex})-2 \mathrm{H}$ |  |

${ }^{*} \mathrm{~F}$ and G are only obtained in reaction no.1.
${ }^{\text {§ }}$ Two different sum formulas are possible with the calculated $\mathrm{m} / \mathrm{z}$ for $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{hex})$ being closer to the experimentally observed value. It could be assumed that this clusters is an intermediate in the reaction pathway to $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}$.

## [ $\left.\mathrm{Ni}(\mathbf{c o d})_{2}\right]$ : NiGa reactions with dpa at room temperature

Table 8: Overview of Ni-Ga-dpa reactions performed at r.t. for several hours in toluene. The reactions were conducted with $10-30 \mathrm{mg}$ of [ $\mathrm{Ni}\left(\mathrm{cod}_{2}\right)_{2}$.

| No. | $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right][$ eq. $]$ | dpa [eq.] | GaCp* $^{\text {[eq.] }}$ | $\mathbf{t}$ [h] |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | 0.5 | $\mathbf{0 . 5}$ | $\mathbf{7}$ |
| $\mathbf{2}$ | 1 | 0.5 | $\mathbf{1}$ | $\mathbf{7}$ |


| $\mathbf{3}$ | 1 | 0.5 | $\mathbf{2}$ | 16 |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{4}$ | 1 | 0.5 | $\mathbf{3}$ | $\mathbf{7}$ |
| $\mathbf{5}$ | 1 | 0.5 | $\mathbf{4}$ | 19 |
| $\mathbf{6}$ | 1 | $\mathbf{2}$ | 1 | 6 |
| $\mathbf{7}$ | $\mathbf{1}$ | $\mathbf{4}$ | 6 |  |



Figure 71: LIFDI mass spectra of the reaction [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}^{*}$ and dpa at room temperature for several hours in toluene. The equivalents used are given in Table 8.

Table 9: Cluster assignment of obtained signals in the reactions of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp} *$ and dpa at room temperature as listed in Table 8. M/z values assigned as product peaks are given in bold.

|  | Experimental [m/z] | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster | Fragment | Observed in No. |
| :--- | :--- | :--- | :--- | :--- | :--- |
| A | 510.13 | 510.1367 | $\left[\mathrm{Ni}_{2}\right](\mathrm{cod})_{2}(\mathrm{dpa})$ |  | $2,6,7$ |
| B | 549.21 | 549.2092 | $\left[\mathrm{Ni}^{2}\right]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{2}$ |  | $2,6,7$ |
| C | 564.19 | 564.1837 | $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})$ |  | $1-5$ |
| D | 640.05 | 640.0519 | $\left[\mathrm{Ni}_{3}\right](\mathrm{cod})(\mathrm{dpa})_{3}$ |  | 6,7 |
| E | 999.95 | 999.9790 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{2}$ | $\mathrm{~J}-2 \mathrm{dpa} / \mathrm{L}-2 \mathrm{GaCp}^{*}$ | $1-5$ |
|  |  |  |  | K-GaCp*-dpa |  |
| F | 1025.93 | 1025.9430 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{1}$ | K-2dpa/L-GaCp*-dpa | $1-5$ |
| G | 1178.05 | 1178.0585 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{3}$ | J-dpa/K-GaCp* | $1-7$ |
| H | 1204.00 | 1204.0215 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}$ | K-dpa/L-GaCp* | $1-5$ |
| J | $\mathbf{1 3 5 6 . 1 2}$ | $\mathbf{1 3 5 6 . 1 3 7 2}$ | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4}$ |  | $\mathbf{1 , 2}$ |
| K | $\mathbf{1 3 8 4 . 0 9}$ | $\mathbf{1 3 8 4 . 0 9 7 3}$ | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ |  | $\mathbf{1 - 6}$ |
| L | $\mathbf{1 4 1 0 . 0 4}$ | $\mathbf{1 4 1 0 . 0 6 3 0}$ | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})_{2}$ |  | $\mathbf{1 - 5}$ |

## [ $\mathrm{Ni}(\operatorname{cod})_{2}$ ]: NiGa reactions with dpa at $60^{\circ} \mathrm{C}$

Table 10: Overview of Ni-Ga-dpa reactions performed at $60^{\circ} \mathrm{C}$ for several hours in toluene. The reactions were conducted with $10-30 \mathrm{mg}$ of [ $\mathrm{Ni}\left(\mathrm{cod}_{2}\right)_{2}$.

| No. | $\left[\mathrm{Ni}(\text { cod })_{2}\right][$ eq. $]$ | dpa [eq.] | GaCp* [eq.] | $\mathbf{t}[\mathrm{h}]$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | 0.5 | $\mathbf{1}$ | 4.5 |
| $\mathbf{2}$ | 1 | $\mathbf{1}$ | $\mathbf{1}$ | 24 |
| $\mathbf{3}$ | 1 | $\mathbf{2}$ | $\mathbf{1}$ | 3.5 |
| $\mathbf{4}$ | 1 | $\mathbf{4}$ | 1 | 4.5 |



Figure 72: LIFDI mass spectra of the reaction [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ], $\mathrm{GaCp} *$ and dpa at $60^{\circ} \mathrm{C}$ for several hours in toluene. The equivalents used are given in Table 10.

Table 11: Cluster assignment of obtained signals in the reactions of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}^{*}$ and dpa at $60^{\circ} \mathrm{C}$ as listed in Table 10. M/z values assigned as product peaks are given in bold.

|  | Experimental [m/z] | Calculated [m/z] | Cluster | Fragment | Observed in No. |
| :---: | :---: | :---: | :---: | :---: | :---: |
| A | 416.11 |  |  |  | 2-4 |
| B | 550.21 | 550.2173 | [ Ni$]\left(\mathrm{Cp}{ }^{*}\right)(\mathrm{dpa})_{2}+\mathrm{H}$ |  | 2-4 |
| C | 564.18 | 564.1837 | [ $\mathrm{Ni}_{2}$ ] $\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})$ |  | 1-4 |
| D | 1178.05 | 1178.0585 | [ $\mathrm{Ni}_{4} \mathrm{Ga}_{2}$ ] $\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{3}$ | J-2dpa/G-GaCp* | 1-3 |
| $\mathrm{E}_{\mathrm{a}}$ | 1204.02 | 1204.0215 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right](\mathrm{Cp} *)_{3}(\mathrm{dpa})_{2}$ | G-dpa/ $\mathrm{H}_{\mathrm{a}}-\mathrm{GaCp} *$ | 1 |
| $\mathrm{E}_{\mathrm{b}}$ | 1208.02 | 1208.0281 | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{1}\right]\left(\mathrm{Cp}^{*}\right)_{1}(\mathrm{dpa})_{4}$ | $\mathrm{H}_{\mathrm{b}}$-GaCp* | 2, 3 |
| F | 1356.13 | 1356.1372 | [ $\mathrm{Ni}_{4} \mathrm{Ga}_{2}$ ] $\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4}$ | J-dpa | 1-3 |
| G | 1384.10 | 1384.0973 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ |  | 1-3 |
| $\mathrm{Ha}_{\mathrm{a}}$ | 1410.06 | 1410.0630 | [ $\mathrm{Ni}_{4} \mathrm{Ga}_{4}$ ] $\left.\mathrm{CPp}^{*}\right)_{4}(\mathrm{dpa})_{2}$ |  | 1 |
| $\mathrm{H}_{\mathrm{b}}$ | 1414.06 | 1410.0630 | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4}$ |  | 1-3 |


| J | 1534.23 | 1534.2131 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}$ | $1-3$ |
| :--- | :--- | :--- | :--- | :--- |
| K | 1553.89 | 1553.9144 | $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})_{1}+2 \mathrm{H}$ | 1 |

## [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ]: NiGa reactions with dpa at $90^{\circ} \mathrm{C}$

Table 12: Overview of Ni-Ga-dpa reactions performed at $90^{\circ} \mathrm{C}$ for several hours in toluene. The reaction was conducted with 35 mg of [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ].

| No. | $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right][$ eq.] | dpa [eq.] | GaCp* [eq.] | $\mathbf{t}$ [h] |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 1 | 0.5 | 0.5 | 19 |



Figure 73: LIFDI mass spectrum of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], G a C p^{*}$ and dpa at $90^{\circ} \mathrm{C}$ for several hours in toluene. The equivalents used are given in Table 12.

Table 13: Cluster assignment of obtained signals in the reaction of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}^{*}$ and dpa at $90^{\circ} \mathrm{C}$ as listed in Table 12. M/z values assigned as product peaks are given in bold.

|  | Experimental $[\mathrm{m} / \mathrm{z}]$ | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster | Fragment |
| :--- | :--- | :--- | :--- | :--- |
| A | $\mathbf{1 3 8 4 . 1 0}$ | $\mathbf{1 3 8 4 . 0 9 7 3}$ | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ |  |
| B | $\mathbf{1 5 5 3 . 8 9}$ | $\mathbf{1 5 5 3 . 9 1 4 4}$ | $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})_{1}+\mathbf{2 H}$ |  |
| C | Mixture: |  |  |  |
|  | 1637.75 | 1637.7943 | $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ | E-dpa |
|  | 1647.74 | 1647.7804 | $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}-\mathrm{H}$ | E-dpa |
| D | $\mathbf{1 7 0 5 . 6 7}$ |  |  |  |
| E | Mixture: | $\mathbf{1 8 1 5 . 8 7 2 6}$ | $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}{ }^{*}\right)_{6}(\mathrm{dpa})$ |  |
|  | $\mathbf{1 8 1 5 . 8 6}$ | $\mathbf{1 8 2 5 . 8 5 8 7}$ | $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right](\mathrm{Cp})_{6}(\mathrm{dpa})-\mathrm{H}$ |  |
|  | $\mathbf{1 8 2 5 . 8 2}$ |  |  |  |

## $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ : Reactions with 3-hexyne at room temperature and $60^{\circ} \mathrm{C}$

General procedure: $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ was dissolved in the respective solvent and 3 -hexyne was added as a 1 m solution in toluene/hexane via a syringe. In dpa containing reactions, dpa was added as a solid in a glovebox instead of 3-hexyne. The reactions were stirred at the mentioned temperatures.

Table 14: Overview of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$-hex reactions performed at room temperature and $60{ }^{\circ} \mathrm{C}$ for several hours in toluene. The reaction was conducted with $15-25 \mathrm{mg}$ of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$.

| No. | $\left[\mathbf{N i}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ [eq.] | 3-hexyne [eq.] | $\mathbf{T}\left[{ }^{\circ} \mathbf{C}\right]$ | $\mathbf{t}[\mathrm{h}]$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | $\mathbf{4}$ | r.t. | 4 |
| $\mathbf{2}$ | 1 | $\mathbf{6}$ | r.t. | 24 |
| $\mathbf{3}$ | 1 | $\mathbf{4}$ | 60 | 6 |
| $\mathbf{4}$ | $\mathbf{1}$ | $\mathbf{6}$ | 60 | 24 |



Figure 74: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{GaCp})_{4}\right]$ and 3-hexyne at room temperature $(\mathbf{1}, \mathbf{2})$ and $60{ }^{\circ} \mathrm{C}(3,4)$, after several hours in toluene. Used equivalents are given in Table 14.

Table 15: Assignment of clusters obtained in the reactions $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ and 3-hexyne as listed in Table 14. M/z values assigned to product peaks are given in bold.

|  | Experimental [m/z] | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster | Fragment | Observed in No. |
| :--- | :--- | :--- | :--- | :--- | :--- |
| A | 468.02 | 468.0204 | $\left[\mathrm{NiGa}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ |  | $1-3$ |
|  | 468.18 | 468.1837 | $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}($ hex $)$ | $1-4$ |  |
| B | 594.86 | 594.8807 | $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ | C-hex | $2-4$ |
| C | 678.97 | 678.9563 | $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{1}$ |  | $\mathbf{2 - 4}$ |
| D | 863.88 | 863.8975 | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{2}$ | K-GaCp*-2hex | 1,2 |


| E | 929.94 | 929.9431 | [ $\mathrm{Ni}_{4} \mathrm{Ga}_{3}$ ] $(\mathrm{Cp})_{3}(\mathrm{hex})_{1}$ | J-GaCp*-hex | 1,2 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| F | 947.97 | 947.9920 | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{3}(-2 \mathrm{H})$ | K-GaCp*-hex | 1-4 |
| G | 1028.05 | 1028.0536 | [ $\left.\mathrm{Ni}_{5} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})_{4}-2 \mathrm{H}$ | K-GaCp* | 1-4 |
| H | 1036.16 | 1036.1653 | [ $\mathrm{Ni}_{3} \mathrm{Ga}_{3}$ ] $\left(\mathrm{Cp}{ }^{*}\right)_{3}(\mathrm{hex})_{3}$ |  | 2-4 |
| J | 1218.06 | 1218.0633 | [ ](Cp*)  ${ }_{4}(\mathrm{hex})_{2}$ |  | 1-4 |
| K | 1234.09 | 1234.1132 | [ $\mathrm{Ni}_{5} \mathrm{Ga}_{3}{ }^{\text {( }}$ (p $\left.{ }^{*}\right)_{3}(\mathrm{hex})_{4}$ |  | 1-4 |

Reaction progress of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ with 4 eq. 3-hexyne at room temperature (reaction no. 1):


Figure 75: Time dependent LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{GaCp})_{4}\right]$ with 4 eq . 3-hexyne at room temperature. The mass spectra show the conversion of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ to $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex}) \quad$ (C), $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(h e x)_{2}$ (F) and afterwards $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}(\mathrm{G})$.

Table 16: Assignment of the obtained clusters as depicted in Figure 75.

|  | Experimental [m/z] | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster | Fragment |
| :--- | :--- | :--- | :--- | :--- |
| A | 468.0186 | 468.0204 | $\left[\mathrm{NiGa}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ |  |
|  | 468.1829 | 468.1837 | $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{hex})$ |  |
| B | 608.0314 | 608.0330 | $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\text { hex })_{1}$ |  |
| C | $\mathbf{8 1 4 . 0 7 5 3}$ | $\mathbf{8 1 4 . 0 7 4 2}$ | $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{1}$ |  |
| D | 929.9419 | 929.9431 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{1}$ | F-GaCp*-hex |
| E | 1152.0206 | 1152.0173 | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}-2 \mathrm{H}$ | G-hex |
| F | $\mathbf{1 2 1 8 . 0 6 6 0}$ | $\mathbf{1 2 1 8 . 0 6 3 3}$ | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ |  |
| G | $\mathbf{1 2 3 4 . 0 9 4 5}$ | $\mathbf{1 2 3 4 . 1 1 3 2}$ | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}$ |  |

## $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ : Reactions with dpa at room temperature

Table 17: Overview of $\left[\mathrm{Ni}(\mathrm{GaCp})_{4}\right]$-dpa reactions performed at room temperature for several hours in toluene. The reaction was conducted with $15-25 \mathrm{mg}$ of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$.

| No. | $\left[\mathbf{N i}\left(\mathrm{GaCp}^{*}\right)_{4}\right][$ eq. $]$ | dpa [eq.] | $\mathbf{t}[\mathrm{h}]$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | $\mathbf{1}$ | 6.5 |
| $\mathbf{2}$ | 1 | $\mathbf{4}$ | 4 |



Figure 76: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{GaCp})_{4}\right]$ and dpa at room temperature after several in toluene. Used equivalents are given in Table 17.

Table 18: Cluster assignment of obtained signals in the reaction [Ni(GaCp*) ${ }_{4}$ ] and dpa at room temperature as listed in Table 17. M/z values assigned as product peaks are given in bold

|  | Experimental [m/z] | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster | Fragment | Observed in No. |
| :--- | :--- | :--- | :--- | :--- | :--- |
| A | 468.02 | 468.0204 | $\left[\mathrm{NiGa}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ | 1 |  |
| B | 534.23 | 534.2348 | $(\mathrm{dpa})_{3}$ | 1,2 |  |
| C | 564.18 | 564.1837 | $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})$ | 1,2 |  |
| D | 1178.06 | 1178.0585 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{3}$ | F-dpa | 1,2 |
| E | 1204.02 | 1204.0215 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}$ | G-dpa | 1,2 |
| F | $\mathbf{1 3 5 6 . 1 3}$ | $\mathbf{1 3 5 6 . 1 3 4 9}$ | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4}$ | 1,2 |  |
| G | $\mathbf{1 3 8 4 . 0 9}$ | $\mathbf{1 3 8 4 . 0 9 7 3}$ | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ | 1,2 |  |
| H | $\mathbf{1 4 1 2 . 0 6}$ | $\mathbf{1 4 1 2 . 0 5 4 6}$ | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4}-\mathbf{2 H}$ | 1,2 |  |
| J | $\mathbf{1 4 6 7 . 9 9}$ | $\mathbf{1 4 6 7 . 9 9 8 7}$ | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})_{2}$ |  |  |

## $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ : Reactivity tests with $\mathrm{PEt}_{3}$

Procedure: 1 was prepared in-situ by reaction of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right](9.1 \mathrm{mg}, 0.033 \mathrm{mmol}, 1.0 \mathrm{eq}$.$) , 3-hexyne$ (1 eq.) and GaCp* (1 eq.) in 0.5 mL toluene-d8. 3-hexyne and GaCp* were added as a 1 m solution in


Table 19: Overview of reactivity tests of 1 with $\mathrm{PEt}_{3}$ performed at room temperature for one day in toluene-d $\mathrm{d}_{8}$.

| No. | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ (hex) ${ }_{2}$ [eq.] | PEt $_{3}$ [eq.] | $\mathbf{t}$ [h] |
| :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | 3 | 24 |
| $\mathbf{2}$ | 1 | 4 | 24 |



Figure 77: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(h e x)_{2}$ and $\mathrm{PEt}_{3}$ at room temperature after one day in toluene-d ${ }_{8}$. Used equivalents are given in Table 19. Right: enlarged experimentally obtained pattern for $1044.1614 \mathrm{~m} / \mathrm{z}$.

Table 20: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(h e x)_{2}$ and $P E t_{3}$ at room temperature as listed in Table 19.

|  | Experimental [m/z] | Calculated [m/z] | Cluster |
| :--- | :--- | :--- | :--- |
| A | 294.1163 | 294.1176 | $\left[\mathrm{Ni}\left(\mathrm{PEt}_{3}\right)_{2}\right]$ |
| B | 326.1064 | 326.1544 | $\mathrm{Ni}\left(\mathrm{Cp}^{*}\right)_{2}-2 \mathrm{H}$ |
| C | 412.2065 | 412.2088 | $\left[\mathrm{Ni}^{\left.\left(\mathrm{PEt}_{3}\right)_{3}\right]}\right.$ |
| D | 1044.1614 | 1044.1606 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{PEt}_{3}\right)_{2}(\mathrm{hex})_{2}$ |
| E | 1218.0621 | 1218.0643 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}(\mathbf{1})$ |

## [ $\left.\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ : Reactivity tests with $\mathrm{PPh}_{3}$

Procedure: 1 was prepared in-situ by reaction of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right](9.1 \mathrm{mg}, 0.033 \mathrm{mmol}, 1.0 \mathrm{eq}$.$) , 3-hexyne$ (1 eq.) and GaCp* (1 eq.) in 0.5 mL toluene-d8. 3-hexyne and GaCp* were added as a 1 m solution in toluene-d ${ }_{8}$. After $4.5 \mathrm{~h}, \mathrm{PPh}_{3}$ was added as solid using a glovebox.

Table 21: Overview of reactivity tests of 1 with $\mathrm{PPh}_{3}$ performed at room temperature for one day in toluene-d ${ }_{8}$.

| No. | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ (hex) ${ }_{2}$ [eq.] | PPh $_{3}$ [eq.] | $\mathbf{t}$ [h] |
| :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | 2.5 | 24 |
| $\mathbf{2}$ | 1 | 3 | 24 |



Figure 78: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(h e x)_{2}$ and $P \mathrm{Ph}_{3}$ at room temperature after one day in toluene-d ${ }_{8}$. Used equivalents are given in Table 21. Right: enlarged experimentally obtained pattern for $1274.1132 \mathrm{~m} / \mathrm{z}$.

Table 22: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(C p^{*}\right)_{4}(\mathrm{hex})_{2}$ and $P P h_{3}$ at room temperature as listed in Table 21. The assignment of the clusters given in italics should be considered with special attention.

|  | Experimental $[\mathrm{m} / \mathrm{z}]$ | Calculated $[\mathrm{m} / \mathbf{z}]$ | Cluster |
| :--- | :--- | :--- | :--- |
| A | 334.0413 |  | Not identified |
| B | 412.0887 | 412.0891 | $\left[\mathrm{Ni}\left(\mathrm{PPh}_{3}\right)(\right.$ tol $\left.)\right]$ |
| C | 582.2280 | 582.1176 | $\left[\mathrm{Ni}\left(\mathrm{PPh}_{3}\right)_{2}\right]$ |
| D | 614.1057 | 614.1802 | $\left[\mathrm{Ni}\left(\mathrm{PPh}_{3}\right)_{2}\right]\left(\mathrm{CH}_{3}\right)_{2}+2 \mathrm{H}$ |
| E | 1218.0621 | 1218.0643 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}(\mathbf{1})$ |
| F | 1274.1140 | 1274.1132 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{PPh}_{3}\right)(\text { hex })_{2}$ |

## $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ : Reactivity tests with dpa

Procedure: 1 was prepared in-situ by reaction of [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right](20.2 \mathrm{mg}, 0.073 \mathrm{mmol}, 1.0 \mathrm{eq}$.$) , 3-hexyne$ (1 eq.) and GaCp* (1 eq.) in 0.5 mL toluene and 0.5 mL hexane. 3-hexyne and GaCp* were added as a 1 M solution in toluene. After 3.5 h , dpa was added as solid using a glovebox and the reaction solution was diluted with 1 mL toluene. The reaction was performed at $40^{\circ} \mathrm{C}$ for two days.

The obtained LIFDI mass spectra are depicted in Figure 23 in chapter 4.1.1.3.

### 6.3.2. Additional experimental data for $\mathrm{Ni} / \mathrm{Al}$ system

General procedure with 3-hexyne: [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right]$ and $A I C p^{*}$ were provided in a reaction vessel as solid and the respective solvent was added to dissolve $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right.$ ]. 3-hexyne was added as a 1 M solution in toluene/hexane via a syringe to observe a burgundy red solution within seconds and AICp* as solid. The reactions were stirred at the mentioned temperatures.

General procedure with dpa: $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ and $A I C p^{*}$ were provided in a reaction vessel as solid and the respective solvent was added to dissolve [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ]. dpa was added as a solid and additional solvent was added to wash down dpa residue on the flask wall to observe a burgundy red solution within minutes and AICp* still as solid. The reactions were stirred at the mentioned temperatures.

## $\left[\mathrm{Ni}(\mathrm{Cod})_{2}\right]$ : NiAl reactions with 3-hexyne at 60 and $90^{\circ} \mathrm{C}$

Table 23: Overview of Ni-Al-hex reactions performed at $60^{\circ} \mathrm{C}$ and $90^{\circ} \mathrm{C}$ for 6 hours in toluene/hexane mixture. The reactions were conducted with 11 mg of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$. The amount of AICp* with different equivalents 3-hexyne was varied.

| No. | [Ni(cod)2] [eq.] | 3-hexyne [eq.] | AICp* ${ }^{\text {[eq.] }}$ | T [ ${ }^{\circ} \mathbf{C}$ ] |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | $\mathbf{1}$ | $\mathbf{1}$ | $\mathbf{2}$ | 60 |
| $\mathbf{2}$ | 1 | 1 | $\mathbf{4}$ | 60 |
| $\mathbf{3}$ | 1 | 4 | $\mathbf{2}$ | 60 |
| $\mathbf{4}$ | $\mathbf{1}$ | 4 | $\mathbf{4}$ | 60 |
| $\mathbf{5}$ | $\mathbf{1}$ | $\mathbf{0 . 5}$ | $\mathbf{2}$ | 90 |
| $\mathbf{6}$ | $\mathbf{1}$ | $\mathbf{8}$ | $\mathbf{2}$ | 90 |



Figure 79: LIFDI mass spectra of the reaction [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right]$, $\mathrm{AlCp} *$ and 3-hexyne at $60^{\circ} \mathrm{C}$ and $90^{\circ} \mathrm{C}$, after 6 h in toluene/hexane. Used equivalents and temperatures are given in Table 23.

Table 24: Assignment of clusters obtained in the reactions of [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{AlCp*}$ and 3-hexyne at $60^{\circ} \mathrm{C}$ and $90^{\circ} \mathrm{C}$ as listed in Table 24. $M / z$ values assigned to product peaks are given in bold.

|  | Experimental $[\mathrm{m} / \mathrm{z}]$ | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster | Fragment | Observed in |
| :--- | :--- | :--- | :--- | :--- | :--- |
| A $^{*}$ | 381.12 | 381.1253 | $\left[\mathrm{NiAl}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}-\mathrm{H}$ | $2-4,6$ |  |
| B* $^{*}$ | 399.13 |  | $\left[\mathrm{Ni}_{1}\right]-$ species | $2-4,6$ |  |
| C $^{*}$ | 415.13 | 415.1446 | $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)(\text { hex })_{2}$ | $2-6$ |  |
| D* | 433.14 |  | $\left[\mathrm{Ni}_{1}\right]-$ species | $2-6$ |  |
| E | $\mathbf{7 0 7 . 3 4}$ | $\mathbf{7 0 7 . 3 3 8 9}$ | $\left[\mathrm{NiAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}+\mathrm{H}$ | $\mathbf{1 - 6}$ |  |
| F | 742.16 | 742.1608 | $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}($ hex $)-2 \mathrm{H}$ | $\mathrm{H}-\mathrm{hex}$ | 5 |
| G | 764.26 | 764.2664 | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ | J -AlCp* | $1,2,5$ |
| H | $\mathbf{8 2 6 . 2 5}$ | $\mathbf{8 2 6 . 2 5 4 7}$ | $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{2}$ |  | $\mathbf{5}$ |
| J | $\mathbf{9 2 7 . 3 7}$ | $\mathbf{9 2 7 . 3 7 3 1}$ | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}+\mathrm{H}$ |  | 1,2 |

*These compounds are only obtained if $707 \mathrm{~m} / \mathrm{z}$ is one of the major products.

## $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]: \mathrm{NiAl}$ reaction with dpa at $90^{\circ} \mathrm{C}$

Table 25: Overview of Ni-Al-dpa reactions performed at $90^{\circ} \mathrm{C}$ for 6 hours in hexane. The reaction was conducted with 30 mg of [Ni(cod)2].

| $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right][$ eq. $]$ | dpa [eq.] | AlCp* $^{*}$ [eq.] | $\mathrm{t}[\mathrm{h}]$ |
| :---: | :---: | :---: | :---: |
| 1 | 8 | 1 | 6 |



Figure 80: LIFDI mass spectra of the reaction [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{AlCp}{ }^{*}$ and dpa (8 eq.) at $90^{\circ} \mathrm{C}$, after 6 h in hexane.

Table 26: Assignment of clusters obtained in the reactions of [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{AlCp}{ }^{*}$ and dpa at $90{ }^{\circ} \mathrm{C}$ after 6 h as listed in Table 25. M/z values assigned to product peaks are given in bold.

|  | Experimental [m/z] | Calculated [m/z] | Cluster | Fragment |
| :--- | :--- | :--- | :--- | :--- |
| A | 414.0902 | 414.0919 | $[\mathrm{Ni}](\mathrm{dpa})_{2}$ |  |
| B | 534.2336 | 534.2348 | $(\mathrm{dpa})_{3}$ |  |
| C | 549.2077 | 549.2092 | $\left[\mathrm{Ni}_{1}\right]\left(\mathrm{Cp}{ }^{*}\right)(\mathrm{dpa})_{2}$ |  |
| D | 576.1910 | 576.1908 | $[\mathrm{NiAl}](\mathrm{Cp} *)(\mathrm{dpa})_{2}$ |  |
| E | 594.2016 | 594.1857 | $[\mathrm{Ni}](\mathrm{dpa})_{3}+2 \mathrm{H}$ |  |
| F | $\mathbf{7 1 2 . 3 0 9 0}$ | $\mathbf{7 1 2 . 3 1 3 0}$ | (dpa) $_{4}$ | H-hex |
| G | $\mathbf{7 5 4 . 2 7 0 4}$ | $\mathbf{7 5 4 . 2 6 9 0}$ | $\left[\mathrm{NiAl](Cp*)(dpa)}_{3}\right.$ |  |

## [ $\left.\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{4}\right]$ : Reactions with 3-hexyne at $60^{\circ} \mathrm{C}$

General procedure: $\left[\mathrm{Ni}\left(\mathrm{AICp}{ }^{*}\right)_{4}\right]$ was dissolved in the respective solvent and 3-hexyne was added as a 1 M solution in toluene/hexane via a syringe. In dpa containing reactions, dpa was added as a solid in a glovebox instead of 3-hexyne. The reactions were stirred at the mentioned temperatures.

Table 27: Overview of $\left[\mathrm{Ni}\left(\mathrm{A} / \mathrm{Cp}^{*}\right)_{4}\right]$ reacted with 3-hexyne performed at $60^{\circ} \mathrm{C}$ for 48 hours in toluene- $d_{8} /$ hexane. The reaction was conducted with 10 mg of $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{4}\right]$.

| No. | $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{4}\right]$ [eq.] | 3-hexyne [eq.] | $\mathbf{t}[\mathrm{h}]$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | 4 | 48 |
| $\mathbf{2}$ | 1 | 8 | 48 |



Figure 81: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}\left(\mathrm{AlCp}{ }^{*}\right)_{4}\right]$ and 3-hexyne at $60{ }^{\circ} \mathrm{C}$ after two days in toluene-d $\mathrm{d}_{8}$ hexane. Used equivalents are given in Table 27.

Table 28: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Ni}\left(\mathrm{AlCp}{ }^{*}\right)_{4}\right]$ and 3-hexyne at $60^{\circ} \mathrm{C}$ as listed in Table 27. $\mathrm{M} / \mathrm{z}$ values assigned as product peaks are given in bold.

|  | Experimental [m/z] | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster | Fragment |
| :--- | :--- | :--- | :--- | :--- |
| A | 320.1457 | 320.1471 | $\left[\mathrm{NiAl}^{2}\right]\left(\mathrm{Cp}^{*}\right)\left(\right.$ tol $\left.-\mathrm{d}_{8}\right)$ | C-AlCp* |
| B | 382.1310 | 382.1332 | $\left[\mathrm{NiAl}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ | E-2AlCp* |
| C | $\mathbf{4 8 2 . 2 4 3 8}$ | 482.2460 | $\left[\mathrm{NiAl}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\right.$ tol-d $\left._{8}\right)$ |  |
| D | 571.2122 | 571.2136 | $\left[\mathrm{NiAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ | E-Cp* |
| E | $\mathbf{7 0 6 . 3 3 0 3}$ | $\mathbf{7 0 6 . 3 3 1 0}$ | $\left[\mathrm{NiAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(+\mathrm{H})$ |  |
| F | 764.2639 | 764.2664 | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ | G-AlCp* |
|  | $\mathbf{7 6 7 . 2 6 9 6}$ | $\mathbf{7 6 7 . 3 2 3 9}$ | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{2}$ |  |
| G | $\mathbf{9 2 8 . 3 6 7 4}$ | $\mathbf{9 2 8 . 3 8 0 9}$ | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ |  |
| H | $\mathbf{1 4 1 2 . 6 4 3 2}$ | $\mathbf{1 4 1 2 . 6 6 2 0}$ | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{8}\right]\left(\mathrm{Cp}^{*}\right)_{8}$ |  |

## [Ni(AICp*) ${ }^{*}$ ]: Reactions with dpa at $60^{\circ} \mathrm{C}$

Table 29: Overview of $\left[\mathrm{Ni}\left(A / C p^{*}\right)_{4}\right]$ reacted with dpa performed at $60^{\circ} \mathrm{C}$ for 72 hours in toluene-d $\mathrm{d}_{8} /$ hexane. The reaction was conducted with 9 mg of $\left[\mathrm{Ni}\left(A / C p^{*}\right)_{4}\right]$.

| No. | $\left.\left[\mathrm{Ni}^{(A I C p *}\right)_{4}\right][$ eq. $]$ | dpa [eq.] | $\mathbf{t}[\mathrm{h}]$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | $\mathbf{4}$ | 72 |
| $\mathbf{2}$ | 1 | $\mathbf{8}$ | 72 |

$\begin{array}{lllllll}A & \text { C } & \text { D F G }\end{array}$


Figure 82: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}\left(\mathrm{AICp}{ }^{*}\right)_{4}\right]$ and dpa at $60^{\circ} \mathrm{C}$ after three days in toluene-d $/$ hexane. Used equivalents are given in Table 29.

Table 30: Cluster assignment of obtained signals in the reaction [Ni(AICp*) ${ }_{4}$ ] and dpa at $60{ }^{\circ} \mathrm{C}$ as listed in Table 29. M/z values assigned as product peaks are given in bold.

|  | Experimental [m/z] | Calculated [m/z] | Cluster | Fragment |
| :---: | :---: | :---: | :---: | :---: |
| A | 320.1465 | 320.1471 | [ NiAI$](\mathrm{Cp} *)\left(\right.$ tol $\left.-\mathrm{d}_{8}\right)$ | C-AlCp* |
| B | 382.1328 | 382.1332 | [ ]((%5Cleft.%5Cmathrm%7BCp%7D%5E%7B*%7D%5Cright) _{2}\) | E-2AICp* |
| C | 482.2448 | 482.2460 |  |  |
| D | 571.2133 | 571.2136 | $\left[\mathrm{NiAl}_{4}\right](\mathrm{Cp})_{3}$ | E-Cp* |
| E | 706.3300 | 706.3310 | [ $\mathrm{NiAl}_{4}$ ](Cp $\left.{ }^{*}\right)_{4}(+\mathrm{H})$ |  |
| F | 764.2623 | 764.2664 | [ ](Cp*)  ${ }_{4}$ | G-AICp* |
| G | 911.3844 | 911.3908 | [ $\mathrm{NiAl}_{5}$ ] $\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})$ |  |
| H | 1381.1451 | 1381.1830 | $\left[\mathrm{Ni}_{6} \mathrm{Al}_{8}\right]\left(\mathrm{Cp}{ }^{*}\right)_{6}+3 \mathrm{H}$ |  |

## $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$ : Reactions with dpa and/or $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]$ at $60{ }^{\circ} \mathrm{C}$

General procedure: [ $\left.\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$ was dissolved in the respective solvent and a mixture consisting of either dpa and $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ or only dpa was added. The reaction mixtures were stirred at the mentioned temperatures.

Table 31: Overview of $\left[\mathrm{Ni}(\mathrm{AlCp})_{3}(H)\left(\mathrm{SiEt}_{3}\right)\right]$ reacted with dpa performed at $60{ }^{\circ} \mathrm{C}$ for several hours in cyclohexane. The reaction was conducted with 7 mg of $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$.

| No. | $\left[\mathrm{Ni}_{\left.\left(\mathrm{AlCp}^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right] \text { [eq.] }}\right.$ | dpa [eq.] | [Ni(cod) ${ }_{2}$ [eq.] | $\mathbf{t}[\mathrm{h}]$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | 1.3 | 1 | 24 |
| 2 | 1 | 2 | 1 | 24 |
| $\mathbf{3}$ | 1 | 4 | 1 | 6 |
| $\mathbf{4}$ | 1 | 1.3 | - | 24 |
| $\mathbf{5}$ | 1 | 4 | - | 6 |
| $\mathbf{6}$ | 1 | - | 1 | 6 |
| 7 | 1 | - |  | 6 |



Figure 83: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}\left(\mathrm{AlCp}{ }^{*}\right)_{3}(\mathrm{H})\left(\operatorname{SiEt}_{3}\right)\right]$ and dpa and/or $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ at $60{ }^{\circ} \mathrm{C}$ after several hours in cyclohexane. Used equivalents are given in Table 31.

Table 32: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Ni}\left(\mathrm{AlCp}{ }^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$ and dpa and/or $\left[\mathrm{Ni}(\mathrm{Cod})_{2}\right]$ at $60{ }^{\circ} \mathrm{C}$ as listed in Table 31. M/z values assigned as product peaks are given in bold.

|  | Experimental $[\mathrm{m} / \mathrm{z}]$ | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster | Fragment | Obtained in |
| :--- | :--- | :--- | :--- | :--- | :---: |
| A | 382.1327 | 382.1332 | $\left[\mathrm{NiAl}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ | D-2AICp* | $1-7$ |
| B | 544.2309 | 544.2321 | $\left[\mathrm{NiAl}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ | D-AlCp* | $1-3,5-7$ |


| C | 576.1889 | 576.1908 | $\left[\mathrm{NiAl}^{2}\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{2}\right.$ |  | $1-3,5$ |
| :--- | :--- | :--- | :--- | :--- | :---: |
| D | $\mathbf{7 0 7 . 3 3 0 0}$ | $\mathbf{7 0 7 . 3 3 8 8}$ | $\left[\mathrm{NiAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}+\mathrm{H}$ |  | $\mathbf{1 , 2 , 4}$ |
| E | 764.2627 | 764.2664 | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ | G-dpa | $1-3,5-7$ |
| F | 782.2755 | 782.2614 | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})(+2 \mathrm{H})$ | $\mathrm{H}-\mathrm{dpa} / \mathrm{G}-\mathrm{AlCp}{ }^{*}$ | 1,2 |
| G | $\mathbf{9 4 2 . 3 4 3 0}$ | $\mathbf{9 4 2 . 3 4 4 6}$ | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})$ |  | $\mathbf{1 , 2}$ |
| H | $\mathbf{9 5 8 . 3 2 1 3}$ | $\mathbf{9 5 8 . 3 2 3 9}$ | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}$ | $\mathbf{1 , 2}$ |  |
| J | $\mathbf{1 0 2 8 . 2 4 8 8}$ | $\mathbf{1 0 2 8 . 2 4 9 1}$ | $\left[\mathrm{Ni}_{3} \mathrm{Al}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})-\mathrm{H}$ |  | $\mathbf{1 , 2}$ |

## $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{7}\right]$ : Reaction with $\mathrm{AlCp}{ }^{*}$ and dpa at $60^{\circ} \mathrm{C}$

General procedure: [ $\mathrm{Ni}_{4}\left(\mathrm{CN}^{*} \mathrm{Bu}\right)$ ]], $A / C p^{*}$ and dpa were provided in the reaction vessel as solid in a glovebox and the respective solvent was added via a syringe. The reactions were stirred at the mentioned temperatures.

Table 33: Overview of $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{7}\right]$ reacted with dpa and $\mathrm{AlCp} *$ performed at $60{ }^{\circ} \mathrm{C}$ for several hours in hexane. The reaction was conducted with 4-10 mg of $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{7}\right]$.

| No. | $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{7}\right]$ [eq.] | dpa [eq.] | AlCp* [eq.] | $\mathbf{t}[\mathrm{h}]$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | 4 | 4 | 6 |
| $\mathbf{2}$ | 1 | 8 | 4 | 7 |
| $\mathbf{3}$ | 1 | 8 | 8 | 7 |



Figure 84: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}_{4}\left(C N^{*} B u\right)_{7}\right]$, dpa and $A I C p^{*}$ at $60^{\circ} \mathrm{C}$ after several hours in hexane. Used equivalents are given in

Table 34: Cluster assignment of obtained signals in the reaction [ $\left.\mathrm{Ni}_{4}\left(\mathrm{CN}^{*} \mathrm{Bu}\right)_{7}\right]$, dpa and $\mathrm{AlCp}{ }^{*}$ at $60{ }^{\circ} \mathrm{C}$ as listed in Table 33. $\mathrm{M} / \mathrm{z}$ values assigned as product peaks are given in bold.

|  | Experimental [m/z] | Calculated [m/z] | Cluster | Fragment | Obtained in |
| :---: | :---: | :---: | :---: | :---: | :---: |
| A | 576.1883 | 576.1908 | [ NiAl$](\mathrm{Cp} *)(\mathrm{dpa})_{2}$ | B-CNtBu | 1-3 |
| B | 659.2620 | 659.2643 | [ NiAlI ] $\left(\mathrm{Cp}{ }^{*}\right)(\mathrm{CNtBu})(\mathrm{dpa})_{2}$ |  | 1-3 |
| C | 689.2869 | 689.2890 | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{3}$ | G-dpa | 1,3 |
| D | 768.3134 | 768.3144 | [ $\left.\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{2}$ |  | 1,3 |
| E | 786.3038 | 786.3094 | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{2}(\mathrm{dpa})+2 \mathrm{H}$ | G-CNtBu | 1-3 |
| F | 832.2940 | 832.2933 | $\left[\mathrm{Ni}_{3} \mathrm{Al}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{4}$ | J-dpa | 1 |
| G | 867.3619 | 867.3673 | [ $\left.\mathrm{Ni}_{2} \mathrm{Al}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{CN}^{+\mathrm{Bu}}\right)_{3}(\mathrm{dpa})$ |  | 1, 3 |
| H | 911.3143 | 911.3187 | $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{\text {tBu}}\right)_{3}$ |  | 1,3 |
| J | 1010.3707 | 1010.3716 | [ $\left.\mathrm{Ni}_{3} \mathrm{Al}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{CN}^{+B u}\right)_{4}(\mathrm{dpa})$ |  | 1 |
| K | 1129.5172 | 1129.5268 | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{2}\right](\mathrm{Cp})_{2} \mathbf{2}^{\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{2}(\mathrm{dpa})_{2}+\mathrm{H}}$ |  | 3 |
| L | 1230.4028 | 1230.4058 | $\left[\mathrm{Ni}_{4} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{4}(\mathrm{dpa})$ |  | 1 |

## [ $\mathrm{Ni}(\operatorname{cod})_{2}$ ]: Reaction with $\mathrm{CN}^{+} \mathrm{Bu}$, dpa and $\mathrm{AICp}^{*}$ at $60^{\circ} \mathrm{C}$

General procedure: [Ni(cod)2] was dissolved in the respective solvent and CNtBu was added as a 1 M solution in toluene/hexane via a syringe. Following, either AICp* or dpa was added first as mentioned at the respective chapters. The reactions were stirred at the mentioned temperatures.

Table 35: Overview of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ reacted with $\mathrm{CN}^{t} \mathrm{Bu}$, dpa and $\mathrm{AlCp}{ }^{*}$ performed at $60^{\circ} \mathrm{C}$ for 7 hours in hexane. The reaction was conducted with 11 mg of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$. Reaction 1 and 2 only differs in the order of the addition of the reagents. Addition order: 1: [Ni(cod) $)_{2}$, CNtBu, dpa, AlCp*; 2: [Ni(cod) $)_{2}$ ], CN*Bu, AICp*, dpa.

| No. | $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]$ [eq.] | CN $^{+}$Bu [eq.] | dpa [eq.] | AlCp* [eq.] |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | 1 | 1 | 1 |
| 2 | 1 | 1 | 1 | 1 |



Figure 85: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ with $\mathrm{CN}^{t} \mathrm{Bu}$, dpa and $\mathrm{AlCp}^{*}$ performed at $60^{\circ} \mathrm{C}$ after 7 hours in hexane. Used equivalents are given in Table 35.

Table 36: Cluster assignment of obtained signals in the reaction [Ni(cod) $)_{2}$ with $\mathrm{CN}^{\star} \mathrm{Bu}$, dpa and $\mathrm{AlCp}{ }^{*}$ performed at $60{ }^{\circ} \mathrm{C}$ for 7 hours in hexane as listed in Table 35. M/z values assigned as product peaks are given in bold.

|  | Experimental $[\mathrm{m} / \mathrm{z}]$ | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster | Fragment |
| :--- | :--- | :--- | :--- | :--- |
| A | 576.1890 | 576.1908 | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{2}$ | B-CNtBu |
| B | 659.2641 | 659.2643 | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{CNtBu})(\mathrm{dpa})_{2}$ |  |
| C | 768.3147 | 768.3144 | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{2}$ |  |
| D | 911.3186 | 911.3187 | $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{3}$ |  |
| E | $\mathbf{1 1 2 9 . 5 2 6 8}$ | 1129.5268 | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{2}(\mathrm{dpa})_{2}+\mathrm{H}$ |  |
| F | $\mathbf{1 2 3 0 . 4 0 4 3}$ | 1230.4058 | $\left[\mathrm{Ni}_{4} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{4}(\mathrm{dpa})$ |  |

## [NiAl](Cp*)(tebd)(cod): Reactivity tests with 3-hexyne or dpa

General procedure reactivity tests: $[\mathrm{NiAA}]\left(\mathrm{CD}^{*}\right)($ tebd $)(\mathrm{cod})$ was dissolved in the respective solvent and either 3-hexyne/GaCp*/PEt ${ }_{3}$ was added as a 1 M solution in toluene/hexane via a syringe or $d p a / A I C p^{*} / P P h_{3}$ as a solid using a glovebox. The reactions were stirred at the mentioned temperatures.

Table 37: Overview of the reactivity test of [NiAl](Cp*)(tebd)(cod) with different alkynes at different equivalents and temperatures in toluene or hexane for one day. The reaction was conducted with $5-25 \mathrm{mg}$ of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(t e b d)(c o d)$.

| No. | [NiAl](Cp*)(tebd)(cod) [eq.] | 3-hexyne [eq.] | $\mathrm{T}\left[{ }^{\circ} \mathrm{C}\right]$ |
| :---: | :---: | :---: | :---: |
| 1 | 1 | 8 | 90 |
|  |  |  |  |
| No. | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd)(cod) [eq.] | dpa [eq.] | $\mathrm{T}\left[{ }^{\circ} \mathrm{C}\right]$ |
| 2 | 1 | 2 | 60 |
| 3 | 1 | 8 | 60 |
| 4 | 1 | 2 | 90 |



Figure 86: LIFDI mass spectra of the reaction [NiAl](Cp*)(tebd)(cod) with different alkynes as listed in Table 37.

Table 38: Cluster assignment of obtained signals in the reaction [NiAl](Cp*)(tebd)(cod) with different alkynes as listed in Table 37.

|  | Experimental [m/z] | Calculated [m/z] | Cluster |
| :--- | :--- | :--- | :--- |
| A | 312.0948 | 312.0969 | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tol $)$ |
| B | 416.1054 | 416.1075 | $[\mathrm{Ni})(\mathrm{dpa})_{2}+2 \mathrm{H}$ |
| C | 466.2682 | 466.2690 | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{hex})$ |
| D | 492.2852 | 492.2847 | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tebd})(\mathrm{cod})$ |
| E | 550.2142 | 550.2170 | $[\mathrm{Ni]}]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{2}+\mathrm{H}$ |
| F | 562.2667 | 562.2690 | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tebd})(\mathrm{dpa})$ |

## [NiAl](Cp*)(tebd)(cod): Reactivity tests with GaCp*

Table 39: Overview of the reactivity test of [NiAl](Cp*)(tebd)(cod) with GaCp* at different equivalents and temperatures in toluene or hexane for one day. The reaction was conducted with 10 mg of [NiAl](Cp*)(tebd)(cod).

| No. | [NiAl](Cp*)(tebd)(cod) [eq.] | GaCp* [eq.] | T [ ${ }^{\circ} \mathrm{C}$ ] |
| :---: | :---: | :---: | :---: |
| 1 | 1 | 2 | 20 |
| 2 | 1 | 1 | 60 |
| 3 | 1 | 2 | 60 |
| 4 | 1 | 8 | 60 |
| 5 | 1 | 2 | 90 |



Figure 87: LIFDI mass spectra of the reaction [NiAl](Cp*)(tebd)(cod) with $\mathrm{GaCp}^{*}$ as listed in Table 39.

Table 40: Cluster assignment of obtained signals in the reaction [NiAl](Cp*)(tebd)(cod) with GaCp* as listed in Table 39.

|  | Experimental [m/z] | Calculated [m/z] | Cluster | Fragment |
| :--- | :--- | :--- | :--- | :--- |
| A | 312.0951 | 312.0969 | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tol $)$ |  |
| B | 384.1900 | 384.1908 | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)$ | C-cod |
| C | 492.2852 | 492.2847 | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})$ |  |

## [ NiAI$]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod}):$ Reactivity tests with $\mathrm{AlCp}^{*}$

Table 41: Overview of the reactivity test of $\left[\mathrm{NiAl]}\left(\mathrm{Cp}^{*}\right)(t e b d)(c o d)\right.$ with $A I C p^{*}$ at different equivalents in toluene or hexane for one day. The reaction was conducted with 10 mg of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(t e b d)(c o d)$.

| No. | [NiAl](Cp*)(tebd)(cod) [eq.] | AlCp* [eq.] | $\mathrm{T}\left[{ }^{\circ} \mathrm{C}\right]$ | Solvent |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 1 | 1 | 60 | Hexane |
| 2 | 1 | 2 | 60 | Hexane |
| 3 | 1 | 2 | 60 | toluene |



Figure 88: LIFDI mass spectra of the reaction $[\mathrm{NiAI}]\left(\mathrm{Cp}^{*}\right)(t e b d)(c o d)$ with $A I C p^{*}$ as listed in Table 41.

Table 42: Cluster assignment of obtained signals in the reaction [NiAl](Cp*)(tebd)(cod) with AICp* as listed in Table 41.

|  | Experimental [m/z] | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster | Fragment |
| :--- | :--- | :--- | :--- | :--- |
| A | 382.1325 | 382.1332 | $\left[\mathrm{NiAl}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ | D-2AICp* |
| B | 492.2828 | 492.2847 | $\left[\mathrm{NiAl}^{*}\right]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})$ |  |
| C | $\mathbf{6 9 9 . 2 9 5 7}$ |  | $\left[\mathrm{Ni}_{1}\right]-$ species |  |
| D | $\mathbf{7 0 6 . 3 2 9 5}$ | $\mathbf{7 0 6 . 3 3 1 0}$ | $\left[\mathrm{NiAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(+\mathrm{H})$ |  |

## [ NiAl$]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod}):$ Reactivity tests with $\mathrm{PPh}_{3}$

Table 43: Overview of the reactivity test of $[\mathrm{NiAl}]\left(C p^{*}\right)(t e b d)(c o d)$ with $P P h_{3}$ at different equivalents and temperatures in toluene or hexane for one day. The reaction was conducted with 10 mg of [NiAI](Cp*)(tebd)(cod).

| No. | $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd (cod) [eq.] | PPh $_{3}$ [eq.] | $\mathrm{T}\left[{ }^{\circ} \mathrm{C}\right]$ |
| :---: | :---: | :---: | :---: |
| 1 | 1 | 2 | 60 |
| 2 | 1 | 4 | 60 |
| 3 | 1 | 2 | 90 |



Figure 89: LIFDI mass spectra of the reaction [NiAl](Cp*)(tebd)(cod) with $P P h_{3}$ as listed in Table 43.

Table 44: Cluster assignment of obtained signals in the reaction [ NiAl$]\left(C p^{*}\right)(t e b d)(c o d)$ with $P P h_{3}$ as listed in Table 43. The assignment of $E$ and $F$ have to be considered carefully.

|  | Experimental [m/z] | Calculated [m/z] | Cluster | Fragment |
| :---: | :---: | :---: | :---: | :---: |
| A | 277.0759 | 277.0628 | $\left.\left[\mathrm{Ni}_{2} \mathrm{Al}_{2}\right]^{(h e x}\right)_{2}+\mathrm{H}$ |  |
| B | 384.1892 | 384.1908 | [ NiAl$]\left(\mathrm{Cp}{ }^{*}\right.$ )(tebd) | C-cod |
| C | 492.2847 | 492.2847 | [ NiAl$](\mathrm{Cp} *)($ tebd)(cod) |  |
| D | 744.2080 | 744.2165 | [ NiAl$]\left(\mathrm{Cp}{ }^{*}\right)\left(\mathrm{PPh}_{3}\right)_{2}$ |  |
| E | 776.1922 | 776.1924 | [ $\mathrm{NiAl}_{5}$ ] $\left(\mathrm{Cp}^{*}\right)\left(\mathrm{PPh}_{3}\right)(\mathrm{tol})_{2}+2 \mathrm{H}$ |  |
| F | 1028.3756 | 1028.3383 | [ $\mathrm{NiAl}_{6}$ ] $\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{PPh}_{3}\right)(\text { tol })_{3}$ |  |
|  |  | 1028.3721 | $\left[\mathrm{Ni}_{2} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}{ }^{*}\right)_{4}\left(\mathrm{PPh}_{3}\right]$ |  |

### 6.3.3. Additional data for Pd-Ga compounds

$\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ : Reaction with GaCp* (and dpa) at $-30^{\circ} \mathrm{C}$
General procedure: $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ was dissolved at $-30^{\circ} \mathrm{C}$ in the respective solvent. GaCp* was added as a 1 M solution in toluene/hexane via a syringe and additionally where mentioned, dpa as a solid. The reactions were stirred at the mentioned temperatures.

Table 45 : Overview of the reactivity test of $\left[\mathrm{Pd}_{2}(d v d s)_{3}\right]$ with GaCp * (and dpa) at $-30{ }^{\circ} \mathrm{C}$ in toluene for two days. The reaction was conducted with 7.5 mg of $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$.

| No. | $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ | GaCp $^{*}$ [eq.] | Dpa [eq.] | $\mathrm{T}\left[{ }^{\circ} \mathrm{C}\right]$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | 2 | - | $-30^{\circ} \mathrm{C}-$ r.t. |
| 2 | 1 | 2 | 2 | $-30^{\circ} \mathrm{C}-$ r.t. |



Figure 90: LIFDI mass spectra of the reaction $\left[\mathrm{Pd}_{2}(d v d s)_{3}\right]$ with $\mathrm{GaCp} / / a n d$ dpa at $-30^{\circ} \mathrm{C}$. Reactions 1 and 2 as listed in Table 45.

Table 46: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Pd}_{2}(d v d s)_{3}\right]$ with $\mathrm{GaCp} * / a n d$ dpa at $-30{ }^{\circ} \mathrm{C}$ as listed in Table 45.

|  | Experimental $[\mathrm{m} / \mathrm{z}]$ | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster | Fragment |
| :--- | :--- | :--- | :--- | :--- |
| A | 1076.8779 | 1076.9555 | $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})+2 \mathrm{H}$ |  |
| B | 1162.8902 | 1162.8913 | $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dvds})(\mathrm{dpa})$ |  |
| C | 1190.8568 | 1190.8558 | $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dvds})$ |  |
| D | 1406.7764 | 1406.7757 | $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{tol})$ |  |
| E | 1500.8030 | 1500.8039 | $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dvds})$ |  |

## $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ : Reaction with $\mathrm{GaCp}^{*}$ (and dpa) at $60^{\circ} \mathrm{C}$

Table 47 : Overview of the reactivity test of $\left[\mathrm{Pd}_{2}(d v d s)_{3}\right]$ with $\mathrm{GaCp}^{*}$ (and dpa) at $60^{\circ} \mathrm{C}$ in toluene for one day. The reaction was conducted with 7.5 mg of $\left[\mathrm{Pd}_{2}(d v d s)_{3}\right]$.

| No. | $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ | GaCp* $^{2}$ [eq.] | Dpa [eq.] | $\mathrm{T}\left[{ }^{\circ} \mathrm{C}\right]$ |
| :---: | :---: | :---: | :---: | :---: |
| 3 | 1 | 2 | - | 60 |
| 4 | 1 | 2 | 2 | 60 |



Figure 91: LIFDI mass spectra of the reaction $\left[\mathrm{Pd}_{2}(d v d s)_{3}\right]$ with $\mathrm{GaCp} * / a n d$ dpa at $60{ }^{\circ} \mathrm{C}$. Reactions 3 and 4 as listed in Table 47.

Table 48: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ with $\mathrm{GaCp}{ }^{*} / a n d$ dpa at $60^{\circ} \mathrm{C}$ as listed in Table 47.

|  | Experimental [m/z] | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster | Fragment |
| :--- | :--- | :--- | :--- | :--- |
| A | 1102.9068 | 1102.9040 | $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ |  |
| B | 1190.8536 | 1190.8558 | $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dvds})$ |  |
| C | 1406.7745 | 1406.7757 | $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{tol})$ |  |
| D | 1500.8021 | 1500.8039 | $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dvds})$ |  |

## $\left[\mathrm{Pd}\left(\mathrm{GaCp}{ }^{*}\right)_{4}\right]$ : Reaction with dpa at $60^{\circ} \mathrm{C}$

General procedure: $\left[\mathrm{Pd}\left((\mathrm{GaCp})_{4}\right]_{4}\right.$ was dissolved in the respective solvent and dpa was added as a solid using a glovebox. The reaction was stirred at the mentioned temperature.


Figure 92: LIFDI mass spectrum of the reaction $\left[\mathrm{Pd}(\mathrm{GaCp})_{4}\right]$ with 2 eq . dpa at $60^{\circ} \mathrm{C}$ after five hours in toluene showing the selective formation of $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(C p^{*}\right)_{5}$ indicated by the fragment peak at $1102 \mathrm{~m} / \mathrm{z}$.

### 6.3.4. Additional data for Pt-E compounds

## $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right]$ : Reaction with GaCp* and dpa at different temperatures

General procedure 3-hexyne: [Pt(cod $)_{2}$ ] was dissolved in the respective solvent and 3-hexyne was added as 0.5 m solution in toluene via a syringe using a glovebox. Subsequently, GaCp* was added as 0.5 m solution in toluene via a syringe, too. The reaction was stirred at the mentioned temperature.

General procedure dpa: $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ was dissolved in the respective solvent and dpa was added solid in a glovebox. Subsequently, GaCp* was added as 0.5 M solution in toluene via a syringe, too. The reaction was stirred at the mentioned temperature.

Table 49: Overview of the reactivity tests of $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ with GaCp * and dpa at different temperatures in toluene. The reaction was conducted with 4.0 mg of $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$.

| No. | $\left[P t(c o d)_{2}\right]$ | GaCp* [eq.] | Dpa [eq.] | $\mathrm{T}\left[{ }^{\circ} \mathrm{C}\right]$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | 1 | $\mathbf{1}$ | RT |
| $\mathbf{2}$ | 1 | 1 | $\mathbf{4}$ | RT |
| $\mathbf{3}$ | 1 | 1 | 4 | $60^{\circ} \mathrm{C}$ |
| $\mathbf{4}$ | 1 | 1 | 4 | $90^{\circ} \mathrm{C}$ |



Figure 93: LIFDI mass spectra of the reaction [Pt(cod) $)_{2}$ (1 eq.), GaCp* (1 eq.) and dpa ( $\Delta$ eq.) at different temperatures in toluene as listed in Table 49. The spectra were recorded after two hours if not otherwise stated.

Table 50: Cluster assignment of obtained signals in the reaction [Pt(cod) ${ }_{2}$ ] (1 eq.), GaCp* (1 eq.) and dpa ( $\Delta$ eq.) at different temperatures in toluene as listed in Table 49. M/z values assigned as product peaks are given in bold.

|  | Experimental $[\mathrm{m} / \mathrm{z}]$ | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster |
| :--- | :--- | :--- | :--- |
| A | 1032.2493 |  | Not identified yet |
| B | 1253.0570 | 1253.0616 | $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})$ |

$\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ : Reaction with AICp * and dpa at different temperatures
General procedure; [Pt(cod)2], A/Cp* and dpa were dissolved in 0.5 mL toluene and stirred at the mentioned temperature.

Table 51: Overview of the reactivity tests of $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ with $A I C p^{*}$ and dpa at different temperatures in toluene. The reaction was conducted with 4.0 mg of $\left[\mathrm{Pt}(\mathrm{COd})_{2}\right]$.

| No. | $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right]$ | AlCp* [eq.] | Dpa [eq.] | $\mathrm{T}\left[{ }^{\circ} \mathrm{C}\right]$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1 | 1 | $\mathbf{0 . 5}$ | $60^{\circ} \mathrm{C}$ |
| $\mathbf{2}$ | 1 | 1 | $\mathbf{1}$ | $60^{\circ} \mathrm{C}$ |
| $\mathbf{3}$ | 1 | 1 | $\mathbf{4}$ | $60^{\circ} \mathrm{C}$ |
| $\mathbf{4}$ | 1 | $\mathbf{4}$ | 4 | $60^{\circ} \mathrm{C}$ |
| $\mathbf{5}$ | 1 | 1 | $\mathbf{4}$ | $90^{\circ} \mathrm{C}$ |



Figure 94: LIFDI mass spectra of the reaction [Pt(cod) ${ }_{2}$ ] (1 eq.), AICp* ( $\Delta$ eq.) and dpa ( $\Delta$ eq.) at different temperatures in toluene as listed in Table 51. The spectra were recorded after two hours.

Table 52: Cluster assignment of obtained signals in the reaction [Pt(cod) ${ }_{2}$ ] (1 eq.), AlCp* ( $\Delta$ eq.) and dpa ( $\Delta$ eq.) at different temperatures in toluene as listed in Table 51. M/z values assigned as product peaks are given in bold.

|  | Experimental [m/z] | Calculated [m/z] | Cluster | Fragment |
| :--- | :--- | :--- | :--- | :--- |
| A | 546.1422 | 546.1441 | $\left[\mathrm{PtAl}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{2}$ | D-Al-2Cp* |
| B | 682.2664 | 682.2697 | $\left[\mathrm{PtAl}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}+\mathrm{H}$ | D-AlCp* |
| C | 713.2145 | 713.2202 | $\left[\mathrm{PtAl}^{*}\right]\left(\mathrm{Cp}^{*}\right)(\mathrm{dpa})_{2}$ | E-dpa |
| D | $\mathbf{8 4 4 . 3 6 2 3}$ | $\mathbf{8 4 4 . 3 6 8 6}$ | $\left[\mathrm{PtAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{\mathbf{4}+\mathrm{H}}$ |  |
| E | $\mathbf{8 9 1 . 2 9 5 2}$ | $\mathbf{8 9 1 . 2 9 8 9}$ | $\left[{\mathrm{PtAl}](\mathrm{Cp*})(\mathrm{dpa})_{\mathbf{3}}}\right.$ |  |
| F $^{*}$ | 1048.4085 | 1048.4207 | $\left[\mathrm{PtAl}_{5}\right](\mathrm{Cp*})_{4}(\mathrm{dpa})$ |  |

*Signal F could not be assigned with high certainty as it would require unusual bonding on the transition metal

### 6.3.5. Additional data for TM-Zn compounds

## $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ : Reaction with $\mathrm{ZnMe}_{2}$ (and 3-hexyne)

General procedure; [ $\left.\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ ( $24 \mathrm{mg}, 0.027 \mathrm{mmol}, 1.0$ eq.) was dissolved in 1 mL toluene. $\mathrm{ZnMe}_{2}$ was added as a 1 m solution in toluene at $-30^{\circ} \mathrm{C}$. The mixture was allowed to reach the respective temperature and stirred for a certain time. Afterwards, all volatiles were removed and the residue was dissolved in toluene for MS analysis.

The obtained NiGaZn library was dissolved in toluene and 3-hexyne was added as a 1 m solution in toluene. The mixture was stirred at the respective temperature.


Figure 95: LIFDI mass spectra of the reaction [ $\left.\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right](75 \mathrm{mg})$ with 2 eq . $\mathrm{ZnMe} \mathrm{e}_{2}(0.17 \mathrm{~mL}, 1 \mathrm{~m}$ in toluene) after two hours at $0^{\circ} \mathrm{C}$ (black trace). The obtained NiGaZn library (1) was further reacted with 4 eq. 3-hexyne for 1.5 hours (red trace) or 18 hours (blue trace) at $60^{\circ} \mathrm{C}$. Peak assignment is given below.

Table 53: Peak assignment of the reactions as depicted in Figure 95.

|  | Experimental [m/z] | Calculated [m/z] | Cluster |
| :---: | :---: | :---: | :---: |
| A | 818.68 | 818.94 | 952-Cp* |
| B | 877.68 | 878.10 | [ $\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}$ ] |
| C | 894.54 | 894.89 | 1029-Cp* |
| D | 953.56 | 954.06 | [ $\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{3}(\mathrm{ZnCp} *)(\mathrm{ZnMe})$ ] |
| E | 970.38 | 970.85 | 1102-Cp* |
| F | 1029.44 | 1030.01 | [ $\left.\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{ZnCp}^{*}\right)_{2}(\mathrm{ZnMe})_{2}\right]$ |
| G | 1105.32 | 1105.96 | [ $\left.\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)(\mathrm{ZnCp})_{3}(\mathrm{ZnMe})_{3}\right]$ |
| H | 1183.17 | 1181.93 | [ $\left.\mathrm{Ni}(\mathrm{ZnCp})_{4}(\mathrm{ZnMe})_{4}\right]$ |

## [ $\left.\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ : Reaction of 1 with $\mathrm{ZnMe}_{2}$

General procedure: 1 was synthesized from [ $\left.\mathrm{Ni}\left(\mathrm{cod}_{2}\right]_{2}\right](8.0 \mathrm{mg}, 0.029 \mathrm{mmol}, 1.0 \mathrm{eq}),$.GaCp * ( $0.03 \mathrm{mmol}, 1.0 \mathrm{eq}$.) and 3 -hexyne ( $0.03 \mathrm{mmol}, 1.0 \mathrm{eq}$.) in 0.8 mL toluene as previously mentioned. After four hours at room temperature, 0.4 mL toluene and $\mathrm{ZnMe}_{2}(0.29 \mathrm{mmol}, 10.0$ eq.) were added, as a 1 M solution in toluene. The reaction was stirred for one day at room temperature.

LIFDI mass spectra have already been displayed in Figure 61 in the main part of this thesis.

## [ $\left.\mathrm{Ni}(\operatorname{cod})_{2}\right]$ : Reaction with $\left[\mathrm{Zn}_{2} \mathrm{Cp}^{\star}{ }_{2}\right]$ and alkynes

General procedure-3-hexyne: [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right]$ and $\left[\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}\right]$ were dissolved in toluene and 3-hexyne was added as 1 m solution in toluene via a syringe using a glovebox. The reaction was stirred at the mentioned temperature.

General procedure- dpa: [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right]$, dpa and $\left[\mathrm{Zn}_{2} \mathrm{Cp}^{*}\right.$ ] $]$ were dissolved in toluene and stirred at the mentioned temperature.

Table 54: Overview of the reaction of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ with $\mathrm{Zn}_{2} \mathrm{Cp}^{*}$ and 3-hexyne (dpa) with different equivalents and at different temperatures in 1.5 mL toluene. The reaction was conducted with 5.5 mg of [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ].

| No. | [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ] | $\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ [eq.] | 3-hexyne [eq.] | $\mathrm{T}\left[{ }^{\circ} \mathrm{C}\right]$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 1 | 1 | 1 | 60 |
| 2 | 1 | 1 | 1 | 90 |
| 3 | 1 | 2 | 1 | 90 |
| 4 | 1 | 2 | 2 | 90 |
| No. | [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ] | $\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ [eq.] | dpa [eq.] | $\mathrm{T}\left[{ }^{\circ} \mathrm{C}\right]$ |
| 5 | 1 | 1 | 1 | 90 |



Figure 96: LIFDI mass spectra of the reaction [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right], Z n_{2} \mathrm{Cp}^{*}{ }_{2}$ and 3-hexyne with different equivalents and at different temperatures in toluene after 5.5 hours. The exact conditions are specified in Table 54.

Table 55: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and 3 -hexyne with different equivalents and at different temperatures in toluene after 5.5 hours as listed in Table 54.

|  | Experimental $[\mathrm{m} / \mathrm{z}]$ | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster |
| :--- | :--- | :--- | :--- |
| A | 328.1702 | 328.1702 | $[\mathrm{Ni}]\left(\mathrm{Cp}^{*}\right)_{2}$ |
| B | 468.1830 | 468.1834 | $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}($ hex $)$ |
| C | 735.1517 | 735.1532 | $\left[\mathrm{Ni}_{2} \mathrm{Zn}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{3}($ hex $)$ |



Figure 97: LIFDI mass spectrum of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and dpa in toluene after one hour. The exact conditions are specified in Table 54.

Table 56: Cluster assignment of obtained signals in the reaction [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and dpa in toluene after one hour as listed in Table 54

|  | Experimental $[\mathrm{m} / \mathrm{z}]$ | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster |
| :--- | :--- | :--- | :--- |
| A | 371.1288 | 371.1309 | $[\mathrm{Ni}]\left(\mathrm{Cp}{ }^{*}\right)(\mathrm{dpa})$ |
| B | 564.1820 | 564.1837 | $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})$ |
| C | 831.1502 | 831.1532 | $\left[\mathrm{Ni}_{2} \mathrm{Zn}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})$ |

## [ $\left.\mathrm{Pt}(\mathrm{cod})_{2}\right]$ : Reaction with $\left[\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}\right]$ and dpa

General procedure: $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right](4.1 \mathrm{mg}, 0.010 \mathrm{mmol}, 1.0 \mathrm{eq}$.) and dpa ( $2.0 \mathrm{mg}, 0.011 \mathrm{mmol}, 1.1 \mathrm{eq}$.) were dissolved in 1 mL toluene. $\left[\mathrm{Zn}_{2} \mathrm{Cp}^{*}\right.$ ] ( $4.0 \mathrm{mg}, 0.010 \mathrm{mmol}, 1.0 \mathrm{eq}$.) was added and the mixture was stirred for several hours at the mentioned temperature.

LIFDI mass spectra have already been displayed in Figure 63 in the main part of this thesis.

## Experimental

### 6.3.6. Experimental for semi-hydrogenation experiments

$\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ (1): 1 was synthesized from $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]$ ( $55 \mathrm{mg}, 0.200 \mathrm{mmol}, 1.0 \mathrm{eq}$.), 3-hexyne ( $0.200 \mathrm{mmol}, 1.0 \mathrm{eq}$.) and GaCp* ( $0.200 \mathrm{mmol}, 1.0$ eq.) in toluene ( 2 mL ) as mentioned above. 3-hexyne and GaCp* were added as a 1 m solution in toluene. After 3.5 hours at room temperature, the mixture was shortly exposed to vacuo. The oily residue was resolved in 2 mL toluene- $\mathrm{d}_{8}$ and divided in four equal parts. The provided NMR tubes were used for different reactions: (A) reference, (B) pressurized with 1 bar $\mathrm{H}_{2}$, (C) pressurized with 1 bar $\mathrm{H}_{2}$ and addition of one drop 3-hexyne, and (D) pressurized with 1 bar $\mathrm{H}_{2}$ and addition of 0.05 mmol Cyclohexane as internal standard. The mixture was reacted at room temperature.
$\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}:\left[\mathrm{Ni}(\mathrm{cod})_{2}\right](35.6 \mathrm{mg}, 0.129 \mathrm{mmol}, 1.9$ eq. $)$ and dpa ( $12.7 \mathrm{mg}, 0.071 \mathrm{mmol}$, 1.0 eq.) was provided in a 3 mL vial. Subsequently, GaCp* ( $0.13 \mathrm{~mL}, 0.13 \mathrm{mmol}, 1.9 \mathrm{eq}$.) as a 1 m solution in toluene- $d_{8}$ and 0.87 mL toluene- $\mathrm{d}_{8}$ were added. The mixture was reacted for one day at room temperature. Afterwards, the mixture was divided in two parts (reference, reaction mixture) and the reaction mixture was pressurized with 1 bar $\mathrm{H}_{2}$ to vacuo. The mixture was reacted at room temperature.
$\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})_{1}:\left[\mathrm{Ni}(\mathrm{cod})_{2}\right](35.5 \mathrm{mg}, 0.129 \mathrm{mmol}, 1.9 \mathrm{eq}$.$) and dpa ( 12.7 \mathrm{mg}, 0.071 \mathrm{mmol}$, 1.0 eq.) was provided in a 3 mL vial. Subsequently, GaCp* ( $0.13 \mathrm{~mL}, 0.13 \mathrm{mmol}, 1.9 \mathrm{eq}$.) as a 1 m solution in toluene- $\mathrm{d}_{8}$ and 0.87 mL toluene- $\mathrm{d}_{8}$ were added. The mixture was reacted for one day at $60^{\circ} \mathrm{C}$. Afterwards, the mixture was divided in two equal parts (reference, reaction mixture) in a NMR tube each and the reaction mixture was pressurized with 1 bar $\mathrm{H}_{2}$ to vacuo. The mixture was reacted at room temperature.
[NiAl](Cp*)(tebd)(cod) (6): 6 was synthesized as described above. The yellow powder $(10.2 \mathrm{mg}, 0.020 \mathrm{mmol}, 1.0 \mathrm{eq})$ was dissolved in 0.34 mL toluene- $\mathrm{d}_{8}$ and 3 -hexyne ( $0.16 \mathrm{~mL}, 0.16 \mathrm{mmol}$, 8.0 eq.) was added as a 1 m solution in toluene- $\mathrm{d}_{8}$. The NMR tube was pressurized with $1 \mathrm{bar} \mathrm{H}_{2}$ on argon atmosphere. The mixture was reacted at room temperature.
[NiAl](Cp*)(tebd)(hex) (7): 7 was synthesized in-situ from 6 ( $4.6 \mathrm{mg}, 0.009 \mathrm{mmol}, 1.0 \mathrm{eq}$ ) and 3-hexyne ( $0.08 \mathrm{~mL}, 0.080 \mathrm{mmol}, 8.9$ eq.) in 0.42 mL toluene- $\mathrm{d}_{8}$ as described above. After six hours at $90^{\circ} \mathrm{C}$, the red mixture was pressurized with 1 bar $\mathrm{H}_{2}$ and reacted at room temperature.

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## 8. Appendix

### 8.1. Supplementary information of the experimental part

### 8.1.1. Appendix for fully analyzed compounds

$\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}(1) .{ }^{140}$
For further information see: P. Heiß, J. Hornung, C. Gemel, R. A. Fischer, Chem. Commun. 2022, 58, 4332-4335.


Figure 98: ${ }^{1} \mathrm{H}$ NMR spectrum of 1 in toluene- $d_{8}$ with assignments of the starting materials as well as side products.


Figure 99: ${ }^{13} \mathrm{C}$ NMR spectrum of 1 (black) in toluene- $d_{8}$ with assignments of the starting materials as well as side products.


Figure 100: ATR IR spectrum of 1 with characteristic band at $1738.5 \mathrm{~cm}^{-1}$ and $1670.2 \mathrm{~cm}^{-1}$ assuming side-on coordinated 3-hexyne.


Figure 101: Comparison of LIFDI mass distribution of 1 measured on either an Exactive Orbitrap System (Thermo Fischer, top) revealing fragmentation or a JEOL AccuTOF instrument where no fragmentation was observed.
[NiAl](Cp*)(tebd)(cod) (6). ${ }^{140}$
For further information see: P. Heiß, J. Hornung, C. Gemel, R. A. Fischer, Chem. Commun. 2022, 58, 4332-4335.


Figure 102: ${ }^{1} \mathrm{H}$ NMR of $[\mathrm{NiAl}]\left(C p^{*}\right)($ tebd $)(\mathrm{cod})(6)$ in toluene- $\mathrm{d}_{8}$.


Figure 103: ${ }^{13} \mathrm{C}$ NMR of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})(6)$ in toluene $-\mathrm{d}_{8}$.


Figure 104: ATR IR spectrum of 6.


Figure 105: UV-vis spectrum of 6 in n-hexane with absorption maxima at 220 nm and 285 nm

## [NiAl](Cp*)(tebd)(hex) (7). ${ }^{140}$

For further information see: P. Heiß, J. Hornung, C. Gemel, R. A. Fischer, Chem. Commun. 2022, 58, 4332-4335.


Figure 106: ${ }^{1} \mathrm{H}$ NMR spectrum of 7 in cyclohexane- $d_{12}$ with signal assignment.


Figure 107: ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{7}$ in cyclohexane- $d_{12}$.


Figure 108: ATR-IR spectrum of 7 with the characteristic band at $1825.0 \mathrm{~cm}^{-1}$ with relates to side-on coordinated 3-hexyne.


Figure 109: UV-vis spectrum of 7 in n-hexane with absorption maxima at 215, 315 and 375 nm .
[NiAl](Cp*)(tpbd)(dpa) (8). ${ }^{140}$
For further information see: P. Heiß, J. Hornung, C. Gemel, R. A. Fischer, Chem. Commun. 2022, 58, 4332-4335.


Figure 110: ${ }^{1} \mathrm{H}$ NMR spectrum of 8 in benzene- $\mathrm{d}_{6}$ with signal assignment.


Figure 111: Enlarged ${ }^{13} \mathrm{C}$ NMR spectrum of 8 in benzene- $d_{6}$ with signal assignment. Orange dots refer to trimerized dpa and green dots are assigned to free dpa.


Figure 112: ATR IR spectrum of 8 with the characteristic band at $1812.2 \mathrm{~cm}^{-1}$ which is assigned to side-on coordinated dpa.


Figure 113: UV-vis spectrum of 8 in n-hexane with absorption maxima at 215, 280 and 330 nm .
$\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{+} \mathrm{Bu}\right)_{4}\left(\mathbf{1 2} \cdot \mathrm{CN}^{+B u}\right)$.


Figure $114:{ }^{1} \mathrm{H}$ NMR spectrum of 12 in toluene- $d_{8}$.


Figure 115: ${ }^{13} \mathrm{C}$ NMR spectrum of 12 in toluene-d 8 . Impurity: 31.3 ppm (free tert-butylisonitrile).


Figure $116:{ }^{1} \mathrm{H}{ }^{13} \mathrm{C}$ HSQC NMR spectrum of 12 in toluene- $\mathrm{d}_{8}$.


Figure 117: ${ }^{1} \mathrm{H} /{ }^{13} \mathrm{C}$ HMBC NMR spectrum of 12 in toluene- $\mathrm{d}_{8}$.

## [PtAl](Cp*)(tpbd)(dpa) (13).



Figure 118: Full range ${ }^{1} \mathrm{H}$ NMR spectrum of 13 in toluene- $d_{8}$. Impurities: dpa (7.45 and 7.01 ppm ), cod (5.54 and 2.21 ppm ) and Cp*H (2.47, 1.72, 1.79 and 0.99 ppm).


Figure 119: ${ }^{\dagger} \mathrm{H}$ NMR spectrum (aromatic range) of 13 in toluene- $\mathrm{d}_{8}$.


Figure 120: Full range ${ }^{13} \mathrm{C}$ NMR spectrum of 13 in toluene-d8. Impurities cod (90.4 and 29.5 ppm ).


Figure 121: ${ }^{1} \mathrm{H}^{\top} \mathrm{H}$ COSY NMR spectrum of 13 in toluene- $\mathrm{d}_{8}$.


Figure 122: ${ }^{1} \mathrm{H} /{ }^{13} \mathrm{C}$ HSQC NMR spectrum of 13 in toluene- $\mathrm{d}_{8}$.


Figure 123: ${ }^{1} \mathrm{H} /{ }^{3} \mathrm{C}$ HMBC NMR spectrum of 13 in toluene- $\mathrm{d}_{8}$.

### 8.1.2. Appendix for further experiments

## Reference LIFDI mass spectrum of $\left[\mathrm{PdGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$



Figure 124: LIFDI mass spectrum of $\left[\mathrm{PdGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ in toluene showing signals for $[M]^{+}=926.0643 \mathrm{~m} / \mathrm{z}(\mathrm{C}$; calc. $926.0751 \mathrm{~m} / \mathrm{z})$, $\left[M-C p^{*}\right]^{+}=790.9463 \mathrm{~m} / \mathrm{z}$ (B; calc. $790.9571 \mathrm{~m} / \mathrm{z}$ ) and $\left[M-G a-2 C p^{*}\right]^{+}=586.9062 \mathrm{~m} / \mathrm{z}$ (A; calc. $586.9140 \mathrm{~m} / \mathrm{z}$ ). Further signals


### 8.1.3. Appendix for semi-hydrogenation experiments

$\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}+\mathrm{H}_{2}$


Figure 125: Time-dependent ${ }^{1} \mathrm{H}$ NMR spectrum of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}(3)$ with 1 bar $\mathrm{H}_{2}$ in toluene- $d_{8}$ showing the signal decrease of 3 (highlighted).


Figure 126: Time-dependent ${ }^{1} \mathrm{H}$ NMR spectrum of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ (3) with 1 bar $\mathrm{H}_{2}$ in toluene-d ${ }_{8}$. Abbreviations: coa, cyclooctane; coe, cyclooctene; cod, 1,5-cyclooctadiene; dpe, diphenylethylene (stilbene); bb, bibenzyl.


Figure 127: LIFDI mass spectra of the reaction of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}(3)$ with $\mathrm{H}_{2}$ (1 bar) (red trace) or without hydrogen (black trace, reference) after one day at room temperature in toluene-d. Signal assignment is listed below.

Table 57: Signal assignment of the reaction of 3 with 1 bar $\mathrm{H}_{2}$ as obtained by LIFDI MS depicted in Figure 127.

|  | Experimental [m/z] | Calculated [m/z] | Cluster | Fragment |
| :--- | :--- | :--- | :--- | :--- |
| A | 510.1356 | 510.1367 | $\left[\mathrm{Ni}_{2}\right](\mathrm{cod})_{2}(\mathrm{dpa})$ |  |
| B | 537.1590 | 537.1602 | $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)(\mathrm{cod})(\mathrm{dpa})$ |  |
| C | 564.1827 | 564.1837 | $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})$ |  |
| D | 1025.9436 | 1025.9431 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{1}$ | F-2dpa/G-GaCp*-dpa |
| E | 1204.0220 | 1204.0215 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}$ | F-dpa/G-GaCp* |
| F | 1384.1004 | 1384.0973 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ |  |
| G | 1410.0647 | 1410.0643 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})_{2}$ |  |
| H | Mixture: |  |  |  |
|  | 1637.7904 | 1637.7943 | $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ |  |
|  | 1649.7734 | 1649.7773 | $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}-\mathrm{H}$ |  |

$\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}{ }^{*}\right)_{5}(\mathrm{dpa})_{1}+\mathrm{H}_{2}$


Figure 128: Time-dependent ${ }^{1} \mathrm{H} N M R$ spectrum of $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})_{1}(\boldsymbol{A})$ with 1 bar $\mathrm{H}_{2}$ in toluene- $d_{8}$. Abbreviations: coa, cyclooctane; coe, cyclooctene; cod, 1,5-cyclooctadiene; dpe, diphenylethylene (stilbene); bb, bibenzyl, dpa, diphenylacetylene.


Figure 129: LIFDI mass spectra of the reaction of $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})_{1}$ with $\mathrm{H}_{2}$ (1 bar) (red trace) or without hydrogen (black trace, reference) after one day at room temperature in toluene-d $\mathrm{d}_{8}$. Signal assignment is listed below.

Table 58: Signal assignment of the reaction of $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})$ with 1 bar $\mathrm{H}_{2}$ as obtained by LIFDI MS depicted in Figure 129.

|  | Experimental $[\mathrm{m} / \mathrm{z}]$ | Calculated $[\mathrm{m} / \mathrm{z}]$ | Cluster | Fragment |
| :--- | :--- | :--- | :--- | :--- |
| A | 564.1825 | 564.1837 | $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})$ |  |
| B | 1204.0193 | 1204.0215 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}$ | D-dpa |
| C | 1237.6709 | 1237.9890 | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{3}$ |  |
| D | 1384.0982 | 1384.0973 | $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ |  |
| E | 1467.9973 | 1467.9996 | $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})_{2}$ |  |
| F | 1553.8948 | 1553.8964 | $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})$ |  |
| G | Mixture: |  |  |  |
|  | 1637.7779 | 1637.7943 | $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ |  |
|  | 1649.7730 | 1649.7773 | $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}-\mathrm{H}$ |  |
| H | 1705.7072 | 1705.6964 | $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}-3 \mathrm{H}$ |  |

### 8.2. Supplementary information of the computational part

Note: All calculated compounds are available on the NAS-server of TU Munich.
[ $\mathrm{Ni}_{4} \mathrm{Ga}_{4}$ ] $\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ : octahedron

| Ni | 1.638209000 | -0.268314000 | 1.290854000 |
| :---: | :---: | :---: | :---: |
| Ni | -0.707372000 | -0.300481000 | 1.671477000 |
| H | 1.060086000 | 4.479823000 | 4.471183000 |
| C | 0.203502000 | 4.856962000 | 3.897878000 |
| H | 0.232067000 | 5.957035000 | 3.953830000 |
| H | -0.715428000 | 4.541960000 | 4.415935000 |
| C | 0.234769000 | 4.386724000 | 2.477445000 |
| C | 1.218074000 | 3.645490000 | 1.858048000 |
| C | 2.501978000 | 3.138007000 | 2.427587000 |
| H | 2.520037000 | 3.196170000 | 3.523899000 |
| H | 3.368827000 | 3.710595000 | 2.055393000 |
| H | 2.669254000 | 2.081521000 | 2.151273000 |
| C | 0.824917000 | 3.442725000 | 0.443881000 |
| C | 1.909290000 | 3.589686000 | -0.615847000 |
| H | 2.741414000 | 2.895516000 | -0.434616000 |
| H | 2.315441000 | 4.614670000 | -0.612075000 |
| H | 1.534213000 | 3.379501000 | -1.625073000 |
| C | -0.459768000 | 4.170221000 | 0.281795000 |
| C | -1.191487000 | 4.282027000 | -1.019301000 |
| H | -1.459077000 | 3.295156000 | -1.432382000 |
| H | -2.122745000 | 4.852524000 | -0.909341000 |
| H | -0.584576000 | 4.791291000 | -1.786312000 |
| Ga | 0.204126000 | 1.466335000 | 0.381286000 |
| C | -0.809473000 | 4.700513000 | 1.507422000 |
| C | -2.030657000 | 5.495233000 | 1.854184000 |
| H | -2.611463000 | 5.018744000 | 2.659758000 |
| H | -1.763356000 | 6.501889000 | 2.213151000 |
| H | -2.698922000 | 5.616724000 | 0.992850000 |
| H | 5.220784000 | -3.168485000 | 1.062053000 |
| C | 5.369082000 | -2.222571000 | 1.597360000 |
| H | 6.308556000 | -2.310557000 | 2.164914000 |
| H | 4.554613000 | -2.120976000 | 2.330715000 |
| C | 5.407285000 | -1.056577000 | 0.659778000 |
| C | 5.452867000 | -1.093872000 | -0.769612000 |
| C | 5.579387000 | -2.306057000 | -1.639328000 |
| H | 5.280360000 | -3.219007000 | -1.111793000 |
| H | 6.620684000 | -2.442369000 | -1.971585000 |
| H | 4.958585000 | -2.227771000 | -2.542541000 |
| C | 5.458773000 | 0.266144000 | -1.245107000 |
| C | 5.580931000 | 0.687233000 | -2.676573000 |
| H | 5.088995000 | -0.027108000 | -3.349716000 |
| H | 6.637166000 | 0.753812000 | -2.983622000 |
| H | 5.127537000 | 1.671570000 | -2.851367000 |
| C | 5.436071000 | 1.134703000 | -0.101190000 |
| C | 5.539533000 | 2.627267000 | -0.144183000 |
| H | 5.043171000 | 3.045213000 | -1.029431000 |
| H | 5.086568000 | 3.093719000 | 0.739348000 |
| H | 6.593511000 | 2.945583000 | -0.180371000 |
| Ga | 3.415087000 | -0.085814000 | -0.244708000 |
| C | 5.393587000 | 0.314827000 | 1.071386000 |
| C | 5.348037000 | 0.774677000 | 2.494273000 |
| H | 4.556250000 | 0.257519000 | 3.055917000 |
| H | 6.302045000 | 0.575747000 | 3.007675000 |
| H | 5.151644000 | 1.850639000 | 2.566923000 |
| H | -5.134154000 | -2.409538000 | 2.373080000 |
| C | -5.576505000 | -2.181573000 | 1.394029000 |
| H | -6.671089000 | -2.231126000 | 1.511442000 |
| H | -5.283595000 | -2.983927000 | 0.704630000 |
| C | -5.140572000 | -0.837003000 | 0.897343000 |
| C | -4.910324000 | 0.319067000 | 1.729449000 |
| C | -5.133458000 | 0.361172000 | 3.209208000 |
| H | -4.613609000 | -0.454322000 | 3.732447000 |
| H | -6.205542000 | 0.266400000 | 3.444291000 |
| H | -4.786584000 | 1.306318000 | 3.642168000 |
| C | -4.579982000 | 1.420651000 | 0.868679000 |
| C | -4.252105000 | 2.821167000 | 1.285100000 |
| H | -4.189078000 | 2.910640000 | 2.375687000 |
| H | -5.015897000 | 3.533480000 | 0.938022000 |
| H | -3.284152000 | 3.149230000 | 0.880111000 |
| C | -4.605568000 | 0.945282000 | -0.480023000 |


| C | -4.294790000 | 1.743336000 | -1.708382000 |
| :---: | :---: | :---: | :---: |
| H | -3.922660000 | 2.741569000 | -1.448637000 |
| H | -3.519787000 | 1.251300000 | -2.314678000 |
| H | -5.187066000 | 1.871696000 | -2.340799000 |
| Ga | -2.883804000 | -0.190338000 | 0.750217000 |
| C | -4.970410000 | -0.437771000 | -0.462966000 |
| C | -5.150630000 | -1.289890000 | -1.677269000 |
| H | -5.257570000 | -2.349739000 | -1.417225000 |
| H | -6.053440000 | -0.994247000 | -2.235036000 |
| H | -4.298436000 | -1.197236000 | -2.363513000 |
| H | 3.214846000 | -3.607135000 | 0.114189000 |
| C | 2.567683000 | -4.051913000 | -0.653590000 |
| H | 2.892547000 | -5.095447000 | -0.799100000 |
| H | 2.756304000 | -3.511885000 | -1.590223000 |
| C | 1.127275000 | -3.969308000 | -0.259079000 |
| C | 0.596909000 | -4.186662000 | 1.059869000 |
| C | 1.432100000 | -4.491999000 | 2.261626000 |
| H | 2.357065000 | -3.898340000 | 2.270011000 |
| H | 1.731822000 | -5.552734000 | 2.274296000 |
| H | 0.897943000 | -4.293390000 | 3.198170000 |
| C | -0.824948000 | -4.142811000 | 0.974492000 |
| C | -1.804430000 | -4.214489000 | 2.103591000 |
| H | -1.297344000 | -4.267108000 | 3.074993000 |
| H | -2.456804000 | -5.098321000 | 2.021799000 |
| H | -2.458080000 | -3.327924000 | 2.117373000 |
| C | -1.187105000 | -3.934586000 | -0.393003000 |
| C | -2.590693000 | -3.777183000 | -0.878893000 |
| H | -3.048552000 | -2.857858000 | -0.479111000 |
| H | -2.638145000 | -3.709715000 | -1.972639000 |
| H | -3.221708000 | -4.624326000 | -0.568931000 |
| Ga | 0.264160000 | -1.945786000 | 0.187587000 |
| C | 0.008236000 | -3.830998000 | -1.164379000 |
| C | 0.131517000 | -3.709838000 | -2.649907000 |
| H | 0.853397000 | -2.931623000 | -2.935740000 |
| H | 0.465469000 | -4.658187000 | -3.100147000 |
| C | 1.570166000 | -1.392236000 | 4.061586000 |
| H | 2.195593000 | -2.123969000 | 3.535229000 |
| H | 2.258878000 | -0.793706000 | 4.683490000 |
| C | 0.553662000 | -2.115687000 | 4.953266000 |
| H | -0.187173000 | -2.639171000 | 4.334268000 |
| H | 1.046115000 | -2.848576000 | 5.607952000 |
| H | 0.004640000 | -1.405313000 | 5.585409000 |
| C | 0.919975000 | -0.448115000 | 3.079545000 |
| C | -0.047263000 | 0.447953000 | 3.253323000 |
| C | -0.487290000 | 1.425403000 | 4.279827000 |
| C | -1.870772000 | 2.015613000 | 4.033769000 |
| H | -2.615265000 | 1.213253000 | 3.972751000 |
| H | -2.162489000 | 2.707817000 | 4.836158000 |
| H | -1.883120000 | 2.555905000 | 3.078230000 |
| H | -0.453513000 | 0.913829000 | 5.260024000 |
| H | 0.263923000 | 2.227773000 | 4.339802000 |
| H | -0.826500000 | -3.443511000 | -3.107529000 |
| C | -0.106311000 | 0.362494000 | -2.530181000 |
| C | 0.311869000 | 1.539147000 | -3.393149000 |
| H | -0.383800000 | 1.629595000 | -4.244436000 |
| C | 1.754276000 | 1.450353000 | -3.900800000 |
| H | 2.011630000 | 2.316036000 | -4.529008000 |
| H | 1.904287000 | 0.536611000 | -4.491621000 |
| H | 2.451858000 | 1.409124000 | -3.050439000 |
| H | 0.189039000 | 2.462457000 | -2.809178000 |
| C | -1.145780000 | -0.460883000 | -2.646782000 |
| C | -1.942673000 | -1.019618000 | -3.772966000 |
| H | -2.804915000 | -0.344266000 | -3.926049000 |
| C | -1.170413000 | -1.189008000 | -5.088345000 |
| H | -1.801480000 | -1.650258000 | -5.861074000 |
| H | -0.816964000 | -0.223209000 | -5.470621000 |
| H | -0.290583000 | -1.827536000 | -4.936388000 |
| H | -2.394870000 | -1.976936000 | -3.471209000 |
| Ni | -1.097883000 | -0.158110000 | -0.794316000 |
| Ni | 1.245039000 | -0.131822000 | -1.153494000 |

[ $\left.\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ : tetrahedron
$\begin{array}{lllll}\mathrm{Ni} & 0.386036000 & -1.451981000 & 1.355630000\end{array}$
$\begin{array}{lrrr}\mathrm{Ni} & -1.148223000 & 0.665011000 & 0.662218000 \\ \mathrm{H} & 0.701740000 & 1.950189000 & -4.871649000\end{array}$
C $0.820621000-0.865421000-4.97990100$

| H | 0.873093000 | 0.639819000 | -6.056717000 |
| :--- | ---: | ---: | ---: |
| H | -0.097377000 | 0.390306000 | -4.594847000 |
| C | 2.034521000 | 0.368447000 | -4.260854000 |
| C | 3.107716000 | 1.149072000 | -3.725438000 |


| C | 3.269167000 | 2.636147000 | -3.786683000 |
| :---: | :---: | :---: | :---: |
| H | 2.344495000 | 3.132941000 | -4.103252000 |
| H | 4.055696000 | 2.916615000 | -4.505536000 |
| H | 3.556739000 | 3.059123000 | -2.812707000 |
| C | 4.088918000 | 0.243992000 | -3.196558000 |
| C | 5.406880000 | 0.655250000 | -2.617551000 |
| H | 5.307013000 | 1.513286000 | -1.937815000 |
| H | 6.114123000 | 0.951376000 | -3.409751000 |
| H | 5.873492000 | -0.161736000 | -2.054369000 |
| C | 3.629457000 | -1.090571000 | -3.415215000 |
| C | 4.369399000 | -2.341484000 | -3.056591000 |
| H | 4.909826000 | -2.236779000 | -2.106365000 |
| H | 3.688650000 | -3.195117000 | -2.956430000 |
| H | 5.112333000 | -2.604609000 | -3.826583000 |
| Ga | 2.020303000 | 0.044820000 | -1.920107000 |
| C | 2.357567000 | -1.018992000 | -4.063239000 |
| C | 1.514823000 | -2.163733000 | -4.531232000 |
| H | 0.452123000 | -1.996531000 | -4.302292000 |
| H | 1.606396000 | -2.308836000 | -5.620193000 |
| H | 1.806355000 | -3.104468000 | -4.047889000 |
| H | 2.859130000 | -2.322774000 | 5.381259000 |
| C | 3.405011000 | -1.371989000 | 5.452649000 |
| H | 4.286033000 | -1.550666000 | 6.090789000 |
| H | 2.762605000 | -0.657487000 | 5.982786000 |
| C | 3.810362000 | -0.863292000 | 4.104292000 |
| C | 4.278813000 | -1.677431000 | 3.018955000 |
| C | 4.383010000 | -3.170658000 | 3.056311000 |
| H | 3.433808000 | -3.641782000 | 3.352241000 |
| H | 5.146428000 | -3.497051000 | 3.779851000 |
| H | 4.663143000 | -3.577942000 | 2.077669000 |
| C | 4.655565000 | -0.809529000 | 1.951047000 |
| C | 5.201362000 | -1.191552000 | 0.611924000 |
| H | 5.200530000 | -2.278885000 | 0.467997000 |
| H | 6.237981000 | -0.840816000 | 0.487433000 |
| H | 4.605262000 | -0.745332000 | -0.198953000 |
| C | 4.433218000 | 0.543431000 | 2.374171000 |
| C | 4.735296000 | 1.752654000 | 1.542523000 |
| H | 4.239503000 | 1.699576000 | 0.558638000 |
| H | 4.396868000 | 2.672940000 | 2.032726000 |
| H | 5.817705000 | 1.852937000 | 1.362744000 |
| Ga | 2.299807000 | -0.536204000 | 2.308309000 |
| C | 3.919829000 | 0.512482000 | 3.709471000 |
| C | 3.605366000 | 1.691074000 | 4.578062000 |
| H | 2.723013000 | 1.506463000 | 5.206461000 |
| H | 4.443172000 | 1.924663000 | 5.254318000 |
| H | 3.403372000 | 2.589484000 | 3.983029000 |
| H | -3.817599000 | -1.369339000 | 0.355694000 |
| C | -4.445497000 | -1.639880000 | -0.508095000 |
| H | -5.481161000 | -1.359384000 | -0.255974000 |
| H | -4.418399000 | -2.730979000 | -0.616915000 |
| C | -3.982717000 | -0.946631000 | -1.750917000 |
| C | -3.710181000 | 0.454636000 | -1.830213000 |
| C | -3.870655000 | 1.412139000 | -0.693737000 |
| H | -3.079925000 | 1.299418000 | 0.093009000 |
| H | -4.831961000 | 1.260976000 | -0.181587000 |
| H | -3.824986000 | 2.454925000 | -1.029131000 |
| C | -3.297905000 | 0.754163000 | -3.167332000 |
| C | -3.031709000 | 2.110299000 | -3.743443000 |
| H | -2.774935000 | 2.839096000 | -2.965750000 |
| H | -3.917507000 | 2.492051000 | -4.276162000 |
| H | -2.202505000 | 2.094649000 | -4.463573000 |
| C | -3.317965000 | -0.475761000 | -3.917663000 |
| C | -3.057775000 | -0.612445000 | -5.386848000 |
| H | -2.334289000 | 0.133806000 | -5.741355000 |
| H | -2.660094000 | -1.605073000 | -5.637684000 |
| H | -3.981489000 | -0.474381000 | -5.972260000 |
| Ga | -1.608703000 | -0.668515000 | -2.369673000 |

## $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{4}:$

| Ni | 1.868891000 | 5.420699000 | 27.825889000 |
| :---: | :---: | :---: | :---: |
| Ni | 2.794290000 | 2.846849000 | 27.621079000 |
| Ni | 5.526411000 | 3.029688000 | 28.367486000 |
| Ni | 3.386124000 | 4.258709000 | 29.868908000 |
| Ni | 4.355630000 | 4.939522000 | 26.677399000 |
| Ga | 4.225574000 | 6.242766000 | 28.802086000 |
| Ga | 4.193423000 | 1.047312000 | 27.882227000 |
| C | 2.633450000 | 8.316135000 | 29.825420000 |
| C | 4.018084000 | 8.373693000 | 30.073554000 |
| C | 4.697865000 | 8.454698000 | 28.787068000 |
| C | 3.672659000 | 8.514522000 | 27.765747000 |
| C | 2.419300000 | 8.374011000 | 28.403995000 |
| C | 1.553208000 | 8.266742000 | 30.857860000 |
| H | 1.158517000 | 9.274936000 | 31.069452000 |
| H | 1.918351000 | 7.858159000 | 31.808561000 |
| H | 0.704185000 | 7.651007000 | 30.535321000 |
| C | 4.685793000 | 8.412591000 | 31.413427000 |


| C | -3.756108000 | -1.521948000 | -3 |
| :---: | :---: | :---: | :---: |
| C | -3.988083000 | -2.945310000 | -3.440183000 |
| H | -4.053458000 | -3.606574000 | -2.567947000 |
| H | -4.929194000 | -3.048766000 | -4.003529000 |
| H | -3.182699000 | -3.328153000 | -4.082646000 |
| H | 0.512070000 | -2.445057000 | 4.690543000 |
| C | -0.501485000 | -2.827691000 | 4.873796000 |
| H | -0.555469000 | -3.150883000 | 5.925812000 |
| H | -0.630951000 | -3.716667000 | 4.243974000 |
| C | -1.530565000 | -1.785032000 | 4.567382000 |
| C | -1.389927000 | -0.379945000 | 4.834598000 |
| C | -0.181868000 | 0.251074000 | 5.452601000 |
| H | 0.738946000 | -0.081367000 | 4.948045000 |
| H | -0.087566000 | -0.014240000 | 6.516980000 |
| H | -0.217926000 | 1.344906000 | 5.384216000 |
| C | -2.582149000 | 0.276827000 | 4.399243000 |
| C | -2.879123000 | 1.742433000 | 4.462416000 |
| H | -1.972009000 | 2.328988000 | 4.653496000 |
| H | -3.598232000 | 1.974655000 | 5.263535000 |
| H | -3.309536000 | 2.104962000 | 3.517833000 |
| C | -3.460217000 | -0.716726000 | 3.850465000 |
| C | -4.827379000 | -0.455325000 | 3.299119000 |
| H | -4.867894000 | 0.504217000 | 2.765521000 |
| H | -5.136356000 | -1.238720000 | 2.595517000 |
| H | -5.582921000 | -0.417001000 | 4.100105000 |
| Ga | -1.534877000 | -0.706564000 | 2.513301000 |
| C | -2.813587000 | -1.994632000 | 3.962428000 |
| C | -3.390088000 | -3.315549000 | 3.556742000 |
| H | -2.605052000 | -4.019851000 | 3.251583000 |
| H | -3.944908000 | -3.781879000 | 4.386272000 |
| H | -4.087530000 | -3.213723000 | 2.714736000 |
| C | -0.258268000 | -2.934346000 | 0.308908000 |
| C | -1.480731000 | -3.772691000 | 0.180799000 |
| H | -1.483782000 | -4.497265000 | 1.014134000 |
| C | -1.571142000 | -4.516371000 | -1.157150000 |
| H | -2.504756000 | -5.092920000 | -1.223204000 |
| H | -0.730094000 | -5.208711000 | -1.286078000 |
| H | -1.540985000 | -3.794260000 | -1.984628000 |
| H | -2.366941000 | -3.140993000 | 0.318424000 |
| C | 1.053249000 | -2.904146000 | 0.334229000 |
| C | 2.317195000 | -3.617812000 | 0.021595000 |
| H | 2.666107000 | -4.118315000 | 0.939648000 |
| C | 2.162879000 | -4.641513000 | -1.108720000 |
| H | 3.128565000 | -5.102789000 | -1.358184000 |
| H | 1.465073000 | -5.439532000 | -0.823976000 |
| H | 1.763136000 | -4.153340000 | -2.008109000 |
| H | 3.090401000 | -2.881271000 | -0.234418000 |
| Ni | 0.168651000 | -1.237533000 | -1.151095000 |
| Ni | 1.571087000 | 0.810752000 | 0.300642000 |
| C | 0.285751000 | 1.985392000 | 1.212620000 |
| C | -0.389742000 | 2.290541000 | 0.102725000 |
| C | -0.654677000 | 3.385835000 | -0.866103000 |
| H | -1.743070000 | 3.485894000 | -1.003126000 |
| H | -0.293852000 | 4.343130000 | -0.451317000 |
| C | 0.002886000 | 3.132020000 | -2.225688000 |
| H | -0.317554000 | 2.158165000 | -2.618051000 |
| H | 1.092459000 | 3.093655000 | -2.110482000 |
| H | -0.257993000 | 3.916817000 | -2.950270000 |
| C | 0.547601000 | 2.648557000 | 2.536418000 |
| H | 1.010019000 | 1.929020000 | 3.227822000 |
| C | 1.451637000 | 3.877104000 | 2.377236000 |
| H | 2.400566000 | 3.592733000 | 1.902883000 |
| H | 1.669575000 | 4.340072000 | 3.350291000 |
| H | 0.977227000 | 4.634675000 | 1.739085000 |
| H | -0.414875000 | 2.947925000 | 2.981908000 |


|  |  |  |  |
| :--- | :---: | :---: | :---: |
| C | 4.963402000 | -0.788639000 | 26.718833000 |
| C | 3.755068000 | -0.653530000 | 25.973940000 |
| C | 2.657619000 | -0.951949000 | 26.837341000 |
| C | 2.374654000 | -1.678187000 | 29.328133000 |
| H | 2.292765000 | -2.775229000 | 29.394853000 |
| H | 1.354735000 | -1.274575000 | 29.302786000 |
| H | 2.840336000 | -1.334054000 | 30.262126000 |
| C | 5.562897000 | -1.553371000 | 29.154705000 |
| H | 5.915778000 | -2.588167000 | 29.013225000 |
| H | 5.104400000 | -1.495303000 | 30.150838000 |
| H | 6.447741000 | -0.899866000 | 29.166239000 |
| C | 6.362394000 | -0.734989000 | 26.191992000 |
| H | 6.798969000 | -1.743661000 | 26.119393000 |
| H | 7.019688000 | -0.140732000 | 26.843584000 |
| H | 6.399949000 | -0.284132000 | 25.192905000 |
| C | 3.623256000 | -0.246798000 | 24.538914000 |
| H | 4.580106000 | 0.090838000 | 24.121366000 |
| H | 2.902199000 | 0.575693000 | 24.419085000 |
| H | 3.267513000 | -1.081548000 | 23.914158000 |
| C | 1.222956000 | -0.929544000 | 26.411886000 |
| H | 1.015578000 | -1.715053000 | 25.667620000 |
| H | 0.952003000 | 0.030182000 | 25.944707000 |
| H | 0.543703000 | -1.091148000 | 27.256998000 |
| C | 0.734513000 | 4.914807000 | 31.728554000 |
| C | 0.244304000 | 4.837493000 | 30.275948000 |
| C | 1.335867000 | 4.355851000 | 29.326666000 |
| C | 1.252131000 | 1.852253000 | 29.934885000 |
| C | C | 1.848000000 | 3.086695000 | 229.310348000

## [ $\mathrm{Ni}_{4} \mathrm{Ga}_{4}$ ] $\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})_{2}$ : octahedron

|  | 1.086629000 | -0.138252000 | 1.003800000 |
| :--- | ---: | ---: | ---: |
| Ni | -1.285594000 | -0.178588000 | 1.247970000 |
| H | 2.421894000 | 2.830906000 | 1.744945000 |
| C | 1.734307000 | 3.651994000 | 1.996948000 |
| H | 2.319220000 | 4.584842000 | 1.988264000 |
| H | 1.383462000 | 3.481959000 | 3.021761000 |
| C | 0.588625000 | 3.703417000 | 1.034928000 |
| C | 0.715691000 | 3.734365000 | -0.396071000 |
| C | 2.003248000 | 3.783009000 | -1.151345000 |
| C | -0.604674000 | 3.707886000 | -0.957289000 |
| C | -0.980081000 | 3.832863000 | -2.398029000 |
| H | -0.108690000 | 3.729329000 | -3.050851000 |
| H | -1.435710000 | 4.815016000 | -2.599639000 |
| H | -1.702137000 | 3.060878000 | -2.700491000 |
| C | -1.538753000 | 3.643381000 | 0.131937000 |
| C | -3.025229000 | 3.612563000 | -0.003719000 |
| H | -3.323491000 | 3.172312000 | -0.963641000 |
| H | -3.476932000 | 3.006611000 | 0.791700000 |
| H | -3.466738000 | 4.621198000 | 0.053929000 |
| Ga | -0.261041000 | 1.684227000 | 0.074131000 |
| C | -0.801666000 | 3.669999000 | 1.358221000 |
| C | -1.419205000 | 3.714532000 | 2.716911000 |
| H | -0.716166000 | 3.419737000 | 3.503428000 |
| H | -1.772731000 | 4.731948000 | 2.950355000 |
| H | -2.285872000 | 3.045652000 | 2.789828000 |
| H | 3.093361000 | -4.066369000 | -1.650721000 |
| C | 2.259398000 | -3.850203000 | -2.331022000 |
| H | 2.298480000 | -4.579603000 | -3.153652000 |


| H | 2.439627000 | -2.856262000 | -2.773099000 |
| :--- | :---: | :---: | :---: |
| C | 0.948162000 | -3.893430000 | -1.613150000 |
| C | 0.764610000 | -3.893961000 | -0.212509000 |
| C | 1.841742000 | -4.033818000 | 0.815781000 |
| H | 2.437076000 | -3.115328000 | 0.917424000 |
| H | 2.531751000 | -4.847288000 | 0.547801000 |
| H | 1.431039000 | -4.258808000 | 1.806126000 |
| C | -0.672420000 | -3.801764000 | 0.044845000 |
| C | -1.353126000 | -4.073281000 | 1.357486000 |
| H | -0.741912000 | -3.742868000 | 2.206829000 |
| H | -1.561468000 | -5.148065000 | 1.488061000 |
| H | -2.309170000 | -3.535903000 | 1.421328000 |
| C | -1.329416000 | -3.824904000 | -1.257006000 |
| C | -2.809790000 | -3.822465000 | -1.451016000 |
| H | -3.272944000 | -2.942036000 | -0.977805000 |
| H | -3.071508000 | -3.794898000 | -2.515256000 |
| H | -3.280290000 | -4.715439000 | -1.009440000 |
| Ga | -0.205372000 | -1.753350000 | -0.296877000 |
| C | -0.333406000 | -3.875355000 | -2.249960000 |
| C | -0.520289000 | -3.927186000 | -3.731242000 |
| H | 0.116623000 | -3.193477000 | -4.242647000 |
| H | -0.248359000 | -4.919681000 | -4.127008000 |
| H | -1.554620000 | -3.723049000 | -4.029795000 |
| Ni | -1.596481000 | 0.043276000 | -1.186754000 |
| Ni | 0.783765000 | 0.052566000 | -1.478189000 |
| H | 1.842697000 | 3.654600000 | -2.228178000 |
| H | 2.680118000 | 2.976058000 | -0.832040000 |
| H | 2.526708000 | 4.739724000 | -0.996149000 |


| C | -0.075909000 | -0.166480000 | 2.747368000 |
| :---: | :---: | :---: | :---: |
| C | 0.955870000 | -1.028583000 | 2.641141000 |
| C | 1.466143000 | -2.033684000 | 3.537833000 |
| C | 2.815242000 | -2.435266000 | 3.512770000 |
| C | 3.292254000 | -3.400229000 | 4.394121000 |
| H | 4.342620000 | -3.692013000 | 4.363564000 |
| C | 2.422873000 | -4.008427000 | 5.306958000 |
| H | 2.791812000 | -4.776979000 | 5.986279000 |
| C | 1.074870000 | -3.630620000 | 5.338529000 |
| H | 0.393086000 | -4.103563000 | 6.046200000 |
| H | 3.473039000 | -1.968204000 | 2.784391000 |
| C | 0.601264000 | -2.651562000 | 4.470229000 |
| H | -0.446439000 | -2.351422000 | 4.486387000 |
| C | -0.443160000 | 0.635447000 | 3.919541000 |
| C | 0.544245000 | 1.266363000 | 4.699868000 |
| H | 1.587017000 | 1.178749000 | 4.395062000 |
| C | 0.192307000 | 1.999558000 | 5.832675000 |
| H | 0.968124000 | 2.491177000 | 6.420915000 |
| C | -1.148658000 | 2.104583000 | 6.218127000 |
| C | -2.136419000 | 1.469416000 | 5.458474000 |
| H | -3.183921000 | 1.544263000 | 5.753724000 |
| H | -1.421105000 | 2.679785000 | 7.102967000 |
| C | -1.787029000 | 0.754372000 | 4.314850000 |
| H | -2.543553000 | 0.267797000 | 3.698084000 |
| C | -0.712433000 | 0.053249000 | -2.962088000 |
| C | 0.396527000 | 0.782082000 | -3.158210000 |
| C | 0.970179000 | 1.575351000 | -4.208575000 |
| C | 2.364873000 | 1.764240000 | -4.273790000 |
| C | 2.940386000 | 2.518576000 | -5.292138000 |
| H | 4.022564000 | 2.649242000 | -5.327683000 |
| C | 2.131742000 | 3.124407000 | -6.260011000 |
| H | 2.579494000 | 3.726754000 | -7.050535000 |
| C | 0.741207000 | 2.959488000 | -6.202862000 |
| H | 0.106326000 | 3.434187000 | -6.951980000 |
| H | 2.967200000 | 1.300140000 | -3.493993000 |
| C | 0.164808000 | 2.192593000 | -5.196086000 |
| H | -0.915730000 | 2.060670000 | -5.151912000 |
| C | -1.490284000 | -0.705151000 | -3.958690000 |
| C | -0.972235000 | -0.954898000 | -5.246306000 |
| H | 0.044504000 | -0.640625000 | -5.477228000 |
| C | -1.739391000 | -1.600323000 | -6.213428000 |
| H | -1.315659000 | -1.787343000 | -7.200826000 |
| C | -3.041323000 | -2.021461000 | -5.920414000 |
| C | -3.566858000 | -1.791947000 | -4.645354000 |
| H | -4.579019000 | -2.117712000 | -4.402596000 |
| H | -3.638289000 | -2.529181000 | -6.678246000 |
| C | -2.796846000 | -1.146024000 | -3.679937000 |
| H | -3.194819000 | -0.963383000 | -2.676677000 |
| Ga | 2.923932000 | 0.041846000 | -0.506086000 |
| C | 5.002100000 | 1.455505000 | 0.064764000 |


| C | 5.117438000 | 2.813915000 | 0.683750000 |
| :---: | :---: | :---: | :---: |
| H | 4.654054000 | 2.848521000 | 1.676863000 |
| H | 6.175984000 | 3.098542000 | 0.806323000 |
| H | 4.644669000 | 3.589248000 | 0.068382000 |
| C | 4.990423000 | 0.220102000 | 0.779341000 |
| C | 5.037007000 | 0.094905000 | 2.271767000 |
| H | 4.054397000 | 0.267041000 | 2.738015000 |
| H | 5.737373000 | 0.825705000 | 2.700182000 |
| H | 5.379613000 | -0.900727000 | 2.578862000 |
| C | 4.989793000 | -0.850618000 | -0.178615000 |
| C | 5.135680000 | -2.310543000 | 0.124466000 |
| H | 4.676540000 | -2.577045000 | 1.084080000 |
| H | 6.197950000 | -2.599694000 | 0.172286000 |
| H | 4.662962000 | -2.934979000 | -0.643777000 |
| C | 5.005122000 | -0.255773000 | -1.496648000 |
| C | 5.114981000 | -0.999480000 | -2.792744000 |
| H | 4.652383000 | -1.992477000 | -2.728269000 |
| H | 4.619775000 | -0.462940000 | -3.612902000 |
| H | 6.168208000 | -1.146637000 | -3.081053000 |
| C | 5.029985000 | 1.168926000 | -1.331500000 |
| C | 5.193588000 | 2.192297000 | -2.412334000 |
| H | 4.405594000 | 2.957954000 | -2.392516000 |
| H | 6.156078000 | 2.715812000 | -2.300917000 |
| H | 5.188424000 | 1.731435000 | -3.406879000 |
| Ga | -3.431094000 | -0.267792000 | 0.334902000 |
| C | -5.598214000 | 0.529869000 | 0.170568000 |
| C | -5.970735000 | 1.692091000 | -0.697644000 |
| H | -5.483397000 | 1.641913000 | -1.681234000 |
| H | -7.057703000 | 1.717423000 | -0.873100000 |
| H | -5.687133000 | 2.646408000 | -0.239863000 |
| C | -5.591387000 | -0.848279000 | -0.257365000 |
| C | -5.939137000 | -1.331641000 | -1.631044000 |
| H | -5.641019000 | -0.607578000 | -2.400697000 |
| H | -7.024706000 | -1.488735000 | -1.733795000 |
| H | -5.445559000 | -2.284552000 | -1.861868000 |
| C | -5.306609000 | -1.661262000 | 0.886925000 |
| C | -5.331866000 | -3.155181000 | 0.960245000 |
| H | -5.326160000 | -3.616131000 | -0.033368000 |
| H | -6.243530000 | -3.496564000 | 1.476374000 |
| H | -4.476777000 | -3.557146000 | 1.520790000 |
| C | -5.123233000 | -0.795684000 | 2.010530000 |
| C | -4.843567000 | -1.253646000 | 3.407945000 |
| H | -3.966169000 | -1.914676000 | 3.456458000 |
| H | -4.660100000 | -0.406763000 | 4.079438000 |
| H | -5.697466000 | -1.817144000 | 3.816211000 |
| C | -5.315161000 | 0.553432000 | 1.577199000 |
| C | -5.269852000 | 1.758402000 | 2.467127000 |
| H | -5.386860000 | 2.686448000 | 1.895678000 |
| H | -6.082125000 | 1.728300000 | 3.209287000 |
| H | -4.323824000 | 1.830368000 | 3.023382000 |

## $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})_{2}$ : tetrahedron

| Ni | 0.185289000 | -1.446036000 | 1.403263000 |
| :--- | :---: | ---: | ---: |
| Ni | -1.245998000 | 0.417886000 | 0.611547000 |
| H | 0.611239000 | 1.573204000 | -5.097417000 |
| C | 0.613785000 | 0.501418000 | -4.865684000 |
| H | 0.480084000 | -0.046712000 | -5.809880000 |
| H | -0.269724000 | 0.297384000 | -4.240482000 |
| C | 1.874299000 | 0.087147000 | -4.174041000 |
| C | 2.945614000 | 0.921918000 | -3.739791000 |
| C | 3.102303000 | 2.398294000 | -3.934010000 |
| H | 2.268751000 | 2.822171000 | -4.505196000 |
| H | 4.027137000 | 2.617987000 | -4.489192000 |
| H | 3.157621000 | 2.944741000 | -2.981340000 |
| C | 3.936838000 | 0.086189000 | -3.126432000 |
| C | 5.268785000 | 0.564707000 | -2.639552000 |
| H | 5.176573000 | 1.430898000 | -1.969414000 |
| H | 5.903045000 | 0.876408000 | -3.485238000 |
| H | 5.807512000 | -0.222142000 | -2.099516000 |
| C | 3.489466000 | -1.276009000 | -3.205639000 |
| C | 4.275563000 | -2.477953000 | -2.787715000 |
| H | 4.861361000 | -2.288676000 | -1.879592000 |
| H | 3.626736000 | -3.334838000 | -2.579570000 |
| H | 4.981144000 | -2.778551000 | -3.578563000 |
| Ga | 1.980327000 | -0.200381000 | -1.805901000 |
| C | 2.203498000 | -1.273339000 | -3.841777000 |
| C | 1.356982000 | -2.464057000 | -4.169911000 |
| H | 0.308064000 | -2.302548000 | -3.880862000 |
| H | 1.378713000 | -2.681000000 | -5.249940000 |
| H | 1.710449000 | -3.356475000 | -3.641528000 |
| H | 3.180164000 | -1.713686000 | 5.687651000 |
| C | 3.383528000 | -0.639377000 | 5.588236000 |
| H | 4.288454000 | -0.425343000 | 6.180685000 |
| H | 2.555193000 | -0.094666000 | 6.057633000 |
| C | 3.579928000 | -0.237931000 | 4.160042000 |
| C | 4.217414000 | -1.037082000 | 3.154257000 |
| C | 4.703006000 | -2.437638000 | 3.368017000 |
|  |  |  |  |

$\left.\begin{array}{lccc} & & 3.905568000 & -3.105969000\end{array}\right] 3.724145000$ H

| C | -2.836428000 | -0.915520000 | -4.952271000 |
| :--- | ---: | :---: | :---: |
| H | -2.226138000 | -0.183791000 | -5.494051000 |
| H | -2.227228000 | -1.818241000 | -4.803872000 |
| H | -3.674795000 | -1.195599000 | -5.610402000 |
| Ga | -2.013597000 | -0.121104000 | -1.715883000 |
| C | -4.026420000 | -1.119059000 | -2.653962000 |
| C | -4.286628000 | -2.591041000 | -2.752090000 |
| H | -4.997990000 | -2.927950000 | -1.991042000 |
| H | -4.703736000 | -2.844583000 | -3.738124000 |
| H | -3.372287000 | -3.188068000 | -2.617828000 |
| H | -1.424992000 | -4.448252000 | 2.939133000 |
| C | -2.311061000 | -4.168448000 | 3.524352000 |
| H | -2.378609000 | -4.868837000 | 4.372042000 |
| H | -3.186324000 | -4.329598000 | 2.886805000 |
| C | -2.221337000 | -2.758965000 | 4.011059000 |
| C | -1.054785000 | -2.176449000 | 4.590855000 |
| C | 0.264891000 | -2.860683000 | 4.757061000 |
| H | 0.471546000 | -3.535235000 | 3.915570000 |
| H | 0.294270000 | -3.459060000 | 5.682937000 |
| H | 1.087028000 | -2.135638000 | 4.801070000 |
| C | -1.371158000 | -0.848731000 | 5.013817000 |
| C | -0.423927000 | 0.062393000 | 5.728275000 |
| H | 0.443748000 | 0.322958000 | 5.101651000 |
| H | -0.036107000 | -0.414878000 | 6.640398000 |
| H | -0.905026000 | 1.000854000 | 6.025119000 |
| C | -2.734295000 | -0.583297000 | 4.662422000 |
| C | -3.544675000 | 0.626780000 | 5.017640000 |
| H | -2.913126000 | 1.506569000 | 5.192693000 |
| H | -4.255035000 | 0.888531000 | 4.221640000 |
| H | -4.131608000 | 0.454452000 | 5.934200000 |
| Ga | -1.758085000 | -0.777636000 | 2.611982000 |
| C | -3.262890000 | -1.778233000 | 4.028829000 |
| C | -4.693542000 | -1.980148000 | 3.63181800 |
| H | -4.800572000 | -2.839840000 | 2.959797000 |
| H | -5.326777000 | -2.166727000 | 4.514013000 |
| H | -5.106375000 | -1.101083000 | 3.117456000 |
| Ni | -0.082164000 | -1.186036000 | -0.957930000 |
| Ni | 1.108268000 | 0.645807000 | 0.207455000 |
| C | -0.641356000 | -2.693274000 | 0.101150000 |
| C | -1.790630000 | -3.579105000 | 0.169856000 |
| C | -1.617671000 | -4.975951000 | 0.064832000 |
| C | -2.708944000 | --8.839359000 | 0.142824000 |
| H | -2.550717000 | -6.915471000 | 0.061643000 |
|  |  |  | 0 |

## $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ : octahedron

| Ni | 1.088867000 | -0.075038000 | 0.891691000 |
| :---: | :---: | :---: | :---: |
| Ni | -1.288763000 | -0.309589000 | 1.001014000 |
| H | 2.111972000 | 2.761012000 | 1.640830000 |
| C | 1.522580000 | 3.688020000 | 1.719281000 |
| H | 2.209097000 | 4.534853000 | 1.565042000 |
| H | 1.143881000 | 3.746023000 | 2.746459000 |
| C | 0.400213000 | 3.684255000 | 0.731136000 |
| C | 0.536234000 | 3.445127000 | -0.673274000 |
| C | 1.818571000 | 3.421830000 | -1.440626000 |
| C | -0.807752000 | 3.422763000 | -1.246939000 |
| C | -1.121057000 | 3.450723000 | -2.712952000 |
| H | -0.397949000 | 2.856195000 | -3.286553000 |
| H | -1.096403000 | 4.479509000 | -3.107641000 |
| H | -2.116220000 | 3.037380000 | -2.920346000 |
| C | -1.727772000 | 3.688873000 | -0.170749000 |
| C | -3.206172000 | 3.868788000 | -0.287049000 |
| H | -3.560852000 | 3.671140000 | -1.302819000 |
| H | -3.762363000 | 3.202099000 | 0.387695000 |
| H | -3.491422000 | 4.901157000 | -0.028288000 |
| Ga | -0.350747000 | 1.429680000 | -0.391760000 |
| C | -0.982032000 | 3.840413000 | 1.025658000 |
| C | -1.576022000 | 4.170331000 | 2.357043000 |
| H | -0.946045000 | 3.833236000 | 3.188263000 |
| H | -1.712866000 | 5.259163000 | 2.467598000 |
| H | -2.562233000 | 3.707441000 | 2.485271000 |
| H | 3.611789000 | -3.984609000 | -2.050698000 |
| C | 2.725755000 | -3.563726000 | -2.547836000 |
| H | 2.689793000 | -3.963877000 | -3.570014000 |
| H | 2.886428000 | -2.475221000 | -2.626684000 |
| C | 1.475239000 | -3.869507000 | -1.788152000 |
| C | 1.374191000 | -3.957890000 | -0.384207000 |
| C | 2.514937000 | -3.946620000 | 0.580278000 |
| H | 3.006247000 | -2.963465000 | 0.618077000 |
| H | 3.280269000 | -4.684283000 | 0.293729000 |
| H | 2.185870000 | -4.182383000 | 1.598239000 |
| C | -0.038030000 | -4.123446000 | -0.045578000 |
| C | -0.556714000 | -4.610916000 | 1.278940000 |
| H | -0.044617000 | -4.130307000 | 2.123319000 |
| H | -0.414646000 | -5.699520000 | 1.379359000 |
| H | -1.626791000 | -4.403529000 | 1.390691000 |
| C | -0.758440000 | -4.211007000 | -1.307450000 |
| C | -2.224250000 | -4.497086000 | -1.419580000 |


| H | -2.826466000 | -3.811763000 | -0.806640000 |
| :--- | :---: | :---: | :---: |
| H | -2.570722000 | -4.412574000 | -2.457686000 |
| H | -2.460656000 | -5.517539000 | -1.078436000 |
| Ga | 0.099408000 | -1.983057000 | -0.253703000 |
| C | 0.173481000 | -4.042231000 | -2.354516000 |
| C | -0.102494000 | -4.007738000 | -3.826949000 |
| H | 0.155073000 | -3.032136000 | -4.267753000 |
| H | 0.492914000 | -4.766555000 | -4.358046000 |
| H | -1.157382000 | -4.203661000 | -4.054054000 |
| Ni | -1.554304000 | -0.521160000 | -1.367888000 |
| Ni | 1.028663000 | -0.253711000 | -1.601692000 |
| H | 1.738772000 | 2.830324000 | -2.360034000 |
| H | 2.615607000 | 2.963670000 | -0.842825000 |
| H | 2.144064000 | 4.438993000 | -1.715467000 |
| C | -0.214989000 | 0.103033000 | 2.564859000 |
| C | 0.793505000 | -0.786433000 | 2.579238000 |
| C | 1.259659000 | -1.789709000 | 3.501277000 |
| C | 2.578288000 | -2.276336000 | 3.428127000 |
| C | 3.044331000 | -3.217658000 | 4.340608000 |
| H | 4.069670000 | -3.582731000 | 4.271950000 |
| C | 2.194664000 | -3.702067000 | 5.341650000 |
| H | 2.554471000 | -4.447246000 | 6.051264000 |
| C | 0.881515000 | -3.224005000 | 5.432826000 |
| H | 0.220704000 | -3.593763000 | 6.217392000 |
| H | 3.215559000 | -1.883420000 | 2.638370000 |
| C | 0.418063000 | -2.274229000 | 4.527812000 |
| H | -0.596588000 | -1.885043000 | 4.601570000 |
| C | -0.660437000 | 1.008106000 | 3.623292000 |
| C | 0.265891000 | 1.611271000 | 4.495601000 |
| H | 1.330136000 | 1.451606000 | 4.321807000 |
| C | -0.172050000 | 2.399902000 | 5.558164000 |
| H | 0.556372000 | 2.869274000 | 6.220450000 |
| C | -1.541349000 | 2.583533000 | 5.781741000 |
| C | -2.468730000 | 1.984146000 | 4.924077000 |
| H | -3.536997000 | 2.126610000 | 5.090136000 |
| H | -1.882026000 | 3.195718000 | 6.616867000 |
| C | -2.032894000 | 1.219990000 | 3.843286000 |
| H | -2.741870000 | 0.763074000 | 3.150954000 |
| C | 1.258216000 | 0.235814000 | -3.460663000 |
| C | 0.069140000 | -0.232065000 | -3.256351000 |
| C | -1.290478000 | -0.406774000 | -3.696813000 |
| C | -2.121270000 | -1.455152000 | -3.190455000 |
|  | 2.0 |  |  |


| C | -3.453839000 | -1.578808000 | -3.628594000 |
| :--- | ---: | ---: | ---: |
| H | -4.060166000 | -2.397122000 | -3.241249000 |
| C | -3.986876000 | -0.671826000 | -4.532904000 |
| H | -5.023580000 | -0.761112000 | -4.855382000 |
| C | -3.184636000 | 0.377360000 | -5.022621000 |
| H | -3.601860000 | 1.090923000 | -5.733836000 |
| H | -1.658487000 | -2.275700000 | -2.632134000 |
| C | -1.868933000 | 0.518727000 | -4.607940000 |
| H | -1.250136000 | 1.331064000 | -4.986182000 |
| C | 2.244944000 | 0.659917000 | -4.416140000 |
| C | 2.292820000 | 1.988125000 | -4.888965000 |
| H | 1.552380000 | 2.706437000 | -4.538502000 |
| C | 3.275730000 | 2.387673000 | -5.792665000 |
| H | 3.296578000 | 3.421528000 | -6.139074000 |
| C | 4.227759000 | 1.475318000 | -6.257524000 |
| C | 4.177261000 | 0.149521000 | -5.813332000 |
| H | 4.904940000 | -0.576718000 | -6.177510000 |
| H | 4.996931000 | 1.791893000 | -6.961353000 |
| C | 3.205149000 | -0.253716000 | -4.900821000 |
| H | 3.166402000 | -1.285199000 | -4.553272000 |
| C | -3.068914000 | -0.406840000 | -0.145042000 |
| C | -2.895625000 | -1.250183000 | 0.877856000 |
| C | -3.535088000 | -2.313942000 | 1.588820000 |
| C | -3.060312000 | -2.722641000 | 2.853919000 |
| C | -3.681184000 | -3.755031000 | 3.548062000 |
| H | -3.299770000 | -4.058578000 | 4.523324000 |
| C | -4.785074000 | -4.412579000 | 2.991097000 |
| H | -5.266322000 | -5.228051000 | 3.530951000 |
| C | -5.266718000 | -4.021439000 | 1.735242000 |
| H | -6.124716000 | -4.533522000 | 1.298301000 |
| H | -2.188020000 | -2.210407000 | 3.258065000 |
| C | -4.653951000 | -2.984103000 | 1.039183000 |
| H | -5.024746000 | -2.673427000 | 0.062416000 |
| C | -4.215011000 | 0.438441000 | -0.486905000 |
| C | -5.278272000 | 0.601699000 | 0.425627000 |
|  |  | -2000 |  |


| H | -5.210375000 | 0.127263000 | 1.404974000 |
| :---: | :---: | :---: | :---: |
| C | -6.395201000 | 1.360786000 | 0.086010000 |
| H | -7.206186000 | 1.482336000 | 0.805059000 |
| C | -6.479691000 | 1.968238000 | -1.173173000 |
| C | -5.429679000 | 1.818643000 | -2.082353000 |
| H | -5.481890000 | 2.292751000 | -3.063127000 |
| H | -7.356238000 | 2.559866000 | -1.438013000 |
| C | -4.304381000 | 1.073754000 | -1.735743000 |
| H | -3.474220000 | 0.971992000 | -2.433502000 |
| Ga | 3.070820000 | 0.066790000 | -0.401922000 |
| C | 4.890816000 | 1.515620000 | 0.179899000 |
| C | 4.868796000 | 2.944544000 | 0.623088000 |
| H | 4.279936000 | 3.083704000 | 1.536539000 |
| H | 5.894504000 | 3.286920000 | 0.838066000 |
| H | 4.462651000 | 3.611727000 | -0.145992000 |
| C | 4.989147000 | 0.387091000 | 1.058184000 |
| C | 4.900339000 | 0.453497000 | 2.552150000 |
| H | 3.882521000 | 0.701248000 | 2.891368000 |
| H | 5.579021000 | 1.219600000 | 2.954515000 |
| H | 5.172154000 | -0.503198000 | 3.013559000 |
| C | 5.203849000 | -0.777554000 | 0.260097000 |
| C | 5.545923000 | -2.147227000 | 0.757844000 |
| H | 5.064020000 | -2.379291000 | 1.715174000 |
| H | 6.633623000 | -2.237356000 | 0.910889000 |
| H | 5.254053000 | -2.927271000 | 0.044966000 |
| C | 5.221510000 | -0.373171000 | -1.121530000 |
| C | 5.572931000 | -1.243629000 | -2.285999000 |
| H | 5.276684000 | -2.286053000 | -2.121047000 |
| H | 5.090057000 | -0.897527000 | -3.207050000 |
| H | 6.661062000 | -1.234729000 | -2.460549000 |
| C | 5.031432000 | 1.051552000 | -1.168327000 |
| C | 5.089748000 | 1.905156000 | -2.397263000 |
| H | 6.079872000 | 2.377458000 | -2.497014000 |
| H | 4.911411000 | 1.318075000 | -3.305401000 |
| H | 4.343096000 | 2.708290000 | -2.377910000 |

## [ $\mathrm{Ni}_{4} \mathrm{Ga}_{3}$ ] $\left(\mathrm{Cp}{ }^{*}\right)_{3}(\mathrm{dpa})_{3}$ : tetrahedron

| Ni | 0.606123000 | -1.600139000 | 1.469104000 |
| :---: | :---: | :---: | :---: |
| Ni | -0.934815000 | 0.288502000 | 1.077389000 |
| H | 0.453948000 | 2.158968000 | -4.745512000 |
| C | 0.428549000 | 1.076983000 | -4.570910000 |
| H | 0.176421000 | 0.587825000 | -5.523124000 |
| H | -0.395670000 | 0.875731000 | -3.872095000 |
| C | 1.735098000 | 0.572040000 | -4.046593000 |
| C | 2.855157000 | 1.343567000 | -3.616189000 |
| C | 3.000937000 | 2.834584000 | -3.618279000 |
| H | 2.133727000 | 3.326791000 | -4.073772000 |
| H | 3.889199000 | 3.135893000 | -4.194214000 |
| H | 3.117114000 | 3.247445000 | -2.605256000 |
| C | 3.890267000 | 0.441357000 | -3.219165000 |
| C | 5.272327000 | 0.855437000 | -2.821066000 |
| H | 5.262768000 | 1.628074000 | -2.040021000 |
| H | 5.815618000 | 1.273849000 | -3.683930000 |
| H | 5.857284000 | 0.008072000 | -2.447250000 |
| C | 3.419759000 | -0.902796000 | -3.424026000 |
| C | 4.250017000 | -2.142963000 | -3.334820000 |
| H | 4.986999000 | -2.091712000 | -2.525023000 |
| H | 3.636332000 | -3.032000000 | -3.157338000 |
| H | 4.803919000 | -2.300590000 | -4.274321000 |
| Ga | 2.063057000 | -0.086744000 | -1.754748000 |
| C | 2.074811000 | -0.818788000 | -3.926804000 |
| C | 1.190394000 | -1.962880000 | -4.321031000 |
| H | 0.273462000 | -1.998215000 | -3.711104000 |
| H | 0.886510000 | -1.881412000 | -5.376056000 |
| H | 1.704995000 | -2.921838000 | -4.192666000 |
| H | 3.180392000 | -2.111047000 | 5.005494000 |
| C | 3.911511000 | -1.293060000 | 5.062168000 |
| H | 4.797504000 | -1.681502000 | 5.590641000 |
| H | 3.473513000 | -0.506587000 | 5.686681000 |
| C | 4.285335000 | -0.780251000 | 3.705422000 |
| C | 4.747417000 | -1.604222000 | 2.620593000 |
| C | 4.904078000 | -3.091315000 | 2.719748000 |
| H | 3.940791000 | -3.614218000 | 2.809167000 |
| H | 5.500209000 | -3.352724000 | 3.607186000 |
| H | 5.418820000 | -3.504076000 | 1.844934000 |
| C | 5.147251000 | -0.738286000 | 1.553995000 |
| C | 5.716138000 | -1.124593000 | 0.225779000 |
| H | 6.011169000 | -2.179915000 | 0.201250000 |
| H | 6.608105000 | -0.523737000 | -0.004867000 |
| H | 4.997217000 | -0.964404000 | -0.591989000 |
| C | 4.942393000 | 0.614903000 | 1.978749000 |
| C | 5.215396000 | 1.821388000 | 1.134859000 |
| H | 4.543653000 | 1.863833000 | 0.263237000 |
| H | 5.072389000 | 2.749462000 | 1.701699000 |
| H | 6.249013000 | 1.819085000 | 0.756548000 |
| Ga | 2.792533000 | -0.489209000 | 1.915156000 |
| C | 4.442290000 | 0.591503000 | 3.319227000 |


|  |  |  |  |
| :--- | ---: | ---: | ---: |
| H | 4.707560000 | -6.084211000 | -2.060063000 |
| C | 4.332318000 | -4.432428000 | -0.715671000 |
| H | 5.346563000 | -4.429373000 | -0.313505000 |
| H | 0.718683000 | -4.440121000 | -2.121279000 |
| C | 3.397701000 | -3.508851000 | -0.249002000 |
| H | 3.654079000 | -2.788475000 | 0.522503000 |
| C | -0.066817000 | 1.895363000 | 0.187119000 |
| C | -0.549850000 | 2.967341000 | -0.667191000 |
| C | 0.018510000 | 3.215754000 | -1.923263000 |
| C | -0.368376000 | 4.325838000 | -2.672074000 |
| H | 0.093434000 | 4.514724000 | -3.642373000 |
| C | -1.344100000 | 5.200286000 | -2.186405000 |
| H | -1.647366000 | 6.067414000 | -2.772835000 |
| C | -1.933218000 | 4.950532000 | -0.941317000 |
| H | -2.696385000 | 5.626027000 | -0.553148000 |
| H | 0.786049000 | 2.532838000 | -2.278862000 |
| C | -1.544039000 | 3.844781000 | -0.187488000 |
| H | -1.985467000 | 3.657732000 | 0.790988000 |
| C | 0.313994000 | 1.815072000 | 1.464182000 |
| C | 0.411966000 | 2.681115000 | 2.619356000 |
| C | -0.716239000 | 2.953493000 | 3.416621000 |
| C | -0.621246000 | 3.813345000 | 4.506347000 |
| H | -1.498170000 | 3.993682000 | 5.128084000 |
| C | 0.595515000 | 4.432025000 | 4.812352000 |
| H | 0.669544000 | 5.102192000 | 5.668780000 |
| C | 1.716075000 | 4.180810000 | 4.016552000 |
| H | 2.666916000 | 4.662778000 | 4.246935000 |


|  | -1.656690000 | 2.455746000 | 3.180006000 |
| :--- | ---: | ---: | ---: |
| C | 1.629402000 | 3.304689000 | 2.935634000 |
| H | 2.497920000 | 3.085573000 | 2.314989000 |
| C | -1.319319000 | -1.265469000 | 2.200599000 |
| C | -2.388144000 | -2.167380000 | 2.576834000 |
| C | -3.728983000 | -1.798389000 | 2.391129000 |
| C | -4.762122000 | -2.623811000 | 2.834732000 |
| H | -5.798970000 | -2.318303000 | 2.689799000 |
| C | -4.471361000 | -3.844312000 | 3.447684000 |
| H | -5.277708000 | -4.499517000 | 3.777213000 |
| C | -3.136445000 | -4.223736000 | 3.632004000 |
| H | -2.900846000 | -5.179506000 | 4.100382000 |
| H | -3.936403000 | -0.846755000 | 1.902879000 |
| C | -2.104260000 | -3.392620000 | 3.211629000 |
| H | -1.063232000 | -3.683488000 | 3.348218000 |
| C | -0.360592000 | -0.624314000 | 2.869022000 |
| C | -0.278996000 | -0.059267000 | 4.206941000 |
| C | -1.454866000 | 0.033194000 | 4.981340000 |
| C | -1.425971000 | 0.596583000 | 6.254115000 |
| H | -2.345058000 | 0.657819000 | 6.838124000 |
| C | -0.227860000 | 1.091736000 | 6.779017000 |
| H | -0.207605000 | 1.546194000 | 7.769617000 |
| C | 0.942402000 | 1.006273000 | 6.020672000 |
| H | 1.877043000 | 1.403493000 | 6.417699000 |
| H | -2.390663000 | -0.337728000 | 4.564843000 |
| C | 0.913736000 | 0.431892000 | 4.752968000 |
| H | 1.818466000 | 0.373019000 | 4.151187000 |

## $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4}:$ octahedron

| Ni | 1.249914000 | -0.124102000 | 1.409338000 |
| :--- | ---: | ---: | ---: |
| Ni | -1.153065000 | -0.280632000 | 1.215874000 |
| H | 3.272408000 | 5.052911000 | 1.135062000 |
| C | 2.366283000 | 5.032291000 | 1.750780000 |
| H | 2.111640000 | 6.071570000 | 2.013603000 |
| H | 2.610513000 | 4.523870000 | 2.697334000 |
| C | 1.231794000 | 4.357361000 | 1.049457000 |
| C | 1.204094000 | 3.896168000 | -0.247710000 |
| C | 2.239697000 | 4.058522000 | -1.311157000 |
| C | -0.140019000 | 3.294528000 | -0.494036000 |
| C | -0.827859000 | 3.631981000 | -1.808288000 |
| H | -0.179831000 | 3.442608000 | -2.670991000 |
| H | -1.094130000 | 4.701547000 | -1.813864000 |
| H | -1.749771000 | 3.056100000 | -1.945950000 |
| C | -0.909447000 | 3.529384000 | 0.772785000 |
| C | -2.350217000 | 3.183599000 | 0.945550000 |
| H | -2.946865000 | 3.46927000 | 0.065703000 |
| H | -2.500190000 | 2.100555000 | 1.085792000 |
| H | -2.776714000 | 3.685415000 | 1.822974000 |
| Ga | 0.371388000 | 1.321039000 | -0.313454000 |
| C | -0.071851000 | 4.138251000 | 1.674051000 |
| C | -0.383944000 | 4.575832000 | 3.067932000 |
| H | 0.183819000 | 3.998526000 | 3.812586000 |
| H | -0.122822000 | 5.635054000 | 3.217358000 |
| H | -1.445341000 | 4.450095000 | 3.307988000 |
| H | 3.504628000 | -5.536283000 | -1.709199000 |
| C | 2.626255000 | -5.371624000 | -2.343695000 |
| H | 2.375728000 | -6.323131000 | -2.838639000 |
| H | 2.921884000 | -4.674153000 | -3.144059000 |
| C | 1.466904000 | -4.842887000 | -1.561656000 |
| C | 1.417359000 | -4.587043000 | -0.205809000 |
| C | 2.463946000 | -4.914333000 | 0.81082000 |
| H | 3.232739000 | -5.564899000 | 0.382236000 |
| H | 2.027519000 | -5.427951000 | 1.678185000 |
| H | 2.989456000 | -4.022822000 | 1.189687000 |
| C | 0.066347000 | -4.039480000 | 0.108224000 |
| C | -0.640925000 | -4.477599000 | 1.379495000 |
| H | -0.890498000 | -5.549111000 | 1.310937000 |
| H | -1.574771000 | -3.92619000 | 1.537451000 |
| H | -0.019163000 | -4.331945000 | 2.269372000 |
| C | -0.694572000 | -4.125793000 | -1.183649000 |
| C | -2.160789000 | -3.876060000 | -1.295885000 |
| H | -2.426529000 | -2.829641000 | -1.074463000 |
| H | -2.523077000 | -4.098535000 | -2.305815000 |
| H | -2.726578000 | -4.496355000 | -0.583082000 |
| Ga | 0.494034000 | -2.024148000 | 0.043679000 |
| C | 0.168186000 | -4.560123000 | -2.162237000 |
| C | -0.114373000 | -4.760935000 | -3.615604000 |
| H | 0.558816000 | -4.154470000 | -4.239070000 |
| H | 0.036245000 | -5.811073000 | -3.912835000 |
| H | -1.138572000 | -4.475801000 | -3.880149000 |
| Ni | -1.073192000 | -0.586316000 | -1.192138000 |
| Ni | 1.305637000 | -0.449907000 | -1.670144000 |
| H | 2.369165000 | 3.140985000 | -1.898313000 |
| H | 3.219419000 | 4.315654000 | -0.890937000 |
| H | 1.956173000 | 4.849821000 | -2.025069000 |
| C | -0.169066000 | 0.150160000 | 2.824232000 |
| C | 0.449256000 | -1.044270000 | 2.849266000 |
|  |  |  |  |


| C | 0.600443000 | -2.131188000 | 3.787153000 |
| :---: | :---: | :---: | :---: |
| C | 1.665355000 | -3.042091000 | 3.664548000 |
| C | 1.824659000 | -4.078585000 | 4.580522000 |
| H | 2.655338000 | -4.775858000 | 4.469392000 |
| C | 0.915968000 | -4.229328000 | 5.633168000 |
| H | 1.032227000 | -5.048120000 | 6.343345000 |
| C | -0.139755000 | -3.320758000 | 5.776878000 |
| H | -0.840267000 | -3.426701000 | 6.605902000 |
| H | 2.362481000 | -2.913796000 | 2.837945000 |
| C | -0.294623000 | -2.276719000 | 4.869645000 |
| H | -1.097955000 | -1.551068000 | 4.995708000 |
| C | -0.580443000 | 1.071092000 | 3.881256000 |
| C | 0.340399000 | 1.455793000 | 4.874735000 |
| H | 1.372862000 | 1.114195000 | 4.796866000 |
| C | -0.065092000 | 2.248817000 | 5.947105000 |
| H | 0.659681000 | 2.538133000 | 6.708828000 |
| C | -1.394896000 | 2.670395000 | 6.049276000 |
| C | -2.313914000 | 2.297578000 | 5.064373000 |
| H | -3.352744000 | 2.621530000 | 5.135918000 |
| H | -1.711175000 | 3.288094000 | 6.889664000 |
| C | -1.909818000 | 1.512422000 | 3.985512000 |
| H | -2.623983000 | 1.211100000 | 3.218669000 |
| C | 2.332011000 | 0.415784000 | -0.177305000 |
| C | 2.361190000 | -1.004171000 | -0.044320000 |
| C | 3.605691000 | -1.781694000 | 0.059137000 |
| C | 4.074626000 | -2.530014000 | -1.030220000 |
| C | 5.267259000 | -3.246369000 | -0.937547000 |
| H | 5.617085000 | -3.826112000 | -1.792281000 |
| C | 6.013177000 | -3.223281000 | 0.244842000 |
| H | 6.943096000 | -3.787305000 | 0.317677000 |
| C | 5.560876000 | -2.469381000 | 1.332446000 |
| H | 6.138733000 | -2.439836000 | 2.256650000 |
| H | 3.480639000 | -2.551027000 | -1.944743000 |
| C | 4.366463000 | -1.755844000 | 1.240591000 |
| H | 4.000947000 | -1.167230000 | 2.083713000 |
| C | 3.550324000 | 1.240627000 | -0.186906000 |
| C | 4.443059000 | 1.178098000 | -1.270085000 |
| H | 4.200136000 | 0.527289000 | -2.111529000 |
| C | 5.619161000 | 1.925320000 | -1.265832000 |
| H | 6.300741000 | 1.866912000 | -2.115101000 |
| C | 5.927179000 | 2.744247000 | -0.174266000 |
| C | 5.052393000 | 2.800439000 | 0.914521000 |
| H | 5.289305000 | 3.429087000 | 1.773285000 |
| H | 6.846004000 | 3.330751000 | -0.170856000 |
| C | 3.871902000 | 2.056969000 | 0.906749000 |
| H | 3.176476000 | 2.105590000 | 1.745961000 |
| C | 0.549078000 | 0.472342000 | -3.102172000 |
| C | -0.300887000 | -0.567212000 | -2.974924000 |
| C | -0.935963000 | -1.353423000 | -4.044445000 |
| C | -2.271883000 | -1.778508000 | -3.946992000 |
| C | -2.883578000 | -2.463101000 | -4.996754000 |
| H | -3.923521000 | -2.777561000 | -4.902517000 |
| C | -2.167477000 | -2.747538000 | -6.162805000 |
| H | -2.642253000 | -3.290040000 | -6.980367000 |
| C | -0.835598000 | -2.333663000 | -6.271556000 |
| H | -0.267731000 | -2.554178000 | -7.176123000 |
| H | -2.833965000 | -1.553247000 | -3.040080000 |
| C | -0.226490000 | -1.643095000 | -5.226198000 |

H
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C

## $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4}$ ：tetrahedron

| Ni | 0.776492000 | －1．154752000 | 1.615902000 |
| :---: | :---: | :---: | :---: |
| Ni | －0．994756000 | 0.558995000 | 0.650806000 |
| H | 2.154298000 | －2．388805000 | 4.684688000 |
| C | 3.084164000 | －1．930160000 | 5.048668000 |
| H | 3.632626000 | －2．707254000 | 5.604487000 |
| H | 2.803369000 | －1．143220000 | 5.755481000 |
| C | 3.920288000 | －1．409534000 | 3.922757000 |
| C | 4.388123000 | －2．228477000 | 2.842320000 |
| C | 4.056536000 | －3．681248000 | 2.697365000 |
| H | 2.984000000 | －3．837165000 | 2.509581000 |
| H | 4.310725000 | －4．230558000 | 3.616627000 |
| H | 4.596812000 | －4．143632000 | 1.864623000 |
| C | 5.241401000 | －1．435083000 | 2.017625000 |
| C | 6.141941000 | －1．902751000 | 0.916155000 |
| H | 6.094802000 | －2．991572000 | 0.805011000 |
| H | 7.185288000 | －1．638262000 | 1.145573000 |
| H | 5.903520000 | －1．463001000 | －0．062059000 |
| C | 5.261995000 | －0．104046000 | 2.556216000 |
| C | 6.140116000 | 1.007822000 | 2.074543000 |
| H | 6.237091000 | 1.003666000 | 0.980710000 |
| H | 5.745746000 | 1.986549000 | 2.370504000 |
| H | 7.156732000 | 0.918967000 | 2.493044000 |
| Ga | 3.068542000 | －0．375131000 | 1.898885000 |
| C | 4.472691000 | －0．099726000 | 3.762104000 |
| C | 4.468994000 | 1.021655000 | 4.753530000 |
| H | 3.798339000 | 0.813655000 | 5.592752000 |
| H | 5.481349000 | 1.165868000 | 5.162920000 |
| H | 4.161012000 | 1.974372000 | 4.303690000 |
| H | －4．396475000 | －3．140853000 | －0．535714000 |
| C | －4．374697000 | －3．182756000 | －1．632728000 |
| H | －5．419452000 | －3．233459000 | －1．977599000 |
| H | －3．890008000 | －4．124539000 | －1．912739000 |
| C | －3．686707000 | －2．003872000 | －2．247163000 |
| C | －4．182969000 | －0．657565000 | －2．144702000 |
| C | －5．462541000 | －0．262990000 | －1．477904000 |
| H | －5．533509000 | －0．649082000 | －0．452547000 |
| H | －6．326003000 | －0．657104000 | －2．039290000 |
| H | －5．565606000 | 0.825950000 | －1．430811000 |
| C | －3．390887000 | 0.174058000 | －3．021133000 |
| C | －3．709018000 | 1.600012000 | －3．347900000 |
| H | －3．852756000 | 2.214781000 | －2．448811000 |
| H | －4．640115000 | 1.659356000 | －3．933068000 |
| H | －2．912281000 | 2.058488000 | －3．941933000 |
| C | －2．393204000 | －0．657653000 | －3．620932000 |
| C | －1．341988000 | －0．251542000 | －4．606056000 |
| H | －1．343076000 | 0.830199000 | －4．779455000 |
| H | －0．334187000 | －0．522292000 | －4．260221000 |
| H | －1．502092000 | －0．750094000 | －5．574810000 |
| Ga | －2．122505000 | －0．503229000 | －1．215715000 |
| C | －2．579712000 | －1．996776000 | －3．145083000 |
| C | －1．717535000 | －3．156643000 | －3．538696000 |
| H | －2．145612000 | －4．110769000 | －3．205422000 |
| H | －1．604620000 | －3．211129000 | －4．631428000 |
| H | －0．703758000 | －3．080338000 | －3．112818000 |
| Ni | 0.163721000 | －1．038992000 | －0．790066000 |
| Ni | 1.665013000 | 0.743893000 | 0.224319000 |
| C | －0．090389000 | －2．567798000 | 0.499500000 |
| C | －1．023957000 | －3．565272000 | 0.992535000 |
| C | －1．114941000 | －3．830402000 | 2.372501000 |
| C | －1．983889000 | －4．807503000 | 2.849910000 |
| H | －2．046797000 | －4．994089000 | 3.922336000 |
| C | －2．778729000 | －5．541668000 | 1.963069000 |
| H | －3．464926000 | －6．300448000 | 2.338695000 |
| C | －2．685807000 | －5．292942000 | 0.591730000 |
| H | －3．298290000 | －5．862366000 | －0．108130000 |
| H | －0．505587000 | －3．240095000 | 3.056981000 |
| C | －1．818318000 | －4．312639000 | 0.109516000 |


| -5.051863000 | -4.031623000 | 2.819157000 |
| ---: | ---: | ---: |
| -5.624607000 | -4.814395000 | 3.316486000 |
| -5.361643000 | -3.666799000 | 1.503053000 |
| -6.175829000 | -4.165931000 | 0.976944000 |
| -2.442576000 | -1.904067000 | 3.358762000 |
| -4.628598000 | -2.676256000 | 0.857091000 |
| -4.853116000 | -2.397060000 | -0.171780000 |
| -3.670570000 | 0.622994000 | -0.890879000 |
| -4.892537000 | 0.918965000 | -0.253096000 |
| -5.087550000 | 0.496985000 | 0.733061000 |
| -5.826059000 | 1.753767000 | -0.860745000 |
| -6.762489000 | 1.979762000 | -0.349690000 |
| -5.562716000 | 2.310002000 | -2.118286000 |
| -4.356432000 | 2.021615000 | -2.762131000 |
| -4.141018000 | 2.451732000 | -3.740422000 |
| -6.292962000 | 2.967203000 | -2.590432000 |
| -3.418675000 | 1.189455000 | -2.153125000 |
| -2.474205000 | 0.967076000 | -2.653273000 |

正

| H | 6.045179000 | -2.100598000 | -4.284984000 |
| ---: | ---: | ---: | ---: |
| C | 3.904378000 | -2.167684000 | -3.977309000 |
| H | 3.731029000 | -2.887610000 | -4.777232000 |
| H | 4.496162000 | 0.341120000 | -1.073691000 |
| C | 2.829970000 | -1.700083000 | -3.228384000 |
| H | 1.817232000 | -2.049089000 | -3.429104000 |
| C | 0.878217000 | 0.559743000 | -1.652087000 |
| C | 0.620221000 | 1.645479000 | -2.586826000 |
| C | -0.546927000 | 2.423729000 | -2.550639000 |


| C | -0.722343000 | 3.495088000 | -3.424811000 |
| :--- | ---: | ---: | ---: |
| H | -1.637748000 | 4.084541000 | -3.368853000 |
| C | 0.263055000 | 3.808066000 | -4.364731000 |
| H | 0.124469000 | 4.644682000 | -5.049745000 |
| C | 1.431823000 | 3.039918000 | -4.415375000 |
| H | 2.208067000 | 3.273879000 | -5.144908000 |
| H | -1.314681000 | 2.180315000 | -1.822517000 |
| C | 1.614393000 | 1.977623000 | -3.533134000 |
| H | 2.529577000 | 1.387767000 | -3.568324000 |

## $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}$

| Ni | 7.293874000 | 7.627225000 |  |
| :---: | :---: | :---: | :---: |
| Ni | 9.302109000 | 10.235162000 | 7.863809000 |
| Ni | 9.522661000 | 8.061560000 | 9.644502000 |
| Ni | 7.570717000 | 9.758859000 | 10.061481000 |
| Ga | 9.946553000 | 11.250365000 | 5.909567000 |
| C | 11.818714000 | 11.190495000 | 4.443794000 |
| C | 12.798807000 | 10.059517000 | 4.395934000 |
| H | 13.054949000 | 9.698407000 | 5.401569000 |
| H | 12.403938000 | 9.201499000 | 3.841391000 |
| H | 13.736584000 | 10.371648000 | 3.909711000 |
| C | 11.948533000 | 12.349583000 | 5.274550000 |
| C | 13.113468000 | 12.641529000 | 6.167986000 |
| H | 12.944750000 | 13.547598000 | 6.761060000 |
| H | 13.326074000 | 11.821729000 | 6.867885000 |
| H | 14.025033000 | 12.801741000 | 5.571034000 |
| C | 10.835945000 | 13.215268000 | 5.016216000 |
| C | 10.589726000 | 14.550320000 | 5.651021000 |
| H | 10.945675000 | 14.575396000 | 6.689405000 |
| H | 11.102707000 | 15.356358000 | 5.102818000 |
| H | 9.519840000 | 14.796415000 | 5.664249000 |
| C | 10.022338000 | 12.594585000 | 4.008401000 |
| C | 8.813044000 | 13.201414000 | 3.366261000 |
| H | 8.195840000 | 13.753970000 | 4.087885000 |
| H | 8.178977000 | 12.438232000 | 2.896093000 |
| H | 9.101827000 | 13.911841000 | 2.575291000 |
| C | 10.631073000 | 11.339573000 | 3.657985000 |
| C | 10.121530000 | 10.372312000 | 2.633670000 |
| H | 10.438358000 | 9.346948000 | 2.862183000 |
| H | 9.024310000 | 10.374684000 | 2.583303000 |
| H | 10.495242000 | 10.615987000 | 1.626788000 |
| Ga | 7.279511000 | 7.200891000 | 6.113692000 |
| C | 5.057266000 | 6.318851000 | 5.628670000 |
| C | 3.895495000 | 6.475505000 | 6.558365000 |
| H | 4.076616000 | 5.977046000 | 7.518152000 |
| H | 3.692461000 | 7.532819000 | 6.772802000 |
| H | 2.977405000 | 6.042900000 | 6.130195000 |
| C | 5.985224000 | 5.229257000 | 5.615538000 |
| C | 5.960099000 | 4.056140000 | 6.546936000 |
| H | 6.959462000 | 3.625812000 | 6.687817000 |
| H | 5.592318000 | 4.349383000 | 7.539666000 |
| H | 5.299289000 | 3.257705000 | 6.174596000 |
| C | 6.940526000 | 5.470240000 | 4.576894000 |
| C | 8.012107000 | 4.533139000 | 4.107255000 |
| H | 8.109611000 | 3.674116000 | 4.781610000 |
| H | 7.771531000 | 4.137821000 | 3.107987000 |
| H | 8.997636000 | 5.015417000 | 4.040912000 |
| C | 6.609758000 | 6.731228000 | 3.959955000 |
| C | 7.273464000 | 7.319643000 | 2.753501000 |
| H | 8.331624000 | 7.034603000 | 2.693251000 |
| H | 7.221172000 | 8.416515000 | 2.758102000 |
| H | 6.790480000 | 6.974723000 | 1.824709000 |
| C | 5.427880000 | 7.237121000 | 4.602444000 |
| C | 4.656515000 | 8.448800000 | 4.189560000 |
| H | 4.153518000 | 8.921836000 | 5.041675000 |
| H | 5.298776000 | 9.208439000 | 3.728894000 |
| H | 3.881594000 | 8.180402000 | 3.453322000 |
| C | 8.019934000 | 6.803230000 | 10.046168000 |
| C | 7.442602000 | 6.295893000 | 11.280472000 |
| C | 7.569161000 | 4.926382000 | 11.582933000 |
| C | 7.014119000 | 4.401252000 | 12.749120000 |
| H | 7.123304000 | 3.338047000 | 12.966247000 |
| C | 6.321381000 | 5.230646000 | 13.636201000 |
| H | 5.884492000 | 4.817879000 | 14.545829000 |
| C | 6.189278000 | 6.591076000 | 13.345604000 |
| H | 5.641649000 | 7.246566000 | 14.022842000 |
| H | 8.103996000 | 4.278384000 | 10.889349000 |
| C | 6.741916000 | 7.115228000 | 12.182207000 |
| H | 6.636028000 | 8.174310000 | 11.953474000 |
| C | 8.658472000 | 6.364008000 | 8.956612000 |
| C | 9.515941000 | 5.271820000 | 8.534474000 |
| C | 10.430383000 | 4.731482000 | 9.466929000 |
| C | 11.291667000 | 3.700523000 | 9.103256000 |
| H | 11.989815000 | 3.299819000 | 9.839260000 |
| C | 11.261253000 | 3.176850000 | 7.805365000 |
| H | 11.935707000 | 2.368531000 | 7.522362000 |
| C | 10.365555000 | 3.707210000 | 6.874822000 |


| H | 00 | 00 | 5.854976000 |
| :---: | :---: | :---: | :---: |
| H | 10.457552000 | 5.141260000 | 10.476705000 |
| C | 9.509495000 | 4.746086000 | 7.234703000 |
| H | 8.827784000 | 5.173064000 | 6.502409000 |
| C | 9.429001000 | 8.750590000 | 11.496501000 |
| C | 10.064764000 | 7.858895000 | 12.460667000 |
| C | 9.517530000 | 7.675567000 | 13.749157000 |
| H | 8.626935000 | 8.235278000 | 14.026556000 |
| C | 10.081909000 | 6.768812000 | 14.641353000 |
| H | 9.628445000 | 6.626790000 | 15.622896000 |
| C | 11.214528000 | 6.031051000 | 14.279294000 |
| C | 11.780756000 | 6.214033000 | 13.013884000 |
| H | 12.667618000 | 5.649601000 | 12.723524000 |
| H | 11.649790000 | 5.315861000 | 14.977687000 |
| C | 11.209631000 | 7.110596000 | 12.113562000 |
| H | 11.639980000 | 7.251814000 | 11.122147000 |
| C | 8.598084000 | 9.772799000 | 11.669885000 |
| C | 8.463127000 | 10.784495000 | 12.699772000 |
| C | 9.570766000 | 11.154919000 | 13.493651000 |
| H | 10.524535000 | 10.655619000 | 13.333294000 |
| C | 9.457962000 | 12.155578000 | 14.454438000 |
| H | 10.330128000 | 12.434367000 | 15.0 |
| C | 8.240476000 | 12.818143000 | 14.646347000 |
| C | 7.129462000 | 12.455169000 | 13.876485000 |
| H | 6.174932000 | 12.962255000 | 14.021158000 |
| H | 8.158098000 | 13.611552000 | 15.389411000 |
| C | 7.240860000 | 11.450793000 | 12.918902000 |
| H | 6.385107000 | 11.170612000 | 12.306326000 |
| C | 12.221185000 | 9.687181000 | 9.628565000 |
| C | 13.326623000 | 9.917606000 | 8.774586000 |
| H | 13.268782000 | 9.573273000 | 7.741543000 |
| C | 14.464879000 | 10.563768000 | 9.244916000 |
| H | 15.310085000 | 10.727853000 | 8.575074000 |
| C | 14.525836000 | 11.008452000 | 10.571916000 |
| C | 13.437097000 | 10.795033000 | 11.423180000 |
| H | 13.471162000 | 11.152176000 | 12.452576000 |
| H | 15.415742000 | 11.521933000 | 10.936344000 |
| C | 12.302279000 | 10.137535000 | 10.960656000 |
| H | 11.442394000 | 9.978426000 | 11.604868000 |
| C | 11.051987000 | 9.034321000 | 9.109500000 |
| C | 10.543225000 | 8.671188000 | 7.923332000 |
| C | 10.986954000 | 7.809782000 | 6.842227000 |
| C | 12.054931000 | 6.911228000 | 7.065502000 |
| H | 12.496918000 | 6.867097000 | 8.060687000 |
| C | 12.523124000 | 6.086557000 | 6.050028000 |
| H | 13.345601000 | 5.400208000 | 6.250888000 |
| C | 11.928529000 | 6.118046000 | 4.781510000 |
| C | 10.857823000 | 6.982076000 | 4.550530000 |
| H | 10.389924000 | 7.017837000 | 3.565884000 |
| H | 12.292801000 | 5.467432000 | 3.986536000 |
| C | 10.388084000 | 7.816254000 | 5.567395000 |
| H | 9.586082000 | 8.527944000 | 5.369080000 |
| C | 7.620609000 | 11.502061000 | 9.392653000 |
| C | 6.501139000 | 12.385583000 | 9.149541000 |
| C | 6.603638000 | 13.429296000 | 8.204088000 |
| H | 7.524503000 | 13.520623000 | 7.627838000 |
| C | 5.542733000 | 14.304467000 | 7.998083000 |
| H | 5.633290000 | 15.098692000 | 7.256264000 |
| C | 4.358935000 | 14.167576000 | 8.732670000 |
| C | 4.239744000 | 13.134591000 | 9.667339000 |
| H | 3.317227000 | 13.015848000 | 10.236554000 |
| H | 3.531564000 | 14.858613000 | 8.570787000 |
| C | 5.292857000 | 12.246477000 | 9.862231000 |
| H | 5.210852000 | 11.425368000 | 10.573957000 |
| C | 8.933411000 | 11.640166000 | 9.107303000 |
| C | 9.947961000 | 12.498233000 | 9.677566000 |
| C | 9.668646000 | 13.236989000 | 10.850702000 |
| H | 8.688919000 | 13.139070000 | 11.314960000 |
| C | 10.636831000 | 14.062794000 | 11.413578000 |
| H | 10.407510000 | 14.612352000 | 12.326513000 |
| C | 11.897222000 | 14.179002000 | 10.818184000 |
| C | 12.184029000 | 13.464309000 | 9.649346000 |
| H | 13.169384000 | 13.537545000 | 9.190715000 |
| H | 12.656750000 | 14.820600000 | 11.265796000 |
| C | 11.223776000 | 12.630781000 | 9.090800000 |
| H | 11.438348000 | 12.057752000 | 8.191086000 |


|  |  |  |  |
| :--- | :---: | :---: | :---: |
| C | 5.581422000 | 8.251404000 | 9.138036000 |
| C | 4.625420000 | 7.711824000 | 10.056268000 |
| C | 4.515637000 | 6.318380000 | 10.236117000 |
| H | 5.188300000 | 5.669725000 | 9.676879000 |
| C | 3.596146000 | 5.790632000 | 11.135676000 |
| H | 3.534219000 | 4.711321000 | 11.271399000 |
| C | 2.783252000 | 6.642037000 | 11.890499000 |
| C | 2.885731000 | 8.028088000 | 11.725243000 |
| H | 2.255873000 | 8.696083000 | 12.313602000 |
| H | 2.078629000 | 6.228628000 | 12.611913000 |
| C | 3.793357000 | 8.561466000 | 10.813828000 |
| H | 3.885843000 | 9.639979000 | 10.687516000 |


|  |  |  |  |
| :--- | :---: | :---: | :---: |
| C | 5.951153000 | 9.045092000 | 8.189603000 |
| C | 5.551738000 | 10.031191000 | 7.223754000 |
| C | 6.438805000 | 10.473321000 | 6.229348000 |
| H | 7.451682000 | 10.064939000 | 6.217080000 |
| C | 6.055647000 | 11.442278000 | 5.307635000 |
| H | 6.768643000 | 11.781929000 | 4.556884000 |
| C | 4.770942000 | 11.986713000 | 5.358111000 |
| C | 3.874219000 | 11.555775000 | 6.343508000 |
| H | 2.874891000 | 11.987170000 | 6.397553000 |
| H | 4.469816000 | 12.752061000 | 4.642768000 |
| C | 4.257836000 | 10.590326000 | 7.270074000 |
| H | 3.567726000 | 10.264108000 | 8.047445000 |

## [NiAl](Cp*)(tebd)(cod)

| Ni | 10.257110000 | 5.590030000 | 7.834240000 |
| :--- | :---: | :---: | :---: |
| Al | 9.211130000 | 3.155310000 | 7.909300000 |
| C | 11.888890000 | 4.805160000 | 6.878690000 |
| H | 11.655520000 | 3.800590000 | 6.520190000 |
| C | 12.166450000 | 4.946660000 | 8.248760000 |
| H | 12.097510000 | 4.039510000 | 8.853270000 |
| C | 13.017410000 | 6.062970000 | 8.838700000 |
| H | 13.801350000 | 6.335070000 | 8.116610000 |
| H | 13.545970000 | 5.680230000 | 9.723410000 |
| C | 12.199700000 | 7.315520000 | 9.238450000 |
| H | 11.932190000 | 7.24148000 | 10.299930000 |
| H | 12.827570000 | 8.221370000 | 9.146440000 |
| C | 10.921510000 | 7.472070000 | 8.441160000 |
| H | 10.094260000 | 7.952710000 | 8.969120000 |
| C | 10.864590000 | 7.430530000 | 7.045250000 |
| H | 9.988150000 | 7.859840000 | 6.558890000 |
| C | 12.088560000 | 7.244650000 | 6.166130000 |
| H | 11.977860000 | 7.84188000 | 5.249840000 |
| H | 12.976920000 | 7.639610000 | 6.678940000 |
| C | 12.303790000 | 5.764420000 | 5.785620000 |
| H | 11.698450000 | 5.533760000 | 4.896830000 |
| H | 13.355800000 | 5.587380000 | 5.491740000 |
| C | 8.695080000 | 1.168420000 | 9.025140000 |
| C | 8.293330000 | 1.096430000 | 7.647340000 |
| C | 9.467390000 | 1.192690000 | 6.836400000 |
| C | 10.588730000 | 1.39045000 | 7.711600000 |
| C | 10.104300000 | 1.347300000 | 9.066660000 |
| C | 7.748070000 | 1.129310000 | 10.185960000 |
| H | 7.114980000 | 2.029230000 | 10.232520000 |
| H | 8.285630000 | 1.061730000 | 11.139530000 |
| H | 7.078300000 | 0.259910000 | 10.119790000 |
| C | 6.887530000 | 0.904140000 | 7.162390000 |
| H | 6.165050000 | 1.449540000 | 7.784740000 |
| H | 6.598620000 | -0.15800000 | 7.18076000 |
| H | 6.765640000 | 1.257250000 | 6.130310000 |
| C | 9.536540000 | 1.028950000 | 5.350900000 |
| H | 8.628270000 | 1.391860000 | 4.854980000 |
| H | 9.654070000 | -0.032990000 | 5.082030000 |
| H | 10.388270000 | 1.569570000 | 4.918720000 |
| C | 12.035560000 | 1.350270000 | 7.317380000 |
|  |  |  |  |


| H | 12.182580000 | 1.632960000 | 6.267680000 |
| :--- | :---: | :---: | :---: |
| H | 12.436810000 | 0.330890000 | 7.437590000 |
| H | 12.653240000 | 2.019800000 | 7.929070000 |
| C | 10.983920000 | 1.450180000 | 10.275020000 |
| H | 11.768420000 | 0.678680000 | 10.255880000 |
| H | 10.412780000 | 1.318380000 | 11.201590000 |
| H | 11.490930000 | 2.424600000 | 10.342970000 |
| C | 7.676360000 | 4.055160000 | 4.348430000 |
| H | 6.871660000 | 4.793490000 | 4.456620000 |
| H | 7.306420000 | 3.111920000 | 4.774660000 |
| H | 7.851430000 | 3.900910000 | 3.273900000 |
| C | 8.953260000 | 4.516800000 | 5.067630000 |
| H | 9.776790000 | 3.842150000 | 4.787650000 |
| H | 9.241360000 | 5.508070000 | 4.673240000 |
| C | 8.824060000 | 4.537470000 | 6.569880000 |
| C | 8.265950000 | 5.639570000 | 7.255870000 |
| C | 8.344020000 | 5.597330000 | 8.742860000 |
| C | 8.976700000 | 4.482800000 | 9.323920000 |
| C | 9.154900000 | 4.373560000 | 10.822790000 |
| H | 8.249430000 | 4.727340000 | 11.343700000 |
| H | 9.246270000 | 3.313830000 | 11.097520000 |
| C | 10.363100000 | 5.119560000 | 11.402790000 |
| H | 11.294670000 | 4.774570000 | 10.936190000 |
| H | 10.442890000 | 4.966300000 | 12.489190000 |
| H | 10.287810000 | 6.198010000 | 11.214790000 |
| C | 7.615710000 | 6.805200000 | 6.542660000 |
| H | 8.020570000 | 6.860240000 | 5.522450000 |
| H | 7.886500000 | 7.757180000 | 7.023050000 |
| C | 6.083370000 | 6.709070000 | 6.464940000 |
| H | 5.678110000 | 7.480390000 | 5.795000000 |
| H | 5.620180000 | 6.847690000 | 7.449010000 |
| H | 5.767460000 | 5.727910000 | 6.087120000 |
| C | 7.698820000 | 6.680850000 | 9.580840000 |
| H | 7.603190000 | 7.613150000 | 9.008040000 |
| H | 8.344040000 | 6.917170000 | 10.438600000 |
| C | 6.312590000 | 6.259340000 | 10.100670000 |
| H | 5.646340000 | 5.976040000 | 9.276230000 |
| H | 5.835360000 | 7.076310000 | 10.659820000 |
| H | 6.387080000 | 5.390770000 | 10.767510000 |
|  |  |  |  |
| H |  |  |  |

## [NiAl](Cp**)(tpbd)(cod)

| 6.218571000 | 3.081145000 | 6.544553000 |
| :---: | ---: | :---: |
| 8.085698000 | 1.437566000 | 5.520561000 |
| 7.883211000 | 4.168195000 | 5.815910000 |
| 8.428598000 | 3.089174000 | 6.535111000 |
| 9.460834000 | 3.302403000 | 7.564288000 |
| 9.261715000 | 3.029668000 | 8.926191000 |
| 10.289286000 | 3.186850000 | 9.857305000 |
| 11.552771000 | 3.618493000 | 9.447878000 |
| 11.769759000 | 3.899525000 | 8.094654000 |
| 10.739735000 | 3.744699000 | 7.168805000 |
| 9.063015000 | -0.159431000 | 4.210598000 |
| 9.996968000 | 0.240348000 | 5.229960000 |
| 11.335498000 | 0.866340000 | 4.978582000 |
| 9.442425000 | -0.097738000 | 6.499265000 |
| 8.135576000 | -0.653486000 | 6.274565000 |
| 7.284023000 | -1.329478000 | 7.307127000 |
| 7.914867000 | -0.713038000 | 4.850072000 |
| 6.707434000 | -1.315940000 | 4.200297000 |
| 10.121633000 | 0.029837000 | 7.825913000 |
| 9.321092000 | -0.054572000 | 2.739175000 |
| 6.769537000 | 2.454222000 | 4.460117000 |
| 5.856631000 | 1.896141000 | 3.445447000 |
| 6.352653000 | 1.531765000 | 2.177382000 |
| 5.540606000 | 0.922587000 | 1.222233000 |
| 4.200410000 | 0.645095000 | 1.509809000 |
| 3.689189000 | 1.000211000 | 2.759567000 |
| 4.506577000 | 1.615539000 | 3.709504000 |
| 6.958336000 | 3.832706000 | 4.696919000 |
| 6.349595000 | 4.926135000 | 3.891623000 |
| 6.280556000 | 4.821278000 | 2.492076000 |


|  |  |  |  |
| :---: | :---: | :---: | :---: |
| H | 4.844783000 | 7.814768000 | 1.706632000 |
| H | 5.708164000 | 5.734030000 | 0.629135000 |
| H | 6.660480000 | 3.928459000 | 2.004911000 |
| H | 5.952686000 | 6.255781000 | 5.553941000 |
| H | 4.981638000 | 8.050048000 | 4.189659000 |
| H | 12.357716000 | 3.739180000 | 10.172740000 |
| H | 10.100883000 | 2.968496000 | 10.909471000 |
| H | 8.283697000 | 2.685681000 | 9.252432000 |
| H | 10.913469000 | 3.972097000 | 6.116713000 |
| H | 12.747744000 | 4.246814000 | 7.758867000 |
| H | 4.107666000 | 1.881752000 | 4.683112000 |
| H | 2.644774000 | 0.796358000 | 3.000141000 |
| H | 3.564942000 | 0.161145000 | 0.768294000 |
| H | 5.957004000 | 0.660147000 | 0.248564000 |
| H | 7.397648000 | 1.736433000 | 1.946224000 |
| C | 4.410706000 | 4.155359000 | 6.605600000 |
| C | 5.181810000 | 4.498565000 | 7.713439000 |
| H | 5.783138000 | 5.408071000 | 7.658919000 |


|  |  |  |  |
| :--- | :---: | :---: | :---: |
| C | 4.885659000 | 3.950549000 | 9.097485000 |
| H | 5.170680000 | 4.691502000 | 9.856788000 |
| C | 5.613942000 | 2.616341000 | 9.393591000 |
| H | 6.539212000 | 2.833945000 | 9.942306000 |
| H | 5.004861000 | 1.993126000 | 10.074626000 |
| C | 5.969973000 | 1.821011000 | 8.155535000 |
| H | 6.872938000 | 1.214505000 | 8.241928000 |
| C | 5.053730000 | 1.478019000 | 7.153562000 |
| H | 5.303760000 | 0.638825000 | 6.501318000 |
| C | 3.575771000 | 1.826456000 | 7.248061000 |
| H | 3.273428000 | 1.777917000 | 8.305423000 |
| H | 2.989810000 | 1.053569000 | 6.731699000 |
| H | 3.798243000 | 3.813082000 | 9.201628000 |
| H | 4.441945000 | 4.807142000 | 5.733305000 |
| C | 3.225791000 | 3.218138000 | 6.664336000 |
| H | 2.409999000 | 3.675867000 | 7.252388000 |
| H | 2.830974000 | 3.105797000 | 5.646457000 |

## [NiAl](Cp*)(tebd)(hex)

| Ni | 9.843280000 | 5.399914000 | 8.128248000 |
| :--- | :---: | :---: | :---: |
| Al | 8.850919000 | 3.135884000 | 7.997255000 |
| C | 8.887312000 | 1.083572000 | 8.966566000 |
| C | 8.408609000 | 0.961580000 | 7.614178000 |
| C | 9.474213000 | 1.333203000 | 6.732078000 |
| C | 10.577967000 | 1.763102000 | 7.530431000 |
| C | 10.218621000 | 1.588109000 | 8.915694000 |
| C | 8.097210000 | 0.715815000 | 10.185727000 |
| H | 7.143918000 | 1.261048000 | 10.246480000 |
| H | 8.656782000 | 0.927734000 | 11.104371000 |
| H | 7.858896000 | -0.358706000 | 10.186221000 |
| C | 7.073751000 | 0.415890000 | 7.203573000 |
| H | 6.301453000 | 0.629405000 | 7.954139000 |
| H | 7.111252000 | -0.677799000 | 7.075109000 |
| H | 6.737594000 | 0.843944000 | 6.249750000 |
| C | 9.440665000 | 1.212529000 | 5.241387000 |
| H | 8.480421000 | 1.535562000 | 4.819711000 |
| H | 9.592058000 | 0.164305000 | 4.938111000 |
| H | 10.230249000 | 1.806011000 | 4.765288000 |
| C | 11.910241000 | 2.247236000 | 7.045826000 |
| H | 11.870445000 | 2.539945000 | 5.989187000 |
| H | 12.679647000 | 1.465916000 | 7.145254000 |
| H | 12.245318000 | 3.126390000 | 7.613437000 |
| C | 11.124530000 | 1.896259000 | 10.066842000 |
| H | 11.917178000 | 1.138178000 | 10.163401000 |
| H | 10.579338000 | 1.932420000 | 11.017113000 |
| H | 11.616673000 | 2.869494000 | 9.932485000 |
| C | 7.444676000 | 4.153194000 | 4.420433000 |
| H | 6.636001000 | 4.887213000 | 4.533899000 |
| H | 7.063387000 | 3.193294000 | 4.797703000 |
| H | 7.656614000 | 4.042425000 | 3.347298000 |
| C | 8.693334000 | 4.589816000 | 5.202016000 |
| H | 9.523801000 | 3.913448000 | 4.952731000 |
| H | 9.006218000 | 5.585607000 | 4.843642000 |
| C | 8.470924000 | 4.570691000 | 6.690971000 |
| C | 7.926655000 | 5.662087000 | 7.384286000 |
| C | 7.860679000 | 5.544942000 | 8.875178000 |
| C | 8.412001000 | 4.397799000 | 9.455502000 |
|  |  |  |  |


|  |  |  |  |
| :---: | :---: | :---: | :---: |
| C | 8.474941000 | 4.239458000 | 10.959771000 |
| H | 7.540527000 | 4.598463000 | 11.422209000 |
| H | 8.531454000 | 3.171512000 | 11.213322000 |
| H | 9.659492000 | 4.949461000 | 11.629022000 |
| H | 9.606900000 | 4.539282000 | 11.261713000 |
| H | 9.663394000 | 6.022429000 | 11.395244000 |
| C | 7.517739000 | 6.951212000 | 6.703002000 |
| H | 8.023434000 | 7.005137000 | 5.729577000 |
| H | 7.888883000 | 7.812656000 | 7.278593000 |
| C | 6.003579000 | 7.099404000 | 6.483390000 |
| H | 5.784514000 | 7.981992000 | 5.866240000 |
| H | 5.463678000 | 7.213988000 | 7.431224000 |
| H | 5.592595000 | 6.217572000 | 5.973906000 |
| C | 7.199100000 | 6.630816000 | 9.697755000 |
| H | 7.212696000 | 7.590569000 | 9.165155000 |
| H | 7.764654000 | 6.789513000 | 10.625809000 |
| C | 5.746738000 | 6.260601000 | 10.050130000 |
| H | 5.156708000 | 6.060715000 | 9.146362000 |
| H | 5.255809000 | 7.070974000 | 10.606937000 |
| H | 5.710296000 | 5.353026000 | 10.666746000 |
| C | 11.473204000 | 5.804875000 | 7.331351000 |
| C | 11.629687000 | 5.747411000 | 8.613884000 |
| C | 11.997492000 | 5.956958000 | 5.953906000 |
| C | 13.527248000 | 5.912725000 | 5.843585000 |
| H | 11.617591000 | 6.905256000 | 5.538976000 |
| H | 11.552999000 | 5.173549000 | 5.319512000 |
| H | 13.988435000 | 6.726210000 | 6.417581000 |
| H | 13.846158000 | 6.008398000 | 4.795992000 |
| H | 13.917957000 | 4.963373000 | 6.234194000 |
| C | 12.554036000 | 5.845129000 | 9.771584000 |
| C | 13.971800000 | 6.306546000 | 9.411918000 |
| H | 12.600461000 | 4.863519000 | 10.272509000 |
| H | 12.115162000 | 6.520054000 | 10.523300000 |
| H | 14.449747000 | 5.603424000 | 8.717656000 |
| H | 14.599486000 | 6.381077000 | 10.311274000 |
| H | 13.949673000 | 7.292441000 | 8.928342000 |
|  |  |  |  |

## [NiAl](Cp*)(tebd)(dpa)

| Ni | 6.359136000 | 3.065097000 | 6.358330000 |
| :--- | :---: | :---: | :---: |
| Al | 7.859614000 | 1.291246000 | 5.524584000 |
| C | 8.083978000 | 4.049549000 | 5.674749000 |
| C | 8.501788000 | 2.946966000 | 6.429491000 |
| C | 9.427844000 | 3.066380000 | 7.560225000 |
| C | 9.135803000 | 2.464574000 | 8.796085000 |
| C | 10.032056000 | 2.525473000 | 9.862362000 |
| C | 11.259623000 | 3.175945000 | 9.713094000 |
| C | 11.570659000 | 3.774538000 | 8.486986000 |
| C | 10.666831000 | 3.726216000 | 7.427307000 |
| C | 7.752143000 | -0.719791000 | 4.529706000 |
| C | 9.118090000 | -0.387479000 | 4.835325000 |
| C | 10.237298000 | -0.263509000 | 3.844944000 |
| C | 9.253809000 | -0.308024000 | 6.267461000 |
| C | 7.963273000 | -0.512973000 | 6.838253000 |
| C | 7.596571000 | -0.579126000 | 8.289774000 |
| C | 7.029717000 | -0.761878000 | 5.760768000 |
| C | 5.587577000 | -1.111013000 | 5.970945000 |
| C | 10.542798000 | -0.060264000 | 6.987277000 |
| C | 7.222004000 | -0.982705000 | 3.155032000 |
| C | 6.768530000 | 2.468411000 | 4.324134000 |
| C | 5.805568000 | 2.033643000 | 3.306795000 |
| C | 6.016705000 | 2.269674000 | 1.933699000 |
| C | 5.138573000 | 1.769210000 | 0.972759000 |
| C | 4.019470000 | 1.022609000 | 1.354081000 |
| C | 3.796070000 | 0.777169000 | 2.711344000 |


| 4.681971000 | 1.267846000 | 3.668332000 |
| :---: | :---: | :---: |
| 7.144140000 | 3.798001000 | 4.545136000 |
| 6.567220000 | 4.974680000 | 3.836850000 |
| 7.020439000 | 5.349040000 | 2.564931000 |
| 6.488288000 | 6.465863000 | 1.918611000 |
| 5.497132000 | 7.229185000 | 2.539760000 |
| 5.049877000 | 6.873687000 | 3.814859000 |
| 5.585420000 | 5.758303000 | 4.459096000 |
| 8.457277000 | 5.452499000 | 5.993574000 |
| 8.079819000 | 6.033308000 | 7.210640000 |
| 8.441961000 | 7.344393000 | 7.516822000 |
| 9.193344000 | 8.093522000 | 6.607407000 |
| 9.574364000 | 7.522995000 | 5.389880000 |
| 9.204697000 | 6.213123000 | 5.083438000 |
| 5.391473000 | 2.841707000 | 7.949718000 |
| 5.548647000 | 2.723873000 | 9.375788000 |
| 4.815363000 | 1.754678000 | 10.094963000 |
| 4.981291000 | 1.612231000 | 11.470433000 |
| 5.872440000 | 2.439949000 | 12.162209000 |
| 6.601385000 | 3.406728000 | 11.463540000 |
| 6.450055000 | 3.541159000 | 10.085402000 |
| 4.599170000 | 2.807078000 | 6.918537000 |
| 3.265193000 | 2.709082000 | 6.386483000 |
| 2.939149000 | 3.313460000 | 5.155907000 |
| 1.649273000 | 3.221291000 | 4.639773000 |
| 0.663855000 | 2.510793000 | 5.331026000 |


| 0.974415000 | 1.899346000 | 6.551280000 |
| :---: | :---: | :---: |
| 2.260026000 | 1.999312000 | 7.077892000 |
| 11.085642000 | 0.799357000 | 6.571802000 |
| 11.202698000 | -0.937929000 | 6.907782000 |
| 10.382024000 | 0.151286000 | 8.049444000 |
| 6.792660000 | 0.124966000 | 8.548741000 |
| 8.455135000 | -0.353541000 | 8.931461000 |
| 7.238633000 | -1.587491000 | 8.548269000 |
| 9.876950000 | 0.089126000 | 2.869837000 |
| 10.729378000 | -1.234921000 | 3.679687000 |
| 11.007394000 | 0.436503000 | 4.194246000 |
| 7.592531000 | -0.250090000 | 2.426173000 |
| 6.128351000 | -0.937130000 | 3.121529000 |
| 7.534861000 | -1.979866000 | 2.808020000 |
| 5.055269000 | -1.205813000 | 5.018779000 |
| 5.066258000 | -0.351879000 | 6.572627000 |
| 5.497383000 | -2.068709000 | 6.506443000 |
| 7.481543000 | 5.444847000 | 7.905437000 |
| 8.133643000 | 7.783989000 | 8.465733000 |
| 9.476635000 | 9.119344000 | 6.843667000 |
| 10.156908000 | 8.102216000 | 4.672986000 |
| 9.496218000 | 5.771841000 | 4.130550000 |
| 5.080522000 | 8.101067000 | 2.035171000 |
| 6.851413000 | 6.741630000 | 0.928174000 |

## $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3}$

| 7.811229000 | 4.770227000 | 2.087686000 |
| :---: | :---: | :---: |
| 5.247814000 | 5.484117000 | 5.460064000 |
| 4.283286000 | 7.468225000 | 4.312320000 |
| 4.128329000 | 1.104034000 | 9.554313000 |
| 4.412433000 | 0.852457000 | 12.007298000 |
| 5.999416000 | 2.328888000 | 13.239089000 |
| 7.303471000 | 4.051575000 | 11.992268000 |
| 7.037633000 | 4.275724000 | 9.538387000 |
| 11.966083000 | 3.220250000 | 10.542113000 |
| 9.765990000 | 2.063635000 | 10.814183000 |
| 8.180439000 | 1.961007000 | 8.915704000 |
| 10.917413000 | 4.198550000 | 6.477625000 |
| 12.523981000 | 4.288519000 | 8.357645000 |
| 2.502472000 | 1.528332000 | 8.030016000 |
| 0.208909000 | 1.344127000 | 7.094285000 |
| -0.343064000 | 2.430082000 | 4.920931000 |
| 1.417093000 | 3.692493000 | 3.684748000 |
| 3.715967000 | 3.846496000 | 4.610716000 |
| 4.503375000 | 1.077435000 | 4.722938000 |
| 2.923245000 | 0.207522000 | 3.032008000 |
| 3.331353000 | 0.637356000 | 0.601603000 |
| 5.330306000 | 1.964513000 | -0.083084000 |
| 6.894712000 | 2.829657000 | 1.618270000 |

15.824347000 14.565149000 13.473234000 12.297701000 12.627028000 14.173069000 14.327097000 13.109257000 16.247147000 16.992060000 18.080179000 18.420066000 17.533539000 15.833991000 15.821471000 14.942495000 15.742530000 17.159672000 16.996790000 19.306132000 20.699608000 19.649709000 20.629004000 20.268348000 21.228494000 17.596388000 17.367441000 19.000509000 18.768897000 20.036916000 20.471654000 17.909570000 18.854813000 17.441597000 18.311910000 18.638681000 19.905861000 20.376293000 21.413584000 21.970483000 21.368700000 22.655278000 21.893083000 13.701480000 14.504828000 12.734122000 12.569654000 11.310575000 12.693038000 14.019292000 14.738320000 15.655751000 15.605634000 14.997820000 16.340869000 11.755437000 12.930677000 13.455353000 12.911881000 12.208671000 13.262556000
エコ

| 2.519471000 | 0.182366000 | 14.560074000 |
| ---: | ---: | ---: |
| 1.595441000 | -1.120409000 | 15.233416000 |
| 6.541856000 | -2.085685000 | 12.086678000 |
| 6.624550000 | -0.813116000 | 10.848872000 |

## $\left[\mathrm{Ni}_{2} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})_{1}$

| Ni | -0.144772000 | 1.265788000 | 1.083101000 |
| :---: | :---: | :---: | :---: |
| Ni | -2.401625000 | 1.009882000 | 0.528824000 |
| AI | -0.680795000 | -0.139108000 | -0.650194000 |
| AI | -1.206036000 | 3.014192000 | 0.098403000 |
| AI | -1.509970000 | 0.323437000 | 2.630954000 |
| C | -5.354365000 | 0.228588000 | -2.296892000 |
| C | -5.986358000 | -0.619404000 | -3.204051000 |
| C | -6.119599000 | -1.983806000 | -2.925500000 |
| C | -5.610363000 | -2.491796000 | -1.725266000 |
| C | -4.960927000 | -1.651837000 | -0.823034000 |
| C | -4.826037000 | -0.274597000 | -1.088622000 |
| C | -6.358029000 | 2.637477000 | 1.245379000 |
| C | -7.099267000 | 3.552892000 | 1.986544000 |
| C | -6.473262000 | 4.360289000 | 2.946505000 |
| C | -5.096561000 | 4.240100000 | 3.156678000 |
| C | -4.349041000 | 3.326661000 | 2.414580000 |
| C | -4.965546000 | 2.510558000 | 1.447821000 |
| C | -4.198462000 | 1.569262000 | 0.682519000 |
| C | -4.165695000 | 0.597884000 | -0.161358000 |
| C | 1.074616000 | -1.066183000 | -1.726856000 |
| C | 0.127777000 | -0.666973000 | -2.720244000 |
| C | 0.384989000 | 0.304305000 | -3.830112000 |
| C | -1.075676000 | -1.417288000 | -2.514057000 |
| C | -2.300609000 | -1.341439000 | -3.371783000 |
| C | -0.863832000 | -2.287830000 | -1.394946000 |
| C | -1.837711000 | -3.276962000 | -0.832526000 |
| C | 0.458926000 | -2.060027000 | -0.899603000 |
| C | 1.091661000 | -2.712575000 | 0.290452000 |
| C | 2.467345000 | -0.554161000 | -1.575084000 |
| C | -2.505924000 | 4.484212000 | -1.055160000 |
| C | -3.985517000 | 4.369967000 | -1.244588000 |
| C | -1.816661000 | 5.199489000 | -0.023032000 |
| C | -2.443205000 | 5.987616000 | 1.086858000 |
| C | -0.411159000 | 5.096006000 | -0.280724000 |
| C | -0.230146000 | 4.319793000 | -1.471736000 |
| C | 1.096893000 | 3.923855000 | -2.043946000 |
| C | 0.681570000 | 5.678529000 | 0.562003000 |
| C | -1.525735000 | 3.938974000 | -1.946495000 |
| C | -1.850071000 | 3.106117000 | -3.148754000 |
| C | 0.000060000 | 0.714509000 | 5.551720000 |
| C | -1.134055000 | 0.027397000 | 4.856027000 |
| C | -2.458247000 | 0.545974000 | 4.698772000 |
| C | -2.953922000 | 1.840842000 | 5.267570000 |
| C | -3.220968000 | -0.406166000 | 3.949268000 |
| C | -2.361385000 | -1.513279000 | 3.643431000 |
| C | -2.778507000 | -2.743776000 | 2.901073000 |
| C | -4.669378000 | -0.307599000 | 3.584457000 |
| C | -1.072008000 | -1.246541000 | 4.206720000 |
| C | 0.150768000 | -2.107365000 | 4.108565000 |
| H | -5.248991000 | 1.291631000 | -2.513956000 |
| H | -6.379417000 | -0.212801000 | -4.136682000 |
| H | -6.614764000 | -2.644822000 | -3.636442000 |
| H | -5.712442000 | -3.553181000 | -1.495401000 |
| H | -2.112052000 | -3.039979000 | 0.204681000 |
| H | -6.839860000 | 2.006908000 | 0.497920000 |
| H | -7.057420000 | 5.076300000 | 3.524741000 |
| H | -8.173248000 | 3.641309000 | 1.818037000 |
| H | -4.602240000 | 4.863745000 | 3.902643000 |
| H | -3.273588000 | 3.216737000 | 2.561299000 |
| H | -0.552099000 | 0.643275000 | -4.286694000 |
| H | 0.991115000 | -0.156609000 | -4.625718000 |
| H | 0.927120000 | 1.192152000 | -3.477260000 |
| H | -2.560057000 | -0.303919000 | -3.620760000 |
| H | -2.150784000 | -1.879838000 | -4.320598000 |
| H | -3.172921000 | -1.777086000 | -2.8737860 |


| H | -4.545885000 | -2.047644000 | 0.103129000 |
| :---: | :---: | :---: | :---: |
| H | -2.763688000 | -3.295385000 | -1.417056000 |
| H | -1.414006000 | -4.292017000 | -0.839424000 |
| H | 0.340593000 | -3.211650000 | 0.915252000 |
| H | 1.837927000 | -3.465980000 | -0.006687000 |
| H | 1.598491000 | -1.967532000 | 0.922164000 |
| H | 2.609172000 | 0.389268000 | -2.115887000 |
| H | 3.206983000 | -1.276789000 | -1.955624000 |
| H | 2.692167000 | -0.362148000 | -0.517336000 |
| H | -4.535095000 | 4.649030000 | -0.338502000 |
| H | -4.326933000 | 5.027150000 | -2.060123000 |
| H | -4.278783000 | 3.341997000 | -1.496332000 |
| H | -3.477049000 | 5.672229000 | 1.268236000 |
| H | -2.458999000 | 7.062389000 | 0.845977000 |
| H | -1.894205000 | 5.870790000 | 2.031387000 |
| H | 1.002661000 | 3.596911000 | -3.087311000 |
| H | 1.803422000 | 4.766175000 | -2.022373000 |
| H | 1.546283000 | 3.094411000 | -1.470607000 |
| H | 0.306308000 | 6.500755000 | 1.184359000 |
| H | 1.124916000 | 4.925002000 | 1.231901000 |
| H | 1.494106000 | 6.076588000 | -0.061790000 |
| H | -2.279725000 | 2.130686000 | -2.866241000 |
| H | -0.955582000 | 2.911548000 | -3.750795000 |
| H | -2.583540000 | 3.613064000 | -3.792592000 |
| H | -0.366820000 | 1.437600000 | 6.291477000 |
| H | 0.639340000 | -0.009045000 | 6.075931000 |
| H | -2.263814000 | 2.671181000 | 5.060638000 |
| H | -3.067728000 | 1.771871000 | 6.360916000 |
| H | -3.929466000 | 2.111130000 | 4.848837000 |
| H | -1.912106000 | -3.299802000 | 2.521017000 |
| H | -3.353813000 | -3.426309000 | 3.546033000 |
| H | -3.415572000 | -2.496084000 | 2.040234000 |
| H | -5.016661000 | 0.731950000 | 3.594273000 |
| H | -4.858351000 | -0.698248000 | 2.575950000 |
| H | -5.293981000 | -0.879393000 | 4.288581000 |
| H | 0.912190000 | -1.655488000 | 3.452316000 |
| H | -0.088336000 | -3.097458000 | 3.701992000 |
| H | 0.610856000 | -2.256563000 | 5.096587000 |
| H | 0.638174000 | 1.260567000 | 4.838253000 |
| AI | 1.995546000 | 1.483143000 | 1.604734000 |
| C | 3.821828000 | 2.869701000 | 1.741240000 |
| C | 3.906397000 | 4.260063000 | 1.192331000 |
| H | 4.952336000 | 4.605748000 | 1.174363000 |
| H | 3.337534000 | 4.972340000 | 1.800812000 |
| H | 3.524971000 | 4.321477000 | 0.164253000 |
| C | 3.435214000 | 2.492256000 | 3.068029000 |
| C | 2.958541000 | 3.425233000 | 4.139817000 |
| H | 3.803130000 | 3.861559000 | 4.695490000 |
| H | 2.374811000 | 4.254976000 | 3.719603000 |
| H | 2.316042000 | 2.910917000 | 4.865442000 |
| C | 3.607317000 | 1.075819000 | 3.186594000 |
| C | 3.412529000 | 0.242272000 | 4.415010000 |
| H | 4.383545000 | -0.084460000 | 4.819040000 |
| H | 2.899181000 | 0.801795000 | 5.204336000 |
| H | 2.822862000 | -0.662308000 | 4.213305000 |
| C | 4.094663000 | 0.579780000 | 1.933804000 |
| C | 4.468056000 | -0.847088000 | 1.670288000 |
| H | 5.415780000 | -1.102376000 | 2.170067000 |
| H | 4.598255000 | -1.044388000 | 0.599716000 |
| H | 3.707076000 | -1.545599000 | 2.045639000 |
| C | 4.234587000 | 1.690758000 | 1.043539000 |
| C | 4.795021000 | 1.679048000 | -0.345383000 |
| H | 5.788980000 | 2.152423000 | -0.365258000 |
| H | 4.907220000 | 0.659479000 | -0.730740000 |
| H | 4.158656000 | 2.232851000 | -1.050250000 |

## $\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}$



## $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}\right)_{4}$

| -6.827950000 | 3.221974000 | 2.508157000 |
| ---: | ---: | ---: |
| -6.114721000 | 4.121493000 | 3.313570000 |
| -4.717769000 | 4.124638000 | 3.273890000 |
| -4.037826000 | 3.236878000 | 2.441272000 |
| -4.742092000 | 2.326564000 | 1.630546000 |
| -4.043313000 | 1.406524000 | 0.780643000 |
| -4.048439000 | 0.505483000 | -0.133066000 |
| 1.131933000 | -1.749142000 | -1.121091000 |
| 0.691342000 | -0.928719000 | -2.210125000 |
| 1.487972000 | 0.089684000 | -2.963449000 |
| -0.680469000 | -1.240278000 | -2.478402000 |
| -1.504713000 | -0.584220000 | -3.541875000 |
| -1.095445000 | -2.256916000 | -1.558010000 |
| -2.425705000 | -2.939879000 | -1.505028000 |
| 0.024096000 | -2.566852000 | -0.716775000 |
| 0.075119000 | -3.670392000 | 0.292185000 |
| 2.508022000 | -1.817728000 | -0.536901000 |
| -2.604575000 | 4.670363000 | -1.191505000 |
| -4.095127000 | 4.612646000 | -1.051582000 |
| -1.680017000 | 5.255853000 | -0.267073000 |
| -2.037675000 | 5.980266000 | 0.993279000 |
| -0.355858000 | 5.071906000 | -0.784233000 |
| -0.465129000 | 4.391808000 | -2.041969000 |
| 0.681084000 | 4.027722000 | -2.933349000 |
| 0.922599000 | 5.499762000 | -0.130333000 |
| -1.853001000 | 4.140476000 | -2.291038000 |
| -2.439981000 | 3.449315000 | -3.482529000 |
| 0.676756000 | 0.856848000 | 5.117921000 |
| -0.575743000 | 0.250893000 | 4.563823000 |
| -1.909516000 | 0.762647000 | 4.692758000 |
| -2.309378000 | 1.994681000 | 5.442550000 |
| -2.800311000 | -0.165090000 | 4.057622000 |
| -2.018485000 | -1.254320000 | 3.550191000 |
| -2.572824000 | -2.416047000 | 2.782835000 |
| -4.293126000 | -0.068215000 | 3.985897000 |
| -0.645694000 | -0.997832000 | 3.863298000 |
| 0.542852000 | -1.832366000 | 3.492045000 |
| 3.294300000 | 3.487477000 | 3.350621000 |
| 3.160511000 | 5.211830000 | 5.137810000 |
| 0.952425000 | 6.163595000 | 5.797027000 |
| -1.120382000 | 5.385397000 | 4.648668000 |
| -0.968607000 | 3.637825000 | 2.861427000 |
| 3.883839000 | 0.480610000 | 2.425526000 |
| 6.698325000 | 0.350897000 | -0.842981000 |
| 6.092837000 | -0.200775000 | 1.512041000 |
| 5.079258000 | 1.602841000 | -2.269919000 |
| 2.850922000 | 2.238419000 | -1.359752000 |
| -4.220903000 | 0.626940000 | -2.805624000 |
| -5.456564000 | -0.938325000 | -4.294091000 |
| -6.661723000 | -2.894872000 | -3.322840000 |
| -6.664684000 | -3.235712000 | -0.852976000 |


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| ---: | ---: | ---: |
| -2.816396000 | -2.996007000 | -0.480252000 |
| -6.704044000 | 1.633188000 | 1.048010000 |
| -6.647544000 | 4.814003000 | 3.965164000 |
| -4.156077000 | 3.215822000 | 2.534146000 |
| -2.948857000 | 3.2193771000 | 3.894704000 |
| 1.096195000 | 1.106192000 | -2.392052000 |
| 1.457555000 | -0.113703000 | -4.044324000 |
| 2.535931000 | 0.089829000 | -2.646607000 |
| -1.704575000 | 0.472985000 | -3.308006000 |
| -0.986051000 | -0.616480000 | -4.511315000 |
| -2.472826000 | -1.082251000 | -3.657722000 |
| -5.458173000 | -1.647478000 | 0.628274000 |
| -3.175901000 | -2.414488000 | -2.104690000 |
| -2.348917000 | -3.970684000 | -1.883935000 |
| -0.895584000 | -3.818469000 | 0.781253000 |
| 0.347808000 | -4.623229000 | -0.189175000 |
| 0.821675000 | -3.472864000 | 1.070502000 |
| 3.129193000 | -0.975106000 | -0.857090000 |
| 3.013557000 | -2.746691000 | -0.842434000 |
| 2.485575000 | -1.802535000 | 0.561123000 |
| -4.409321000 | 4.795730000 | -0.017234000 |
| -4.584684000 | 5.364863000 | -1.689481000 |
| -4.488005000 | 3.627040000 | -1.337124000 |
| -2.957936000 | 5.582906000 | 1.439785000 |
| -2.203271000 | 7.050515000 | 0.793409000 |
| -1.239853000 | 5.905494000 | 1.742839000 |
| 0.430598000 | 3.187025000 | -3.593001000 |
| 0.971778000 | 4.874110000 | -3.575174000 |
| 1.566942000 | 3.743388000 | -2.349464000 |
| 0.792781000 | 5.639121000 | 0.949939000 |
| 1.712874000 | 4.748226000 | -0.263106000 |
| 1.290380000 | 6.449669000 | -0.548612000 |
| -3.286806000 | 2.810407000 | -3.195130000 |
| -1.700607000 | 2.815092000 | -3.988469000 |
| -2.813142000 | 4.174237000 | -4.222737000 |
| 0.556039000 | 1.927720000 | 5.316849000 |
| 0.961292000 | 0.370080000 | 6.064073000 |
| -1.514145000 | 2.749961000 | 5.424812000 |
| -2.518873000 | 1.757432000 | 6.497376000 |
| -3.214985000 | 2.448187000 | 5.020166000 |
| -1.848618000 | -3.237795000 | 2.731265000 |
| -3.485125000 | -2.803967000 | 3.256662000 |
| -2.830892000 | -2.136169000 | 1.748047000 |
| -4.641979000 | 0.948941000 | 4.198254000 |
| -4.669105000 | -0.337482000 | 2.990119000 |
| -4.764779000 | -0.743392000 | 4.717275000 |
| 1.089584000 | -1.402258000 | 2.636411000 |
| 0.242704000 | -2.849873000 | 3.215626000 |
| 1.248356000 | -1.906188000 | 4.330849000 |
| 1.517300000 | 0.748838000 | 4.420000000 |
|  |  |  |


| -1.196941000 | 0.803343000 | -0.020334000 |
| ---: | ---: | ---: |
| 1.188222000 | 0.643355000 | -0.006876000 |
| -0.122147000 | -1.463272000 | 0.007359000 |
| 0.118210000 | 2.666331000 | -0.137589000 |
| -0.090412000 | 0.066670000 | 1.882875000 |
| -0.065508000 | 0.003429000 | -1.881707000 |
| -0.191386000 | 4.569524000 | 1.058758000 |
| 1.094363000 | -0.700409000 | 3.639571000 |
| 1.211565000 | 4.448989000 | 0.764415000 |
| 6.494710000 | 1.569709000 | 0.136278000 |
| 5.500295000 | -0.552889000 | 1.113926000 |
| -2.390567000 | 4.815733000 | -0.324080000 |
| -1.218711000 | -0.931973000 | 3.580844000 |
| -0.852333000 | 4.564767000 | 2.404878000 |
| -0.925215000 | 0.432936000 | 3.929103000 |
| 0.510458000 | 0.578117000 | 3.965395000 |
| 0.066525000 | 4.670797000 | -1.250778000 |
| 3.119175000 | -4.020694000 | 0.181120000 |
| -0.900637000 | 4.697575000 | -0.186421000 |
| 1.370149000 | 4.500127000 | -0.663697000 |
| 0.753197000 | 0.524313000 | -3.885803000 |
| 1.504082000 | -2.148024000 | 0.091839000 |
| -2.581880000 | -1.533456000 | 3.414140000 |
| 2.561275000 | -0.994380000 | 3.520024000 |
| 1.287862000 | 1.813802000 | 4.310442000 |
| 5.628743000 | -0.256290000 | -1.393207000 |
| -3.899942000 | -4.278328000 | -1.558397000 |
| 2.686714000 | 4.406062000 | -1.379636000 |
| -6.497870000 | 1.807454000 | -0.114541000 |
| 2.344051000 | 4.261739000 | 1.731451000 |
| 4.119829000 | -4.165253000 | -0.981067000 |
| -0.137664000 | -3.085702000 | -3.187595000 |
| 2.928507000 | 0.863954000 | -0.020746000 |
| -0.688040000 | 0.584292000 | -3.935759000 |
|  |  |  |


| -3.483880000 | -3.911357000 | -0.120803000 |
| ---: | ---: | ---: |
| -1.195885000 | -0.737904000 | -3.669604000 |
| -0.231533000 | 4.892295000 | -2.703152000 |
| -2.644792000 | -1.117634000 | -3.578053000 |
| -2.460138000 | -4.927479000 | 0.420619000 |
| 3.838898000 | -4.259324000 | 1.522169000 |
| 1.951149000 | -5.010407000 | 0.014416000 |
| -1.542337000 | 1.794165000 | -4.186740000 |
| 1.717567000 | 1.664908000 | -4.048053000 |
| -2.926689000 | 1.107080000 | -0.010060000 |
| 5.438116000 | 0.465143000 | -0.043221000 |
| -1.744177000 | -2.140187000 | -0.079000000 |
| -4.117240000 | 1.332143000 | 0.017491000 |
| 2.628258000 | -2.632686000 | 0.171612000 |
| -2.890062000 | -2.567107000 | -0.154991000 |
| -5.429139000 | 0.709784000 | 0.031316000 |
| 4.122106000 | 1.076762000 | -0.037739000 |
| -0.073949000 | -1.614651000 | -3.471101000 |
| 1.127668000 | -0.835274000 | -3.593039000 |
| 0.024070000 | -1.632487000 | 3.420224000 |
| -5.589929000 | -0.034907000 | 1.372742000 |
| 2.524380000 | -1.345934000 | -3.394724000 |
| -4.725920000 | -3.859067000 | 0.787335000 |
| 0.154501000 | -3.090854000 | 3.093134000 |
| -1.958596000 | 1.488230000 | 4.207455000 |
| -5.502785000 | -0.290340000 | -1.141250000 |
| -6.357055000 | 2.361723000 | -1.063788000 |
| -6.429934000 | 2.532339000 | 0.721182000 |
| -7.513213000 | 1.362733000 | -0.113347000 |
| -4.817296000 | -0.822687000 | 1.459627000 |
| -6.591381000 | -0.507596000 | 1.436370000 |
| -5.477873000 | 0.665841000 | 2.224225000 |
| -4.702734000 | -1.049809000 | -1.032900000 |
| -5.362134000 | 0.233360000 | -2.107667000 |
| -5.3 |  |  |


|  |  | -192000 |  |
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| H | -6.490769000 | -0.795039000 | -1.158759000 |
| H | -1.539991000 | -4.919111000 | -0.196566000 |
| H | -2.885159000 | -5.951667000 | 0.421995000 |
| H | -2.169256000 | -4.668080000 | 1.458022000 |
| H | -3.014241000 | -4.319073000 | -2.222694000 |
| H | -4.604552000 | -3.527196000 | -1.966504000 |
| H | -4.395054000 | -5.270414000 | -1.575509000 |
| H | -5.219638000 | -4.851116000 | 0.825183000 |
| H | -5.454977000 | -3.116256000 | 0.409122000 |
| H | -4.444663000 | -3.570143000 | 1.819369000 |
| H | -1.664695000 | 3.811182000 | 2.452199000 |
| H | -1.302102000 | 5.553295000 | 2.638193000 |
| H | -0.132395000 | 4.328911000 | 3.211303000 |
| H | 2.853402000 | 3.286866000 | 1.572210000 |
| H | 1.993693000 | 4.292760000 | 2.779793000 |
| H | 3.108628000 | 5.057868000 | 1.610447000 |
| H | -2.721278000 | 4.581203000 | -1.354507000 |
| H | -2.745763000 | 5.841277000 | -0.082430000 |
| H | -2.915285000 | 4.106592000 | 0.347334000 |
| H | 0.509817000 | 4.394788000 | -3.358255000 |
| H | -0.209425000 | 5.975718000 | -2.951441000 |
| H | -1.234487000 | 4.512973000 | -2.977364000 |
| H | 2.548433000 | 4.262085000 | -2.468419000 |
| H | 3.290715000 | 3.554655000 | -1.004330000 |
| H | 3.287804000 | 5.331033000 | -1.240867000 |
| H | 7.513630000 | 1.133487000 | 0.146737000 |
| H | 6.332905000 | 2.110013000 | 1.090220000 |
| H | 6.435042000 | 2.304790000 | -0.691080000 |
| H | 4.863908000 | -1.048200000 | -1.509275000 |
| H | 6.635255000 | -0.719312000 | -1.445126000 |
| H | 5.526753000 | 0.456868000 | -2.235396000 |
| H | 4.693612000 | -1.302759000 | 0.989259000 |
| H | 5.357013000 | -0.044438000 | 2.087901000 |
| H | 6.483798000 | -1.065913000 | 1.128356000 |
| H | 4.553868000 | -5.185584000 | -0.994795000 |
| H | 4.944033000 | -3.432458000 | -0.877214000 |
| H | 3.619414000 | -3.985983000 | -1.953238000 |
|  |  |  |  |


|  |  |  |  |
| :--- | ---: | ---: | ---: |
| H | 4.268276000 | -5.281167000 | 1.553060000 |
| H | 3.133855000 | -4.154231000 | 2.370254000 |
| H | 4.659387000 | -3.528550000 | 1.662415000 |
| H | 2.320516000 | -6.055946000 | 0.012501000 |
| H | 1.414718000 | -4.821865000 | -0.936552000 |
| H | 1.218340000 | -4.892290000 | 0.836368000 |
| H | 2.766427000 | -1.660782000 | 2.660149000 |
| H | 2.959693000 | -1.480310000 | 4.436795000 |
| H | 3.140316000 | -0.065974000 | 3.353263000 |
| H | 2.162999000 | 1.937355000 | 3.642735000 |
| H | 1.663098000 | 1.778780000 | 5.355723000 |
| H | 0.667520000 | 2.723599000 | 4.208062000 |
| H | -0.404539000 | -3.346336000 | 2.170693000 |
| H | -0.225530000 | -3.721280000 | 3.925532000 |
| H | 1.210397000 | -3.364681000 | 2.912923000 |
| H | -2.649318000 | -2.115499000 | 2.474020000 |
| H | -3.364102000 | -0.752893000 | 3.373505000 |
| H | -2.828387000 | -2.216924000 | 4.255440000 |
| H | -2.622046000 | 1.655154000 | 3.332520000 |
| H | -1.489705000 | 2.457416000 | 4.458366000 |
| H | -2.602031000 | 1.199034000 | 5.064785000 |
| H | 2.613027000 | -1.900220000 | -2.438610000 |
| H | 3.251971000 | -0.514473000 | -3.356333000 |
| H | 2.831507000 | -2.028768000 | -4.215557000 |
| H | 0.701400000 | -3.405190000 | -2.540556000 |
| H | -0.093154000 | -3.678081000 | -4.127696000 |
| H | -1.072578000 | -3.351955000 | -2.659189000 |
| H | -2.832091000 | -1.777469000 | -2.708723000 |
| H | -2.990996000 | -1.647920000 | -4.491303000 |
| H | -3.280507000 | -0.222182000 | -3.444963000 |
| H | -2.189988000 | 1.652919000 | -5.076953000 |
| H | -0.921147000 | 2.690481000 | -4.363278000 |
| H | -2.200731000 | 2.014879000 | -3.319458000 |
| H | 2.382706000 | 1.517492000 | -4.924421000 |
| H | 2.356540000 | 1.783928000 | -3.148152000 |
| H | 1.179614000 | 2.620251000 | -4.194427000 |
|  |  |  |  |
|  |  |  |  |

## $\left[\mathrm{Pd}_{3} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dvds})$

| Pd | 7.448151000 | 3.308590000 | 4.481903000 |
| :---: | :---: | :---: | :---: |
| Pd | 9.809413000 | 2.241903000 | 4.813770000 |
| Pd | 7.013957000 | 1.005315000 | 5.805087000 |
| Ga | 9.421047000 | 4.504315000 | 3.680352000 |
| Ga | 8.028863000 | 0.988499000 | 3.510722000 |
| Ga | 5.281793000 | 4.174052000 | 4.141728000 |
| Ga | 8.331653000 | 2.853822000 | 6.841912000 |
| Si | 8.463699000 | -1.628140000 | 6.845314000 |
| C | 9.344352000 | 4.566970000 | 8.071799000 |
| O | 9.664205000 | -1.128194000 | 5.812406000 |
| C | 11.045882000 | 5.979616000 | 2.899373000 |
| C | 8.832455000 | -0.370612000 | 1.763034000 |
| C | 8.891899000 | 6.820905000 | 2.997462000 |
| C | 6.831033000 | 0.767423000 | 1.522597000 |
| C | 8.225162000 | 0.801002000 | 1.203659000 |
| C | 10.616504000 | 5.159553000 | 7.553917000 |
| H | 10.804088000 | 6.157089000 | 7.980703000 |
| H | 10.585511000 | 5.267890000 | 6.458961000 |
| H | 11.480428000 | 4.526920000 | 7.792290000 |
| C | 3.049887000 | 3.537483000 | 3.729661000 |
| C | 8.921159000 | 1.887600000 | 0.452618000 |
| H | 8.818347000 | 1.766657000 | -0.637584000 |
| H | 9.992821000 | 1.906740000 | 0.684609000 |
| H | 8.512840000 | 2.871601000 | 0.719888000 |
| C | 10.158781000 | 6.817340000 | 3.656085000 |
| C | 5.866644000 | -0.383763000 | 6.994566000 |
| H | 6.078815000 | -0.139312000 | 8.037255000 |
| H | 4.810304000 | -0.340150000 | 6.715989000 |
| C | 10.943260000 | 4.717615000 | 0.629791000 |
| C | 3.096797000 | 4.140330000 | 5.029658000 |
| C | 7.090805000 | 4.196241000 | 8.442015000 |
| C | 8.028039000 | 5.036930000 | 7.769060000 |
| C | 7.807967000 | -1.137194000 | 2.410562000 |
| C | 10.326888000 | 5.497836000 | 1.749768000 |
| C | 2.633225000 | 2.123575000 | 3.465639000 |
| H | 1.543492000 | 2.005234000 | 3.575430000 |
| H | 3.107336000 | 1.424061000 | 4.168478000 |
| H | 2.894939000 | 1.802465000 | 2.450245000 |
| C | 6.785076000 | -1.105939000 | 6.217832000 |
| H | 6.397409000 | -1.577283000 | 5.310015000 |
| C | 7.817737000 | 3.208767000 | 9.174384000 |
| C | 10.346309000 | 2.697089000 | 9.598813000 |
| H | 10.623517000 | 3.164759000 | 10.557421000 |
| H | 11.245763000 | 2.691822000 | 8.969210000 |
| H | 10.086430000 | 1.651875000 | 9.811356000 |
| C | 2.752234000 | 3.431855000 | 6.304346000 |
| C | 5.227895000 | -0.837341000 | 2.783482000 |
| C | 5.603700000 | 4.294091000 | 8.336405000 |


| H | 5.190521000 | 5.075796000 | 8.994072000 |
| :---: | :---: | :---: | :---: |
| H | 5.122974000 | 3.344707000 | 8.603844000 |
| H | 5.305530000 | 4.529298000 | 7.305225000 |
| C | 7.644549000 | 7.520056000 | 3.437185000 |
| H | 7.317776000 | 8.264446000 | 2.694442000 |
| H | 7.786542000 | 8.042467000 | 4.390808000 |
| H | 6.816637000 | 6.805446000 | 3.570191000 |
| C | 8.030673000 | -2.461561000 | 3.071193000 |
| H | 8.272850000 | -3.238944000 | 2.329696000 |
| H | 7.139928000 | -2.797397000 | 3.615848000 |
| H | 8.859853000 | -2.417547000 | 3.790842000 |
| C | 7.213890000 | 2.164987000 | 10.060716000 |
| C | 6.571569000 | -0.433291000 | 2.261854000 |
| C | 10.264826000 | -0.778494000 | 1.629787000 |
| H | 10.420116000 | -1.416095000 | 0.744429000 |
| H | 10.600918000 | -1.349019000 | 2.504907000 |
| H | 10.926247000 | 0.091538000 | 1.523963000 |
| C | 3.479500000 | 5.512112000 | 4.869455000 |
| C | 9.217533000 | 3.430870000 | 8.945106000 |
| C | 10.554042000 | 7.647216000 | 4.837961000 |
| H | 10.921976000 | 8.633857000 | 4.512781000 |
| H | 11.360581000 | 7.177787000 | 5.415113000 |
| H | 9.716239000 | 7.821163000 | 5.524163000 |
| C | 5.816547000 | 1.799067000 | 1.150085000 |
| H | 5.301654000 | 1.546101000 | 0.208718000 |
| H | 6.277176000 | 2.787587000 | 1.023638000 |
| H | 5.054871000 | 1.898732000 | 1.933491000 |
| C | 8.992474000 | 6.010760000 | 1.824152000 |
| C | 3.401074000 | 4.386938000 | 1.272787000 |
| H | 2.494282000 | 4.832824000 | 0.834278000 |
| H | 3.428996000 | 3.334639000 | 0.967719000 |
| H | 4.263126000 | 4.888372000 | 0.811379000 |
| C | 8.557956000 | -3.506528000 | 6.911744000 |
| H | 9.538734000 | -3.841246000 | 7.280146000 |
| H | 8.409148000 | -3.943152000 | 5.914238000 |
| H | 7.786262000 | -3.918334000 | 7.577946000 |
| C | 8.716151000 | -0.908574000 | 8.560350000 |
| H | 8.794443000 | 0.184796000 | 8.495162000 |
| H | 9.626731000 | -1.294844000 | 9.034982000 |
| H | 7.866816000 | -1.151046000 | 9.213827000 |
| C | 3.400222000 | 4.535274000 | 2.762876000 |
| C | 12.500168000 | 5.752271000 | 3.176638000 |
| H | 13.126998000 | 6.533553000 | 2.716472000 |
| H | 12.838834000 | 4.787329000 | 2.776304000 |
| H | 12.712685000 | 5.756623000 | 4.254106000 |
| C | 7.699869000 | 6.187204000 | 6.872762000 |
| H | 7.884904000 | 7.154676000 | 7.367705000 |
| H | 6.647274000 | 6.164184000 | 6.563957000 |


| H | 8.300520000 | 6.156185000 | 5.953772000 |
| :---: | :---: | :---: | :---: |
| C | 3.581811000 | 6.548842000 | 5.946006000 |
| H | 2.670442000 | 7.166166000 | 5.985893000 |
| H | 4.426852000 | 7.230509000 | 5.778170000 |
| H | 3.714977000 | 6.097125000 | 6.935907000 |
| C | 3.676277000 | 5.753054000 | 3.467875000 |
| C | 7.856523000 | 5.751725000 | 0.883443000 |
| H | 7.501538000 | 6.683919000 | 0.417113000 |
| H | 6.999317000 | 5.302366000 | 1.411893000 |
| H | 8.142795000 | 5.067722000 | 0.075153000 |
| Si | 11.240019000 | -0.615744000 | 5.784754000 |
| C | 3.999999000 | 7.070828000 | 2.834438000 |
| H | 3.083064000 | 7.590759000 | 2.512856000 |
| H | 4.634776000 | 6.952175000 | 1.946154000 |
| H | 4.525007000 | 7.737104000 | 3.530234000 |
| C | 11.843714000 | -0.196833000 | 7.511873000 |
| H | 11.777619000 | -1.063718000 | 8.182720000 |
| H | 11.254633000 | 0.616188000 | 7.954031000 |
| H | 12.894875000 | 0.122273000 | 7.478808000 |
| C | 12.247543000 | -2.040900000 | 5.082605000 |

## $\left[\mathrm{Pd}_{4} \mathrm{Al}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{7}$

| C | 7.935605000 | 17.639326000 | 2.139963000 |
| :---: | :---: | :---: | :---: |
| Al | 5.842548000 | 16.951825000 | 1.453650000 |
| Pd | 3.615392000 | 16.271233000 | 0.659389000 |
| C | 8.033739000 | 16.306942000 | 1.629951000 |
| AI | 2.291678000 | 18.252998000 | 1.072911000 |
| Pd | 4.665371000 | 15.432883000 | 3.065926000 |
| C | 7.645809000 | 16.335365000 | 0.251989000 |
| Al | 2.613593000 | 14.496114000 | 2.045478000 |
| Pd | 4.195358000 | 18.281374000 | 2.713989000 |
| Pd | 1.993106000 | 16.675730000 | 3.035538000 |
| C | 7.311284000 | 17.687417000 | -0.087476000 |
| C | 7.493369000 | 18.491555000 | 1.079504000 |
| C | 8.210087000 | 18.073854000 | 3.542525000 |
| H | 9.128038000 | 18.678668000 | 3.612393000 |
| H | 8.329573000 | 17.207472000 | 4.201173000 |
| H | 7.372188000 | 18.672296000 | 3.935804000 |
| C | 8.457075000 | 15.091048000 | 2.394265000 |
| H | 8.279018000 | 15.216002000 | 3.469736000 |
| H | 9.527201000 | 14.875641000 | 2.245170000 |
| H | 7.884729000 | 14.206005000 | 2.086957000 |
| C | 7.561173000 | 15.164219000 | -0.671603000 |
| H | 6.584236000 | 15.140602000 | -1.176910000 |
| H | 7.664216000 | 14.217976000 | -0.126721000 |
| H | 8.347382000 | 15.195082000 | -1.442973000 |
| C | 6.824547000 | 18.160732000 | -1.418055000 |
| H | 5.977886000 | 17.548488000 | -1.760461000 |
| H | 7.614507000 | 18.111179000 | -2.182671000 |
| H | 6.472003000 | 19.197995000 | -1.365867000 |
| C | 7.281018000 | 19.967297000 | 1.178444000 |
| H | 6.597363000 | 20.328538000 | 0.399727000 |
| H | 8.229872000 | 20.518701000 | 1.082071000 |
| H | 6.829893000 | 20.228117000 | 2.145188000 |
| C | 2.681237000 | 12.279111000 | 2.633599000 |
| C | 2.476873000 | 12.408586000 | 1.222874000 |
| C | 1.218662000 | 13.065452000 | 1.015786000 |
| C | 3.867057000 | 11.636726000 | 3.283855000 |
| H | 4.805753000 | 11.945155000 | 2.804273000 |
| H | 3.801281000 | 10.537967000 | 3.237276000 |
| H | 3.946520000 | 11.925123000 | 4.339325000 |
| C | 1.556639000 | 12.860260000 | 3.296254000 |
| C | 0.651926000 | 13.342673000 | 2.299267000 |
| C | 3.427632000 | 11.956788000 | 0.162905000 |
| H | 3.584280000 | 12.747045000 | -0.585733000 |
| H | 3.057788000 | 11.060735000 | -0.358878000 |
| H | 4.407536000 | 11.715335000 | 0.592934000 |
| C | 0.610686000 | 13.429585000 | -0.300789000 |
| H | 1.350034000 | 13.922635000 | -0.948341000 |
| H | -0.220986000 | 14.132953000 | -0.168763000 |
| H | 0.222079000 | 12.545383000 | -0.830058000 |
| C | 1.374541000 | 12.986473000 | 4.772043000 |
| H | 2.343102000 | 12.931783000 | 5.282781000 |
| H | 0.726484000 | 12.195270000 | 5.181308000 |
| H | 0.934675000 | 13.961145000 | 5.028024000 |
| C | -0.661620000 | 14.009168000 | 2.555488000 |
| H | -0.659375000 | 14.507124000 | 3.532578000 |
| H | -1.491332000 | 13.283950000 | 2.542519000 |
| H | -0.875095000 | 14.783861000 | 1.807340000 |
| C | 2.018285000 | 19.688861000 | -0.694301000 |
| C | 0.901821000 | 18.792475000 | -0.667882000 |
| C | 0.201392000 | 18.987206000 | 0.561941000 |
| C | 0.888507000 | 20.004754000 | 1.299392000 |
| C | 2.982630000 | 21.502546000 | 0.908902000 |
| H | 3.969328000 | 21.326261000 | 0.462104000 |
| H | 3.129621000 | 21.506081000 | 1.996245000 |


| H | 2.643002000 | 22.505259000 | 0.602666000 |
| :---: | :---: | :---: | :---: |
| C | 0.538697000 | 20.478981000 | 2.670316000 |
| H | -0.173409000 | 21.320276000 | 2.656949000 |
| H | 1.437758000 | 20.801170000 | 3.210653000 |
| H | 0.098039000 | 19.660986000 | 3.253885000 |
| C | -1.000366000 | 18.230506000 | 1.032430000 |
| H | -1.905892000 | 18.856092000 | 1.024006000 |
| H | -0.847765000 | 17.859444000 | 2.057557000 |
| H | -1.190020000 | 17.354985000 | 0.399197000 |
| C | 0.570836000 | 17.815622000 | -1.744826000 |
| H | 0.224950000 | 18.323420000 | -2.659661000 |
| H | -0.213684000 | 17.115585000 | -1.433826000 |
| H | 1.456180000 | 17.213779000 | -2.000042000 |
| C | 3.036782000 | 19.765767000 | -1.786784000 |
| H | 3.518167000 | 18.787179000 | -1.939661000 |
| H | 3.827998000 | 20.486400000 | -1.545715000 |
| H | 2.585616000 | 20.072221000 | -2.742668000 |
| C | 2.004031000 | 20.445096000 | 0.515750000 |
| AI | 5.434605000 | 14.688182000 | 5.119576000 |
| C | 6.563833000 | 14.130945000 | 7.053939000 |
| C | 5.207662000 | 13.686587000 | 7.194230000 |
| C | 4.767322000 | 12.268939000 | 7.400369000 |
| H | 4.809095000 | 11.988685000 | 8.464843000 |
| H | 3.735003000 | 12.111293000 | 7.061334000 |
| H | 5.405359000 | 11.562055000 | 6.852911000 |
| C | 4.363894000 | 14.839253000 | 7.146434000 |
| C | 2.876808000 | 14.882748000 | 7.281717000 |
| H | 2.433791000 | 13.881279000 | 7.275641000 |
| H | 2.597267000 | 15.358863000 | 8.234102000 |
| H | 2.409483000 | 15.461695000 | 6.469781000 |
| C | 5.189196000 | 15.991571000 | 6.964494000 |
| C | 4.680981000 | 17.385483000 | 6.769436000 |
| H | 3.709595000 | 17.382527000 | 6.255550000 |
| H | 4.559435000 | 17.912297000 | 7.729549000 |
| H | 5.355699000 | 17.975295000 | 6.135743000 |
| C | 7.784857000 | 13.263337000 | 7.097273000 |
| H | 8.164167000 | 13.158884000 | 8.126435000 |
| H | 7.575862000 | 12.252623000 | 6.722570000 |
| H | 8.599722000 | 13.679757000 | 6.490105000 |
| C | 6.550724000 | 15.557099000 | 6.929867000 |
| C | 7.753082000 | 16.440861000 | 6.824974000 |
| H | 8.557610000 | 15.977484000 | 6.237668000 |
| H | 8.166117000 | 16.664284000 | 7.821548000 |
| H | 7.501338000 | 17.397245000 | 6.352558000 |
| AI | 3.685327000 | 15.570452000 | -1.583491000 |
| C | 2.542735000 | 15.056028000 | -3.588042000 |
| C | 3.245577000 | 13.870739000 | -3.206789000 |
| C | 2.640717000 | 12.504839000 | -3.113659000 |
| H | 2.431940000 | 12.128460000 | -4.128884000 |
| H | 3.317310000 | 11.789409000 | -2.635052000 |
| H | 1.693239000 | 12.492258000 | -2.564346000 |
| C | 4.645216000 | 14.155075000 | -3.226419000 |
| C | 5.732135000 | 13.149771000 | -2.991805000 |
| H | 5.778976000 | 12.426126000 | -3.820659000 |
| H | 6.714432000 | 13.629064000 | -2.917773000 |
| H | 5.571661000 | 12.577997000 | -2.067250000 |
| C | 4.812695000 | 15.511782000 | -3.647708000 |
| C | 6.110247000 | 16.153427000 | -4.030646000 |
| H | 6.929706000 | 15.880944000 | -3.355662000 |
| H | 6.400013000 | 15.836958000 | -5.045637000 |
| H | 6.037442000 | 17.246752000 | -4.038903000 |
| C | 1.064990000 | 15.130700000 | -3.822805000 |
| H | 0.788592000 | 14.543936000 | -4.713450000 |
| H | 0.488437000 | 14.728119000 | -2.978820000 |

## [PtAI](Cp**)(tebd)(dpa)

| Pt | 6.284985000 | 3.050206000 | 6.416234000 |
| :--- | :---: | :---: | :---: |
| Al | 7.930229000 | 1.319393000 | 5.437591000 |
| C | 8.158239000 | 4.089498000 | 5.618794000 |
| C | 8.627569000 | 2.967349000 | 6.315271000 |
| C | 9.528215000 | 3.088444000 | 7.469112000 |
| C | 9.176264000 | 2.56373000 | 8.72130000 |
| C | 10.052123000 | 2.624497000 | 9.804793000 |
| C | 11.313177000 | 3.208028000 | 9.656000000 |
| C | 11.679114000 | 3.737265000 | 8.413707000 |
| C | 10.797996000 | 3.682384000 | 7.334627000 |
| C | 7.722725000 | -0.713825000 | 4.512893000 |
| C | 9.101104000 | -0.445954000 | 4.825760000 |
| C | 10.235603000 | -0.417216000 | 3.845254000 |
| C | 9.222666000 | -0.325076000 | 6.255977000 |
| C | 7.916200000 | -0.447823000 | 6.815587000 |
| C | 7.526750000 | -0.439519000 | 8.261813000 |
| C | 6.984669000 | -0.681499000 | 5.734881000 |
| C | 5.518681000 | -0.921074000 | 5.929710000 |
| C | 10.511735000 | -0.110900000 | 6.987004000 |
| C | 7.191800000 | -0.990340000 | 3.141166000 |
| C | 6.918193000 | 2.511346000 | 4.185334000 |
| C | 5.965690000 | 2.111954000 | 3.140661000 |
| C | 6.271725000 | 2.285983000 | 1.777097000 |
| C | 5.405409000 | 1.832210000 | 0.782918000 |
| C | 4.208288000 | 1.194763000 | 1.123190000 |
| C | 3.892607000 | 1.013105000 | 2.471982000 |
| C | 4.765520000 | 1.457181000 | 3.464293000 |
| C | 7.231611000 | 3.844545000 | 4.468459000 |
| C | 6.632391000 | 5.009931000 | 3.760739000 |
| C | 7.119726000 | 5.412620000 | 2.51052000 |
| C | 6.558740000 | 6.504449000 | 1.845910000 |
| C | 5.503305000 | 7.211493000 | 2.426529000 |
| C | 5.017115000 | 6.822427000 | 3.677173000 |
| C | 5.580335000 | 5.731317000 | 4.339502000 |
| C | 8.516150000 | 5.485677000 | 5.979717000 |
| C | 8.170318000 | 6.015075000 | 7.229325000 |
| C | 8.537751000 | 7.313927000 | 7.577373000 |
| C | 9.261819000 | 8.101819000 | 6.67832000 |
| C | 9.611717000 | 7.582072000 | 5.429508000 |
| C | 9.238026000 | 6.283543000 | 5.081233000 |
| C | 5.244877000 | 2.795436000 | 8.111128000 |
| C | 5.424688000 | 2.698943000 | 9.535927000 |
| C | 4.657093000 | 1.797114000 | 10.303441000 |
| C | 4.860454000 | 1.682257000 | 11.676372000 |
| C | 5.825862000 | 2.469063000 | 12.313946000 |
| C | 6.590258000 | 3.369825000 | 11.565628000 |
| C | 6.397197000 | 3.479987000 | 10.190981000 |
| C | 4.429546000 | 2.703058000 | 7.080014000 |
| C | 3.089655000 | 2.528458000 | 6.585683000 |
| C | 2.731942000 | 3.067311000 | 5.332899000 |
|  |  |  |  |


| C | 1.439784000 | 2.913950000 | 4.837560000 |
| :---: | :---: | :---: | :---: |
| C | 0.481508000 | 2.215172000 | 5.578250000 |
| C | 0.822080000 | 1.676699000 | 6.824438000 |
| C | 2.111475000 | 1.832643000 | 7.327085000 |
| H | 11.093884000 | 0.715832000 | 6.557884000 |
| H | 11.137781000 | -1.015191000 | 6.939911000 |
| H | 10.345125000 | 0.134000000 | 8.041284000 |
| H | 6.733019000 | 0.292103000 | 8.471335000 |
| H | 8.378728000 | -0.201428000 | 8.907759000 |
| H | 7.142907000 | -1.426970000 | 8.560865000 |
| H | 9.908427000 | -0.063482000 | 2.858705000 |
| H | 10.665437000 | -1.421756000 | 3.705644000 |
| H | 11.046676000 | 0.238849000 | 4.187183000 |
| H | 7.578207000 | -0.279999000 | 2.398619000 |
| H | 6.099254000 | -0.921399000 | 3.106742000 |
| H | 7.481187000 | -2.000996000 | 2.813656000 |
| H | 4.991790000 | -0.976719000 | 4.971077000 |
| H | 5.053631000 | -0.118690000 | 6.521420000 |
| H | 5.346085000 | -1.866689000 | 6.466328000 |
| H | 7.595839000 | 5.395081000 | 7.916929000 |
| H | 8.255797000 | 7.713601000 | 8.551752000 |
| H | 9.548482000 | 9.118502000 | 6.947767000 |
| H | 10.173512000 | 8.191271000 | 4.721016000 |
| H | 9.508434000 | 5.881111000 | 4.105410000 |
| H | 5.064189000 | 8.063797000 | 1.907745000 |
| H | 6.948079000 | 6.803288000 | 0.872306000 |
| H | 7.952969000 | 4.871796000 | 2.061431000 |
| H | 5.209605000 | 5.424382000 | 5.319200000 |
| H | 4.196848000 | 7.370791000 | 4.141008000 |
| H | 3.919590000 | 1.170361000 | 9.803307000 |
| H | 4.266105000 | 0.973361000 | 12.253492000 |
| H | 5.983268000 | 2.377423000 | 13.388645000 |
| H | 7.347187000 | 3.984109000 | 12.053496000 |
| H | 7.000000000 | 4.168535000 | 9.601787000 |
| H | 12.002545000 | 3.256218000 | 10.499026000 |
| H | 9.742691000 | 2.219659000 | 10.769442000 |
| H | 8.191617000 | 2.113971000 | 8.838340000 |
| H | 11.088017000 | 4.102710000 | 6.371415000 |
| H | 12.657265000 | 4.202719000 | 8.286293000 |
| H | 2.375911000 | 1.413524000 | 8.297030000 |
| H | 0.077265000 | 1.132065000 | 7.405402000 |
| H | -0.528474000 | 2.089816000 | 5.187517000 |
| H | 1.182031000 | 3.335510000 | 3.865993000 |
| H | 3.487573000 | 3.603378000 | 4.760205000 |
| H | 4.520552000 | 1.310610000 | 4.513332000 |
| H | 2.959677000 | 0.526353000 | 2.758905000 |
| H | 3.530090000 | 0.844906000 | 0.344878000 |
| H | 5.666386000 | 1.979585000 | -0.265777000 |
| H | 7.209255000 | 2.765635000 | 1.499296000 |

### 8.3. Table of Figures

Figure 1: Distribution of the European fossil-based plastics demand in 2018/2019 (left) and European fossil-based plastics demand by application in 2018 / 2019 (right). ${ }^{2}$

Figure 2: Left: Energy diagram of the hydrogenation process of acetylene on a Pd (black) or PdAg (red) surface calculated from Studt et al.. Right: Diagram of the conversion of acetylene dependent on the metal ratios with respect to the observed ethane concentration. ${ }^{10}$ Adapted reprinted with permission from The American Association for the Advancement of Science. Copyright in 2008. 2

Figure 3: Cross sections of nanoparticle showing different types of metal distribution: core-shell (A), cluster-in-cluster (B), intermetallic alloy with ordered metal atoms (C), intermetallic alloy with randomly distributed metal atoms (D), multi-shell alloy (E)

Figure 4: Different steps of nanoparticle synthesis: Reduction, nucleation and growth to obtain nanostructured metal colloids. ${ }^{32-34}$.
Figure 5: Synthesis of NHC and phosphine stabilized Iron-Sulfur clusters. ${ }^{68}$ Adapted reprinted with permissions from L. Deng, R. H. Holm, J. Am. Chem. Soc. 2008, 130, 9878-9886. Copyright 2008, American Chemical Society.
.7
Figure 6: Schematic representation of the synthesis of different Pd-Ga compounds as published by Fischer et al. in 2002 and 2005. ${ }^{72-73}$

Figure 7: Molecular structures of $\left[\mathrm{CuZn} n_{2}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ (left), $\left[\mathrm{Cu}_{2} \mathrm{Zn}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}{ }^{+}$(middle) and $\left[\mathrm{Cu}_{3} \mathrm{Zn} 4\right]\left(\mathrm{Cp}^{*}\right)_{5}$ (right) as determined by SC- XRD. ${ }^{75-76,78}$ Color code: Cu, orange; Zn , light blue; C, grey. H atoms are omitted for clarity. $\mathrm{Cp}^{*}$ rings are depicted in wireframes.
Figure 8: Schematic representation of different synthetic pathways for Cu -Al clusters including cluster degradation from $\left[\mathrm{Cu}_{4} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{Mes})$ to embryonic $\left[\mathrm{Cu}_{2} \mathrm{Al}_{1}\right]\left(\mathrm{Cp}^{*}\right)_{3}$, thermal cluster growth from $\left[\mathrm{Cu}_{4} \mathrm{Al}_{4}\right]$ or chemical cluster growth from $\left[\mathrm{Cu}_{2} \mathrm{Al}_{1}\right]\left(\mathrm{Cp}^{*}\right)_{3}$ to obtain $\left[(\mathrm{H}) \mathrm{Cu}_{7 / 8} \mathrm{Al}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$. Organic residues are omitted for clarity. Color code: Cu, red; Al, blue. ${ }^{81}$ Reprinted with permission from M. Schütz, C. Gemel, M. Muhr, C. Jandl, S. Kahlal, J.-Y. Saillard, R. A. Fischer, Chem. Sci. 2021, 12, 6588-6599. Copyright 2021, by the Royal Society of Chemistry. Permission conveyed through Copyright Clearance Center, Inc.. 11
Figure 9: Schematic representation of the reaction between $\left[\mathrm{Pd}_{3}(\operatorname{lnCp})_{8}\right]$ with $\mathrm{PPh}_{3}$ yielding $\left[\mathrm{Pd}_{3}\left(\operatorname{InCp}{ }^{*}\right)_{3}\left(\mathrm{PPh}_{3}\right)_{3}\right] .{ }^{73}$ 13

Figure 10: Schematic representation of the reaction between $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ and AlCp * in different solvents resulting in $\mathrm{C}-\mathrm{H}$ and $\mathrm{Si}-\mathrm{H}$ bond activated products. ${ }^{82}$ Reprinted with permissions from T. Steinke, C. Gemel, M. Cokoja, M. Winter, R. A. Fischer, Angew. Chem. Int. Ed. 2004, 43, 2299-2302. Copyright 2004, John Wiley and Sons. 14

Figure 11: Left: Molecular structure of $\left[\mathrm{Pd}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{CN}^{\dagger} \mathrm{Bu}_{4}{ }_{4}\left(\mathrm{Cp}^{*}\right)_{4}\right.$ and the core structure (middle left) showing two interconnected tetrahedra. Pd, red; Ga, blue; N, yellow. ${ }^{98}$ Right: Molecular structure of $\left[\mathrm{Cu}_{4} \mathrm{Zn}_{4}\right]\left(\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}\right)_{4}\left(\mathrm{Cp}^{*}\right) 4^{74}$ and the respective core structure ${ }^{78}$ showing two inverted tetrahedra with $\mathrm{Zn}_{4}$ forming the outer sphere and $\mathrm{Cu}_{4}$ the inner spherical tetrahedron. Cu , dark red; Zn , green; N , yellow. Left and middle left: Adapted reprinted with permissions from M. Molon, K. Dilchert, C. Gemel, R. W. Seidel, J. Schaumann, R. A. Fischer, Inorg. Chem. 2013, 52, 14275-14283. Copyright 2013, American Chemical Society. Middle right: Adapted reprinted with permissions from K. Freitag, C. Gemel, P. Jerabek, I. M. Oppel, R. W. Seidel, G. Frenking, H. Banh, K. Dilchert, R. A. Fischer, Angew. Chem. Int. Ed. 2015, 54, 4370-4374. Copyright in 2015, John Wiley and Sons. Right: Adapted reprinted with permissions from K. Freitag, H. Banh, C. Gemel, R. W. Seidel, S. Kahlal, J.-Y. Saillard, R. A. Fischer, Chem. Commun., 2014, 50, 8681-8684. Copyright 2014, Royal Society of Chemistry; Permission conveyed through Copyright Clearance Center, Inc. 17

Figure 12: Molecular structure of [Cp*AI-Fe(CO)4] as determined by SC-XRD. H atoms are omitted for clarity. Color code: Fe, orange; O, red; Al, yellow; C, grey. ${ }^{104}$
Figure 13: Left: Molecular structure of $\left[\mathrm{Cu}_{4} \mathrm{Zn}_{4}\right]\left(\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}\right)_{4}\left(\mathrm{Cp}^{*}\right)_{4}$ as molecular model for $\gamma$-brass. The same structural motif of the two interpenetrated polyhedra of [ $\mathrm{Cu}_{4} \mathrm{Zn}_{4}$ ] cluster core is also found in solid-state structure of $\gamma$-brass $\mathrm{Cu}_{10} \mathrm{Zn}_{16}$ (right) where a tetrahedral $\mathrm{Zn}_{4}$ is surrounded by tetrahedral $\mathrm{Cu}_{4}$ being inverse to ligand protected $\left[\mathrm{Cu}_{4} \mathrm{Zn}_{4}\right](\mathrm{L})_{8 .}{ }^{74}$ Color code: Cu , red; Zn , green. (Adapted) reprinted with permission from K. Freitag, H. Banh, C. Gemel, R. W. Seidel, S. Kahlal, J.-Y. Saillard, R. A. Fischer, Chem. Commun. 2014, 50, 8681-8684. Copyright 2014, Royal Society of Chemistry; permission conveyed through Copyright Clearance Center, Inc.

Figure 14: Overview of the Ni-Ga clusters discussed in this chapter. It has to be noted, these are all calculated structures with ORCA4.0 or ORCA5.0.

Figure 15: LIFDI mass spectra of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}(\mathbf{1}, 1218.0627 \mathrm{~m} / \mathrm{z})$ at different collision energies of the HCD cell (Orbitrap system from Thermo Fisher) enables unambiguous identification of product, intermediate or fragment signals. Following signals/intermediates or fragments were assigned to 1 ( $1218.0633 \mathrm{~m} / \mathrm{z}$, calc. $1218.0633 \mathrm{~m} / \mathrm{z}$ ), $1-G a C p^{*}\left(\mathrm{~m} / \mathrm{z} 1012.0188\right.$ ), $1-G a C p^{*}-h e x$ at $\mathrm{m} / \mathrm{z} 929.9385$, 1-GaCp*-2hex at $m / z 845.8494,1-2 G a C p^{*}$ at $m / z 807.9739$ and for $1-2 G a C p^{*}-h e x$ at $m / z 721.8676$. RF voltages of CE10.0 are required as the lowest collision energy for detection with this setup and are used in all experiments unless otherwise stated. ${ }^{140}$

26
Figure 16: LIFDI mass spectra of the reaction [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ] (1eq.) and $\mathrm{GaCp}^{*}$ (1eq.) at $90^{\circ} \mathrm{C}$ after 6 h in toluene showing the influence of additive on cluster formation: Black trace: with 3-hexyne ( 0.5 eq. ) as additive, red: without any additive. Additive containing reaction led to Ni-rich clusters as $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ ( $1637.7517 \mathrm{~m} / \mathrm{z} ; \mathrm{F}),\left[\mathrm{Ni}_{8} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}-2 \mathrm{H}(1693.6507 \mathrm{~m} / \mathrm{z}, \mathrm{G})$ and $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}(\mathrm{hex})(1719.8331 \mathrm{~m} / \mathrm{z})$ while the reaction without any additive favors Ga-enriched clusters as $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}(1649.7700 \mathrm{~m} / \mathrm{z})$ and $\left[\mathrm{Ni}_{7} \mathrm{Ga}_{7}\right]\left(\mathrm{Cp}^{*}\right)_{6}-2 \mathrm{H}(1706.6904 \mathrm{~m} / \mathrm{z})$. Further signals assigned: $\mathrm{A}:[\mathrm{NiGa} 2]\left(\mathrm{Cp}^{*}\right)_{2}(468.0185 \mathrm{~m} / \mathrm{z})$ for reaction without additive, $\left[\mathrm{Ni}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}($ hex $)(468.1774 \mathrm{~m} / \mathrm{z})$ for reaction with additive; $\mathrm{B}:\left[\mathrm{Ni}_{6} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ (1169.7576 m/z) C: [ $\left.\mathrm{Ni}_{6} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}-2 \mathrm{H}(1333.8977 \mathrm{~m} / \mathrm{z})$; D: [ $\left.\mathrm{Ni}_{5} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{hex})(1399.9414 \mathrm{~m} / \mathrm{z})$; $\mathrm{E}:\left[\mathrm{Ni}_{5} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{hex})_{2}+2 \mathrm{H}(1484.8918 \mathrm{~m} / \mathrm{z}) .{ }^{140}$27

Figure 17: Left: LIFDI mass distribution of the reaction [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ] (1eq.), GaCp* (1eq.) and 3-hexyne (0.5eq.) after 5 h at $60^{\circ} \mathrm{C}$ showing a library of clusters in solution. ${ }^{140}$ Highlighted signals are assigned as products and are related to clusters given in the right table. Figure left is reprinted with permission from P. Heiß, J. Hornung, C. Gemel, R. A. Fischer, Chem. Commun. 2022, 58, 4332-4335. Copyright 2022, Royal Society of Chemistry; permission conveyed through Copyright Clearance Center, Inc. .. 28
Figure 18: Left: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ and $\mathrm{GaCp}^{*}$ with different equivalents 3-hexyne at $60^{\circ} \mathrm{C}$ in toluene. Right: Overview of assigned clusters in the spectra left. Sum formulas assigned as products are given in bold.

29
Figure 19: Left: LIFDI mass spectra of the reaction [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ] (1 eq.) with dpa ( 0.5 eq .) and different equivalents of GaCp* in toluene at room temperature. Right: Cluster assignment of obtained compounds. Sum formulas related to products are given in bold. 31

Figure 20: Exchange reaction of 1 with AICp* monitored by in-situ LIFDI MS measurements. Left: LIFDI mass spectrum of the reaction of 1 with 1 eq . AlCp * (related to Ni ) in hexane after one day at $40^{\circ} \mathrm{C}$. Right: Table of experimentally observed $\mathrm{m} / \mathrm{z}$ values and assigned clusters. 34

Figure 21: Enlarged ${ }^{31} \mathrm{P}$ NMR spectrum of the reaction $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ with 3 eq. $\mathrm{PEt}_{3}$ showing free $\mathrm{PEt}_{3}(-19.98 \mathrm{ppm}),\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right](16.5 \mathrm{ppm})$ and $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{PEt}_{3}\right)_{2}\right](31.3 \mathrm{ppm})$ as literature known compounds. 35
Figure 22: Enlarged ${ }^{31} \mathrm{P}$ NMR spectrum of the reaction $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ with 2.5 eq. $\mathrm{PPh}_{3}$ showing free $\mathrm{PPh}_{3}(-5.3 \mathrm{ppm}),\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{PPh}_{3}\right)_{2}\right](40.5 \mathrm{ppm})$ as literature known compounds. ..................... 36
Figure 23: LIFDI mass spectra of the reaction of 1 (black trace) with 1 eq. dpa (red trace) after two days at $40^{\circ} \mathrm{C}$ in toluene. The assignment of the signals is given in the table right. 37
Figure 24: LIFDI mass spectrum of $\left[\mathrm{Ni}\left(\mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right) 4\right.$ after 4.5 hours at $60^{\circ} \mathrm{C}$ in toluene. The assignment of the signals is given in the table right.

38
Figure 25: Left: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ with 3-hexyne ( $\Delta \mathrm{eq}$. related to Ni ) in toluene at room temperature after one day showing strong interaction. Right: Table of LIFDI MS signal assignment.

39
Figure 26: Left: Reaction progress monitored by LIFDI MS of [Ni(GaCp*)4] with 4 eq. 3-hexyne (related to Ni ) at $60^{\circ} \mathrm{C}$ in toluene. Right: Cluster assignment of obtained compounds. Sum formulas related to products are given in bold. 40

Figure 27: Left: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ with dpa ( $\Delta \mathrm{eq}$.) at room temperature after one day (1 eq.) and three days (4 eq.). Right: Table includes cluster assignment of the obtained compounds. Compounds related to products are given in bold.

41
 calculated by ORCA4.0 (BP86-D3/def2-tzvpp) while D and E could not be optimized to a minimum. Color code: Ni, green; Ga, blue; C, grey. Hydrogen atoms are omitted and $\mathrm{Cp}^{*}$ rings are depicted in wireframe for clarity. C was previously suggested by J. Hornung ${ }^{134}$.

Figure 29: Metal arrangement of possible $\mathrm{Ni}_{4} \mathrm{Ga}_{4}$ clusters compared with already published $\mathrm{Pd}_{4} \mathrm{Ga}_{4}$ clusters. Left: square planar $\mathrm{Ni}_{4}$-core with two $\mathrm{Ni}_{2}$-edge-bridging $\mathrm{GaCp}^{*}$ and two $\mathrm{Ni}_{4}$-face-bridging $\mathrm{GaCp}^{*}$. The same structure motif was obtained for $\left[\mathrm{Pd}_{4}\left(\mathrm{GaCp}^{*}\right)_{4}\left(\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}\right)_{4}\right]$ from $\left[\left\{\mathrm{Pd}\left(\mathrm{CN}{ }^{\mathrm{t}} \mathrm{Bu}\right)_{2}\right\}_{3}\right]^{98}$ (middle left). Middle right: Tetrahedrally arranged $\mathrm{Ni}_{4}$ core with four $\mathrm{Ni}_{2}$-edge-bridging $\mathrm{GaCp}^{*}$ ligands. Right: Metal arrangement of $\left[\mathrm{Pd}_{4}\left(\mathrm{GaCp}^{*}\right)_{4}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)_{4}\right]$ originating from $\left[\mathrm{Pd}_{3}\left(\mathrm{GaCp}^{*}\right)_{4}\left(\mathrm{CN}^{+1} \mathrm{Bu}\right)_{3}\right]^{98}$ featuring a $\mathrm{Pd}_{4}$ tetrahedra with four $\mathrm{Pd}_{4}$-face-bridging $\mathrm{GaCp}^{*}$ ligands. Color code: Ni, green; Ga, blue; Pd, red 44
Figure 30: Left: Structure suggestion for $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{4}$ as calculated by ORCA4.0 (BP86-D3/def2tzvpp). Right: Crystal structure of $\left[\mathrm{Pd}_{3} \mathrm{Al}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}$ as determined by SC-XRD from Fischer et al. ${ }^{73}$. Color code: Ni, green; Ga, blue; Pd, red; Al, yellow, C, grey. H atoms are omitted for clarity. Cp* and ethyl moieties are depicted in wireframe. 45

Figure 31: Structure suggestions for $\left[\mathrm{Ni}_{4} \mathrm{Gan}_{n}\right]^{\left(C p^{*}\right)_{n}(\mathrm{dpa})_{6-n}(\mathrm{n}=2-4) \text { as calculated by ORCA5.0 }}$ (BP86-D3/def2-tzvpp). Top: square-planar $\mathrm{Ni}_{4}$ core structures; bottom: Tetrahedrally arranged $\mathrm{Ni}_{4}$-core structures. Left: $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})_{2}$; middle: $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$; right: $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{4}$. H atoms are omitted for clarity. Phenyl- and $\mathrm{Cp}^{*}$-rings are depicted in wireframe. Color code: Ni, green; Ga, blue; C, grey. 46

Figure 32: Comparison of different $\mathrm{Ni}_{4}$ compounds. Left: Structure suggestion for the herein reported $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{5}$ calculated with ORCA5.0 (BP86-D3/def2-tzvpp); middle left: molecular structure of $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{\dagger} \mathrm{Bu}\right)_{7}\right]$ determined by SC-XRD ${ }^{146}$; middle right: molecular structure of $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{\dagger} \mathrm{Bu}\right)_{4}(\mathrm{dpa})_{3}\right]$ as determined by SC-XRD ${ }^{147}$; right: molecular structure of $\left[\mathrm{Ni}_{4}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{CN}^{\star} \mathrm{Bu}\right)_{4}\right]$ as determined by SCXRD $^{98}$. Middle left and middle right are reprinted with permission from M. G. Thomas, W. R. Pretzer, B. F. Beier, F. J. Hirsekorn, E. L. Muetterties, J. Am. Chem. Soc. 1977, 99, 743-748 and E. L. Muetterties, E. Band, A. Kokorin, W. R. Pretzer, M. G. Thomas, Inorg. Chem. 1980, 19, 1552-1560. Copyright 1977 (middle left) and 1980 (middle right), American Chemical Society.

47
Figure 33: Overview of the herein discussed structures of $\mathrm{Ni}-\mathrm{Al}$ compounds. The structures were either determined by SC-XRD or proposed with ORCA4.0 or ORCA5.0.
Figure 34: Left: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ (1eq.), $\mathrm{AlCp}^{*}$ (1eq.) and 3-hexyne ( $\Delta \mathrm{eq}$.) after 6 h at $60^{\circ} \mathrm{C}$ in toluene/hexane. Right: Cluster assignment of observed signals. Compounds related to a product peak are given in bold.

51
Figure 35: Left: LIFDI mass spectra of the reaction [ $\mathrm{Ni}(\operatorname{cod})_{2}$ ] (1eq.), AICp* (1eq.) and 3-hexyne ( $\Delta$ eq.) after 6.5 h at $90^{\circ} \mathrm{C}$ in toluene/hexane. Right: Signal assignment of obtained compounds. Clusters related to product peaks are given in bold.

52
Figure 36: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ (1 eq.), AICp* ( $\Delta$ eq.) and 3-hexyne after 6 h at $60^{\circ} \mathrm{C}$ in toluene/hexane. Left: 1 eq. 3-hexyne, right: 4 eq. 3-hexyne.

53
Figure 37: LIFDI mass spectra of the reaction [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right]$ ( 1 eq. ), $\mathrm{AICp}^{*}$ (1 eq.) and dpa ( $\left.\Delta \mathrm{eq}.\right)$ after 6 h at $60^{\circ} \mathrm{C}$ in toluene/hexane.54

Figure 38: LIFDI mass spectrum of the reaction of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})$ with 2 eq. dpa at $90^{\circ} \mathrm{C}$ after one day in hexane. MS samples were measured in a solvent mixture (toluene/hexane)

55
Figure 39: Left: Molecular structure of [Ni(AICp*)(tebd)(cod)] (6) determined by single crystal X-ray diffraction.. Middle: Measured dihedral angle between the plane $\mathrm{C}_{\text {tebd }}-\mathrm{Al}-\mathrm{C}_{\text {tebd }}$ (grey) and the plane of the four ring-C's (red) of the metallacycle. Right: Molecular structure of [Ni(AICp*)(tpbd)(dpa)] (8) determined by single crystal x-ray diffraction. Hydrogen atoms are omitted for clarity and cod and $\mathrm{Cp}^{*}$ ring are depicted in wireframe Color code: green, Ni; orange, Al; grey, C. 58
Figure 40: Calculated structure of $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]_{\left(\mathrm{Cp}^{*}\right)_{3}(\text { hex })_{3} \text { (left) using ORCA5.0 (BP86-D3/def2-tzvpp) and }}$ crystal structure of $\left[\mathrm{Pd}_{3} \mathrm{Al}_{6}\right]\left(\mathrm{Cp}^{*}\right)_{6}{ }^{73}$ (right) showing the same structural motif in the metal core as $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]$. Color code: yellow: Al; green: Ni; blue: Pd.

59
Figure 41: Calculated structures of $\left[\mathrm{Ni}_{2} \mathrm{Al}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})$ (left) and $\left[\mathrm{Ni}_{2} \mathrm{Al}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{2}$ (right) using BP86-D3/def2-tzvpp level of theory. Color code: yellow: AI; green: Ni. Cp* rings are depicted in wireframe. H atoms are omitted for clarity.

60
Figure 42: LIFDI mass spectrum of the reaction $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$ with DPA (black) and DPA/Ni(cod)2 mixture (red) after 1 d at $60^{\circ} \mathrm{C}$ in cyclohexane.

61
Figure 43: Time dependent LIFDI mass spectra of the reactions [ $\left.\mathrm{Ni}_{4}\left(\mathrm{CN}^{\dagger} \mathrm{Bu}\right)_{7}\right]$ with 4 eq. $\mathrm{AlCp}^{*}$ and 4 eq . acetylene at $60^{\circ} \mathrm{C}$. Left: 3-hexyne, right: dpa. Clusters given in bold are referred to product peaks... 63
Figure 44: Left: Molecular structure of $\left[\mathrm{Ni}_{3} \mathrm{Al}_{3}\right]_{\left(\mathrm{Cp}^{*}\right)_{3}\left(\mathrm{CN}^{*} \mathrm{Bu}\right)_{4} \text { (12) determined by single crystal x-ray }}$ diffraction. Hydrogen atoms are omitted for clarity. Color code: green, Ni; orange, Al; light blue, N; grey,
C. Right: Core structure of 12 showing a trigonal bipyramid consisting of a Ni ${ }_{3}$ triangle which is face-
capped by two Al atoms. Further one Al atom is bridging the Ni-Ni bond........................................... 64

Figure 45: LIFDI mass spectra of the reaction $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ with $\mathrm{GaCp}^{*}$ (2 eq.) in toluene (black trace) or toluene- $\mathrm{d}_{8}$ (red trace) or with GaCp*Et (blue trace) after one day at $-30^{\circ} \mathrm{C}$. Cluster assignments are given on the right. 67
Figure 46: LIFDI mass spectra of the reaction $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ with $\mathrm{GaCp}^{*}$ (2 eq.) in toluene (black trace) or toluene-d8 (red trace) or with $\mathrm{GaCp}^{* E t}$ (blue trace) after one day at room temperature. Cluster assignments are given on the right.

68
Figure 47: LIFDI mass spectra of the reaction $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ and $\mathrm{GaCp}^{*}(2 \mathrm{eq}$.$) at -30^{\circ} \mathrm{C}$ (black trace) or at $60^{\circ} \mathrm{C}$ (blue trace) and additional with dpa (2 eq.) at $-30^{\circ} \mathrm{C}$ (red trace) or at $60^{\circ} \mathrm{C}$ (green trace). The spectra were recorded after one or two days in toluene. Observed peaks are assigned in the table on the right. 69
Figure 48: Time dependent LIFDI mass spectra of the reaction $\left[\mathrm{PdGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ with excess 3-hexyne at room temperature in toluene/benzene-d . $_{6}$

71
Figure 49: Time-dependent LIFDI mass spectra of the reaction $\left[\mathrm{PdAl}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ with 100 -fold excess 3-hexyne at $90^{\circ} \mathrm{C}$ in toluene/benzene- $\mathrm{d}_{6}$. Clusters assigned to products are given in bold. 73
Figure 50: Molecular structure of $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{\dagger} \mathrm{Bu}\right)_{7}\right]$ determined by SC-XRD ${ }^{146}$ (left) and structural suggestion for $\left[\mathrm{Pd}_{4}\left(\mathrm{AlCp}^{*}\right)_{7}\right]$ as proposed by ORCA5.0 (BP86-D3/def2-tzvpp).

73
Figure 51: Left: Time dependent LIFDI mass spectra of the reaction $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right]$ ( 1 eq .), GaCp* (1 eq.) and 3-hexyne ( 1 eq.) in toluene at room temperature. Right: Cluster assignment of observed peaks. Signals which are related to product signals are given in bold.

76
Figure 52: Crystal structure of $\left[\mathrm{Pd}_{3}\left(\operatorname{InCp}^{*}\right)_{3}\left(\mathrm{PPh}_{3}\right)_{3}\right]$ as determined by SC-XRD from Fischer et al. ${ }^{73}$ resembling a structural analog of $\left[\mathrm{Pt}_{3} \mathrm{Ga}_{3}\right]_{\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{3} . \mathrm{H} \text { atoms are omitted for clarity. Phenyl rings are }}$ depicted in wireframe. Color code: Pd, red; In, light yellow; P, light blue; C, grey.

77
Figure 53: Left: LIFDI mass spectra of the reaction $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ ( 1 eq .) with $\mathrm{GaCp}^{*}$ ( $1 \mathrm{eq}$. ) and dpa ( $\Delta \mathrm{eq}$.) at room temperature after six hours in toluene. Right: Cluster assignment related to the obtained signals.
.78
Figure 54: Left: Proposed structure for $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{dpa})$; Structure of $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right){ }_{4}\left(\mathrm{PPh}_{3}\right)$ (middle) and $\left[\mathrm{Pt}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ (right) as published from Fischer et al. ${ }^{71,73}$.

79
Figure 55: Left: LIFDI mass spectra of the reaction $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ (1 eq.) with dpa (4 eq.) and $\operatorname{AICp}{ }^{*}(\Delta$ eq.) at $60^{\circ} \mathrm{C}$ after two hours in toluene. Right: Cluster assignment of the obtained signals. Peaks which could be assigned as product are given in bold.

81
Figure 56: Left: Structural suggestion of $[\mathrm{PtAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tpbd})(\mathrm{dpa})$ as proposed by theoretical calculations (BP86-D3/def2-tzvpp). Color code: light blue, Pt; yellow, Al; grey, C. Phenyl and $\mathrm{Cp}^{*}$ rings are partly depicted in wireframe. H-atoms are omitted for clarity. Right: ${ }^{1} \mathrm{H} /{ }^{1} \mathrm{H}$ COSY NMR spectrum of [PtAl](Cp*)(tpbd)(dpa) with signal assignment.

82
Figure 57: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ with $\Delta \mathrm{eq} . \mathrm{ZnMe} \mathrm{Zn}_{2}$ after one hour at $-30^{\circ} \mathrm{C}$ in toluene. 85

Figure 58: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ with $\Delta$ eq. $\mathrm{ZnMe}{ }_{2}$ after one/two hour at $0^{\circ} \mathrm{C}$ in toluene 86
Figure 59: LIFDI mass spectra of the reaction $\left[\mathrm{NiGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ and $\left[\mathrm{NiGa}_{3} \mathrm{Zn}_{2}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{Me})$ (black trace) with 4 eq. (red) or 8 eq. 3-hexyne after one day at $60^{\circ} \mathrm{C}$ in toluene.

87
Figure 60: Top: LIFDI mass spectrum of the reaction $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})\right]$ with 3-hexyne as solvent after one day at $60^{\circ} \mathrm{C}$. Peaks are assigned as follows: A: $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right) 4\right](877.59 \mathrm{~m} / \mathrm{z})$; B: $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{3}\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})\right] \quad(953.77 \mathrm{~m} / \mathrm{z})$; C: see below left ( $1017.29 \mathrm{~m} / \mathrm{z}$ ); D: $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{ZnCp}^{*}\right)_{2}(\mathrm{ZnMe})_{2}\right](1032.31 \mathrm{~m} / \mathrm{z})$; $\mathrm{E}: \mathrm{H}-\mathrm{Cp}^{*}(1047.29 \mathrm{~m} / \mathrm{z}) ; \mathrm{F}:\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)\left(\mathrm{ZnCp}{ }^{*}\right)_{3}(\mathrm{ZnMe})_{3}\right]$ ( $1105.19 \mathrm{~m} / \mathrm{z}$ ); G: see below, middle ( $1170.96 \mathrm{~m} / \mathrm{z}$ ); H: [ $\left.\mathrm{Ni}\left(\mathrm{ZnCp}^{*}\right)_{4}(\mathrm{ZnMe}) 4\right](1181.00 \mathrm{~m} / \mathrm{z})$; J: see below, right ( $1246.81 \mathrm{~m} / \mathrm{z}$ ). 89
Figure 61: Left: LIFDI mass spectrum of the reaction of 1 with 10 eq . $\mathrm{ZnMe}_{2}$ after one day at room temperature. Right: Calculated pattern for $\left[\mathrm{Ni}_{4}\left(\mathrm{GaCp}^{*}\right)_{2}\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})(\mathrm{hex})_{3}\right]+\mathrm{H}(1171.0608 \mathrm{~m} / \mathrm{z})$ and [ $\mathrm{Ni}_{6} \mathrm{Ga}_{2}$ ](Cp*) ${ }_{2}(\text { hex })_{5}-\mathrm{H}(\mathrm{m} / \mathrm{z} 1171.0735)$ vs. measured $\mathrm{m} / \mathrm{z} 1171.0782$.

Figure 62: LIFDI mass spectrum of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ with $1.9 \mathrm{eq} . \mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and 1.9 eq .3 -hexyne recorded after 6 hours at $90^{\circ} \mathrm{C}$ in toluene. Peak assignment is given in the table on the right 91

Figure 63: LIFDI mass spectra of the reaction [ $\mathrm{Pt}(\mathrm{cod})_{2}$ ] with $1 \mathrm{eq} . \mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and 1 eq . dpa at different temperatures in toluene. The spectrum was recorded after five hours. Peak assignment are given in the table on the right. 93

Figure 64: Structural suggestion of $\left[\mathrm{Pt}_{3} \mathrm{Zn}\right]\left(\mathrm{Cp}^{*}\right)_{2}(\mathrm{dpa})_{2}(\mathrm{cod})$ revealing a $\mathrm{Pd}_{3}$ triangular metal core with
two face-capping dpa units.

93

Figure 65: Time-dependent ${ }^{1} \mathrm{H}$ NMR spectra of the reaction of 1 with 1 bar $\mathrm{H}_{2}$ and excess 3 -hexyne. Color code: orange all components referring to a derivative of cod or cod-containing species, light blue: species that originates from 3-hexyne, grey: starting material. Abbreviations: cod: 1,5-cyclooctadiene; coe: cyclooctene; coa: cyclooctane; tol-d8: deuterated toluene.

96
Figure 66: Hydrogen experiment of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})(\mathbf{A})$ with 8 eq. 3-hexyne and 1 bar $\mathrm{H}_{2}$. Abbreviations: A, [NiAl](Cp*)(tebd)(cod); B, [NiAl](Cp*)(tebd)(hex); coa, cyclooctane; coe, cyclooctene; cod, 1,5-cyclooctadiene; tol-d8, deuterated toluene.

98

> Figure 67: Hydrogen experiment of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)($ hex $)(\mathbf{B})$ with 8 eq. 3-hexyne and 1 bar $\mathrm{H}_{2}$ at room temperature. Abbreviations: A, [NiAl](Cp*)(tebd)(cod); B, [NiAl](Cp*)(tebd)(hex); coa, cyclooctane; coe, cyclooctene; cod, 1,5-cyclooctadiene; tol- $\mathrm{d}_{8}$, deuterated toluene.
> 99

> Figure 68: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}^{*}$ and 3-hexyne at room temperature for several hours in toluene. The equivalents used are given in Table $2 . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . ~$ 109
Figure 69: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}^{*}$ and 3 -hexyne at $60^{\circ} \mathrm{C}$, after $4-6 \mathrm{~h}$ in toluene. Used equivalents are given in Table 4. ..... 110
Figure 70: LIFDI mass spectra obtained of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$, $\mathrm{GaCp}^{*}$ and 3 -hexyne at $90^{\circ} \mathrm{C}$, after 6h in toluene. Used equivalents are given in Table 6. ..... 111
Figure 71: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}^{*}$ and dpa at room temperature for several hours in toluene. The equivalents used are given in Table 8. ..... 112
Figure 72: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}^{*}$ and dpa at $60^{\circ} \mathrm{C}$ for several hours in toluene. The equivalents used are given in Table 10 ..... 113
Figure 73: LIFDI mass spectrum of the reaction [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right]$, $\mathrm{GaCp}{ }^{*}$ and dpa at $90^{\circ} \mathrm{C}$ for several hours in toluene. The equivalents used are given in Table 12. ..... 114
Figure 74: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ and 3 -hexyne at room temperature $(\mathbf{1}, \mathbf{2})$ and $60^{\circ} \mathrm{C}(3,4)$, after several hours in toluene. Used equivalents are given in Table 14. ..... 115
Figure 75: Time dependent LIFDI mass spectra of the reaction $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right) 4\right]$ with 4 eq. 3-hexyne at room temperature. The mass spectra show the conversion of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ to $\left[\mathrm{Ni}_{2} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}($ hex $)$ (C), $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}(\mathrm{~F})$ and afterwards $\left[\mathrm{Ni}_{5} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{hex})_{4}(\mathrm{G})$ ..... 116
Figure 76: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right) 4\right]$ and dpa at room temperature after several in toluene. Used equivalents are given in Table 17. ..... 117
Figure 77: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}$ and $\mathrm{PEt}_{3}$ at room temperature afterone day in toluene-d8. Used equivalents are given in Table 19. Right: enlarged experimentally obtainedpattern for $1044.1614 \mathrm{~m} / \mathrm{z}$.118
Figure 78: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\text { hex })_{2}$ and $\mathrm{PPh}_{3}$ at room temperature afterone day in toluene- $\mathrm{d}_{8}$. Used equivalents are given in Table 21. Right: enlarged experimentally obtainedpattern for $1274.1132 \mathrm{~m} / \mathrm{z}$.119
Figure 79: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{AlCp}^{*}$ and 3 -hexyne at $60^{\circ} \mathrm{C}$ and $90^{\circ} \mathrm{C}$, after6h in toluene/hexane. Used equivalents and temperatures are given in Table 23.121
Figure 80: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right], \mathrm{AICp}^{*}$ and dpa (8 eq.) at $90^{\circ} \mathrm{C}$, after 6 h inhexane.122
Figure 81: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{AICp})_{4}\right]$ and 3 -hexyne at $60^{\circ} \mathrm{C}$ after two days in toluene-d $\mathrm{d}_{8} /$ hexane. Used equivalents are given in Table 27 ..... 123
Figure 82: LIFDI mass spectra of the reaction $\left.\left[\mathrm{Ni}(\mathrm{AlCp})^{*}\right)_{4}\right]$ and dpa at $60^{\circ} \mathrm{C}$ after three days in toluene- dz/hexane. Used equivalents are given in Table 29. ..... 124

Figure 83: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}\left(\mathrm{AICp}^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$ and dpa and/or $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ at $60^{\circ} \mathrm{C}$ after several hours in cyclohexane. Used equivalents are given in Table 31. 125

Figure 84: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{\star} \mathrm{Bu}\right)_{7}\right]$, dpa and $\mathrm{AICp}^{*}$ at $60^{\circ} \mathrm{C}$ after several hours
in hexane. Used equivalents are given in.
126

| Figure 85: LIFDI mass spectra of the reaction [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right]$ with $\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}$, dpa and $\mathrm{AICp}^{*}$ performed at $60^{\circ} \mathrm{C}$ |
| :--- |
| after 7 hours in hexane. Used equivalents are given in Table $35 . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . ~$ | after 7 hours in hexane. Used equivalents are given in Table 35.

Figure 86: LIFDI mass spectra of the reaction $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})$ with different alkynes as listed in Table 37
Figure 87: LIFDI mass spectra of the reaction $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})$ with $\mathrm{GaCp}^{*}$ as listed in Table 39.
130
Figure 88: LIFDI mass spectra of the reaction $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tebd})(\mathrm{cod})$ with $\mathrm{AICp}{ }^{*}$ as listed in Table 41.
Figure 89: LIFDI mass spectra of the reaction $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tebd})(\mathrm{cod})$ with $\mathrm{PPh}_{3}$ as listed in Table 43.
132
Figure 90: LIFDI mass spectra of the reaction $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ with $\mathrm{GaCp}^{*} /$ and dpa at $-30^{\circ} \mathrm{C}$. Reactions 1 and 2 as listed in Table 45.................................................................................................................. 133
Figure 91: LIFDI mass spectra of the reaction $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ with $\mathrm{GaCp}{ }^{*} /$ and $d p a$ at $60^{\circ} \mathrm{C}$. Reactions 3 and 4 as listed in Table 47................................................................................................................. 134
Figure 92: LIFDI mass spectrum of the reaction $\left[\mathrm{Pd}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ with 2 eq. dpa at $60^{\circ} \mathrm{C}$ after five hours in toluene showing the selective formation of $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ indicated by the fragment peak at $1102 \mathrm{~m} / \mathrm{z}$.

135
Figure 93: LIFDI mass spectra of the reaction $\left[\operatorname{Pt}(\operatorname{cod})_{2}\right]$ ( 1 eq .), $\mathrm{GaCp}^{*}$ ( 1 eq. ) and dpa ( $\Delta \mathrm{eq}$.) at different temperatures in toluene as listed in Table 49. The spectra were recorded after two hours if not otherwise stated.

136

> Figure 94: LIFDI mass spectra of the reaction $\left[\operatorname{Pt}(\mathrm{cod})_{2}\right](1 \mathrm{eq}),. \mathrm{AICp}^{*}(\Delta$ eq. $)$ and dpa ( $\Delta$ eq.) at different temperatures in toluene as listed in Table 51 . The spectra were recorded after two hours. .............. 137

Figure 95: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right](75 \mathrm{mg})$ with 2 eq . $\mathrm{ZnMe}_{2}(0.17 \mathrm{~mL}, 1 \mathrm{~m}$ in toluene) after two hours at $0^{\circ} \mathrm{C}$ (black trace). The obtained NiGaZn library (1) was further reacted with 4 eq. 3-hexyne for 1.5 hours (red trace) or 18 hours (blue trace) at $60^{\circ} \mathrm{C}$. Peak assignment is given below.

139
Figure 96: LIFDI mass spectra of the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and 3 -hexyne with different equivalents
and at different temperatures in toluene after 5.5 hours. The exact conditions are specified in Table 54 .
Figure 97: LIFDI mass spectrum of the reaction $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right], \mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and dpa in toluene after one hour. The exact conditions are specified in Table 54.

141
Figure $98:{ }^{1} \mathrm{H}$ NMR spectrum of 1 in toluene- $\mathrm{d}_{8}$ with assignments of the starting materials as well as side
products. ................................................................................................................................ 149

Figure 99: ${ }^{13} \mathrm{C}$ NMR spectrum of 1 (black) in toluene- $\mathrm{d}_{8}$ with assignments of the starting materials as
well as side products.
149
Figure 100: ATR IR spectrum of 1 with characteristic band at $1738.5 \mathrm{~cm}^{-1}$ and $1670.2 \mathrm{~cm}^{-1}$ assuming side-on coordinated 3-hexyne. ..... 150
Figure 101: Comparison of LIFDI mass distribution of 1 measured on either an Exactive Orbitrap System (Thermo Fischer, top) revealing fragmentation or a JEOL AccuTOF instrument where no fragmentation was observed ..... 150
Figure 102: ${ }^{1} \mathrm{H}$ NMR of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})(6)$ in toluene- $\mathrm{d}_{8}$. ..... 151
Figure 103: ${ }^{13} \mathrm{C}$ NMR of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})(6)$ in toluene- $\mathrm{d}_{8}$. ..... 151
Figure 104: ATR IR spectrum of 6. ..... 152
Figure 105: UV-vis spectrum of 6 in n-hexane with absorption maxima at 220 nm and 285 nm . ..... 152
Figure 106: ${ }^{1} \mathrm{H}$ NMR spectrum of 7 in cyclohexane- $\mathrm{d}_{12}$ with signal assignment. ..... 153
Figure 107: ${ }^{13} \mathrm{C}$ NMR spectrum of 7 in cyclohexane- $\mathrm{d}_{12}$. ..... 153
Figure 108: ATR-IR spectrum of 7 with the characteristic band at $1825.0 \mathrm{~cm}^{-1}$ with relates to side-on coordinated 3-hexyne. ..... 154
Figure 109: UV-vis spectrum of 7 in n-hexane with absorption maxima at 215, 315 and 375 nm ..... 154
Figure 110: ${ }^{1} \mathrm{H}$ NMR spectrum of 8 in benzene- $\mathrm{d}_{6}$ with signal assignment. ..... 155
Figure 111: Enlarged ${ }^{13} \mathrm{C}$ NMR spectrum of 8 in benzene- $\mathrm{d}_{6}$ with signal assignment. Orange dots refer to trimerized dpa and green dots are assigned to free dpa. ..... 155
Figure 112: ATR IR spectrum of 8 with the characteristic band at $1812.2 \mathrm{~cm}^{-1}$ which is assigned to side- on coordinated dpa ..... 156
Figure 113: UV-vis spectrum of 8 in n-hexane with absorption maxima at 215, 280 and 330 nm ..... 156
Figure 114: ${ }^{1} \mathrm{H}$ NMR spectrum of 12 in toluene-d 8 . ..... 157
Figure 115: ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 2}$ in toluene-d8. Impurity: 31.3 ppm (free tert-butylisonitrile) ..... 157
Figure 116: ${ }^{1} \mathrm{H} /{ }^{13} \mathrm{C}$ HSQC NMR spectrum of 12 in toluene-d8. ..... 157
Figure 117: ${ }^{1} \mathrm{H} /{ }^{13} \mathrm{C}$ HMBC NMR spectrum of 12 in toluene- $\mathrm{d}_{8}$. ..... 158
Figure 118: Full range ${ }^{1} \mathrm{H}$ NMR spectrum of 13 in toluene-d8. Impurities: dpa ( 7.45 and 7.01 ppm ), cod
(5.54 and 2.21 ppm) and Cp*H (2.47, 1.72, 1.79 and 0.99 ppm) ..... 158
Figure 119:| ${ }^{1} \mathrm{H}$ NMR spectrum (aromatic range) of 13 in toluene- $\mathrm{d}_{8}$ ..... 159
Figure 120: Full range ${ }^{13} \mathrm{C}$ NMR spectrum of 13 in toluene- $\mathrm{d}_{8}$. Impurities cod (90.4 and 29.5 ppm ). ..... 159
Figure 121: ${ }^{1} \mathrm{H} /{ }^{1} \mathrm{H}$ COSY NMR spectrum of 13 in toluene-d 8. ..... 160
Figure 122: ${ }^{1} \mathrm{H} /{ }^{13} \mathrm{C}$ HSQC NMR spectrum of 13 in toluene- $\mathrm{d}_{8}$. ..... 160
Figure 123: ${ }^{1} \mathrm{H} /{ }^{13} \mathrm{C}$ HMBC NMR spectrum of 13 in toluene- $\mathrm{d}_{8}$ ..... 161
Figure 124: LIFDI mass spectrum of $\left[P d G_{4}\right]\left(\mathrm{Cp}^{*}\right) 4$ in toluene showing signals for $[\mathrm{M}]^{+}=926.0643 \mathrm{~m} / \mathrm{z}$(C; calc. $926.0751 \mathrm{~m} / \mathrm{z}$ ), $\left[\mathrm{M}-\mathrm{Cp}^{\star}\right]^{+}=790.9463 \mathrm{~m} / \mathrm{z}\left(\mathrm{B}\right.$; calc. $790.9571 \mathrm{~m} / \mathrm{z}$ ) and $\left[\mathrm{M}-\mathrm{Ga}-2 \mathrm{Cp}^{\star}\right]^{+}=$$586.9062 \mathrm{~m} / \mathrm{z}$ (A; calc. $586.9140 \mathrm{~m} / \mathrm{z}$ ). Further signals caused by instrumental induced fragmentation:[ $\left.\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right): 1102.8891 \mathrm{~m} / \mathrm{z}$ (D; calc. $1102.9051 \mathrm{~m} / \mathrm{z}$ ).161
Figure 125: Time-dependent ${ }^{1} \mathrm{H}$ NMR spectrum of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}$ (3) with $1 \mathrm{bar} \mathrm{H}_{2}$ in toluene-d8showing the signal decrease of 3 (highlighted).162
Figure 126: Time-dependent ${ }^{1} \mathrm{H}$ NMR spectrum of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}(3)$ with 1 bar $\mathrm{H}_{2}$ in toluene- $\mathrm{d}_{8}$.Abbreviations: coa, cyclooctane; coe, cyclooctene; cod, 1,5-cyclooctadiene; dpe, diphenylethylene(stilbene); bb, bibenzyl163
Figure 127: LIFDI mass spectra of the reaction of $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{3}\right]\left(\mathrm{Cp}^{*}\right)_{3}(\mathrm{dpa})_{3}(3)$ with $\mathrm{H}_{2}$ (1 bar) (red trace) orwithout hydrogen (black trace, reference) after one day at room temperature in toluene-d8. Signalassignment is listed below.163

Figure 128: Time-dependent ${ }^{1} \mathrm{H}$ NMR spectrum of $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})_{1}(\mathbf{A})$ with $1 \mathrm{bar} \mathrm{H}_{2}$ in toluene- $\mathrm{d}_{8}$. Abbreviations: coa, cyclooctane; coe, cyclooctene; cod, 1,5-cyclooctadiene; dpe, diphenylethylene (stilbene); bb, bibenzyl, dpa, diphenylacetylene. 165

Figure 129: LIFDI mass spectra of the reaction of $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})_{1}$ with $\mathrm{H}_{2}$ (1 bar) (red trace) or without hydrogen (black trace, reference) after one day at room temperature in toluene-d8. Signal assignment is listed below.
8.4. List of Tables
Table 1: Selected interatomic distances or angles of 6, 7, $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tpbd})(\mathrm{cod})$ and 8 . Abbreviations: tebd: tetraethylbutadiene; tpbd: tetraphenylbutadiene. ..... 58
Table 2: Overview of Ni-Ga-hex reactions performed at room temperature for several hours in toluene. The reactions were conducted with $5-20 \mathrm{mg}$ of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ ..... 108
Table 3: Assignment of clusters obtained in the reactions of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}^{*}$ and 3-hexyne at room temperature as listed in Table 2. $\mathrm{M} / \mathrm{z}$ values assigned to product peaks are given in bold ..... 109
Table 4: Overview of Ni-Ga-hex reactions performed at $60^{\circ} \mathrm{C}$ for $4-6$ hours in toluene. The reactions were conducted with $5-20 \mathrm{mg}$ of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$. ..... 109
Table 5: Assignment of clusters obtained in the reactions of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}^{*}$ and 3 -hexyne at $60^{\circ} \mathrm{C}$ as listed in Table 4. $\mathrm{m} / \mathrm{z}$ values assigned to product peaks are given in bold. ..... 110
Table 6: Overview of Ni-Ga-hex reactions performed at $90^{\circ} \mathrm{C}$ for 6 hours in toluene. The reactions were conducted with $10-30 \mathrm{mg}$ of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$. ..... 111
Table 7: Assignment of clusters obtained in the reactions of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{GaCp}^{*}$ and 3 -hexyne at $90^{\circ} \mathrm{C}$ as listed in Table 4. M/z values assigned to product peaks are given in bold. ..... 111
Table 8: Overview of $\mathrm{Ni}-\mathrm{Ga}$-dpa reactions performed at r.t. for several hours in toluene. The reactions were conducted with $10-30 \mathrm{mg}$ of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$. ..... 111
Table 9: Cluster assignment of obtained signals in the reactions of [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ], $\mathrm{GaCp}^{*}$ and dpa at room temperature as listed in Table 8. M/z values assigned as product peaks are given in bold. ..... 112
Table 10: Overview of Ni-Ga-dpa reactions performed at $60^{\circ} \mathrm{C}$ for several hours in toluene. The reactions were conducted with $10-30 \mathrm{mg}$ of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$. ..... 113
Table 11: Cluster assignment of obtained signals in the reactions of [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right]_{, ~ G a C p *}$ and dpa at $60^{\circ} \mathrm{C}$ as listed in Table 10. $\mathrm{M} / \mathrm{z}$ values assigned as product peaks are given in bold. ..... 113
Table 12: Overview of Ni-Ga-dpa reactions performed at $90^{\circ} \mathrm{C}$ for several hours in toluene. The reaction was conducted with 35 mg of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$. ..... 114
Table 13: Cluster assignment of obtained signals in the reaction of $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right], \mathrm{GaCp}^{*}$ and dpa at $90^{\circ} \mathrm{C}$ as listed in Table 12. $\mathrm{M} / \mathrm{z}$ values assigned as product peaks are given in bold. ..... 114
Table 14: Overview of [ $\left.\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right) 4\right]$-hex reactions performed at room temperature and $60^{\circ} \mathrm{C}$ for several hours in toluene. The reaction was conducted with $15-25 \mathrm{mg}$ of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right) 4\right]$. ..... 115
Table 15: Assignment of clusters obtained in the reactions $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)_{4}\right]$ and 3 -hexyne as listed in Table14. $\mathrm{M} / \mathrm{z}$ values assigned to product peaks are given in bold.115
Table 16: Assignment of the obtained clusters as depicted in Figure 75. ..... 116
Table 17: Overview of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right) 4\right]$-dpa reactions performed at room temperature for several hours in toluene. The reaction was conducted with $15-25 \mathrm{mg}$ of $\left[\mathrm{Ni}\left(\mathrm{GaCp}{ }^{*}\right)_{4}\right]$. ..... 117
Table 18: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right) 4\right.$ ] and dpa at room temperature as listed in Table 17. $\mathrm{M} / \mathrm{z}$ values assigned as product peaks are given in bold ..... 117
Table 19: Overview of reactivity tests of 1 with $\mathrm{PEt}_{3}$ performed at room temperature for one day in toluene-d ${ }_{8}$ ..... 118
Table 20: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}$ and $\mathrm{PEt}_{3}$ at room temperature as listed in Table 19. ..... 118
Table 21: Overview of reactivity tests of 1 with $\mathrm{PPh}_{3}$ performed at room temperature for one day in toluene-d8. ..... 119
Table 22: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Ni}_{4} \mathrm{Ga}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}(\mathrm{hex})_{2}$ and $\mathrm{PPh}_{3}$ at room temperature as listed in Table 21. The assignment of the clusters given in italics should be considered with special attention. ..... 119
Table 23: Overview of Ni-Al-hex reactions performed at $60^{\circ} \mathrm{C}$ and $90^{\circ} \mathrm{C}$ for 6 hours in toluene/hexanemixture. The reactions were conducted with 11 mg of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$. The amount of $\mathrm{AICp}^{*}$ with differentequivalents 3 -hexyne was varied.121
Table 24: Assignment of clusters obtained in the reactions of [ $\mathrm{Ni}(\operatorname{cod})_{2}$ ], $\mathrm{AlCp}^{*}$ and 3 -hexyne at $60^{\circ} \mathrm{C}$ and $90^{\circ} \mathrm{C}$ as listed in Table 24. $\mathrm{M} / \mathrm{z}$ values assigned to product peaks are given in bold. 122
Table 25: Overview of Ni-Al-dpa reactions performed at $90^{\circ} \mathrm{C}$ for 6 hours in hexane. The reaction was conducted with 30 mg of [ $\mathrm{Ni}(\mathrm{cod}) 2$ ]. ..... 122
Table 26: Assignment of clusters obtained in the reactions of $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right], \mathrm{AlCp}^{*}$ and dpa at $90{ }^{\circ} \mathrm{C}$ after 6 h as listed in Table 25. $\mathrm{M} / \mathrm{z}$ values assigned to product peaks are given in bold. ..... 122
Table 27: Overview of $\left[\mathrm{Ni}\left(\mathrm{AICp}^{*}\right) 4\right]$ reacted with 3-hexyne performed at $60^{\circ} \mathrm{C}$ for 48 hours in toluene-d8/hexane. The reaction was conducted with 10 mg of $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{4}\right]$ ..... 123
Table 28: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{4}\right]$ and 3-hexyne at $60^{\circ} \mathrm{C}$ as listed in Table 27. $\mathrm{M} / \mathrm{z}$ values assigned as product peaks are given in bold. ..... 123
Table 29: Overview of $\left[\mathrm{Ni}\left(\mathrm{AlCp}{ }^{*}\right) 4\right]$ reacted with dpa performed at $60^{\circ} \mathrm{C}$ for 72 hours in toluene- $\mathrm{d}_{8} /$ hexane. The reaction was conducted with 9 mg of $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right) 4\right]$. ..... 124
Table 30: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Ni}\left(\mathrm{AICp}^{*}\right) 4\right]$ and dpa at $60^{\circ} \mathrm{C}$ as listed in Table 29. $\mathrm{M} / \mathrm{z}$ values assigned as product peaks are given in bold. ..... 124
Table 31: Overview of $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$ reacted with dpa performed at $60{ }^{\circ} \mathrm{C}$ for several hours in cyclohexane. The reaction was conducted with 7 mg of $\left[\mathrm{Ni}\left(\mathrm{AlCp}^{*}\right)_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$. ..... 125
Table 32: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Ni}(\mathrm{AlCp})_{3}(\mathrm{H})\left(\mathrm{SiEt}_{3}\right)\right]$ and dpa and/or [ $\mathrm{Ni}(\operatorname{cod})_{2}$ ] at $60^{\circ} \mathrm{C}$ as listed in Table 31. $\mathrm{M} / \mathrm{z}$ values assigned as product peaks are given in bold. ..... 125
Table 33: Overview of $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{+} \mathrm{Bu}_{7}\right)_{7}\right]$ reacted with dpa and $\mathrm{AICp}^{*}$ performed at $60^{\circ} \mathrm{C}$ for several hours in hexane. The reaction was conducted with $4-10 \mathrm{mg}$ of $\left[\mathrm{Ni}_{4}\left(\mathrm{CN}^{\dagger} \mathrm{Bu}\right)_{7}\right]$ ..... 126
Table 34: Cluster assignment of obtained signals in the reaction [ $\mathrm{Ni}_{4}\left(\mathrm{CN}^{+\mathrm{Bu}}\right)_{7}$ ], dpa and $\mathrm{AlCp}^{*}$ at $60^{\circ} \mathrm{C}$ as listed in Table 33. $\mathrm{M} / \mathrm{z}$ values assigned as product peaks are given in bold. ..... 127
Table 35: Overview of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ reacted with $\mathrm{CN}^{+} \mathrm{Bu}$, dpa and $\mathrm{AlCp}^{*}$ performed at $60^{\circ} \mathrm{C}$ for 7 hours in hexane. The reaction was conducted with 11 mg of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$. Reaction 1 and 2 only differs in the order of the addition of the reagents. Addition order: 1: [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{CN}^{+} \mathrm{Bu}, \mathrm{dpa}, \mathrm{AlCp}^{*}$; 2: [ $\left.\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{CN}^{\mathrm{t}} \mathrm{Bu}$, AICp*, dpa ..... 127
Table 36: Cluster assignment of obtained signals in the reaction [ $\mathrm{Ni}(\operatorname{cod})_{2}$ ] with CNtBu , dpa and $\mathrm{AlCp}^{*}$ performed at $60^{\circ} \mathrm{C}$ for 7 hours in hexane as listed in Table $35 . \mathrm{M} / \mathrm{z}$ values assigned as product peaks are given in bold. ..... 128
Table 37: Overview of the reactivity test of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})$ with different alkynes at different equivalents and temperatures in toluene or hexane for one day. The reaction was conducted with $5-25 \mathrm{mg}$ of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod})$ ..... 128
Table 38: Cluster assignment of obtained signals in the reaction $[\mathrm{NiAl}](\mathrm{Cp} *)(\mathrm{tebd})(\mathrm{cod})$ with different alkynes as listed in Table 37. ..... 129
Table 39: Overview of the reactivity test of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tebd})(\mathrm{cod})$ with $\mathrm{GaCp}^{*}$ at different equivalents and temperatures in toluene or hexane for one day. The reaction was conducted with 10 mg of [NiAl](Cp*)(tebd)(cod). ..... 129
Table 40: Cluster assignment of obtained signals in the reaction [NiAl](Cp*)(tebd)(cod) with GaCp* as listed in Table 39. ..... 130
Table 41: Overview of the reactivity test of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tebd})(\mathrm{cod})$ with $\mathrm{AICp}^{*}$ at different equivalents intoluene or hexane for one day. The reaction was conducted with 10 mg of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)($ tebd $)(\mathrm{cod}) . . .130$
Table 42: Cluster assignment of obtained signals in the reaction [NiAl](Cp*)(tebd)(cod) with AICp* as listed in Table 41. ..... 131
Table 43: Overview of the reactivity test of $[\mathrm{NiAl}]\left(\mathrm{Cp}^{*}\right)(\mathrm{tebd})(\mathrm{cod})$ with $\mathrm{PPh}_{3}$ at different equivalents and temperatures in toluene or hexane for one day. The reaction was conducted with 10 mg of [NiAl](Cp*)(tebd)(cod). ..... 131
Table 44: Cluster assignment of obtained signals in the reaction [ NiAl$]\left(\mathrm{Cp}{ }^{*}\right)($ tebd $)(\mathrm{cod})$ with $\mathrm{PPh}_{3}$ as listed in Table 43. The assignment of $E$ and $F$ have to be considered carefully. ..... 132
Table 45 : Overview of the reactivity test of $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ with GaCp (and dpa ) at $-30{ }^{\circ} \mathrm{C}$ in toluene for two days. The reaction was conducted with 7.5 mg of $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ ..... 133
Table 46: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ with $\mathrm{GaCp} /$ and dpa at - $30^{\circ} \mathrm{C}$ as listed in Table 45. ..... 133
Table 47 : Overview of the reactivity test of $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ with GaCp (and dpa) at $60{ }^{\circ} \mathrm{C}$ in toluene for one day. The reaction was conducted with 7.5 mg of $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$. ..... 134
Table 48: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ with $\mathrm{GaCp} /$ and dpa at $60^{\circ} \mathrm{C}$ as listed in Table 47 ..... 134
Table 49: Overview of the reactivity tests of $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ with $\mathrm{GaCp}^{*}$ and dpa at different temperatures in toluene. The reaction was conducted with 4.0 mg of $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$. ..... 136
Table 50: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right]$ ( 1 eq. ), $\mathrm{GaCp}^{*}$ ( 1 eq.$\left.\right)$ and dpa ( $\Delta$ eq.) at different temperatures in toluene as listed in Table $49 . \mathrm{M} / \mathrm{z}$ values assigned as product peaks are given in bold. ..... 137
Table 51: Overview of the reactivity tests of $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$ with $\mathrm{AlCp}^{*}$ and dpa at different temperatures in toluene. The reaction was conducted with 4.0 mg of $\left[\mathrm{Pt}(\mathrm{cod})_{2}\right]$. ..... 137
Table 52: Cluster assignment of obtained signals in the reaction $\left[\operatorname{Pt}(\operatorname{cod})_{2}\right]$ ( 1 eq.$\left.\right)$, $\operatorname{AlCp}^{*}$ ( $\Delta$ eq.) and dpa ( $\Delta$ eq.) at different temperatures in toluene as listed in Table 51. $\mathrm{M} / \mathrm{z}$ values assigned as product peaks are given in bold. ..... 138
Table 53: Peak assignment of the reactions as depicted in Figure 95. ..... 139
Table 54: Overview of the reaction of $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right]$ with $\mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and 3-hexyne (dpa) with different equivalents and at different temperatures in 1.5 mL toluene. The reaction was conducted with 5.5 mg of [ $\left.\mathrm{Ni}(\operatorname{cod})_{2}\right]$. ..... 140
Table 55: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Ni}(\mathrm{cod})_{2}\right], \mathrm{Zn}_{2} \mathrm{Cp}^{*} 2$ and 3-hexyne with different equivalents and at different temperatures in toluene after 5.5 hours as listed in Table 54.. ..... 141
Table 56: Cluster assignment of obtained signals in the reaction $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right], \mathrm{Zn}_{2} \mathrm{Cp}^{*}{ }_{2}$ and dpa in toluene after one hour as listed in Table 54. ..... 142
Table 57: Signal assignment of the reaction of 3 with 1 bar $\mathrm{H}_{2}$ as obtained by LIFDI MS depicted in Figure 127 ..... 164
Table 58: Signal assignment of the reaction of $\left[\mathrm{Ni}_{6} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}(\mathrm{dpa})$ with 1 bar $\mathrm{H}_{2}$ as obtained by LIFD MS depicted in Figure 129 ..... 166

### 8.5. List of Schemes

Scheme 1: Schematic representation of the performed substitution reactions of $\left[\mathrm{TM}_{2}\left(\mathrm{ECp}^{*}\right)_{5}\right]$ with $\mathrm{TM}=$$\mathrm{Pd}, \mathrm{Pt} .{ }^{73}$12
Scheme 2: Proposed mechanisms for ligand exchanged reactions based on fluxional processes. $M=$ Pd, Pt. ${ }^{73}$ Reprinted with permissions from T. Steinke, C. Gemel, M. Winter, R. A. Fischer, Chem. Eur. J. 2005, 11, 1636-1646. Copyright 2005, John Wiley and Sons ..... 13
Scheme 3: Synthesis of full $\mathrm{E} / \mathrm{Zn}$ exchanged compounds of the formula $\left[\mathrm{Ni}\left(\mathrm{ZnCp}^{*}\right)_{n}(\mathrm{ZnMe})_{n}\left(\mathrm{PEt}_{3}\right)_{4-n}\right]$$(\mathrm{n}=1-3)$ originating from $\left[\mathrm{Ni}\left(\mathrm{ECp}^{*}\right)_{n}\left(\mathrm{PEt}_{3}\right) 4-\mathrm{n}\right]$ precursors. Partial exchange was observed due to thesynthesis of $\left[\mathrm{Ni}\left(\mathrm{GaCp}^{*}\right)\left(\mathrm{ZnCp}^{*}\right)(\mathrm{ZnMe})\left(\mathrm{PEt}_{3}\right)_{2]}\right] .{ }^{92}$ Reprinted with permission from P. Heiß, J. Hornung,X. Zhou, C. Jandl, A. Pöthig, C. Gemel, R. A. Fischer, Inorg. Chem. 2020, 59, 514-522. Copyright 2020,American Chemical Society.15
Scheme 4: Isolobal priniciple applied for $\mathrm{CO}, \mathrm{NHC}, \mathrm{PR}_{3}$ and ECp * ligands. ..... 18
Scheme 5: Electronic situation in ER-ligands applying the Dewar-Chatt-Duncanson donor-acceptor- model. Adapted reprinted with permission from G. Frenking, K. Wichmann, N. Fröhlich, C. Loschen, M. Lein, J. Frunzke, V. c. M. Rayón, Coord. Chem. Rev. 2003, 238-239, 55-82. Copyright 2003, Elsevier.19
Scheme 6: Overview of the reactions including $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right], \mathrm{GaCp}^{*}$ and 3 -hexyne discussed in this chapter. The reactions were investigated depending on additive or temperature control. ..... 25
Scheme 7: Overview of the herein reported products obtained during the reaction of $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right], \mathrm{GaCp}$ *and dpa dependent on the metal amount (variation of $\mathrm{GaCp}^{*}$, left) and additive concentration (right). 30
Scheme 8: Overview of herein discussed products of the reactivity test of 1 with $\mathrm{AlCp}^{*}, \mathrm{PR}_{3}$ and dpa.33
Scheme 9: Overview of the herein discussed products which are formed during the reaction of [ NiGa 4$]\left(\mathrm{Cp}^{*}\right)_{4}$ with 3-hexyne (left) or diphenylacetylene (dpa; right). ..... 38
Scheme 10: Overview of the herein discussed products which are formed during the reaction [ $\mathrm{Ni}(\mathrm{cod})_{2}$ ] with $\mathrm{AlCp}^{*}$ and either 3-hexyne (left) or diphenylacetylene (dpa; right). Additionally, the Ni-Al ratio was varied (bottom). ..... 50
Scheme 11: Overview of the isolated compounds starting from $\mathrm{Ni}(c o d)$ 2. As 3-hexyne (3-hex) or diphenyl acetylene (dpa) are dimerized in the molecular structure they are named as tebd (tetraethylbudadiene) or tpbd (tetraphenylbutadiene). ..... 57
Scheme 12: Overview of the herein discussed products obtained from the reactions of [ $\left.\mathrm{Ni}_{4}\left(\mathrm{CN}^{\dagger} \mathrm{Bu}_{4}\right)_{7}\right]$ with AICp* and 3-hexyne (left) or diphenylacetylene (dpa; right). ..... 62
Scheme 13: Overview of the herein discussed products obtained from the reactions of $\left[\mathrm{Pd}_{2}(\mathrm{dvds})_{3}\right]$ withGaCp * dependent on the temperature (left) and with dpa as additive dependent on temperature (right).66
Scheme 14: Overview of the herein discussed products obtained from the reaction of $[\mathrm{PdGa} 4]\left(\mathrm{Cp}^{*}\right)_{4}$ witheither 3-hexyne or dpa resulting in the formation of dinuclear $\left[\mathrm{Pd}_{2} \mathrm{Ga}_{5}\right]\left(\mathrm{Cp}^{*}\right)_{5}$ regardless of the additive.70
Scheme 15: Overview of the herein discussed products obtained during the reaction of $\left[\mathrm{PdAl}_{4}\right]\left(\mathrm{Cp}^{*}\right) 4$ with 3-hexyne. ..... 72
Scheme 16: Reaction of $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right]$ with different $E C p^{*}$ and additives as performed in this thesis. ..... 75
Scheme 17: Overview of the herein discussed products obtained during the reaction of $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right], \mathrm{GaCp} *$ and either 3-hexyne (left) or dpa (right) dependent on additive or temperature control. ..... 75
Scheme 18: Overview of the herein discussed products obtained during the reaction of $\left[\mathrm{Pt}(\operatorname{cod})_{2}\right], \mathrm{AlCp}$ * and dpa depending on the additive concentration (left) or on the metal ratio (right). ..... 80
Scheme 19: Overview of the herein discussed products obtained during the reaction of $\left[\mathrm{NiGa}_{4}\right]\left(\mathrm{Cp}^{*}\right)_{4}$ and $\mathrm{ZnMe} \mathrm{Z}_{2}$ depending on the metal ratio (left) and with 3-hexyne as additive depending on the additive concentration and temperature (right). ..... 84

Scheme 20: Overview of the herein discussed products obtained during the reaction of $\left[\mathrm{Ni}(\operatorname{cod})_{2}\right]$ with $\mathrm{Zn}_{2} \mathrm{Cp}^{*}$ and alkynes ( 3 -hexyne and dpa). The product were obtained regardless of temperature and alkyne.

91
Scheme 21: Overview of the herein discussed products obtained during the reaction of $\left[\mathrm{Pt}(\mathrm{Cod})_{2}\right]$ with $\mathrm{Zn}_{2} \mathrm{Cp}^{*}$ and dpa dependent on the temperature.

### 8.6. List of Publications

## Thesis-based publications:

P. Heiß, J. Hornung, C. Gemel and R. A. Fischer, Chem. Commun., 2022, 58, 4332-4335.
(A combinatorial coordination-modulated approach to all-hydrocarbon-ligated intermetallic clusters)
M. Muhr ${ }^{\ddagger}$, P. Heiß ${ }^{\ddagger}$, M. Schütz, R. Bühler, C. Gemel, M. H. Linden, H. B. Linden and R. A. Fischer, Dalton Trans., 2021, 50, 9031-9036. (Enabling LIFDI-MS measurements of highly air sensitive organometallic compounds: a combined MS/glovebox technique)

## Other publications:

P. Heiß ${ }^{\ddagger}$, J. Hornung ${ }^{\ddagger}$, X. Zhou, C. Jandl, A. Pöthig, C. Gemel, R. A. Fischer, Inorg. Chem. 2020, 59 (1), 514-522. (Combined Experimental and Theoretical Study on Hampered Phosphine Dissociation in Heteroleptic Ni/Zn Complexes)

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Clusters [Ma(GaCp*)b(CNR)c] (M = Ni, Pd, Pt): Synthesis Structure, and $G a / Z n$ Exchange Reactions

Author: Mariusz Molon, Katharina Dilchert, Christian Gemel, et al
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B) Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text, which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section $14(\mathrm{~b})(\mathrm{i})(\mathrm{A})$ above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;
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