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N-Heterocyclic-Imine Stabilized Heavier Tetrylenes Towards Small Molecule Activation and Catalysis

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“[…] some are so ignorant, that they grow sullen and silent,
and are chilled with horror at the sight of any thing that bears the semblance of learning,
in whatever shape it may appear;
and should the *spectre* appear in the shape of *woman*,
the pangs which they suffer are truly dismal."
Elisabeth Fulhame

“Don't ask me how I did it. I just did it. It was hard!”
Chandler Matkins

LIST OF ABBREVIATIONS

Alk	alkyl group	
AO	atomic orbital	
BO	bond order	
cf.	Latin (confer): “compare”	
C	chalcogen	
DABCO	1,4-Diazabicyclo[2.2.2]octane	
DBU	1,8-Diazabicyclo[5.4.0]undec-7-en	
Dipp	2,6-di-isopropyl-phenyl	2,6-$i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$
$^{\mathrm{Dipp}}$Ter	1,3-bis-diisopropylphenyl-benzene	
E	main group element	
e.g.	Latin (exempli gratia): “for example”	
EDA	Energy Deposition Analysis	
$\mathrm{E}_{\mathrm{hyb}}$	hybridization energy/efficiency of s-p mixing	
Eind	1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl	
HOMO	highest occupied molecular orbital	
i.e.	Latin (id est): “that is”	
IDipp	1,3-bis(2,6-diisopropylphenyl)imidazoline-2-ylidene	
IMe_4	1,3,4,5-tetramethyl-imidazol-2-ylidene	
IMes	1,3,4,5-tetramethylimidazolin-2-ylidene	
*i*Pr	*iso*-propyl	$\mathrm{C}_3\mathrm{H}_7$
I*t*Bu	1,3-*tert*-butyl-2-ylidene	
L	ligand	
LDA	di-iso-propylamide	
LUMO	lowest occupied molecular orbital	

M	transition metal	
Mes	mesityl	$C_6H_3(CH_3)_3$
^{Mes}Ter	1,3-di-mesityl-benzene	
Naph	naphthalenide	$C_{10}H_8^-$
NHC	*N*-heterocyclic carbene	
NHCP	*N*-heterocyclic carbene-phosphinidene	
NHI	*N*-heterocyclic imine	
Nuc	nucleophile	
Ph	phenyl	C_6H_5
QTAIM	Quantum Theory of Atoms in Molecules	
red	reduction / reducing agent	
*t*Bu	*tert*-butyl	$C(CH_3)_3$
Ter	1,3-diphenylbenzene	
Tipp	2,4,6-tri-isopropylphenyl	2,4,6-*i*$Pr_2C_6H_3$
^{Tipp}Ter	1,3-bis-triisopropylphenyl-benzene	
X	halide	
ΔE_{ST}	singlet-triplet gap energy	

LIST OF PUBLICATIONS AND CONFERENCE CONTRIBUTIONS

Results of the work on hand have been published in the following contributions:

Publications

- **Ligand Assisted CO_2 Activation and Catalytic Valorization by an NHI-Stabilized Stannylene**
  Debotra Sarkar$^+$, Lisa Groll$^+$, Dominik Munz, Franziska Hanusch, Shigeyoshi Inoue
  ChemCatChem, **2022**, *14*, e202201048

- **Reactivity of NHI-Stabilized Heavier Tetrylenes towards CO_2 and N_2O**
  Lisa Groll, John A. Kelly, Shigeyoshi Inoue
  Chem. Asian J., **2024**, *19*, e2023009

Conference Contributions

- Poster: **Synthesis and Reactivity of N-Heterocyclic Imine Stabilized Tetrylenes**
  Lisa Groll, Shiori Fujimori, Shigeyoshi Inoue
  44th International Conference on Coordination Chemistry (ICCC), Rimini, Italy, August 2022

- Oral Contribution: **CO_2 Activation and Catalytic Reduction by NHI-stabilized Stannylenes - Ligand Influences**
  Lisa Groll, Debotra Sarkar, Shigeyoshi Inoue
  29th International Conference on Organometallic Chemistry (ICOMC), Prague, Czech Republic, July 2022

ABSTRACT

Heavier tetrylenes, such as germylenes and stannylenes, display a unique reactivity due to their ambiphilic nature. With their filled s-orbital and empty p-orbital, they can engage in donor-acceptor type reactivity and are capable of activating a range of strong bonds in small molecules such as CO_2, NH_3, H_2, ethylene, and so on. Promising research has already been done, that showcases the potential of heavier tetrylenes for small molecule activation and catalysis, but there is still lots of work to be done to demonstrate the full potential of those complexes. This doctoral thesis attempts to contribute a small part to this endeavor by presenting the synthesis and reactivity of *N*-heterocyclic imine (NHI) stabilized germanium and tin complexes.

To begin with, the reactivity of aryl(imino)stannylene ^{Mes}Ter(IDippN)Sn: with CO_2 is considered. By reacting equimolar amounts of the lithiated ligand precursor (IDippN)Li with the chloro-stannylene ^{Mes}Ter(Cl)Sn:, the heteroleptic stannylene ^{Mes}Ter(IDippN)Sn: was obtained in good yields. Reaction with CO_2 revealed the unique stabilization capability of the NHI ligand, which allows the oxidation state +II of the tin center to stay intact upon activation of the small molecule. Instead of oxidation of the metal center, a tin-carboxylate is formed, which then can release C1 feedstock upon reduction with HBpin stoichiometrically and catalytically. Experimental and computational comparison of ^{Mes}Ter(IDippN)Sn:, ^{Mes}Ter(IDippP)Sn:, and ^{Mes}Ter(Ph_2N)]Sn: reveals the inherent character of the Sn-L bond to be the deciding factor that enables reversible CO_2 uptake. While the Sn–N bond in the aryl(imino)stannylene is a strongly polarized single bond, the Sn–P bond of ^{Mes}Ter(IDippP)Sn: exhibits double-bond character and is too stable to allow CO_2 insertion. In contrast, ^{Mes}Ter(Ph_2N)Sn: does react with CO_2, but the Sn–N bonds affinity to re-form the stannylene upon reduction with HBpin is too low due to the low bond order single bond. Instead, the ammine-borane Ph_2N–Bpin is formed. Only ^{Mes}Ter(IDippN)Sn: is capable of reversible dissociation of the Sn–N bond, enabling efficient catalytic hydroboration of CO_2 with HBpin under mild conditions.

Secondly, the synthesis of I*t*BuN stabilized tetrylenes [$(Me_3Si)_2N$](I*t*BuN)Sn:, (I*t*BuN)$_2$Sn:, and (I*t*BuN)$_2$Ge: as well as their reactivity towards CO_2 and N_2O are discussed. While [$(Me_3Si)_2N$](I*t*BuN)Sn: can be obtained *via* ligand exchange reaction of [$(Me_3Si)_2N$]$_2$Sn: with free (I*t*BuN)H, the homoleptic tetrylenes are synthesized by reacting (I*t*BuN)Li with the respective ECl_2·dioxane salt (E = Ge, Sn). While (I*t*BuN)$_2$Sn: forms a dimer in solid-state as well as in solution at −80 °C, as determined by SC-XRD and VT-NMR, the other tetrylenes

could only be observed as monomers. Upon reaction of CO_2 with the germylene, one molecule of CO_2 bridges each of the Ge–N bonds respectively, while they themselves stay intact, forming 4-rings. In the case of the homoleptic stannylene, the Sn–N bonds dissociate and form carbamato groups upon insertion of CO_2. Upon reaction of (I*t*BuN)$_2$Sn: with N_2O, partial oxidation can be observed, giving a bis-stannylene with a central Sn_2N_2 ring coordinated by stannanolate moieties. In contrast, the heteroleptic stannylene [(Me$_3$Si)$_2$N](I*t*BuN)Sn: does not react selectively with CO_2 or N_2O.

ZUSAMMENFASSUNG

Schwere Tetrylene wie Germylene und Stannylene weisen aufgrund ihres ambiphilen Charakters eine einzigartige Reaktivität auf. Aufgrund eines gefüllten s-Orbitals und eines leeren p-Orbital können sie Donor-Akzeptor-Reaktivität mit einer Reihe starker Bindungen in kleinen Molekülen wie CO_2, NH_3, H_2, Ethylen usw. zeigen. Es wurden bereits vielversprechende Forschungsarbeiten durchgeführt, die das Potenzial schwerer Tetrylene für die Aktivierung und Katalyse kleiner Moleküle demonstrieren, aber es bleibt noch viel zu tun, um das volle Potenzial dieser Komplexe auszuschöpfen. Diese Doktorarbeit versucht, einen kleinen Teil zu diesem Unterfangen beizutragen, indem sie die Reaktivität von *N*-heterozyklisch-Imin (NHI) stabilisierten Germanium- und Zinnkomplexen zeigt.

Zunächst wird die Reaktivität des Aryl(imino)stannylens ^{Mes}Ter(IDippN)Sn: mit CO_2 betrachtet. Durch Reaktion äquimolarer Mengen des lithiierten Ligandenvorläufers (IDippN)Li mit dem Chlorostannylen ^{Mes}Ter(Cl)Sn: wurde das heteroleptische Stannylen ^{Mes}Ter(IDippN)Sn: in guten Ausbeuten erhalten. Die Reaktion mit CO_2 offenbarte die bemerkenswerte Stabilisierungsfähigkeit des NHI-Liganden, der es ermöglicht, dass der Oxidationszustand +II des Zinnzentrums bei Aktivierung des kleinen Moleküls erhalten bleibt. Anstelle der Oxidation des Metallzentrums wird ein Zinncarboxylat gebildet. Das Stannylen ist zudem in der katalytischen Hydroborierung von CO_2 mit Pinacolboran als Reduktionsmittel aktiv. Der Vergleich mit ^{Mes}Ter(IDippN)Sn:, ^{Mes}Ter(IDippP)Sn: und ^{Mes}Ter(Ph_2N)]Sn: zeigt, dass der Charakter der Sn–L Bindung der entscheidende Faktor ist, der eine reversible CO_2-Aufnahme und somit Katalyse ermöglicht. Während die Sn–N Bindung im Aryl(imino)stannylen eine stark polarisierte Einfachbindung ist, weist die Sn–P Bindung von ^{Mes}Ter(IDippP)Sn: Doppelbindungscharakter auf und ist zu stabil, um eine CO_2-Insertion zu ermöglichen. ^{Mes}Ter(Ph_2N)Sn: reagiert zwar mit CO_2, hier ist jedoch die Sn–N Bindung zu schwach und die Affinität zur Neubildung des Stannylens bei Reduktion mit HBpin zu gering. Stattdessen wird das Amminboran Ph_2N–Bpin gebildet. Nur ^{Mes}Ter(IDippN)Sn: ist zur reversiblen Dissoziation der Sn–N Bindung fähig, was eine effiziente katalytische Hydroborierung von CO_2 mit HBpin unter milden Bedingungen ermöglicht.

Zweitens werden die Synthesen der I*t*BuN-stabilisierten Tetrylene $[(Me_3Si)_2N]$(I*t*BuN)Sn:, (I*t*BuN)$_2$Sn: und (I*t*BuN)$_2$Ge: sowie deren Reaktivität gegenüber CO_2 und N_2O diskutiert. Während $[(Me_3Si)_2N]$(I*t*BuN)Sn: durch Ligandenaustauschreaktion von $[(Me_3Si)_2N]_2$Sn: mit freiem (I*t*BuN)H erhalten wird, werden die homoleptischen Tetrylene durch Reaktion von

(I*t*BuN)Li mit dem jeweiligen Chlorid-salz (ECl_2·dioxane, E = Ge, Sn) synthetisiert. Während (I*t*BuN)$_2$Sn: sowohl als Feststoff als auch in Lösung bei −80 °C ein Dimer bildet, wie durch SC-XRD und VT-NMR verifiziert, konnten die anderen Tetrylene nur als Monomere beobachtet werden. Bei der Reaktion von CO_2 mit dem Germylen überbrückt jeweils ein Molekül CO_2 die Ge–N Bindungen, während die Bindungen selbst intakt bleiben, wodurch sich 4-Ringe bilden. Im Fall des homoleptischen Stannylens dissoziieren die Sn–N Bindungen und bilden bei Insertion von CO_2 Carbamatogruppen. Bei der Reaktion von (I*t*BuN)$_2$Sn: mit N_2O kann eine partielle Oxidation beobachtet werden, bei der ein Bis-Stannylen mit einem zentralen Sn_2N_2-Ring gebildet wird.

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1. INTRODUCTION

In research, as well as the chemical industry, catalytic processes are an established cornerstone that receives continuing attention and study. While already utilized in the enzymatic fermentation to drinking alcohol and vinegar for thousands of years, the chemical concept behind catalysis was first described by Elizabeth Fulhame in 1794 in her book on oxidation-reduction reactions.[1-3] Almost 40 years later, in 1836, Berzelius coined the term *catalysis* based on his research. The word is derived from the Greek word καταλύειν (katalū́ō), meaning “to loosen”.[1] Followed by several breakthroughs in the early 20th century, such as the Haber-Bosch- or the Ostwald-process, which both utilize catalytic processes, industrial chemistry is no longer imaginable without them.[4-6]

> ***“Anyone who knows about Mozart, Ravel, and Gershwin***
> ***should know about catalysis as well.***
> ***There is no life without the miracles of catalytic reactions in***
> ***plants, animals, and human beings.”***
>
> Excerpt from
> Catalysis from A to Z: A Concise Encyclopedia[7]

In the last decades, however, arguments for environmentally friendly and more cost-effective chemistry have become an increasingly more burning topic. Transition metals and their catalytically active complexes are often toxic and hard to source. Naturally, an effort to utilize more abundant elements and ecological alternatives has been made and continues to be explored. One effort to create novel catalytic systems is to move away from transition metals to other elements in the periodic table.

As such, elements of the p-block have received increasing attention. Among them are elements that are much more abundant and more eco-friendly than many industrially relevant transition metals (e.g. platinum, vanadium, etc.).[8-11] Long overlooked, however, was their potential to exist in previously unobserved oxidation states and coordination environments, enabling them to perform outstanding reactivity. Before several seminal breakthroughs in the late 1970s and 80s, chemists believed that heavier p-block elements followed quite rigid and predictable patterns. For example, it was generally believed that they could not form stable double bonds (known as the “double bond rule”).[12-13] This rule was, however, thoroughly refuted by the early pioneers in this field. As such, Lappert presented the first heavy alkene analogs of germanium and tin, followed by the synthesis of disilene, diphosphene, and silaethene by West, Yoshifuji, and Brook.[14-18]

With the previously untapped potential of those elements now made clear, the rush towards new developments picked up and has not slowed down since. In the last 40 years, many milestones were reached, and heavier main-group compounds showed reactivity in small molecule and bond activation as well as in an increasing number of catalytic applications, slowly attempting to close the gap toward transition-metal organometallic chemistry.

Special attention has been given to heavier elements of group 14 (*i.e.* Si, Ge, Sn, Pb). While the high reactivity of low-coordinate and low-oxidation-state congeners (e.g., tetrylenes, tetrylones, tetryliumylidene ions, etc.) of this group makes them challenging to stabilize, it is also crucial for enabling activation of enthalpically strong bonds. With deliberately constructed ligands, highly active but stable complexes with free coordination sites can be created and utilized in small molecule activation and catalysis.[19-22] Especially germanium and tin complexes, whose central elements contain an inherent flexibility between the +II and +IV oxidation states, have resulted in big strides in that field.[23-25] Facile switching between oxidation states is imperative for enabling redox-based catalysis (*i.e.* oxidative addition and reductive elimination).[26]

2. STATE OF THE ART

2.1. CARBENES

BASICS

Carbon, the lightest element of group 14 in the periodic table, can be observed in a virtually unmatched diversity of structures. The range of appearances of the pure element alone, such as graphite, diamond, or fullerene, already demonstrates this. The variety is further expanded exponentially once hydrogen and other heteroatoms (*i.e.* N, O) are introduced, giving way to the entire field of organic chemistry.[27]

One class of carbon compounds that is now indispensable in organic and organometallic chemistry is the carbenes. Here, a neutral carbon atom forms two covalent bonds, leaving two free valence electrons. While they initially have only been observed as highly reactive transient intermediates, a wide variety of persistent carbenes are known today and are applied as catalysts and ligands.[28-30] Due to their electronic configuration, carbenes can be observed in the singlet (spin-paired) as well as triplet (unpaired) ground state (Figure 1).

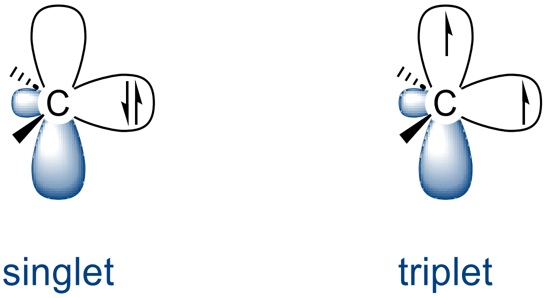
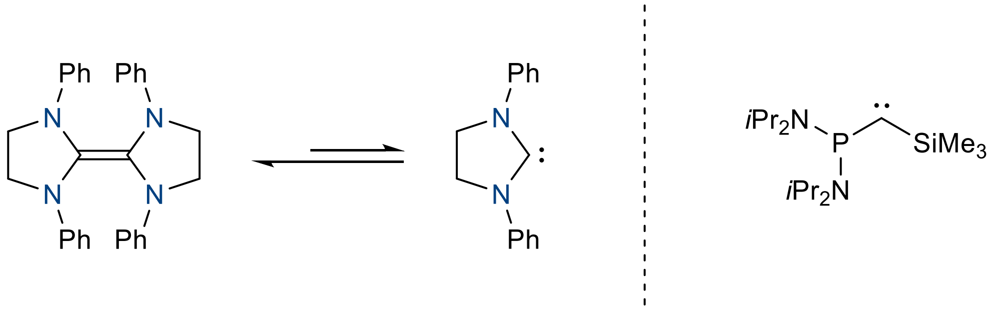


Figure 1. Non-bonding orbital depiction of the singlet and triplet states of carbenes.

While the simplest congener, transient methylene (H_2C:), is a ground state triplet (ΔE_{ST} = – 14.0 kcal mol^{-1})[31], persistent carbenes are more often observed in the singlet ground state, significantly influenced by the electronic and steric environment around the central carbon.[31-32] Consequently, carbenes can be stabilized by introducing strong electron donors and sterically demanding moieties as substituents.[29, 33-34]

Initial attempts to isolate a stable carbene employed amino moieties.[33, 35-36] The most promising first attempt was presented by Wanzlick in 1962 with a bis-(1,3-diphenyl-2-imdazolinylidene). The compound can be interpreted as a dimer with a considerable tendency to dissociate into the respective carbenes. In fact, reactivity studies revealed a carbene-like reactivity, indicating an equilibrium between monomer and dimer.



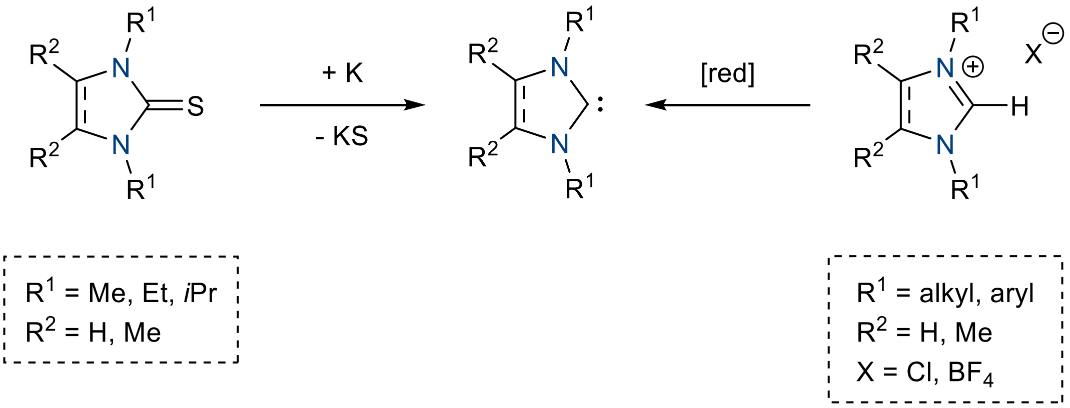
Scheme 1. Left: Dissociation of bis-(1,3-diphenyl-2-imdazolinylidene) to respective un-isolated carbene monomer.[33] Right: first stable carbene.[37]

Still, it took over 20 years until the first instance of a persistent carbene was reported in 1988. Bertrand *et al.* isolated a (phosphino)(silyl)carbene, presumably stabilized by a strong P–C multiple bond character and a push-pull effect between the phosphine and the silyl moiety.[36-38]

N-HETEROCYCLIC CARBENES – STRUCTURE AND SYNTHESIS

Remarkably stable *N*-heterocyclic carbenes (NHCs), discovered in 1991 by Arduengo *et al.,* are arguably the most popular and widely applied carbenes. While other types of NHCs are known, the term is usually understood to refer to imidazoline-2-ylidenes. NHCs are ground-state singlets, where the carbene carbon is neighbored by nitrogen atoms in a five-membered heterocycle (Scheme 2, middle).

Thermodynamic stabilization is provided on the one hand by the *N*-lone-pairs, donating electron density into the empty carbon p-orbital perpendicular to the ring plane, resulting in 6π aromaticity.[29-30] On the other hand, σ-donation from the carbene to the nitrogen centers also contributes to thermodynamic stability. Additionally, kinetic stability can be influenced by the steric bulk of substituents on the imine moieties, which can be varied relatively easily depending on the required properties. This results in a stable but electron-rich, nucleophilic carbene that is suitable as a ligand for a wide variety of organometallic complexes as well as an organocatalyst on its own.[29-30, 39-41]



Scheme 2. Synthesis of Arduengo-type NHCs from thione**[42]** (left) or imidazolium salt**[43-44]** (right). [red] = reducing agent (*e.g.*, KO*t*Bu, NaH).

Depending on the steric bulk of the amine substituents, two synthesis pathways towards NHCs are applied most frequently. Smaller NHCs, such as IMe_4 (1,3,4,5-tetramethyl-imidazol-2-ylidene), can be obtained *via* reductive desulfurizing of the respective imidazole-2-(3H)-thiones.[42] Larger congeners are usually synthesized by reduction of imidazolium salts (Scheme 2).[43, 45]

2.2. N-HETEROCYCLIC IMINES

STRUCTURE

As the name suggests, *N*-heterocyclic imines (NHIs) are a structural evolution from NHCs, in which an exocyclic imine nitrogen is introduced at the 2-position of the ring. Along the ylidic C=N bond, the nitrogen atom accepts σ- and π-electron density. At the same time, due to the orthogonal orientation of the nitrogen lone pair, no π-back-donation can occur. Therefore, the electron-rich aromatic cycle pushes further electron density into the terminal imino-nitrogen.

NHIs can act as 2σ,2π-electron donors as well as 2σ,4π-electron donors (Figure 2). All this results in a more basic and stronger donor ligand than the parent NHC, making them ideal candidates for stabilizing early transition metals and other more electrophilic metal centers.[46-49]

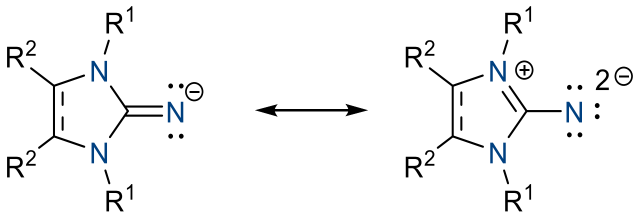
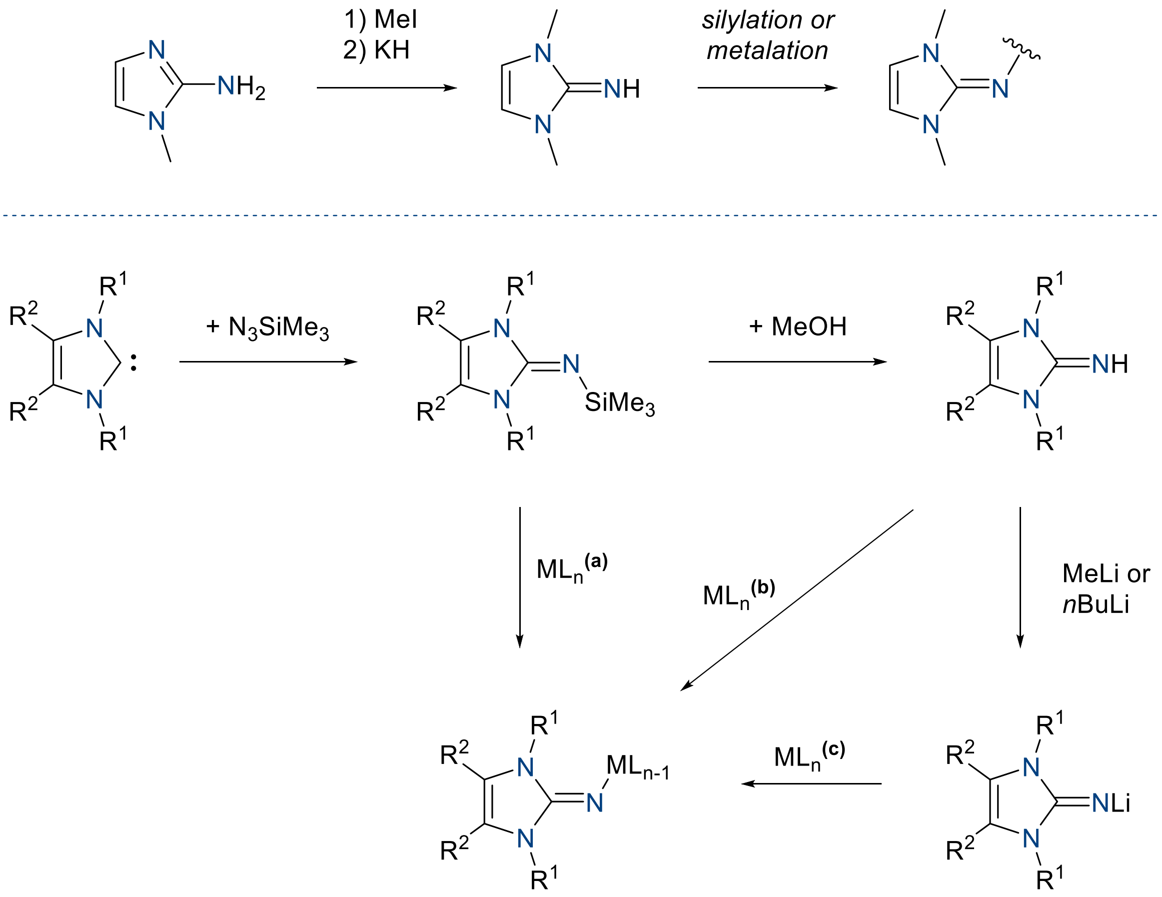


Figure 2. Canonical resonance structures of the anionic NHI Ligand (R = organyl). Adapted from Inoue *et al.*[49]

Besides anionic monodentate NHIs, donor-functionalized, neutral imine moieties can also act as ligands. Consequently, this opens up the possibility of bi- or even tri-dentate ligand systems.[50]

SYNTHESIS

While the seemingly most clear-cut synthesis towards *N*-heterocyclic imines - introducing NH_3 to parent carbene - does not lead to the desired product, several pathways to NHIs with varying steric composition have been reported.[51] The first established synthesis of 1,3-dimethyl-2-imino-imidazoline with satisfactory yield ensues by reaction of 1-methyl-1H-imidazole-2-amine with iodomethane and subsequent reduction with potassium hydride (Scheme 3, top).[52] This route is, however, not transferable to longer iodoalkanes.



Scheme 3. *Top:* Synthesis of 1,3-dimethyl-2-imino-imidazoline.[51-53] *Bottom:* Synthesis of commonly used NHI-ligand transfer reagents (R^1 = alkyl, aryl; R^2 = CH_3, H) and introduction to various metal centers as a ligand. $ML_n^{(a)}$ = *e.g.*, $GeCl_4$, $CpTiCl_3$, Re_2O_7, $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_3$; $ML_n^{(b)}$ = *e.g.*, $[(Me_3Si)_2N]_2Sn$:; $ML_n^{(c)}$ = *e.g.*, $SnCl_2$·Dioxane, $Me_3CC{\equiv}W(OCCMe_3)_3$.[54-60]

The most versatile route for bigger NHIs up to date was first established by Tamm *et al.* and involves a *Staudinger*-type mechanism of the respective NHC with trimethylsilylazide, giving *N*-silylated imines (Scheme 3, bottom).[55, 61] *Via* this approach, it is possible to generate NHIs with a wide variety of substituents on the endocyclic nitrogen moieties, ranging from small methyl groups up to much more sterically demanding substituents, such as Dipp (2,6-di-isopropyl-phenyl). These *N*-silylated precursors can then either be introduced directly to a variety of metal centers or desilylated with methanol to give free NHI–H, which opens up further reaction pathways to organometallic complexes.[55, 61] If silylated or free NHIs do not show sufficient reactivity to be introduced to a metal center, additional lithiation of the ligand can be interposed.[60, 62]

NHI SUPPORTED COMPLEXES

Due to the 2σ and up to 4π electron-donating nature of the NHI, metal complexes can display a degree of metalla-2-aza-allene or metalimide character (Figure 3). In terms of structure, this can be observed in a wide C–N–M bond angle, approaching 180°, and an elongation of the C–N bond alongside a respective shortening of the N–M bond.[49]

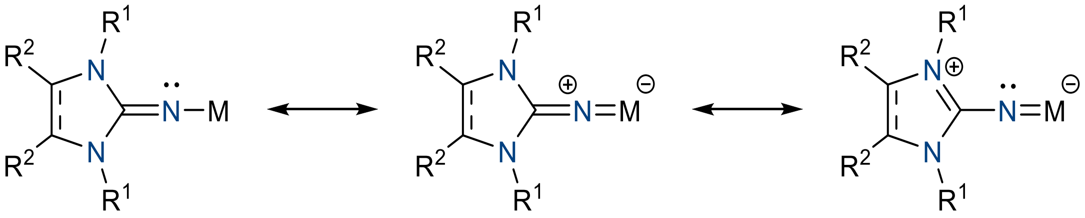
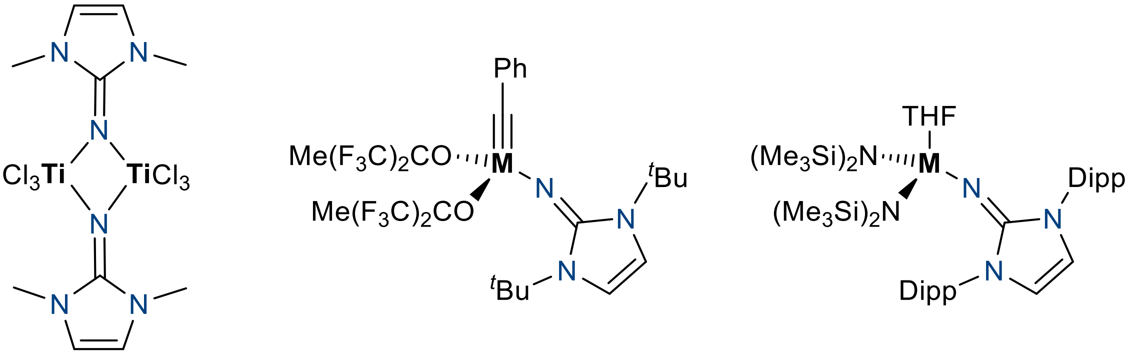


Figure 3. Selected resonance structures of a model complex of anionic NHI Ligand with M^+ (R = organyl). Adapted from Inoue *et al.*[49]

As a result of their exceptional donor properties, NHIs have been employed as ligands in many compounds. In fact, examples of transition metal complexes with NHIs can be found along the whole d-block of the periodic table, as well as among lanthanides and actinides (*e.g.,* Figure 4, **1-3**).[50, 63-65] The first NHI-supported organometallic compound, the dimeric titanium complex (**1**), was published in 1997 by Kuhn *et al*.[66]

Since then, a number of transition metal complexes that utilize NHIs have been developed for catalysis.[50, 67] Examples include transfer hydrogenation by actinidine complexes, alkyne metathesis by tungsten and molybdenum compounds (*e.g.*, $PhC{\equiv}M[OC(CF_3)_2Me]_2$(I*t*BuN); M = Mo, W; Figure 4, **2a,b**), hydroboration by hafnium complexes, and more.[60, 62, 68-70] Especially titanium complexes seem to benefit from the stabilization by NHIs and were shown to enable various polymerization as well as the catalytic synthesis of urea derivates.[71-74]



1

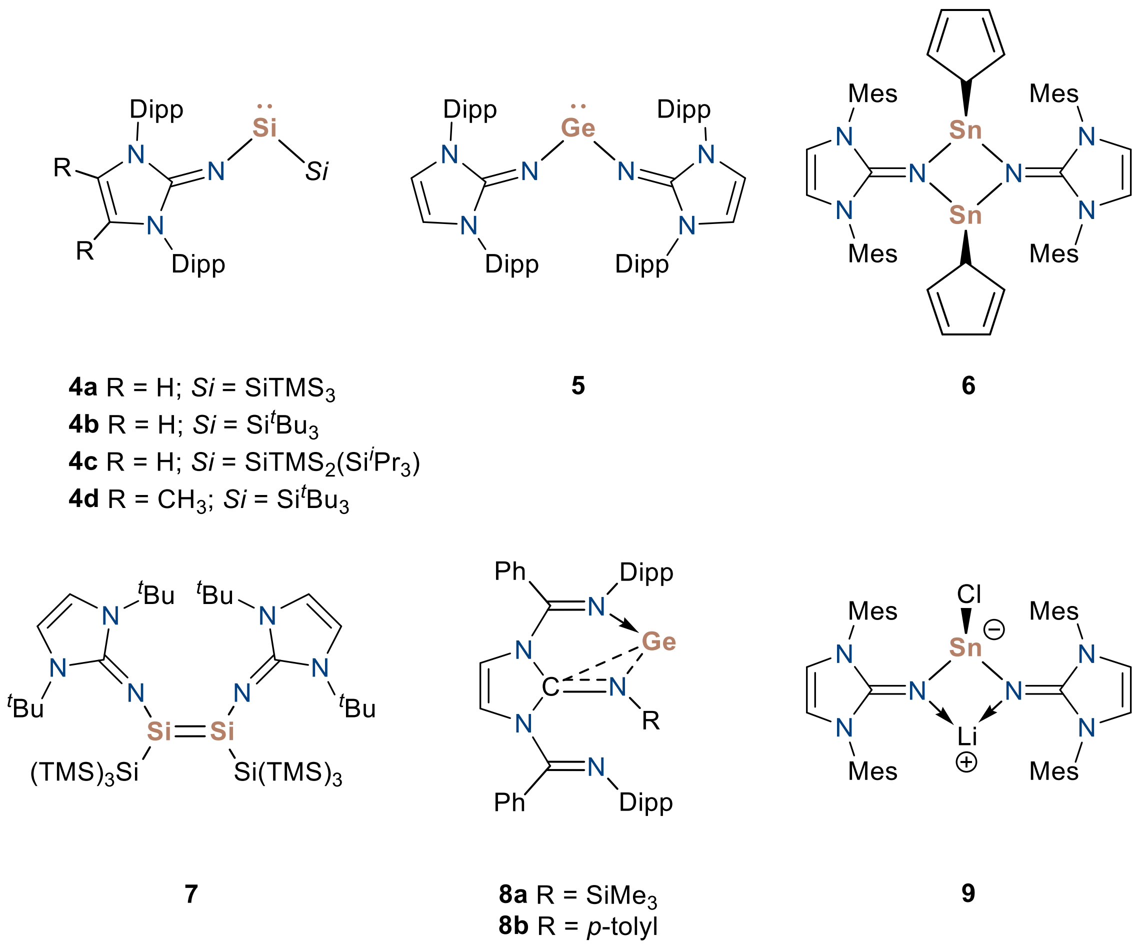
2a M = Mo
2b M = W

3a M = Sc
3b M = Y
3c M = Lu
3d M = Gd

Figure 4. Selected examples of NHI-supported transition metal complexes.[66, 68, 75]

Besides application in transition-metal compounds, NHIs have proven to be particularly suitable for stabilizing a considerable selection of electron-deficient low-valent p-block complexes. It could be shown that the electrophilic main-group-metal center benefits from kinetic and thermodynamic stabilization by NHIs.

Pertinent group 13 complexes span for examples from dimeric aluminum-hydride [μ-IDippNAlH$_2$]$_2$, capable of catalytic reduction of CO$_2$, and bis-Ga(I) [IDippN-Ga]$_2$, both with a central E$_2$N$_2$ ring (E = Al, Ga), to cyclic five-membered E(I) carbenoids (E = Ga, In, Tl).[76-78] Moving further to group 14, a compelling number of homo- and heteroleptic tetrel compounds can be mentioned. The selected examples **4-9** [54, 59, 79-85] (Figure 5) illustrate the structural influence of a sterically demanding substituent at the endocyclic *N*-moieties. While the use of bulky ligands tends to result in the formation of monomeric structures with one coordination center, smaller NHIs can lead to dimerization, as in disilene **7**. Besides that, dimerization can also occur *via* bridging of two element centers by the NHI, such as in compounds **1** and **6**.



4a R = H; *Si* = $SiTMS_3$
4b R = H; *Si* = Si^tBu_3
4c R = H; *Si* = $SiTMS_2(Si^iPr_3)$
4d R = CH_3; *Si* = Si^tBu_3

5

6

7

8a R = $SiMe_3$
8b R = *p*-tolyl

9

Figure 5. Selected examples of low valent group 14 complexes stabilized by *N*-heterocyclic imines.[54, 59, 79-85]

In some cases, further stabilization by silylene ligands has proven beneficial. For example, the homoleptic $IDippN_2Si$: (the silylene congener of **5**) could not be isolated but instead undergoes an irreversible ligand rearrangement after N–C bond cleavage on the side-arms.[54] However, upon the introduction of a silyl moiety to form heteroleptic silylenes, **4a**-**d** were described.[79-82, 86] Here, it should be mentioned that the NHI's backbone significantly affects the complex's structure. While transient silylenes **4a**-**c**, which bear ligands with unsubstituted backbones, undergo reversible intramolecular C–C bond activation to the respective silepins (*i.e.* sila-2,4,6-heptatrienes), complex **4d**, which is ligated by an NHI with a methylated backbone, can be isolated in acyclic form. Notably, **4d** can still undergo C–C bond activation. In fact, reversible intermolecular C–C insertion of the silicon center can be observed with benzene and fluorobenzene as well as ring opening of pyridine and DMAP.[82] The first Ge(0) π-complex **8** was recently reported, utilizing a modified NHI ligand with imino-moieties on the wingtips, allowing additional σ-donation towards the germanium center.[85]

2.3. HEAVIER TETRYLENES

BASICS

As carbenes (*vide supra*), heavier analogs of group 14 contain a central atom in the oxidation state +II, coordinated by two ligands. In contrast to the lightest congener, heavier tetrylenes R_2E: (E = Si, Ge, Sn, Pb) show markedly different electronic and chemical behavior (*cf.* Figure 6). This aspect can be best explained by taking a step back and looking at quantum-mechanic considerations of the bonding nature in heavier carbon analogs.

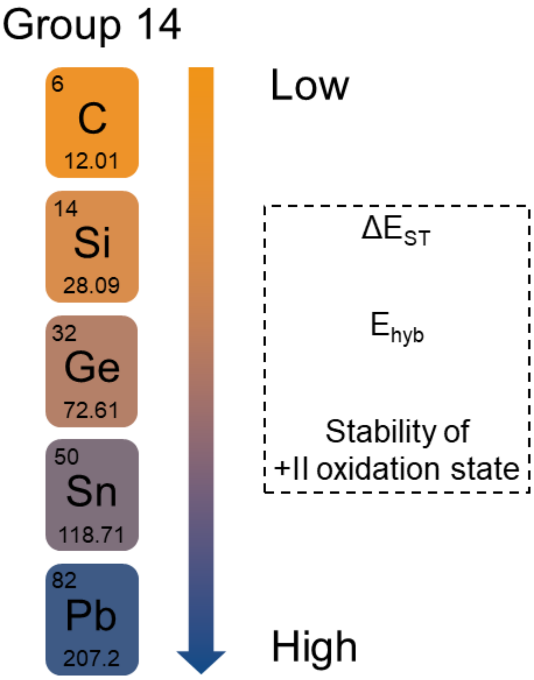


Figure 6. Trend of the singlet/triplet gap (ΔE_{ST}), hybridization energy (ΔE_{hyb}), and stability of the +II oxidation state along group 14 from carbon to lead.

Unlike carbon, which shows very effective hybridization, s-p mixing becomes increasingly less efficient descending group 14.[87] This can be traced back to an increasing difference in diffusion (*i.e.* “size”) of the valence s- and p-orbitals (Figure 7). In the case of carbon, the valence s- and p-orbital are close in energy due to them experiencing a similar amount of attraction towards the nucleus. This results in a very similar amount of diffusion of the valence 2s and 2p orbitals in the carbon atom, enabling facile hybridization.[88]

Moving on to heavier elements, relativistic effects lead to a contraction of the s-orbitals, resulting in a larger energy separation between np- and ns- valence orbitals. In other words, the valence p-orbital becomes "bigger" faster than the respective valence s-orbital, hindering hybridization. This effect increases the further the respective valence shell is from the core, i.e. the heavier the element becomes.

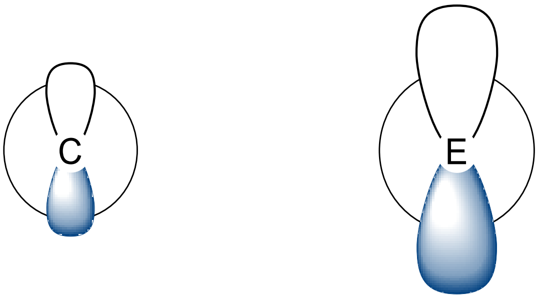


Figure 7. Similar size of 2s- and 2p- valence orbitals in carbon (left) compared to an increased size separation of ns- and np- valence orbitals in heavier group 14 elements (right). Adapted from Gernot *et al.*[88]

Returning to tetrylenes, the consequence is increasing the stability of the singlet ground state with growing energy difference of the valence orbitals going down the group. This can, for example, be observed in the trend of singlet-triplet gaps of parent tetrylenes H_2E: (E = C, Si, Ge, Sn, Pb). While the carbene is a ground-state triplet with a negative ΔE_{ST} (*c.f.* chapter 2.1), the heavier congeners are ground-state singlets with increasing singlet-triplet energy differences (Table 1). In regards to structure, this can be observed in a narrowing of the L–E–L angle with increased ΔE_{ST} due to the lone pair occupying more space.[89]

Table 1. Calculated singlet-triplet energy gaps (ΔE_{ST}) for tetrylenes H_2E: (E = group 14 element) and their respective ground states.[31]

tetrylene	ΔE_{ST} [kcal/mol^{-1}]	ground state
H_2C:	– 12.7	triplet
H_2Si:	16.7	**singlet**
H_2Ge:	21.8	
H_2Sn:	24.8	
H_2Pb:	34.8	

Another consequence of the s-orbital being so much lower in energy is the so-called *inert-pair-effect*.[23-25] This relativistic effect describes the increased hesitancy of the lone pair to participate in bonding, which can, for example, be observed in the decreasing tendency of tetrylenes to dimerize with the increasing size of the central element. While disilenes form strong Si=Si bonds, which have been observed to persist in solution, digermenes already tend to dissociate at least partially to form an equilibrium between the monomer and the dimer. Going down the group, this inertia increases and the E=E bonds get longer and weaker.

With the lone pair (predominantly s-character) capable of electron donation, and the vacant orbital (predominantly p-character) being electrophilic in ground-state triplet tetrylenes, they can display ambiphilic reactivity and are capable of multifaceted follow-up reactivity.[23, 89] In turn, tetrylenes are highly reactive and require deliberate ligand stabilization.

LIGAND INFLUENCES

The rational synthesis of tetrylenes is a balancing act between stabilization and ensuring selective reactivity. The electronic and steric properties of the ligands have a significant influence on the reactivity of the compound.

So far, a combination of both thermodynamic and kinetic stabilization, often realized in the same ligand, has been proven effective (*cf.* Figure 8). On the one hand, thermodynamic stabilization can be achieved by the inductive effect of σ-accepting groups, which increase the s-character of the non-bonding σ-orbital (*i.e.* lowering the HOMO energy level). On the other hand, electronegative, π-donating moieties push electron density into the vacant p-orbital, thereby increasing the energy of the LUMO, providing a mesomeric effect. Similarly, the LUMO energy can be increased by employing additional *Lewis* bases, donating electron density into the vacant p-orbital. In all cases, the result is a widened HOMO-LUMO gap and, therefore, increased stability of the tetrylene. [23, 28]

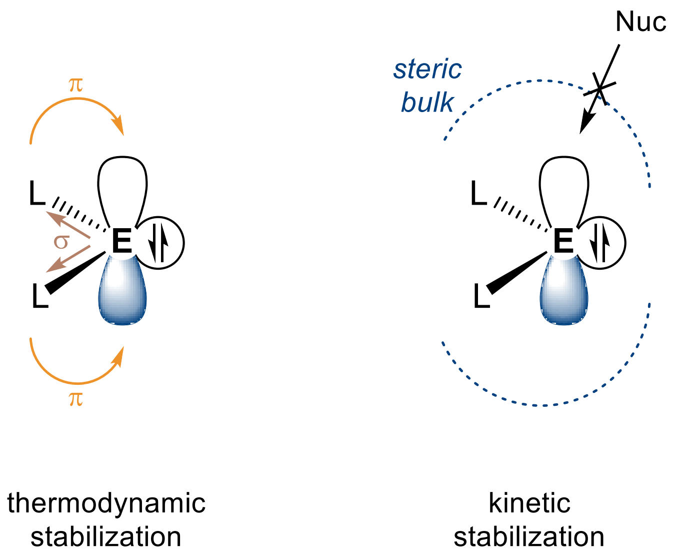


Figure 8. Thermodynamic and kinetic approaches to stabilize heavier tetrylenes in their singlet state and protect the empty p-orbital from nucleophilic attack (nuc = nucleophile) Adapted from Tokitoh *et al.*[23]

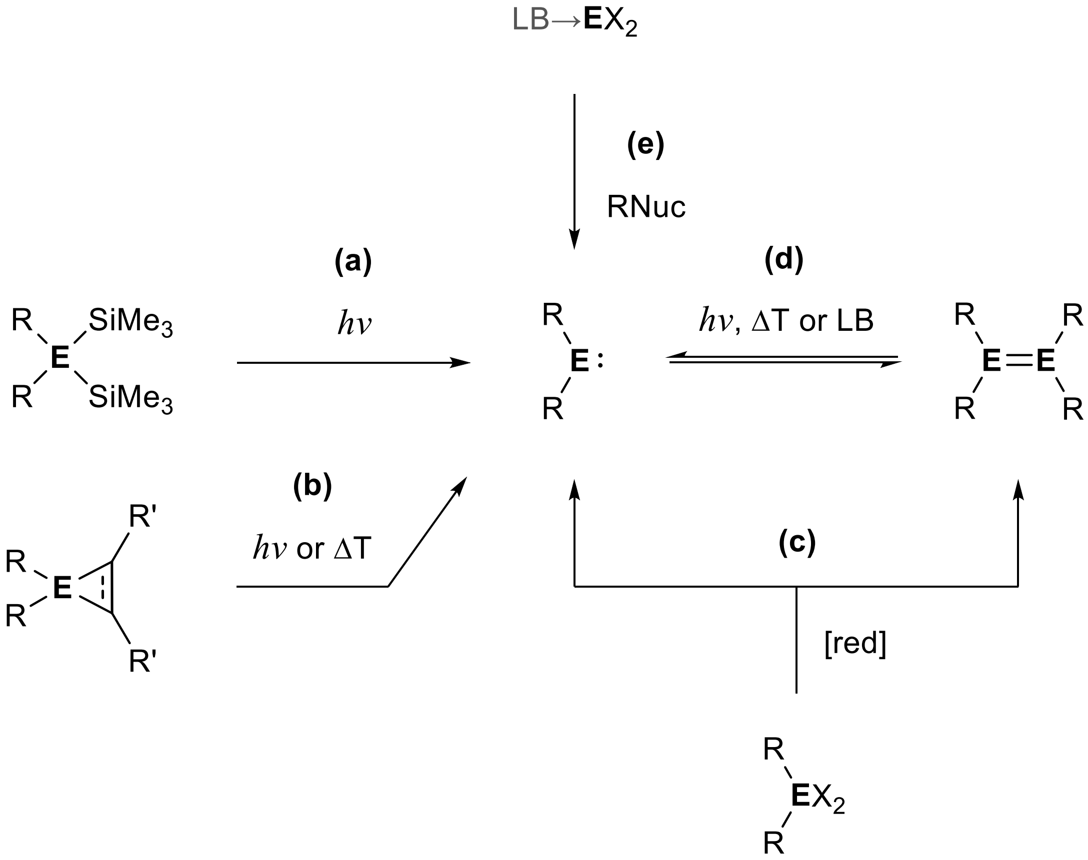
Kinetic stabilization can be achieved by shielding the metal center with sterically encumbering substituents. Bulky Ligands protect the empty p-orbital from nucleophilic attacks by steric repulsion. This can also prevent the tetrylene from reacting with itself and prevents dimerization or oligomerization, which is often observed for smaller E(II) complexes or salts, such as ECl_2·dioxane.[60, 89] Another thing to consider with bulky ligands is their influence on the L–E–L angle and, therefore, the singlet-triplet gap due to changes in geometry. With the widening of the L–E–L angle, the p-character of the lone pair increases, lowering ΔE_{ST}.[90-91]

While stabilizing the central atom is of fundamental importance to obtain an isolable tetrylene, ligand properties that potentially increase reactivity can also be incorporated into the design of suitable ligands. Especially for heavier tetrylenes, where the singlet ground state is inherently more stable and ΔE_{ST} is larger, increasing reactivity by utilizing ligands that decrease the HOMO-LUMO or singlet-triplet gap can enable follow-up reactivity. One approach that seems to be a productive middle ground is using strongly σ-donating but sterically demanding ligands, such as bulky boryls[92-94] and silyls[95], to provide kinetic stabilization but increased reactivity at the same time. The NHI-Ligands combine these aspects by providing (activating) σ-donation and (stabilizing) π-donation with sterically demanding wingtips.

SYNTHESIS

Tetrylenes are most commonly synthesized by the following pathways, with their respective efficacy depending on the central atom (Scheme 4).[23, 96-97] The first method is the reduction of a precursor in the +IV oxidation state. This can be achieved by reductive elimination *via* photochemical or thermal reduction or with the use of a reducing agent.

The Photochemical reduction can be applied to silyl-substituted precursors $R_2E(SiR'_3)_2$ *via* liberation of a disilene (route **(a)**, Scheme 4). Furthermore, metalliranes or metallirenes (3-membered heterocycles resembling the [2+1] cycloaddition product of a tetrylene and an alkene or alkyne) can be driven to photochemical or thermal reductive elimination by means of releasing the respective olefin or alkyne (route **(b)**, Scheme 4). Using an additional reducing agent, such as KC_8, NaNaph or alkali metals, halide substituted species R_2EX_2 (E = Si, Ge, Sn, Pb; X = Cl, Br, I) can be reduced as well (route **(c)**, Scheme 4). Depending on the compound, this can lead to the tetrylene or the respective dimeric dimetallene.



Scheme 4. Common synthetic routes to generate stable tetrylenes ([red] = reducing agent (e.g. KC_8, NaNaph, alkali metals), LB = *Lewis* base (e.g. polar solvent, NHC, dioxane, etc.), Nuc = Li, MgBr, $SiMe_3$, X = Cl, Br, I).[23, 96-97]

The second pathway starts from precursors already in the +II oxidation state. As such, the splitting of dimetallene can be achieved by photochemical or thermal means, or using an additional *Lewis* base, such as IMe_4 or dioxane (route **(d)**, Scheme 4). Another route starting from +II precursors is the salt-metathesis reaction from a halide-salt EX_2 (E = Si, Ge, Sn, Pb; X = Cl, Br, I) with an organometallic nucleophile, such as RLi or RMgBr (route **(e)**, Scheme 4). This method was initially only used for germanium, tin, and lead since their di-halides are easily accessible. Silicon(II)-halides are highly reactive and require bulky donors for stabilization. Still, since the synthesis of *Lewis* base stabilized compounds, such as $IDipp \rightarrow SiCl_2$ or $CAAC \rightarrow SiI_2$, this route also became accessible for silylenes.[98-100] Generally, using additional *Lewis* bases for heavier halides can improve solubility and aid in stabilizing potential transition states. Similar to silicon, but to a lesser degree, the +II oxidation state of germanium also profits from additional stabilization by a donor.[101]

SMALL MOLECULE ACTIVATION AND CATALYSIS BY HEAVIER TETRYLENES

The reason why transition metals are so predestined for small molecule activation and catalysis is their flexibility to switch between oxidation states and their reactivity on multiple coordination sites, due to their access to (partially occupied) valence d-orbitals of low energy difference.[26, 102] This made them the prime target for the exploration of new catalytic routes and applications in organometallic chemistry. However, the research on (heavier) tetrylenes for small molecule activation and catalysis was long neglected and only gradually got more widespread attention. This is due to the initial motivation of imitating bonding motifs found in carbon chemistry, such as double or triple bonds. Chemists at that time were more interested in the similarities with the lightest element of the group than exploring the potential in the marked differences from it.

Power first highlighted the potential and similarities of tetrylenes with transition metal catalysts in his seminal 2010 review *"Main-group elements as transition metals"*.[102] Due to their ambiphilic nature and low HOMO-LUMO or singlet-triplet energy gaps, they can react similarly to transition metals.

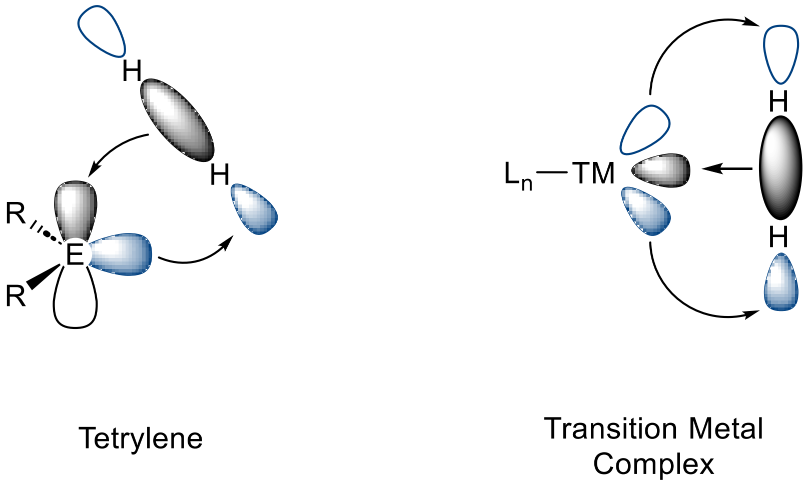
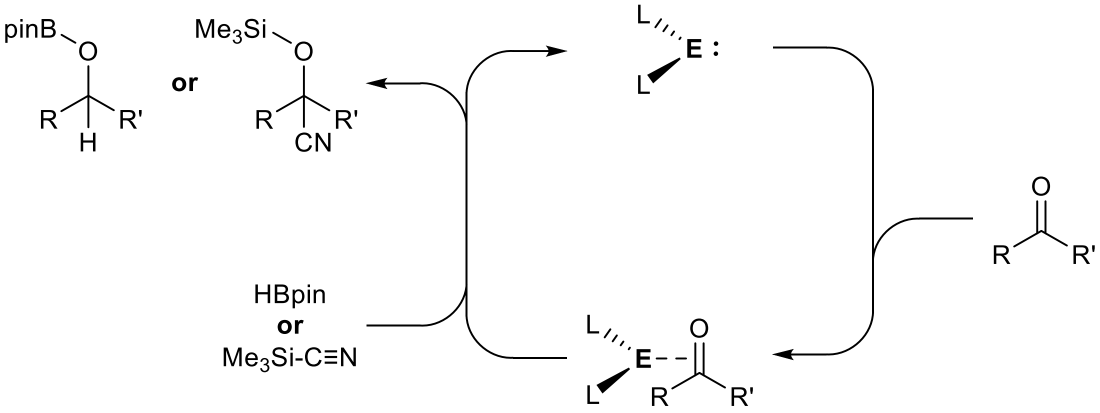


Figure 9. Frontier orbital interaction of tetrylenes (left) and transition metal complexes (right) with small molecules, specifically H_2. Adapted from Power *et al.* and Inoue *et al.*[26, 102]

Their reactivity towards small molecules can be illustrated by looking at the frontier orbital interaction of tetrylenes as well as transition metals with H_2 (Figure 9).[20, 26, 102] Adding H_2 to transition metal complexes can occur under mild conditions and signify the first step in a catalytic cycle, the oxidative addition. In the case of a tetrylene, the filled s-orbital attacks the antibonding σ*-orbital of H_2, weakening and polarizing the H-H bond. In turn, the electrophilic p-orbital of the tetrylene accepts electron density from the H_2 σ-orbital. Under the right conditions, the H_2 bond is sufficiently weakened, and oxidative addition occurs. Pertinent to this, the first activation of H_2 by a stable main-group complex was achieved in 2005 by Power and coworkers with a germanium alkyne analog.[103] The digermyne was irreversibly oxidated to a mixture Ge(II) and Ge(IV) compounds under mild conditions. In terms of stable heavier tetrylenes, H_2 could first be activated by the diaryl-stannylene $^{Dipp}Ter_2Sn$: giving bridged $(^{Dipp}TerSn(\mu\text{-}H))_2$ dimer *via* ligand elimination in 2008 (*c.f.* Scheme 17).[104]

A persistent challenge of applying tetrylenes in catalysis is their lack of coordinative or oxidative flexibility in contrast to transition metals. While they have proven capable of oxidative addition in many instances, closing the catalytic cycle and recovering the low oxidation state is still a significant obstacle. The oxidized product tends to be very stable, and reductive elimination is unfavored. Because of this, progress has primarily been made in redox-based catalytic cycles that utilize external, stochiometric reducing agents that are strong enough to provide the required driving force to close the cycle and release the product. As such, hydroboration or cyanosilylation has been successfully achieved by heavier tetrylenes (*c.f.* Scheme 5).[19, 105-108]

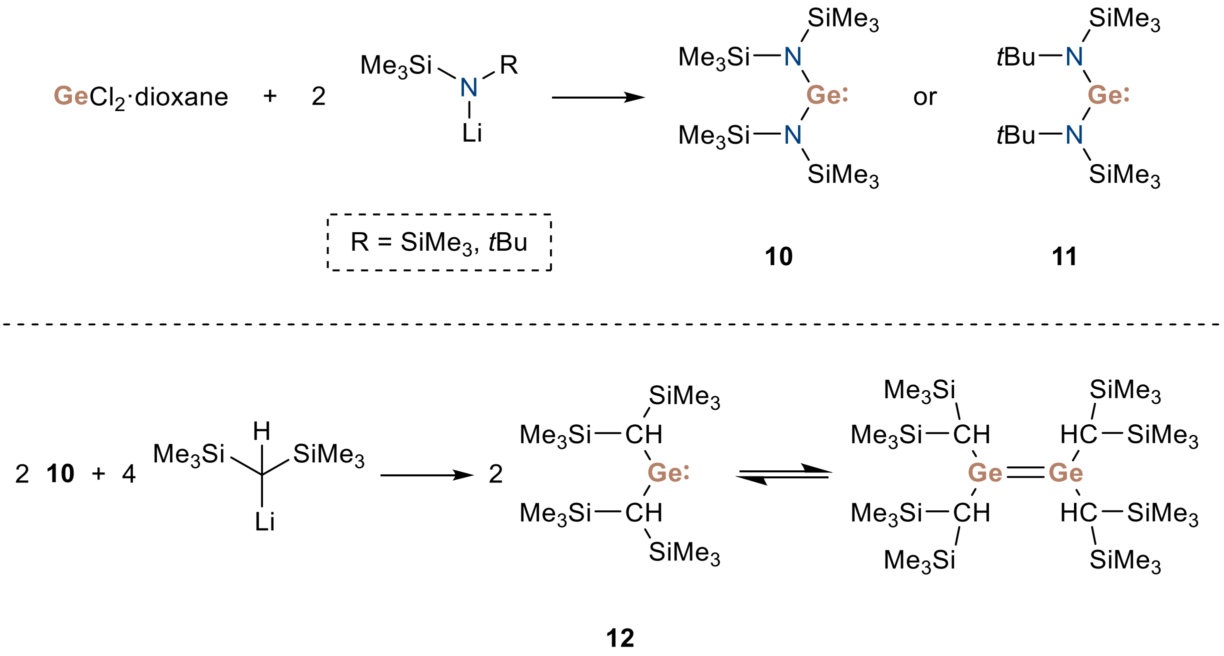


Scheme 5. Schematic catalytic cycle for the cyanosilylation or hydroboration of carbonyl compounds by tetrylenes (R = alkyl, aryl; R' = alkyl, aryl, H).

Since those first discoveries, the number of examples of small molecule activation and catalysis by tetrylenes has grown steadily and the drive towards more efficient and novel catalytic applications is still going strong. In the following chapters, a selection of acyclic germylenes and stannylenes and their reactivity will be illuminated in more detail, since the results of this present work concerns tetrylenes of germanium and tin.

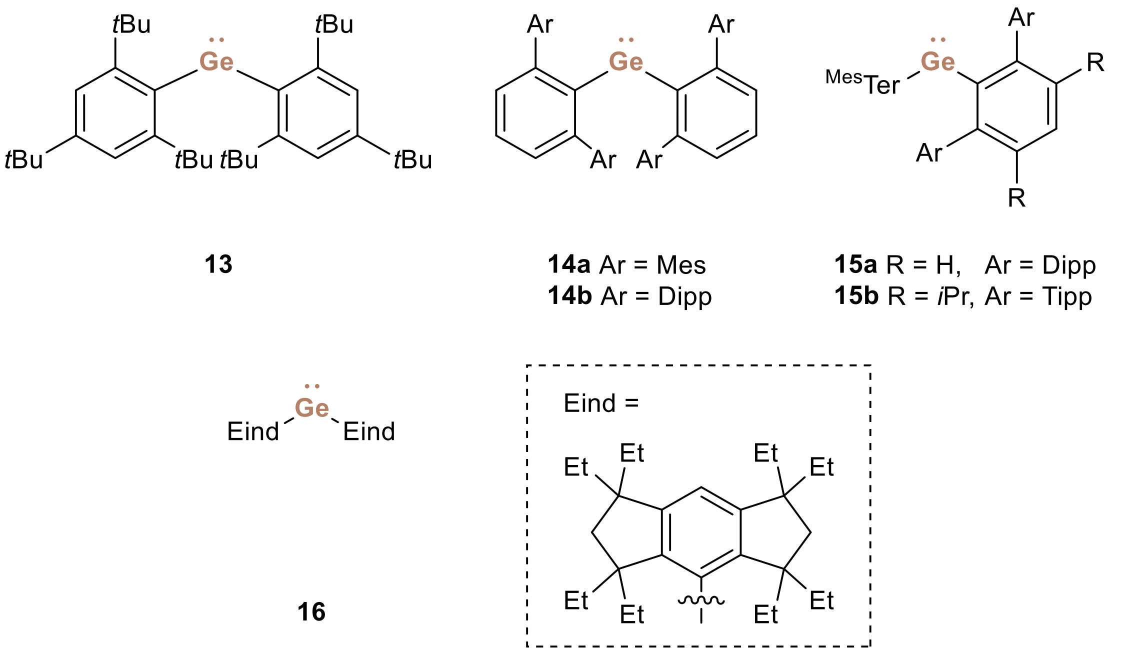
2.3.1. Germylenes

In the infancy of germylene chemistry, the generation of transient, small germylenes as a proof of concept was the contemporary research focus. They were more seen as starting materials or precursors for other compounds, not only owing to limited synthetical and characterization methods.[109-111] The first stable germylenes were reported in 1974 by Lappert *et al.* with the amido-germylenes $[(Me_3Si)_2N]_2Ge$: (**10**) and $[(Me_3Si)(Me_3C)N]_2Ge$: (**11**) (Scheme 6, top).[112] The complexes were obtained *via* the aforementioned salt-metathesis route (*c.f.* route (e), Scheme **4**) with the lithiated amides $[(Me_3Si)_2N]Li$ or $[(Me_3Si)(Me_3C)N]Li$ respectively.



Scheme 6. Top: Synthesis of the first stable germylenes (**10** and **11**), published by Lappert *et al.* in 1974 (R = $SiMe_3$, *t*Bu).[112] Bottom: Synthesis of germylene **12**, which can be observed as dimer in solid state.[14, 113]

Shortly after, the same group isolated the homoleptic alkyl derivative $[(Me_3Si)_2CH]_2Ge$: by reacting complex **10** with $[(Me_3Si)_2CH]Li$. The resulting germylene **12** is monomeric in solution and the gas phase, but dimerizes in solid state to the digermene $[(Me_3Si)_2CH]_2Ge{=}Ge[CH(SiMe_3)_2]_2$ (Scheme 6, bottom).[14, 113] Increasing the steric bulk of one of the alkyl ligands by an additional trimethylsilyl-group (*i.e.* $(Me_3Si)_3C$ *vs.* $(Me_3Si)_2CH$), prevents this dimerization.[97, 111]



13

14a Ar = Mes
14b Ar = Dipp

15a R = H, Ar = Dipp
15b R = *i*Pr, Ar = Tipp

16

Figure 10. A selection of aryl-stabilized germylenes (Eind = 1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl).[114-118]

Thermodynamically stabilized aryl-germylenes also belong to one of the earlier congeners of the compound class and continue to show interesting reactivity towards small molecules (Figure 10). The first upon them, 2,4,6-tri-*t*-butylphenyl-stabilized germylene **13**, was prepared in 1987 by du Mont *et al.* *via* the by now familiar salt-metathesis route from $GeCl_2$·dioxane and the lithiated ligand precursor.[114]

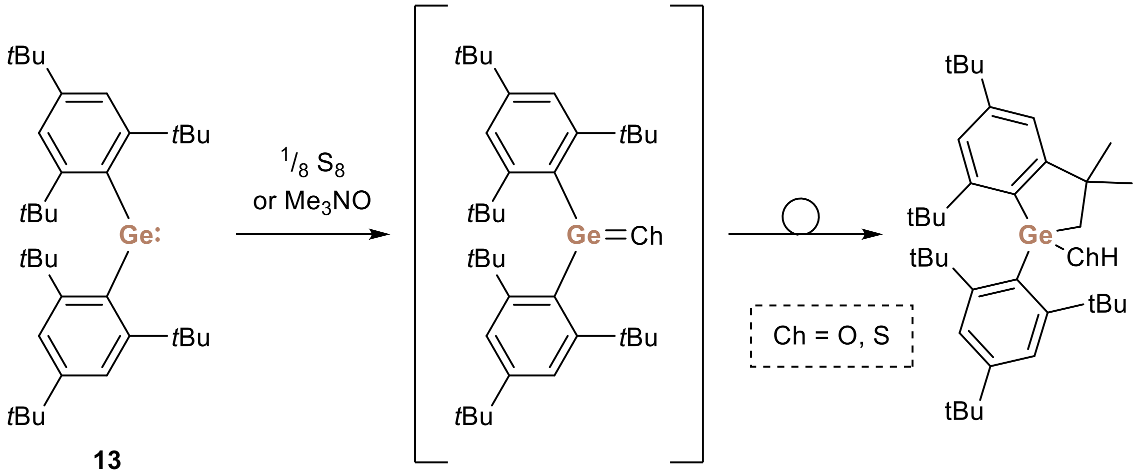
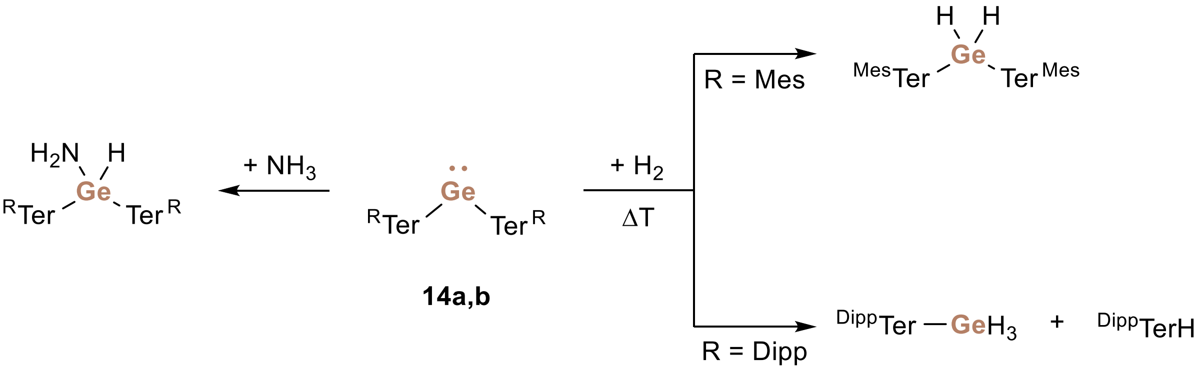


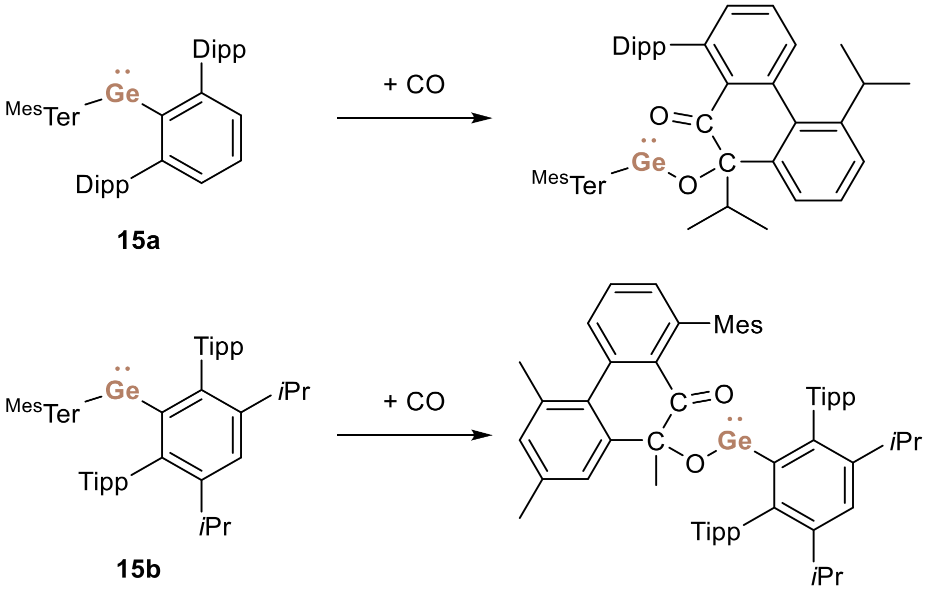
Figure 11. Reactivity of aryl-germylene 13 with sulfur and trimethylamine N-oxide (Ch = O, S).[114, 119]

They observed reactivity towards sulfur, giving a transient germathion, which undergoes intermolecular C–H insertion by the germanium center into one of the ortho-*tert*-butyl groups. Later, Jutzi and coworkers observed the formation of a germaindanol upon treatment of complex **13** with trimethylamine *N*-oxide, postulated *via* an intermediate germanone similar to the reaction with sulfur.[119]



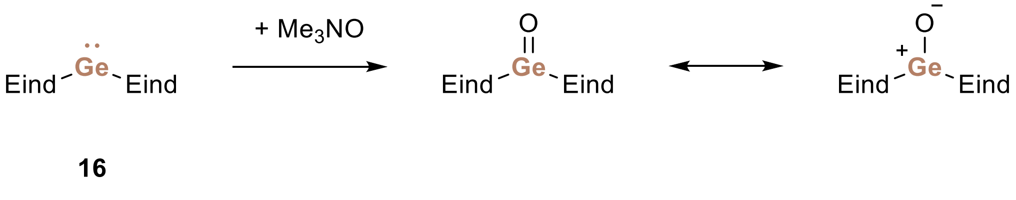
Scheme 7. Contrasting reactivity of germylenes **14a** (R = Mes) and **14b** (R = Dipp) with NH_3 and H_2.[115-116]

Complexes **14a** and **14b**, which were again obtained *via* salt metathesis, were investigated on their reactivity towards NH_3 and H_2.[115-116] While both compounds reacted with NH_3 at elevated temperatures to the oxidative addition products $L_2GeH(NH_2)$ (L = Mes or Dipp respectively), they showed contrasting reactivity towards hydrogen (Scheme 7). On one hand, the sterically less encumbered metal center in complex **14a** reacts with hydrogen in the same fashion as with ammonia, giving the oxidative addition product. Germylene **14b** on the other hand decomposes to ^{Dipp}Ter–GeH_3 and free ligand. Theoretical calculations revealed, that ligand elimination to give hydrido-germylene ^{Dipp}Ter–GeH is more favored than the oxidative addition to $^{Dipp}Ter_2GeH_2$ due to the increased steric bulk. The intermediate then reacts further to ^{Dipp}Ter–GeH_3 with an additional equivalent of H_2. Compound **14a** also showed oxidative addition reactivity towards Methanol and H_2O as well as reversible activation of P_4.[120-121]



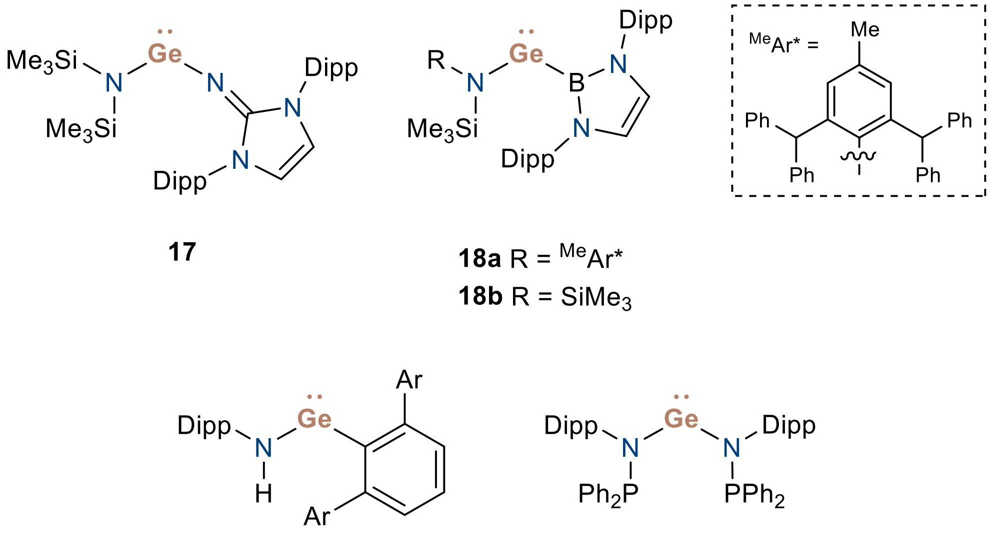
Scheme 8. Contrasting reactivity of germylenes **15a** and **15b** with CO.[117]

The first reactivity towards CO at room temperature was observed with the heteroleptic germylenes **15a** and **15b**.[117] In both cases, the authors observed the insertion of two equivalents of CO into one of the respective Ge–C bonds. Calculations propose the formation of an intermediate germaketene with a weak Ge–CO bond. Pertinently, this bonding motif is similar to the later discovered room-temperature stable silicon-carbonyl complexes $[(Me_3Si)_3Si](^tBu_3Si)Si{:}–CO$ and $[L(Br)Ga]_2Si{:}–CO$ ($L = HC[C(CH_3)N(2,6\text{-}^iPr_2\text{-}C_6H_3)]_2$) by our group and Schulz *et al.* respectively.[122-123] Reaction with another CO molecule and rearrangement subsequently leads to the formation of cyclic decomposition products (Scheme 8). The authors also observed reactivity of previously discussed germylenes **14a** and **14b** towards CO, however no selective product formation was reported.



Scheme 9. Synthesis of the first stable germanone from germylene **16** with trimethylamine *N*-oxide.[118]

A milestone in mimicking common carbon bonding motives with heavier congeners was achieved with Eind (Eind = 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl)-stabilized germylene **16**.[118] The rigid and bulky Eind ligand enabled the formation of a stable germanone upon reaction of complex **16** with trimethylamine *N*-oxide (Scheme 9). While the Ge=O bond is highly polarized, the shortened bond length compared to a single bond and theoretical calculations support the existence of a double bond.



17

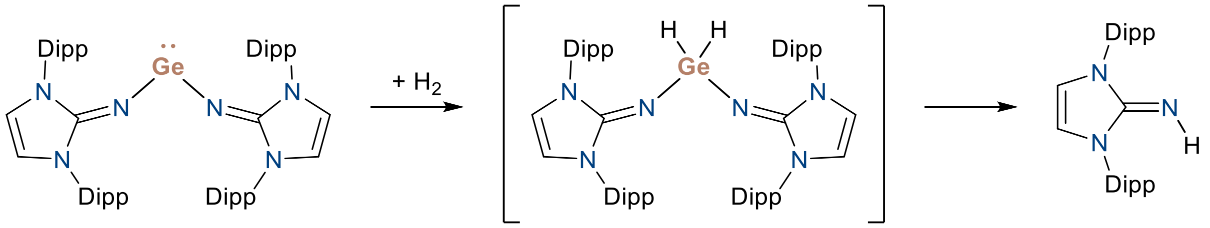
18a R = $^{Me}Ar^*$
18b R = $SiMe_3$

19a Ar = Mes
19b Ar = Dipp

20

Figure 12. Selected examples of amine- and imine-stabilized germylenes.[94, 124-127]

Since the discovery of Lappert's amido-germylene, the use of amine- and imine-type ligands continues to be a lucrative approach to stabilizing germylenes (**17-20**, Figure 12; **5**, Figure 5).[54, 94, 96, 105, 124-130] The *N*-moieties' σ-accepting and π-donating properties make them a suitable target for stabilization, as discussed earlier. Most amido-ligands are also markedly bulky, using Mes, Dipp or even larger substituents, and therefore also provide thermodynamic stabilization. As such, $(IDippN)_2Ge$: (**5**, Figure 5), stabilized by two bulky NHI ligands, reacts with H_2 to give (IDippN)H, presumed by the authors *via* the oxidative addition product $(IDippN)_2GeH_2$, which could however not be observed (Scheme 10).[54]

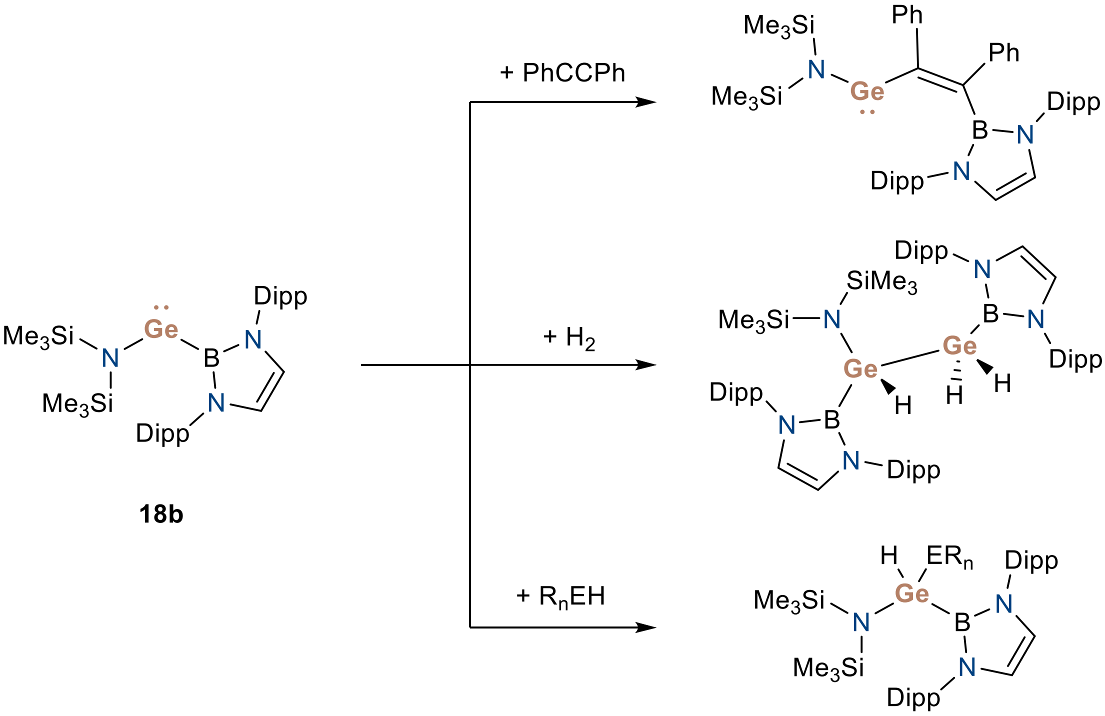


5

proposed intermediate

Scheme 10. Reaction of the NHI-stabilized germylene **5** with H_2 *via* the proposed intermediate oxidative addition product $(IDippN)_2GeH_2$.[54]

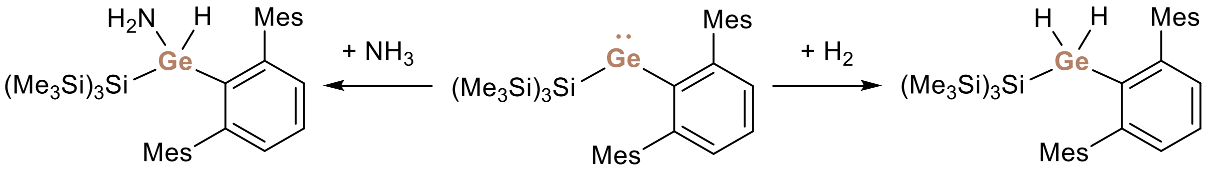
The first heteroleptic NHI-stabilized germylene was synthesized by our group with complex **17**.[124] The compound was obtained by a ligand exchange reaction using Lappert's germylene (**10**) and the free ligand (IDippN)H. While no small molecule activation was presented, the nucleophilicity of the germanium center could be demonstrated by its use as a ligand to form the respective iron carbonyl complex.



18b

Scheme 11. Selected reacitivty of imino(boryl)germylene **18b**.[125-126]

Nevertheless, combining amido-ligands with other substituents, to give heteroleptic compounds, opens the possibility to fine-tune certain properties, such as increased reactivity, of the complex and the element-ligand bonds. For example, boryl-substituted amido germylene **18b** irreversibly inserts one equivalent of phenylacetylene into the Ge–B bond under mild conditions (Scheme 11).[126] The authors proposed an activation route *via* a [2+1] cycloaddition to a Ge(IV) intermediate, followed by reduction back to Ge(II) in the insertion product. While they could not isolate the germanium intermediate, they were able to isolate said [2+1] cycloaddition product with the respective silylene analog. In that case, however, reduction of the Si(IV) center and insertion of the substrate into the Si–B bond, could not be observed. Complex **18b** was also found to activate hydrogen and other E–H bonds.[125] In the reaction with compounds with polarized E–H bonds, such as SiH_3 and $BH_2 \cdot NMe_3$, oxidative addition took place to give the respective Ge(IV) product. Upon reaction with H_2 however, an unsymmetrical digermane forms.

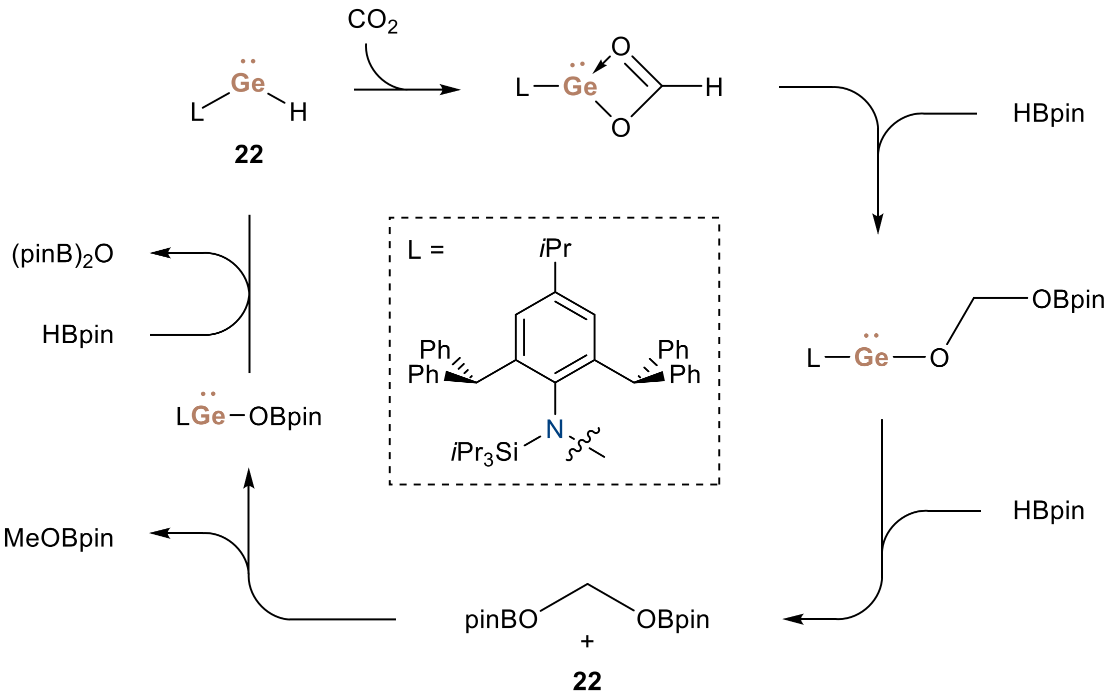


21

Scheme 12. Activation of NH_3 and H_2 by aryl(silyl)germylene **21** via oxidative addition.[125]

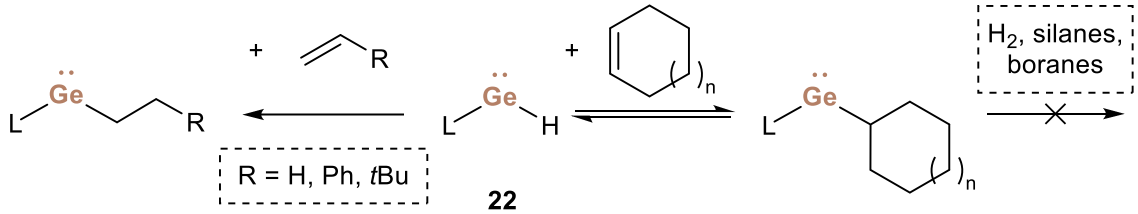
In the case of germylenes **19a,b** an amine- alongside a bulky aryl-moiety does not provide sufficient activation of the germanium center.[125] This was investigated in a reactivity study of a number of mesityl-terphenyl-stabilized germylenes with a variety of additional ligands possessing weak to strong π-donor capabilities. While boryl-substituted germylene ^{Mes}Ter[B(NDippCH)$_2$]Ge: is too reactive to be isolated and undergoes intramolecular C–H activation, the silyl-substituted compound ^{Mes}Ter[(Me$_3$Si)$_3$Si]Ge: (**21**) selectively forms oxidative addition products with H_2 and NH_3 (Scheme 12).[125]

The use of germylenes for catalytic applications is still a relatively young field, nevertheless noteworthy examples can be named.[19] While the first instance of a germylene-based catalysis – a cyanosilylation – was achieved by a *N*-heterocyclic germylene, the first hydroboration was achieved by an acyclic germylene and stannylene (*vide infra*) with impressive TOF.[131] Using **22**, the authors first observed hydrogermylation of carbonyl substrates at a much faster rate and under milder conditions than with previously reported three-coordinate (^{Dip}Nacnac)GeH.[105, 132] Subsequently, they explored hydroboration using HBpin and a selection of aldehydes and ketones. They could observe TOFs up to 6000 h^{-1} with least sterically encumbered cyclohexane-carboxaldehyde. As expected, more sterically demanding substrates required a higher catalyst loading and longer reaction times for quantitative yields and aldehydes generally performed better than ketones. While the reactions were overall slower than with the respective stannylene, **22** was more stable under catalytic conditions. Also, significant *cis/trans* selectivity was observed in the hydroboration of 2-methylcyclohexanon, which could not be achieved with the corresponding stannylene-hydride (*vide infra*) as the catalyst.



Scheme 13. One of the two proposed reaction mechanisms for the catalytic hydroboration of CO_2 with hydrido-germylene **2**.[129]

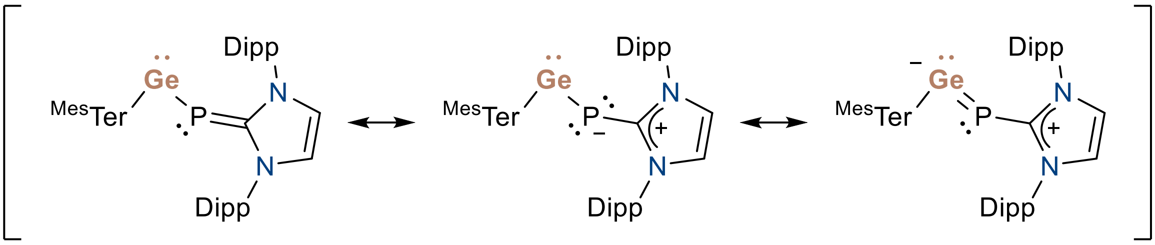
The substrate scope was later expanded to CO_2, catalytically accessing methanol equivalents (>99 % MeOBpin and $O(Bpin)_2$) upon hydroboration with HBpin.[129] Here, the mechanism was investigated using DFT calculations. The authors found two main viable pathways. In both cases, the first two steps are the insertion of CO_2 into the Ge–H bond of the germylene to give a germanium-formate, followed by reaction with HBpin to give an acetal intermediate (Scheme 13). The following steps either involve the release of formaldehyde from the intermediate or the introduction of another HBpin molecule to release MeOBpin. In both cases, the resulting borate ester then releases $(pinB)_2O$ with a last equivalent of HBpin and re-forms germylene **22**. Both routes have a similar energy profile and can be assumed to take place simultaneously.



22

Scheme 14. Reactivity of hydrido-germylene **22** towards acyclic and cyclic alkenes. Valorization of hydrogermylation products with cyclic alkenes by reacting with H_2 or hydridic reagents was unsuccessful.[128]

Germylene **22** is also active in the hydrometalation of various alkenes (Scheme 14).[128] While reactions with acyclic alkenes and alkynes irreversibly led to anti-Markovnikov insertion products, hydrogermylation of cyclohexene and cyclooctene were reversible. The authors observed a temperature-dependent equilibrium of the germylene, the cycloalkene, and the hydrogermylation product. DFT calculations and experimental confirmation revealed a β-hydride elimination mechanism for the reverse reaction. Despite this reversibility, none of the hydrogermylation products further reacted with hydrogen, boranes or silanes, preventing further catalytic utilization.



23

Scheme 15. Resonance structures of NHCP-stabilized germylene **23**, illustrating the partial double bond character of the Ge–P bond.[133]

A *N*-heterocyclic carbene-phosphinidene (NHCP) stabilized germylene **23** was presented by our group in 2019 (Scheme 15).[133] While the ligand class is structurally very similar to NHIs, the decreased electronegativity and hardness of phosphor compared to nitrogen leads to a more pronounced double bond character between germanium and phosphor according to DFT calculations. Consequently, calculations also revealed a strong dative character of the NHC–P bond. Despite this, efforts to remove the carbene from the complex by a strong *Lewis* acid were unsuccessful. The complex was however moderately active in the hydroboration of benzaldehyde (5 mol% cat. loading, r.t., 3h, 67% conversion) with HBpin.

More and more instances mainly of catalytic cyanosilylation and hydroboration by different types of Ge(II) species have been published in recent years and efforts to improve reaction conditions and develop new applications are ongoing.[19, 106-107, 133-135]

2.3.2. STANNYLENES

As with germylenes, Lappert *et al.* set the first milestone in regards to stable acyclic stannylenes with several alkyl- and amine-stannylenes published in 1974 and 1976 (Figure 13).[14, 112, 136] The compounds were either obtained *via* salt metathesis of $SnCl_2$ and the respective lithiated ligand precursor (**24** and **25**) or from ligand exchange of the previously isolated amine-stannylene (**26**).

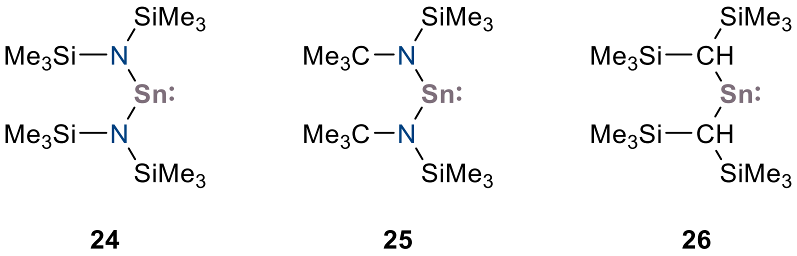
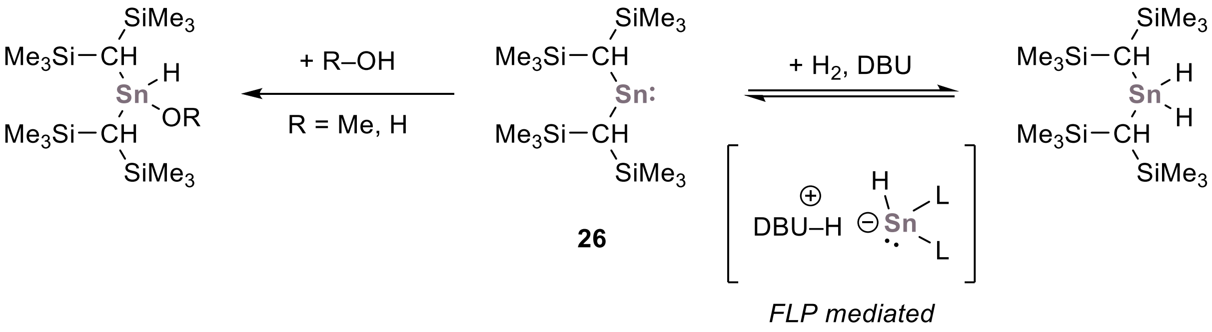


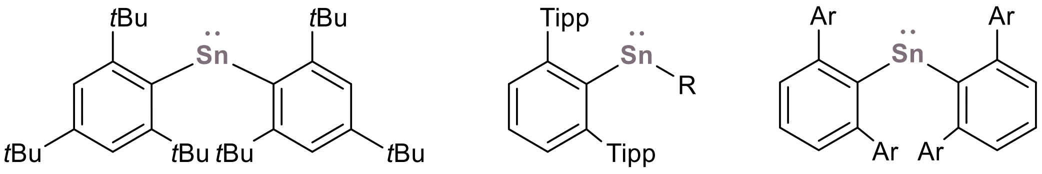
Figure 13. The first stable stannylenes, published by Lappert *et al.* in 1974 and 1976.[14, 112, 136-137]

While the focus was not yet on small molecule activation at that time, their high reactivity was already recognized. Lappert and coworkers reported insertion-, redistribution-, photochemical- and metathesis-reactions as well as oxidative addition with the methyl iron complex $Cp(OC)_2FeMe$ upon reaction with stannylene **24**.[112] Similar to the respective alkyl germylene (**12**), stannylene **26** could be observed as a dimer in solid state.[14] Furthermore, the weak *Lewis*-acid and strong *Lewis*-base properties of complex **26** could be illustrated upon reaction with a selection of transition metal complexes. Also, oxidative addition reactivity could be demonstrated with a number of alkyl-halides as well as 2,3-dimethylbuta-1,3-diene.[136] The reactivity of **26** with H_2O and MeOH was later investigated, resulting in the respective Sn(IV) oxidative addition products (Scheme 16.).[120]



Scheme 16. Oxidative addition of stannylene **26** upon reaction with methanol or water as well as DBU catalyzed and reversible H_2 activation.[120, 138]

Stannylene $(Me_3Si)_2CH]_2Sn$: (**26**) was also investigated regarding its reactivity towards hydrogen.[138] While the compound alone did not react with the small molecule, the addition of amines as catalysts enables oxidative addition at the metal center. When DBU (1,8-Diazabicyclo[5.4.0]undec-7-en) was used, the reaction was observed to be reversible, therefore also enabling reductive elimination. The authors proposed a mechanism involving **26** as a *Lewis* acid in a frustrated *Lewis* pair. Respective hydrogenation catalysis has not yet been reported.



27

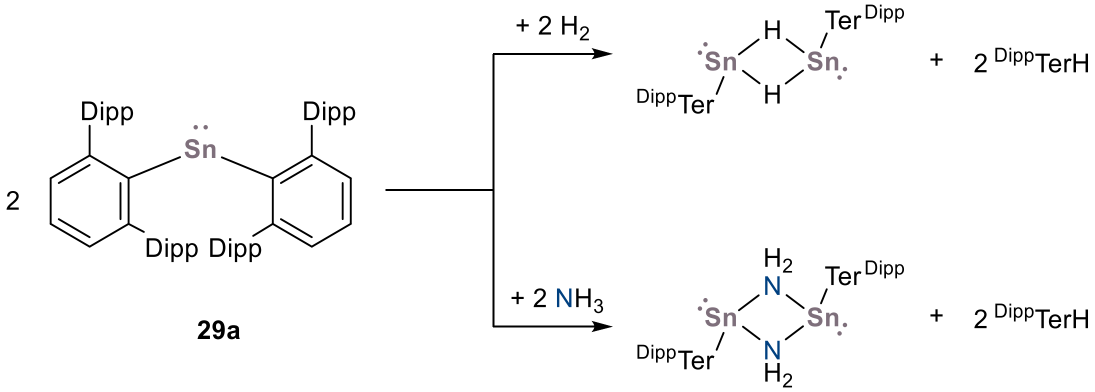
28a R = Me
28b R = *t*Bu

29a Ar = Dipp
29b Ar = Mes

Figure 14. A selection of aryl-stabilized stannylenes.[104, 115, 139-140]

Following a similar pattern as the previous chapter, the next iteration of acyclic stannylenes were aryl-ligated ones (Figure 14). Complex **27** was the first aryl stannylene that did not dimerize to the distannene due to the extremely bulky 2,4,6-tri-tert-butylphenyl ligands.[139] The compound was obtained by ligand exchange reaction of stannylene **24** with the lithiated ligand precursor. The heteroleptic stannylenes **28a** and **28b** were obtained by reacting the terphenyl-substituted chloro-stannylene precursor with MeLi or *t*BuLi respectively.[140] **28a** could then be further reacted to a valence isomer of an alkene, $^{Tipp}TerSn–SnMe_2Mes^{Tipp}$. **28b** did not show further reactivity, presumably due to the increased steric bulk of the *t*Bu- compared to the methyl-group.

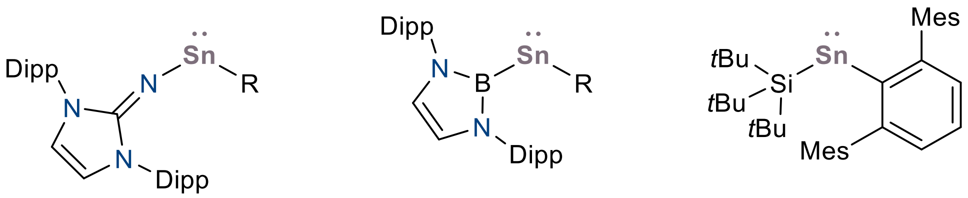
The first account of reactivity towards hydrogen with an acyclic tetrylene was observed with the ^{Dipp}Ter-stabilized stannylene **29a** (Scheme 17).[104] In contrast to the previously discussed terphenyl-substituted germylenes **14a** and **14b**, the oxidation state +II of the tin center stays intact and a bridging hydride is formed alongside arene elimination.



Scheme 17. Reactivity of stannylene $^{Dipp}Ter_2Sn$: (**29a**) with hydrogen and ammonia.[104]

Reacting **29a** with ammonia, a similar bonding pattern is observed, giving a dimeric structure with symmetrically bridged NH_2 moieties. This bonding motif has also been reported earlier, however not *via* direct synthesis from the stannylene.[141-142] Interestingly, **29b**[115] did not show any reactivity towards H_2, in contrast to the respective germylene $^{Mes}Ter_2Ge$: (**14a**). The authors presumed the wider bite angle of **29a** necessary to sufficiently lower the HOMO-LUMO gap in order to enable reactivity with hydrogen.[141-142]

Power *et al.* continued to explore the reactivity of **29b** and again observed the formation of bridged $[^{Mes}TerSn(\mu\text{-}OH)]_2$ and $[^{Mes}TerSn(\mu\text{-}OMe)]_2$ upon reaction with water or methanol respectively.[120] Furthermore, alkene- and alkyne-arylstannylation of **29a** could be achieved with terminal and non-terminal alkynes as well as ethylene.[143-144] Here, the mono-insertion into the Sn–L bond is observed for ethylene, phenylacetylene, diphenylacetylene and 1-hexyne. If trimethylsilyl acetylene is used, ligand exchange takes place giving distannene $[(^{Dipp}Ter)Sn(CCSiMe_3)]_2$.



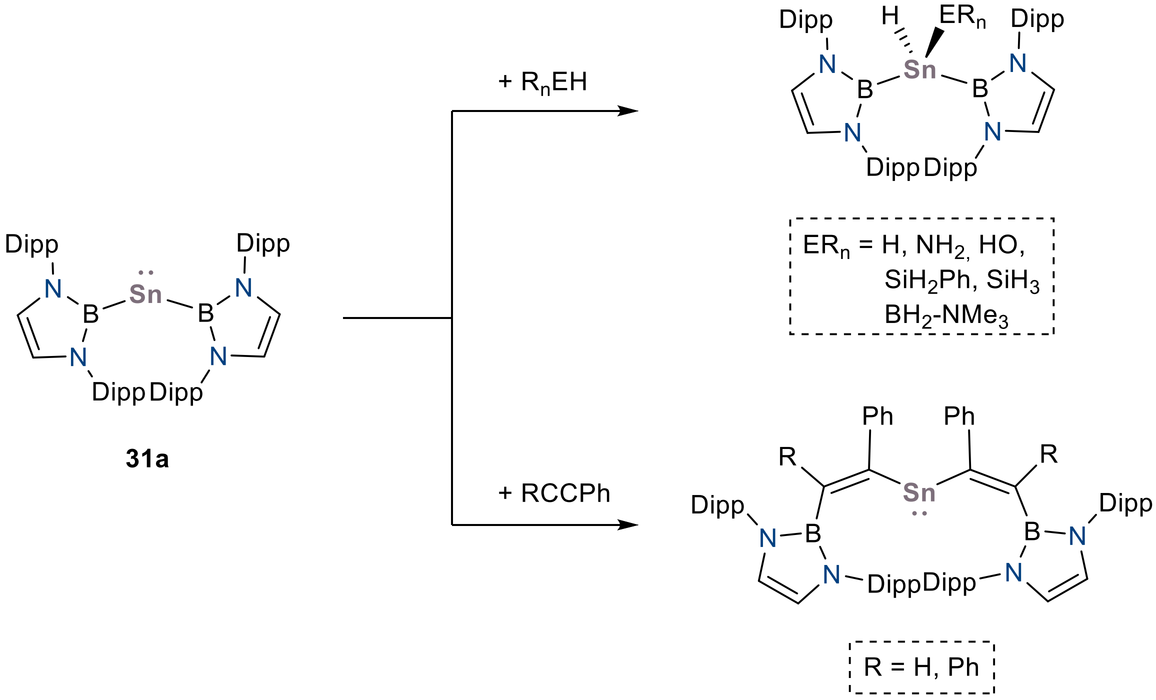
30a R = $N(SiMe_3)_2$
30b R = N(Dipp)(Si*i*Pr_3)
30c R = IDipp

31a R = $(HCDippN)_2B$
32b R = $Me_3Si(Dipp)N$

32

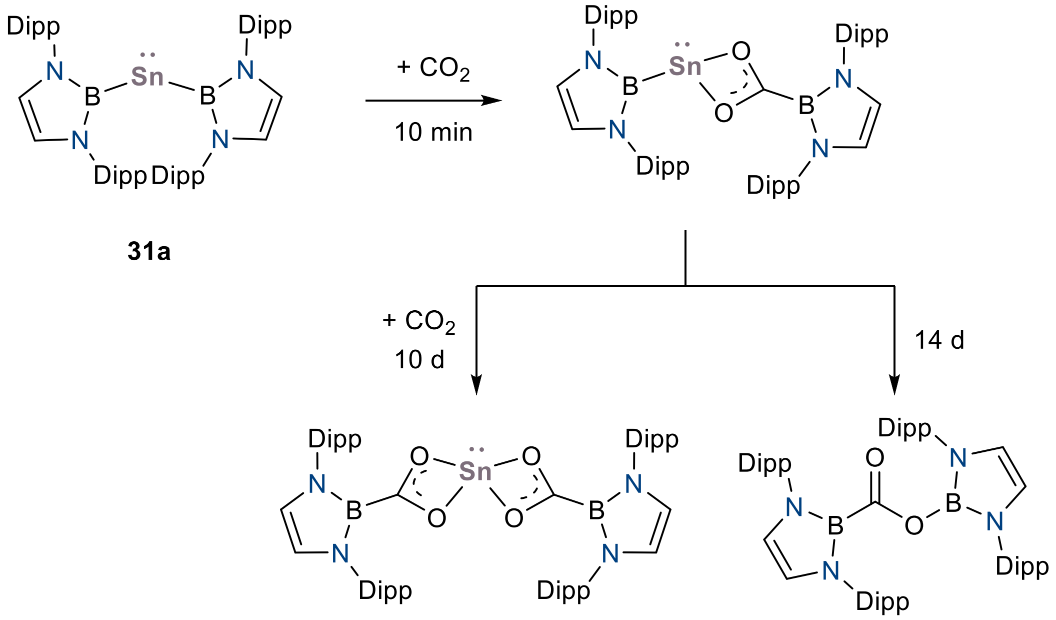
Figure 15. Selected examples of imino-, boryl- and silyl-substituted stannylenes.[58, 92, 126, 145-147]

Pertinent to this work, some examples of homo- and heteroleptic NHI-stabilized stannylenes have been reported in our group (**6**, Figure 5; **30a-c**, Figure 15), however, no small molecule activation could be achieved with these compounds at that point.[58, 83, 145-146]



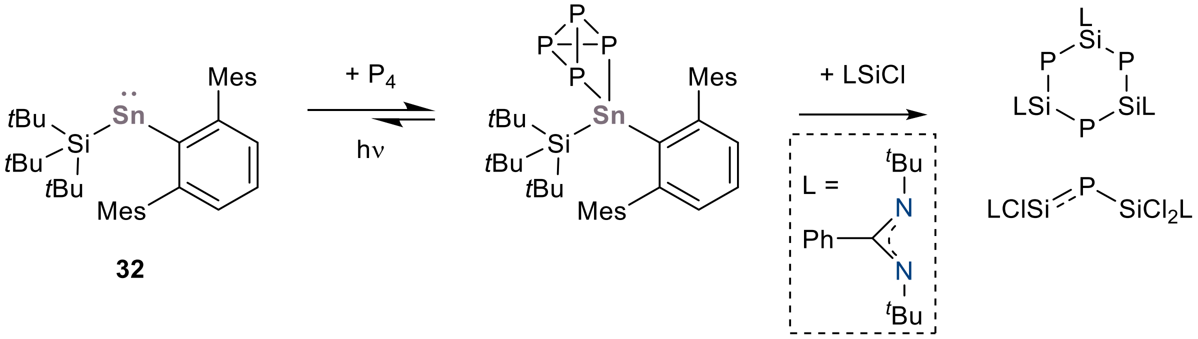
Scheme 18. Reactivity of bis-borylstannylene **31a** with various E-H bonds and phenylacetylenes. [92, 126]

In terms of reactivity, other heteroatom-substituted stannylenes showed more potential. As such, Aldridge *et al.* showcased the oxidative addition capability of bis-borylstannylene **31a** with H_2, NH_3, and H_2O as well as silanes and amineborane BH_3–NMe_3 (Scheme 18).[92] Upon reaction with ammonia, adduct formation takes place first, followed by oxidative addition as with the other R_nEH-type substrates. After 4 days, reductive elimination products $(HCDippN_2)B$–H and $(HCDippN_2)B$–NH_2 alongside the reduction of the metal center to mostly elemental tin could be observed. Furthermore, **31a** as well as **31b** cleanly insert phenylacetylene into the respective Sn–B bond(s) to give vinylstannylenes without oxidizing the metal center.[126]



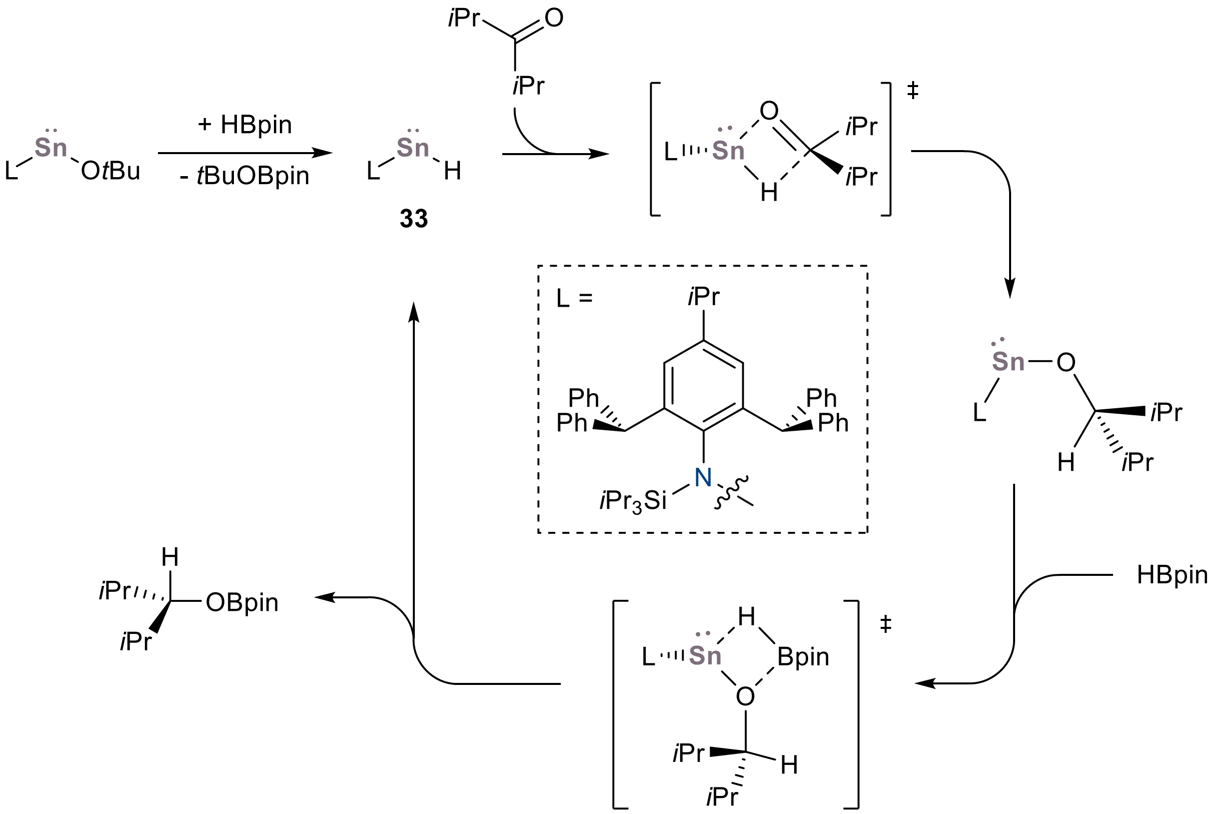
Scheme 19. Insertion reaction of CO_2 with bis-borylstannylene **31a**.[93]

The reaction of CO_2 and N_2O with **31a** was also investigated.[93] Rather than oxidative addition taking place, the molecule inserts into one of the Sn–B bonds, initially giving a mono-carboxylate (Scheme 19). If the solution is left under a CO_2 atmosphere, the double insertion product is formed. Reductive elimination is observed however, when the mono-carboxylate is left in hexane for 14 days in the absence of CO_2. Similarly, upon the reaction of complex **31a** with N_2O, the initial insertion of one oxygen atom into the Sn–B bond is observed. The compound slowly dissociates in solution to again give stannylene **31a** alongside the bis(boryloxy)stannylene product.



Scheme 20. Reversible activation of P_4 by heteroleptic silyl-stannylene **32** and irreversible P-atom transfer to a silylene chloride.[147]

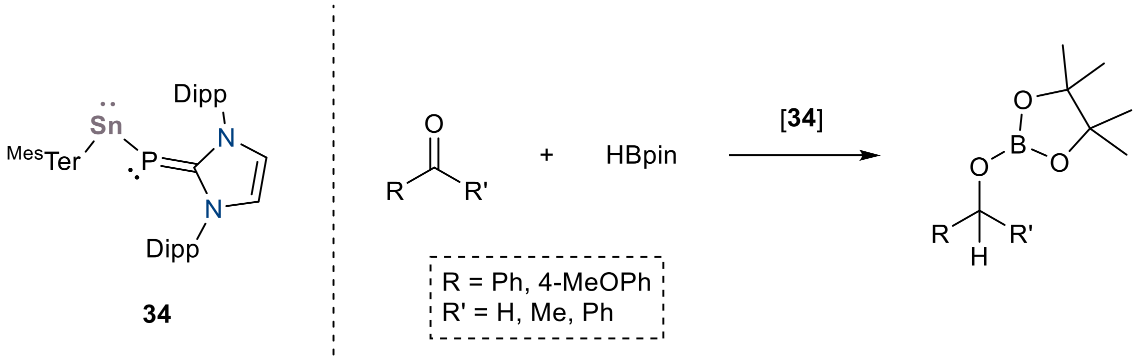
Silyl-substituted stannylene **32** can activate P_4 and displays phosphorus transfer reactivity (Scheme 20).[147] Upon reaction of **32** with white phosphorus, oxidative addition takes place, coordinating a P_4 cluster at the metal center. The reaction proved to be reversible with the use of UV light. Attempts to further utilize the activated phosphorus were successful in the P-atom transfer with the silylene chloride PhC(N*t*Bu)$_2$SiCl. Theoretical calculations revealed a higher nucleophilicity and a more electron rich metal center compared to the homoleptic stannylene **29a**, rationalizing the increased reactivity of **32**.



Scheme 21. Proposed mechanism for the catalytic hydroboration of diisopropylketone with hydrido-stannylene **33** and HBpin.[105]

Moving on to catalytic applications, the parallels to germylenes are again apparent. A hydrido-stannylene presented by Jones *et al.* in the same course as the previously discussed germylene showed hydroboration capability as well.[105, 129] Compared to the germylene (**22**), hydrido-stannylene **33** L(H)Sn: (L = N(Ar†)[Si*i*Pr$_3$], Ar† = C_6H_2-2,6-[C(H)Ph_2]$_2$-4-*i*Pr) showed a significantly faster reaction rate in the hydroboration of utilized ketones, aldehydes, and CO_2. With a catalyst loading of only 0.5 mol% they achieved a TOF of up to 1330 h^{-1}, which is similar to commonly used transition metal complexes for those types of reactions. Due to **33** slowly decomposing in solution, pre-catalyst L(O*t*Bu)Sn: was used after initial investigations (Scheme 21). While the mechanism for the CO_2 reduction could not be identified conclusively by DFT calculations, they suggested a mechanism for hydroboration of the bulky ketone O=C*i*Pr$_2$. Here, the authors propose an initial attack of the substrate's oxygen moiety on the stannylene center, forming an alkoxide *via* a four-membered transition state. In the next step, HBpin and the alkoxide react in a σ-bond metathesis to give borate ester as the product and regenerate the hydrido-stannylene (**33**).

Analogously to the respective hydrido-germylene (**22**), complex **33** also displayed hydroelementation activity.[128] While the hydrostannylation of acyclic alkenes irreversibly gave isolable products, the reversible hydrostannylation of cyclopentene showed the slow formation of decomposition products over time. Since no decomposition can be observed when an excess of cyclopentene is used, this observation can be attributed to the instability of the hydrido stannylene. Again, the hydrostannylation products could not be utilized in any follow up reactivity.



Scheme 22. NHCP stabilized stannylene **34** (left) and catalytic hydroboration of aldehydes and ketones by **34** (right).[133]

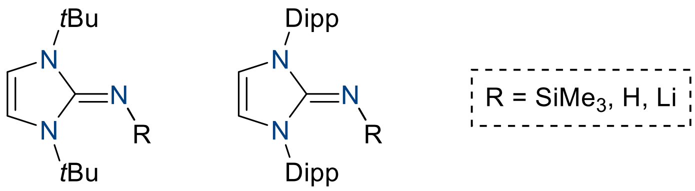
NHCP-substituted stannylene ^{Mes}Ter(IDippP)Sn: (**34**), the tin analog of germylene **23**, shows very similar structural properties with a partial double bond character of the Sn–P bond. Theoretical calculations revealed a slightly lower Wiberg bond index of the element-phosphor bond (Ge–P in **23**: 1.300, Sn–P in **34**: 1.063) and slightly smaller HOMO-LUMO gap (**23** = 3.49 eV, **34** = 3.34 eV) of **34**, which is in accordance to the higher reactivity of the stannylene (**41**) in hydroboration. Full conversion could be achieved in the hydroboration of several aldehydes and ketones in ≤ 2.5 hours with a catalyst loading of ≤ 0.5 mol% with HBpin as reducing agent. While **23** was only active towards benzaldehyde with conversion of 67 % after three hours, **34** fully consumed (> 99% conversion) the compound in less than 15 minutes with a catalyst loading of 0.1 mol%.

As with germylenes, investigations into broader and more effective applications of stannylenes and other Sn(II) species for small molecule activations and catalysis continue to be published and indicate ongoing interest and further development in the future.[19, 107, 148-151]

3. SCOPE OF THIS WORK

As elaborated in the previous chapter, heavier tetrylenes – especially germylenes and stannylenes – bear an inherent potential for application in small molecule activation and catalysis. While a lot of early work has been done and showed great promise, there is still much room for further exploration. As such, deliberately designed ligands can enhance the desired properties of novel tetrylenes, and the resulting complexes could display more efficient or new applications than previously observed. As such, this work aims to design novel, imine-ligand stabilized germylenes and stannylenes and explore their suitability for small molecule activation and catalysis.

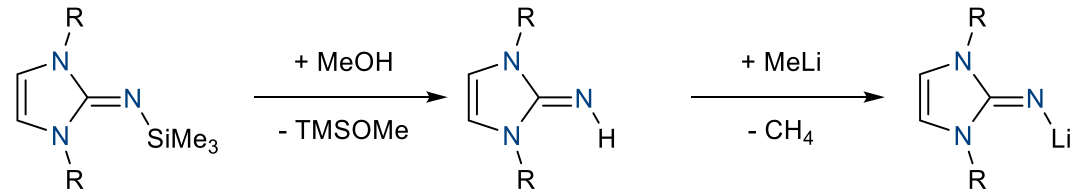
The goal of the present work can be separated into multiple parts. The first step is synthesizing a library of NHI-stabilized germanium and tin complexes. The choice of *N*-heterocyclic imines (NHIs) as ligand types comes down to their strong donor abilities and their variability in steric bulk, providing thermodynamic and kinetic stabilization of the metal center. Selected ligands **35** and **36** were the most promising candidates (Figure 16).[55-56, 61, 152]



35-R **36-R**

Figure 16. Selected examples of applied ligands with leaving groups –SiMe3, –H, and –Li.

A few avenues can be explored to introduce the ligand to the metal center. Suitable leaving groups on the ligand include $–SiMe_3$ and –Li. The free ligand (NHI–H) can also be utilized in some cases, given a strong enough driving force to form the new complex. Generally, trimethylsilyl as a leaving group provides the best reaction economy since the free and the lithiated ligands are generated from it (Scheme 23).



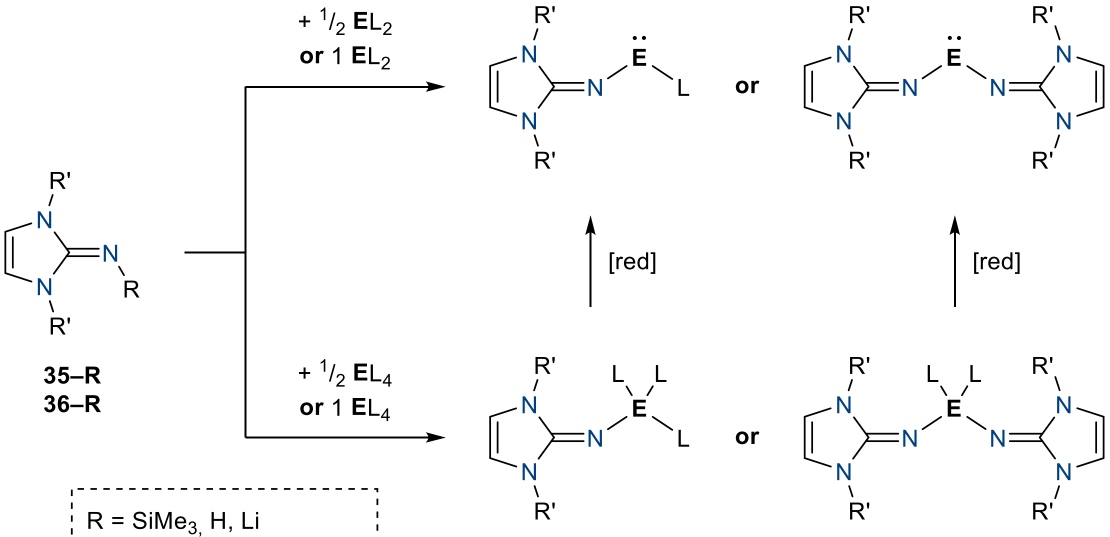
35–SiMe$_3$ R = Dipp
36–SiMe$_3$ R = *t*Bu

35–H R = Dipp
36–H R = *t*Bu

35–Li R = Dipp
36–Li R = *t*Bu

Scheme 23. Synthesis of free and lithiated ligand precursors NHI ligands from trimethylsilyl-substituted congener.[55, 60-61, 153]

This ligand class has previously been utilized in similar low-valent group 14 complexes as well as late transition metal complexes, showcasing their suitability.[49, 55-56, 59-61, 79, 84, 146, 152-153] Introduction of the ligand to the metal center can occur by metathesis reactions of a tetrylene salt or complex (Scheme 24). Preferably, a compound with the oxidation state +II is utilized, such as ECl$_2$·dioxane, ^{Mes}Ter(Cl)Sn: or [(Me$_3$Si)$_2$N]$_2$E: (E = Ge, Sn), to obtain novel complexes in a one-step synthesis. In the case of ECl$_2$·dioxane or [(Me$_3$Si)$_2$N]$_2$E:, homo- or heteroleptic complexes can be obtained depending on the equivalents of the ligand used.



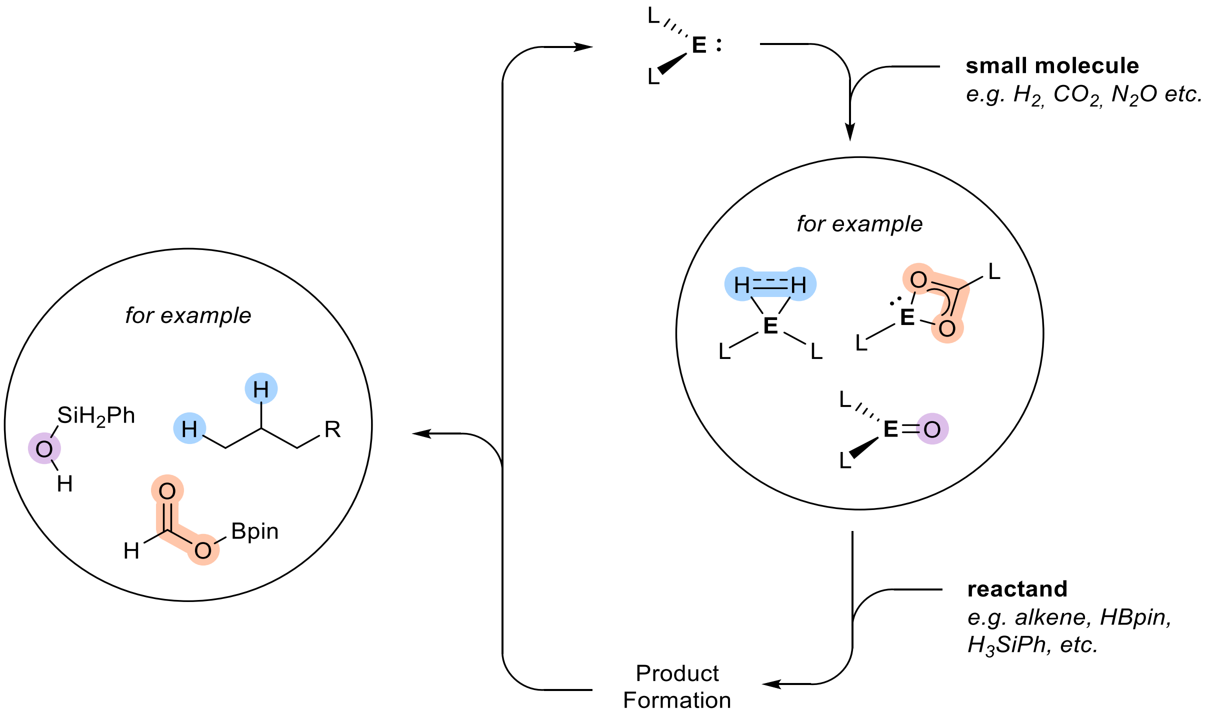
35–R
36–R

R = SiMe$_3$, H, Li
R ' = *t*Bu, Dipp
E = Ge, Sn
L = Hal, N(SiMe$_3$), ^{Mes}Ter
[red] = KC$_8$, NaNaph etc.

Scheme 24. Synthesis of NHI and stabilized homo- and heteroleptic germylenes and stannylenes.

Alternatively, the ligand can be introduced to a +IV germanium or tin precursor, such as the respective halide salts, to first obtain a tetravalent complex. The following reduction, for example, by common reducing agents KC_8 or NaNaph, leads then to the desired low-oxidation state compound.

With the imine-stabilized tetrylenes in hand, the next step is the exploration of their reactivity towards small molecules. For that, different bonding types and molecules can be considered. Of the most interest are industrially relevant compounds, such as H_2, CO_2, ethylene, NH_3, N_2O, and more.



Scheme 25. Selected potential pathways of activation and catalytic utilization of small molecules with tetrylenes.

Activation should occur either by the metal center's oxidative addition or by insertion into the metal-ligand bond (Scheme 25). In both cases, the reversibility of the reaction is an important aspect of the potential future utilization of the activated small molecule. If a selective activation can be observed, catalytic applications such as hydroboration or hydrosilylation must be considered. For that, suitable reducing substrates, such as boranes or silanes of varying steric demand and reactivity, must be compared. Ideally, a tetrylene that can activate and catalytically metabolize small molecules under mild conditions and with high selectivity should be obtained.

4. LIGAND ASSISTED CO_2 ACTIVATION AND CATALYTIC VALORIZATION BY AN NHI-STABILIZED STANNYLENE

TITLE: “Ligand Assisted CO_2 Activation and Catalytic Valorization by an NHI-Stabilized Stannylene”[154]

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AUTHORS: Dr. Debotra Sarkar[†], Lisa Groll[†], Prof. Dominik Munz, Dr. Franziska Hanusch, Prof. Shigeyoshi Inoue[a]

[†] Authors contributed equally

[a] D. Sarkar and L. Groll planned and carried out the experiments, analyzed experimental data and co-wrote the manuscript. D. Munz performed theoretical calculations and contributed to writing the manuscript. F. Hanusch carried out the SC-XRD measurements and refined the crystallographic data. All work was carried out under the supervision of S. Inoue.

CONTENT:

Aryl(imino)stannylene ^{Mes}Ter(IDippN)Sn: was obtained by the metathesis reaction of cloro-stannylene ^{Mes}Ter(Cl)Sn: with lithiated ligand (IDippN)–Li. In many previous instances where activation of CO_2 *via* insertion into the ligand–metal bond of an acyclic stannylene could be observed, the resulting Sn(II)carboxylates quickly decomposed due to the relatively high oxophilicity of the corresponding ligands. In the case of ^{Mes}Ter(IDippN)Sn: however, with the introduction of a strongly donating and nucleophilic NHI-ligand to the Sn-center, a highly polarized but stable (Löwdin’s Partial Charges, Sn: +0.4 a.u., N: –0.4 a.u.; Mayer Bond Order

Sn–N: 1.1) Sn–N bond was formed, enabling formation of a persistent Sn(II)carboxylate upon CO_2 insertion and regeneration of the complex *via* catalytic conversion.

Insertion of CO_2 into the Sn–N bond takes place under mild conditions and leads to the quantitative formation of a thermodynamically stable Sn(II)-carboxylate within 10 minutes. Addition of HBpin led to the formation of hydroboration products, indicating catalytic activity. In fact, the optimal conditions for CO_2 hydroboration by ^{Mes}Ter(IDippN)Sn: with HBpin as reductant (5 mol% cat. Loading, THF, 50 °C, 1 bar CO_2) lead to complete conversion of HBpin to MeOBpin and pinBOBpin with a TOF of 4.2 h^{-1}.

Theoretical and experimental comparison of the catalyst with aryl(amido)stannylene ^{Mes}Ter(Ph_2N)Sn: and aryl(phosphinidene)stannylene ^{Mes}Ter(IDippP)Sn:, revealed the intrinsic properties of the Sn–N bond in the catalyst to be the deciding factor for the observed reactivity.

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Ligand Assisted CO_2 Activation and Catalytic Valorization by an NHI-Stabilized Stannylene

Debotra Sarkar+,[a] Lisa Groll+,[a] Dominik Munz,*[b, c] Franziska Hanusch,[a] and Shigeyoshi Inoue*[a]

The aryl(imino)stannylene $^{Mes}Ter[N(IDipp)]Sn$ could be obtained by treating NHILi (NHI = N(IDipp), IDipp = $C[N\text{-}(2,6\text{-}{}^{i}Pr_2C_6H_3)CH]_2$) with $^{Mes}TerSnCl$ ($^{Mes}Ter = 2,6\text{-}Mes_2C_6H_3$) and offers a unique reactivity pattern compared to conventional single site tetrylene catalyzed CO_2 reduction reactions. The Sn(II) center, stabilized by the NHI ligand enabled the sequestration and valorization of CO_2 to C1 feedstock stoichiometrically, as well as catalytically, utilizing HBpin (pin = pinacolato) as reductant. The experimental comparison with aryl(amido)stannylene $^{Mes}Ter(NPh_2)Sn$ and aryl(phosphinidene)stannylene $^{Mes}Ter[P(IDipp)]Sn$, as well as computational analysis, rationalize the electronic features and key role of the NHI ligand in the CO_2 reduction process. In case of the phosphorus congener, Sn–P bonding with pronounced double-bond character is obtained, which prevents swift dissociation, thus preventing CO_2 uptake. Instead, hard/soft mismatch between tin and the NHI induces zwitterionic and single-bond character, switching on the intermediate dissociation of Sn(II)/NHI, followed by a tin hydride mediated reduction step, and thus allows for efficient catalysis under mild conditions.

Introduction

CO_2 is ubiquitous in our environment and therefore presents an attractive resource for value-added C1 feedstock, especially in the face of current challenges associated with climate change and increasing global energy demands.[1] A lot of efforts to activate this thermodynamically robust molecule have been made. Frequently, transition-metal complexes with dynamic oxidation state variability, usually in redox-based mechanisms are applied, but also the use metal free systems and main group complexes, has been reported.[2] Particularly, the use of low valent p-block compounds in small molecule (*e.g.* CO_2) activation and catalysis has made great progress in recent years.[2a,c,3] In this context, low valent heavier group 14 carbene homologues, namely tetrylenes [R_2E:] (E = Si, Ge, Sn), which are in the +II oxidation state, gave new impetus.[3b,4] While silylene, germylene and stannylene mediated CO_2 activation is known, their catalytic application in CO_2 conversion is still scarce.[4l] The main challenge for utilizing tetrylenes in redox-based catalysis is enabling reductive elimination, and thereby release of the functionalized substrates.[2c,5]

An elegant approach to circumvent this challenge is reversible metal–ligand σ-bond cleavage and subsequent valorization to commodity chemicals. Here, the spatial proximity between nucleophilic and electrophilic reaction sites of ligand and metal allows for the insertion of CO_2 to form a new M–O bond, leaving the metal's oxidation state unchanged (Scheme 1a).[6] Initial decrease of C–O bond strength upon CO_2 insertion into the M–L bond, with concomitant formation of a relatively weak M–O bond, enables functionalization.[6e] To date, a plethora of homogeneous transition-metal catalysts have been developed for thermal, photochemical, and electrochemical conversion of CO_2, utilizing this strategy.[1] Additionally, fine-tuning of the ancillary ligand could also promote CO_2 insertion and facilitate catalyst regeneration. Therefore, appropriate metal choice, understanding the impact of the ancillary ligand, and additional effects, such as solvent, temperature, *etc.* on CO_2 activation is crucial for rational catalyst design. In contrast to transition-metals, a limited number of low valent main-group metal-initiated CO_2 activations and catalytic functionalizations have been reported.[3a,4m, 7] Pertinent to this work, insertion of CO_2 *via* stanna-amination by ($Sn[N(SiMe_2R)_2]_2$ (R = Me, Ph) **I**,[4g,h] stanna-borylation by $Sn[B(NDippCH)_2]_2$ **II**,[4i] as well as reversible CO_2 uptake by P,P-chelated stannylene $[(i\text{-}Pr_2P)_2N]_2Sn$ **III**,[4j] rendering Sn(II)carboxylates, could be demonstrated (Scheme 1b). Nonetheless, poor stability of these Sn(II)carboxylates

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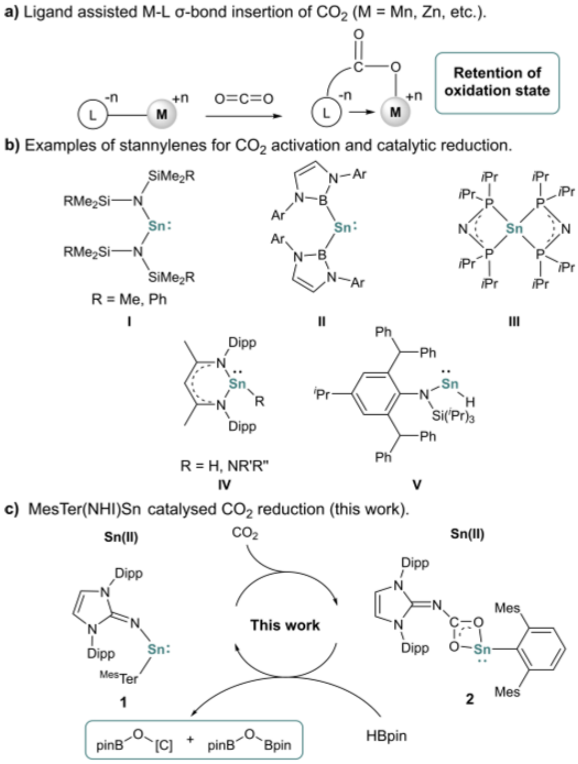


Scheme 1. a) Insertion of CO$_2$ by transition metal-ligand bond cleavage. b) Recent examples of stannylenes for CO$_2$ activation and catalytic reduction.[4g–l] c) Two- coordinate stannylene-NHI synergy (Dipp = 2,6-^{i}Pr$_2$(C$_6$H$_3$), Mes = 2,4,6-Me$_3$(C$_6$H$_2$), ^{Mes}Ter = 2,6-Mes$_2$C$_6$H$_3$, pin = pinacolato, R′R″ = ^{i}Pr$_2$; R′ = H, R″ = Dipp).

leads to undesired rearrangement reactions, such as diboration of CO$_2$ in case of **II** or the 1,3-shift of a trimethylsilyl group from the ligand to inserted CO$_2$ in case of **I**.[4g–i] This is attributed to the comparatively high oxophilicity of the corresponding ligand functional groups, which impede their catalytic use in CO$_2$ reduction.[4g–j,8]

To the best of our knowledge, merely one example of tetrylene-mediated single-site CO$_2$ activation and catalytic conversion has been reported to date, where the high reactivity of the E(II)–H group facilitates the reduction of CO$_2$ (**V**, Scheme 1b).[4l] However, synergistic activation of CO$_2$ *via* tetrylene-ligand cooperation and subsequent conversion to value added products is not yet reported. Based on these previous accounts, and considering the high electrophilicity of stannylenes, a Sn(II) center connected to an electron-rich and consequently nucleophilic ligand should therefore be an excellent choice to procure CO$_2$ activation and conversion while bypassing the requirement for Sn(II)-Sn(IV) redox shuttling.[4h–k,8a,9] Additionally, the reduced bond strength of Sn(II)–O in comparison to E(II)–O (E = Si, Ge) bonds renders Sn(II) an ideal metal center for CO$_2$ functionalization.[10]

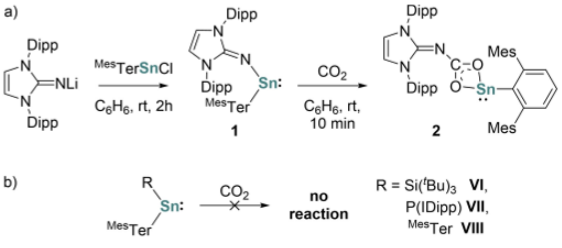
Engineering the Sn-ligand bond, *viz.* polarization or zwitterionic character, may likewise allow to achieve small HOMO-LUMO energy gaps, and thus control of bond activation, elimination, and eventually catalysis.[11] A convenient method to control the polarization of formal multiple bonds is hard-soft mismatch. Recently, we reported *N*-heterocyclic phosphinidene (NHCP)-supported stannylene NHCP=SnAr, which can be regarded as heavier nitrile congener with multiple bonded character between P and Sn.[9b] Moving from the "*N*-heterocyclic phosphinidene (NHCP)" to an *N*-heterocyclic imine (NHI), featuring an electronegative nitrogen atom, should strongly enhance charge separation in the Sn=E bond and consequently facilitate CO$_2$ activation.[12] Due to the readily adjustable steric and electronic properties of NHIs, they are frequently applied in various metalorganic complexes and are an ideal candidate for our purpose.[12a,13]

Results and Discussion

With this insight in mind, the heteroleptic NHI stannylene **1** ^{Mes}Ter(NHI)Sn was synthesized *via* treatment of chlorostannylene ^{Mes}Ter(Cl)Sn with one equivalent of LiN(IDipp), (^{Mes}Ter = 2,6-Mes$_2$C$_6$H$_3$, NHI = N(IDipp), IDipp = C[N-(2,6-^{i}Pr$_2$C$_6$H$_3$)CH]$_2$), (Scheme 2a). Compound **1** was isolated in 75 % yield as a dark red solid and is highly soluble in tetrahydrofuran, benzene, or toluene, but poorly soluble in pentane, hexane, or heptane. The ^{119}Sn{^{1}H} NMR spectrum of compound **1** shows a characteristic signal for the tin center at 967.8 ppm, which falls in the range of reported heteroleptic, two-coordinate (aryl)stannylenes (δ = 197-1919 ppm).[9b,14]

Single crystal X-ray diffraction (SC-XRD) analysis confirmed the structural identity of compound **1**, with the two-coordinate Sn center bound by one NHI and one *m*-terphenyl group (Figure 1). The Sn–N bond length in complex **1** is 2.041(2) Å, which is longer than a Sn–N double bond (1.92 Å) and slightly shorter than a Sn–N single bond of amido-stannylenes (2.08–2.09 Å).[14b,16] The ∠C1–Sn1–N1 bond angle in **1** is 95.62(10)° and is acute in regard to other heteroleptic two coordinate aryl Sn(II) complexes (96.9–117.6°).[9b,14]

To understand the electronic structure of **1**, we performed a computational analysis (PBE0). The HOMO relates to the



Scheme 2. a) Synthesis and reactivity of ^{Mes}Ter(NHI)Sn, b) Heteroleptic two coordinated (aryl)stannylenes inert towards CO$_2$ (IDipp = C[N-(2,6-^{i}Pr$_2$C$_6$H$_3$)CH]$_2$, Dipp = 2,6-^{i}Pr$_2$(C$_6$H$_3$), Mes = 2,4,6-Me$_3$(C$_6$H$_2$), ^{Mes}Ter = 2,6-Mes$_2$C$_6$H$_3$).[9b,14a, 15]

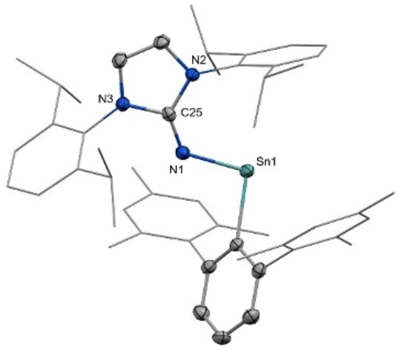


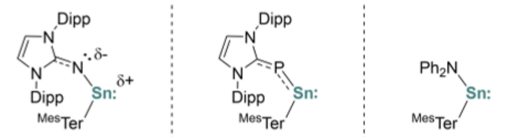
Figure 1. Molecular structure of compound **1** in the solid state. Ellipsoids are set at the 50 % probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1–N1 2.041(2), Sn1–C1 2.232(3), N1–Sn1–C1 95.62(10).

stannylene's lone pair, whereas the LUMO is associated with the Sn–N antibonding π-type orbital, which features strong Sn(p_z) character. The two frontier orbitals are separated by 3.83 eV ($E^{s/t}=241$ kJ mol^{-1}; Figure 2), which is larger than in **VI** (^{Mes}Ter(Si^{t}Bu$_3$)Sn, 3.08 eV) yet in the same order of magnitude as found in **VII** (^{Mes}Ter[P(IDipp)]Sn, 3.88 eV).[9b,14a] However, the Sn–N bonding in **1** differs distinctly from Sn–P bonding in **VII** (Figure S21). In **1**, the HOMO-2 relates to the lone pair at the NHI, which profits from delocalization within the π-system of the imidazoline substituent, thus leading to a weak Sn–N π-interaction. In contrast, the HOMO-1 of **VII** demonstrates a genuine Sn–P π-bond.[9b] Accordingly, Mayer's Bond Order and Löwdin's partial charge analysis corroborate the strongly polarized nature of the Sn$^{\delta+}$–N$^{\delta-}$ single bond (Mayer Bond Order, Sn–N: 1.1; Löwdin's Partial Charges, Sn: +0.4 a.u., N: −0.4 a.u.), whereas the Sn–P bond is rather multiple-covalent in **VII** (Sn=P: 1.6; Sn: +0.2 a.u., P: +0.2 a.u.). In case of **3** (*vide infra*), the electronic structure changes, and the HOMO (-5.41 eV) represents the amine's lone pair, which is delocalized within the aryl substituents, while the HOMO-1 relates to the Sn lone pair (−6.11 eV).

Motivated by our interest in small molecule activation, we were enticed to determine, whether compound **1** shows reactivity towards CO$_2$. A trial NMR scale reaction of **1** with CO$_2$ (1 bar) at room temperature in C$_6$D$_6$ afforded a color change from red to colorless within 10 min. Heteronuclear NMR analysis confirmed the quantitative conversion of **1** to a tin-carboxylate complex **2**. The ^{119}Sn{^{1}H} NMR spectrum revealed resonances for a distinct ^{119}Sn nucleus at 323.3 ppm, which resonates in the up-field region compared to **1** and literature reported tin-carbamate complex (δ = +393 ppm).[8a] Further, in the ^{13}C NMR of **2**, a characteristic signal was observed at 175.6 ppm, which is indicative of a carbamate carbon. Compound **2** evolved thermodynamically stable and did not convert back to **1**, neither at elevated temperatures nor under reduced pressure. [^{Mes}TerSn(CO$_2$)N(IDipp)] was therefore isolated on a preparative scale as a colorless solid in 96 % yield. SC-XRD of **2** confirmed the insertion of CO$_2$ into the Sn–NHI bond, yielding a tetrahedral tin center, κ^2*O,O′* coordinated by the carbamato group (Figure 3, Sn1–O1 2.2066(12), Sn1–O2 2.1971(12)).

This facile access to a tin-carbamate complex directly from CO$_2$ presents an attractive entry to carbon dioxide valorization.[4i,j, 8a] Notably, ^{Mes}Ter(Si^{t}Bu$_3$)Sn **VI** (3.08 eV) and ^{Mes}Ter(^{Mes}Ter)Sn **VIII** (3.51 eV) are not able to activate CO$_2$, despite their lower HOMO-LUMO gaps (Scheme 2b). Also **VII**, which 1,2 adds ketenes and catalytically reduces aldehydes and ketones, does not react with CO$_2$.[9b]

The mechanisms for the CO$_2$ activation by **1** and **VII** were calculated (DLPNO-CCSD(T)/def2-TZVPP//PBE0-D3/def2-SVP) including correction for solvation in benzene. The computations reveal that two mechanisms are feasible in case of **1** (Scheme 3). The transition state, which is higher in energy ($\Delta G^{\neq}=+81$ kJ mol^{-1}), is to be understood as nucleophilic attack of the *N*-heterocyclic imine at carbon dioxide. Note that the comparatively higher barrier is consistent with the HOMO being located at tin, whereas the NHI lone pair is the HOMO-2. The other,



1		**VII**		**3**	
E(LUMO)	= -1.23 eV	*E*(LUMO)	= -1.10 eV	*E*(LUMO)	= -1.85 eV
E(HOMO)	= -5.06 eV	*E*(HOMO)	= -4.98 eV	*E*(HOMO)	= -5.41 eV
q(Sn)	= +0.4 a.u.	*q*(Sn)	= +0.2 a.u.	*q*(Sn)	= +0.6 a.u.
q(**N**)	= -0.4 a.u.	*q*(**P**)	= +0.2 a.u.	*q*(**N**)	= +0.1 a.u.
BO(Sn—**N**)	= 1.1	BO(Sn⋯**P**)	= 1.6	BO(Sn—**N**)	= 0.8
BO(C⋯**N**)	= 1.8	BO(C⋯**P**)	= 1.5		

Figure 2. Frontier orbital energies and population analysis (Löwdin charges, Mayer Bond Order, PBE0/def-TZVPP//PBE0-D3/def2-SVP) of **1** and comparison with **VII** and **3**. (Dipp = 2,6-^{i}Pr$_2$(C$_6$H$_3$), Mes = 2,4,6-Me$_3$(C$_6$H$_2$), ^{Mes}Ter = 2,6-Mes$_2$C$_6$H$_3$).

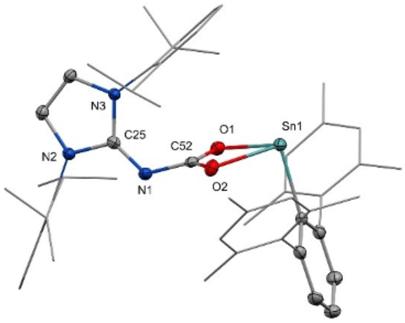
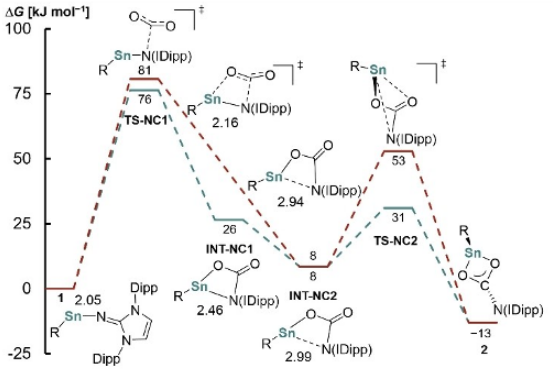


Figure 3. Molecular structures of compound **2** in the solid state. Ellipsoids are set at the 50 % probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1–O1 2.2066(12), Sn1–O2 2.1971(12), O1–C52 1.2842(19), O2–C52 1.2787(19), N1–C52 1.360(2), N1–C25 1.300(2), N2–C25 1.3729(19), N3–C25 1.3721(19), O1–Sn1–O2 59.71(4).

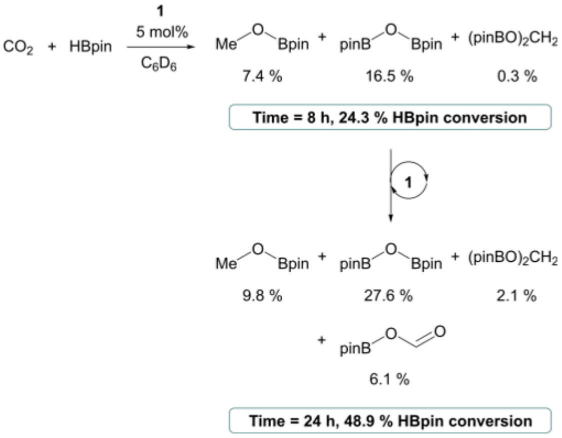


Scheme 3. Computed mechanism for the CO_2 activation by **1**. (R = ^{Mes}Ter, ^{Mes}Ter = 2,6-Mes$_2$C$_6$H$_3$, Mes = 2,4,6-Me$_3$(C$_6$H$_2$), Dipp = 2,6-^{i}Pr$_2$(C$_6$H$_3$), IDipp = C-[N-(2,6-^{i}Pr$_2$C$_6$H$_3$)CH]$_2$.

more favorable transition state relates to the 1,2-addition across the strongly polarized π-system of the Sn–N moiety (**TS-NC1**, $\Delta G^{\neq} = +76$ kJ mol^{-1}). This latter mechanism affords first intermediate **INT-NC1** ($\Delta G = +26$ kJ mol^{-1}), where a Sn–N bond is still present. Barrierless dissociation gives **INT-NC2** ($\Delta G = +8$ kJ mol^{-1}), which affords the μ^3-coordinate adduct **2** ($\Delta G = -13$ kJ mol^{-1}) *via* **TS-NC2** ($\Delta G^{\neq} = +31$ kJ mol^{-1}).

In case of the phosphorus congener, where the phosphorus atom lacks distinct nucleophilic properties, the activation proceeds through the 1,2-addition mechanism only (*cf.* Scheme S1). The activation of CO_2 is predicted to be facile with $\Delta G^{\neq} = +84$ kJ mol^{-1} for **TS-PC1**. However, the transition state **TS-PC2**, which breaks the Sn–P bond, is high in energy ($\Delta G^{\neq} = +128$ kJ mol^{-1}). Accordingly, Sn–P bond cleavage to give **PC2**, which is the P-congener of **2**, proceeds overall endergonic ($\Delta G = +39$ kJ mol^{-1}). We thus conclude that enhanced covalency in the phosphorus-tin compound **VII** thermodynamically disfavors CO_2 activation, whereas hard-soft mismatch (orbital-energy mismatch, respectively) facilitates bond activation through strong polarization of the Sn–N bond in **1**.

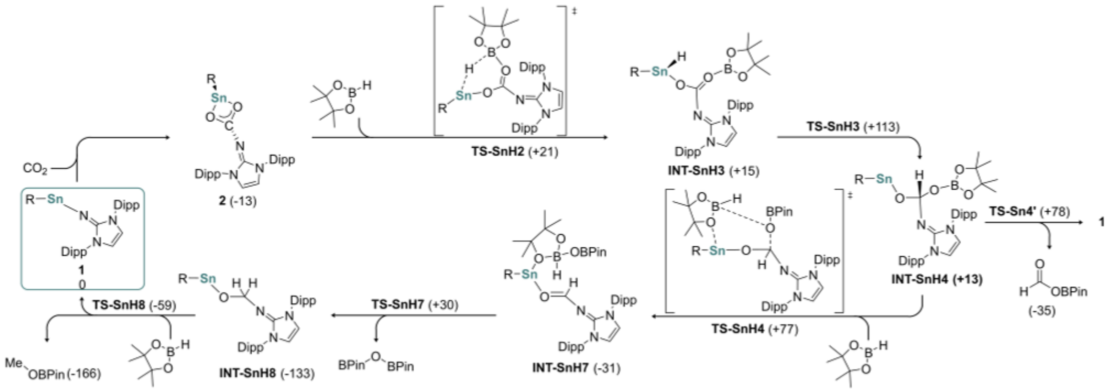
Consequently, we were interested, if **1** would be applicable for the hydroboration of CO_2 using HBpin (pin = pinacolato) as reductant. As anticipated, treating **2** with equimolar amounts of HBpin in C_6D_6 at room temperature led to the formation of MeOBpin (9%) and pinBOBpin (5%) after 30 minutes. Additionally, in this mixture a new septet was observed at 3.19 ppm (*cf.* Figure S14), which possibly stems from an unidentified active catalyst species. Despite several attempts, isolation of this active catalyst from the reaction mixture was unsuccessful. However, alternating addition of 1 bar of CO_2 and one equivalent of HBpin to this reaction mixture clearly shows the increasing formation of MeOBpin (31% yield after three alternating additions). This observation implies, that **1** could also act as a precatalyst. Indeed, 5 mol% of **1** catalytically converts CO_2 to MeOBpin, pinBOBpin, (pinBO)$_2$CH$_2$ and pinBO(C=O)H (Scheme 4).



Scheme 4. Hydroboration products obtained from the reaction of HBpin with CO_2 (1 bar) with **1** (5 mol%) as catalyst at 25 °C (in C_6D_6). Overall HBpin conversion based on ^{11}B NMR integrals, ratio of products based on ^{1}H NMR integrals relative to 0.33 eq. of 1,3,5-trimethoxybenzene as internal standard.

Solvent optimization studies revealed a moderately higher reaction rate in polar (*e.g.*, rt, THF-d$_8$, *TOF* = 1.8 h^{-1}) than in non-polar solvents (*e.g.*, rt, C_6D_6, *TOF* = 1.2 h^{-1}). With the above points in mind and after temperature optimization, we found that using 5 mol% of **1** with HBpin in THF at 50 °C provides the optimal reaction conditions for complete conversion of HBpin to MeOBpin, and pinBOBpin (*TOF* = 4.2 h^{-1}, 1 bar CO_2). The longevity of the catalyst could be demonstrated by repeating the reaction multiple times, where gradual decrease of the catalytic activity was observed (*e.g.*, 50 °C, THF-d$_8$ *TOF*(Run 1) = 4.2 h^{-1} vs. *TOF*(Run 4) = 2.9 h^{-1}). After the seventh run, no catalytic conversion was observed and the formation of black precipitate at the bottom of the NMR tube indicated decomposition of the catalyst into metallic tin. To rule out hidden boron catalysis by *in situ* formed BH_3 (BH_4^-, respectively) and to assess the stability of **1**, we conducted a stoichiometric reaction of **1** with HBpin in absence of CO_2.[17] Here, no reaction between the complex and the reductant, as well as no formation of aforementioned boranes, could be observed. Additionally, a control experiment with the free NHI ligand HN(IDipp) (5 mol% HN(IDipp), 1 eq. HBpin, 1 bar CO_2, in C_6D_6 at 25 °C) was performed, which showed no notable conversion of HBpin after eight hours.

To elucidate the mechanism for CO_2 reduction, further computations were conducted. Especially the hydrogenation step proved intriguing. The computations for two isomers corroborate that the direct borylation of the CO_2 group by HBpin is indeed facile (Scheme S3, **TS-BH1**, $\Delta G^{\neq} = +59$ kJ mol^{-1}). In contrast, the hydride transfer from the borohydride to the central carbon atom of the CO_2 group (Scheme S3, **TS-BH2**) is associated with a high activation energy of at least $\Delta G^{\neq} = +132$ kJ mol^{-1}. These values are hardly consistent with an experimental reaction temperature of 50 °C, which relates to a barrier around $\Delta G^{\neq} = +100$ kJ mol^{-1}, even

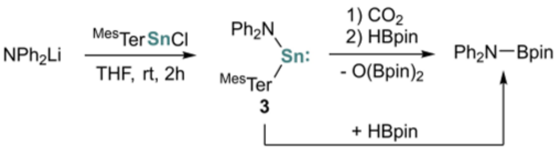


Scheme 5. Proposed mechanism of ^{Mes}Ter[N(IDipp)]Sn catalyzed hydroboration of CO_2. ΔG (kJ mol^{-1}) values are given in parentheses. (R = ^{Mes}Ter = 2,6-$Mes_2C_6H_3$, Dipp = 2,6-$^iPr_2(C_6H_3)$, Mes = 2,4,6-$Me_3(C_6H_2)$, ^{Mes}Ter = 2,6-$Mes_2C_6H_3$, pin = pinacolato). See Schemes S3, S4, S6 for more details including intermediates, which have been omitted for clarity.

more so if considering that **2** (*cf.* Scheme 3, $\Delta G = -13$ kJ mol^{-1}) is the resting state of the catalytic cycle. However, forming the stanna-hydride **INT-SnH3** is very facile (Scheme 5, $\Delta G^{\neq} = +21$ kJ mol^{-1}, $\Delta G = +15$ kJ mol^{-1}). Also, the subsequent migration of the hydride to give the formyl derivative **INT-SnH4**, is predicted to occur under comparatively mild conditions ($\Delta G^{\neq} = +113$ kJ mol^{-1}, $\Delta G = +13$ kJ mol^{-1}). These values are in much better agreement with the experimental conditions.

The release of the reduced products through hydrogenation by HBpin proceeds with lower barriers as was found for the previous step, which thus represents the rate-determining transition state of the overall catalytic cycle. A second borylation step (**TS-SnH4**, $\Delta G^{\neq} = +77$ kJ mol^{-1}) may give **INT-SnH7**, ($\Delta G = -31$ kJ mol^{-1}). Subsequent hydride transfer *via* **TS-SnH7** ($\Delta G^{\neq} = +30$ kJ mol^{-1}) affords **INT-SnH8** ($\Delta G = -133$ kJ mol^{-1}), which may reversibly eliminate ($\Delta G = -127$ kJ mol^{-1}) formaldehyde (Scheme S5; **TS-Sn8**, $\Delta G^{\neq} = -59$ kJ mol^{-1}), thereby regenerating **1**. Analogously, H-(CO)OBpin may be released reversibly from a conformer of **INT-SnH4** (Scheme S5; **TS-Sn4′**, $\Delta G^{\neq} = +78$ kJ mol^{-1}; $\Delta G = -35$ kJ mol^{-1}), whereas borylation of, for instance, **INT-SnH8** will eventually lead to the formation of MeOBPin ($\Delta G = -166$ kJ mol^{-1}).

In order to highlight the relevance of the NHI ligand in the catalytic CO_2 reduction with **1**, we synthesized ^{Mes}Ter(NPh_2)Sn **3** with a similarly low oxophilic –NPh_2 group replacing the NHI moiety.[4g–j,8a] **3** was obtained *via* the reaction of ^{Mes}Ter(Cl)Sn with $LiNPh_2$ (Scheme 6) and characterized by single-crystal XRD and standard NMR techniques (*cf.* SI). Treatment of **3** with 1 bar CO_2 in C_6D_6 leads to a gradual color change from deep red to yellow in about 10 minutes. According to ^{1}H and ^{13}C NMR, as well as mass spectrometry (*cf.* SI), the formation of a new compound, which we hypothesize to be a CO_2 adduct of **3**, presumably a tin-carboxylate, is observed. In agreement, the computational analysis indicates that the insertion of CO_2 into **3** should be exergonic by -27 kJ mol^{-1} (Scheme S2). However, the compound could not be isolated and the characterization by ^{119}Sn{^{1}H} NMR spectroscopy was unsuccessful. Upon addition of equimolar amounts of HBpin to the mixture, the formation of amineborane Ph_2N-Bpin and pinBOBpin was observed, rendering the regeneration of **3** unsuccessful (Scheme 6). Unlike the conversion of CO_2 with NHI stabilized stannylene **1**, no other products indicative of a hydroboration reaction, were found. Similarly, **3** is unstable in the presence of HBpin, leading to the formation of aforementioned amineborane, protonated ligand, and deposition of elemental tin.



Scheme 6. Synthesis and reactivity of ^{Mes}Ter(NPh_2)Sn with CO_2 and HBpin. (Mes = 2,4,6-$Me_3(C_6H_2)$, ^{Mes}Ter = 2,6-$Mes_2C_6H_3$, pin = pinacolato).

This outcome is in good agreement with the computational analysis of the electronic structure of **3** (*cf.* Figure 2). Indeed, and as expected due to the small HOMO-LUMO energy gap of only 3.56 eV and the polarized character of the Sn–N bond (Sn: +0.6 a.u., N: +0.1 a.u.), **3** activates CO_2 readily. However, the low bond order indicates a weaker Sn–N bond and a more nucleophilic amide, rendering it susceptible to the irreversible and undesired reaction with HBpin. Thus, this study signifies the importance of the unique donor abilities of the NHI, enabling stabilization of tin-carboxylate complex **2** as well as regeneration of **1** in this stannylene-mediated CO_2 reduction.

Conclusion

In summary, the ligand assisted activation and catalytic reduction of CO_2 to commodity chemicals by an NHI-stabilized stannylene is reported for the first time. Both experimental and computational investigations revealed the effectiveness of the tunable Sn/NHI interaction, involving Sn/NHI dissociation and the intermediate formation of tin hydrides. Thus, our design protocol to translate the concept of ligand assisted transition-metal ligand σ-bond cleavage to main group chemistry indicates a promising avenue towards the cooperativity between a heavy p-block element and a ligand.

Experimental Section

General Information

All experiments and manipulations were carried out under a dry argon atmosphere using standard *Schlenk* techniques or a glovebox. All glass junctions were coated with PTFE-based grease *Merkel* Triboflon III. N-hexane, n-pentane, THF, benzene and toluene were refluxed over sodium/benzophenone, freshly distilled and deoxygenated prior to use. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were measured on *Bruker* 400 MHz and 500 MHz spectrometers. Chemical shifts were referenced to residual solvent signals (^{1}H and ^{13}C NMR). ^{119}Sn NMR chemical shifts were referenced to Me_4Sn (^{119}Sn). Deuterated solvent C_6D_6 and THF-d_8 were obtained from *Deutero* Deutschland GmbH and were dried over 4 Å molecular sieves prior to use. Unless otherwise stated, all reagents were purchased from commercial sources and used as received. Elemental analyses (EA) were conducted with a EURO EA (*HEKA tech*) instrument equipped with a CHNS combustion analyzer. Thereby, all samples were prepared in THF solutions, filtered and injected into the spectrometers. TOF analyzation in cationic mode resulted in the obtained spectra (see SI), which were resolved by mass-to-charge values. Liquid Injection Field Desorption Ionization Mass Spectrometry (LIFDI-MS) was performed in an inert atmosphere glovebox with a *Thermo Fisher* Scientific Exactive Plus Orbitrap equipped with an ion source from Linden CMS.S7.[18] NHILi, [^{Mes}TerSnCl] and Ph_2NLi were synthesized according to literature procedures.[15a,19]

^{Mes}Ter[N(IDipp)]Sn (1)

A benzene (5 mL) solution of NHILi (0.5 g, 1.22 mmol, 1.00 eq) was added to ^{Mes}TerSnCl (0.57 g, 1.22 mmol, 1.00 eq) in benzene (3 mL) at room temperature. The color of the solution rapidly changed from orange to dark red. After stirring the solution for 2 h, the solvent was removed *in vacuo*. The obtained residue was washed with pentane (3×2 mL), extracted with a mixture of toluene (10 mL) + hexane (2 mL) and filtered through a microfiber glass filter. The solution was concentrated to approximately 2 mL and placed at −25 °C and after two weeks compound **1** was obtained as an analytically pure red crystalline material (0.77 g, 0.54 mmol, 75 %). **^{1} H NMR** (400.13 MHz, 298 K, C_6D_6): δ = 1.09, 1.11, 1.14 (m, 24H, $CH(CH_3)_2$, NHI), 2.08 (s, 12H, 4×$C^{2,6}$-CH_3, Mes), 2.29 (s, 6H, 2xC^{4}-CH_3, Mes), 3.06 (hept, $^{3}J_{H-H}$ = 6.7 Hz, 4H, $CH(CH_3)_2$), 5.94 (s, 2H, N-CH), 6.65 (s, 4H, 2×$C^{3,5}$-H, Mes), 6.85, 6.88 (2H, $C^{3,5}$-C_6H_3), 7.04-7.06 (4H, 2×$C^{3,5}$-H, Dipp, NHI), 7.16-7.23 (3H, C^{4}-C_6H_3, 2×C^{4}-H, Dipp) ppm. **^{13}C{^{1}H} NMR** (125.83 MHz, 298 K, C_6D_6): δ = 21.6–21.9 ($C^{2,4,6}$-CH_3, Mes), 23.4 ($CH(CH_3)_2$), 24.9 ($CH(CH_3)_2$), 29.2 ($CH(CH_3)_2$), 114.8 (N-CH-, NHI), 124.3-148.1 (Ar-C, Mes, NHI), 155.8 (NCN) ppm. **^{119}Sn{^{1}H} NMR** (149.20 MHz, 298 K, THF-d_8): 967.8 ppm. **Anal. Calcd. [%] for $C_{51}H_{61}N_3Sn$**: C, 73.38; H, 7.37; N, 5.03. Found C, 73.12; H, 7.21; N, 4.89.

[^{Mes}TerSn(CO_2)N(IDipp)] (2)

The benzene (2 mL) solution of **1** (100 mg, 0.11 mmol, 1.00 eq) in a Schlenk flask was freeze-pump-thaw degassed two times before being refilled with 1 bar of CO_2. After refilling with CO_2, the red solution immediately turned colorless. The solution was stirred for 15 minutes, followed by the removal of all volatiles. The resulting solid was dissolved in a mixture of THF (2 mL) and n-hexane (2 mL) and placed at −35 °C for eight days, which yielded colorless crystals of compound **2** (102 mg, 0.12 mmol, 97 %). **^{1}H NMR** (400.13 MHz, 298 K, C_6D_6): δ = 1.09–1.31 (m, 24H, $CH(CH_3)_2$, NHI), 2.12 (s, 12H, 4×$C^{2,6}$-CH_3, Mes), 2.30 (s, 6H, 2×C^{4}-CH_3, Mes), 2.92 (hept, $^{3}J_{H-H}$ = 6.7 Hz, 4H, $CH(CH_3)_2$), 5.90 (s, 2H, N-CH), 6.86 (s, 4H, 2×$C^{3,5}$-H, Mes), 6.98-7.03 {6H, (2H, $C^{3,5}$-C_6H_3), (4H, 2×$C^{3,5}$-H, Dipp, NHI)}, 7.10–7.21 {3H, C^{4}-C_6H_3, (2×C^{4}-H, Dipp)} ppm. **^{13}C{^{1}H} NMR** (125.83 MHz, 298 K, C_6D_6): δ = 21.3–21.5 ($C^{2,4,6}$-CH_3, Mes), 23.6 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 29.1 ($CH(CH_3)_2$), 115.9 (N-CH-, NHI), 124.2-147.6 (Ar-C, Mes, NHI), 169.9 (NCN), 175.6 (OCO) ppm. **^{119}Sn{^{1}H} NMR** (149.20 MHz, 298 K, C_6D_6): 323.1 ppm. **Anal. Calcd. [%] for $C_{52}H_{61}N_3O_2Sn$**: C, 71.07; H, 7.00; N, 4.78. Found C, 70.88; H, 6.81; N, 4.71.

^{Mes}Ter(NPh_2)Sn (3)

^{Mes}TerSnCl (100 mg, 0.21 mmol, 1.00 eq.) and Ph_2NLi (37.46 mg, 0.21 mmol, 1.00 eq.) were each dissolved in THF (5 ml) respectively. The Ph_2NLi solution was then added dropwise to the ^{Mes}TerSnCl solution at room temperature while stirring, giving an orange mixture. The mixture was then stirred for another 60 minutes. Subsequently, the volatiles were removed *in vacuo* and the red residue was extracted with Et_2O (2×3 mL) and filtered through a microfiber glass filter. After once more drying *in vacuo*, the raw product was recrystallized in a minimal amount of pentane at −35 °C, resulting in the formation of dark red crystals of compound **3** (65.5 mg, 0.11 mmol, 51 %). **^{1}H NMR** (400.13 MHz, 298 K, C_6D_6): δ = 2.15 (s, 12H, 4x$C^{2,6}$-CH_3), 2.17 (s, 6H, 2xC^{4}-CH_3, Mes), 6.48 (d, $^{3}J_{H-H}$ = 7.7 Hz, 4H, 2x$C^{2,6}$-H, Ph), 6.88-6.79 (m, 6H, 2x$C^{3,5}$-H, Mes, 2xC^{4}, Ph), 7.06-6.95 (m, 6H, 2x$C^{3,5}$-H, Ph, $C^{3,5}$-H, Ter), 7.23 (t, $^{3}J_{H-H}$ = 7.5 Hz, 1H, C^{4}-H, Ter) ppm. **^{13}C{^{1}H} NMR** (75 MHz, 298 K, C_6D_6): δ = 21.14–21.55 ($C^{2,4,6}$-CH_3, Mes), 118.24-129.55 (Ar-C, ^{Mes}Ter, Ph), 135.79 (Sn-C), 153.82 (N-C) ppm. **^{119}Sn{^{1}H} NMR** (149.20 MHz, 298 K, C_6D_6): 903.81 ppm. **LIFDI-MS Calcd. for $C_{36}H_{35}NSn$**: 601.17914 Found: 601.17546. **Anal. Calcd. [%] for $C_{36}H_{35}NSn$**: C, 72.02; H, 5.88; N, 2.33; Sn, 19.77. Found: C, 68.56; H, 5.88; N, 2.29; Sn, 19.70. (N.B. Despite several attempts, elemental analysis showed consistently low C values with simultaneously excellent agreement of H and N values, presumably due to formation of incombustible material).

Adduct-formation upon Reaction of 3 with CO_2

^{Mes}Ter(NPh_2)Sn (20 mg, 0.07 mmol; 1.00 eq.) was dissolved in 0.5 mL benzene in a Schlenk flask and freeze-pump-thaw degassed two times. Subsequently, the flask was refilled with 1 bar of CO_2, resulting in a color change from deep red to yellow in the span of about 10 minutes. The reaction was quantitative according to NMR spectroscopy, however the product could not be isolated in solid state. **^{1}H NMR** (400.13 MHz, 298 K, C_6D_6): δ = 2.17 (s, 12H, 4x$C^{2,6}$-CH_3, Mes), 2.27 (s, 6H, 2×C^{4}-CH_3, Mes), 6.84 (s, 4H, 2×$C^{3,5}$-H, Mes), 7.01 (d, $^{3}J_{H-H}$ = 7.5 Hz, 2H, $C^{3,5}$-H, Ter), 7.08–7.15 (m, 10H, Ar-H, Ph), 7.25 (t, $^{3}J_{H-H}$ = 7.5 Hz, 1H, C^{4}-H, Ter) **^{13}C{^{1}H} NMR** (101 MHz, 298 K, C_6D_6): δ = 21.41 (C^{4}-CH_3, Mes), 21.68 ($C^{2,6}$-CH_3, Mes), 124.35–128.96 (Ar-CH, Mes, Ph), 136.37 (Ar-CH, Mes), 138.83 ($C^{3,5}$-CH, Ter) 142.90 (Ar-C, Ph), 147.98 (C^{4}-CH, Ter), 160.81 (OCO) ppm. **LIFDI-MS Calcd. for $C_{37}H_{36}NO_2Sn$**: 645.16897 Found: 645.16863.

Catalytic Hydroboration of CO_2 by 1

All catalytic reactions were performed according to the following procedure in either C_6D_6 at room temperature, or in THF-d_8 at room temperature or 50 °C respectively. 2.9 mg of ^{Mes}Ter[N(IDipp)]Sn (0.003 mmol, 0.05 eq.) were dissolved in 0.4 ml of the respective deuterated solvent in a *J-young* NMR tube. Then, 10 µl of HBpin (8.82 mg, 0.063 mmol, 1.0 eq.) and 0.046 ml of a 0.5 M solution of 1,3,5-methoxybenzene in C_6D_6 (0.023 mmol, 0.33 eq.) were added. The NMR tube was freeze-pump-thaw degassed two times before being refilled with 1 bar of CO_2. The reactions at room temperature were terminated after 24 h, the reaction at 50 °C after 6 h. Time course data of product yields and overall conversion were determined by ^{1}H- and ^{11}B-NMR data.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Tin · Small Molecule Activation · CO_2 Activation · Stannylene · Tetrylenes

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5. REACTIVITY OF NHI-STABILIZED HEAVIER TETRYLENES TOWARDS CO_2 AND N_2O

TITLE: “Reactivity of NHI-Stabilized Heavier Tetrylenes towards CO_2 and N_2O”[155]

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AUTHORS: Lisa Groll, Dr. John A. Kelly, Prof. Shigeyoshi Inoue[a]

[a] L. Groll planned and carried out the experiments, analyzed experimental data and wrote the manuscript. J. Kelly carried out the SC-XRD measurements, refined the crystallographic data and helped in writing the manuscript. All work was carried out under the supervision of S. Inoue.

CONTENT:

This paper expands the library of highly reactive but stably acyclic heavier tetrylenes by three new compounds. Firstly, the heteroleptic stannylene $[(Me_3Si)_2N](ItBuN)Sn$: could be obtained via ligand exchange reaction of $[(Me_3Si)_2N]_2Sn$: with the free ligand (I*t*BuN)H. Secondly, the homoleptic congeners $(ItBuN)_2E$: (E = Ge, Sn) were isolated from the reaction of ECl_2·dioxane and (I*t*BuN)Li. While $[(Me_3Si)_2N](ItBuN)Sn$: and $(ItBuN)_2Ge$: appear monomeric in solid state as well as in solution (determined by SC-XRD and NMR-spectroscopy), the solid state structure of $(ItBuN)_2Sn$: is dimeric according to SC-XRD. However, solution state VT-NMR experiments (^1H- and ^{119}Sn-NMR) reveal an approximate 1:1 ratio of monomer and dimer at – 80 °C with the monomer being the predominant state at room temperature.

While $[(Me_3Si)_2N](\mathrm{I}t\mathrm{BuN})Sn$: did not show selective reactivity towards CO_2 or N_2O, the homoleptic congeners showed interesting and contrasting reactivity with CO_2. Stannylene $(\mathrm{I}t\mathrm{BuN})_2Sn$: activates CO_2 by inserting one equivalent of the molecule into each Sn–N bond, to give two carbamato groups. In contrast, the metal-ligand bonds in germylene stay intact upon reaction with CO_2. Instead, the small molecule bridges each of the Ge–N bonds in an N,O coordination mode, giving two 4-membered metallacycles.

Upon reaction of $(\mathrm{I}t\mathrm{BuN})_2Sn$: with N_2O, partial oxidation takes place, giving a bis-stannylene with a central Sn_2N_2 ring ligated by two stannanolate-type ligands ($(\mathrm{I}t\mathrm{BuN})_3SnO$–). Germylene $(\mathrm{I}t\mathrm{BuN})_2Ge$: showed no selective reactivity towards N_2O and gave only free ligand as determinable decomposition product.

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Reactivity of NHI-Stabilized Heavier Tetrylenes towards CO_2 and N_2O

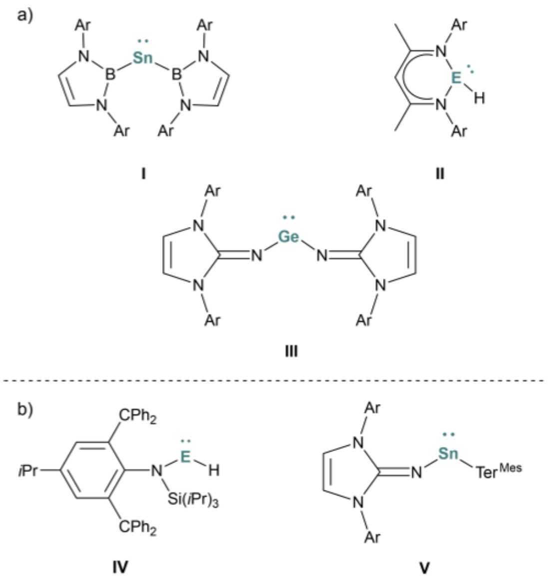
Lisa Groll,[a] John A. Kelly,[a] and Shigeyoshi Inoue*[a]

A heteroleptic amino(imino)stannylene $(TMS_2N)(I^tBuN)Sn$: (TMS = trimethylsilyl, $I^tBu = C[(N{-}^tBu)CH]_2$) as well as two homoleptic NHI-stabilized tetrylenes, $(I^tBuN)_2E$: (NHI = *N*-heterocyclic imine, E=Ge, Sn) are presented. VT-NMR investigations of $(I^tBuN)_2Sn$: (**2**) reveal an equilibrium between the monomeric stannylene at room temperature and the dimeric form at −80 °C as well as in the solid state. Upon reaction of the homoleptic tetrylenes with CO_2, both compounds insert two equivalents of CO_2, however differing bonding modes can be observed. $(I^tBuN)_2Sn$: (**2**) inserts one equivalent of CO_2 into each Sn–N bond, giving carbamato groups coordinated $\kappa^2 O,O'$ to the metal center. With $(I^tBuN)_2Ge$: (**3**), the Ge–N bonds stay intact upon activation, being bridged by one molecule of CO_2 respectively, forming 4-membered rings. Furthermore, the reactivity of **2** towards N_2O was investigated, resulting in partial oxidation to form stannylene dimer $[((I^tBuN)_3SnO)(I^tBuN)Sn:]_2$ (**6**).

Introduction

One of the most pressing goals in contemporary chemical research is the utilization of CO_2 as a source of a C_1 building block. This is due to its ubiquity and status as a greenhouse gas. CO_2 as well as N_2O, contribute significantly to climate change, due to their considerable heat-trapping potency.[1] One approach to curb global warming, is the utilization of these climate critical gases in the production of value added chemicals, which can be achieved with the use of transition-metal compounds as catalysts.[2] However, due to their often costly and toxic nature, there have been efforts towards more economically viable alternatives. As such, metal-free systems as well as abundant main-group element compounds have been investigated.[3] Pertinent to this, low valent group 14 compounds are of interest, since they have been shown to mimic the reactivity of transition metal complexes when isolated in a low oxidation state.[3a,4] In particular, heavier tetrylenes R_2E: (E = Si, Ge, Sn) demonstrated considerable potential in this respect due to their ambiphilic nature and small HOMO-LUMO gap. For example the uptake of CO_2 and N_2O by diborylstannylene $[(CHDippN)_2B]_2Sn$: **I** (Dipp = 2,6-*i*$Pr_2(C_6H_3)$ and *N*-heterocyclic tetrylene hydrides $CH[(CMe)(DippN)]_2EH$ **II**, the formation of a germanone $(IDippN)_2Ge{=}O$ (IDipp = $C[(N{-}Dipp)CH]_2$) upon reaction of $(IDippN)_2Ge$: **III** with N_2O with subsequent O-atom transfer, or the catalytic reduction of CO_2 to methanol by tetrylene hydride complexes $N(Ar)(Si^iPr_3)EH$ ($Ar = C_6H_2Pr^i\{C(H)Ph_2\}_2$-4,2,6, E = Ge, Sn) **IV** have been reported (*cf.* Scheme 1).[5]

With our recently reported aryl(imino)stannylene $(^{Mes}Ter)(IDippN)Sn$: **V** ($^{Mes}Ter = 2,6\text{-}Mes_2C_6H_3$), which showed catalytic activity in CO_2 hydroboration with HBpin, we could showcase the notable suitability of NHI (*N*-heterocyclic imine) ligated stannylenes for small molecule activation and catalysis.[6] Here, the zwitterionic nature of the Sn–Imine bond due to



Scheme 1. Selected tetrylenes E_2R (E = Ge, Sn) capable of activating CO_2 and/or N_2O (a),[5a,b,e–g] as well as catalytic reduction of CO_2 (b)[5d,6] (Ar = Dipp = 2,6-*i*$Pr_2(C_6H_3)$, $^{Mes}Ter = 2,6\text{-}Mes_2C_6H_3$, Mes = 2,4,6-$Me_3(C_6H_2)$,).

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distinct properties of the NHI ligand allows activation and subsequent reduction of CO_2 under mild conditions. In comparison, amine or NHCP (*N*-heterocyclic phospinidine) substituted congeners were not able to reduce CO_2. NHIs are exceptionally strong π- as well as σ-donors and also allow facile modification of their steric demand at the endocyclic nitrogen moieties and backbone, making them excellent ligands for an electrophilic metal center.[7] With this in mind, we set out to further expand the library of NHI stabilized tetrylenes and explore their capabilities in small molecule activation.

Results and Discussion

Heteroleptic stannylene $(TMS_2N)(I^tBuN)Sn$: **1** ($I^tBu = C[(N{-}^tBu)CH]_2$) was synthesized *via* a ligand exchange reaction with Lappert's stannylene[8] $(TMS_2N)_2Sn$: with protonated ligand, $(I^tBuN)H$ at room temperature (Scheme 2a) and characterized by standard NMR and SC-XRD techniques (see SI). Subsequent introduction of a second equivalent of $(I^tBuN)H$ to **1** gave bis-NHI-substituted stannylene $(I^tBuN)_2Sn$: **2**, however in poor yield and purity. Alternatively, introduction of two equivalents lithiated ligand, $(I^tBuN)Li$ to $SnCl_2 \cdot$dioxane with one additional equivalent of DMAP lead to the formation of **2** more selectively. In a similar manner, the analogous germylene $(I^tBuN)_2Ge$: (**3**) could be obtained by the reaction of $GeCl_2 \cdot$dioxane with $(I^tBuN)Li$ (Scheme 2b). It should be noted that parent amino-germylene $(TMS_2N)_2Ge$: showed no reactivity towards $(I^tBuN)H$.

The ^{119}Sn-NMR Signal of **2** (122.07 ppm) is significantly up-field shifted compared to **1** (401.35 ppm) as well as $(TMS_2N)_2Sn$: (767 ppm), but within the range of previously reported two-coordinate, NHI-stabilized stannylenes (−208.0–967.8 ppm).[6,8–9] While solution state ^{1}H-NMR characterization shows one set of signals attributed to the ligand indicating a symmetrical molecule, the solid state structure of **2** exhibits a dimer with two distinct ligand environments (Figure 1). The compound displays a nearly planar Sn_2N_2 ring (sum of internal bond angles = 359.5°) with terminal ligand moieties *trans* oriented in respect to the Sn_2N_2 ring, and two imines bridging the Sn centers. The Sn–N bond lengths are in the range of previously reported amido- and iminato-stannylene single bonds (2.041(2)–2.227(7) Å).[6,9c,10]

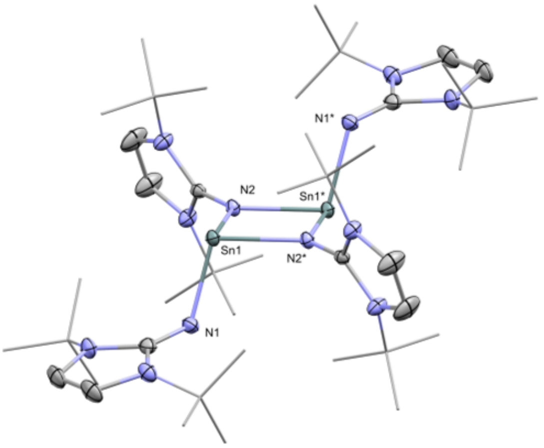
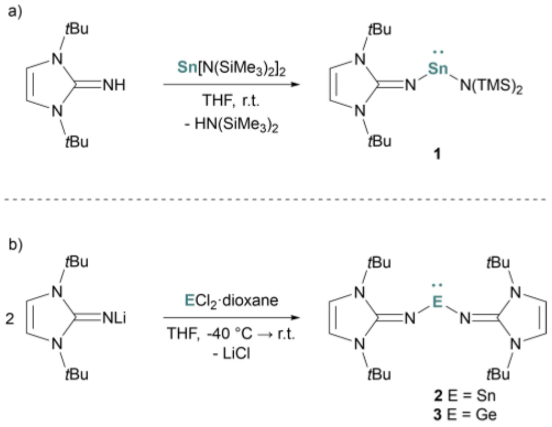


Figure 1. Molecular structure of Stannylene **2** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1–N1 2.0985(16), Sn1–N2 2.1841(16), Sn1–N2* 2.1880(16), N2–Sn1–N2* 75.96(6), Sn1–N2–Sn1* 104.04(6).

In order to elucidate the structure of **2** in solution, VT-NMR experiments in toluene-d_8 were conducted (Figure 2). ^{1}H- and ^{119}Sn-NMR measurements show the gradual appearance of a second species upon cooling, with an approximate 1:1 ratio at −80 °C (determined by ^{1}H-NMR integral ratios, *cf.* Figure S18). The new ^{119}Sn signal displays further up-field at 130.6 ppm, while the ^{1}H-NMR shows the emergence of two new distinct sets of ligand signals, as expected according to the molecular



Scheme 2. a) Synthesis of heteroleptic stannylene **1** *via* ligand exchange of Lappert's stannylene with free $(I^tBuN)H$. b) Homoleptic tetrylenes **2** and **3** obtained *via* imination of $ECl_2 \cdot$dioxane with $(I^tBuN)Li$ ($I^tBu = C[(N{-}^tBu)CH]_2$, E = Sn, Ge).

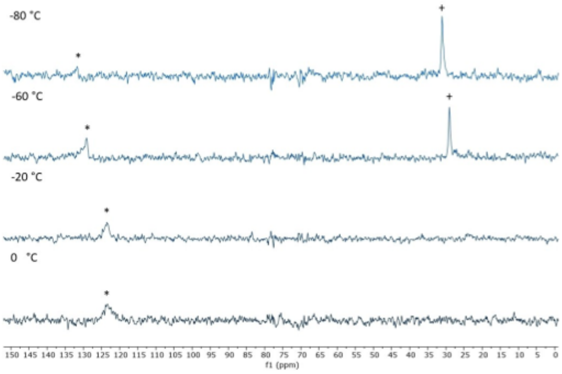


Figure 2. Truncated variable temperature ^{119}Sn NMR spectra of stannylene **2** in Toluene-d_8 at −80 °C, −60 °C, −20 °C and 0 °C. (* = signals corresponding to monomeric stannylene, + = signals corresponding to di-stannylene). For experimental details and corresponding 1H NMR spectra see supporting information.

structure of **2** in the solid state. This confirms an equilibrium between the monomer and dimer of **2** in solution, with the monomer being the preferred form at room temperature.

Germylene **3** displays a monomeric molecular structure in solution as well as in solid state, according to ^{1}H-NMR and SC-XRD characterization (Figure 3). Compared to previously reported germylene (IDippN)$_2$Ge: (**III**), Ge–N bond lengths of 1.8739(17) Å are elongated and the Ge–N–Ge angle of 94.17(9) is more acute (**III**: 1.819(15) Å, 99.48(10)°). Overall, **3** is highly symmetrical with the imidazole rings being perpendicular to the N–Ge–N moiety (Ge1–N1–C1–N2 = 90°).

With **1–3** in hand, we wanted to explore their reactivity towards small molecules, in particular CO$_2$ and N$_2$O. Both homoleptic tetrylenes **2** and **3** reacted with 1 bar of CO$_2$ at room temperature instantaneously to give colorless crystals suitable for SC-XRD analysis (Scheme 3). In contrast, **1** did not selectively react with CO$_2$, likely due to decomposition of the amido-ligand via silyl migration, a commonly observed phenomenon when utilizing silyl-amido-ligands.[11]

Stannylene **2** inserts one molecule of CO$_2$ into each Sn–N bond, giving a distorted seesaw structure with both carbamato groups coordinated κ^2*O,O′* around the metal center (Compound **4**, Figure 4, Sn1–O 2.1578(15)–2.2410(15) Å). The ^{1}H- as well as ^{13}C-NMR spectroscopic analysis confirms a quantitative conversion and a ^{13}C-NMR signal at 167.40 ppm, characteristic for the formation of a tin-carbamate carbon (161.6–175.6 ppm)[6,12] can be observed. Compound **4** shows very poor solubility in THF and C$_6$H$_6$ but is soluble in acetonitrile, nevertheless no ^{119}Sn-NMR signal could be observed. The insertion of CO$_2$ is irreversible and **2** could not be recovered upon heating or under reduced pressure.

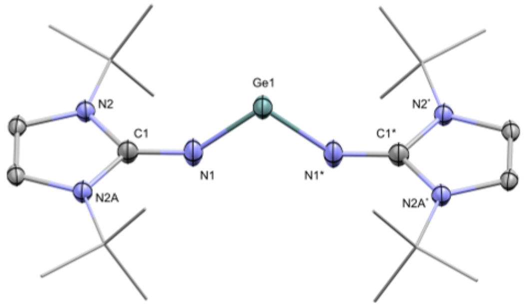
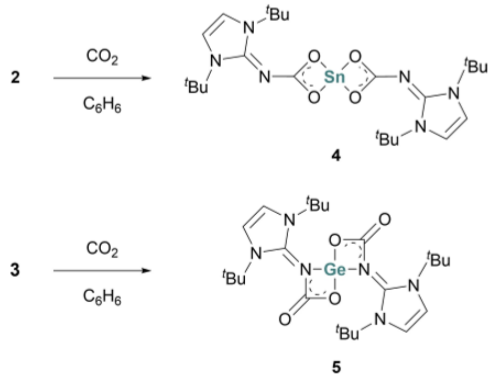


Figure 3. Molecular structure of compound **3** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ge1–N1 1.8738(17), Ge1–N1* 1.8739(17), N1–Ge–N1* 94.17(9), Ge1–N1–C1–N2 90.000(1).



Scheme 3. Reaction of tetrylenes **2** and **3** with 1 bar of CO$_2$ in benzene at room temperature.

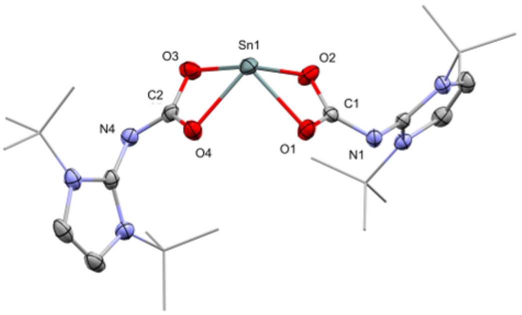


Figure 4. Molecular structure of compound **4**. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1–O1 2.1846(16), Sn1–O2 2.2054(15), Sn1–O3 2.1578(15), Sn1–O4 2.2410(15), O1–Sn1–O2 59.79(5), O1–Sn1–O3 83.71(6).

Germylene **3** also irreversibly activates two equivalents of CO$_2$ to give compound **5**. Here, the Ge–N bonds stay intact, and we observe a N,O coordination mode as opposed to the O,O mode as seen in **4**. This is presumably due to the higher bond strength of Ge–N bonds (364 kJ/mol) compared to Sn–N bonds (324 kJ/mol).[13] The central germanium is surrounded by the ligands in a distorted seesaw fashion, with an almost perpendicular O–Ge–O angle (94.4(3)°) and nearly planar four membered metallacycles (sum of internal bond angles = 178.4°) (*cf.* Figure 5).

Reaction of **2** with N$_2$O gives bis-stannylene $[((\mathrm{I}^t\mathrm{BuN})_3\mathrm{SnO})(\mathrm{I}^t\mathrm{BuN})\mathrm{Sn:}]_2$ (**6**) with a central Sn$_2$N$_2$ ring (Scheme 4). The +II oxidation state is retained by the central Sn atoms, which are bridged by imine moieties similarly to stannylene **2**. However, the other two Sn centers get oxidized and form stannanolate (IDippN)$_3$SnO– ligands. We propose that

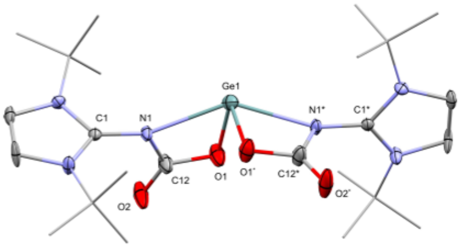
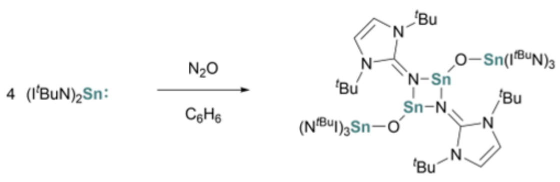


Figure 5. Molecular structure of compound **5** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ge1–O1 1.904(5), Ge1–N1 2.288(5), O1*–Ge1–O1 94.4(3), O1–Ge1–N1 63.64(18), O1–Ge1–N1* 91.25(19).



2 **6**

Scheme 4. Reaction of tetrylene **2** with 1 bar of N_2O in benzene at room temperature.

the initial step in the mechanism is the formation of a transient stannone intermediate, as suggested for the reaction of **I** and N_2O. This transient stannone reacts with one equivalent of **2** giving the final product **6** after dimerising (a proposed mechanism is in the SI, Figure S22)[5a] Pertinently, the formation of a silanolate-ligated bis-stannylene when $(TMS_2N)_2Sn$: was treated with CO_2 as well as NHI ligand rearrangements have been reported.[11a,14] The ^{1}H- and ^{13}C-NMR spectra show two sets of signals corresponding to the distinct ligand environments. Due to the low solubility of compound **6** in most common NMR solvents and only slight solubility in acetonitrile, no ^{119}Sn-NMR signal could be observed. The molecular structure of **6** displays a planar Sn_2N_2 ring (sum of internal bond angles = 360.0°) with Sn–N bond lengths (Sn2–N1 2.185(6) Å, Sn2–N1* 2.173(6) Å) shorter than **2** and the stannanolate moieties *trans* oriented to the ring center (Figure 6).

Treatment of **1** as well as **3** with N_2O, lead to the formation of mostly protonated ligand and indeterminable decomposition products. The reaction outcome for **3** and N_2O is in stark contrast to the previously reported reaction of $(IDippN)_2Ge$: with N_2O, which leads to the isolation of a stable germanone.[5c] This is likely due to the $I^{tBu}N$ ligands not offering sufficient kinetic protection to the polarized Ge=O bond compared to the more sterically imposing IDippN. The comparison of **1** and **2** in terms of small molecule activation showcases once again the benefits of utilizing the robust NHI ligand system for the stabilization of low valent tin compounds, enabling selective reactivity.

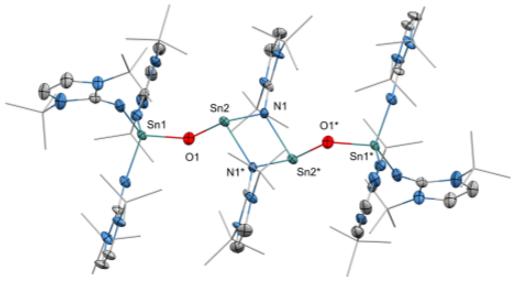


Figure 6. Molecular structure of compound **6**. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: **1**: Sn1–O1 1.930(6), Sn2–O1 2.022(7), Sn2–N1 2.185(6), Sn2–N1* 2.173(6), O1–Sn2–N1 98.8(2), O1–Sn2–N1* 97.0(3), Sn2–N1–Sn2* 102.4(3), N1–Sn2–N1* 77.6(3).

Conclusions

The isolation and reactivity of three novel NHI-stabilized tetrylenes has been reported. While the heteroleptic amino(imino)stannylene $(TMS_2N)(I^tBuN)Sn$: (**1**) does not selectively react with N_2O or CO_2, the homoleptic congener $(I^tBuN)_2Sn$: (**2**) shows defined activation of both small molecules. Also, the reaction of $(I^tBuN)_2Ge$: (**3**) with CO_2 could be observed, which led to a rare bonding mode (N,O) for germanium. These tetrylenes expand the library of low valent group 14 compounds capable of small molecule activation and the investigation of their reactivity towards a broader substrate scope as well as their potential catalytic applications is currently underway.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Germylene · Stannylene · *N*-heterocyclic Imine · CO_2 Activation · N_2O Activation

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6. SUMMARY AND OUTLOOK

NHI ligands have long been discussed for their inherent suitability to stabilize electron-deficient metal centers since their introduction to the scientific community by Tamm *et al.* [49-50, 55, 60-61, 64, 153] Nevertheless, instances of NHI-stabilized heavier tetrylenes, especially those active in small molecule activation, have mostly been reserved for silylenes.[20, 80, 86, 156] NHI-stabilized germylenes and stannylenes, on the other hand, often did not show activity towards small molecules or have simply not been explored for that purpose.[58, 83, 124, 145-146] This is somewhat surprising since the increased stability of the +II oxidation state going down group 14 should facilitate the synthesis of those complexes as well as reductive elimination, which is a crucial step in redox-based catalysis. NHIs can support this reactivity by providing strong σ- as well as π-donation to the metal center, which can stabilize and increase the reactivity of the compound at the same time. With this work, this gap could be partially bridged, and a collection of NHI-stabilized germylenes and stannylenes active in small molecule activation and/or catalysis were presented.

6.1. HYDROBORATION OF CO_2 BY AN NHI-STABILIZED TETRYLENE

The aryl(imino)stannylene ^{Mes}Ter(IDippN)Sn: (**I**) was synthesized as a dark red solid via salt metathesis of (IDippN)Li and ^{Mes}Ter(Cl)Sn: in a 75 % yield. The compound was thoroughly characterized by ^{1}H-, ^{13}C{^{1}H}-, and ^{119}Sn-NMR, as well as elemental analysis and SC-XRD. The length of the Sn–N bond is in the range of a short single bond (2.042(2) Å), and density functional theory calculations identified a highly polarized single bond with a weak π-component. The compound was also compared theoretically with the known NHCP-stabilized stannylene ^{Mes}Ter(IDippP)Sn: (**34**)[133] as well as amido stannylene ^{Mes}Ter(Ph_2N)Sn: (**III**), which was also synthesized and fully characterized for this account. The calculations revealed the lowest HOMO-LUMO gap in **III** (3.56 eV) and similar values for stannylenes **34** and **I** (3.88 eV and 3.83 eV respectively). Furthermore, Löwdin's Partial Charges and Mayer's Bond Orders indicated a strong covalent Sn–P bond with double bond character in ^{Mes}Ter(IDippP)Sn: and a weak and polarized single bond in ^{Mes}Ter(Ph_2N)Sn:.

The reactivity of **I** towards CO_2 was then examined. It turned out that the stannylene reacts readily with CO_2 (1 bar) at room temperature in less than 10 minutes, and the product [^{Mes}TerSn(CO_2)N(IDipp)] (**II**) could be isolated in a 96 % yield as a colorless solid. ^{13}C{^{1}H}-NMR revealed a signal at 175.6 ppm characteristic for a carbamate carbon and SC-XRD confirmed the identity of the compound. One molecule of CO_2 inserts into the Sn–N bond of ^{Mes}Ter(IDippN)Sn: (**I**) to give a tetrahedral tin center. Calculations of the mechanism suggest a 1,2-addition of CO_2 across the Sn–N bond followed by a barrierless dissociation of the metal-ligand bond. Comparing this to ^{Mes}Ter(IDippP)Sn: (**34**), which does not react with CO_2, a similar 1,2-addition is theoretically feasible, however the bond dissociation is unfavored. This indicates that the nature of the Sn–N is the deciding factor that allows CO_2 activation with the imino-stannylene.

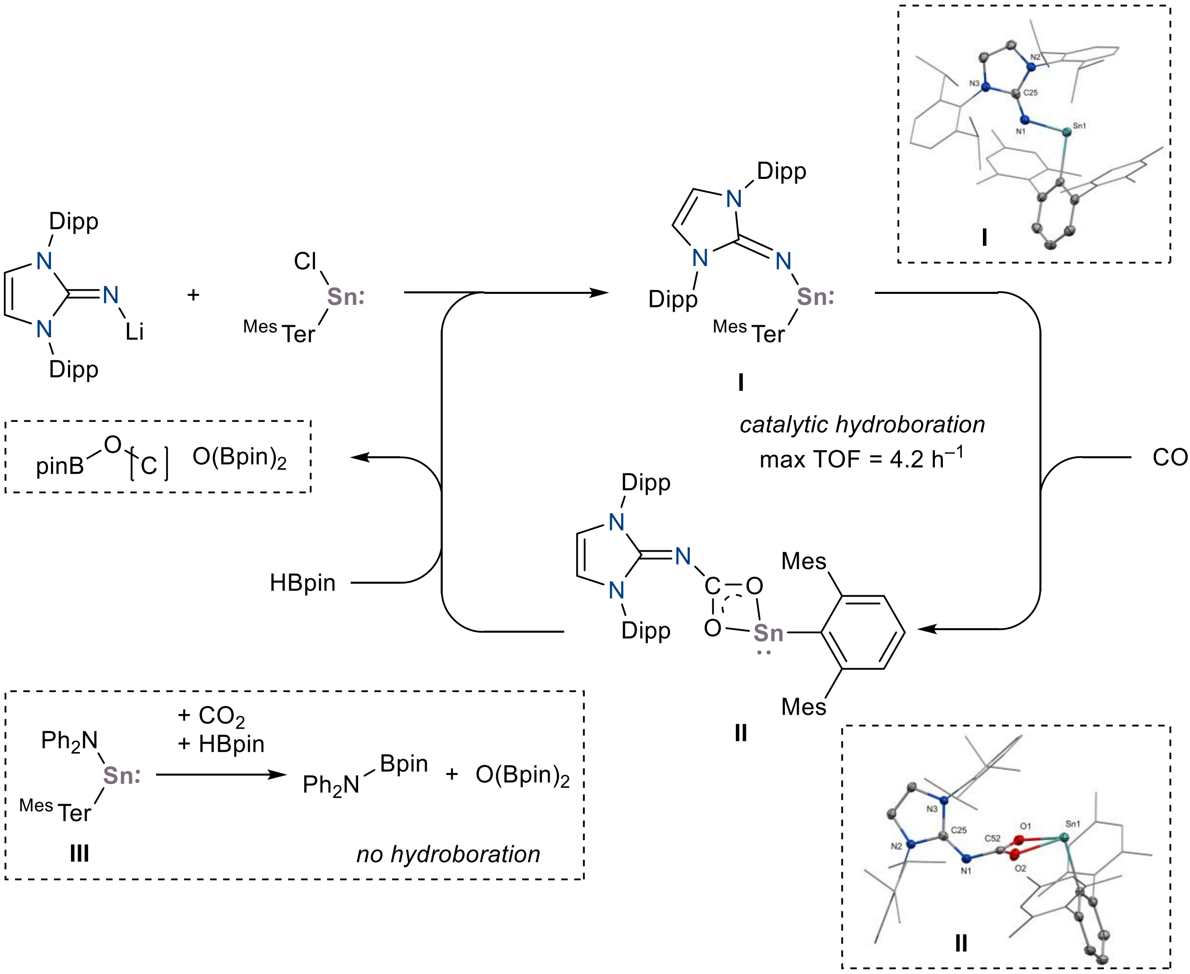


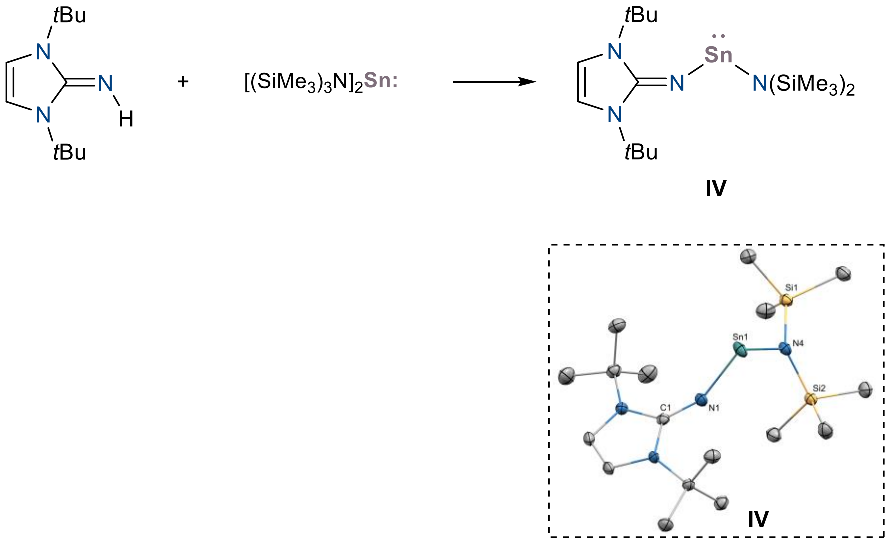
Figure 17. Synthesis, CO_2 activation, and catalytic hydroboration activity of NHI-stabilized stannylene (**I**) and comparison with amine-stabilized stannylene (**III**).

This rapid and mild activation of CO_2 gave impetus to explore the utilization of the activated molecule in follow-up reactivity. While the direct release of CO_2 from compound **II** could not be observed, even at reduced pressure or elevated temperatures, it reacted with stoichiometrical amounts of pinacolborane (Figure 17). In fact, alternating between addition of 1 bar of CO_2 and one equivalent of HBpin three times led to the formation of 31 % yield of MeOBpin. Under optimized catalytic conditions (THF, 50 °C, 5 mol% catalyst loading), 1 bar of CO_2 and equimolar amounts of HBpin led to the full conversion of CO_2 to MeOBpin and $O(Bpin)_2$ with a TOF of 4.2 h^{-1}. Theoretical calculations revealed the tin carboxylate (**II**) to be the resting state of the catalytic cycle and the rate-determining step to be the hydrogenation of the reduced products by HBpin. Overall, three equivalents of HBpin are consumed per equivalent of CO_2 in one cycle, and the calculated mechanism is in agreement with the applied reaction conditions.

The importance of the NHI ligand for the observed catalysis could further be illustrated by comparing the reactivity of $^{Mes}Ter(Ph_2N)Sn$: (**III**) with CO_2. The $-NPh_2$ moiety was chosen for its similarly low oxophilicity compared to the NHI ligand. While stannylene **III** reacts with CO_2 to presumably give a tin-carboxylate analogously to the NHI-stabilized congener (not isolated, but in line with ^1H- and ^{13}C-NMR as well as mass spectroscopic measurements), the addition of HBpin to the reaction mixture led to the formation of Ph_2N–Bpin and $O(Bpin)_2$. This is in good agreement with the calculated weak Sn–N bond and low HOMO–LUMO gap of complex **III**. While reactivity can be observed, the regeneration of the tetrylene is unfavored upon the addition of HBpin, giving the respective decomposition products.

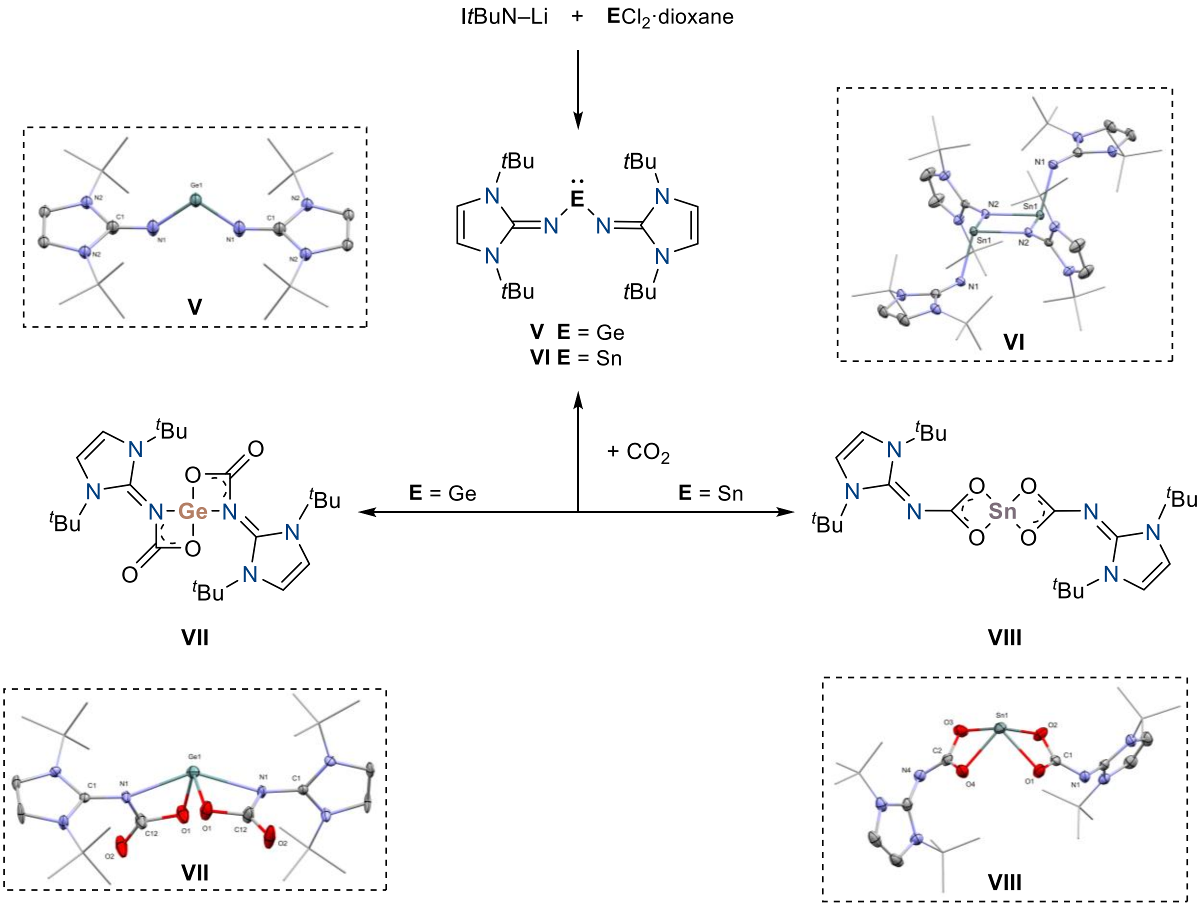
6.2. SMALL MOLECULE ACTIVATION BY HEAVIER BIS-NHI-TETRYLENES

The differences in structure and reactivity of heteroleptic stannylene $[(Me_3Si)_2N](I\textit{t}BuN)Sn$: (**IV**) homoleptic tetrylenes $(I\textit{t}BuN)_2Ge$: (**V**) and $(I\textit{t}BuN)_2Sn$: (**VI**) have been discussed in this chapter. Stannylene **IV** readily forms upon treatment of Lappert's stannylene $[(Me_3Si)_2N]_2Sn$:[112, 137] with the free NHI ligand $(I\textit{t}BuN)H$ (Scheme 26). In the case of the bis-NHI-stabilized tetrylenes **V** and **VI**, a salt metathesis route *via* treating ECl_2·dioxane (E = Ge, Sn) with the lithiated ligand precursor $(I\textit{t}BuN)Li$ gave the best results. All compounds have been fully characterized by multinuclear NMR experiments, SC-XRD, as well as elemental analysis. According to NMR experiments, all tetrylenes appear monomeric in solution at room temperature. SC-XRD spectroscopy, however, showed a dimeric structure for stannylene **VI** in the solid state. Due to this observation, ^1H and ^{119}Sn VT-NMR experiments were performed, which revealed an equilibrium between the monomeric and dimeric form with about a 1:1 ratio of both at – 80 °C (according to ^1H integral ratios).



Scheme 26. Synthesis and molecular structure of heteroleptic stannylene **IV**.

Next, the tetrylenes were evaluated regarding their reactivity towards CO_2 and N_2O. While **IV** reacted with both small molecules, no selective product formation could be observed. In Contrast, homoleptic tetrylenes **V** and **VI** both reacted selectively with CO_2 in swift reactions at room temperature. The activations are irreversible, and even under elevated temperatures or reduced pressure, no release of CO_2 could be observed in both cases. Germylene **V** undergoes a [2+2]-cycloaddition alongside each of the Ge–N bonds of the complex to give a doubly N,O-coordinated germylene (**VII**). In the case of stannylene **VI**, insertion of CO_2 into each of the Sn–N bonds take place and the doubly κ^2O,O’ coordinated bis-carbamate (**VIII**) is formed. The difference between these activation modes is presumed to be due to a stronger Ge–N bond than the Sn–N bond in the respective complexes.



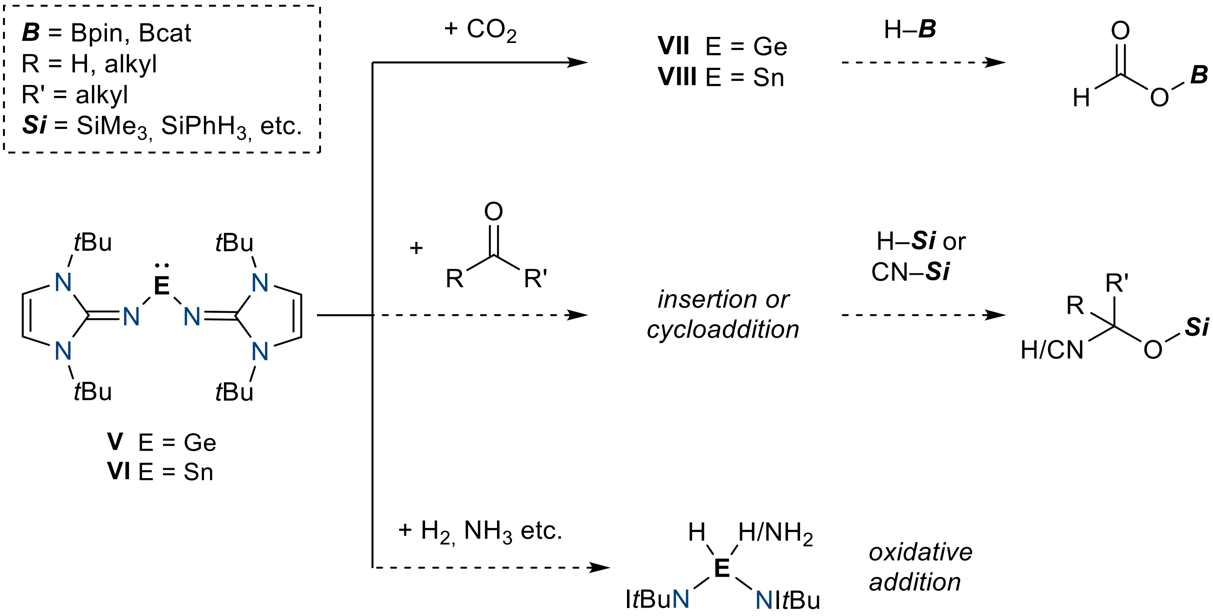
Scheme 27. Synthesis and reactivity towards CO_2 of NHI-stabilized tetrylenes **V** and **VI**.

While the reaction of germylene **V** led to decomposition upon exposure to N_2O, stannylene **VI** reacted selectively with N_2O in a partial oxidation. The compound can be described as a stannanolate-ligated bis-stannylene with a central Sn_2N_2 ring, confirmed by SC-XRD measurements. The mechanism potentially follows the transient formation of a stannone followed by a reaction with another equivalent of unreacted stannylene and rearrangement.

6.3. OUTLOOK

UNEXPLORED REACTIVITY

As a first step into further research, the scope of small molecule activation and catalysis with the presented tetrylenes should be expanded (Scheme 28). As such, other industrially relevant small molecules (*e.g.* H_2, NH_3, or CO) should be explored in regard to their reactivity with the tetrylenes. If the reactivity of the respective tetrylene is not high enough, the introduction of an amine or another *Lewis* base could increase activity. In previous accounts, for example in the case of dialkyl-stannylene **33** (*c.f.* chapter 2.3.2, Scheme 16) or a cyclic alkylsilylene (2,2,5,5-tetrakis(trimethylsilyl)silacyclopentane-1,1-diyl), frustrated *Lewis* pairs of a tetrylene with an amine enabled activation of hydrogen.[138, 157]



Scheme 28. Unexplored reactivity with NHI-stabilized tetrylenes **V** and **VI**.

Since aryl(imino)stannylene **I** showed activity in hydroboration of CO_2, the homoleptic tetrylenes (I*t*BuN)$_2$Ge: (**V**) and (I*t*BuN)$_2$Sn: (**VI**) should also be investigated in that regard. As such, the reactivity of the respective carbamates (**VII** and **VIII**) towards HBpin or other boranes should be investigated. Besides hydroboration, (catalytic) silylation of CO_2 or cyanosilylation of aldehydes and ketones should also be investigated not only for tetrylenes **V** and **VI**, but also for stannylene **I**.

LIGAND MODIFICATION

Modification of the NHI ligand, not only on the endocyclic *N*-substituents but also in the backbone area, could lead to interesting new compounds (Figure 18). Introducing a methylated backbone to the NHI has proven to have a notable impact on the structure and reactivity of silylenes. While (IDippN)(silyl)silylenes with an unmodified backbone (*c.f.* **4a-c**, Figure 5) react with the aromatic wingtip moiety to form silepins, (^{Me}IDippN)(Si*t*Bu$_3$)Si: (**4d**) is stable as an acyclic silylene.

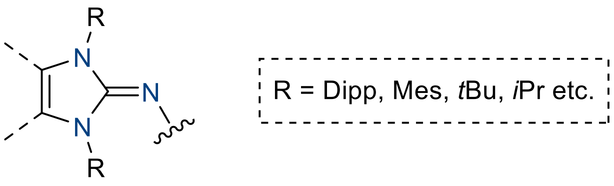
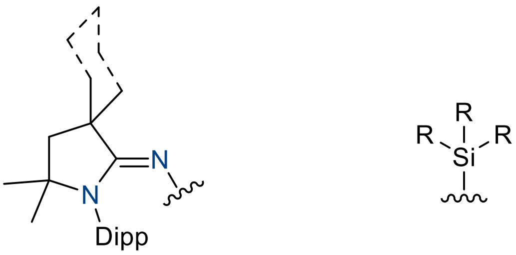


Figure 18. Potential ligand modifications of the backbone or wingtips of the NHI ligand.

It would be interesting to see, what impact backbone modification could have on the respective germylene or stannylene analog. Modification of the wingtips would mostly change the steric bulk of the ligand and therefore the geometry around the metal center of a potential tetrylene. This could have an influence on dimerization tendencies as well as the HOMO–LUMO gap (and therefore the reactivity) of the compound as well, as previously observed in similar silylenes and silepins.[79-82, 86]

ALTERNATIVE SYNTHESIS ROUTE AND LIGANDS

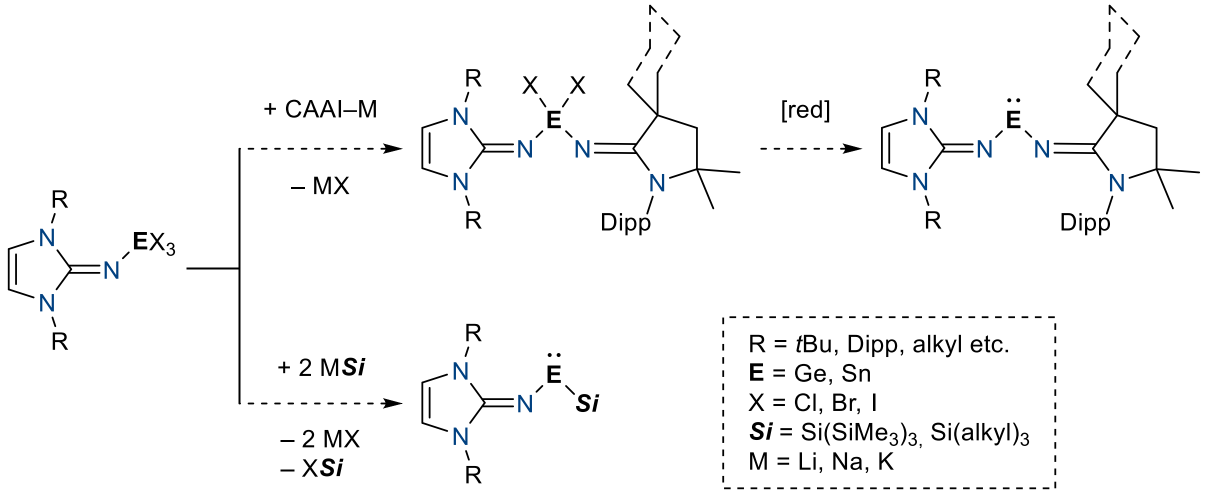
While the previously presented accounts all utilize the direct synthesis of tetrylenes *via* introduction of a ligand precursor to a metal source of the oxidation state +II (*i.e.* EX_2·dioxane, $[(Me_3Si)_2N]_2Sn$:, $^{Mes}Ter(Cl)Sn$:), using reagents where the group 14 element is in the +IV oxidation state can also lead to useful precursor compounds. While this route requires a multi-step synthesis, that ultimately leads to the desired tetrylene *via* reduction (*c.f.* Scheme 4), intermediary compounds can be more stable and easier to handle. This is especially the case for germanium (and silicon) complexes, where hybridization is still more effective than for tin or led, making the tetravalent compound generally more stable. The stoichiometric introduction of ligands to the metal center tends to be more selective, allowing a potentially more facile synthesis of heteroleptic compounds.



CAAI **Silyl**

Figure 19. CAAI and Silyl moieties as secondary ligands for the synthesis of heteroleptic tetrylenes (R = $SiMe_3$, *t*Bu, Me, etc).

The introduction of silyl or cyclic alkyl(amino)iminate (CAAI) groups as secondary ligands could for example be considered (Figure 19). As mentioned above (*c.f.* chapter 2.3), silyl ligands are strong σ-donors and can be varied in steric bulk relatively easily. By this, they can theoretically increase reactivity and provide thermodynamic stabilization to the metal center at the same time. CAAIs are a newer evolution of imine ligands derived from the respective parent carbenes. First published in 2019 by Braunschweig *et al.*, this compound class has found quick acceptance in the scientific community.[152] As in NHIs, CAAIs bear a terminal imine introduced at the former carbene position. The presence of only one endocyclic nitrogen leads to a less electron-rich heterocycle with a weaker inductive effect on the 2-position of the ring, just as in the parent CAAC. Looking at the structure and comparing earlier accounts regarding NHIs, one can expect CAAIs to be weaker π-donors and stronger σ-donors, respectively.[158] Nevertheless, CAAIs can also be described as 2σ- and up to 4π-electron donors, visualized by the resonance structures. Synthesizing heteroleptic tetrylenes with one NHI and one CAAI ligand could also lead to new highly reactive compounds.



Scheme 29. Proposed synthesis routes to NHI- and silyl- or CAAI-substituted heteroleptic tetrylenes.

Both silyl and CAAI moieties could be introduced as alkali metal salts (e.g. R$_3$Si–K or CAAI–Li) to an NHI-substituted E(IV) halide via salt metathesis (Scheme 29), followed by reduction to give a tetrylene. Reduction of L$_2$EX$_2$ type compounds to the respective tetrylenes L$_2$E: could for example successfully demonstrated for a number of silyl ligated silylenes and disilenes, such as [(Me$_3$Si)$_3$Si](*t*Bu$_3$Si)Si: and (*t*Bu$_2$MeSi)$_2$Si=Si(SiMe*t*Bu$_2$)$_2$ as well as (IDippN)$_2$Ge: (**5**, Figure 5).[54, 159-160] Furthermore, if the secondary ligand is a strong enough reductant, which is often the case for silanides, introduction of the secondary ligand and reduction can occur in one step. *In situ* reduction and ligand exchange using LEX$_3$ complexes and silanides as ligand precursor and reducing agent proved successful in NHI-stabilized silylenes and disilenes, such as **4a-c** (Figure 5) and (RSi)(I*t*BuN)Si=Si(I*t*BuN)(SiR) (R = $(SiMe_3)_3$, *t*Bu_3, *t*Bu_2Me).[84, 161]

In conclusion, the obtained NHI-stabilized tetrylenes and stannylenes showcased their capability in small molecule activation and catalysis. The introduction of modified NHIs or other new ligands in combination with NHIs to low-valent germanium and tin centers could further advance the field and give more insights into the yet unrealized possibilities of these compounds.

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8. APPENDIX

8.1. SUPPORTING INFORMATION FOR CHAPTER 4

Table of Contents

1. Experimental Procedures

1.1 General Information

All experiments and manipulations were carried out under a dry argon atmosphere using standard *Schlenk* techniques or in a glovebox. All glass junctions were coated with PTFE-based grease *Merkel* Triboflon III. N-hexane, n-pentane, THF, benzene and toluene were refluxed over sodium/benzophenone, freshly distilled and deoxygenated prior to use. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were measured on *Bruker* 400 MHz and 500 MHz spectrometers. Chemical shifts were referenced to residual solvent signals (^{1}H and ^{13}C NMR). ^{119}Sn NMR chemical shifts was referenced to Me_4Sn (^{119}Sn). Deuterated solvent C_6D_6 and THF-d_8 were obtained from *Deutero* Deutschland GmbH and were dried over 4 Å molecular sieves prior to use. Unless otherwise stated, all reagents were purchased from commercial sources and used as received. Abbreviations: s = singlet, br = broad, d = doublet, t = triplet, m = multiplet. Elemental analyses (EA) were conducted with a EURO EA (*HEKA tech*) instrument equipped with a CHNS combustion analyzer. Thereby, all samples were prepared in THF solutions, filtered and injected into the spectrometers. TOF analyzation in cationic mode resulted in the obtained spectra, which were resolved by mass-to-charge values. Liquid Injection Field Desorption Ionization Mass Spectrometry (LIFDI-MS) was performed in an inert atmosphere glovebox with a *Thermo Fisher* Scientific Exactive Plus Orbitrap equipped with an ion source from Linden CMS.S7.[S1] NHILi, [^{m}TerSnCl] and Ph_2NLi were synthesized according to literature procedures.[S2]

1.2 Spectra of Compound 1

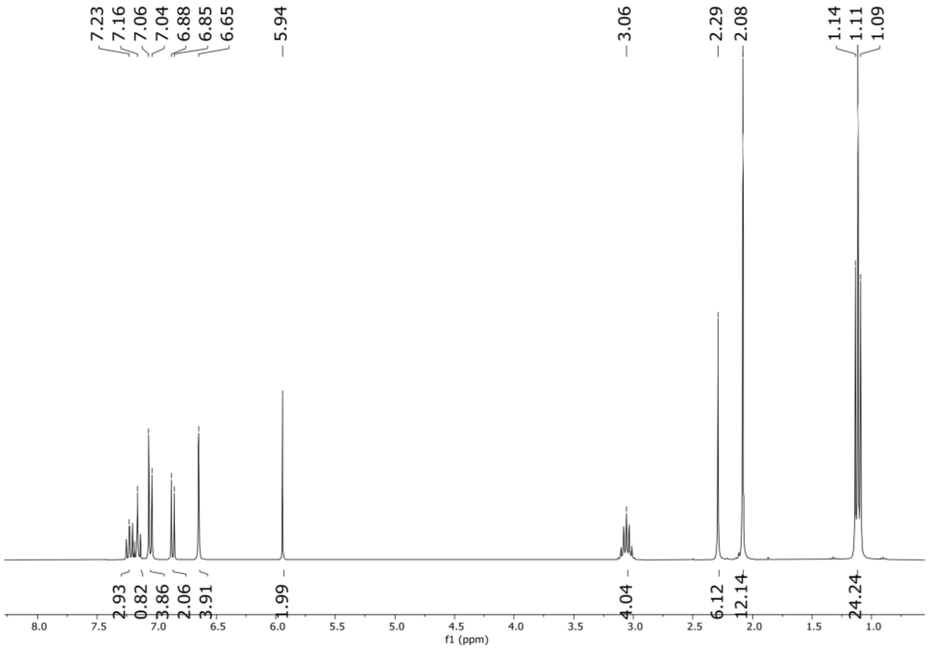


Figure S1. ^{1}H NMR spectrum of compound **1** in C_6D_6 at 298 K.

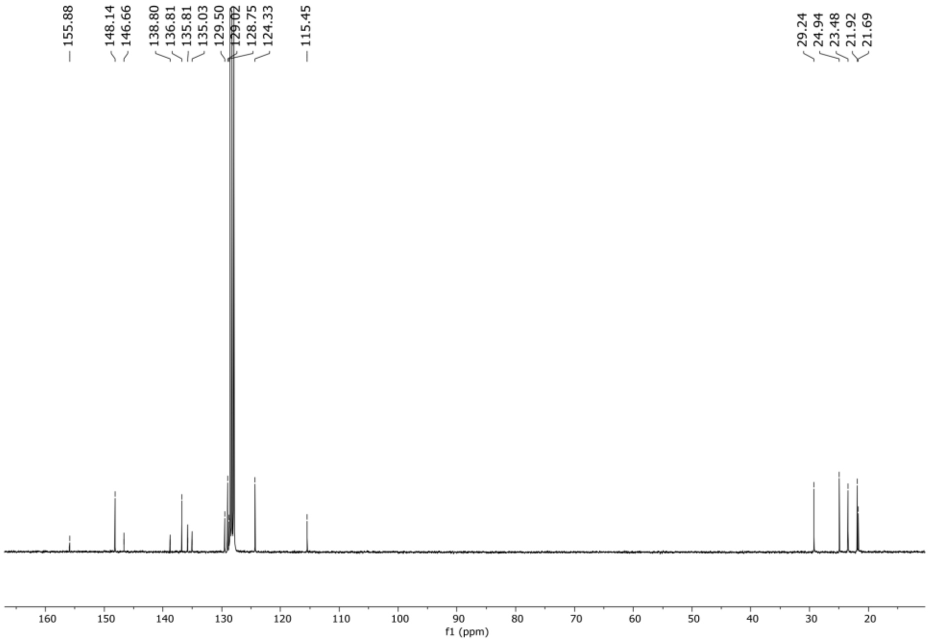


Figure S2. $^{13}C\{^1H\}$ NMR spectrum of compound **1** in C_6D_6 at 298 K.

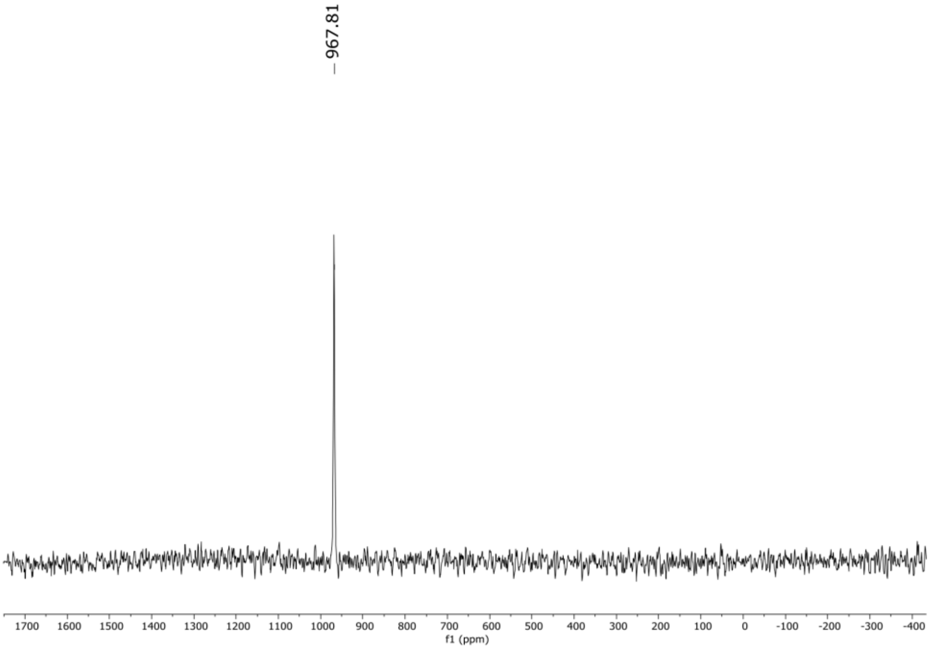


Figure S3. $^{119}Sn\{^1H\}$ NMR spectrum of compound **1** in THF-d_8 at 298 K.

abc

1.3 Spectra of Compound 2

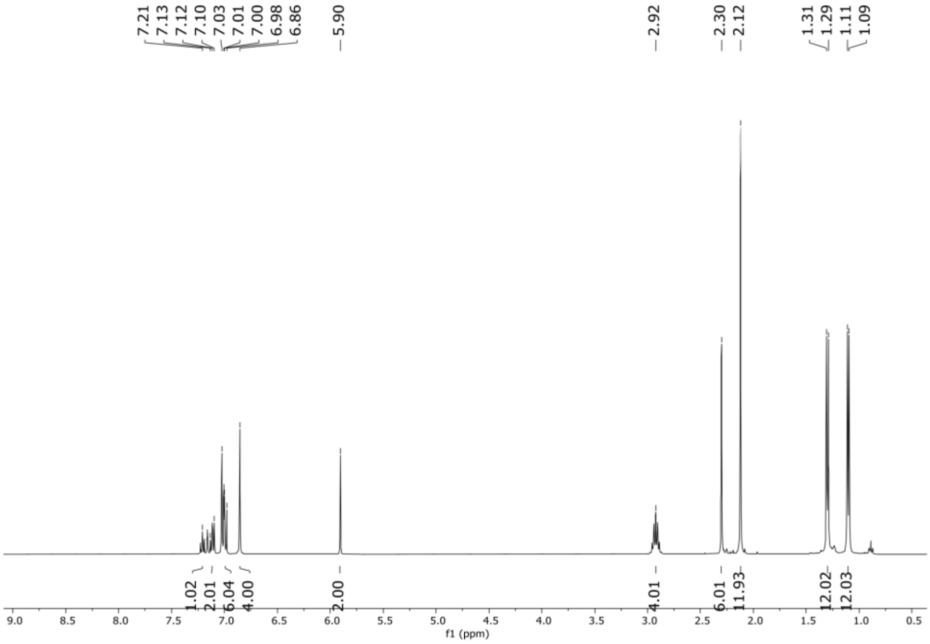


Figure S4. ^{1}H NMR spectrum of compound **2** in C_6D_6 at 298 K.

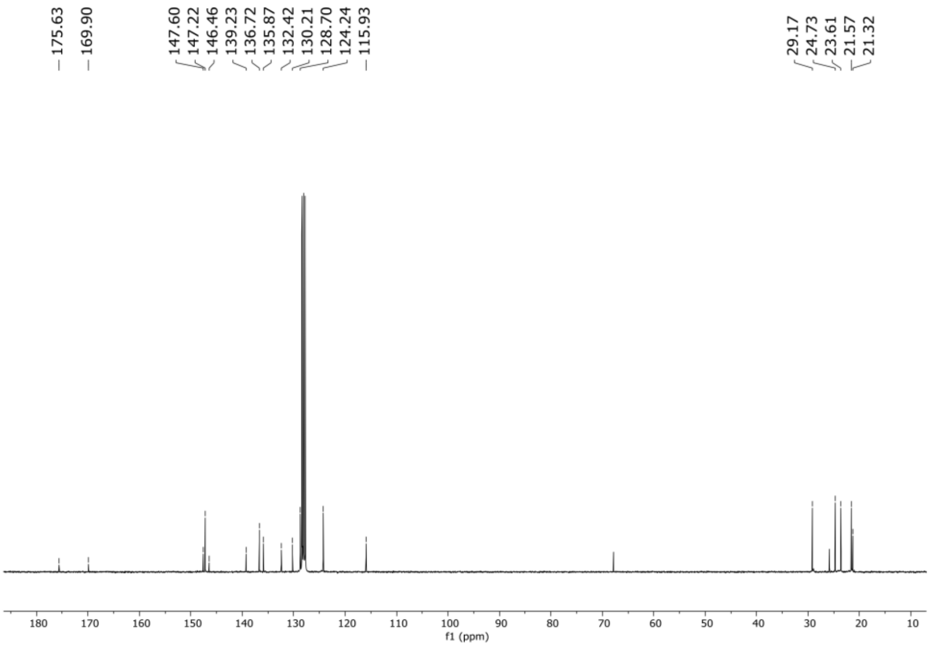


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2** in C_6D_6 at 298 K.

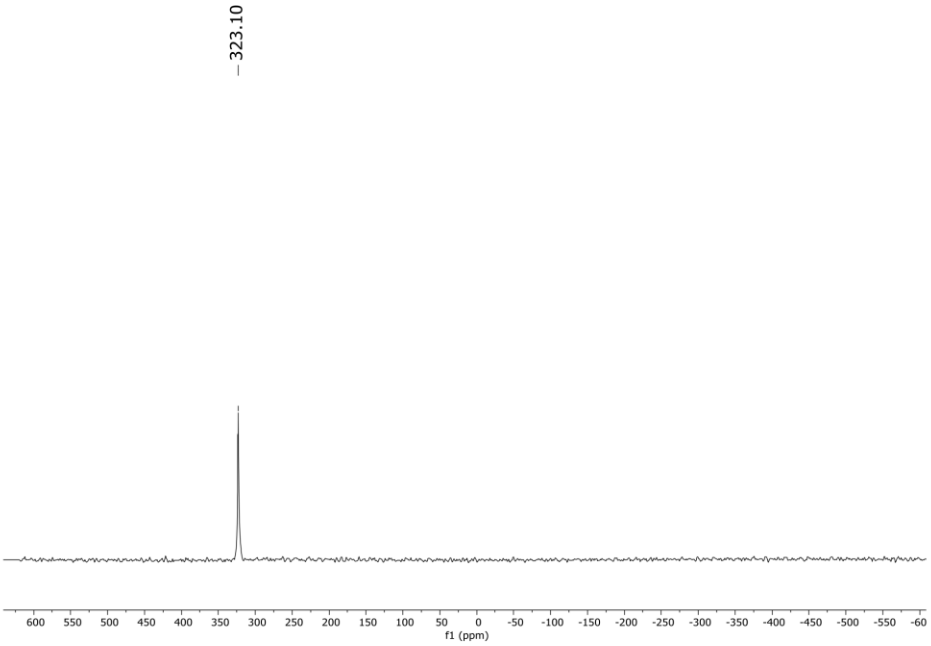


Figure S6. $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **2** in C_6D_6 at 298 K.

1.4 Spectra of Compound 3

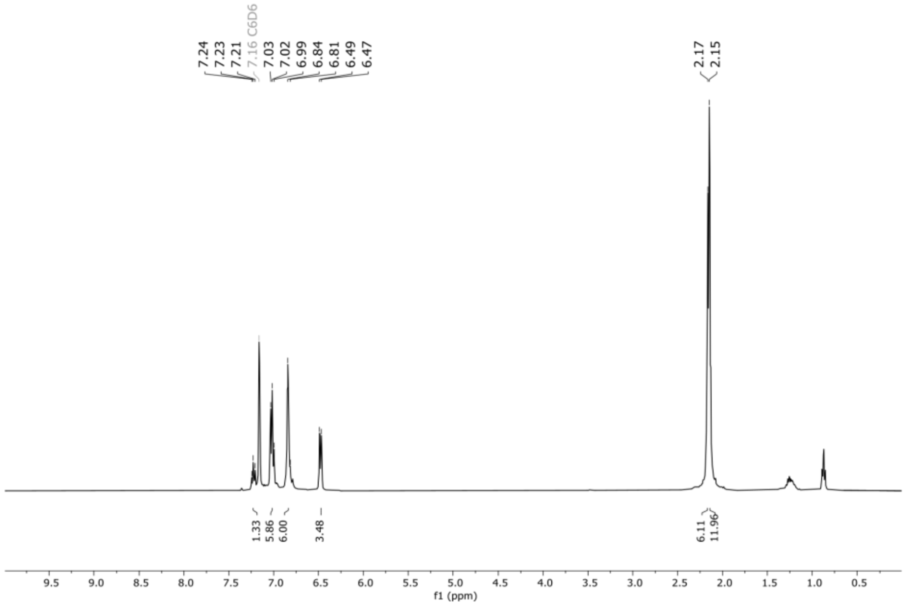


Figure S7. ^{1}H NMR spectrum of compound **3** (in C_6D_6 at 298 K).

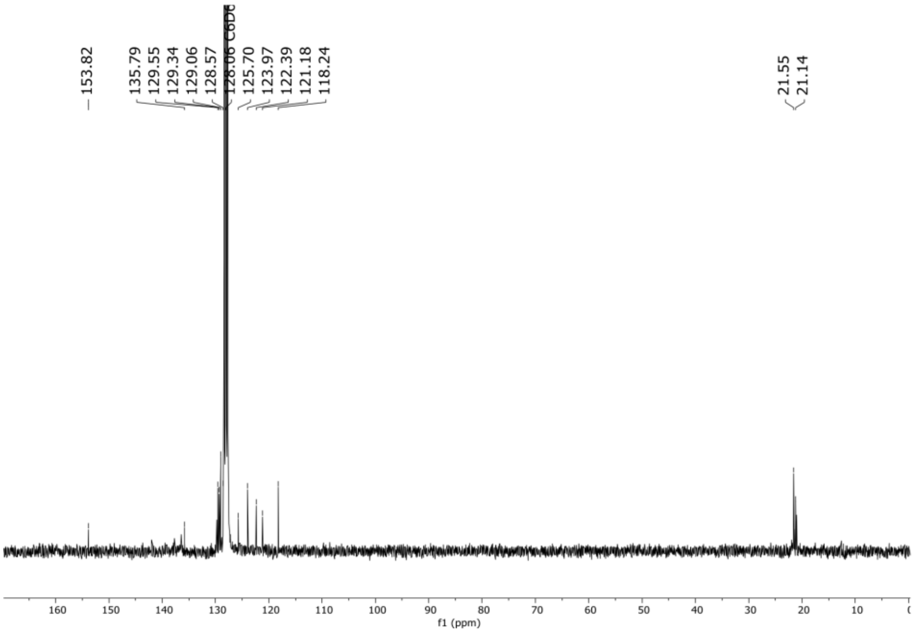


Figure S8. ^{13}C NMR spectrum of compound **3** (in C_6D_6 at 298 K).

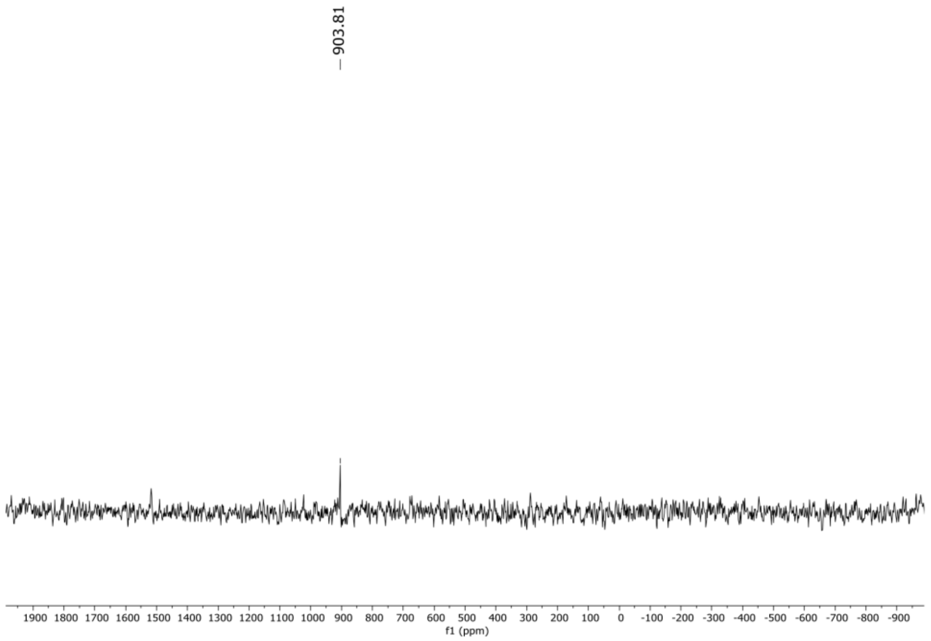


Figure S9. ^{119}Sn NMR spectrum of compound **3** (in C_6D_6 at 298 K).

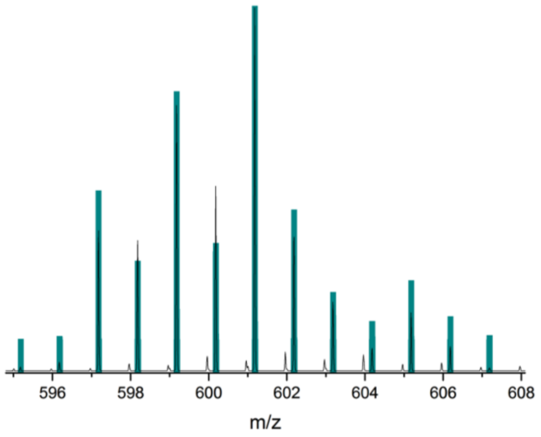


Figure S10. Measured (black) and calculated (teal) LIFDI-MS for **3**.

1.5 Spectra of Adduct-formation upon Reaction of 3 with CO_2

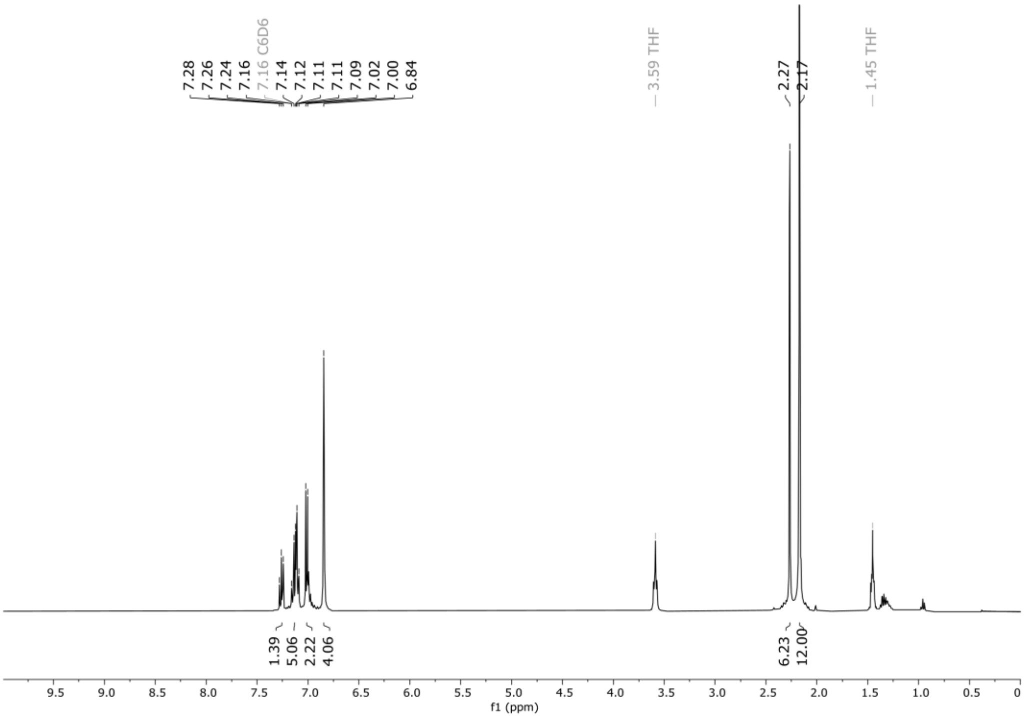


Figure S11. ^1H NMR spectrum of the reaction of compound **3** with CO_2 (in C_6D_6 at 298 K).

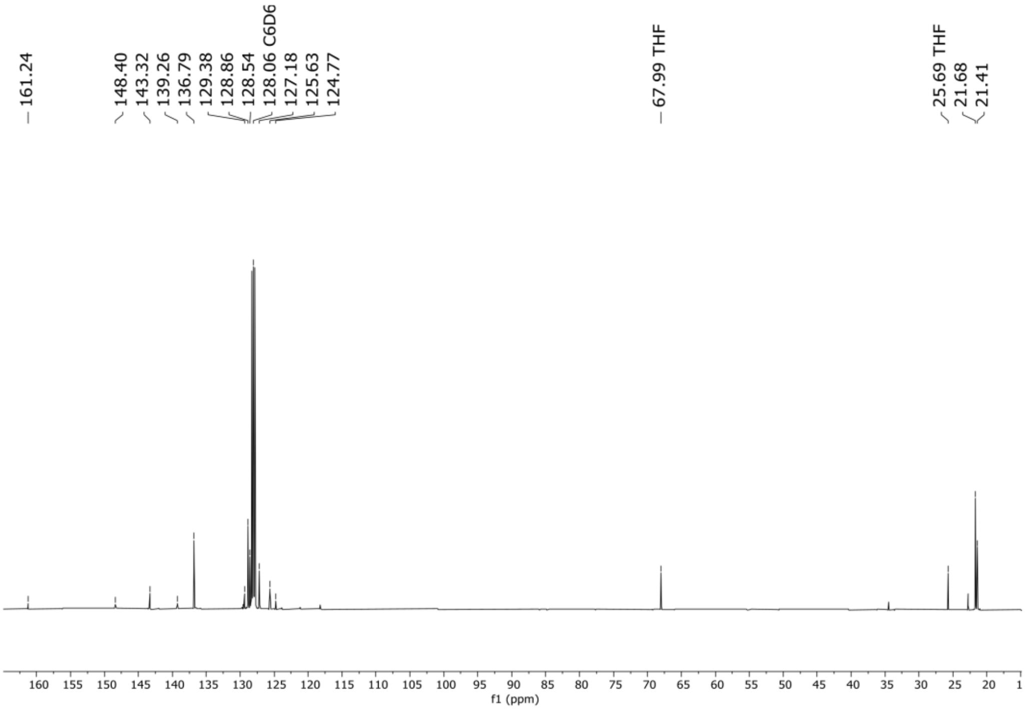


Figure S12. ^{13}C NMR spectrum of the reaction of compound **3** with CO_2 (in C_6D_6 at 298 K).

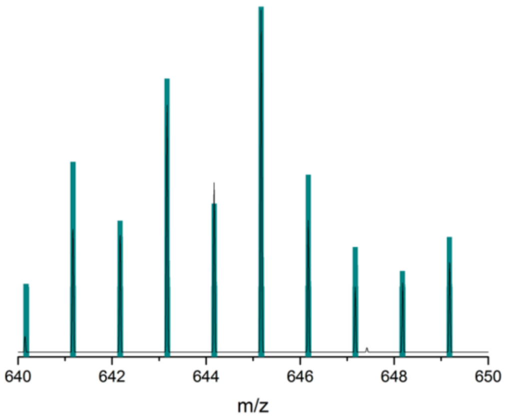
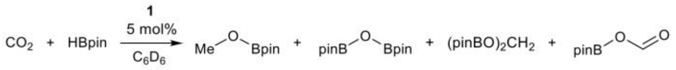


Figure S13. Measured (black) and calculated (teal) LIFDI-MS of CO_2 adduct with **3**.

1.6 Catalytic Hydroboration of CO_2 by ^{Mes}Ter[N(IDipp)]Sn

All catalytic reactions were performed according to the following procedure. As an internal standard, 0,33 equivalents of 1,3,5-Methoxybenzene were added before the start of the reaction, with the characteristic signal at 6.25 ppm in C_6D_6 (6.07 ppm in THF-d_8 respectively) chosen for referencing product yields. Identity of pinBO(C=O)H[S3], pinBO(CH_2)OBpin[S4], MeOBpin[S3b, 5] and pinBOBpin[S3b, 5] were determined by ^{1}H- and ^{11}B-NMR.



2,9 mg of ^{Mes}Ter[N(IDipp)]Sn (0.003 mmol, 0,05 eq.) were dissolved in 0,4 ml of the respective deuterated solvent in a *J-young* NMR tube. Then, 10 µl of HBpin (8.82 mg, 0.063 mmol, 1.0 eq.) and 0.046 ml of a 0.5 M solution of 1,3,5-Methoxybenzene in C_6D_6 (0.023 mmol, 0.33 eq.) were added. The NMR tube was freeze-pump-thaw degassed two times before being refilled with 1 bar of CO_2. For respective solvent and temperature conditions see Table **S1** below.

Table S1. Overview of reaction conditions of performed Hydroboration reactions. All Reactions were performed with 2,9 mg of ^{Mes}Ter[N(IDipp)]Sn (0.003 mmol), 10 µl of HBpin (8.82 mg, 0.063 mmol, 1.0 eq.) and 0,046 ml of a 0,5 M solution of 1,3,5-Methoxybenzene in C_6D_6 as internal standard. [a] Overall conversion calculated from ^{11}B NMR, due to too much overlap in methyl region of ^{1}H spectra.

Entry	Catalyst Loading [mol%]	Temperature [°C]	Solvent	Time [h]	Conversion[a] [%]
1	5	25	C_6D_6	24	48.87
2	5	25	THF-d_8	24	94.94
3	5	50	THF-d_8	6	96.81

Catalysis in C_6D_6 at 25 °C

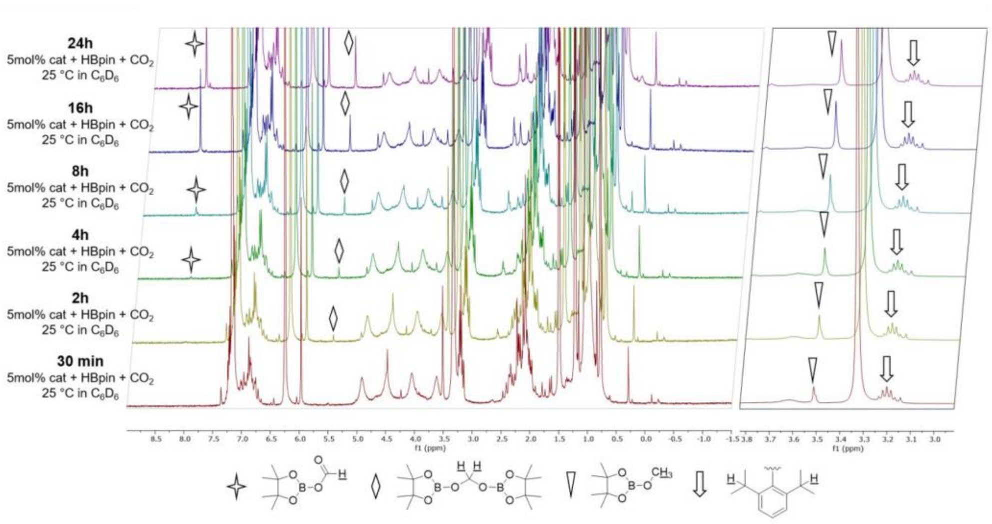


Figure S14. Stacked ^{1}H NMR spectra, compound **1** (5.0 mol%) in C_6D_6, with HBpin (8.8 mg), 25° C and CO_2 (1 bar). ***Left:*** Full spectra with pinBO(C=O)H and pinBO(CH_2)OBpin assigned. ***Right:*** truncated spectra with pinBOMe and characteristic signal of isopropyl protons of [N(IDipp)] moiety of the active catalyst assigned. full conversion reaction time was not measured. pinBOBpin cannot be unambiguously identified in the ^{1}H NMR due to too much overlap in the methyl region.

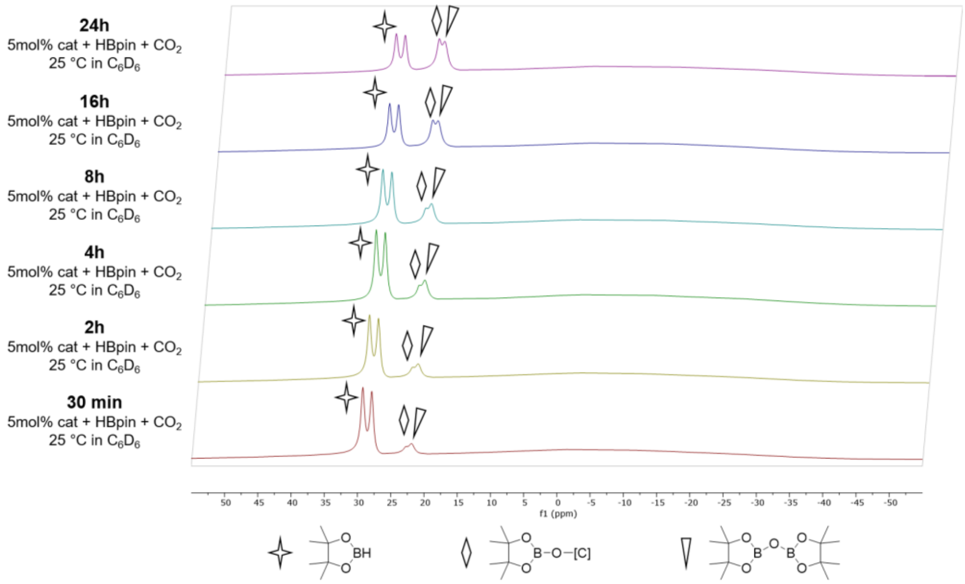


Figure S15. Stacked ^{11}B NMR spectra, compound **1** (5.0 mol%) in C_6D_6, with HBpin (8.8 mg), 25° C and CO_2 (1 bar), full conversion reaction time was not measured.

Table S2. Product distribution in % over time in the catalytic CO_2 reduction by **1**. Reaction conditions: (5.0 mol%) **1** in C_6D_6, with HBpin (10.0 μl), 25° C and CO_2 (1 bar). Individual product yields were calculated based on 1,3,5-trimethoxybenzene as internal standard. [a] Overall conversion calculated from ^{11}B-NMR, due to overlap in methyl region of ^{1}H-NMR spectra.

Reaction Time	Conversion[a] [%]	pinBOMe [%]	H(CO)OBpin [%]	$CH_2(OBpin)_2$ [%]	$O(Bpin)_2$ [%]
30 min	15.68	4.73	-	-	10.90
2h	19.90	5.37	-	0.13	14.36
4h	24.26	7.39	-	0.27	16.53
8h	28.85	8.02	0.34	0.50	19.96
16h	42.26	9.59	5.15	1.22	25.97
24h	48.87	9.77	6.09	2.07	27.63

Catalysis in THF-d₈ at 25 °C

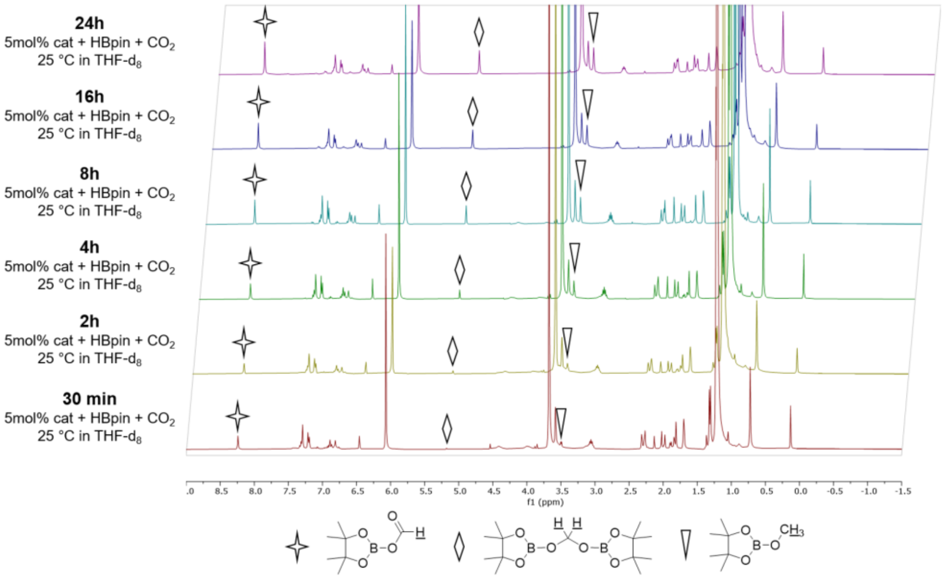


Figure S16. Stacked ^{1}H NMR spectra, compound **1** (5.0 mol%) in THF-d$_8$, with HBpin (8.8 mg), 25° C and CO$_2$ (1 bar). PinBOBpin cannot be unambiguously identified in the ^{1}H NMR due to too much overlap in the methyl region.

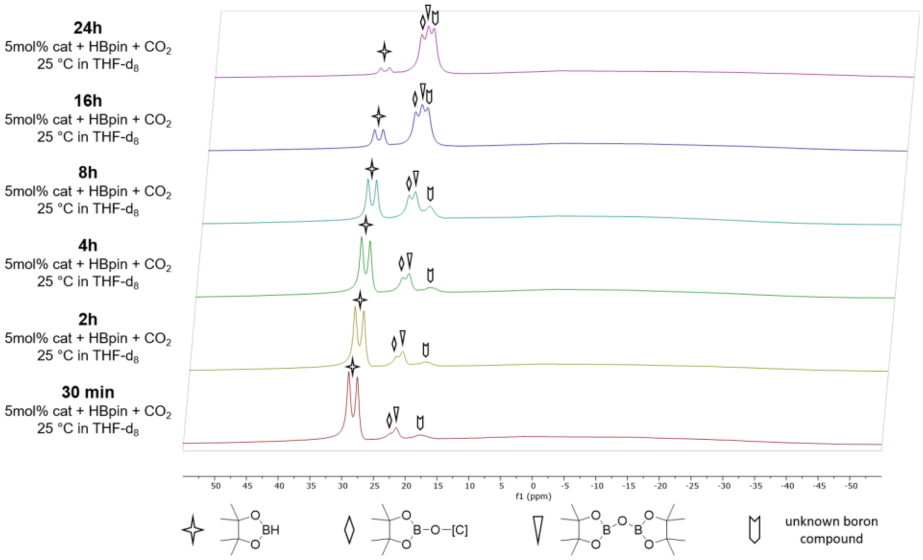


Figure S17. Stacked ^{11}B NMR spectra, compound **1** (5.0 mol%) in THF-d$_8$, with HBpin (8.8 mg), 25° C and CO$_2$ (1 bar).

Table S3. Product distribution over time in the catalytic CO_2 reduction by **1**. Reaction conditions: (5.0 mol%) **1**, with HBpin (10.0 µl), and CO_2 (1 bar), in THF-d_8 at 25 C. HBpin conversion and Product yields are given in [%] and were calculated based on 1,3,5-trimethoxybenzene as internal standard. [a] Overall conversion calculated from ^{11}B-NMR, due to overlap in methyl region of ^{1}H-NMR spectra.

Reaction Time	Conversion[a] [%]	pinBOMe [%]	H(CO)OBpin [%]	$CH_2(OBpin)_2$ [%]	$O(Bpin)_2$ [%]
30 min	26.88	-	10.51	0.19	-
2h	31.52	6.46	10.89	1.82	-
4h	35.19	6.77	11.13	2.65	14,84
8h	66.07	7.56	14.53	5.42	21,41
16h	87.69	11.69	23.03	9.60	23,33
24h	94.94	13.13	27.04	10.85	29,40

Catalysis in THF-d_8 at 50 °C

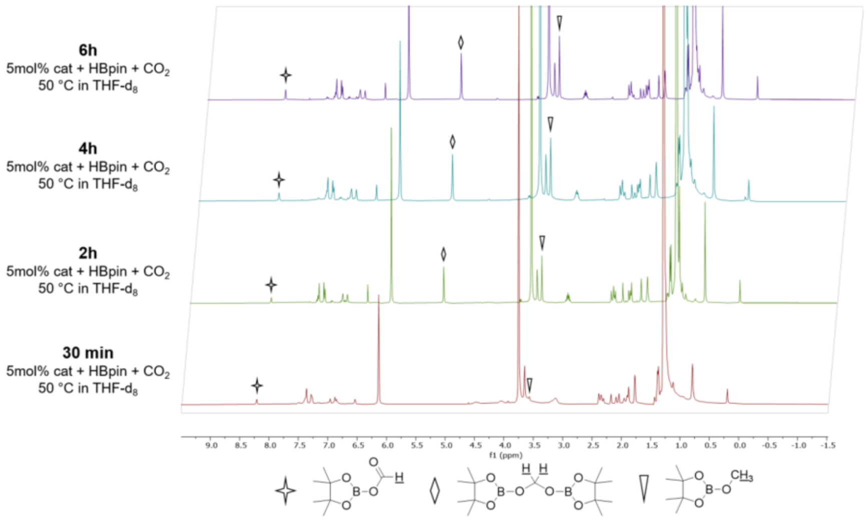


Figure S18. Stacked ^{1}H NMR spectra, compound **1** (5.0 mol%) in THF-d_8, with HBpin (8.8 mg), 50° C and CO_2 (1 bar). PinBOBpin cannot be unambiguously identified in the ^{1}H NMR due to too much overlap in the methyl region.

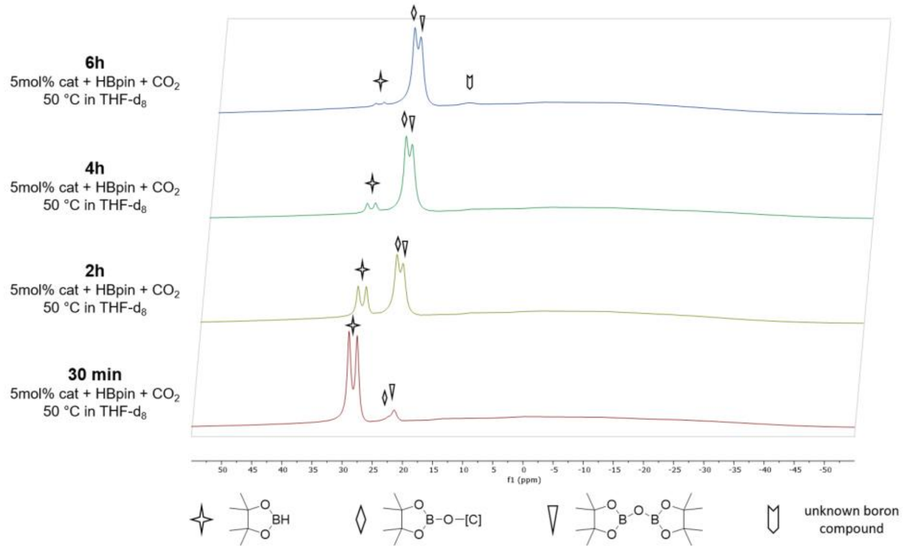


Figure S19. Stacked ^{11}B NMR spectra, compound 1 (5.0 mol%) in THF-d_8, with HBpin (8.8 mg), 50° C and CO_2 (1 bar).

Table S4. Product distribution over time in the catalytic CO_2 reduction by **1**. Reaction conditions: (5.0 mol%) **1** in THF-d_8, with HBpin (10.0 µl), 50 °C and CO_2 (1 bar). Product yields were calculated based on 1,3,5-trimethoxybenzene as internal standard. [a] HBpin conversion calculated as sum of product yields. [a] Overall conversion calculated from ^{11}B-NMR, due to overlap in methyl region of ^{1}H-NMR spectra.

Reaction Time	Conversion[a] [%]	pinBOMe [%]	H(CO)OBpin [%]	$CH_2(OBpin)_2$ [%]	$O(Bpin)_2$ [%]
30 min	14.38	7,07	5.22	0,20	-
2h	73.23	13,38	5,60	14.36	32.53
4h	91.83	20.50	8,00	18.75	36.68
6h	96.81	20.82	8,78	19.10	37.47

2. X-Ray Crystallography

2.1 General Information

Single crystal diffraction data were recorded on a Bruker instrument equipped with a Helios optic monochromator, a Mo IMS microsource (λ = 0.71073 Å) and a CMOS plate or Photon area detector. The data collection was performed, using the APEX III software package[S6] on single crystals coated with Fomblin ® Y as perfluorinated ether. The single crystals were picked on a micro sampler, transferred to the diffractometer and measured frozen under a stream of cold nitrogen (100 K). A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT.[S7] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[S7] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using the APEX III software in conjunction with SHELXL-2014[S8] and SHELXLE.[S9] H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 and 0.95 Å, respectively, and Uiso(H) = 1.2·Ueq(C). Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme.[S10] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.[S11] The images of the crystal structures were generated by Mercury.[S12] The CCDC numbers CCDC-2166130 to CCDC-2166132 contain the supplementary crystallographic data for the structures **1** to **3**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

2.2 Crystal Data and Structure Refinement for Compound 1, 2, and 3

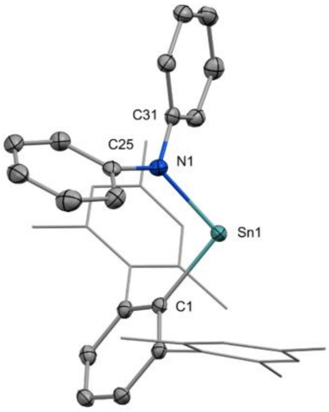


Figure S20. Molecular structures of compound **3** in the solid state. Ellipsoids are set at 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1-C1 2.202(2), Sn1-N1 2.118(2), N1-C25 1.416(2), N1-C31 1.402(2), C1-Sn1-N1 98.63(7).

Table S5. Crystal data and structure refinement for compound 1, 2, and 3.

Compound #	**1**	**2**	**3**
CCDC Number	2166130	2166131	2166132
Chemical formula	C51 H61 N3 Sn	C52 H61 N3 O2 Sn, 2(C7 H8)	C36 H35 N Sn
Formula weight	834.74 g mol^{-1}	1063.02 g/mol	600.36 g/mol
Temperature	100 K	100 K	100 K
Wavelength	0.71073 Å	0.71073 Å	1.54178 Å
Crystal size	0.199 x 0.187 x 0.126 mm	0.328 x 0.264 x 0.200 mm	0.228 x 0.195 x 0.117 mm
Crystal habit	clear orange fragment	clear colourless fragment	clear red fragment
Crystal system	triclinic	triclinic	triclinic
Space group	*P* −1	*P* −1	*P* −1
Unit cell dimensions	a = 10.5490(13) Å; α = 86.474(4)°	a = 12.235(3) Å; α = 89.851(7)°	a = 9.833(6) Å; α = 109.69(2)°
	b = 11.1754(10) Å; β = 88.379(4)°	b = 12.398(3) Å; β = 89.874(7)°	b = 12.487(7) Å; β = 105.32(3)°
	c = 20.812(3) Å; γ = 63.707(3)°	c = 19.346(4) Å; γ = 75.165(7)°	c = 14.536(9) Å; γ = 97.02(2)°
Volume	2195.5(5) Å^3	2836.8(11) Å^3	1576.3(17) Å^3
Z	2	2	2
Density (calculated)	1.263 g/cm^3	1.245 g/cm^3	1.265 g/cm^3
Radiation source	IMS microsource	IMS microsource	IMS microsource
Theta range for data collection	2.04 to 25.35°	2.00 to 25.35°	2.21 to 25.35°
Index ranges	−12<=h<=12, −13<=k<=13, −25<=l<=25	−14<=h<=14, −14<=k<=14, −22<=l<=23	−11<=h<=11, −15<=k<=15, −17<=l<=17
Reflections collected	36727	116862	58406
Independent reflections	8019	10376	5763
Completeness	0.998	0.999	0.999
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	0.7452 and 0.6355	0.7453 and 0.7073	0.7453 and 0.6860
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Function minimized	Σ w(F$_o^2$ - F$_c^2$)^2	Σ w(F$_o^2$ - F$_c^2$)^2	Σ w(F$_o^2$ - F$_c^2$)^2
Data / restraints / parameters	8019 / 0 / 510	10376 / 0 / 664	5763 / 0 / 349
Goodness-of-fit on F^2	0.963	0.992	0.988
Final R indices [I>2sigma(I)]	R1 = 0.0343, wR2 = 0.0726	R1 = 0.0225, wR2 = 0.0603	R1 = 0.0189, wR2 = 0.0492
R indices (all data)	R1 = 0.0542, wR2 = 0.0811	R1 = 0.0237, wR2 = 0.0613	R1 = 0.0198, wR2 = 0.0498
Largest diff. peak and hole	0.576 and −0.564 eÅ^{-3}	0.339 and −0.329 eÅ^{-3}	0.879 and −0.300 eÅ^{-3}

3. Computations

All calculations were performed with ORCA v4.2.1, except the ones depicted in Scheme S2 (Table S6, respectively), which were run with ORCA v5.0.3.[S10]

The geometric parameters of all compounds were optimized without constraints using the PBE0 functional,[S13] with dispersion correction D3(BJ)[S14] and the def2-SVP basis set.[S15] PBE0 has been chosen, since it is a robust functional with good performance for structural parameters of main-group compounds in combination with reasonable barrier heights at reasonable computational cost and convergence.[S16] For tin, the def2-ECP was used.[S17] The RIJCOSX approximation[S18] was used in combination with the def/J[S18] auxiliary basis set. Tighter than default scf ("*tightscf*") and optimization criteria ("*tightopt*") were chosen in conjunction with finer than default grid values ("*grid5*"; "*nofinalgrid*"; "*gridx4*"). The optimized geometric parameters were verified as true minima by the absence of negative eigenvalues in the harmonic vibrational frequency analysis. The connectivity of all transition states with the respective ground states was verified through following the imaginary modes to the respective ground states. A plethora of further isomers and transition states were calculated, turned out to be considerably higher in energy, and are consequently not shown for clarity. For refinement of the electronic energies, single-point calculations were performed at the DLPNO-CCSD(T)[S19] level of theory using "*normalpno*" and frozen-core settings and the def2-TZVPP basis set for all atoms ("*def2/J*", "*def2-TZVPP/C*", "*RIJCOSX*", "*tightscf*).[S15, 20] PBE0-D3BJ(SMD)/def2-TZVPP single-points with likewise tightened convergence criteria ("*tightscf*"; "*grid6*", "*finalgrid7*") were used to account for solvation effects in benzene using the SMD model.[S21] This approach follows the suggested procedure by Neese and colleagues prior to inclusion of PCM in DLPNO-CCSD.[S22] Note that the potential energy surface is very flat for a couple of transitions states (*vide infra*) and, thus, some transitions states could not be located.

DLPNO-CCSD(T) energies have been reported to overestimate reaction barriers, particularly for large molecules.[S23] This seems to be also the case herein (the rate determining transition state is calculated at $\Delta G^{\ddagger}$ = 112.5+12.5 kJ = 125.0 mol^{-1}; PBE0-D3(SMD)/def2-TZVPP//PBE0-D3/def2-SVP predicts $\Delta G^{\ddagger}$ = 82+33 kJ mol^{-1}= 115.0 kJ mol^{-1}, which is better in agreement with the experiment (slow reaction at room temperature). That said, both energy profiles (*cf.* Fig. Scheme S6) are consistent. Overall, we chose to show the DLPNO-CCSD(T) values in the main manuscript for clarity.

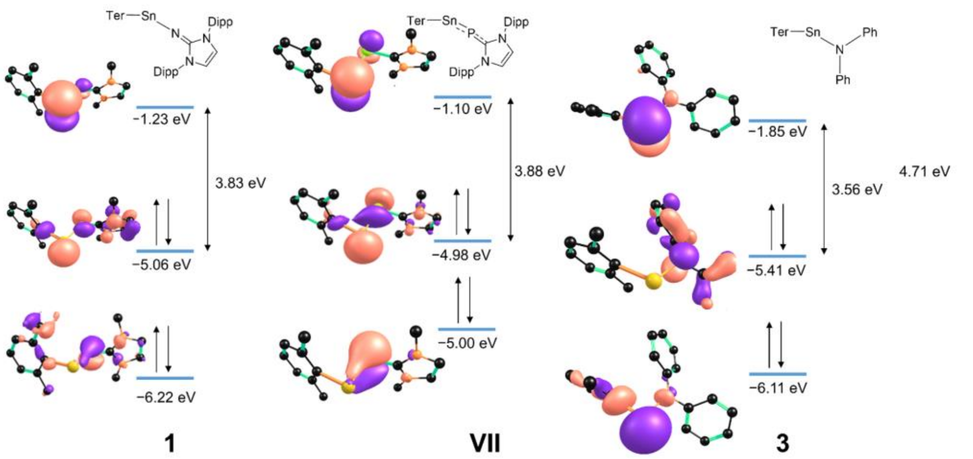
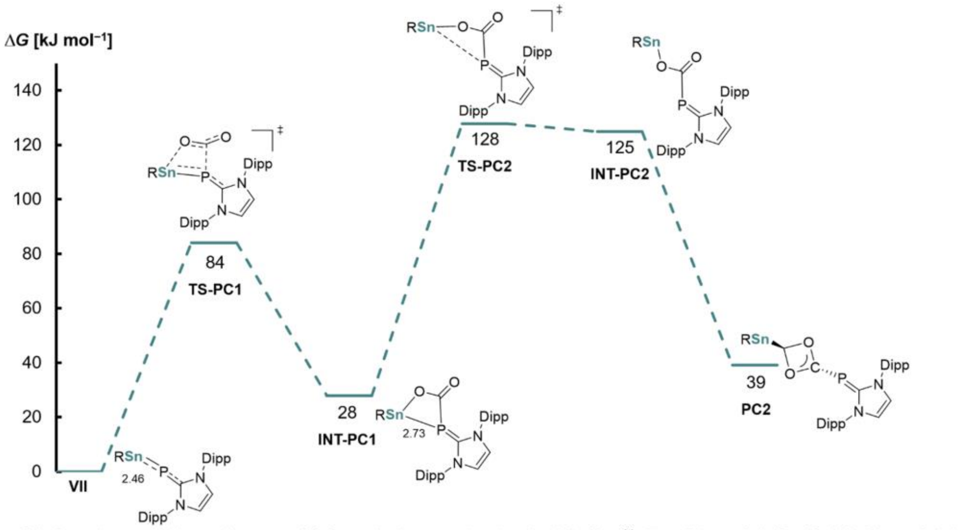
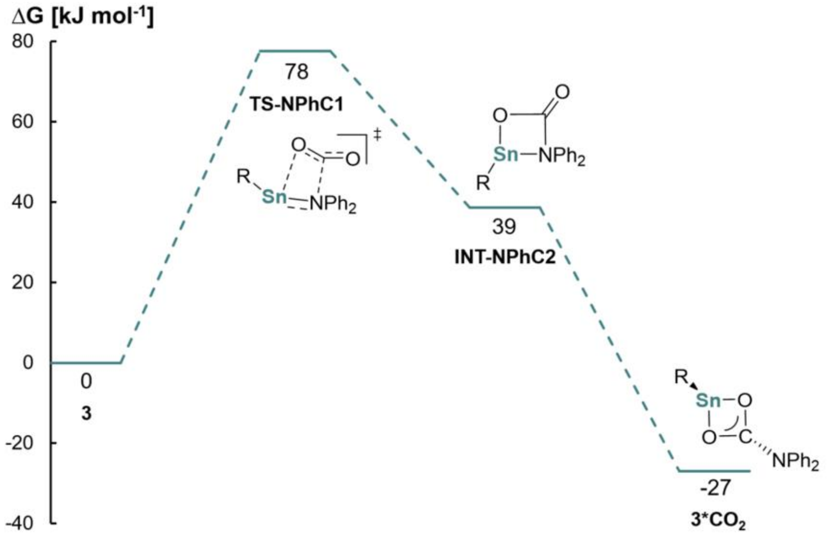


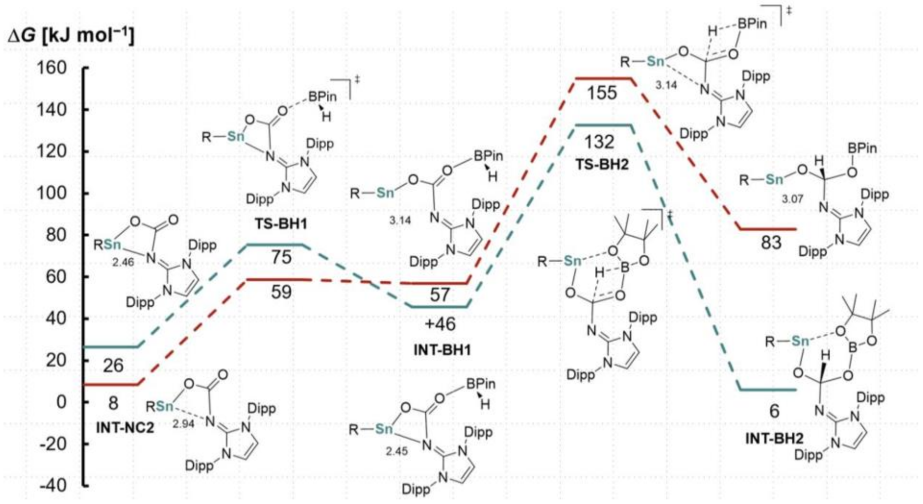
Figure S21. Frontier orbitals of **1** (left), **VII** (middle) and **3** (right). Ter-substituents are truncated for clarity in this Figure, yet were included in the calculations.



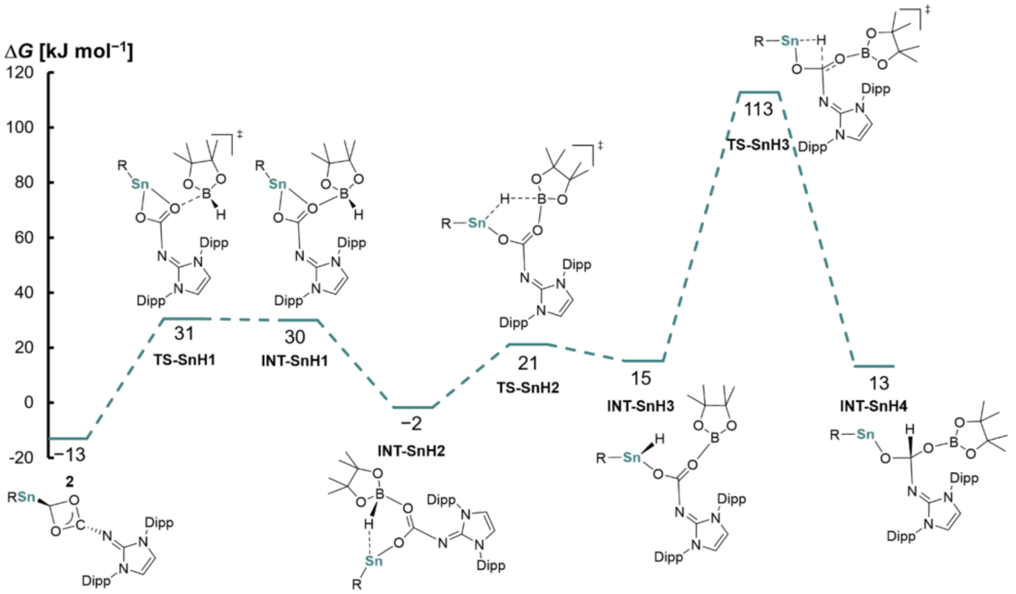
Scheme S1. Reaction coordinate diagram of CO_2 activation mechanism by **VII**. (R = ^{Mes}Ter, Dipp = 2,6-iPr$_2$(C$_6$H$_3$), Mes = 2,4,6-Me$_3$(C$_6$H$_2$), MesTer = 2,6-Mes$_2$C$_6$H$_3$).



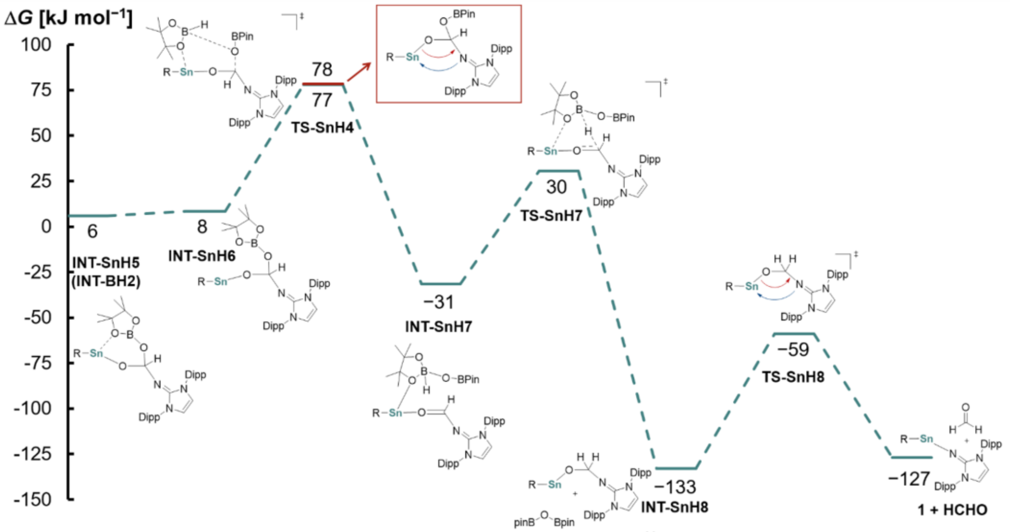
Scheme S2. Reaction coordinate diagram of CO_2 activation mechanism by **3**. (R = ^{Mes}Ter, ^{Mes}Ter = 2,6-$Mes_2C_6H_3$).



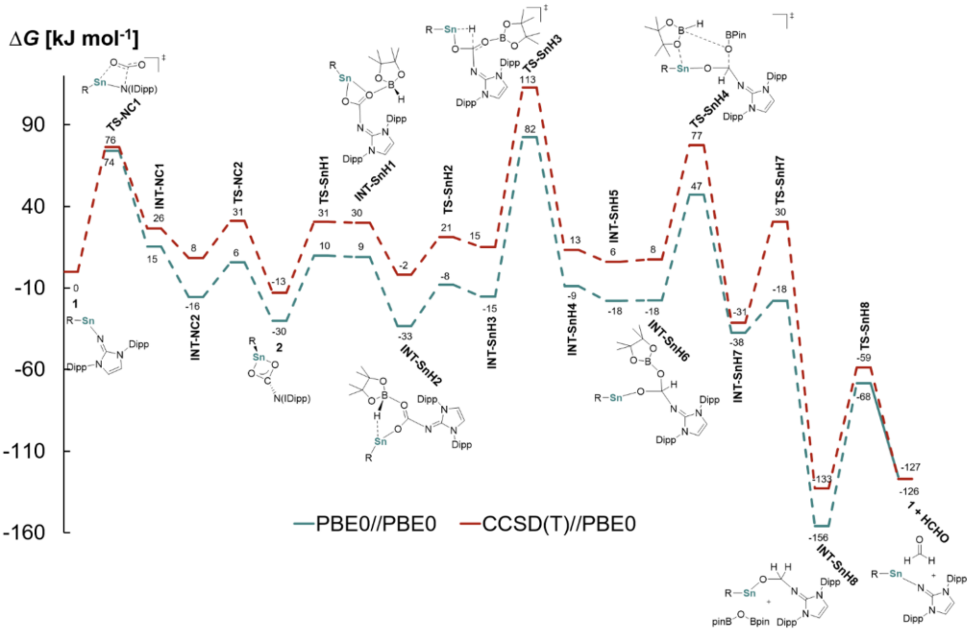
Scheme S3. Reaction coordinate diagram of direct hydride transfer from borohydride. (R = ^{Mes}Ter, Dipp = 2,6-$iPr_2(C_6H_3)$, Mes = 2,4,6-$Me_3(C_6H_2)$, MesTer = 2,6-$Mes_2C_6H_3$).



Scheme S4. Reaction coordinate diagram of hydride transfer via transient stanna-hydride. (R = ^{Mes}Ter, Dipp = 2,6-iPr$_2$(C$_6$H$_3$), Mes = 2,4,6-Me$_3$(C$_6$H$_2$), MesTer = 2,6-Mes$_2$C$_6$H$_3$).



Scheme S5. Reaction coordinate diagram of reduced product release. (R = ^{Mes}Ter, Dipp = 2,6-iPr$_2$(C$_6$H$_3$), Mes = 2,4,6-Me$_3$(C$_6$H$_2$), MesTer = 2,6-Mes$_2$C$_6$H$_3$, pin = pinacolato).



Scheme S6. Comparison of computational methods for the whole mechanism: PBE0(SMD)//PBE0 *vs.* DLPNO-CCSD(T)(SMD)//PBE0.

Energies:

Table S3. Energies for structures of small molecules.

	N	*E* [Eh]	*G* [Eh]	*E*(SP) [Eh]	*E*(SMD,SP) [Eh]	*E*(CCSD(T)) [Eh]
CO_2	0	-188.244338	-188.254517	-188.467345	-188.467731	-188.331725
CO	0	-113.096486	-113.109776	-113.231305	-113.226993	-113.15806
BPinH	0	-411.106476	-410.947321	-411.558783	-411.566091	-411.184837
Bpin_OMe	0	-525.485346	-525.295793	-526.067106	-526.075761	-525.603554
Bpin_O_Bpin	0	-896.241482	-895.91635	-897.226822	-897.242083	-896.427501
H2CO	0	-114.284899	-114.278714	-114.420105	-114.422496	-114.336457

Table S4. Energies and imaginary frequencies of structures shown in Scheme 3.

	NImag/ Frequency [cm^{-1}]	*E* [Eh]	*G* [Eh]	*E*(SP) [Eh]	*E*(SMD,SP) [Eh]	*E*(CCSD(T)) [Eh]
1	0	-2354.91507	-2353.99868	-2357.15706	-2357.19466	-2354.23483
TS-NC1	-285	-2543.15454	-2542.22868	-2545.61096	-2545.65014	-2542.5522
TS-NC1isomer	-234	-2543.16005	-2542.23193	-2545.61591	-2545.65456	-2542.55337
INT-NC1	0	-2543.18675	-2542.25608	-2545.63971	-2545.67756	-2542.57753
INT-NC2	0	-2543.19058	-2542.26281	-2545.64514	-2545.6865	-2542.57805
TS_NC2	-29	-2543.18119	-2542.25292	-2545.63613	-2545.67879	-2542.56859
TS-NC2isomer	-12	-2543.16718	-2542.24033	-2545.6238	-2545.66603	-2542.55917
2	0	-2543.2061	-2542.27768	-2545.66019	-2545.69276	-2542.59578

Table S5. Energies and imaginary frequencies of structures shown in Scheme S1.

	***NImag/ Frequency* [cm^{-1}]**	***E* [Eh]**	***G* [Eh]**	***E*(SP) [Eh]**	***E*(SMD,SP) [Eh]**	***E*(CCSD(T)) [Eh]**
VII	-	-2641.39323	-2640.48099	-2643.68745	-2643.72719	-2640.47112
TS-PC1	i261	-2829.62488	-2828.70467	-2832.13588	-2832.17705	-2828.78418
INT-PC1	-	-2829.64889	-2828.72521	-2832.15939	-2832.20141	-2828.80846
TS-PC2	i41	-2829.62143	-2828.69785	-2832.13318	-2832.16618	-2828.77892
INT-PC2	-	-2829.62205	-2828.70028	-2832.13367	-2832.16618	-2828.77872
PC2	-	-2829.64052	-2828.71931	-2832.15298	-2832.19536	-2828.80127

Table S6. Energies and imaginary frequencies of structures shown in Scheme S2.

	***NImag/ Frequency* [cm^{-1}]**	***E* [Eh]**	***G* [Eh]**	***E*(SP) [Eh]**	***E*(SMD,SP) [Eh]**	***E*(CCSD(T)) [Eh]**
3	-	-1659.27249	-1658.73127	-1660.89953	-1660.93377	-1658.69054
TS-NArC1	i264	-1847.50393	-1846.95246	-1849.35534	-1849.38916	-1847.01019
INT-NArC1	-	-1847.51879	-1846.96598	-1849.36931	-1849.40723	-1847.02241
INT-NArC2	-	-1847.55705	-1847.00558	-1849.39661	-1849.434	-1847.04686

Table S7. Energies and imaginary frequencies of structures shown in Scheme S3.

	***NImag/ Frequency* [cm^{-1}]**	***E* [Eh]**	***G* [Eh]**	***E*(SP) [Eh]**	***E*(SMD,SP) [Eh]**	***E*(CCSD(T)) [Eh]**
TS-BH1	i100	-2954.30304	-2953.19073	-2957.20218	-2957.24675	-2953.7632
INT-BH1	-	-2954.31425	-2953.20028	-2957.21067	-2957.25668	-2953.77492
TS-BH2	i746	-2954.28902	-2953.17863	-2957.18521	-2957.23098	-2953.73812
INT-BH2	-	-2954.33609	-2953.21992	-2957.23461	-2957.27934	-2953.79361
TS-BH1isomer	i77	-2954.31445	-2953.20088	-2957.21449	-2957.25895	-2953.77102
INT-BH1isomer	-	-2954.31852	-2953.20364	-2957.2163	-2957.2614	-2953.77243
TS-BH2isomer	i656	-2954.27961	-2953.16929	-2957.17768	-2957.2241	-2953.72879
INT-BH2isomer	-	-2954.32927	-2953.19073	-2957.22832	-2957.27142	-2953.78812

Table S8. Energies and imaginary frequencies of structures shown in Scheme S4.

	***NImag/ Frequency* [cm^{-1}]**	***E* [Eh]**	***G* [Eh]**	***E*(SP) [Eh]**	***E*(SMD,SP) [Eh]**	***E*(CCSD(T)) [Eh]**
TS-SNH1	i70	-2954.32492	-2953.21124	-2957.22321	-2957.26617	-2953.78347
INT-SnH1	-	-2954.32558	-2953.21243	-2957.22303	-2957.26606	-2953.78305
INT-SnH2	-	-2954.34214	-2953.22850	-2957.23751	-2957.28314	-2953.79316
TS-SnH2	i23	-2954.3351	-2953.22281	-2957.23226	-2957.27846	-2953.78929
INT-SnH3	-	-2954.32791	-2953.21526	-2957.22622	-2957.27483	-2953.7827
TS-SnH3	i859	-2954.29359	-2953.18119	-2957.19326	-2957.237	-2953.74972
INT-SnH4	-	-2954.33078	-2953.21627	-2957.23049	-2957.27424	-2953.79015

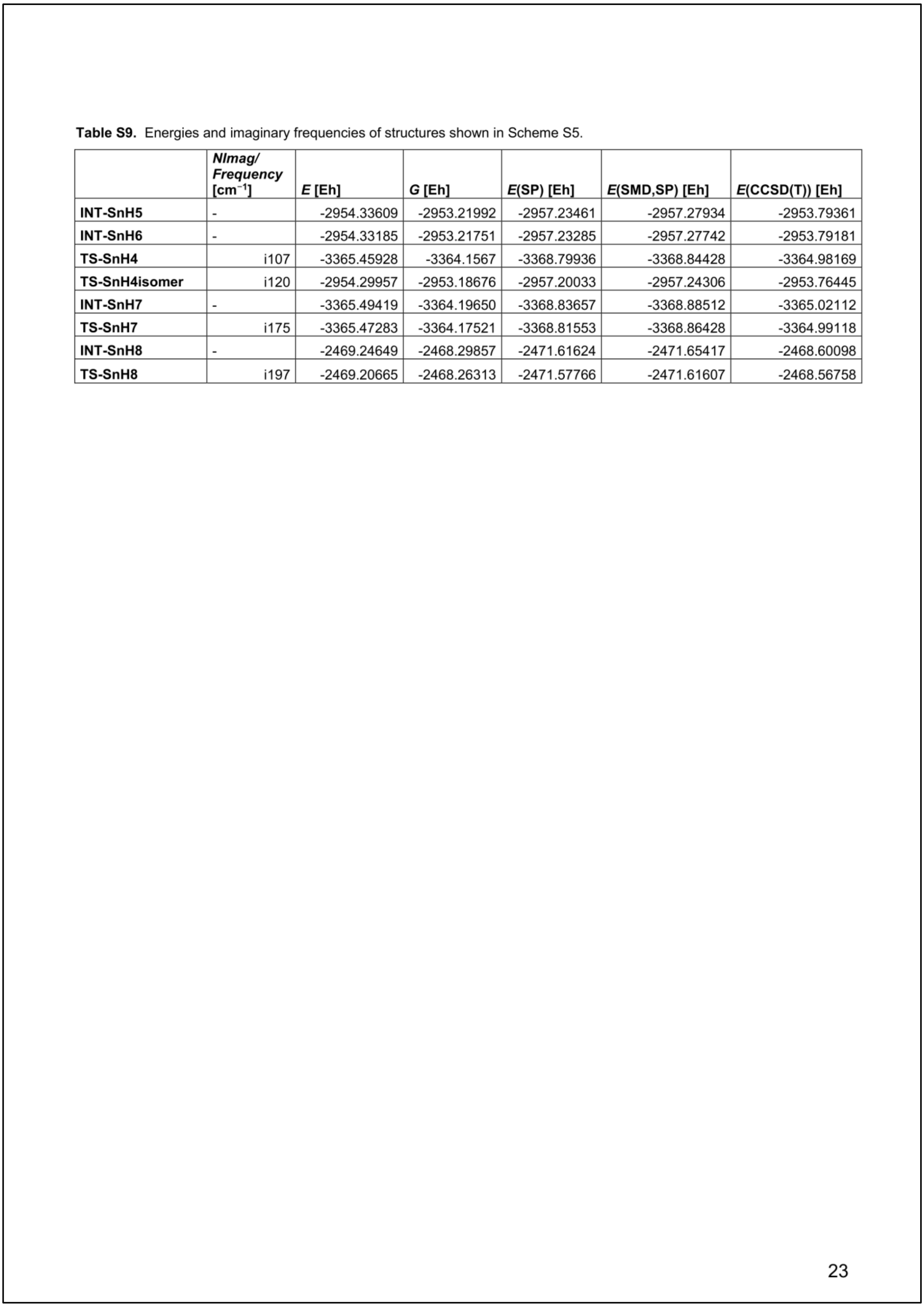
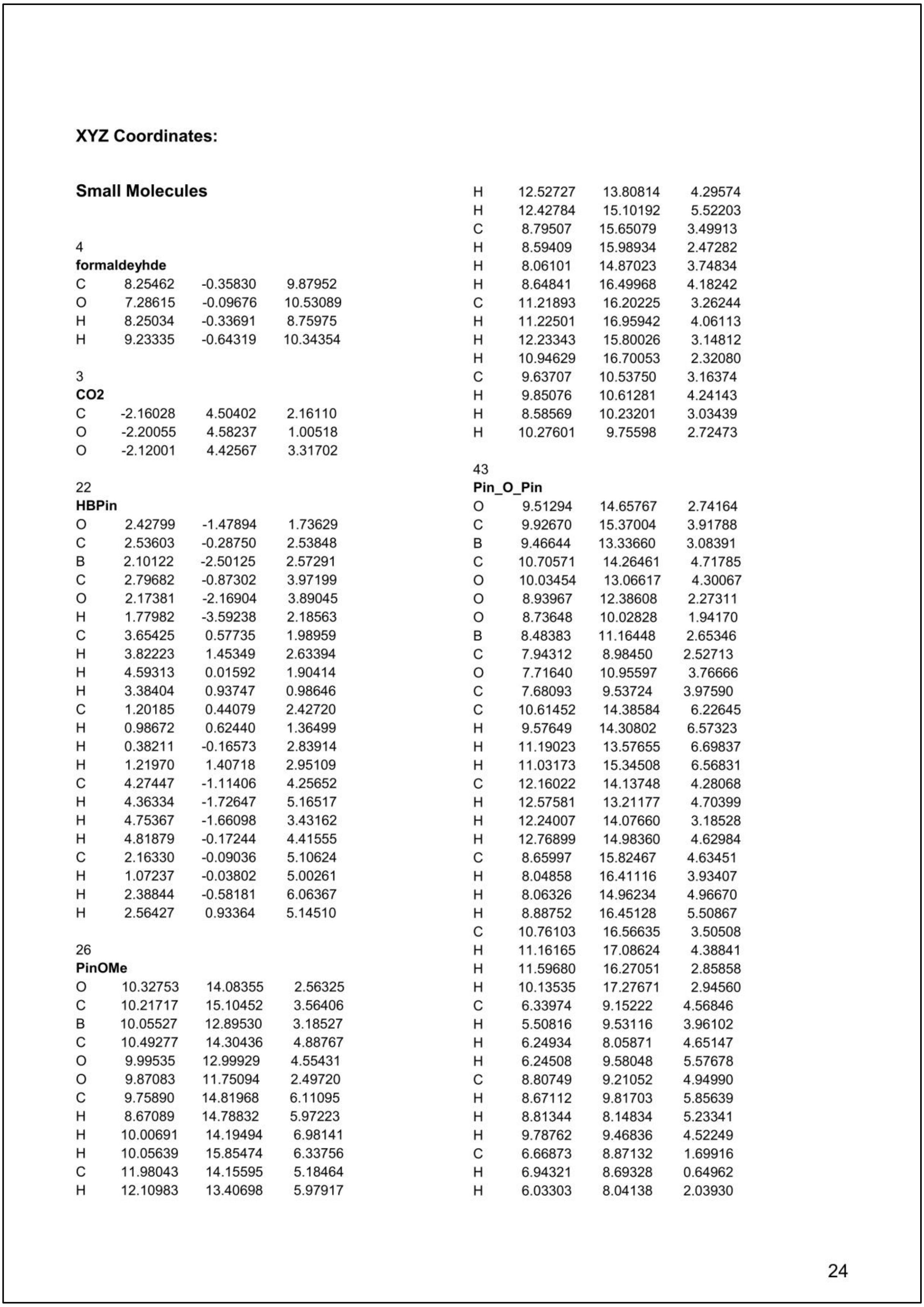


Table S9. Energies and imaginary frequencies of structures shown in Scheme S5.

	NImag/ Frequency [cm^{-1}]	*E* [Eh]	*G* [Eh]	*E*(SP) [Eh]	*E*(SMD,SP) [Eh]	*E*(CCSD(T)) [Eh]
INT-SnH5	-	-2954.33609	-2953.21992	-2957.23461	-2957.27934	-2953.79361
INT-SnH6	-	-2954.33185	-2953.21751	-2957.23285	-2957.27742	-2953.79181
TS-SnH4	i107	-3365.45928	-3364.1567	-3368.79936	-3368.84428	-3364.98169
TS-SnH4isomer	i120	-2954.29957	-2953.18676	-2957.20033	-2957.24306	-2953.76445
INT-SnH7	-	-3365.49419	-3364.19650	-3368.83657	-3368.88512	-3365.02112
TS-SnH7	i175	-3365.47283	-3364.17521	-3368.81553	-3368.86428	-3364.99118
INT-SnH8	-	-2469.24649	-2468.29857	-2471.61624	-2471.65417	-2468.60098
TS-SnH8	i197	-2469.20665	-2468.26313	-2471.57766	-2471.61607	-2468.56758



XYZ Coordinates:

Small Molecules

4

formaldeyhde

C	8.25462	-0.35830	9.87952
O	7.28615	-0.09676	10.53089
H	8.25034	-0.33691	8.75975
H	9.23335	-0.64319	10.34354

3

CO2

C	-2.16028	4.50402	2.16110
O	-2.20055	4.58237	1.00518
O	-2.12001	4.42567	3.31702

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HBPin

O	2.42799	-1.47894	1.73629
C	2.53603	-0.28750	2.53848
B	2.10122	-2.50125	2.57291
C	2.79682	-0.87302	3.97199
O	2.17381	-2.16904	3.89045
H	1.77982	-3.59238	2.18563
C	3.65425	0.57735	1.98959
H	3.82223	1.45349	2.63394
H	4.59313	0.01592	1.90414
H	3.38404	0.93747	0.98646
C	1.20185	0.44079	2.42720
H	0.98672	0.62440	1.36499
H	0.38211	-0.16573	2.83914
H	1.21970	1.40718	2.95109
C	4.27447	-1.11406	4.25652
H	4.36334	-1.72647	5.16517
H	4.75367	-1.66098	3.43162
H	4.81879	-0.17244	4.41555
C	2.16330	-0.09036	5.10624
H	1.07237	-0.03802	5.00261
H	2.38844	-0.58181	6.06367
H	2.56427	0.93364	5.14510

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PinOMe

O	10.32753	14.08355	2.56325
C	10.21717	15.10452	3.56406
B	10.05527	12.89530	3.18527
C	10.49277	14.30436	4.88767
O	9.99535	12.99929	4.55431
O	9.87083	11.75094	2.49720
C	9.75890	14.81968	6.11095
H	8.67089	14.78832	5.97223
H	10.00691	14.19494	6.98141
H	10.05639	15.85474	6.33756
C	11.98043	14.15595	5.18464
H	12.10983	13.40698	5.97917
H	12.52727	13.80814	4.29574
H	12.42784	15.10192	5.52203
C	8.79507	15.65079	3.49913
H	8.59409	15.98934	2.47282
H	8.06101	14.87023	3.74834
H	8.64841	16.49968	4.18242
C	11.21893	16.20225	3.26244
H	11.22501	16.95942	4.06113
H	12.23343	15.80026	3.14812
H	10.94629	16.70053	2.32080
C	9.63707	10.53750	3.16374
H	9.85076	10.61281	4.24143
H	8.58569	10.23201	3.03439
H	10.27601	9.75598	2.72473

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Pin_O_Pin

O	9.51294	14.65767	2.74164
C	9.92670	15.37004	3.91788
B	9.46644	13.33660	3.08391
C	10.70571	14.26461	4.71785
O	10.03454	13.06617	4.30067
O	8.93967	12.38608	2.27311
O	8.73648	10.02828	1.94170
B	8.48383	11.16448	2.65346
C	7.94312	8.98450	2.52713
O	7.71640	10.95597	3.76666
C	7.68093	9.53724	3.97590
C	10.61452	14.38584	6.22645
H	9.57649	14.30802	6.57323
H	11.19023	13.57655	6.69837
H	11.03173	15.34508	6.56831
C	12.16022	14.13748	4.28068
H	12.57581	13.21177	4.70399
H	12.24007	14.07660	3.18528
H	12.76899	14.98360	4.62984
C	8.65997	15.82467	4.63451
H	8.04858	16.41116	3.93407
H	8.06326	14.96234	4.96670
H	8.88752	16.45128	5.50867
C	10.76103	16.56635	3.50508
H	11.16165	17.08624	4.38841
H	11.59680	16.27051	2.85858
H	10.13535	17.27671	2.94560
C	6.33974	9.15222	4.56846
H	5.50816	9.53116	3.96102
H	6.24934	8.05871	4.65147
H	6.24508	9.58048	5.57678
C	8.80749	9.21052	4.94990
H	8.67112	9.81703	5.85639
H	8.81344	8.14834	5.23341
H	9.78762	9.46836	4.52249
C	6.66873	8.87132	1.69916
H	6.94321	8.69328	0.64962
H	6.03303	8.04138	2.03930

H	6.08347	9.80152	1.74342
C	8.72517	7.68641	2.47722
H	9.71982	7.80195	2.92592
H	8.18777	6.88481	3.00596
H	8.86032	7.37599	1.43106

Scheme 2

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3

C	3.19507	-5.61882	10.16110
C	3.37785	-6.86802	10.79015
C	3.33184	-4.44336	10.93071
C	3.64392	-6.94929	12.16167
C	3.60169	-4.54561	12.30367
H	3.77799	-7.92874	12.63006
H	3.70865	-3.63061	12.89304
C	3.74985	-5.78597	12.91836
H	3.96293	-5.84409	13.98884
Sn	3.13698	-5.85819	7.92487
C	3.31786	-8.11704	9.96503
C	4.46406	-8.54432	9.25482
C	2.13624	-8.89399	9.92614
C	4.38265	-9.69668	8.46297
C	2.10667	-10.03880	9.12763
C	3.21303	-10.45247	8.37753
H	5.26994	-10.01845	7.90976
H	1.18722	-10.63128	9.09507
C	3.21785	-3.08244	10.32311
C	4.24933	-2.59053	9.49422
C	2.10161	-2.26579	10.59913
C	4.11331	-1.33011	8.90905
C	1.99929	-1.01781	9.97559
C	2.98473	-0.53435	9.11498
H	4.92021	-0.95704	8.27049
H	1.11868	-0.40023	10.17941
C	5.77725	-7.82362	9.39077
H	6.11737	-7.82760	10.43829
H	6.55207	-8.29795	8.77304
H	5.71397	-6.76389	9.09601
C	0.95008	-8.53292	10.77150
H	0.06878	-9.12520	10.49248
H	1.16406	-8.71870	11.83680
H	0.68834	-7.46951	10.68246
C	3.13483	-11.67714	7.51176
H	2.44844	-11.51875	6.66370
H	4.11799	-11.94728	7.10153
H	2.75107	-12.54149	8.07565
C	5.50591	-3.38004	9.24256
H	5.81231	-3.95763	10.12652
H	5.38793	-4.10050	8.41250
H	6.33256	-2.71305	8.95893
C	2.83238	0.78918	8.42217
H	3.80412	1.28312	8.27402
H	2.37844	0.65958	7.42516
H	2.18334	1.47195	8.98962
C	1.03519	-2.66859	11.58244
H	0.05382	-2.27018	11.28441
H	0.95376	-3.75727	11.69570
H	1.25764	-2.26143	12.58345
N	0.93908	-5.97809	7.40104
C	-0.12173	-6.13388	8.31733
C	-1.10635	-7.12867	8.17418
C	-0.23021	-5.26075	9.41532
C	-2.14900	-7.23966	9.09216
C	-1.27191	-5.38033	10.32781
C	-2.24348	-6.37125	10.17664
H	-1.05511	-7.82252	7.33402
H	0.51875	-4.47819	9.55393
H	-2.89916	-8.02270	8.95123
H	-1.32848	-4.68307	11.16749
H	-3.06454	-6.45852	10.89151
C	0.79713	-6.70402	6.17737
C	1.52360	-7.88086	5.94533
C	-0.07300	-6.25150	5.17250
C	1.41767	-8.56265	4.73303
C	-0.18431	-6.94039	3.96781
C	0.56544	-8.09413	3.73652
H	2.16403	-8.28438	6.73564
H	-0.66588	-5.35304	5.34827
H	2.00330	-9.47190	4.57484
H	-0.86429	-6.56681	3.19781
H	0.48059	-8.62717	2.78661

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INT-NArC1

C	4.50006	-3.36904	8.65201
C	5.22819	-4.52630	8.98691
C	4.37373	-2.33238	9.59553
C	5.77078	-4.65102	10.27322
C	4.92081	-2.47287	10.87641
H	6.33319	-5.55307	10.53155
H	4.81090	-1.66422	11.60505
C	5.61057	-3.63549	11.21411
H	6.03899	-3.74600	12.21374
Sn	3.69687	-2.89763	6.62814
C	5.45334	-5.60182	7.97408
C	6.50427	-5.47835	7.04489
C	4.61399	-6.73370	7.93989
C	6.68146	-6.47940	6.08246
C	4.82642	-7.70733	6.96426
C	5.85186	-7.59868	6.02071
H	7.49929	-6.37886	5.36191
H	4.15745	-8.57286	6.93073
C	3.66915	-1.07500	9.19241
C	4.38148	-0.05509	8.52313
C	2.29718	-0.90319	9.47562
C	3.70037	1.09926	8.12350
C	1.65891	0.26604	9.05705
C	2.33840	1.27740	8.37288
H	4.25714	1.88610	7.60536
H	0.59317	0.38857	9.27271
C	7.45267	-4.31043	7.09019
H	7.93670	-4.22516	8.07559

H	8.23855	-4.41185	6.32874
H	6.94208	-3.34899	6.91843
C	3.49589	-6.89078	8.93001
H	2.86290	-7.75232	8.67590
H	3.87889	-7.03515	9.95317
H	2.85934	-5.99367	8.95927
C	6.04429	-8.65902	4.97405
H	5.13554	-8.78115	4.36294
H	6.87605	-8.41401	4.29838
H	6.25800	-9.63906	5.43035
C	5.85634	-0.18456	8.26115
H	6.41319	-0.37677	9.19104
H	6.08441	-1.02839	7.58917
H	6.25668	0.72824	7.79879
C	1.61667	2.50636	7.89951
H	2.30625	3.35016	7.75290
H	1.11549	2.31986	6.93480
H	0.83934	2.81808	8.61291
C	1.53832	-1.95551	10.23001
H	0.46432	-1.72504	10.25684
H	1.67096	-2.93981	9.75928
H	1.89996	-2.04178	11.26704
N	0.48768	-5.29135	6.58308
C	-0.78508	-4.82912	7.03245
C	-1.88250	-4.92241	6.17065
C	-0.95944	-4.31619	8.32003
C	-3.14135	-4.50524	6.59391
C	-2.21938	-3.88956	8.73295
C	-3.31448	-3.98318	7.87538
H	-1.74079	-5.32923	5.16703
H	-0.10469	-4.24634	8.99226
H	-3.99210	-4.58295	5.91257
H	-2.34552	-3.48750	9.74127
H	-4.30199	-3.65280	8.20594
C	0.57186	-6.61051	6.04690
C	-0.05083	-7.65950	6.73288
C	1.24050	-6.87348	4.84725
C	-0.00191	-8.95556	6.22651
C	1.29376	-8.17463	4.35358
C	0.67483	-9.22082	5.03665
H	-0.57761	-7.45089	7.66653
H	1.73139	-6.06062	4.31356
H	-0.49238	-9.76524	6.77241
H	1.82161	-8.36861	3.41649
H	0.71683	-10.23847	4.64145
C	1.59987	-4.48697	6.66907
O	1.50987	-3.31726	7.15309
O	2.71887	-4.90960	6.25110

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INT-NArC2

C	3.15693	-5.33100	9.93342
C	3.31018	-6.59271	10.54826
C	3.26840	-4.16601	10.72375
C	3.51938	-6.68707	11.92978
C	3.48193	-4.28421	12.10461
H	3.63370	-7.67191	12.39193
H	3.57324	-3.37744	12.70895
C	3.59805	-5.53436	12.70614
H	3.76853	-5.60948	13.78327
Sn	3.10575	-5.39774	7.69445
C	3.28483	-7.84664	9.72800
C	4.44247	-8.25249	9.02805
C	2.12560	-8.65493	9.69108
C	4.39668	-9.41641	8.25129
C	2.12809	-9.80902	8.90440
C	3.24910	-10.20448	8.16692
H	5.29546	-9.72094	7.70664
H	1.22361	-10.42480	8.87430
C	3.20034	-2.80393	10.11432
C	4.25205	-2.34792	9.29130
C	2.09998	-1.95859	10.36549
C	4.15435	-1.09029	8.69183
C	2.03940	-0.71414	9.73385
C	3.04618	-0.26399	8.87975
H	4.97622	-0.74413	8.05705
H	1.16894	-0.07569	9.91459
C	5.72754	-7.47880	9.12844
H	5.96821	-7.23372	10.17359
H	6.56299	-8.04993	8.70048
H	5.67931	-6.51818	8.58659
C	0.91958	-8.31413	10.51741
H	0.05576	-8.92834	10.23011
H	1.11817	-8.48764	11.58758
H	0.63686	-7.25711	10.41823
C	3.21687	-11.45466	7.33448
H	2.40239	-11.42165	6.59326
H	4.16141	-11.60484	6.79313
H	3.04231	-12.34472	7.96019
C	5.49551	-3.16653	9.05513
H	5.72223	-3.83306	9.89868
H	5.41938	-3.80096	8.15093
H	6.36274	-2.51142	8.88672
C	2.92957	1.05223	8.16755
H	3.91687	1.48993	7.95876
H	2.41631	0.92375	7.19977
H	2.34711	1.77999	8.75140
C	0.99442	-2.33819	11.31464
H	0.02879	-1.93776	10.97117
H	0.89996	-3.42488	11.44007
H	1.17881	-1.91937	12.31862
N	0.64272	-5.53093	7.14297
C	-0.37285	-5.83982	8.11278
C	-1.28303	-6.88557	7.93914
C	-0.45281	-5.04835	9.26632
C	-2.25283	-7.13489	8.91096
C	-1.42919	-5.29786	10.22300
C	-2.33531	-6.34622	10.05459
H	-1.24638	-7.50182	7.04061
H	0.25293	-4.22828	9.41101
H	-2.95920	-7.95461	8.75742
H	-1.47883	-4.66417	11.11186
H	-3.10199	-6.54123	10.80758
C	0.57113	-6.28344	5.90748
C	1.16894	-7.54809	5.86219
C	-0.08234	-5.78490	4.77754
C	1.11996	-8.30426	4.69428

C	-0.11356	-6.54419	3.60757
C	0.48298	-7.80197	3.55968
H	1.66283	-7.94929	6.75225
H	-0.56328	-4.80760	4.82734
H	1.59398	-9.28850	4.67162
H	-0.61825	-6.14314	2.72520
H	0.45328	-8.39069	2.63979
C	0.75648	-4.01228	6.93554
O	-0.19595	-3.39618	6.54557
O	1.92411	-3.61483	7.25100

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TS-NArC1

C	3.19507	-5.61882	10.16110
C	3.37785	-6.86802	10.79015
C	3.33184	-4.44336	10.93071
C	3.64392	-6.94929	12.16167
C	3.60169	-4.54561	12.30367
H	3.77799	-7.92874	12.63006
H	3.70865	-3.63061	12.89304
C	3.74985	-5.78597	12.91836
H	3.96293	-5.84409	13.98884
Sn	3.13698	-5.85819	7.92487
C	3.31786	-8.11704	9.96503
C	4.46406	-8.54432	9.25482
C	2.13624	-8.89399	9.92614
C	4.38265	-9.69668	8.46297
C	2.10667	-10.03880	9.12763
C	3.21303	-10.45247	8.37753
H	5.26994	-10.01845	7.90976
H	1.18722	-10.63128	9.09507
C	3.21785	-3.08244	10.32311
C	4.24933	-2.59053	9.49422
C	2.10161	-2.26579	10.59913
C	4.11331	-1.33011	8.90905
C	1.99929	-1.01781	9.97559
C	2.98473	-0.53435	9.11498
H	4.92021	-0.95704	8.27049
H	1.11868	-0.40023	10.17941
C	5.77725	-7.82362	9.39077
H	6.11737	-7.82760	10.43829
H	6.55207	-8.29795	8.77304
H	5.71397	-6.76389	9.09601
C	0.95008	-8.53292	10.77150
H	0.06878	-9.12520	10.49248
H	1.16406	-8.71870	11.83680
H	0.68834	-7.46951	10.68246
C	3.13483	-11.67714	7.51176
H	2.44844	-11.51875	6.66370
H	4.11799	-11.94728	7.10153
H	2.75107	-12.54149	8.07565
C	5.50591	-3.38004	9.24256
H	5.81231	-3.95763	10.12652
H	5.38793	-4.10050	8.41250
H	6.33256	-2.71305	8.95893
C	2.83238	0.78918	8.42217
H	3.80412	1.28312	8.27402
H	2.37844	0.65958	7.42516
H	2.18334	1.47195	8.98962
C	1.03519	-2.66859	11.58244
H	0.05382	-2.27018	11.28441
H	0.95376	-3.75727	11.69570
H	1.25764	-2.26143	12.58345
N	0.93908	-5.97809	7.40104
C	-0.12173	-6.13388	8.31733
C	-1.10635	-7.12867	8.17418
C	-0.23021	-5.26075	9.41532
C	-2.14900	-7.23966	9.09216
C	-1.27191	-5.38033	10.32781
C	-2.24348	-6.37125	10.17664
H	-1.05511	-7.82252	7.33402
H	0.51875	-4.47819	9.55393
H	-2.89916	-8.02270	8.95123
H	-1.32848	-4.68307	11.16749
H	-3.06454	-6.45852	10.89151
C	0.79713	-6.70402	6.17737
C	1.52360	-7.88086	5.94533
C	-0.07300	-6.25150	5.17250
C	1.41767	-8.56265	4.73303
C	-0.18431	-6.94039	3.96781
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H	2.16403	-8.28438	6.73564
H	-0.66588	-5.35304	5.34827
H	2.00330	-9.47190	4.57484
H	-0.86429	-6.56681	3.19781
H	0.48059	-8.62717	2.78661
C	1.06622	-3.81910	6.99778
O	-0.00976	-3.50845	6.68383
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Scheme 3

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Sn	9.48648	7.11348	13.82910
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C	7.66786	8.99504	10.07188
H	7.94031	9.21983	9.03671
C	6.39655	9.31501	10.54444
H	5.67074	9.78758	9.87767
C	6.04929	9.03352	11.86503
H	5.05352	9.28247	12.24276
C	9.96319	8.04973	10.38097
C	6.98453	8.42987	12.70967
C	12.26689	8.64833	9.98674
H	13.08619	9.36188	10.10790
C	11.02105	8.96263	10.53608

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C	11.43678	6.54636	9.19358
H	11.59601	5.59543	8.67547
C	10.81813	10.24468	11.28707
H	10.03185	10.86092	10.82326
H	11.74732	10.82929	11.32703
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C	13.82793	7.15125	8.68365
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H	13.78715	7.24603	7.58580
H	14.15280	6.12320	8.90651
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H	8.65222	5.53588	10.55554
H	9.38179	4.93158	9.04476
H	8.20202	6.26830	9.02118
C	6.69482	8.10380	14.14033
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C	6.78873	8.68437	16.48549
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H	5.71480	6.13831	18.46752
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H	15.42352	8.98401	11.46429
C	14.70596	10.77553	12.41979
H	14.85788	11.39480	11.53220
C	14.17581	11.34057	13.57407
H	13.91154	12.40042	13.58494
C	13.98144	10.57355	14.72711
C	14.33240	9.21513	14.66523
C	14.59338	7.17143	17.60923
H	15.02264	6.64169	18.45374
C	15.16397	7.96375	16.67246
H	16.19399	8.27421	16.52911
C	12.95092	7.89837	16.24282
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H	6.96020	5.48070	12.89831
H	5.35629	6.15983	12.65454
C	13.43063	11.21128	15.98712
H	13.28807	10.41378	16.73173
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H	14.05595	12.62320	17.52025
H	14.60938	13.04750	15.88385
C	12.06565	11.85744	15.75111
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H	14.88329	6.77301	11.29931
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H	12.29401	5.56483	14.94587
H	11.58544	3.94783	15.11650
H	13.21396	4.13915	14.41665
C	13.54154	2.91611	16.84865
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H	12.69135	2.22666	16.72688
H	13.94222	2.78386	17.86529
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H	11.62539	9.71953	20.85465
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H	5.07760	11.68060	14.12399
C	6.30135	12.98798	12.90877
H	5.53845	13.76911	12.85526
C	7.52239	13.17160	12.25669

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C	6.84223	9.51257	14.39958
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C	7.20368	9.37971	15.75539
C	7.14339	8.11164	16.34525
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C	6.01755	8.51965	12.22259
H	5.20611	9.25399	12.10474
H	5.68187	7.55856	11.80943
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H	7.78037	10.31300	17.60833
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C	12.19157	12.76393	11.65549
H	13.05321	13.21434	12.15530
C	12.37082	12.13526	10.42527
C	11.25257	11.56871	9.80437
H	11.36709	11.07788	8.83307
C	9.98756	11.61791	10.38956
C	8.80349	11.01054	9.69173
H	7.98605	11.73918	9.58322
H	8.38169	10.16914	10.26550
H	9.07687	10.64016	8.69420
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H	14.49444	12.53176	10.40196
H	13.72410	12.57632	8.79907
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H	11.82165	6.00978	11.91341
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H	12.93050	7.70588	10.48870
C	13.91741	8.67698	12.13814
H	14.40762	9.41323	11.49857
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C	10.83390	13.46235	13.64342
H	11.56673	14.27431	13.75477
H	11.04410	12.70873	14.42122
H	9.82844	13.86164	13.82995
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H	14.87430	9.77485	15.19855

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H	16.67907	8.21498	14.38999
H	17.24670	9.90143	14.43734
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C	14.92954	11.12469	13.56650
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H	13.90328	11.47222	13.74237
C	11.95337	5.71990	14.61326
H	12.29991	5.85152	15.64959
C	12.34740	4.30581	14.18640
H	11.90185	3.56205	14.86502
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H	10.01457	5.82694	13.60608
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C	11.18485	6.27060	19.10015
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H	9.05635	6.68584	18.94988
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Sn	9.70484	9.12250	15.28785
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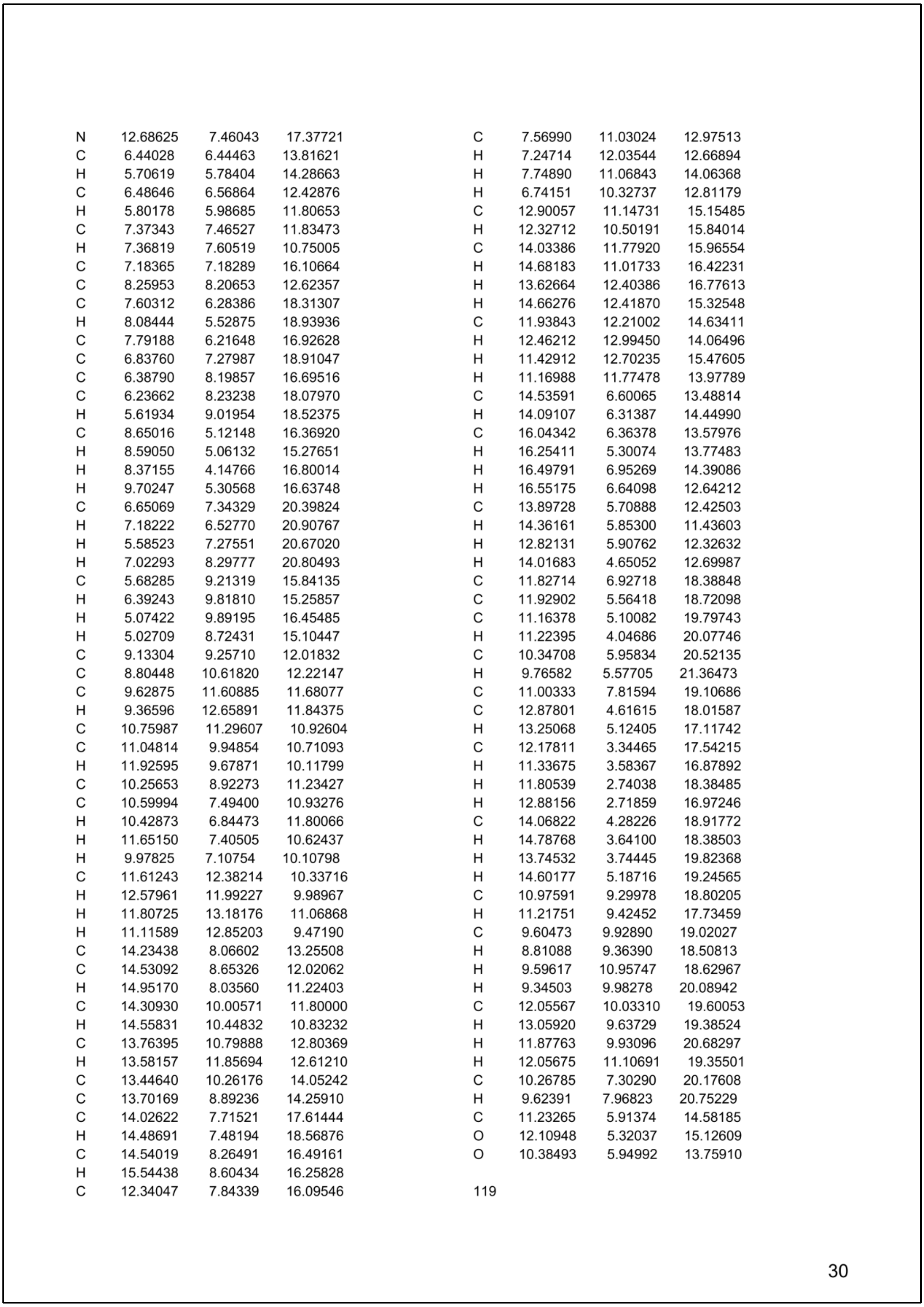

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H	5.02709	8.72431	15.10447
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H	11.11589	12.85203	9.47190
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C	13.76395	10.79888	12.80369
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C	7.56990	11.03024	12.97513
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H	14.09107	6.31387	14.44990
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C	11.82714	6.92718	18.38848
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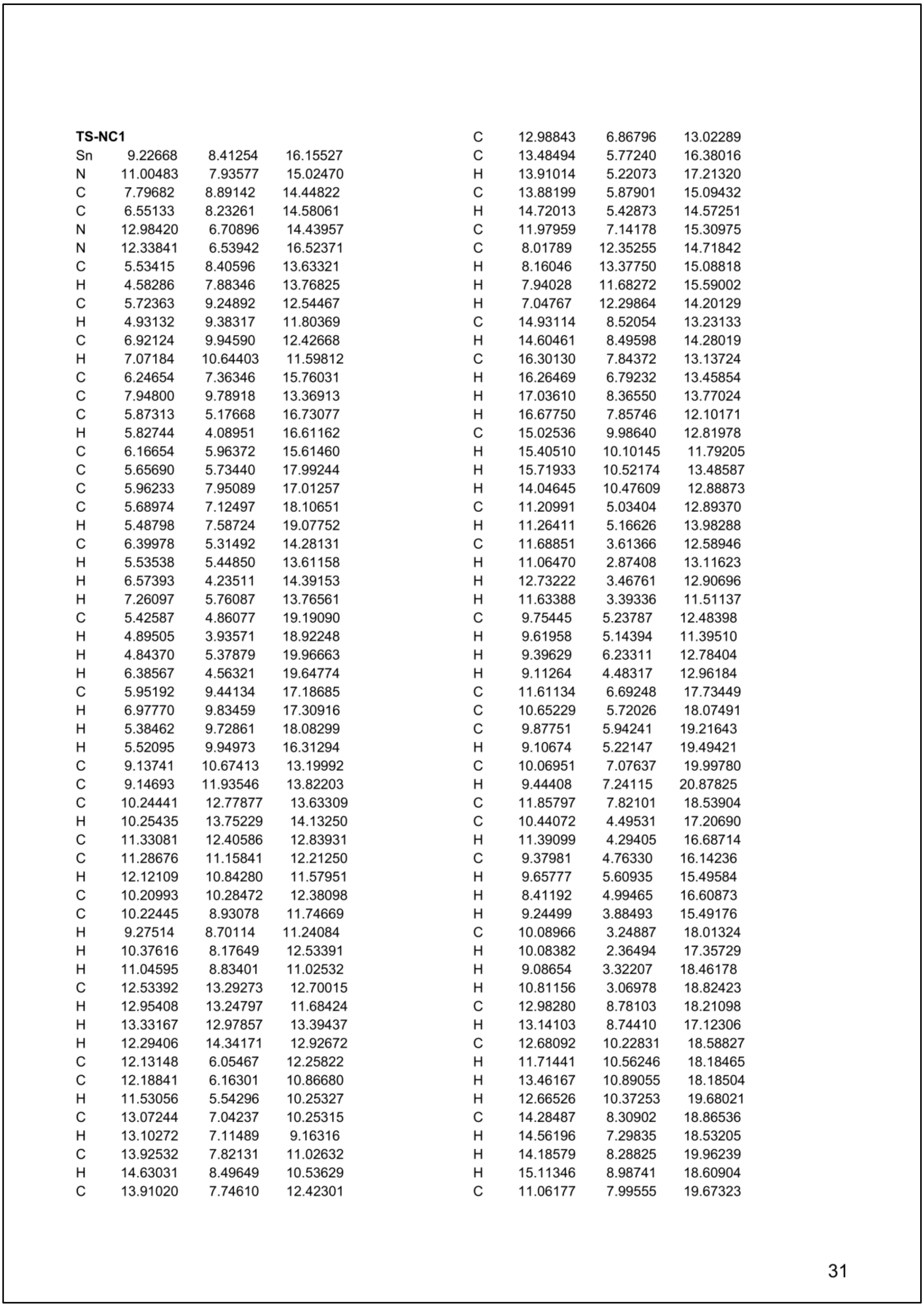

TS-NC1

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C	5.68974	7.12497	18.10651
H	5.48798	7.58724	19.07752
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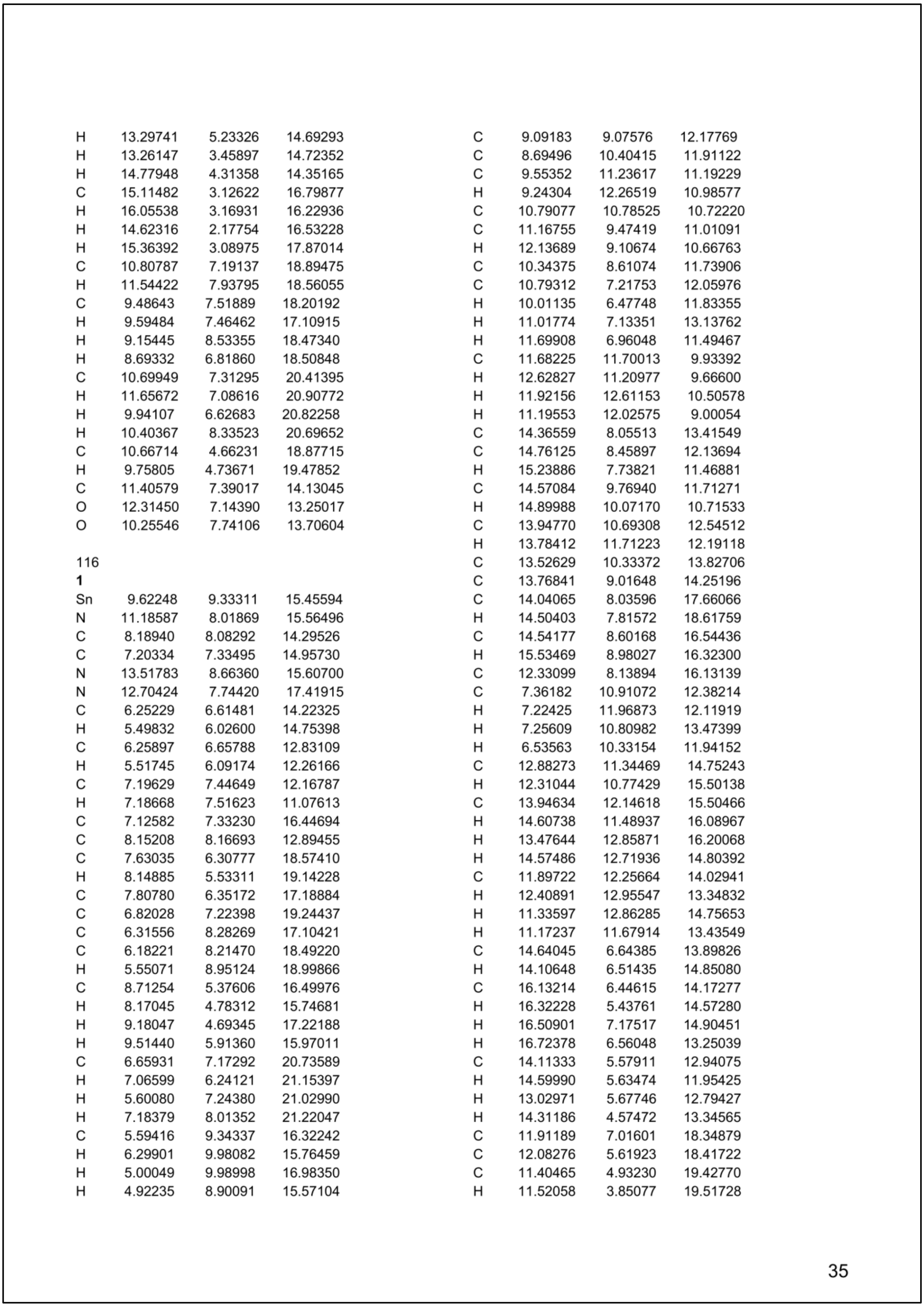

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H	14.77948	4.31358	14.35165
C	15.11482	3.12622	16.79877
H	16.05538	3.16931	16.22936
H	14.62316	2.17754	16.53228
H	15.36392	3.08975	17.87014
C	10.80787	7.19137	18.89475
H	11.54422	7.93795	18.56055
C	9.48643	7.51889	18.20192
H	9.59484	7.46462	17.10915
H	9.15445	8.53355	18.47340
H	8.69332	6.81860	18.50848
C	10.69949	7.31295	20.41395
H	11.65672	7.08616	20.90772
H	9.94107	6.62683	20.82258
H	10.40367	8.33523	20.69652
C	10.66714	4.66231	18.87715
H	9.75805	4.73671	19.47852
C	11.40579	7.39017	14.13045
O	12.31450	7.14390	13.25017
O	10.25546	7.74106	13.70604

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Sn	9.62248	9.33311	15.45594
N	11.18587	8.01869	15.56496
C	8.18940	8.08292	14.29526
C	7.20334	7.33495	14.95730
N	13.51783	8.66360	15.60700
N	12.70424	7.74420	17.41915
C	6.25229	6.61481	14.22325
H	5.49832	6.02600	14.75398
C	6.25897	6.65788	12.83109
H	5.51745	6.09174	12.26166
C	7.19629	7.44649	12.16787
H	7.18668	7.51623	11.07613
C	7.12582	7.33230	16.44694
C	8.15208	8.16693	12.89455
C	7.63035	6.30777	18.57410
H	8.14885	5.53311	19.14228
C	7.80780	6.35172	17.18884
C	6.82028	7.22398	19.24437
C	6.31556	8.28269	17.10421
C	6.18221	8.21470	18.49220
H	5.55071	8.95124	18.99866
C	8.71254	5.37606	16.49976
H	8.17045	4.78312	15.74681
H	9.18047	4.69345	17.22188
H	9.51440	5.91360	15.97011
C	6.65931	7.17292	20.73589
H	7.06599	6.24121	21.15397
H	5.60080	7.24380	21.02990
H	7.18379	8.01352	21.22047
C	5.59416	9.34337	16.32242
H	6.29901	9.98082	15.76459
H	5.00049	9.98998	16.98350
H	4.92235	8.90091	15.57104
C	9.09183	9.07576	12.17769
C	8.69496	10.40415	11.91122
C	9.55352	11.23617	11.19229
H	9.24304	12.26519	10.98577
C	10.79077	10.78525	10.72220
C	11.16755	9.47419	11.01091
H	12.13689	9.10674	10.66763
C	10.34375	8.61074	11.73906
C	10.79312	7.21753	12.05976
H	10.01135	6.47748	11.83355
H	11.01774	7.13351	13.13762
H	11.69908	6.96048	11.49467
C	11.68225	11.70013	9.93392
H	12.62827	11.20977	9.66600
H	11.92156	12.61153	10.50578
H	11.19553	12.02575	9.00054
C	14.36559	8.05513	13.41549
C	14.76125	8.45897	12.13694
H	15.23886	7.73821	11.46881
C	14.57084	9.76940	11.71271
H	14.89988	10.07170	10.71533
C	13.94770	10.69308	12.54512
H	13.78412	11.71223	12.19118
C	13.52629	10.33372	13.82706
C	13.76841	9.01648	14.25196
C	14.04065	8.03596	17.66066
H	14.50403	7.81572	18.61759
C	14.54177	8.60168	16.54436
H	15.53469	8.98027	16.32300
C	12.33099	8.13894	16.13139
C	7.36182	10.91072	12.38214
H	7.22425	11.96873	12.11919
H	7.25609	10.80982	13.47399
H	6.53563	10.33154	11.94152
C	12.88273	11.34469	14.75243
H	12.31044	10.77429	15.50138
C	13.94634	12.14618	15.50466
H	14.60738	11.48937	16.08967
H	13.47644	12.85871	16.20068
H	14.57486	12.71936	14.80392
C	11.89722	12.25664	14.02941
H	12.40891	12.95547	13.34832
H	11.33597	12.86285	14.75653
H	11.17237	11.67914	13.43549
C	14.64045	6.64385	13.89826
H	14.10648	6.51435	14.85080
C	16.13214	6.44615	14.17277
H	16.32228	5.43761	14.57280
H	16.50901	7.17517	14.90451
H	16.72378	6.56048	13.25039
C	14.11333	5.57911	12.94075
H	14.59990	5.63474	11.95425
H	13.02971	5.67746	12.79427
H	14.31186	4.57472	13.34565
C	11.91189	7.01601	18.34879
C	12.08276	5.61923	18.41722
C	11.40465	4.93230	19.42770
H	11.52058	3.85077	19.51728

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C	10.59686	5.61158	20.33474
H	10.08615	5.05767	21.12662
C	11.08085	7.71764	19.23716
C	12.96810	4.89476	17.41978
H	13.78184	5.58722	17.14906
C	12.19869	4.57633	16.13572
H	11.76189	5.48186	15.68874
H	11.37801	3.87173	16.34161
H	12.86636	4.10949	15.39485
C	13.62242	3.64135	17.99056
H	14.35393	3.23869	17.27366
H	12.88794	2.84285	18.18094
H	14.14945	3.84933	18.93422
C	10.94792	9.22417	19.15648
H	11.21511	9.51669	18.12862
C	9.52344	9.70543	19.40830
H	8.79668	9.17814	18.77253
H	9.44440	10.78284	19.19858
H	9.22130	9.55485	20.45714
C	11.94097	9.90753	20.09784
H	12.97802	9.61728	19.87267
H	11.73613	9.63823	21.14671
H	11.86964	11.00294	20.00810
C	10.43064	6.98777	20.23573
H	9.78390	7.50455	20.94708

Scheme S1

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VII

Sn	9.59641	9.15742	15.32884
P	11.15904	7.27195	15.13086
C	8.12486	8.03029	14.08265
C	7.14400	7.24067	14.70689
N	13.64710	8.53549	15.66321
N	12.79241	7.61593	17.42098
C	6.22459	6.51926	13.93433
H	5.46819	5.90691	14.43407
C	6.26407	6.58970	12.54390
H	5.54457	6.02494	11.94560
C	7.21005	7.39922	11.91929
H	7.23047	7.48209	10.82852
C	7.03287	7.20561	16.19648
C	8.13646	8.12391	12.67965
C	7.40360	6.12681	18.32781
H	7.83236	5.29947	18.89867
C	7.58210	6.14371	16.94022
C	6.69864	7.12514	18.99746
C	6.31362	8.22840	16.85525
C	6.16222	8.17148	18.24138
H	5.59960	8.96458	18.74373
C	8.36976	5.05886	16.27267
H	7.85587	4.66345	15.38474
H	8.57491	4.23118	16.96599
H	9.33848	5.46523	15.93068
C	6.52078	7.08938	20.48774
H	6.96378	6.18343	20.92541
H	5.45513	7.11137	20.76604
H	6.99363	7.96210	20.96744
C	5.69688	9.35548	16.07690
H	6.46758	9.98754	15.60695
H	5.08396	9.99630	16.72613
H	5.06686	8.97834	15.25724
C	9.09786	9.03565	11.99175
C	8.80324	10.41396	11.91485
C	9.68870	11.26273	11.24783
H	9.45242	12.32975	11.18645
C	10.85969	10.78530	10.65361
C	11.13066	9.42010	10.74079
H	12.04547	9.02544	10.29055
C	10.26771	8.53313	11.39165
C	10.59959	7.07446	11.46591
H	10.79930	6.79010	12.51314
H	11.49314	6.83941	10.87124
H	9.76714	6.44716	11.11551
C	11.78150	11.72164	9.92746
H	12.72798	11.23050	9.66125
H	12.01525	12.60797	10.53861
H	11.32358	12.08823	8.99395
C	14.48361	7.98178	13.44770
C	14.81201	8.40643	12.15717
H	15.26833	7.69885	11.46087
C	14.56722	9.71277	11.75215
H	14.83983	10.02927	10.74244
C	13.95964	10.61516	12.61871
H	13.74569	11.62850	12.27671
C	13.60242	10.23831	13.91465
C	13.89949	8.92358	14.30931
C	14.04043	8.08566	17.78070
H	14.43186	7.95516	18.78481
C	14.57701	8.66390	16.67738
H	15.53648	9.14459	16.51474
C	12.53631	7.87612	16.10533
C	7.54214	10.96334	12.51834
H	7.42723	12.03202	12.28959
H	7.53549	10.84721	13.61403
H	6.65589	10.42610	12.14725
C	12.92245	11.21242	14.85473
H	12.36310	10.61049	15.59024
C	13.94247	12.05791	15.61983
H	14.62984	11.43799	16.21417
H	13.43183	12.74750	16.31003
H	14.55035	12.66088	14.92616
C	11.90400	12.09201	14.13660
H	12.39113	12.83138	13.48084
H	11.30209	12.65042	14.86909
H	11.21801	11.49278	13.51968
C	14.75983	6.55447	13.87381
H	14.42097	6.44343	14.91467
C	16.25567	6.24533	13.84677

H	16.44554	5.22341	14.21035
H	16.82252	6.94412	14.48091
H	16.66332	6.31506	12.82591
C	13.95302	5.56228	13.03865
H	14.23364	5.60664	11.97424
H	12.87792	5.77483	13.12477
H	14.12938	4.53284	13.38821
C	11.95323	6.85146	18.29129
C	12.07864	5.45318	18.27340
C	11.31764	4.72864	19.19516
H	11.39101	3.63855	19.21237
C	10.47260	5.37609	20.08894
H	9.89059	4.79284	20.80689
C	11.07847	7.53093	19.15478
C	13.00116	4.73635	17.30744
H	13.42002	5.48920	16.62405
C	12.23782	3.73710	16.44116
H	11.42749	4.24244	15.89691
H	11.80152	2.92446	17.04314
H	12.91203	3.27831	15.70137
C	14.17247	4.08273	18.03966
H	14.85297	3.59697	17.32260
H	13.82399	3.31257	18.74597
H	14.75297	4.82249	18.61245
C	10.93609	9.03862	19.11127
H	11.27189	9.36542	18.11329
C	9.48744	9.49060	19.26221
H	8.82212	8.96223	18.56403
H	9.40539	10.56916	19.06091
H	9.11080	9.31877	20.28315
C	11.83288	9.71245	20.15096
H	12.89278	9.45351	20.01150
H	11.54633	9.40815	21.17061
H	11.74311	10.80808	20.08660
C	10.34742	6.76130	20.06177
H	9.65571	7.25294	20.74785

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Sn	5.68102	3.59115	4.01574
O	3.40682	2.86530	6.82070
O	3.78339	3.83239	4.83507
N	2.33237	7.76807	5.78012
N	1.36753	5.98469	4.99674
P	3.50269	5.55807	6.89955
C	6.38669	2.07950	5.47222
C	7.12017	2.37296	6.62950
C	7.54262	1.32340	7.45407
H	8.11864	1.54361	8.35675
C	7.24284	0.00290	7.12208
H	7.58151	-0.80861	7.77073
C	6.52203	-0.28993	5.96453
H	6.29502	-1.32708	5.70220
C	6.09368	0.75022	5.13512
C	5.34089	0.52306	3.86465
C	3.95547	0.24682	3.88739
C	3.28136	0.10793	2.67197
H	2.20905	-0.10656	2.69341
C	3.92690	0.23527	1.43948
C	5.29879	0.48997	1.43854
H	5.83090	0.56575	0.48573
C	6.02243	0.62562	2.62853
C	7.51579	0.80000	2.58326
H	7.85220	1.72821	3.07110
H	7.87950	0.80985	1.54699
H	8.01893	-0.01669	3.12364
C	3.22256	0.10711	5.18452
H	3.64000	-0.71156	5.79072
H	2.15682	-0.09555	5.01221
H	3.30727	1.02805	5.78549
C	3.16216	0.12240	0.15343
H	2.82266	1.11477	-0.18838
H	2.26869	-0.50787	0.26957
H	3.78155	-0.30315	-0.64950
C	7.43187	3.79782	6.93529
C	8.35361	4.49913	6.12821
C	8.58102	5.85710	6.37774
H	9.30081	6.39555	5.75319
C	7.92902	6.53522	7.40677
C	7.03679	5.81548	8.20452
H	6.50560	6.33153	9.00919
C	6.78292	4.45863	8.00063
C	5.83318	3.73067	8.90737
H	6.37281	3.03675	9.57184
H	5.10075	3.13525	8.34351
H	5.28029	4.43958	9.53871
C	9.14109	3.80954	5.04455
H	9.33764	2.75745	5.29303
H	10.10241	4.31827	4.88503
H	8.62004	3.81579	4.07041
C	8.19801	7.98610	7.67919
H	8.91828	8.10548	8.50609
H	7.27612	8.51273	7.96517
H	8.62187	8.49102	6.79885
C	3.51285	3.86123	6.13129
C	2.41216	6.39636	5.79280
C	1.24420	8.19402	5.04025
H	1.00834	9.24811	4.93077
C	0.64523	7.08521	4.55178
H	-0.24701	6.96506	3.94672
C	0.91728	4.64217	4.79695
C	1.15078	4.02279	3.55432
C	0.64196	2.73682	3.36874
H	0.81056	2.22664	2.41916
C	-0.04965	2.08494	4.38515
H	-0.43108	1.07386	4.22317
C	-0.24718	2.71003	5.60902
H	-0.78185	2.18707	6.40457
C	0.22721	4.00479	5.84124
C	-0.04417	4.68926	7.16539
H	0.60231	5.57599	7.22094
C	0.33697	3.80996	8.35382
H	-0.32618	2.93512	8.44914
H	0.25576	4.38629	9.28859
H	1.37317	3.45426	8.25267
C	-1.49550	5.16518	7.23615

H	-1.73542	5.84735	6.40561
H	-1.68093	5.70248	8.17989
H	-2.19786	4.31746	7.18660
C	1.93779	4.70977	2.45549
H	2.61531	5.42159	2.95403
C	2.79691	3.73383	1.65528
H	3.34637	3.04273	2.31013
H	3.52231	4.27958	1.03311
H	2.18494	3.12056	0.97463
C	1.02700	5.49004	1.50388
H	0.31412	4.81218	1.00750
H	1.62079	5.98749	0.72085
H	0.44615	6.26565	2.02027
C	3.26800	8.62914	6.42043
C	4.43367	8.98470	5.72054
C	5.31260	9.87437	6.34119
H	6.22565	10.17617	5.82271
C	5.04666	10.37191	7.61377
H	5.74750	11.06792	8.08160
C	3.90060	9.97873	8.29645
H	3.71105	10.36217	9.30182
C	2.98701	9.09387	7.71522
C	1.75177	8.65066	8.47212
H	1.21273	7.93316	7.83488
C	2.12622	7.91029	9.75571
H	2.76411	7.04366	9.52706
H	1.21998	7.54451	10.26346
H	2.66304	8.56538	10.46049
C	0.81207	9.82541	8.74023
H	1.28848	10.58510	9.38019
H	-0.10061	9.48313	9.25222
H	0.51180	10.32045	7.80387
C	4.74571	8.41890	4.35087
H	3.94523	7.70930	4.09491
C	6.05134	7.62690	4.37517
H	6.91985	8.27713	4.56759
H	6.21883	7.12688	3.40822
H	6.02290	6.86160	5.16547
C	4.75293	9.50968	3.28153
H	3.79101	10.04355	3.24647
H	4.93727	9.07454	2.28687
H	5.54177	10.25494	3.47162

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TS-PC1

Sn	4.95258	4.15853	4.50858
O	2.28607	2.48322	7.22044
O	2.86870	2.59651	4.99868
N	3.03916	7.58519	5.30418
N	1.48446	6.12058	4.97956
P	3.72658	5.14383	6.51450
C	6.19513	2.62054	5.56713
C	6.95449	2.82889	6.73624
C	7.78504	1.81230	7.22855
H	8.36645	1.99940	8.13580
C	7.87758	0.58691	6.57718
H	8.52847	-0.19807	6.97011
C	7.14202	0.37242	5.41618
H	7.20930	-0.58197	4.88656
C	6.31295	1.37806	4.90541
C	5.55897	1.10121	3.64576
C	4.38606	0.32159	3.68437
C	3.69421	0.08047	2.49566
H	2.77569	-0.51313	2.53348
C	4.13801	0.57337	1.26697
C	5.32131	1.31347	1.24592
H	5.70161	1.68944	0.29110
C	6.04502	1.57977	2.41132
C	7.32610	2.35885	2.33674
H	7.18685	3.38951	2.70958
H	7.68609	2.42965	1.30097
H	8.11303	1.90386	2.95586
C	3.89154	-0.27499	4.97004
H	4.38442	-1.24215	5.16580
H	2.80773	-0.45062	4.93028
H	4.10567	0.37028	5.83134
C	3.34972	0.33503	0.01204
H	3.98411	0.40408	-0.88361
H	2.54624	1.08312	-0.09567
H	2.87141	-0.65563	0.01760
C	6.94571	4.12265	7.47693
C	7.76660	5.17768	7.04062
C	7.79021	6.36991	7.77113
H	8.43161	7.18778	7.42981
C	7.04853	6.52669	8.94221
C	6.24337	5.46373	9.35689
H	5.65003	5.56709	10.27051
C	6.17520	4.26451	8.64712
C	5.28177	3.15700	9.12320
H	5.82045	2.20053	9.19255
H	4.44138	2.99772	8.43051
H	4.85630	3.39055	10.10925
C	8.67388	5.00473	5.85351
H	9.46318	4.26717	6.07217
H	9.15966	5.95265	5.58264
H	8.14535	4.62046	4.96831
C	7.16338	7.76690	9.77948
H	7.79446	7.58254	10.66496
H	6.18039	8.09791	10.14597
H	7.61534	8.59461	9.21605
C	2.65585	2.81479	6.15615
C	2.72868	6.27148	5.52653
C	2.01863	8.22926	4.63467
H	2.07753	9.28391	4.38404
C	1.04346	7.31142	4.43167
H	0.07130	7.39205	3.95675
C	0.67284	4.94052	4.98692
C	0.53666	4.21678	3.79151
C	-0.33365	3.12352	3.79805
H	-0.45962	2.53353	2.88820
C	-1.01740	2.76218	4.95196
H	-1.68619	1.89818	4.93958
C	-0.84014	3.48114	6.12993
H	-1.36155	3.16745	7.03481
C	0.00699	4.58981	6.17687
C	0.19343	5.39008	7.45160

H	1.23925	5.73675	7.45614
C	0.02496	4.55761	8.71694
H	-1.01765	4.23496	8.86870
H	0.30737	5.15872	9.59457
H	0.67117	3.66955	8.68722
C	-0.72047	6.61671	7.46968
H	-0.56189	7.26533	6.59531
H	-0.53436	7.22219	8.37099
H	-1.78018	6.31508	7.47698
C	1.30830	4.57692	2.53752
H	2.12458	5.25486	2.83579
C	1.95595	3.35574	1.88750
H	2.53176	2.76657	2.61300
H	2.64009	3.67064	1.08510
H	1.20218	2.69187	1.43464
C	0.42008	5.31798	1.53613
H	-0.41653	4.67939	1.21047
H	0.99672	5.60013	0.64152
H	-0.01204	6.23560	1.96145
C	4.14359	8.28699	5.88236
C	5.29076	8.51829	5.10999
C	6.30021	9.30180	5.67593
H	7.20694	9.50509	5.10226
C	6.16463	9.82701	6.95587
H	6.96216	10.44414	7.37654
C	5.02255	9.56519	7.70534
H	4.93278	9.97314	8.71449
C	3.98707	8.78513	7.18754
C	2.74970	8.50198	8.01575
H	2.08465	7.86229	7.41825
C	3.09584	7.71669	9.27950
H	3.64465	6.79911	9.02129
H	2.17758	7.43389	9.81771
H	3.71402	8.31378	9.96912
C	1.97588	9.78128	8.32828
H	2.57250	10.47688	8.93956
H	1.05822	9.54608	8.88971
H	1.68510	10.30967	7.40734
C	5.43270	7.96402	3.70836
H	4.66913	7.17834	3.58735
C	6.79061	7.30425	3.49098
H	7.60779	8.04236	3.46098
H	6.80297	6.75786	2.53564
H	7.01599	6.59092	4.29679
C	5.16517	9.04162	2.65680
H	4.15909	9.47412	2.76393
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H	5.89246	9.86477	2.74285

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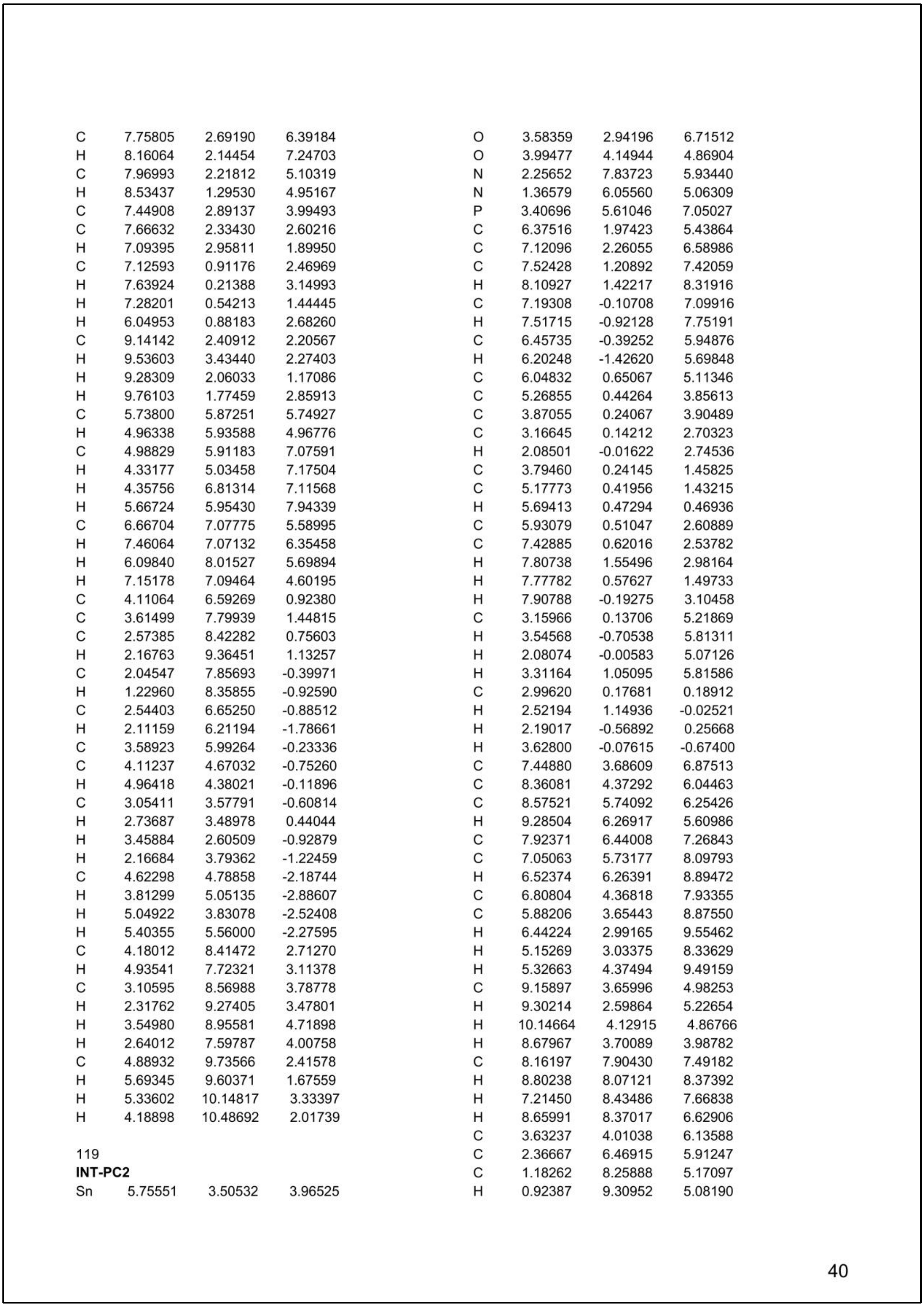
PC2

Sn	4.31373	1.10219	5.82447
O	3.47255	3.20178	5.51153
O	4.40991	2.20867	3.81061
N	5.19066	5.95966	1.60488
N	6.30334	4.83975	3.09737
P	3.41114	4.69971	3.26004
C	2.27875	0.23645	5.54245
C	1.39696	0.41985	6.62392
C	0.12597	-0.16135	6.60630
H	-0.55275	-0.00861	7.45033
C	-0.26707	-0.93540	5.51512
H	-1.25902	-1.39358	5.50006
C	0.60435	-1.13065	4.44558
H	0.29797	-1.74045	3.59094
C	1.88040	-0.54984	4.45146
C	2.81319	-0.77305	3.30866
C	2.72239	0.02188	2.15033
C	3.61172	-0.21378	1.09880
H	3.53803	0.40938	0.20257
C	4.58746	-1.20859	1.16075
C	4.66447	-1.98100	2.32156
H	5.42031	-2.76953	2.39197
C	3.79246	-1.78335	3.39541
C	3.89129	-2.65650	4.61571
H	4.22442	-2.09047	5.50158
H	4.60460	-3.47719	4.45785
H	2.91392	-3.08782	4.87990
C	1.72769	1.13905	2.04132
H	0.83283	0.96156	2.65128
H	1.41859	1.29369	0.99788
H	2.18232	2.08125	2.39013
C	5.50706	-1.45783	0.00040
H	5.03844	-2.12567	-0.74190
H	6.44525	-1.93257	0.32213
H	5.75846	-0.52155	-0.51992
C	1.88255	1.25156	7.76570
C	2.76107	0.68746	8.71419
C	3.33430	1.51551	9.68739
H	4.02568	1.07747	10.41342
C	3.04778	2.87854	9.75230
C	2.13013	3.40332	8.83662
H	1.87900	4.46739	8.88117
C	1.54100	2.61875	7.84554
C	0.59260	3.22519	6.85585
H	-0.35652	2.67150	6.81293
H	1.03496	3.19941	5.84924
H	0.37690	4.27295	7.10597
C	3.06710	-0.78448	8.69907
H	2.14350	-1.38181	8.67644
H	3.65332	-1.07378	9.58194
H	3.64219	-1.08034	7.80590
C	3.71587	3.77018	10.75849
H	4.31812	3.19343	11.47465
H	2.98078	4.35976	11.32816
H	4.38525	4.48886	10.25700
C	3.85066	3.23580	4.29925
C	5.02745	5.08383	2.64949
C	6.52717	6.24758	1.40511
H	6.85092	6.92921	0.62484
C	7.22165	5.54202	2.32421
H	8.28690	5.47166	2.51942
C	6.72983	4.07631	4.22926
C	6.49062	4.57545	5.52465
C	7.01322	3.84844	6.59820
H	6.83720	4.19957	7.61560



C	7.75805	2.69190	6.39184
H	8.16064	2.14454	7.24703
C	7.96993	2.21812	5.10319
H	8.53437	1.29530	4.95167
C	7.44908	2.89137	3.99493
C	7.66632	2.33430	2.60216
H	7.09395	2.95811	1.89950
C	7.12593	0.91176	2.46969
H	7.63924	0.21388	3.14993
H	7.28201	0.54213	1.44445
H	6.04953	0.88183	2.68260
C	9.14142	2.40912	2.20567
H	9.53603	3.43440	2.27403
H	9.28309	2.06033	1.17086
H	9.76103	1.77459	2.85913
C	5.73800	5.87251	5.74927
H	4.96338	5.93588	4.96776
C	4.98829	5.91183	7.07591
H	4.33177	5.03458	7.17504
H	4.35756	6.81314	7.11568
H	5.66724	5.95430	7.94339
C	6.66704	7.07775	5.58995
H	7.46064	7.07132	6.35458
H	6.09840	8.01527	5.69894
H	7.15178	7.09464	4.60195
C	4.11064	6.59269	0.92380
C	3.61499	7.79939	1.44815
C	2.57385	8.42282	0.75603
H	2.16763	9.36451	1.13257
C	2.04547	7.85693	-0.39971
H	1.22960	8.35855	-0.92590
C	2.54403	6.65250	-0.88512
H	2.11159	6.21194	-1.78661
C	3.58923	5.99264	-0.23336
C	4.11237	4.67032	-0.75260
H	4.96418	4.38021	-0.11896
C	3.05411	3.57791	-0.60814
H	2.73687	3.48978	0.44044
H	3.45884	2.60509	-0.92879
H	2.16684	3.79362	-1.22459
C	4.62298	4.78858	-2.18744
H	3.81299	5.05135	-2.88607
H	5.04922	3.83078	-2.52408
H	5.40355	5.56000	-2.27595
C	4.18012	8.41472	2.71270
H	4.93541	7.72321	3.11378
C	3.10595	8.56988	3.78778
H	2.31762	9.27405	3.47801
H	3.54980	8.95581	4.71898
H	2.64012	7.59787	4.00758
C	4.88932	9.73566	2.41578
H	5.69345	9.60371	1.67559
H	5.33602	10.14817	3.33397
H	4.18898	10.48692	2.01739

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INT-PC2

Sn	5.75551	3.50532	3.96525
O	3.58359	2.94196	6.71512
O	3.99477	4.14944	4.86904
N	2.25652	7.83723	5.93440
N	1.36579	6.05560	5.06309
P	3.40696	5.61046	7.05027
C	6.37516	1.97423	5.43864
C	7.12096	2.26055	6.58986
C	7.52428	1.20892	7.42059
H	8.10927	1.42217	8.31916
C	7.19308	-0.10708	7.09916
H	7.51715	-0.92128	7.75191
C	6.45735	-0.39252	5.94876
H	6.20248	-1.42620	5.69848
C	6.04832	0.65067	5.11346
C	5.26855	0.44264	3.85613
C	3.87055	0.24067	3.90489
C	3.16645	0.14212	2.70323
H	2.08501	-0.01622	2.74536
C	3.79460	0.24145	1.45825
C	5.17773	0.41956	1.43215
H	5.69413	0.47294	0.46936
C	5.93079	0.51047	2.60889
C	7.42885	0.62016	2.53782
H	7.80738	1.55496	2.98164
H	7.77782	0.57627	1.49733
H	7.90788	-0.19275	3.10458
C	3.15966	0.13706	5.21869
H	3.54568	-0.70538	5.81311
H	2.08074	-0.00583	5.07126
H	3.31164	1.05095	5.81586
C	2.99620	0.17681	0.18912
H	2.52194	1.14936	-0.02521
H	2.19017	-0.56892	0.25668
H	3.62800	-0.07615	-0.67400
C	7.44880	3.68609	6.87513
C	8.36081	4.37292	6.04463
C	8.57521	5.74092	6.25426
H	9.28504	6.26917	5.60986
C	7.92371	6.44008	7.26843
C	7.05063	5.73177	8.09793
H	6.52374	6.26391	8.89472
C	6.80804	4.36818	7.93355
C	5.88206	3.65443	8.87550
H	6.44224	2.99165	9.55462
H	5.15269	3.03375	8.33629
H	5.32663	4.37494	9.49159
C	9.15897	3.65996	4.98253
H	9.30214	2.59864	5.22654
H	10.14664	4.12915	4.86766
H	8.67967	3.70089	3.98782
C	8.16197	7.90430	7.49182
H	8.80238	8.07121	8.37392
H	7.21450	8.43486	7.66838
H	8.65991	8.37017	6.62906
C	3.63237	4.01038	6.13588
C	2.36667	6.46915	5.91247
C	1.18262	8.25888	5.17097
H	0.92387	9.30952	5.08190

C	0.63007	7.15062	4.62832
H	-0.24044	7.02766	3.99280
C	0.95788	4.70808	4.80818
C	1.23921	4.13478	3.55246
C	0.74659	2.85240	3.30390
H	0.94537	2.38005	2.34097
C	0.02654	2.15861	4.27109
H	-0.34554	1.15348	4.05771
C	-0.21221	2.73537	5.51107
H	-0.76768	2.17964	6.26962
C	0.24152	4.02466	5.80530
C	-0.07965	4.64982	7.14719
H	0.52053	5.56470	7.24095
C	0.33709	3.74509	8.30465
H	-0.28256	2.83555	8.35976
H	0.22416	4.27959	9.26062
H	1.39060	3.44605	8.19848
C	-1.55389	5.04725	7.22001
H	-1.82163	5.74522	6.41138
H	-1.77404	5.54052	8.18013
H	-2.21243	4.16788	7.13486
C	2.05334	4.86497	2.50199
H	2.73339	5.53711	3.04961
C	2.90840	3.91548	1.66596
H	3.42524	3.17038	2.28800
H	3.66467	4.47711	1.09759
H	2.29990	3.36128	0.93340
C	1.17462	5.70391	1.56994
H	0.45673	5.06314	1.03300
H	1.79307	6.21971	0.81843
H	0.60271	6.47144	2.10706
C	3.20734	8.70449	6.54529
C	4.35841	9.04544	5.81226
C	5.25640	9.93654	6.40268
H	6.15930	10.22620	5.86003
C	5.02181	10.45264	7.67450
H	5.73754	11.14962	8.11753
C	3.88770	10.07796	8.38650
H	3.72219	10.47668	9.39015
C	2.95661	9.19049	7.83751
C	1.73874	8.75946	8.62852
H	1.17709	8.04563	8.00651
C	2.14377	8.01776	9.90236
H	2.77024	7.14673	9.65951
H	1.24985	7.65841	10.43576
H	2.70453	8.67062	10.59038
C	0.81625	9.94156	8.92231
H	1.31585	10.69720	9.54931
H	-0.08465	9.60654	9.45929
H	0.49458	10.43955	7.99463
C	4.64662	8.44544	4.45130
H	3.77194	7.84511	4.16061
C	5.83747	7.49008	4.52945
H	6.76893	8.02816	4.76556
H	5.98400	6.97629	3.56615
H	5.67344	6.73335	5.31166
C	4.84076	9.51577	3.38001
H	3.96887	10.18458	3.31570
H	4.98549	9.04793	2.39380
H	5.72700	10.13838	3.58146

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INT-PC1

Sn	5.08601	4.13498	4.34606
O	2.39571	2.83217	6.96718
O	3.18767	3.12141	4.89339
N	3.05402	7.55426	5.27615
N	1.49376	6.08312	4.97256
P	3.79187	5.18338	6.50845
C	6.25088	2.61855	5.52760
C	6.96593	2.82629	6.72281
C	7.75783	1.79857	7.25621
H	8.30900	1.98335	8.18265
C	7.84781	0.56318	6.62394
H	8.47270	-0.22730	7.04693
C	7.13426	0.34127	5.45027
H	7.18789	-0.62635	4.94334
C	6.34230	1.35678	4.90214
C	5.59158	1.08443	3.63895
C	4.35225	0.40902	3.68165
C	3.67819	0.17131	2.48219
H	2.71749	-0.35103	2.51745
C	4.18733	0.57941	1.24665
C	5.42492	1.22288	1.22624
H	5.85701	1.52661	0.26785
C	6.14269	1.47233	2.40020
C	7.49535	2.12296	2.33084
H	7.47711	3.14644	2.74359
H	7.84789	2.19057	1.29237
H	8.23836	1.56558	2.92045
C	3.75094	-0.03648	4.98136
H	4.50025	-0.49340	5.64305
H	2.94485	-0.76378	4.80944
H	3.31962	0.82398	5.51744
C	3.41255	0.34371	-0.01723
H	4.05646	0.41341	-0.90588
H	2.60868	1.09033	-0.13113
H	2.93427	-0.64733	-0.01770
C	6.92485	4.11308	7.47543
C	7.71945	5.19688	7.06158
C	7.72367	6.37146	7.82029
H	8.35008	7.20824	7.49778
C	6.98442	6.48558	8.99834
C	6.19323	5.40146	9.38337
H	5.59901	5.47207	10.29966
C	6.14379	4.21767	8.64471
C	5.25718	3.09223	9.09416
H	5.80161	2.13825	9.14308
H	4.41513	2.93512	8.40122
H	4.83197	3.30195	10.08571
C	8.61325	5.07406	5.85889
H	9.37292	4.29128	6.01349
H	9.13147	6.02026	5.64910
H	8.06087	4.77682	4.95441
C	7.08926	7.70057	9.87331
H	7.72135	7.49305	10.75279

H	6.10416	8.01258	10.25099
H	7.53702	8.54878	9.33762
C	2.95001	3.48060	6.10988
C	2.73671	6.24662	5.50232
C	2.02531	8.19398	4.61323
H	2.08165	9.24806	4.36082
C	1.05123	7.27429	4.42118
H	0.07479	7.34747	3.95423
C	0.65492	4.91895	5.00859
C	0.48446	4.18533	3.82432
C	-0.41855	3.12082	3.85655
H	-0.57447	2.52339	2.95618
C	-1.09960	2.79751	5.02381
H	-1.79562	1.95524	5.03087
C	-0.88039	3.52052	6.19077
H	-1.39423	3.23139	7.10803
C	0.00427	4.59943	6.21311
C	0.24824	5.39203	7.48269
H	1.28758	5.75487	7.44344
C	0.15896	4.54001	8.74351
H	-0.86979	4.20268	8.94754
H	0.48453	5.13018	9.61387
H	0.81551	3.66344	8.65134
C	-0.67154	6.61169	7.55403
H	-0.55188	7.26910	6.67928
H	-0.45349	7.20867	8.45388
H	-1.72806	6.30297	7.60027
C	1.25125	4.50687	2.55788
H	2.07883	5.17961	2.83514
C	1.87883	3.25850	1.94176
H	2.43796	2.68813	2.69505
H	2.57139	3.53846	1.13319
H	1.11526	2.59531	1.50437
C	0.36804	5.23605	1.54372
H	-0.48134	4.60353	1.24023
H	0.94268	5.48484	0.63790
H	-0.04657	6.17211	1.94686
C	4.16305	8.24813	5.85800
C	5.30878	8.48703	5.08289
C	6.33098	9.23968	5.66712
H	7.23830	9.44573	5.09619
C	6.20707	9.73237	6.96125
H	7.01569	10.32571	7.39478
C	5.06301	9.47258	7.70730
H	4.98051	9.86158	8.72416
C	4.01500	8.71926	7.17510
C	2.76493	8.45907	7.99192
H	2.11542	7.78912	7.41114
C	3.08223	7.73833	9.30035
H	3.65166	6.81774	9.10640
H	2.15098	7.46615	9.82081
H	3.66715	8.37522	9.98303
C	1.97940	9.74898	8.22463
H	2.56372	10.47641	8.81007
H	1.05180	9.53846	8.77919
H	1.70458	10.22875	7.27272
C	5.42260	7.99432	3.65549
H	4.70613	7.16494	3.53639

C	6.80760	7.44005	3.33825
H	7.56774	8.23573	3.28844
H	6.79815	6.93210	2.36223
H	7.12962	6.71207	4.09559
C	5.03915	9.09618	2.66490
H	4.01607	9.46386	2.83257
H	5.09783	8.72383	1.63054
H	5.72111	9.95668	2.75487

Scheme S3

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TS-BH2_isomer

Sn	8.92227	9.15418	15.30019
N	11.45371	7.51097	16.16463
C	7.30918	8.75499	13.83588
C	6.22499	8.08024	14.41695
N	13.81727	8.05506	15.84355
N	13.08626	7.58849	17.84691
C	5.09960	7.75382	13.65615
H	4.26210	7.22150	14.11586
C	5.06401	8.10006	12.30592
H	4.18992	7.84606	11.70105
C	6.14430	8.75821	11.71935
H	6.11791	9.01509	10.65666
C	6.37473	7.70704	15.85612
C	7.27678	9.08922	12.47600
C	7.20725	6.18914	17.54701
H	7.70654	5.25208	17.80871
C	6.99995	6.48380	16.19482
C	6.78319	7.04537	18.56462
C	5.95077	8.59473	16.87139
C	6.15876	8.24428	18.20650
H	5.82706	8.93116	18.99054
C	7.40592	5.51086	15.12991
H	6.55961	5.28046	14.46589
H	7.76613	4.57413	15.57391
H	8.21006	5.90367	14.48908
C	6.95945	6.67333	20.00739
H	7.80108	5.98005	20.14270
H	6.05300	6.17905	20.39535
H	7.13790	7.56053	20.63254
C	5.29030	9.89525	16.51479
H	5.97410	10.55382	15.95377
H	4.96080	10.43349	17.41390
H	4.42039	9.73559	15.86014
C	8.42984	9.78529	11.83560
C	8.47872	11.19521	11.83637
C	9.53826	11.84004	11.19710
H	9.56844	12.93423	11.19417
C	10.55596	11.12248	10.56093
C	10.49431	9.72955	10.58615
H	11.28543	9.14890	10.10314
C	9.44762	9.03909	11.20936
C	9.43317	7.54003	11.21281
H	8.43458	7.14316	10.97986
H	9.70936	7.14901	12.20459
H	10.15013	7.13747	10.48460
C	11.68886	11.83938	9.88396

H	12.35800	11.13756	9.36572
H	12.29533	12.40972	10.60778
H	11.31820	12.56362	9.14164
C	14.69071	7.41354	13.66592
C	14.82219	7.69649	12.30401
H	15.40400	7.02184	11.67142
C	14.20924	8.80865	11.74221
H	14.31275	9.00654	10.67234
C	13.45885	9.67154	12.53446
H	12.97837	10.53480	12.07670
C	13.31115	9.44550	13.90399
C	13.93312	8.30482	14.44147
C	14.41766	7.94990	17.97112
H	14.91629	7.95996	18.93504
C	14.87146	8.23499	16.73094
H	15.84652	8.56095	16.38364
C	12.69461	7.65646	16.53202
C	7.39957	11.99376	12.51190
H	7.56321	13.07303	12.38604
H	7.35462	11.77930	13.59200
H	6.40473	11.74338	12.11250
C	12.54501	10.41377	14.78655
H	11.99329	9.81130	15.52702
C	13.49500	11.33539	15.55529
H	14.20365	10.76963	16.17771
H	12.92785	12.00664	16.21982
H	14.07911	11.95933	14.85993
C	11.50670	11.22327	14.02081
H	11.96632	11.95416	13.33741
H	10.87694	11.79476	14.72037
H	10.85761	10.58083	13.40422
C	15.36486	6.19048	14.25564
H	15.04791	6.10458	15.30589
C	16.88603	6.35369	14.23775
H	17.37457	5.49614	14.72610
H	17.20922	7.26953	14.75673
H	17.26659	6.41098	13.20548
C	14.93257	4.89944	13.56445
H	15.16543	4.91346	12.48804
H	13.85627	4.73182	13.69977
H	15.46329	4.04158	14.00698
C	12.29967	7.00620	18.88446
C	12.60113	5.69414	19.28361
C	11.84130	5.14583	20.32310
H	12.05068	4.12800	20.66014
C	10.82461	5.87486	20.92552
H	10.24248	5.43074	21.73700
C	11.26701	7.76339	19.46640
C	13.71442	4.88213	18.64883
H	14.14897	5.47771	17.83239
C	13.19676	3.59108	18.01815
H	12.50392	3.80488	17.19214
H	12.69182	2.94956	18.75803
H	14.03713	3.01583	17.59822
C	14.82976	4.61438	19.65988
H	15.66605	4.08222	19.18073
H	14.47305	3.99179	20.49569
H	15.22087	5.55003	20.08875
C	10.99583	9.18248	19.00871
H	11.15454	9.19568	17.91919
C	9.55774	9.62601	19.24397
H	8.83911	8.91755	18.80606
H	9.38684	10.60705	18.77533
H	9.32695	9.73369	20.31617
C	11.98245	10.15831	19.65394
H	13.02689	9.89164	19.43476
H	11.86043	10.17036	20.74892
H	11.81411	11.18164	19.28256
C	10.53954	7.16967	20.49843
H	9.73478	7.72697	20.97847
C	11.01159	6.99314	14.99052
O	11.84585	6.36020	14.14823
O	9.96314	7.56632	14.44319
B	11.12645	5.11118	14.40725
O	10.22236	4.62847	13.42302
O	11.92558	4.03316	14.87550
C	10.53417	3.27003	13.17205
C	11.25989	2.83638	14.49740
C	10.26849	2.45883	15.59652
H	9.50381	3.24005	15.71400
H	9.76510	1.50308	15.39016
H	10.80754	2.36523	16.55020
C	9.25177	2.51177	12.87233
H	8.81572	2.89086	11.93602
H	9.44102	1.43373	12.75135
H	8.50839	2.65595	13.66725
C	11.46415	3.21803	11.96061
H	12.40993	3.73672	12.17267
H	11.68594	2.18726	11.64451
H	10.97527	3.74264	11.12692
C	12.29569	1.73843	14.33138
H	11.83997	0.81570	13.94066
H	13.09941	2.05146	13.65274
H	12.74897	1.50855	15.30749
H	10.39412	5.64584	15.42017

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Sn	9.07041	8.83851	15.30904
N	11.41239	7.45916	16.45769
C	7.31025	8.49050	14.00258
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N	13.78112	7.89498	16.16258
N	12.95367	7.94579	18.18121
C	5.00246	7.73152	14.08574
H	4.19295	7.21516	14.60891
C	4.79054	8.28072	12.82012
H	3.80603	8.20333	12.35181
C	5.83119	8.91210	12.13924
H	5.66489	9.31248	11.13512
C	6.66132	7.23259	15.97790
C	7.09907	9.02479	12.72639
C	7.69795	5.40967	17.17397
H	8.09507	4.39139	17.17682
C	7.15292	5.90813	15.99162
C	7.78600	6.17993	18.33669

C	6.70235	8.02060	17.15297
C	7.27240	7.47654	18.31288
H	7.31030	8.08455	19.22147
C	7.14908	5.07575	14.74733
H	6.20385	5.17053	14.19506
H	7.32249	4.01774	14.98216
H	7.96253	5.39115	14.07491
C	8.46346	5.63389	19.55438
H	9.54789	5.81626	19.49314
H	8.31519	4.54783	19.64432
H	8.10469	6.11556	20.47478
C	6.07342	9.38672	17.18468
H	6.35419	10.00100	16.31528
H	6.34923	9.93117	18.09839
H	4.97494	9.30324	17.15654
C	8.23862	9.64505	11.99278
C	8.38365	11.04672	11.93821
C	9.45064	11.59182	11.22362
H	9.56046	12.68016	11.18459
C	10.38071	10.78437	10.56048
C	10.22497	9.40093	10.63849
H	10.94222	8.75075	10.12852
C	9.17117	8.81019	11.34691
C	9.04808	7.31640	11.40723
H	8.00118	6.99200	11.32322
H	9.42505	6.91390	12.36270
H	9.62412	6.84918	10.59674
C	11.52671	11.39930	9.81033
H	12.11664	10.63894	9.27907
H	12.20764	11.93685	10.49157
H	11.17341	12.13300	9.06896
C	14.59063	6.75385	14.17549
C	14.70205	6.72304	12.78280
H	15.23101	5.89506	12.30549
C	14.11934	7.71122	11.99851
H	14.19243	7.65406	10.90970
C	13.43527	8.77096	12.58839
H	12.98041	9.53460	11.95685
C	13.32437	8.86728	13.97749
C	13.89993	7.83522	14.74306
C	14.29919	8.27772	18.27532
H	14.75876	8.50745	19.23137
C	14.81192	8.24157	17.02659
H	15.81334	8.44056	16.65909
C	12.62084	7.69746	16.87294
C	7.40999	11.93841	12.65439
H	7.66207	12.99893	12.51563
H	7.39842	11.72684	13.73591
H	6.37998	11.77830	12.30133
C	12.65733	10.05636	14.64620
H	12.06590	9.66492	15.49009
C	13.69652	11.02428	15.21696
H	14.36550	10.53717	15.94001
H	13.19858	11.85899	15.73480
H	14.31628	11.44611	14.40975
C	11.68905	10.80152	13.73875
H	12.21232	11.34662	12.93799
H	11.12184	11.54626	14.31725
H	10.96855	10.12868	13.24869
C	15.22019	5.67369	15.03143
H	14.85593	5.81554	16.05972
C	16.74333	5.82141	15.04226
H	17.19979	5.08710	15.72403
H	17.06247	6.82608	15.36015
H	17.16110	5.65037	14.03711
C	14.80621	4.26815	14.61092
H	15.16957	4.02743	13.59900
H	13.71474	4.14378	14.63465
H	15.24956	3.52667	15.29387
C	12.09499	7.79538	19.30956
C	12.24172	6.64207	20.10113
C	11.48307	6.56501	21.27270
H	11.57643	5.69073	21.91870
C	10.59804	7.58150	21.61653
H	10.01195	7.50177	22.53525
C	11.18682	8.82298	19.61641
C	13.12804	5.49706	19.64875
H	13.98838	5.93316	19.11609
C	12.37435	4.61361	18.64814
H	12.02005	5.17619	17.77279
H	11.49596	4.15203	19.12676
H	13.02230	3.80347	18.27980
C	13.68900	4.66964	20.79938
H	14.41438	3.93762	20.41432
H	12.90217	4.09805	21.31657
H	14.20000	5.29729	21.54572
C	11.05650	10.03749	18.71724
H	11.17062	9.67336	17.68370
C	9.68549	10.69778	18.79622
H	8.88068	9.96543	18.63714
H	9.59628	11.46843	18.01599
H	9.51854	11.19378	19.76582
C	12.16396	11.05753	18.99068
H	13.16595	10.62621	18.85468
H	12.09659	11.44192	20.02092
H	12.07509	11.91314	18.30309
C	10.43657	8.68745	20.78816
H	9.72080	9.46394	21.06195
C	11.09517	6.68605	15.36921
O	11.73652	5.68216	15.03902
O	9.99605	7.03615	14.74908
B	10.57646	3.99918	14.48333
O	10.00429	4.33683	13.26881
O	11.54905	3.01848	14.31889
C	10.81738	3.76935	12.24045
C	11.43931	2.53803	12.97688
C	10.49434	1.33845	13.00066
H	9.48916	1.64159	13.32804
H	10.41299	0.85510	12.01585
H	10.87901	0.60202	13.72084
C	9.93454	3.43001	11.05382
H	9.54558	4.35726	10.60815
H	10.50180	2.89108	10.27928
H	9.07514	2.81751	11.35568
C	11.87623	4.79169	11.84500
H	12.51619	5.03692	12.70111

H	12.49976	4.43369	11.01202
H	11.38223	5.72143	11.53603
C	12.80104	2.10637	12.46648
H	12.73371	1.76759	11.42099
H	13.53121	2.92059	12.52626
H	13.17491	1.26867	13.07394
H	9.97357	4.13198	15.51830

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Sn	9.06801	8.57462	16.35737
N	11.39201	8.00421	15.50457
C	7.32644	8.92270	14.93545
C	6.11040	8.44745	15.48694
N	13.50283	6.84363	15.02186
N	12.23266	6.11342	16.62881
C	4.87277	8.90875	15.01824
H	3.95461	8.51610	15.46527
C	4.81242	9.85135	13.99919
H	3.84698	10.22249	13.64587
C	5.99328	10.30212	13.42017
H	5.96277	11.02226	12.59756
C	6.05491	7.39289	16.54834
C	7.24070	9.84155	13.86271
C	5.76778	5.06143	17.13741
H	5.65040	4.01853	16.82568
C	5.91716	6.04509	16.15635
C	5.72954	5.37592	18.49792
C	5.99441	7.73364	17.91478
C	5.84089	6.71847	18.86267
H	5.78775	6.99128	19.92127
C	5.85323	5.67519	14.70136
H	4.89207	5.99040	14.26389
H	5.95013	4.58952	14.56030
H	6.63369	6.18100	14.11521
C	5.59373	4.30223	19.53827
H	5.06879	3.41987	19.14462
H	5.04451	4.66154	20.42061
H	6.58306	3.96125	19.89089
C	6.08253	9.16481	18.35415
H	7.11395	9.54854	18.25095
H	5.80001	9.27656	19.40987
H	5.44265	9.81710	17.74280
C	8.42833	10.31227	13.09424
C	9.13921	11.46157	13.46989
C	10.23198	11.85689	12.69484
H	10.80262	12.72662	13.01918
C	10.62266	11.16389	11.55180
C	9.86445	10.05576	11.16516
H	10.13570	9.51087	10.25556
C	8.77521	9.61595	11.91883
C	7.97882	8.41940	11.47720
H	6.94078	8.69425	11.23193
H	7.91436	7.66288	12.27487
H	8.42638	7.95040	10.58984
C	11.85327	11.56582	10.79234
H	11.78869	11.28436	9.73047
H	12.74357	11.06871	11.21444
H	12.02720	12.65058	10.85016
C	13.30762	7.35814	12.66303
C	13.75229	8.09369	11.56063
H	13.23119	7.99992	10.60514
C	14.86389	8.92292	11.66276
H	15.19896	9.49157	10.79200
C	15.57150	9.01113	12.85862
H	16.46676	9.63415	12.90987
C	15.14816	8.32546	13.99812
C	13.98930	7.54123	13.87460
C	13.30016	5.23835	16.52787
H	13.39777	4.38097	17.18650
C	14.08981	5.69388	15.52999
H	15.01754	5.30871	15.12179
C	12.33804	7.10136	15.68948
C	8.76805	12.28198	14.66974
H	8.25503	13.20829	14.35997
H	9.67508	12.55425	15.22777
H	8.08638	11.74418	15.34223
C	15.96606	8.33803	15.27501
H	15.32510	7.94501	16.07911
C	17.17071	7.40280	15.12209
H	16.88414	6.38898	14.80415
H	17.72112	7.31938	16.07213
H	17.86703	7.79328	14.36290
C	16.41991	9.72442	15.71316
H	17.10309	10.18032	14.97766
H	16.97908	9.64738	16.65890
H	15.56805	10.39894	15.87471
C	12.21526	6.31773	12.51602
H	11.98145	5.92723	13.51667
C	12.73110	5.13549	11.69233
H	11.96923	4.34176	11.63665
H	13.64262	4.70538	12.13551
H	12.97431	5.44155	10.66254
C	10.92269	6.88457	11.95142
H	11.05643	7.26027	10.92555
H	10.55633	7.71926	12.56328
H	10.14365	6.10762	11.91939
C	11.21616	6.06123	17.62886
C	10.15866	5.15270	17.45841
C	9.17081	5.12707	18.44533
H	8.32208	4.45292	18.33807
C	9.24267	5.97049	19.54764
H	8.45154	5.94110	20.30045
C	11.31181	6.93516	18.72677
C	10.05373	4.29384	16.21207
H	11.07736	4.03176	15.89740
C	9.41053	5.09361	15.07669
H	9.99203	5.99049	14.81937
H	8.40204	5.41621	15.37280
H	9.31660	4.48028	14.16686
C	9.29832	2.98938	16.44027
H	9.37319	2.34959	15.54818
H	8.22715	3.17106	16.61960
H	9.69882	2.42797	17.29799
C	12.46393	7.91360	18.86291
H	12.73263	8.25569	17.85074

C	12.09842	9.16432	19.65408
H	11.18965	9.63854	19.25494
H	12.91218	9.90023	19.58439
H	11.93889	8.94534	20.72198
C	13.69544	7.23087	19.46353
H	14.02404	6.36908	18.86421
H	13.48253	6.87224	20.48321
H	14.53541	7.94061	19.51963
C	10.29999	6.86254	19.68753
H	10.33163	7.52894	20.55045
C	11.57243	9.38370	15.38583
O	12.67285	9.93493	15.27197
O	10.45317	10.00789	15.51534
B	12.79869	11.71143	16.35211
O	14.15991	11.97753	16.25616
O	12.06753	12.69166	15.68111
C	14.33019	12.99016	15.26196
C	12.97131	13.75107	15.36589
C	12.94204	14.73829	16.53202
H	13.29907	14.26059	17.45590
H	13.55537	15.63023	16.33617
H	11.90267	15.05868	16.69492
C	15.55752	13.81218	15.60871
H	16.45855	13.18790	15.51216
H	15.66370	14.67074	14.92774
H	15.51304	14.18144	16.64144
C	14.50490	12.32213	13.90094
H	13.62615	11.71280	13.64926
H	14.68041	13.06134	13.10536
H	15.37184	11.65127	13.93934
C	12.54313	14.45822	14.09427
H	13.24257	15.27313	13.85243
H	12.50456	13.77281	13.24014
H	11.54341	14.89662	14.23028
H	12.35448	11.13049	17.31324

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Sn	8.30537	9.71366	15.96782
N	11.37666	6.92602	15.89799
C	7.22193	9.79516	14.00692
C	6.03201	9.04295	14.06693
N	13.36233	6.38751	14.56333
N	13.23209	5.73040	16.64168
C	5.13045	9.03820	12.99785
H	4.21844	8.43783	13.06255
C	5.40280	9.79335	11.86003
H	4.70052	9.79717	11.02227
C	6.57844	10.53669	11.78752
H	6.80474	11.11799	10.88904
C	5.75748	8.24827	15.30378
C	7.49538	10.53991	12.84823
C	6.07268	6.26462	16.65076
H	6.49370	5.26146	16.76416
C	6.28478	6.94776	15.44746
C	5.34895	6.82455	17.70306
C	5.00614	8.82724	16.35201
C	4.81855	8.10736	17.53165
H	4.24741	8.56447	18.34534
C	7.08418	6.30437	14.35278
H	8.12369	6.67024	14.37950
H	6.67683	6.53948	13.35949
H	7.10725	5.21263	14.47673
C	5.11836	6.06375	18.97619
H	5.84513	5.24751	19.09483
H	4.11095	5.61525	18.99082
H	5.19279	6.72066	19.85580
C	4.43782	10.20907	16.20294
H	5.23258	10.95221	16.02492
H	3.88138	10.50959	17.10127
H	3.76335	10.27417	15.33556
C	8.77039	11.29133	12.68025
C	8.83157	12.67423	12.92015
C	10.02911	13.35194	12.67316
H	10.07425	14.43110	12.85267
C	11.16470	12.68900	12.19954
C	11.08530	11.30981	11.99608
H	11.96444	10.76448	11.64236
C	9.90628	10.59755	12.22577
C	9.84896	9.12049	11.98408
H	9.08559	8.86916	11.23038
H	9.58478	8.58688	12.90880
H	10.81933	8.74192	11.64543
C	12.42997	13.43886	11.89535
H	12.52970	14.33689	12.52257
H	12.45065	13.76936	10.84322
H	13.31691	12.80868	12.05770
C	12.10735	6.07700	12.48833
C	11.98767	6.37292	11.12852
H	11.25634	5.83440	10.52481
C	12.78065	7.34748	10.52996
H	12.67303	7.55544	9.46271
C	13.68384	8.07666	11.29246
H	14.27848	8.86327	10.82236
C	13.84038	7.82308	12.65883
C	13.06791	6.79738	13.22485
C	14.41391	5.22438	16.13326
H	15.08235	4.61757	16.73602
C	14.49846	5.63417	14.84821
H	15.24651	5.44198	14.08630
C	12.56413	6.45724	15.68371
C	7.62861	13.41209	13.43668
H	7.87192	14.45741	13.67411
H	7.22628	12.93635	14.34534
H	6.80716	13.40962	12.70275
C	14.81405	8.64240	13.47985
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H	16.95797	8.89542	13.75284
H	16.48241	8.53509	12.07684
C	14.54425	10.13728	13.33042
H	14.76658	10.49038	12.31029
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H	13.49629	10.36455	13.56235
C	11.25232	5.00488	13.13935

H	11.01443	5.35979	14.15443
C	12.01232	3.68153	13.25797
H	11.39087	2.92525	13.76332
H	12.94265	3.78851	13.83479
H	12.27624	3.29169	12.26168
C	9.91471	4.80029	12.43715
H	10.03044	4.33019	11.44743
H	9.37928	5.75221	12.30831
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C	12.76355	5.59442	17.97945
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H	10.49815	3.86398	19.81580
C	11.88873	5.31575	20.58594
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H	11.59062	4.08879	16.21431
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H	9.15512	3.76128	16.11921
C	11.18773	2.37096	17.40532
H	10.75190	1.80453	16.56759
H	10.65715	2.06469	18.32088
H	12.24034	2.06679	17.51082
C	14.40930	7.42786	18.65474
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O	10.46428	10.91785	15.81343
C	12.39610	11.92634	16.61483
C	10.83609	11.93279	16.76947
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H	10.88689	10.57470	18.48261
H	10.66405	12.29475	18.90526
H	9.31994	11.36377	18.20731
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H	12.94562	11.70053	18.71095
C	12.84884	12.74423	15.41179
H	12.28165	12.45383	14.51775
H	12.72144	13.82431	15.57598
H	13.91373	12.54498	15.22792
C	10.15964	13.23154	16.37920
H	10.53179	14.06472	16.99429
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INT-BH2

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C	1.59404	-1.31675	6.37869
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C	2.49646	-3.66835	7.65213
H	2.85381	-4.57798	8.14162
C	1.15071	-3.53487	7.31973
H	0.43694	-4.32822	7.56020
C	0.70163	-2.36473	6.70026
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C	-1.36071	-2.50531	5.24221
C	-0.57267	-3.23664	4.19612
H	0.28324	-2.63303	3.85139
H	-1.19306	-3.48061	3.32288
H	-0.14367	-4.16837	4.59434
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H	-1.60240	-0.63844	9.43772
H	0.00949	-0.54458	8.67865
C	-4.84555	-0.99846	5.66735
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C	3.90810	-0.32685	6.56312
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C	4.67696	1.88349	7.15671
H	4.59742	2.76873	7.79315
C	3.85736	0.78531	7.42152
C	2.92014	0.82332	8.59176
H	2.71568	-0.17973	8.99083
H	1.96521	1.26990	8.27847
H	3.32837	1.44510	9.40020
C	5.02974	-1.62284	4.71202
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C	-2.39821	2.55716	5.80534
H	-2.80136	1.80724	6.48901
C	-1.54097	3.54776	6.29270
C	-1.23472	3.65499	7.77305
H	-0.34257	4.28694	7.88755
C	-0.90925	2.30815	8.40352
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C	-2.38840	4.35441	8.49534
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H	-3.31693	3.76642	8.41446
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H	-0.46119	4.06380	1.36865
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H	1.36552	6.11298	9.20266
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H	2.23373	3.85636	8.51244
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H	3.49127	5.94388	11.40991
H	1.73543	6.00480	11.61097
H	2.60441	7.42272	10.96681
C	3.52181	7.18676	4.80508
H	2.42775	7.07868	4.75205
C	4.12672	6.14033	3.87017
H	5.22718	6.20161	3.86380
H	3.78020	6.29972	2.83629
H	3.83721	5.12445	4.17525
C	3.85575	8.61163	4.36550
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H	3.49411	8.79309	3.34113
H	4.94247	8.79274	4.36722
B	2.97136	2.05075	3.40896
O	3.65292	2.29439	2.24897
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H	0.94128	2.02618	1.43676
H	0.86579	0.62251	0.33735
H	0.14337	0.52990	1.96696
C	3.41075	1.60910	-0.03125
H	4.33829	2.10569	-0.35014
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C	2.34440	-1.10582	1.87397
H	2.41098	-1.41618	0.82081
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N	13.04520	7.91745	18.16611
C	5.08091	7.32532	13.61728
H	4.28405	6.75017	14.09636
C	4.96890	7.70976	12.27981
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C	5.99189	8.42680	11.66065
H	5.90769	8.70375	10.60604
C	6.52579	7.31674	15.74796
C	7.14119	8.78660	12.37844
C	7.59898	5.82433	17.30951
H	8.04406	4.84840	17.52032
C	7.05322	6.04183	16.04274
C	7.65412	6.82430	18.28475
C	6.51238	8.33218	16.73970
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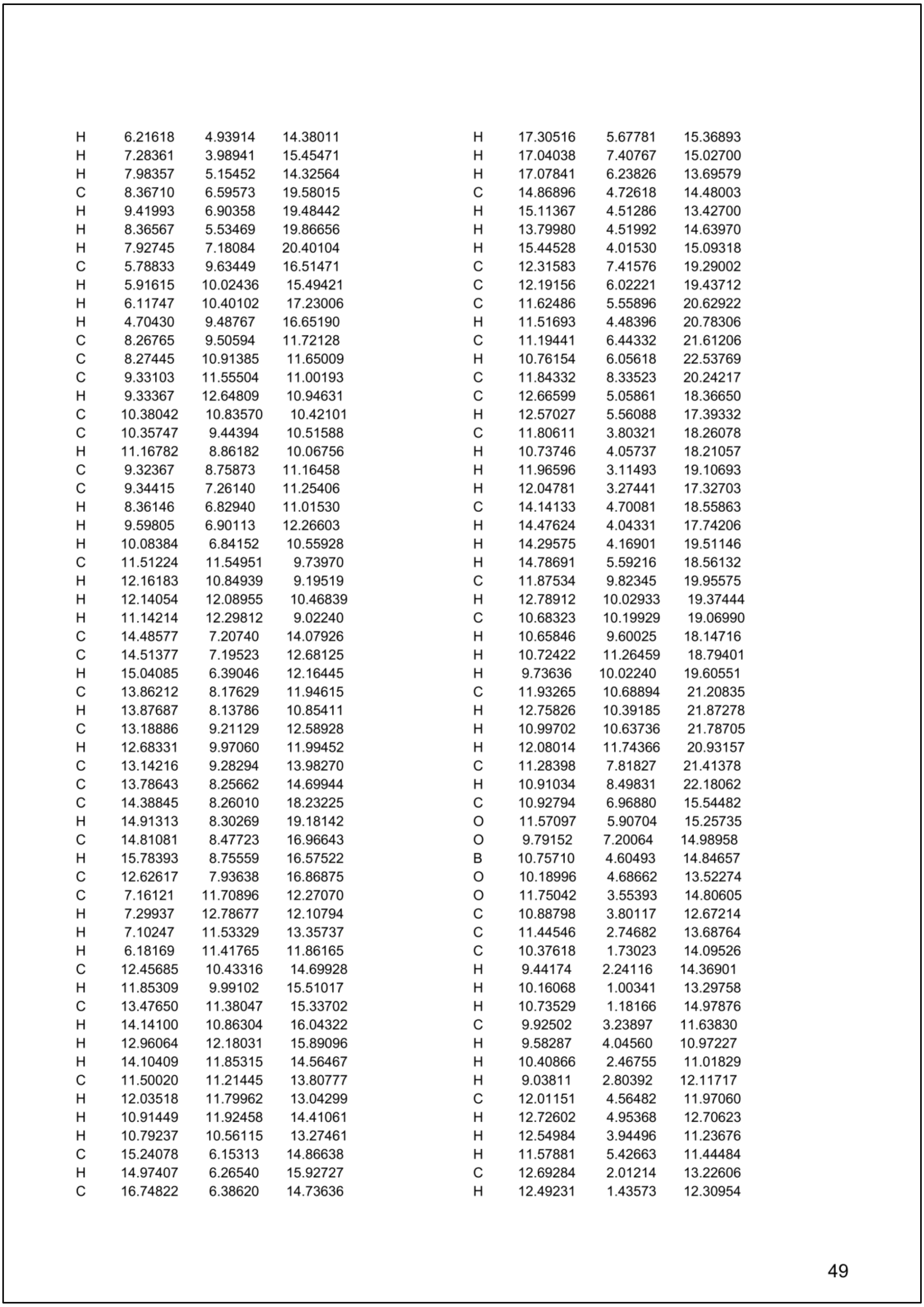

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H	9.41993	6.90358	19.48442
H	8.36567	5.53469	19.86656
H	7.92745	7.18084	20.40104
C	5.78833	9.63449	16.51471
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H	4.70430	9.48767	16.65190
C	8.26765	9.50594	11.72128
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C	10.35747	9.44394	10.51588
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H	8.36146	6.82940	11.01530
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C	11.51224	11.54951	9.73970
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H	11.14214	12.29812	9.02240
C	14.48577	7.20740	14.07926
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H	15.04085	6.39046	12.16445
C	13.86212	8.17629	11.94615
H	13.87687	8.13786	10.85411
C	13.18886	9.21129	12.58928
H	12.68331	9.97060	11.99452
C	13.14216	9.28294	13.98270
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H	14.91313	8.30269	19.18142
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H	15.78393	8.75559	16.57522
C	12.62617	7.93638	16.86875
C	7.16121	11.70896	12.27070
H	7.29937	12.78677	12.10794
H	7.10247	11.53329	13.35737
H	6.18169	11.41765	11.86165
C	12.45685	10.43316	14.69928
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H	11.51693	4.48396	20.78306
C	11.19441	6.44332	21.61206
H	10.76154	6.05618	22.53769
C	11.84332	8.33523	20.24217
C	12.66599	5.05861	18.36650
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H	10.65846	9.60025	18.14716
H	10.72422	11.26459	18.79401
H	9.73636	10.02240	19.60551
C	11.93265	10.68894	21.20835
H	12.75826	10.39185	21.87278
H	10.99702	10.63736	21.78705
H	12.08014	11.74366	20.93157
C	11.28398	7.81827	21.41378
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C	10.92794	6.96880	15.54482
O	11.57097	5.90704	15.25735
O	9.79152	7.20064	14.98958
B	10.75710	4.60493	14.84657
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C	10.88798	3.80117	12.67214
C	11.44546	2.74682	13.68764
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C	5.18969	8.88436	12.65696
H	4.37430	8.93159	11.93018
C	6.31295	9.69024	12.50137
H	6.38338	10.37911	11.65487
C	5.99422	7.08393	15.87381
C	7.36859	9.65078	13.42381
C	6.08504	4.88660	16.88222
H	6.23904	3.80780	16.77859
C	6.19219	5.69378	15.74782
C	5.78165	5.41422	18.14007
C	5.63386	7.62950	17.12339
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H	7.25570	5.65738	13.86316
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H	5.35457	3.52823	19.11198
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C	5.35773	9.09780	17.27927
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C	10.63713	11.06612	12.15581
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H	12.85654	7.32843	9.13359
C	13.57481	8.29450	10.91856
H	14.13435	9.04759	10.36369
C	13.60367	8.32557	12.31822
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C	13.90663	6.43356	15.04452
H	14.73939	6.02484	14.48210
C	12.03338	7.61459	15.36423
C	7.37418	12.30330	14.64614
H	7.42769	13.37991	14.85815
H	7.43689	11.77321	15.61134
H	6.38349	12.07766	14.22345
C	14.44719	9.36377	13.02674
H	13.93403	9.62825	13.96401
C	15.83614	8.80603	13.35365
H	15.80197	7.96726	14.06294
H	16.45800	9.59036	13.80991
H	16.34452	8.46081	12.43882
C	14.58523	10.65038	12.22060
H	15.24759	10.52443	11.34874
H	15.00133	11.43607	12.85929
H	13.60933	11.01304	11.87371
C	11.31279	5.29402	13.04034
H	11.07230	5.67716	14.04278
C	12.15484	4.02576	13.20395
H	11.59322	3.24833	13.74486
H	13.08370	4.21680	13.75989
H	12.43223	3.61796	12.21919
C	9.98423	4.97198	12.36003
H	10.13191	4.46824	11.39260
H	9.38804	5.87855	12.18420
H	9.39283	4.29067	12.98845
C	11.51754	6.85484	17.66554
C	10.74033	5.67925	17.69139
C	9.81962	5.52780	18.73087
H	9.19033	4.63594	18.76222
C	9.68894	6.49833	19.71506
H	8.95393	6.37090	20.51344
C	11.42501	7.84061	18.66213
C	10.87723	4.57400	16.66400
H	11.56791	4.91206	15.88019
C	9.54662	4.26105	15.99064
H	9.11856	5.15579	15.51655
H	8.80218	3.89052	16.70952
H	9.67652	3.49010	15.21628
C	11.49810	3.32396	17.28839
H	11.64258	2.54129	16.52720
H	10.85376	2.91112	18.08027
H	12.47680	3.54413	17.74081
C	12.31733	9.05926	18.70085
H	12.62581	9.32114	17.67745
C	11.62453	10.29065	19.27508
H	10.66400	10.47664	18.77145
H	12.25906	11.16538	19.08608
H	11.44434	10.20124	20.35847

C	13.58551	8.72730	19.49271
H	14.16130	7.91253	19.02612
H	13.33655	8.41603	20.52021
H	14.23604	9.61213	19.55198
C	10.49235	7.63006	19.68416
H	10.39043	8.38466	20.46478
C	11.09756	9.75275	15.43646
O	12.24930	10.27846	15.34761
O	10.03382	10.33861	15.78402
B	12.62882	11.75263	15.84069
O	13.29683	11.63476	17.12346
O	13.65016	12.20861	14.91364
C	14.67214	11.89451	16.95486
C	14.66567	12.80966	15.68756
C	14.24881	14.24385	16.02535
H	13.34183	14.24644	16.64642
H	15.04189	14.79839	16.54956
H	14.01874	14.77116	15.08773
C	15.21600	12.55232	18.21324
H	15.18993	11.83828	19.05135
H	16.26035	12.87464	18.07765
H	14.60928	13.42232	18.49647
C	15.40992	10.57915	16.69682
H	15.04735	10.11885	15.76854
H	16.50047	10.71321	16.62829
H	15.20315	9.88391	17.52245
C	15.97453	12.83655	14.91653
H	16.78614	13.24379	15.53956
H	16.26845	11.83519	14.57704
H	15.87411	13.48070	14.02987
H	11.58177	12.37901	15.87791

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INT-BH2_isomer

Sn	9.24388	8.63121	15.22740
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C	7.55411	8.30411	13.80623
C	6.57065	7.48227	14.38140
N	13.80579	7.78920	16.18432
N	12.88979	7.78406	18.17831
C	5.33306	7.30300	13.75834
H	4.57838	6.65468	14.21288
C	5.07633	7.94803	12.54874
H	4.11130	7.81528	12.05324
C	6.05306	8.74989	11.95957
H	5.85768	9.23255	10.99754
C	6.96353	6.79320	15.64825
C	7.29534	8.93477	12.58210
C	8.12434	4.98396	16.75301
H	8.66268	4.03330	16.69476
C	7.65611	5.56278	15.57246
C	7.95093	5.58898	17.99956
C	6.73510	7.40094	16.90449
C	7.23987	6.78942	18.05683
H	7.07703	7.26947	19.02612
C	7.93098	4.91435	14.24872
H	7.05073	4.93761	13.59097
H	8.24339	3.86895	14.38373
H	8.74403	5.44773	13.72750
C	8.56462	4.98569	19.22464
H	9.60998	5.31953	19.31997
H	8.57137	3.88697	19.17448
H	8.04018	5.29249	20.14043
C	5.96262	8.68591	16.99781
H	6.44725	9.49488	16.42642
H	5.86718	9.01687	18.04099
H	4.95364	8.57530	16.57202
C	8.35562	9.74919	11.92348
C	8.36404	11.15313	12.04930
C	9.36556	11.88645	11.41197
H	9.37120	12.97610	11.51608
C	10.35886	11.26581	10.64724
C	10.33317	9.87586	10.54080
H	11.10183	9.36974	9.94854
C	9.35337	9.10066	11.17279
C	9.39522	7.60546	11.06875
H	8.38670	7.17382	11.00195
H	9.87830	7.15752	11.95437
H	9.96594	7.29704	10.18146
C	11.43106	12.07934	9.98151
H	12.10226	11.44889	9.38108
H	12.04737	12.61171	10.72488
H	11.00046	12.84465	9.31656
C	14.91003	6.94013	14.17885
C	15.05178	6.99092	12.78938
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C	14.33324	7.90715	12.02946
H	14.43788	7.91541	10.94143
C	13.49776	8.83157	12.64903
H	12.96051	9.56094	12.04175
C	13.34116	8.83708	14.03691
C	14.01440	7.84509	14.77519
C	14.18177	8.26747	18.31900
H	14.57597	8.56155	19.28665
C	14.74648	8.26912	17.09655
H	15.72993	8.59034	16.77246
C	12.62716	7.45185	16.85251
C	7.31851	11.84686	12.87517
H	7.45627	12.93697	12.86193
H	7.35075	11.50885	13.92371
H	6.30350	11.62133	12.51429
C	12.53824	9.91486	14.74116
H	11.94881	9.41967	15.53150
C	13.45577	10.93199	15.42559
H	14.12672	10.46309	16.15769
H	12.85569	11.68552	15.95995
H	14.07402	11.45705	14.67976
C	11.56088	10.64538	13.83298
H	12.08219	11.27437	13.09513
H	10.91752	11.31594	14.42333
H	10.91818	9.95880	13.25945
C	15.75392	5.99154	15.00852
H	15.28954	5.93198	16.00480
C	17.16699	6.56187	15.16849
H	17.76875	5.93227	15.84261
H	17.16557	7.58565	15.56985

H	17.67911	6.59810	14.19369
C	15.82588	4.57099	14.45677
H	16.35632	4.53707	13.49104
H	14.82825	4.14016	14.30778
H	16.39060	3.93132	15.15317
C	12.03163	7.49585	19.27480
C	12.26342	6.32415	20.01713
C	11.48348	6.11018	21.15759
H	11.64517	5.21538	21.76152
C	10.49298	7.01529	21.52307
H	9.89125	6.83085	22.41640
C	11.01659	8.40993	19.60758
C	13.25821	5.28572	19.53815
H	14.01670	5.80684	18.93262
C	12.54614	4.29051	18.61628
H	12.03571	4.81353	17.79416
H	11.79168	3.71593	19.17818
H	13.26407	3.57772	18.18117
C	13.99429	4.57560	20.66898
H	14.76589	3.90830	20.25601
H	13.31960	3.94905	21.27359
H	14.48814	5.29026	21.34509
C	10.79409	9.65163	18.76728
H	11.01442	9.36680	17.72612
C	9.35250	10.14349	18.79388
H	8.65107	9.33528	18.53956
H	9.21633	10.94869	18.05644
H	9.07150	10.55062	19.77855
C	11.75847	10.77069	19.16578
H	12.80837	10.45597	19.08267
H	11.58028	11.08883	20.20565
H	11.62135	11.64765	18.51359
C	10.24943	8.14306	20.74507
H	9.45296	8.83173	21.03121
C	11.08841	6.32235	15.31368
O	12.18422	5.67855	14.67934
O	10.41132	7.13592	14.43640
B	12.03336	4.92883	13.56561
O	11.04597	5.03476	12.61920
O	12.90207	3.89343	13.29530
C	11.41045	4.17477	11.53153
C	12.31751	3.11589	12.24516
C	11.50872	2.00370	12.90429
H	10.68934	2.42080	13.50855
H	11.08023	1.31315	12.16372
H	12.16870	1.43305	13.57347
C	10.14667	3.62696	10.89872
H	9.58169	4.45121	10.43921
H	10.38607	2.89347	10.11400
H	9.49746	3.15144	11.64524
C	12.19514	5.01252	10.52897
H	13.11752	5.40255	10.98308
H	12.45607	4.43448	9.63090
H	11.58286	5.87144	10.22568
C	13.42018	2.52856	11.38576
H	13.00013	2.00346	10.51472
H	14.11003	3.30507	11.03245
H	14.00076	1.80354	11.97468

H	10.41152	5.50170	15.62492

Scheme S4

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TS-SnH3

Sn	3.01147	0.97173	4.33416
O	3.02303	0.29607	7.43475
O	3.05552	2.17406	6.24035
N	-0.05442	3.59281	8.31900
N	2.07054	3.50361	8.88805
N	1.16660	1.72950	7.50334
C	1.62498	2.31810	3.21058
C	0.41595	1.78059	2.72673
C	-0.42126	2.54308	1.90358
H	-1.35742	2.10807	1.54218
C	-0.05354	3.83388	1.53275
H	-0.70865	4.42802	0.89014
C	1.16326	4.35548	1.96323
H	1.47757	5.35331	1.64393
C	2.01224	3.60365	2.78774
C	3.35867	4.17657	3.09562
C	3.53057	5.11007	4.13597
C	4.76882	5.73260	4.29441
H	4.88679	6.47267	5.09206
C	5.86130	5.42815	3.47874
C	5.68073	4.47658	2.47531
H	6.52086	4.22074	1.82265
C	4.44654	3.85409	2.26000
C	4.29364	2.86788	1.13670
H	4.18515	1.83804	1.51755
H	5.17069	2.88299	0.47494
H	3.39533	3.07432	0.53629
C	2.39863	5.42868	5.06392
H	1.58516	5.94952	4.53914
H	2.73038	6.06374	5.89698
H	1.97953	4.49914	5.47765
C	7.19628	6.07140	3.71541
H	7.09070	7.13476	3.97816
H	7.84529	5.99857	2.83108
H	7.72214	5.58085	4.55252
C	0.06523	0.35657	3.00949
C	0.58293	-0.65259	2.16961
C	0.25835	-1.98589	2.42919
H	0.66074	-2.76424	1.77365
C	-0.58156	-2.34635	3.48649
C	-1.08727	-1.32999	4.29745
H	-1.75248	-1.58653	5.12779
C	-0.77292	0.01596	4.08572
C	-1.28802	1.06714	5.01700
H	-1.64763	1.95444	4.47872
H	-0.48856	1.40105	5.69933
H	-2.10635	0.68460	5.64113
C	1.44572	-0.30224	0.98967
H	0.90440	0.34291	0.28014
H	1.77386	-1.20521	0.45676
H	2.34167	0.26474	1.28750
C	-0.91893	-3.78826	3.73629

H	-0.03378	-4.35061	4.07549
H	-1.28004	-4.28034	2.81977
H	-1.69538	-3.89406	4.50728
C	2.30968	1.33518	6.86992
C	1.09645	2.85316	8.14589
C	0.20907	4.67803	9.15006
H	-0.56904	5.38911	9.40722
C	1.51247	4.62578	9.49538
H	2.10459	5.27042	10.13753
C	3.22421	2.83668	9.42780
C	3.02019	1.97414	10.52320
C	4.12702	1.30533	11.05024
H	3.99125	0.62645	11.89549
C	5.39570	1.49935	10.52031
H	6.25132	0.96391	10.93853
C	5.57724	2.37917	9.46166
H	6.57848	2.52841	9.05594
C	4.50213	3.06763	8.89118
C	4.74268	4.04879	7.76604
H	3.80883	4.10715	7.19233
C	5.83097	3.57059	6.81068
H	6.83300	3.61682	7.26713
H	5.84610	4.20164	5.91285
H	5.63274	2.53861	6.49068
C	5.06208	5.43765	8.32163
H	4.24727	5.82545	8.95176
H	5.22011	6.15326	7.49925
H	5.97808	5.41999	8.93439
C	1.66757	1.78440	11.17942
H	0.91595	2.31444	10.57955
C	1.25871	0.31557	11.22465
H	1.20858	-0.11142	10.21346
H	0.26871	0.20593	11.69193
H	1.96594	-0.28063	11.82185
C	1.64549	2.41817	12.57053
H	2.36688	1.92956	13.24444
H	0.64515	2.32458	13.02142
H	1.89964	3.48779	12.52567
C	-1.35083	3.31551	7.78077
C	-2.11578	2.26782	8.32796
C	-3.42213	2.09607	7.86454
H	-4.03445	1.29420	8.28173
C	-3.95807	2.93363	6.89403
H	-4.98529	2.78919	6.55126
C	-3.18041	3.94858	6.35465
H	-3.59926	4.59506	5.58062
C	-1.86238	4.15406	6.77453
C	-1.04759	5.25793	6.13481
H	-0.00962	5.15212	6.48287
C	-1.03840	5.11284	4.61568
H	-0.58495	4.16132	4.30581
H	-0.46148	5.92409	4.14927
H	-2.05418	5.15612	4.19419
C	-1.54441	6.63957	6.56075
H	-2.57953	6.81052	6.22436
H	-0.91380	7.42792	6.12125
H	-1.52777	6.76182	7.65422
C	-1.59239	1.38202	9.43535
H	-0.50128	1.47832	9.44433
C	-1.87919	-0.09509	9.19019
H	-2.95773	-0.31747	9.16990
H	-1.43510	-0.69993	9.99383
H	-1.42524	-0.41952	8.24280
C	-2.13068	1.86339	10.78393
H	-1.84421	2.90888	10.97786
H	-1.73972	1.24654	11.60789
H	-3.23061	1.80882	10.81409
B	2.57736	-0.92523	7.82923
O	1.28161	-1.29884	8.05530
O	3.47872	-1.93448	8.01748
C	1.28233	-2.73399	8.15962
C	2.76777	-3.04435	8.57393
C	2.98998	-3.01258	10.08151
H	2.57503	-2.09612	10.52182
H	2.53854	-3.88102	10.58224
H	4.07200	-3.01927	10.27598
C	0.24430	-3.16571	9.17643
H	-0.76176	-2.91832	8.81003
H	0.29147	-4.25336	9.33653
H	0.38774	-2.66325	10.14132
C	0.92442	-3.26922	6.78034
H	1.66866	-2.96756	6.02895
H	0.83642	-4.36486	6.77501
H	-0.03730	-2.83599	6.47607
C	3.32658	-4.32757	7.98822
H	2.74788	-5.19922	8.32929
H	3.31896	-4.30394	6.89135
H	4.36807	-4.45743	8.31601
H	1.72344	0.48498	5.67584

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TS-SnH1

Sn	5.24044	1.36469	6.25373
O	3.08089	0.43987	6.39181
O	3.45917	2.49882	7.01161
N	-0.19625	3.56318	6.77273
N	0.83219	3.32267	8.69057
N	1.29197	1.74469	6.90517
C	5.04597	2.54972	4.37117
C	4.52125	2.01287	3.18357
C	4.41755	2.81743	2.04116
H	4.01410	2.38914	1.11951
C	4.84600	4.14230	2.07141
H	4.76392	4.76374	1.17592
C	5.40238	4.66837	3.23540
H	5.77371	5.69690	3.25348
C	5.51402	3.87622	4.38524
C	6.21771	4.43065	5.58351
C	5.57628	5.33505	6.45650
C	6.30365	5.90197	7.50320
H	5.80119	6.61300	8.16635
C	7.64376	5.58211	7.73639
C	8.25629	4.67418	6.87413
H	9.30825	4.41642	7.02871
C	7.57354	4.10066	5.79544
C	8.30165	3.16608	4.87039

H	8.04550	2.11233	5.07286
H	9.38973	3.26308	4.98912
H	8.04150	3.35114	3.81841
C	4.13398	5.69669	6.26766
H	4.00324	6.36683	5.40428
H	3.73761	6.21103	7.15443
H	3.53003	4.79699	6.08627
C	8.38025	6.18244	8.89770
H	8.21579	7.26915	8.95913
H	9.46244	6.00360	8.82842
H	8.03098	5.74858	9.84990
C	4.15909	0.56861	3.13580
C	5.19588	-0.38834	3.11918
C	4.86714	-1.74658	3.13443
H	5.67395	-2.48638	3.12759
C	3.54293	-2.18176	3.14271
C	2.53640	-1.21628	3.10713
H	1.49144	-1.53771	3.10876
C	2.81419	0.15056	3.11712
C	1.68445	1.13544	3.18337
H	1.86910	2.03520	2.58169
H	1.51999	1.46387	4.22287
H	0.74317	0.68204	2.84403
C	6.64210	0.02330	3.04064
H	6.78958	0.85297	2.33368
H	7.26883	-0.82202	2.72370
H	7.03733	0.37146	4.00993
C	3.20355	-3.63640	3.25314
H	2.96950	-3.86353	4.30606
H	4.04037	-4.27736	2.93945
H	2.32200	-3.89712	2.64872
C	2.59772	1.56563	6.80300
C	0.74088	2.81162	7.42198
C	-0.67695	4.54655	7.62534
H	-1.42589	5.26197	7.30115
C	-0.04094	4.39760	8.81072
H	-0.13763	4.94267	9.74415
C	1.34894	2.60253	9.82244
C	0.49551	1.66000	10.42695
C	0.96450	0.98599	11.55676
H	0.32037	0.25093	12.04415
C	2.23267	1.23489	12.06304
H	2.58497	0.69391	12.94442
C	3.05493	2.17156	11.44867
H	4.04974	2.35980	11.85434
C	2.63376	2.88024	10.31880
C	3.52876	3.93100	9.70027
H	3.25634	3.99988	8.63900
C	5.00100	3.53739	9.75975
H	5.40587	3.59527	10.78298
H	5.59882	4.20863	9.12938
H	5.15231	2.51172	9.39207
C	3.29345	5.29421	10.35319
H	2.24965	5.62494	10.24204
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H	3.52192	5.26508	11.43081
C	-0.90642	1.37749	9.92877
H	-1.06196	1.94684	9.00237
C	-1.09095	-0.09850	9.58560
H	-0.34317	-0.42628	8.84788
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H	-0.99268	-0.73375	10.48054
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H	-2.96501	1.71583	10.54397
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C	-1.48357	2.21508	5.19011
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H	-0.47835	4.66092	2.32165
C	-0.24618	4.20001	4.41409
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H	1.14202	5.22628	5.65852
C	1.88440	5.27564	3.65918
H	2.43643	4.32920	3.74710
H	2.59447	6.09393	3.84099
H	1.54151	5.36992	2.61761
C	0.01131	6.69321	4.58591
H	-0.42987	6.86364	3.59086
H	0.71928	7.51276	4.78419
H	-0.80269	6.76068	5.32370
C	-1.90402	1.27235	6.29844
H	-1.07847	1.22989	7.02093
C	-2.10506	-0.16237	5.82323
H	-2.97319	-0.26762	5.15294
H	-2.27866	-0.81863	6.68855
H	-1.20809	-0.53159	5.30535
C	-3.14989	1.81601	7.00070
H	-2.97911	2.82322	7.41095
H	-3.44835	1.15994	7.83285
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B	1.95390	-1.15530	6.45933
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O	1.50609	-1.16350	7.78852
C	3.25768	-2.68882	7.53772
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H	3.76441	-4.62085	8.39780
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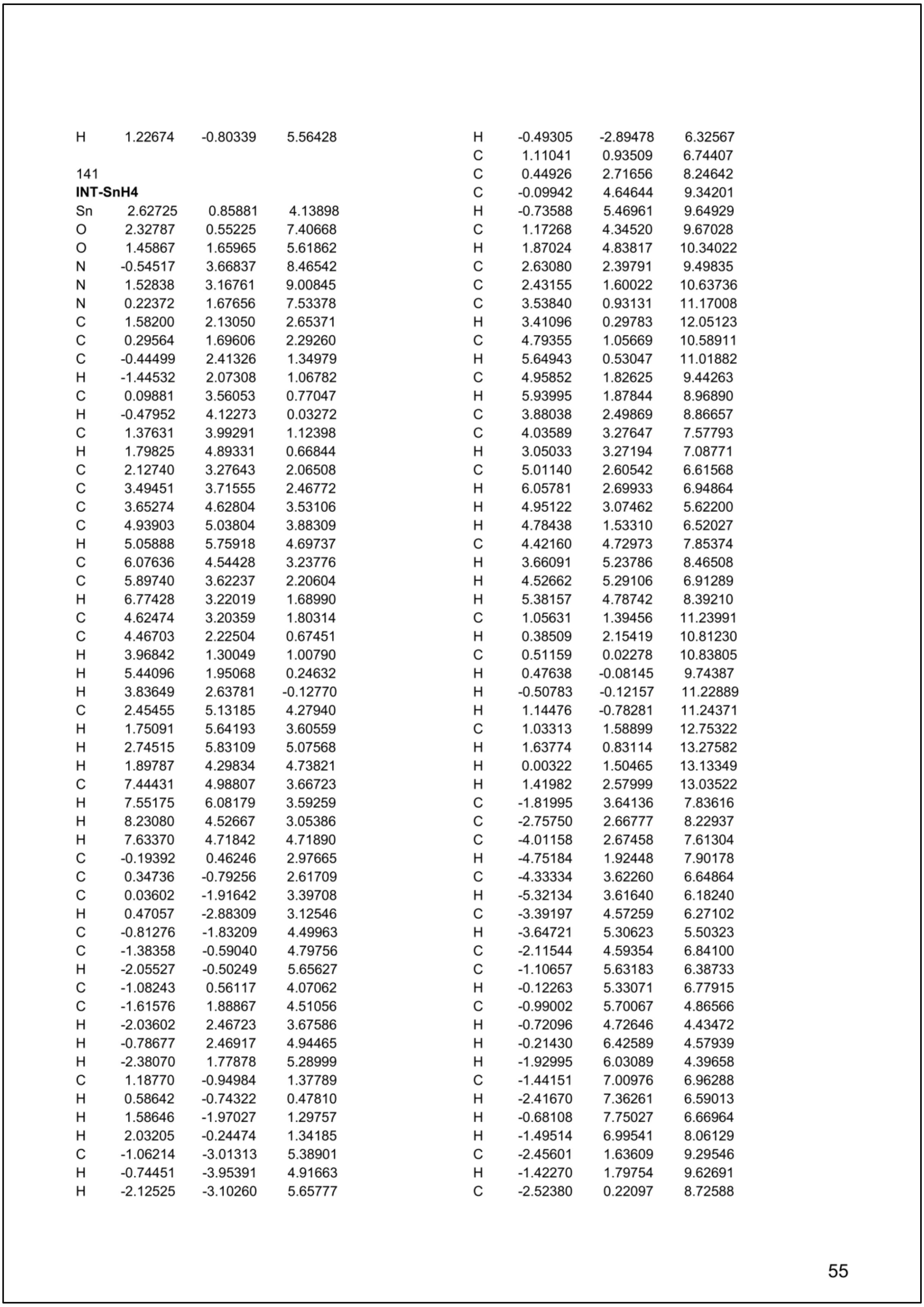

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INT-SnH4

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C	1.58200	2.13050	2.65371
C	0.29564	1.69606	2.29260
C	-0.44499	2.41326	1.34979
H	-1.44532	2.07308	1.06782
C	0.09881	3.56053	0.77047
H	-0.47952	4.12273	0.03272
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H	1.79825	4.89331	0.66844
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C	3.49451	3.71555	2.46772
C	3.65274	4.62804	3.53106
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H	5.05888	5.75918	4.69737
C	6.07636	4.54428	3.23776
C	5.89740	3.62237	2.20604
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C	4.62474	3.20359	1.80314
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H	3.96842	1.30049	1.00790
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H	3.83649	2.63781	-0.12770
C	2.45455	5.13185	4.27940
H	1.75091	5.64193	3.60559
H	2.74515	5.83109	5.07568
H	1.89787	4.29834	4.73821
C	7.44431	4.98807	3.66723
H	7.55175	6.08179	3.59259
H	8.23080	4.52667	3.05386
H	7.63370	4.71842	4.71890
C	-0.19392	0.46246	2.97665
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H	0.47057	-2.88309	3.12546
C	-0.81276	-1.83209	4.49963
C	-1.38358	-0.59040	4.79756
H	-2.05527	-0.50249	5.65627
C	-1.08243	0.56117	4.07062
C	-1.61576	1.88867	4.51056
H	-2.03602	2.46723	3.67586
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H	-2.38070	1.77878	5.28999
C	1.18770	-0.94984	1.37789
H	0.58642	-0.74322	0.47810
H	1.58646	-1.97027	1.29757
H	2.03205	-0.24474	1.34185
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H	-0.74451	-3.95391	4.91663
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H	1.87024	4.83817	10.34022
C	2.63080	2.39791	9.49835
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C	3.53840	0.93131	11.17008
H	3.41096	0.29783	12.05123
C	4.79355	1.05669	10.58911
H	5.64943	0.53047	11.01882
C	4.95852	1.82625	9.44263
H	5.93995	1.87844	8.96890
C	3.88038	2.49869	8.86657
C	4.03589	3.27647	7.57793
H	3.05033	3.27194	7.08771
C	5.01140	2.60542	6.61568
H	6.05781	2.69933	6.94864
H	4.95122	3.07462	5.62200
H	4.78438	1.53310	6.52027
C	4.42160	4.72973	7.85374
H	3.66091	5.23786	8.46508
H	4.52662	5.29106	6.91289
H	5.38157	4.78742	8.39210
C	1.05631	1.39456	11.23991
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C	-1.81995	3.64136	7.83616
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C	-1.44151	7.00976	6.96288
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H	-1.42270	1.79754	9.62691
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H	-3.53258	-0.02055	8.35341
H	-2.26774	-0.52064	9.49785
H	-1.80213	0.12445	7.90281
C	-3.36093	1.81175	10.51420
H	-3.28401	2.82919	10.92719
H	-3.08001	1.10066	11.30753
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B	2.68254	-0.73473	7.56409
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C	2.72865	-2.97399	7.31340
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H	3.72766	-3.74340	9.98756
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H	1.17179	-4.45874	7.17096
H	2.65820	-5.03809	7.95883
H	1.53608	-3.96040	8.83761
C	3.12498	-3.20364	5.85933
H	3.69397	-2.34735	5.46729
H	3.72908	-4.11394	5.73469
H	2.21074	-3.30191	5.25609
C	5.27674	-3.08072	7.81514
H	5.27082	-4.17742	7.90577
H	5.54870	-2.81151	6.78645
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INT-SnH2

Sn	4.53520	1.70729	4.08789
O	3.07723	0.23519	6.82555
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N	1.48587	1.70893	7.26669
C	2.81003	1.59511	2.63638
C	1.94191	0.50340	2.43583
C	0.94396	0.56977	1.45462
H	0.28567	-0.29085	1.30656
C	0.79291	1.70971	0.66909
H	0.01074	1.75088	-0.09372
C	1.64997	2.79154	0.85052
H	1.55076	3.68673	0.22947
C	2.65948	2.73438	1.81972
C	3.60844	3.88549	1.93603
C	3.29333	5.00829	2.72706
C	4.18439	6.08257	2.76840
H	3.92639	6.95799	3.37224
C	5.39338	6.06975	2.06874
C	5.69354	4.94266	1.30274
H	6.63468	4.90922	0.74606
C	4.82043	3.85482	1.21638
C	5.17917	2.66400	0.37605
H	5.33385	1.76643	0.99840
H	6.10215	2.84272	-0.19220
H	4.37316	2.40941	-0.32836
C	2.01647	5.05486	3.51295
H	1.14642	5.12257	2.84385
H	1.99509	5.92181	4.18778
H	1.88401	4.14066	4.11131
C	6.34743	7.22425	2.16836
H	5.81999	8.18822	2.10666
H	7.10283	7.19562	1.37030
H	6.88332	7.20990	3.13217
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C	3.12546	-1.63543	3.02243
C	3.26837	-2.74229	3.86037
H	4.09607	-3.43634	3.68363
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H	0.67774	-2.22432	5.97880
C	1.17288	-0.95885	4.31455
C	0.05274	0.00197	4.58265
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H	-0.47097	-0.24239	5.51523
C	4.12271	-1.40290	1.92214
H	3.66587	-0.93602	1.03805
H	4.60009	-2.34538	1.61779
H	4.93528	-0.72974	2.25238
C	2.66834	-4.07866	5.90715
H	3.39184	-3.72852	6.66159
H	3.09637	-4.96299	5.41202
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C	2.58950	1.41039	6.58699
C	1.02829	2.90519	7.49846
C	-0.46843	4.54165	7.89272
H	-1.44413	5.01605	7.89652
C	0.73413	4.97782	8.33067
H	1.02063	5.90364	8.81911
C	2.93644	3.89982	8.74491
C	2.97145	3.32798	10.03136
C	4.19479	3.31098	10.70627
H	4.24912	2.86705	11.70249
C	5.33831	3.84350	10.12629
H	6.28701	3.82245	10.66792
C	5.28036	4.39061	8.85072
H	6.18792	4.78939	8.39680
C	4.08351	4.42933	8.12947
C	4.04601	5.04184	6.74678
H	3.24365	4.53031	6.19576
C	5.34776	4.80949	5.98568
H	6.16716	5.43674	6.37257
H	5.21990	5.06309	4.92370
H	5.66310	3.75783	6.05367
C	3.71339	6.53345	6.81451
H	2.72420	6.71742	7.25941
H	3.71231	6.97142	5.80469
H	4.46005	7.07618	7.41608
C	1.75509	2.71348	10.69179
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H	2.13064	0.73174	9.86962

H	1.04239	0.74517	11.28441
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H	2.22202	3.24207	12.76470
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H	1.27357	4.47097	11.89728
C	-1.32687	2.43967	6.84391
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C	-2.83196	0.58378	7.08038
H	-3.18866	-0.28291	7.64145
C	-3.44172	0.92343	5.87997
H	-4.27818	0.33022	5.50340
C	-2.97531	2.00972	5.15126
H	-3.44593	2.25948	4.19838
C	-1.90199	2.78123	5.60566
C	-1.41009	3.93857	4.75825
H	-0.45357	4.28502	5.18012
C	-1.14208	3.50269	3.31788
H	-0.37165	2.72088	3.26119
H	-0.79647	4.35585	2.71728
H	-2.05079	3.11631	2.83189
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C	-1.13924	0.90527	8.90186
H	-0.31074	1.58960	9.11723
C	-0.53832	-0.49565	8.78702
H	-1.30411	-1.24394	8.52791
H	-0.08763	-0.80134	9.74304
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C	-2.13349	1.01596	10.05733
H	-2.53936	2.03574	10.14217
H	-1.64255	0.76491	11.01083
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B	4.39740	-0.15106	6.31082
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H	8.50579	-0.16444	7.82107
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C	5.93300	0.08292	8.95461
H	4.93202	-0.34645	9.10626
H	6.63831	-0.40417	9.64493
H	5.87785	1.15320	9.20092
C	6.39068	-2.61647	7.93050
H	7.43704	-2.59904	8.27223
H	5.73012	-2.53604	8.80325
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INT-SnH1

Sn	5.23508	1.35245	6.19577
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O	3.43709	2.45782	6.94493
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C	5.03521	2.56339	4.33520
C	4.49718	2.03319	3.15154
C	4.38222	2.84473	2.01567
H	3.96828	2.42433	1.09512
C	4.81307	4.16921	2.05231
H	4.72331	4.79697	1.16198
C	5.37971	4.68874	3.21470
H	5.74994	5.71758	3.23572
C	5.50140	3.88911	4.35839
C	6.20525	4.43072	5.56202
C	5.56326	5.32964	6.44071
C	6.28831	5.88511	7.49483
H	5.78572	6.59177	8.16235
C	7.62631	5.55818	7.73109
C	8.23878	4.65466	6.86439
H	9.28910	4.39175	7.02123
C	7.55868	4.09288	5.77761
C	8.28907	3.16449	4.84790
H	8.04989	2.10762	5.05600
H	9.37693	3.27537	4.95595
H	8.01679	3.34344	3.79806
C	4.12221	5.69570	6.25092
H	3.99466	6.37243	5.39232
H	3.72455	6.20389	7.14062
H	3.51620	4.79929	6.05996
C	8.35983	6.14614	8.90041
H	8.19603	7.23229	8.97201
H	9.44202	5.96690	8.83285
H	8.00696	5.70306	9.84699
C	4.13271	0.58949	3.11910
C	5.17131	-0.36755	3.10941
C	4.84408	-1.72475	3.16087
H	5.65117	-2.46409	3.16157
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C	2.51242	-1.19723	3.15414
H	1.46837	-1.51936	3.18182
C	2.78830	0.16990	3.12611
C	1.65538	1.15159	3.18732
H	1.85457	2.06885	2.61811
H	1.45731	1.44700	4.23095
H	0.72564	0.70620	2.80786
C	6.61550	0.04373	2.99498
H	6.74911	0.85272	2.26159
H	7.23797	-0.80950	2.69149
H	7.02815	0.42179	3.94563
C	3.18476	-3.61017	3.36340
H	2.98069	-3.79799	4.43020
H	4.01344	-4.26123	3.04897
H	2.28706	-3.88911	2.79197
C	2.55493	1.53987	6.79091

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C	-0.68407	4.54775	7.63251
H	-1.42841	5.26952	7.31199
C	-0.04957	4.38763	8.81758
H	-0.14258	4.92723	9.75454
C	1.33786	2.57834	9.81516
C	0.48719	1.63265	10.41742
C	0.96166	0.95322	11.54137
H	0.32134	0.21288	12.02553
C	2.23253	1.19868	12.04220
H	2.58892	0.65240	12.91858
C	3.05449	2.13407	11.42557
H	4.05352	2.31537	11.82406
C	2.62828	2.84704	10.30048
C	3.52788	3.88804	9.67189
H	3.23688	3.97206	8.61632
C	4.99381	3.46742	9.70017
H	5.41844	3.51317	10.71579
H	5.59246	4.13083	9.06222
H	5.11805	2.43980	9.32766
C	3.32842	5.24981	10.33942
H	2.28718	5.59649	10.25576
H	3.97313	6.00891	9.86934
H	3.58086	5.20802	11.41118
C	-0.90980	1.33903	9.91307
H	-1.07444	1.92514	8.99847
C	-1.06123	-0.13332	9.53804
H	-0.28905	-0.43421	8.81289
H	-2.05729	-0.31734	9.10674
H	-0.96851	-0.78215	10.42378
C	-1.96234	1.79044	10.92577
H	-1.87543	1.22909	11.86927
H	-2.97575	1.62254	10.52925
H	-1.86248	2.86070	11.16364
C	-0.66059	3.33366	5.43277
C	-1.49561	2.22615	5.18201
C	-1.96861	2.05870	3.87941
H	-2.61445	1.20958	3.65212
C	-1.63122	2.95267	2.86862
H	-2.01989	2.80536	1.85832
C	-0.78515	4.01868	3.13741
H	-0.50392	4.70108	2.33294
C	-0.26654	4.22300	4.42080
C	0.69423	5.36861	4.66236
H	1.12641	5.24085	5.66735
C	1.84619	5.33354	3.66100
H	2.40666	4.38991	3.72185
H	2.55126	6.15393	3.85317
H	1.49106	5.44847	2.62565
C	-0.03005	6.71504	4.63111
H	-0.48234	6.89704	3.64314
H	0.67186	7.53810	4.83619
H	-0.83781	6.76275	5.37714
C	-1.91471	1.27171	6.28094
H	-1.09663	1.23318	7.01150
C	-2.09248	-0.16249	5.79471
H	-2.94632	-0.27333	5.10727
H	-2.27629	-0.82464	6.65333
H	-1.18061	-0.52028	5.29469
C	-3.17192	1.79800	6.97604
H	-3.01511	2.80585	7.39074
H	-3.46716	1.13549	7.80424
H	-4.01543	1.85483	6.26935
B	2.10038	-1.01456	6.51651
O	3.00699	-2.09413	6.32256
O	1.65137	-1.06526	7.87789
C	3.36428	-2.61136	7.59160
C	2.09652	-2.28042	8.44955
C	0.99223	-3.32273	8.26651
H	0.81531	-3.51245	7.19786
H	1.22643	-4.27641	8.76335
H	0.06100	-2.92814	8.69915
C	3.67031	-4.09340	7.44978
H	4.56688	-4.22538	6.82518
H	3.86393	-4.55807	8.42915
H	2.84200	-4.62658	6.96515
C	4.60745	-1.88538	8.10638
H	4.39014	-0.82653	8.30269
H	4.99989	-2.33553	9.03082
H	5.39075	-1.93850	7.33504
C	2.37080	-2.07272	9.93034
H	2.83853	-2.96289	10.37957
H	3.02043	-1.20331	10.09589
H	1.42628	-1.88261	10.46011
H	1.26349	-0.84165	5.64629

Scheme S5

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TS-SnH7

Sn	1.10021	4.80885	5.61369
O	1.34615	1.79655	3.25539
O	-0.22695	3.46941	6.69569
N	-0.27191	-0.64857	7.48538
N	-2.21211	-0.69670	6.48633
N	-1.25163	1.44706	6.70529
C	0.32215	6.49630	6.98466
C	-0.83956	7.28760	7.06015
C	-0.94679	8.28816	8.03999
H	-1.86280	8.88480	8.08162
C	0.07391	8.51902	8.95607
H	-0.03256	9.30127	9.71215
C	1.22273	7.73565	8.90747
H	2.03249	7.88519	9.62796
C	1.34136	6.73872	7.93508
C	2.55568	5.86579	7.90680
C	2.53938	4.63027	8.58970
C	3.62395	3.76272	8.43831
H	3.59270	2.79631	8.94495
C	4.73121	4.09213	7.65379
C	4.74952	5.34116	7.02910
H	5.61281	5.62298	6.41941
C	3.68053	6.23318	7.13852
C	3.69909	7.54294	6.40635
H	2.90308	7.58056	5.64378
H	4.66150	7.70510	5.90222

H	3.50851	8.38666	7.08623
C	1.38033	4.24778	9.46187
H	1.25575	4.96437	10.28842
H	1.52774	3.24469	9.88381
H	0.43883	4.24573	8.89390
C	5.85026	3.11130	7.46254
H	6.02439	2.51690	8.37185
H	6.79032	3.61437	7.19478
H	5.60973	2.40518	6.65032
C	-2.02053	7.11513	6.16668
C	-2.21349	7.99479	5.08406
C	-3.36867	7.87783	4.30956
H	-3.50812	8.55385	3.46009
C	-4.33432	6.90305	4.57408
C	-4.13135	6.05576	5.66386
H	-4.88216	5.29444	5.89695
C	-2.99295	6.14456	6.47221
C	-2.82079	5.21568	7.63807
H	-2.45044	5.74990	8.52541
H	-2.08293	4.43126	7.40394
H	-3.77108	4.72854	7.89481
C	-1.17698	9.02943	4.75096
H	-1.07415	9.77632	5.55362
H	-1.42748	9.55728	3.82013
H	-0.18289	8.57009	4.63385
C	-5.52452	6.73513	3.67560
H	-6.36241	6.25076	4.19772
H	-5.27087	6.10051	2.80866
H	-5.87544	7.69995	3.28007
C	-0.14930	2.19317	6.53504
C	-1.20199	0.15001	6.86299
C	-0.72425	-1.96177	7.51542
H	-0.14729	-2.74431	7.99752
C	-1.92614	-1.98804	6.90003
H	-2.61070	-2.80729	6.70932
C	-3.34472	-0.34770	5.68513
C	-4.37829	0.41332	6.26530
C	-5.49079	0.69305	5.46979
H	-6.30912	1.28642	5.87841
C	-5.57159	0.23131	4.15883
H	-6.45150	0.46433	3.55457
C	-4.53369	-0.51011	3.61148
H	-4.60116	-0.85505	2.57783
C	-3.39107	-0.81464	4.35971
C	-2.28876	-1.65696	3.74426
H	-1.40632	-1.58299	4.39922
C	-1.86102	-1.16300	2.36424
H	-2.67597	-1.25495	1.62829
H	-1.03000	-1.78400	1.99555
H	-1.52556	-0.11670	2.39700
C	-2.71049	-3.12810	3.67916
H	-3.01053	-3.52831	4.65906
H	-1.88478	-3.74919	3.29833
H	-3.56709	-3.25568	2.99806
C	-4.28433	0.89385	7.70147
H	-3.25357	1.25709	7.83497
C	-5.19867	2.07501	8.00227
H	-5.05395	2.88696	7.27495

H	-4.97401	2.47644	9.00195
H	-6.26340	1.79180	7.99643
C	-4.53790	-0.24785	8.69011
H	-5.56543	-0.63238	8.58918
H	-4.40981	0.10482	9.72580
H	-3.84856	-1.09124	8.53969
C	0.83529	-0.21492	8.27731
C	0.58675	0.14571	9.61294
C	1.69394	0.45176	10.41063
H	1.54193	0.73750	11.45379
C	2.98410	0.38520	9.89557
H	3.83685	0.61167	10.54010
C	3.19558	0.05599	8.55932
H	4.21130	0.04149	8.16010
C	2.12359	-0.23736	7.71324
C	2.33770	-0.55629	6.24561
H	1.39294	-0.33873	5.72103
C	3.41107	0.31925	5.60425
H	3.22320	1.38750	5.79191
H	3.41343	0.17821	4.51408
H	4.41669	0.07324	5.98254
C	2.63530	-2.04260	6.03945
H	3.57269	-2.32906	6.54269
H	2.74212	-2.26194	4.96610
H	1.83212	-2.68123	6.43615
C	-0.82136	0.23433	10.16898
H	-1.49723	-0.24330	9.44412
C	-1.26217	1.69340	10.30200
H	-0.63688	2.23394	11.02993
H	-2.30617	1.74829	10.64855
H	-1.19726	2.21959	9.33934
C	-0.97681	-0.52564	11.48323
H	-0.66381	-1.57564	11.38028
H	-2.02944	-0.51357	11.80517
H	-0.38285	-0.07312	12.29272
B	1.65507	1.03519	2.20964
O	0.89404	0.82564	1.07416
O	2.85142	0.33334	2.15112
C	1.71407	0.14578	0.12419
C	2.76621	-0.56574	1.04710
C	2.25869	-1.90009	1.58729
H	1.25392	-1.78705	2.02053
H	2.22156	-2.67699	0.80980
H	2.93660	-2.23888	2.38441
C	0.84937	-0.79018	-0.70107
H	0.14923	-0.20180	-1.31207
H	1.46391	-1.40185	-1.37933
H	0.25571	-1.45671	-0.06275
C	2.34865	1.20536	-0.77122
H	2.99288	1.87817	-0.18613
H	2.94738	0.75975	-1.57879
H	1.54935	1.81035	-1.22337
C	4.14361	-0.73772	0.43463
H	4.09828	-1.36290	-0.47013
H	4.59004	0.23061	0.17521
H	4.80900	-1.23126	1.15849
H	0.84765	1.73185	6.64774
B	0.09824	2.35018	3.70550

O	-1.07680	1.86899	3.05967
O	0.00481	3.83143	3.65192
C	-1.96199	2.94461	2.81200
C	-0.98152	4.14949	2.65751
H	0.08297	2.05289	4.96251
C	-1.58405	5.49781	2.96733
H	-1.95484	5.53708	3.99707
H	-0.83628	6.29549	2.83486
H	-2.42485	5.71785	2.29333
C	-0.28377	4.16496	1.29980
H	-0.96379	4.50852	0.50596
H	0.56848	4.85891	1.34789
H	0.09210	3.16677	1.03495
C	-2.89239	3.11562	4.00915
H	-2.33346	3.39418	4.91306
H	-3.66488	3.87606	3.82445
H	-3.38493	2.15536	4.20876
C	-2.76578	2.63747	1.55934
H	-3.35979	3.50974	1.24454
H	-2.10559	2.33286	0.73683
H	-3.46135	1.80993	1.76377

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TS-SnH4_isomer

Sn	4.08862	3.25539	7.12226
O	1.78442	1.55784	5.19146
O	1.81972	2.15456	7.34969
N	1.99825	6.14963	7.11759
N	0.64201	5.57854	5.49199
N	2.52587	4.12878	5.83253
C	4.65242	1.33638	6.09185
C	4.51058	0.11557	6.78390
C	4.89317	-1.08478	6.17198
H	4.77139	-2.02571	6.71655
C	5.44215	-1.08304	4.89143
H	5.73375	-2.02432	4.41833
C	5.66275	0.12587	4.23737
H	6.14408	0.14280	3.25544
C	5.28891	1.33369	4.84119
C	5.67445	2.62001	4.18894
C	4.91514	3.17350	3.14358
C	5.37573	4.33887	2.52029
H	4.80016	4.75028	1.68907
C	6.54751	4.98179	2.91489
C	7.28141	4.42126	3.96291
H	8.21187	4.89995	4.28383
C	6.87301	3.24822	4.59850
C	7.73169	2.64336	5.67304
H	7.19585	2.56134	6.63047
H	8.63753	3.24316	5.83764
H	8.03388	1.61831	5.40713
C	3.61857	2.55525	2.71770
H	3.61261	1.46505	2.83937
H	3.38983	2.79285	1.66923
H	2.80403	2.94262	3.35194
C	7.00801	6.24487	2.24705
H	6.91435	7.10824	2.92691
H	6.41655	6.46381	1.34647
H	8.06711	6.18275	1.95269
C	4.01251	0.09453	8.19386
C	4.84331	0.57110	9.23038
C	4.34950	0.61030	10.53961
H	4.99756	0.99093	11.33494
C	3.06628	0.17015	10.85934
C	2.28082	-0.34903	9.82836
H	1.27350	-0.71282	10.05485
C	2.73033	-0.39892	8.50912
C	1.83064	-0.97043	7.45354
H	1.77477	-2.06909	7.53553
H	2.20279	-0.73005	6.45166
H	0.80856	-0.57675	7.54788
C	6.25648	1.01489	8.97295
H	6.71635	0.45194	8.14917
H	6.87243	0.88856	9.87483
H	6.29879	2.08415	8.69999
C	2.53196	0.26398	12.25898
H	2.08878	-0.68899	12.58749
H	1.74042	1.02871	12.32667
H	3.32066	0.53721	12.97435
C	1.35028	2.29618	6.22947
C	1.83498	5.16917	6.11984
C	0.97652	7.08764	7.07358
H	0.95758	7.93662	7.75034
C	0.14121	6.73569	6.07862
H	-0.74424	7.22791	5.69135
C	0.00135	4.96061	4.38518
C	0.55389	5.10271	3.09311
C	-0.15097	4.53116	2.02904
H	0.24537	4.60681	1.01716
C	-1.36681	3.88373	2.22558
H	-1.90191	3.46364	1.37052
C	-1.90189	3.77704	3.50128
H	-2.85833	3.27121	3.64723
C	-1.22698	4.30288	4.60652
C	-1.84640	4.18182	5.98885
H	-1.06485	4.43416	6.72366
C	-2.34057	2.76678	6.29751
H	-3.23233	2.51368	5.70180
H	-2.62946	2.69303	7.35719
H	-1.58262	1.99752	6.09292
C	-2.99184	5.18167	6.16818
H	-2.66970	6.21759	5.99518
H	-3.40185	5.12161	7.18838
H	-3.80982	4.96508	5.46266
C	1.84692	5.86924	2.85568
H	2.61131	5.40067	3.50209
C	2.32734	5.78358	1.41172
H	2.46270	4.74759	1.07254
H	3.29319	6.29884	1.31359
H	1.62391	6.28147	0.72481
C	1.74459	7.35094	3.23681
H	0.94322	7.84622	2.66479
H	2.69043	7.85977	2.99424
H	1.55125	7.51385	4.30351
C	2.98409	6.13041	8.13874
C	4.19118	6.81790	7.92257

C	5.16895	6.73933	8.91801
H	6.12586	7.24492	8.77650
C	4.93631	6.02825	10.09084
H	5.71501	5.97447	10.85584
C	3.71848	5.38988	10.30012
H	3.55358	4.83457	11.22470
C	2.71738	5.42036	9.32678
C	1.39432	4.70909	9.53688
H	1.00952	4.44431	8.53995
C	1.53086	3.40627	10.31648
H	2.29639	2.74786	9.88438
H	0.57938	2.85434	10.29219
H	1.77996	3.58576	11.37488
C	0.37790	5.63874	10.20436
H	0.72541	5.94167	11.20526
H	-0.59081	5.12797	10.32267
H	0.20661	6.55031	9.61463
C	4.42940	7.57637	6.63181
H	3.44015	7.87332	6.24815
C	5.07117	6.67610	5.57564
H	6.06409	6.32853	5.90107
H	5.19942	7.22283	4.62862
H	4.45719	5.78807	5.36226
C	5.24184	8.85180	6.83257
H	4.80415	9.49586	7.61066
H	5.27985	9.42658	5.89461
H	6.28344	8.63527	7.11827
B	1.01498	0.66888	4.50770
O	1.46512	0.03568	3.39153
O	-0.23160	0.27908	4.90893
C	0.57491	-1.06881	3.16340
C	-0.74286	-0.59377	3.88277
C	-1.63576	0.24685	2.98315
H	-1.06625	1.05508	2.50368
H	-2.11646	-0.36211	2.20462
H	-2.42036	0.70990	3.59779
C	0.43743	-1.28816	1.66968
H	1.40332	-1.61233	1.25656
H	-0.30586	-2.07092	1.45627
H	0.14145	-0.36697	1.15247
C	1.20560	-2.28873	3.82389
H	1.28887	-2.15532	4.91118
H	0.63100	-3.20453	3.62520
H	2.22244	-2.41567	3.42628
C	-1.53951	-1.70267	4.54127
H	-1.86586	-2.44234	3.79510
H	-0.95318	-2.21494	5.31433
H	-2.43569	-1.28114	5.01901
H	0.39289	2.80448	6.03842

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TS-SnH4

Sn	0.31789	4.60874	6.09586
O	0.00416	2.02965	4.37398
O	-0.40018	2.69701	6.59995
N	-1.11537	-1.22818	6.81969
N	-2.95846	-0.93321	5.67508
N	-1.53649	0.91707	5.66608
C	0.64518	5.30086	8.19327
C	-0.26115	6.16968	8.81589
C	0.08362	6.79440	10.02042
H	-0.63202	7.46106	10.51091
C	1.34062	6.57505	10.58418
H	1.60564	7.06285	11.52566
C	2.26856	5.75524	9.94090
H	3.26372	5.60590	10.36967
C	1.92477	5.12525	8.74041
C	2.87400	4.27053	7.96930
C	2.82655	2.87108	8.12378
C	3.66438	2.07420	7.34308
H	3.61236	0.98801	7.46073
C	4.53796	2.62423	6.40210
C	4.57282	4.01349	6.26709
H	5.25034	4.46320	5.53480
C	3.75756	4.84962	7.03479
C	3.82062	6.34085	6.86346
H	2.83368	6.76098	6.61103
H	4.52497	6.61901	6.06760
H	4.13355	6.83959	7.79377
C	1.85295	2.24955	9.07524
H	1.79094	2.80765	10.02031
H	2.11948	1.20876	9.28855
H	0.84758	2.25591	8.62404
C	5.35702	1.73915	5.51315
H	6.24215	2.25983	5.11932
H	4.73933	1.41461	4.65992
H	5.69287	0.83416	6.04094
C	-1.56118	6.43502	8.13371
C	-1.65709	7.49408	7.20825
C	-2.86595	7.70299	6.53718
H	-2.93563	8.52305	5.81562
C	-3.98548	6.90312	6.77457
C	-3.86615	5.85911	7.69454
H	-4.73074	5.21869	7.88687
C	-2.67107	5.60148	8.36983
C	-2.54885	4.43206	9.30099
H	-1.99892	4.69587	10.21548
H	-1.98485	3.62105	8.81297
H	-3.53585	4.04103	9.58527
C	-0.47835	8.38624	6.94213
H	-0.10694	8.84593	7.87043
H	-0.73657	9.18584	6.23432
H	0.36939	7.81973	6.52266
C	-5.29193	7.16839	6.08352
H	-5.97758	7.73249	6.73791
H	-5.80080	6.23081	5.81304
H	-5.15195	7.75910	5.16665
C	-0.32391	1.62106	5.79535
C	-1.77907	-0.29008	6.03392
C	-1.89550	-2.38223	6.94540
H	-1.55102	-3.22108	7.54177
C	-3.02723	-2.19580	6.24401
H	-3.88675	-2.84003	6.08669
C	-3.95829	-0.43811	4.79528
C	-4.89980	0.48345	5.27755
C	-5.94344	0.85474	4.42228

H	-6.69016	1.57314	4.76881
C	-6.05291	0.30580	3.15035
H	-6.88426	0.59344	2.50226
C	-5.10047	-0.60090	2.69071
H	-5.19125	-1.00992	1.68351
C	-4.02444	-0.98013	3.49578
C	-2.92625	-1.89781	2.99084
H	-2.60780	-2.52725	3.83739
C	-1.70714	-1.07865	2.55820
H	-1.94731	-0.44940	1.68780
H	-0.87521	-1.74297	2.27765
H	-1.35695	-0.40427	3.35147
C	-3.37461	-2.83768	1.87888
H	-4.27368	-3.40688	2.16037
H	-2.57460	-3.55732	1.64905
H	-3.59397	-2.29461	0.94600
C	-4.80038	1.05890	6.67230
H	-3.97880	0.53683	7.18359
C	-4.43015	2.53852	6.62787
H	-3.48890	2.69458	6.08214
H	-4.29350	2.91861	7.64944
H	-5.22480	3.13646	6.15109
C	-6.07050	0.81577	7.48503
H	-6.93567	1.35115	7.06211
H	-5.93594	1.17604	8.51694
H	-6.32634	-0.25405	7.52786
C	0.08495	-1.13689	7.58661
C	-0.04661	-0.95085	8.97793
C	1.09791	-1.10683	9.76339
H	1.03193	-0.98395	10.84529
C	2.32490	-1.40969	9.18206
H	3.21046	-1.52663	9.81147
C	2.43565	-1.55062	7.80308
H	3.40755	-1.77857	7.36442
C	1.31560	-1.43430	6.97308
C	1.41272	-1.67721	5.47649
H	0.75645	-0.94325	4.97884
C	2.81750	-1.46372	4.92733
H	3.20390	-0.46514	5.16933
H	2.79907	-1.54173	3.83107
H	3.51903	-2.22807	5.29794
C	0.90975	-3.07558	5.10447
H	1.52186	-3.85033	5.59348
H	0.98206	-3.22362	4.01563
H	-0.13811	-3.23595	5.39311
C	-1.38879	-0.58203	9.58307
H	-2.16072	-1.12834	9.01670
C	-1.67265	0.91172	9.40542
H	-0.96936	1.51407	10.00105
H	-2.69274	1.15014	9.74599
H	-1.57780	1.23852	8.36012
C	-1.53451	-0.99164	11.04378
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H	-2.56447	-0.80460	11.38316
H	-0.87009	-0.40984	11.70198
B	-0.99974	2.67641	3.65805
O	-1.22989	2.45299	2.33725
O	-1.78899	3.65620	4.19093

C	-2.37366	3.24708	1.96410
C	-2.40662	4.34391	3.08840
C	-1.53051	5.54894	2.76863
H	-0.50721	5.23467	2.51470
H	-1.94685	6.14151	1.94142
H	-1.47344	6.19255	3.65866
C	-2.16358	3.78445	0.56252
H	-2.12846	2.94856	-0.15139
H	-2.99515	4.44497	0.27432
H	-1.22440	4.34439	0.47872
C	-3.57703	2.32382	2.01485
H	-3.71069	1.91224	3.02414
H	-4.50236	2.83643	1.71714
H	-3.41375	1.48225	1.32840
C	-3.79197	4.78726	3.51328
H	-4.31775	5.27833	2.68041
H	-4.39385	3.94166	3.86786
H	-3.69927	5.50619	4.33961
H	0.56091	1.00046	6.03511
B	1.71314	2.54020	4.06771
O	1.54899	3.45508	3.01202
O	2.46542	1.44370	3.64196
C	2.39775	3.04096	1.94373
C	2.57896	1.50547	2.21909
H	1.94578	2.93625	5.20588
C	3.93493	0.95491	1.80932
H	4.75610	1.45372	2.33937
H	3.98367	-0.11923	2.04184
H	4.09288	1.07392	0.72639
C	1.47682	0.65110	1.60011
H	1.58816	0.57830	0.50806
H	1.54472	-0.36381	2.01907
H	0.47925	1.04791	1.82348
C	3.70354	3.81911	2.08484
H	4.19829	3.57799	3.03747
H	4.40301	3.61933	1.25997
H	3.46818	4.89317	2.09190
C	1.73237	3.36300	0.61883
H	2.32961	2.98163	-0.22375
H	0.72735	2.92792	0.57245
H	1.64245	4.45394	0.50490

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Sn	2.48960	1.40765	5.21159
H	1.81149	1.97339	2.11844
O	0.93194	0.78177	3.53853
N	2.01474	5.05768	5.69793
N	0.38223	5.00348	4.23974
N	1.98023	3.21374	4.10956
C	4.30913	0.42272	4.22045
C	5.17180	-0.14339	5.19037
C	6.28780	-0.90740	4.82295
H	6.92343	-1.32867	5.60710
C	6.58286	-1.12773	3.48408
H	7.45651	-1.71802	3.19647
C	5.73996	-0.59797	2.51480
H	5.94138	-0.77569	1.45439

C	4.60888	0.15420	2.86674
C	3.76366	0.58911	1.71918
C	2.80299	-0.29482	1.19252
C	2.06054	0.10028	0.07571
H	1.30018	-0.58057	-0.31893
C	2.26406	1.33389	-0.54797
C	3.24665	2.17811	-0.02669
H	3.43487	3.14241	-0.50620
C	3.98901	1.83437	1.10618
C	4.97622	2.79829	1.69125
H	4.62048	3.14012	2.67538
H	5.10360	3.68011	1.04817
H	5.95943	2.33181	1.85228
C	2.53391	-1.61542	1.85088
H	3.46164	-2.17687	2.03318
H	1.86208	-2.23472	1.24036
H	2.05557	-1.45549	2.83014
C	1.41805	1.76546	-1.71037
H	1.02573	0.90339	-2.26912
H	1.98331	2.39945	-2.40953
H	0.55069	2.35297	-1.36243
C	4.94907	0.02984	6.65892
C	5.67147	1.01415	7.35835
C	5.49082	1.13735	8.73856
H	6.04880	1.90960	9.27564
C	4.62000	0.30625	9.44394
C	3.93155	-0.68062	8.73358
H	3.25021	-1.34921	9.26859
C	4.08958	-0.84349	7.35631
C	3.34652	-1.92487	6.62862
H	4.02412	-2.53247	6.00996
H	2.59651	-1.49990	5.93886
H	2.81863	-2.58685	7.32880
C	6.63183	1.90731	6.62902
H	7.39328	1.32004	6.09458
H	7.14025	2.59287	7.31853
H	6.11347	2.51287	5.87015
C	4.44167	0.44852	10.92780
H	5.05338	-0.28700	11.47637
H	3.39440	0.28494	11.22334
H	4.74134	1.44798	11.27550
C	0.93045	1.70750	2.71417
C	1.52619	4.29127	4.63068
C	1.20228	6.16600	5.92529
H	1.44474	6.89433	6.69253
C	0.19811	6.13111	5.02771
H	-0.63260	6.81051	4.86112
C	-0.57462	4.53271	3.30628
C	-0.50060	4.98469	1.97663
C	-1.44155	4.49228	1.06805
H	-1.40684	4.81385	0.02544
C	-2.42880	3.59977	1.47883
H	-3.15643	3.22497	0.75494
C	-2.49692	3.18512	2.80531
H	-3.27713	2.48559	3.11233
C	-1.56673	3.63766	3.74627
C	-1.62974	3.18090	5.18997
H	-0.65058	3.40068	5.64195

C	-1.85751	1.67741	5.32565
H	-2.86087	1.38005	4.98064
H	-1.77797	1.38043	6.38277
H	-1.10819	1.10871	4.75527
C	-2.67872	3.98410	5.96053
H	-2.47609	5.06427	5.91100
H	-2.68947	3.68996	7.02168
H	-3.68697	3.81131	5.55058
C	0.60297	5.93243	1.55238
H	0.87959	6.52129	2.44107
C	1.83877	5.13697	1.13238
H	2.15631	4.43934	1.92179
H	2.67960	5.81065	0.90121
H	1.61979	4.54318	0.23154
C	0.17668	6.91166	0.46457
H	0.00003	6.40546	-0.49776
H	0.96968	7.65540	0.29362
H	-0.74322	7.45124	0.73693
C	3.20127	4.84332	6.44982
C	4.44037	5.21192	5.88408
C	5.56139	5.19485	6.71467
H	6.53384	5.48255	6.31289
C	5.45914	4.81862	8.05181
H	6.34811	4.83019	8.68750
C	4.24078	4.40590	8.57217
H	4.17831	4.07797	9.61184
C	3.08675	4.40332	7.78157
C	1.76078	3.96363	8.37041
H	1.05311	3.85879	7.53266
C	1.86488	2.60394	9.05876
H	2.29621	1.84459	8.39081
H	0.86616	2.25861	9.36863
H	2.49101	2.65152	9.96324
C	1.20032	5.01626	9.32811
H	1.87309	5.16166	10.18854
H	0.21924	4.70202	9.71766
H	1.07066	5.99115	8.83675
C	4.52933	5.63860	4.43055
H	3.83894	4.98300	3.87396
C	5.91975	5.44033	3.83776
H	6.65254	6.14386	4.26397
H	5.89359	5.61853	2.75268
H	6.29249	4.41815	4.00059
C	4.07072	7.08541	4.23070
H	3.03886	7.24510	4.57303
H	4.11303	7.35300	3.16296
H	4.72425	7.78146	4.78091
H	-0.02934	2.15737	2.39890

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Sn	3.95482	1.81259	2.58993
H	0.87530	2.16321	4.81752
O	2.30506	2.60566	3.44441
N	1.77838	6.08430	5.51170
N	0.20046	4.95726	4.48443
N	2.12015	3.76877	5.44992
C	4.38212	0.35610	4.23356

C	5.45946	0.56699	5.10489
C	5.72466	-0.36233	6.11854
H	6.56437	-0.19569	6.79907
C	4.91992	-1.49226	6.25946
H	5.13342	-2.21510	7.05097
C	3.84638	-1.70807	5.39477
H	3.22078	-2.59787	5.50657
C	3.57609	-0.78753	4.37750
C	2.43858	-0.91438	3.42226
C	1.11067	-0.71858	3.85471
C	0.10005	-0.59153	2.90030
H	-0.91996	-0.39380	3.24051
C	0.35217	-0.68250	1.52987
C	1.65865	-0.95490	1.12399
H	1.87356	-1.08620	0.05853
C	2.70697	-1.08318	2.04369
C	4.07374	-1.47850	1.54082
H	4.58040	-0.65848	1.00296
H	3.98319	-2.31027	0.82562
H	4.73299	-1.79560	2.35878
C	0.75636	-0.65368	5.31303
H	0.66974	-1.66676	5.73884
H	-0.21090	-0.15149	5.45551
H	1.51701	-0.12566	5.90267
C	-0.74547	-0.49857	0.52306
H	-0.75439	-1.31174	-0.21918
H	-0.61258	0.44512	-0.03019
H	-1.73191	-0.46522	1.00628
C	6.29742	1.78671	4.90603
C	7.26669	1.79056	3.87713
C	8.01006	2.94953	3.64262
H	8.75507	2.94708	2.84087
C	7.83583	4.10007	4.41561
C	6.89659	4.06318	5.44573
H	6.74410	4.94989	6.06612
C	6.11099	2.93468	5.70298
C	5.06554	3.00307	6.77490
H	4.85392	2.01984	7.21582
H	4.11743	3.39613	6.35930
H	5.37053	3.69255	7.57494
C	7.52155	0.55470	3.06109
H	7.76883	-0.30204	3.70697
H	8.34825	0.71053	2.35454
H	6.63344	0.25109	2.48401
C	8.60475	5.35583	4.12398
H	9.56614	5.14143	3.63538
H	8.80488	5.92849	5.04143
H	8.03435	6.01499	3.44664
C	1.92294	2.51675	4.78785
C	1.40935	4.79604	5.15303
C	0.82958	7.00126	5.08100
H	0.93603	8.06413	5.27493
C	-0.13994	6.31162	4.44521
H	-1.06230	6.64555	3.98098
C	-0.70201	3.92842	4.08586
C	-0.82904	3.63038	2.71925
C	-1.79875	2.69457	2.34324
H	-1.92785	2.45263	1.28643

C	-2.58277	2.05584	3.29488
H	-3.33526	1.32712	2.98214
C	-2.39913	2.32396	4.64949
H	-3.00149	1.79261	5.38811
C	-1.45862	3.26448	5.07411
C	-1.24724	3.56225	6.54778
H	-0.17743	3.78914	6.67663
C	-1.54388	2.37086	7.45272
H	-2.61709	2.12350	7.48043
H	-1.23953	2.60029	8.48507
H	-0.99242	1.47389	7.13328
C	-2.04442	4.79200	6.98753
H	-1.77973	5.68116	6.39727
H	-1.84611	5.02142	8.04672
H	-3.12638	4.61701	6.87482
C	0.05642	4.28631	1.68080
H	0.92298	4.69260	2.22214
C	0.59535	3.27456	0.67331
H	1.02905	2.41085	1.19603
H	1.37961	3.73636	0.05384
H	-0.19028	2.91762	-0.01211
C	-0.66555	5.43564	0.97505
H	-1.55593	5.07051	0.43778
H	-0.00310	5.91809	0.23920
H	-0.99806	6.20826	1.68316
C	2.96878	6.38520	6.22561
C	4.08379	6.86920	5.51430
C	5.22954	7.19068	6.24572
H	6.10735	7.57956	5.72691
C	5.27269	7.01160	7.62609
H	6.18109	7.26494	8.17841
C	4.16756	6.50859	8.30216
H	4.21487	6.36538	9.38432
C	2.98941	6.19443	7.61720
C	1.78866	5.64974	8.36311
H	0.95069	5.61668	7.65053
C	2.04137	4.21734	8.83564
H	2.29427	3.57495	7.98043
H	1.14297	3.80974	9.32673
H	2.86811	4.17870	9.56383
C	1.36643	6.56057	9.51436
H	2.13337	6.60476	10.30394
H	0.44051	6.18530	9.97829
H	1.18193	7.58904	9.16854
C	4.05112	6.97934	4.00177
H	3.02321	7.25879	3.71729
C	4.34438	5.61888	3.36113
H	5.36042	5.28084	3.61784
H	4.27144	5.68620	2.26394
H	3.64245	4.84774	3.70861
C	4.98327	8.05168	3.44933
H	4.81763	9.02987	3.92647
H	4.82205	8.16798	2.36698
H	6.04283	7.78323	3.58723
H	2.53161	1.76586	5.32496

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INT-SnH7

Sn	0.91987	4.45601	5.15710
O	-0.12270	1.96541	3.44974
O	-0.05979	2.95383	6.45812
N	-0.02855	-1.32058	7.99692
N	-1.82685	-0.86001	6.84702
N	-0.31225	0.94801	7.42558
C	0.17354	5.94019	6.72676
C	-0.95893	6.77515	6.82079
C	-1.10886	7.63701	7.92062
H	-2.00397	8.26342	7.97576
C	-0.15581	7.69976	8.92993
H	-0.29024	8.38100	9.77418
C	0.96191	6.87649	8.85748
H	1.72018	6.89477	9.64618
C	1.12246	6.00279	7.77673
C	2.31476	5.09622	7.78475
C	2.27207	3.89902	8.52991
C	3.37456	3.04036	8.49592
H	3.32654	2.10291	9.05760
C	4.52753	3.34789	7.77122
C	4.56752	4.56022	7.07777
H	5.46980	4.83080	6.52095
C	3.48459	5.44173	7.07495
C	3.55953	6.73392	6.31468
H	2.88058	6.72739	5.44401
H	4.57626	6.91818	5.94127
H	3.24973	7.58516	6.93895
C	1.07248	3.54903	9.35788
H	0.91832	4.28346	10.16372
H	1.18711	2.55338	9.80556
H	0.16607	3.54146	8.73720
C	5.69099	2.40022	7.72714
H	5.62835	1.65138	8.52970
H	6.64905	2.93262	7.82715
H	5.72014	1.85719	6.76793
C	-2.08220	6.81221	5.83781
C	-2.23302	7.92763	4.99618
C	-3.37434	8.03055	4.19301
H	-3.48057	8.89706	3.53288
C	-4.37244	7.05711	4.20634
C	-4.19859	5.95340	5.04589
H	-4.96446	5.17169	5.07047
C	-3.07559	5.81324	5.86236
C	-2.95799	4.63945	6.78564
H	-2.89608	4.96769	7.83566
H	-2.04739	4.05947	6.58639
H	-3.81609	3.96340	6.67621
C	-1.18195	9.00037	4.94322
H	-1.20672	9.63911	5.84053
H	-1.32181	9.64706	4.06519
H	-0.17096	8.56798	4.90217
C	-5.57843	7.16143	3.31957
H	-6.50592	6.95999	3.87769
H	-5.52584	6.42622	2.49941
H	-5.66311	8.15960	2.86695
C	-0.25367	1.71741	6.35983
C	-0.68966	-0.31309	7.36707
C	-0.76428	-2.49045	7.90441
H	-0.41289	-3.41879	8.34375
C	-1.88933	-2.20039	7.20846
H	-2.74293	-2.81597	6.94670
C	-2.92900	-0.10810	6.31370
C	-3.74091	0.57389	7.23867
C	-4.83578	1.28458	6.74024
H	-5.48306	1.82643	7.43340
C	-5.10154	1.31737	5.37912
H	-5.95346	1.88757	5.00152
C	-4.27587	0.64396	4.48726
H	-4.47968	0.71632	3.42016
C	-3.16722	-0.08667	4.92361
C	-2.27496	-0.79591	3.91511
H	-1.22945	-0.58125	4.20001
C	-2.48269	-0.29291	2.48869
H	-3.45967	-0.62033	2.09727
H	-1.72024	-0.72384	1.82575
H	-2.41522	0.79855	2.39019
C	-2.46543	-2.31690	3.93152
H	-2.15017	-2.78252	4.87295
H	-1.86746	-2.77675	3.12989
H	-3.52127	-2.57711	3.75401
C	-3.47514	0.57764	8.73205
H	-2.58360	-0.03525	8.92919
C	-3.17244	1.99080	9.23024
H	-2.29427	2.40848	8.71809
H	-2.96810	1.98470	10.31123
H	-4.02224	2.66781	9.05525
C	-4.62912	-0.06264	9.50383
H	-5.55909	0.51674	9.39395
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H	4.55075	-0.75433	10.56841
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C	2.77032	-2.42904	5.90509
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H	2.72308	-2.45183	4.80589
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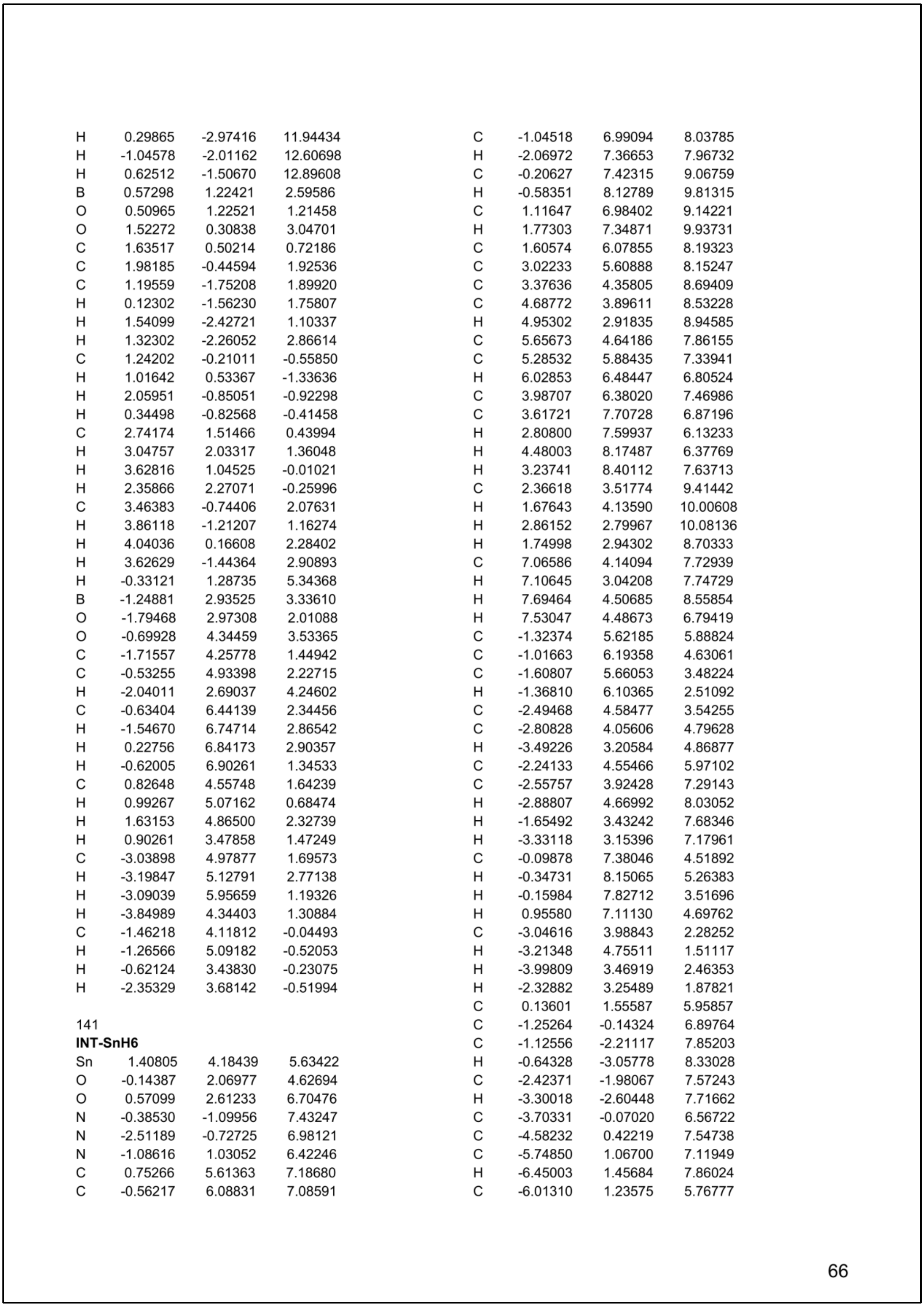

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INT-SnH6

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H	-0.45729	2.13639	9.02229
C	-0.49657	-0.41489	11.39941
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H	0.79514	-1.36997	0.74773
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H	1.31281	3.56974	0.81112
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H	3.09467	-0.05865	0.59505
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INT-SnH5

Sn	0.59977	0.28254	5.12764
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C	2.49646	-3.66835	7.65213
H	2.85381	-4.57798	8.14162
C	1.15071	-3.53487	7.31973
H	0.43694	-4.32822	7.56020
C	0.70163	-2.36473	6.70026
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H	-3.14744	-2.39648	4.04728
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C	-0.89340	-1.16415	8.78422
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H	-5.54993	-1.42847	6.39693
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C	1.71856	3.03908	5.27821
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H	-1.43255	7.13013	6.04400
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C	3.52181	7.18676	4.80508
H	2.42775	7.07868	4.75205
C	4.12672	6.14033	3.87017
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C	3.85575	8.61163	4.36550
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H	3.49411	8.79309	3.34113
H	4.94247	8.79274	4.36722
B	2.97136	2.05075	3.40896
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O	2.32639	0.80349	3.36209
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C	2.29221	0.40414	1.97108
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H	0.14337	0.52990	1.96696
C	3.41075	1.60910	-0.03125
H	4.33829	2.10569	-0.35014
H	3.22979	0.75743	-0.70429
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C	2.34440	-1.10582	1.87397
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H	3.20216	-1.51961	2.41593
H	1.42568	-1.54354	2.29208
H	0.85793	3.20153	4.59331

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Author Contributions

D. Sarkar, L. Groll, and S. Inoue conceived and designed the experiments. D. Sarkar and L. Groll carried out the synthetic experiments and analyzed experimental data. D. Munz performed the theoretical calculations. F. Hanusch collected and refined the crystallographic data. S. Inoue supervised the study. D. Sarkar, L. Groll, D. Munz, and S. Inoue wrote the manuscript. All the authors discussed the results and commented on the manuscript.

8.2. SUPPORTING INFORMATION FOR CHAPTER 5

Table of Contents

1. Experimental Procedures

1.1 General Information

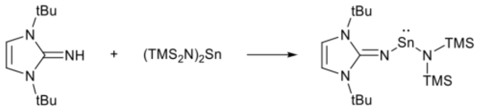
All experiments were carried out under a dry argon atmosphere using standard *Schlenk* techniques or a glovebox. All glass junctions were coated with PTFE-based grease *Merkel* Triboflon III. All used reaction solvents were refluxed over sodium/benzophenone, freshly distilled and deoxygenated prior to use. Unless otherwise stated, all reagents were purchased from commercial sources and used as received. ^{tBu}NHIH[S1], ^{tBu}NHILi[S2] and $(TMS_2N)_2Sn$[S3] were synthesized according to literature procedures.

The ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra were measured on *Bruker* 400 MHz and 500 MHz spectrometers. All NMR samples were prepared in PTFE valve J-Young NMR tubes in an argon atmosphere. Chemical shifts were referenced to residual solvent signals (^{1}H and ^{13}C NMR). ^{119}Sn NMR chemical shifts were referenced to Me_4Sn (^{119}Sn). Deuterated solvents C_6D_6, THF-d_8 and CD_3CN were obtained from *Deutero* Deutschland GmbH. C_6D_6 and THF-d_8 were dried over 4 Å molecular sieves prior to use, CD_3CN was dried with CaH_2, distilled and stored over 3 Å molecular sieves prior to use. Abbreviations: s = singlet. The spectra were processed and analyzed with the Mestrenova software.

Elemental Analysis (CHNS) was carried out by the central analytics laboratory of the TUM Catalysis Research Center on a EURO EA (HEKAtech) instrument equipped with a CHNS combustion analyzer. The highly reactive and air-sensitive nature impaired the accuracy of the measurements.

Liquid Injection Field Desorption Ionization Mass Spectrometry (LIFDI-MS) was performed in an inert atmosphere glovebox with a *Thermo Fisher* Scientific Exactive Plus Orbitrap equipped with an ion source from Linden CMS.S7.[S4] Thereby, all samples were prepared in THF solutions, filtered and injected into the spectrometers. TOF analyzation in cationic mode resulted in the obtained spectra, which were resolved by mass-to-charge values. Due to the very poor solubility of the CO_2 and N_2O activation products (Compounds **4**, **5** and **6**) in conventional solvents suitable for LIFDI-MS (such as THF and Toluene) as well as decomposition in Propanenitrile, no satisfactory Mass Spectrometry could be obtained for those compounds.

1.2 Synthesis of $(TMS_2N)(I^{t}BuN)Sn$: (1)



A solution of ^{tBu}NHIH (1.0 eq., 1.28 mmol, 250.0 mg) in 10 ml Pentane was added to a stirring solution of $(TMS_2N)_2Sn$ (1.1 eq., 1.41 mmol, 618.8 mg) in Pentane. After stirring at room temperature for 30 min, a bright red solution was obtained, which was then reduced to approximately halve its volume *in vacuo*. The solution was left to crystallize over night at -35 °C, to give bright 587.0 mg of red crystals suitable for SC-XRD characterization. After removing all volatiles, 587.0 mg (1.24 mmol, 97 %) of a bright red solid was obtained.

^{1}H-NMR (400MHz, C_6D_6): δ (ppm) = 6.05 (s, 2H, NC***H***), 1.41 (s, 18H, C(C***H***$_3$)$_3$), 0.49 (s, 18H, Si(C***H***$_3$)$_3$).

^{13}C{^{1}H NMR (125.83 MHz, 298 K,C_6D_6): δ (ppm) = 149.79 (N***C***N), 107.91 (N***CC***N), 54.82 (***C***(CH$_3$)$_3$), 29.64 (C(***C***H$_3$)$_3$), 5.85 (Si(***C***H$_3$)$_3$).

^{29}Si{^{1}H} NMR (99.41 MHz, 298 K, C_6D_6): δ (ppm) = -3.66 (2H, ***Si***(CH$_3$)$_3$).

^{119}Sn{^{1}H} NMR (149.20 MHz, 298 K, C_6D_6): δ (ppm) = 401.35.

LIFDI-MS calcd. for $C_{17}H_{38}N_4Si_2Sn$: 474.16569; Found: 474.16369.

Anal. Calcd. [%] for $C_{17}H_{38}N_4Si_2Sn$: C 43.13, H 8.09, N 11.84. Found: C 42.91, H 8.14, N 11,46.

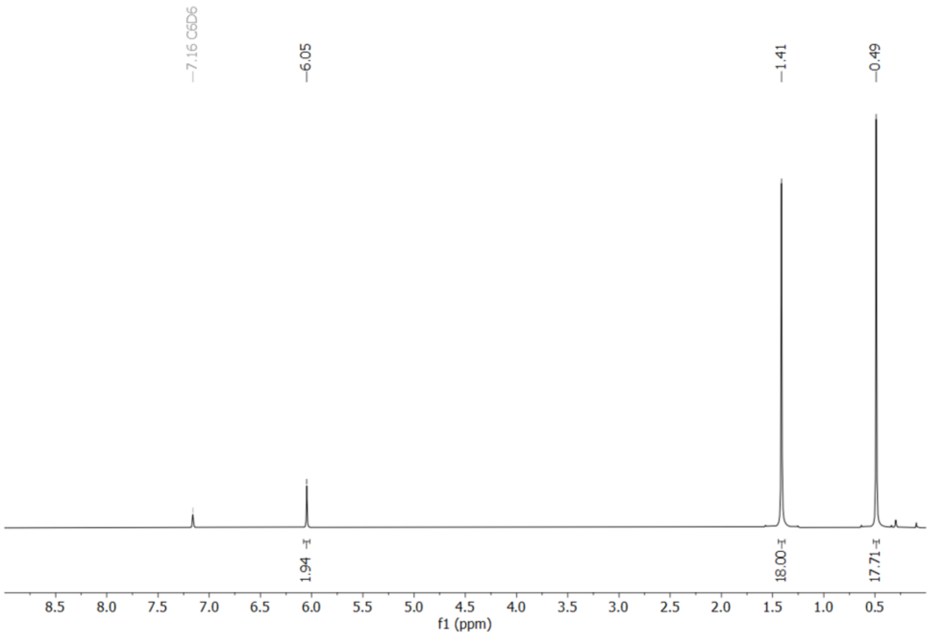


Figure S1: ^{1}H NMR spectrum of compound **1** in C_6D_6 at 298 K.

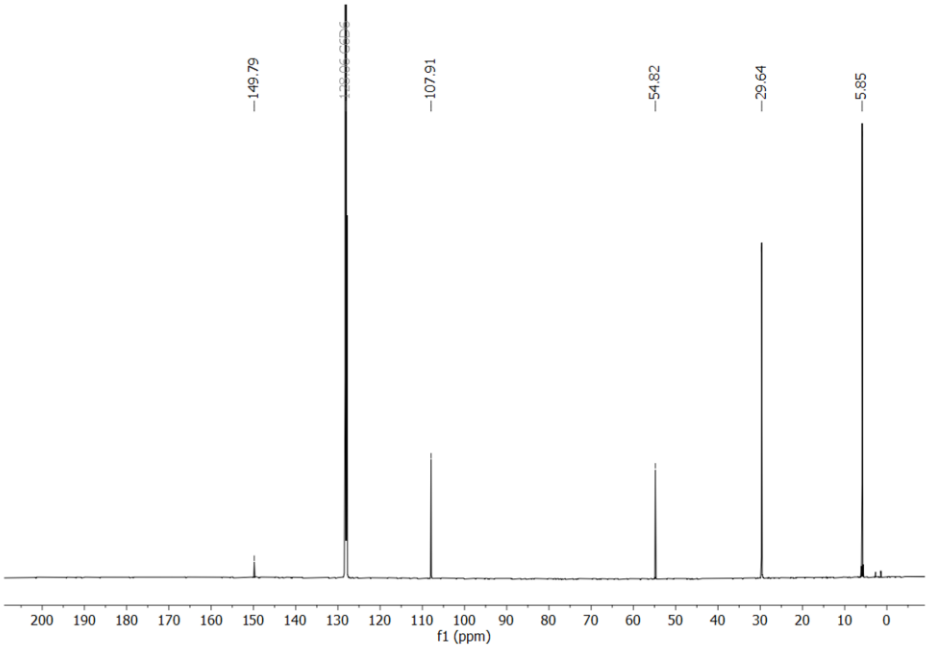


Figure S2: $^{13}C\{^1H\}$ NMR spectrum of compound **1** in C_6D_6 at 298 K.

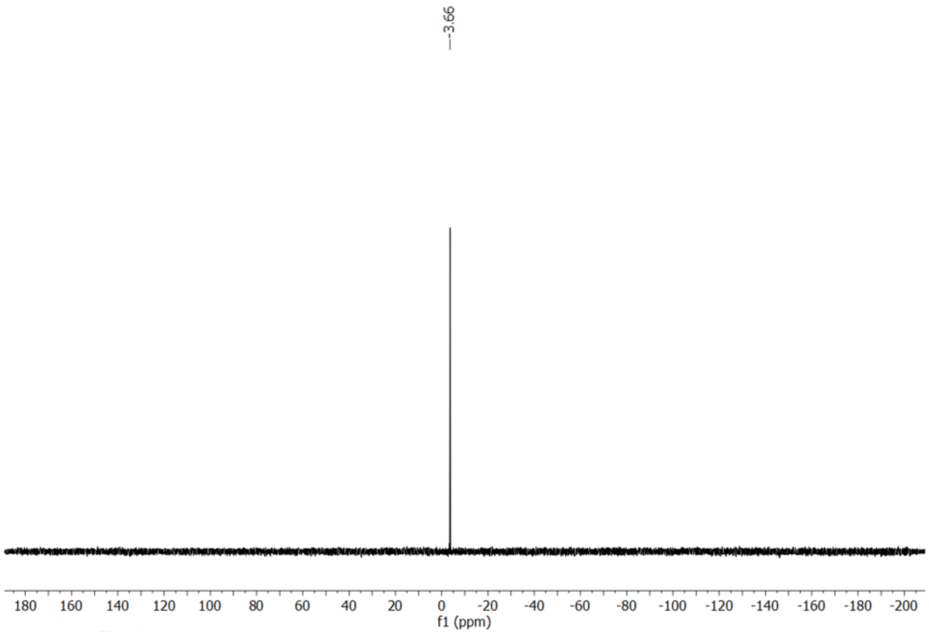


Figure S3: ^{29}Si{^{1}H} NMR spectrum of compound **1** in C_6D_6 at 298 K.

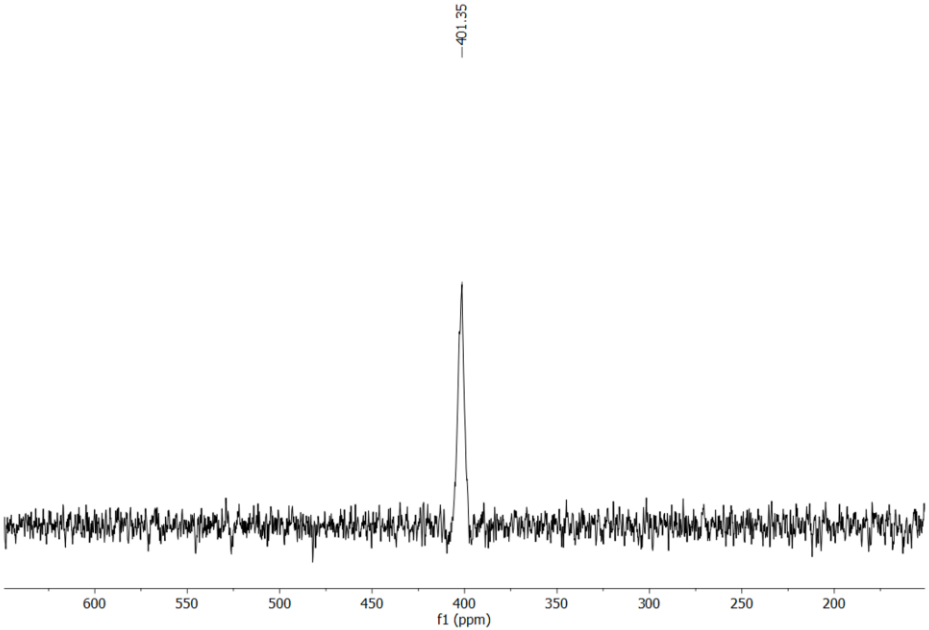


Figure S4: ^{119}Sn{^{1}H} NMR spectrum of compound **1** in C_6D_6 at 298 K.

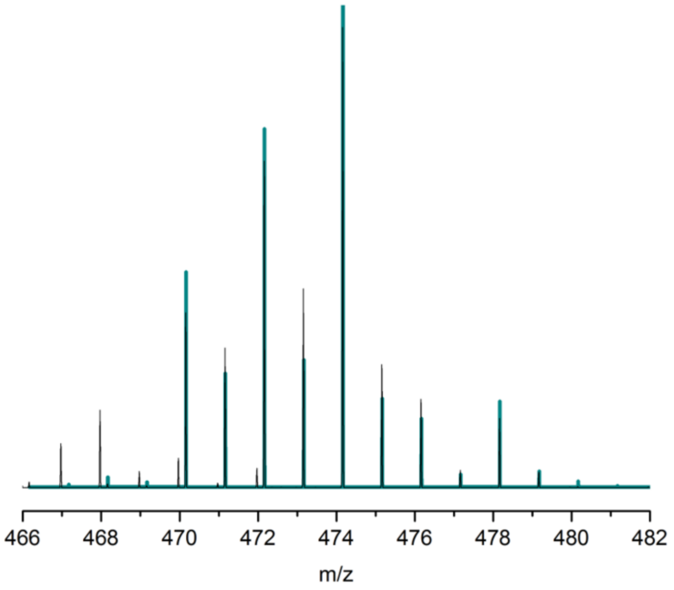
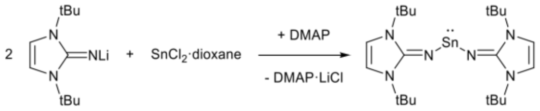


Figure S5. Measured (black) and calculated (teal) LIFDI-MS for **1**.

1.3 Synthesis of (I^{t}BuN)$_2$Sn: (2)



A solution of ^{tBu}NHILi in 10 ml C_6H_6 (2.0 eq., 1.22 mmol, 250.0 mg) was added to a stirring solution of $SnCl_2$·dioxane (1.0 eq., 0.61 mmol, 170.0 mg) and 4-(Dimethylamino)pyridine (1.0 eq., 0.61 mmol, 74.5 mg) in 10 ml of THF at -40 °C. The solution, which turned red after about 10 min, was allowed to gradually warm to room temperature in the course of 2h. All volatiles were removed *in vacuo* and the residue was extracted with C_6H_6 (3 x 5 ml). The resulting solution was dried *in vacuo* once more and recrystallized in pentane giving a yellow powder (226.2 mg, 0.446 mmol) with a yield of 73 %. Crystals suitable for SC-XRD characterization were obtained by vapor diffusion of pentane into a solution of ^{tBu}NHI$_2$Sn in a minimal amount of THF.

^{1}H-NMR (400MHz, C_6D_6): δ (ppm) = 6.16 (s, 4H, NC***H***), 1.59 (s, 36H, C(C***H***$_3$)$_3$).

^{13}C{^{1}H} NMR (125.83 MHz, 298 K,C_6D_6): δ (ppm) = 200.02 (N***C***N), 107.26 (N***CC***N), 54.51 (***C***(CH$_3$)$_3$), 29.34 (C(***C***H$_3$)$_3$).

^{119}Sn{^{1}H} NMR (149.20 MHz, 298 K, C_6D_6): 122.07 ppm.

Anal. Calcd. [%] for $C_{22}H_{40}N_6Sn$: C 52.09, H 7.95, N 16.57. Found: C 52.09, H 8.20, N 16.19.

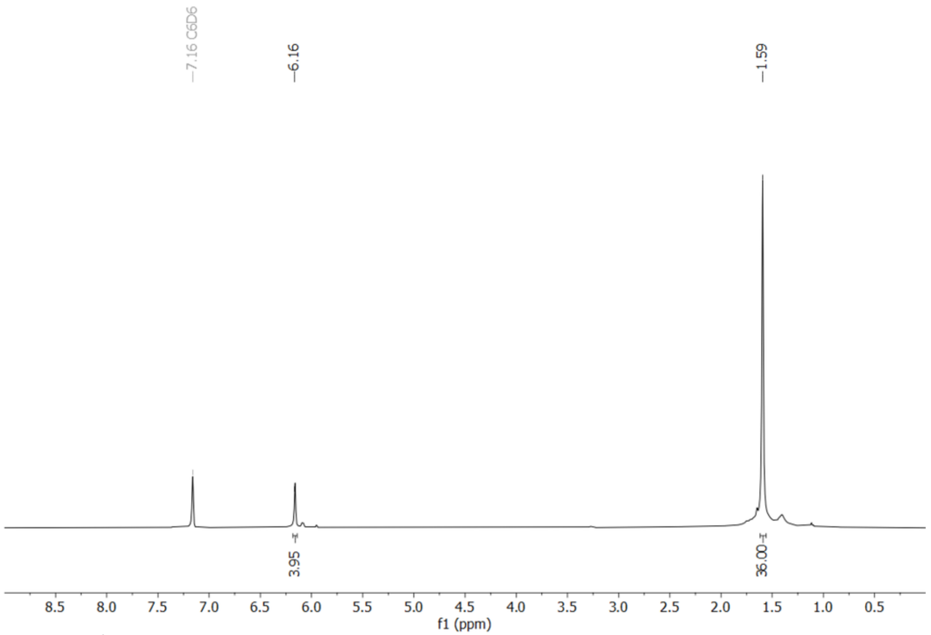


Figure S6: ^{1}H NMR spectrum of compound **2** in C_6D_6 at 298 K.

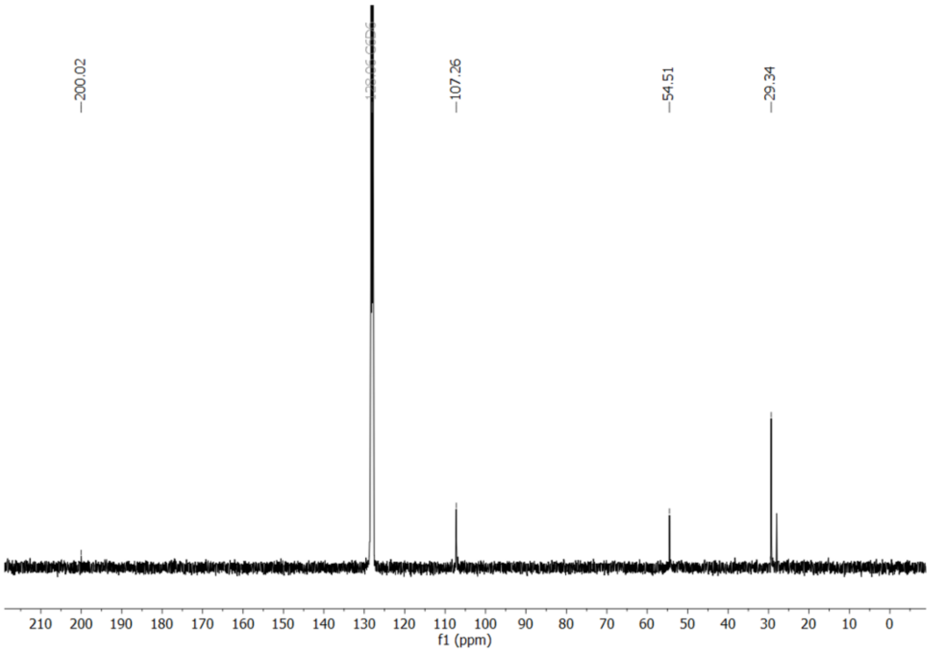


Figure S7: ^{13}C{^{1}H} NMR spectrum of compound **2** in C_6D_6 at 298 K.

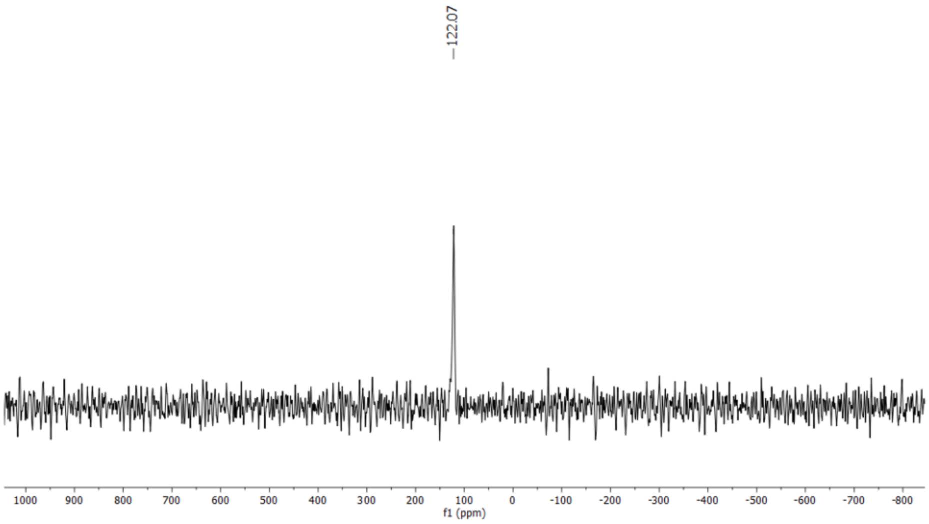
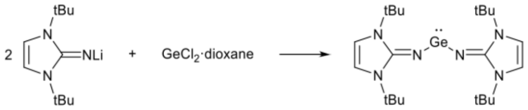


Figure S8: ^{119}Sn{^{1}H} NMR spectrum of compound **2** in C_6D_6 at 298 K.

1.4 Synthesis of (I^{t}BuN)$_2$Ge: (3)



A solution of 460.43 mg $GeCl_2$·dioxane (1.0 eq., 1.99 mmol) in 15 ml of THF was added to a stirring solution of ^{tBu}NHILi in 80 ml THF (2.0 eq., 3.98 mmol, 800.0 mg) at - 40 °C. The solution, which turned orange after about 10 minutes, was allowed to gradually warm to room temperature in the span of two hours. After filtration of the reaction mixture through a microfiber glass filter, all volatiles were removed and the residue was extracted with Et_2O (3 x 10 ml). Subsequently, the solution was dried *in vacuo* once more. The obtained raw product was then washed with cold pentane (3 x 2.5 ml) and stripped of all volatiles a third time, giving a yellow powder (1.43 mmol, 660.85 mg) with a yield of 72 %. Crystals suitable for SC-XRD characterization were obtained by slow evaporation of a solution of the compound in a minimal amount of Et_2O.

^{1}H-NMR (400MHz, C_6D_6): δ (ppm) = 6.17 (s, 4H, NC***H***), 1.62 (s, 36H, C(C***H***$_3$)$_3$).

^{13}C{^{1}H} NMR (125.83 MHz, 298 K,C_6D_6): δ (ppm) = 146.54 (N***C***N), 107.78 (N***CC***N), 54.80 (***C***(CH$_3$)$_3$), 29.61 (C(***C***H$_3$)$_3$).

LIFDI-MS calcd. for $C_{22}H_{40}GeN_6$: 462.25262; found: 462.25181.

Anal. Calcd. [%] for $C_{22}H_{40}GeN_6$: C 57.29, H 8.74, N 18.22. Found: C 56.62, H 8.82, N 17.94.

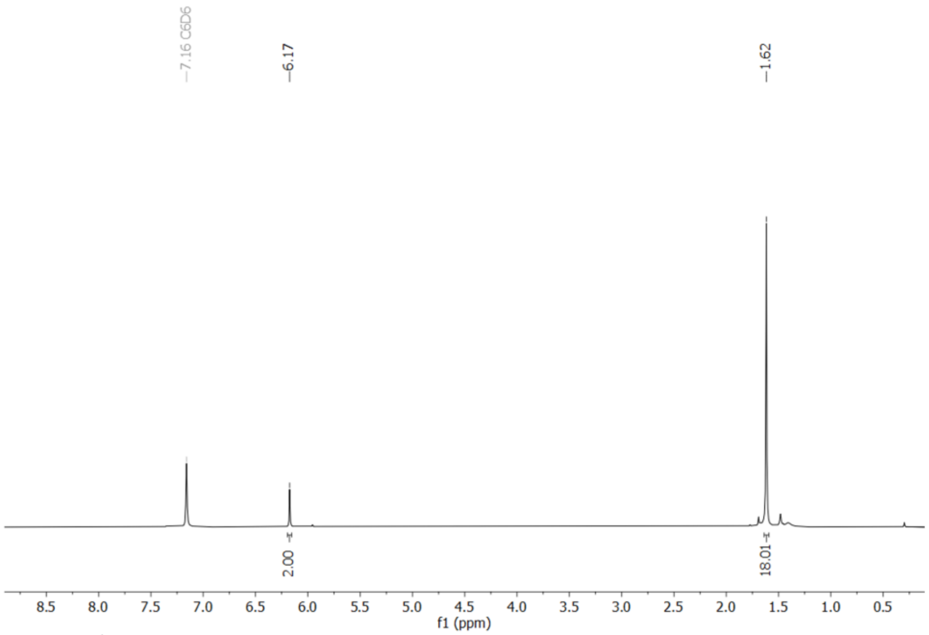


Figure S9. ^{1}H NMR spectrum of compound **3** in C_6D_6 at 298 K.

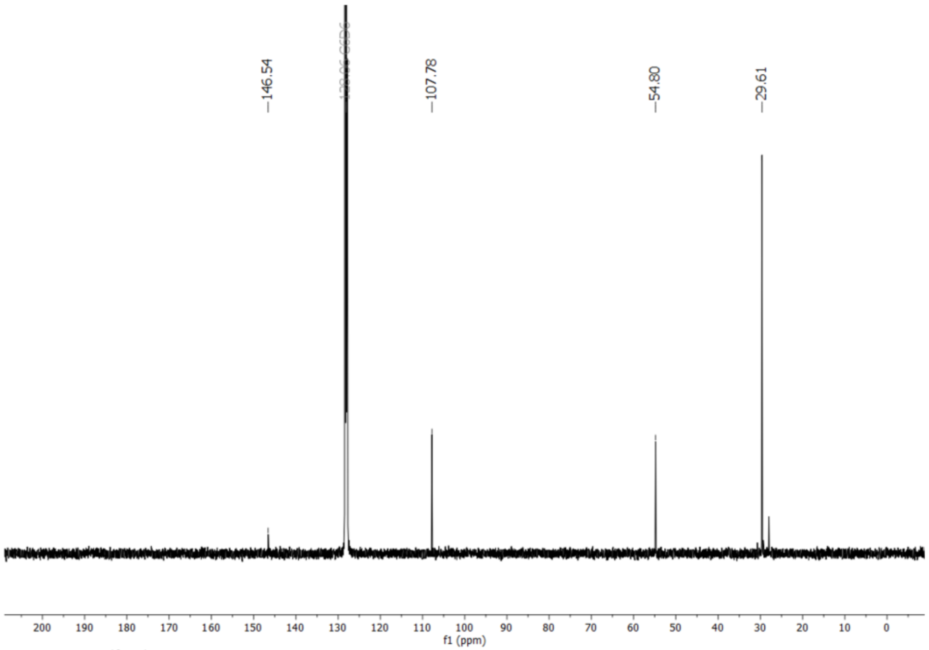


Figure S10. $^{13}C\{^1H\}$ NMR spectrum of compound **3** in C_6D_6 at 298 K.

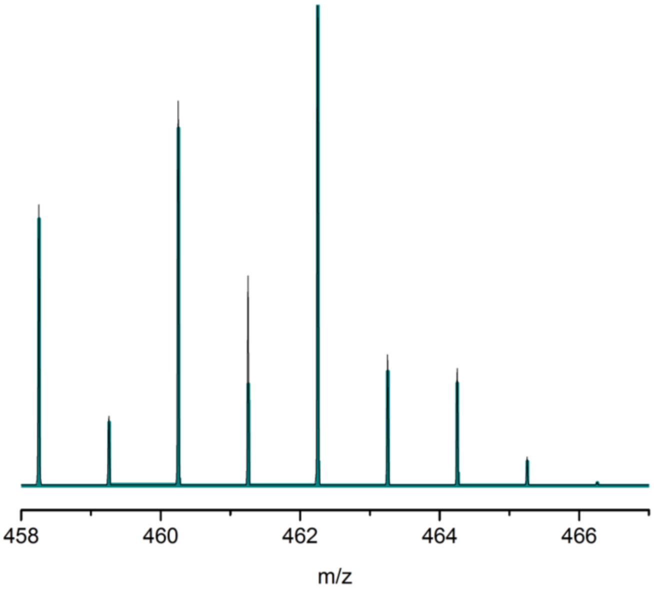
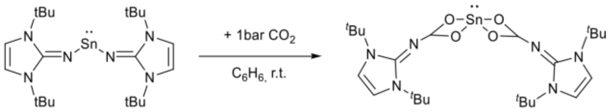


Figure S11. Measured (black) and calculated (teal) LIFDI-MS for **3**.

1.5 Synthesis of (I^{t}BuN-CO$_2$)$_2$Sn: (4)



10 mg of ^{tBu}NHI$_2$Sn (1.0 eq., 0.019 mmol) were dissolved in 0.4 ml C$_6$H$_6$ in a *J-Young* NMR tube. After freeze-pump-thaw degassing the orange-red solution two times, 1 bar of CO$_2$ was added, resulting in rapid loss of color followed by formation of a crystalline precipitate after about 10 minutes. The suspension was treated with 1 ml of pentane in order to preticipate all product. The residue was isolated and washed three more times with 0.5 ml of pentane and dried *in vacuo*, giving 11.3 mg (0.019 mmol, 96 %) of a colorless solid. Due to poor solubility of the product in C$_6$H$_6$ and THF, NMR characterization was carried out in MeCN-d$_3$. SC-XRD characterization could be performed directly from the initially obtained crystalline precipitate in Benzene.

^{1}H-NMR (400MHz, CD$_3$CN): δ (ppm) = 6.97 (s, 4H, NC***H***), 1.60 (s, 36H, C(C***H***$_3$)$_3$).

^{13}C{^{1}H} NMR (125.83 MHz, 298 K, CD$_3$CN): δ (ppm) = 167.40 (N**C**O$_2$),149.51 (N**C**N), 114.12 (N***CC***N), 59.80 (***C***(CH$_3$)$_3$), 29.62 (C(***C***H$_3$)$_3$).

Anal. Calcd. [%] for C$_{30}$H$_{46}$N$_6$O$_4$Sn (**4***C$_6$D$_6$): C 53.51, H 6.89, N 12.48. Found: C 53.61, H 6.87, N 11.54

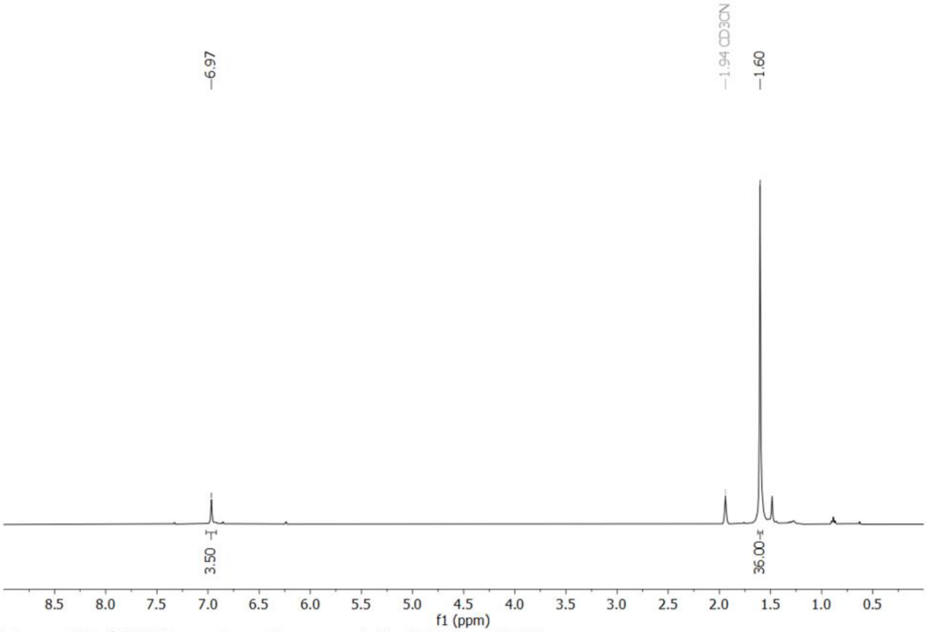


Figure S12: ^{1}H NMR spectrum of compound **4** in CD_3CN at 298 K.

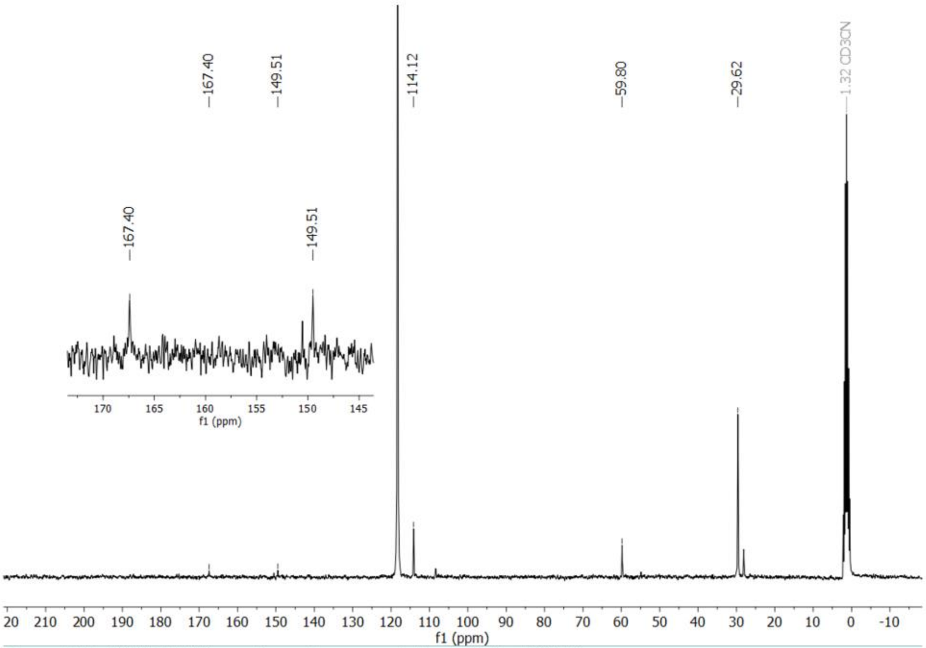
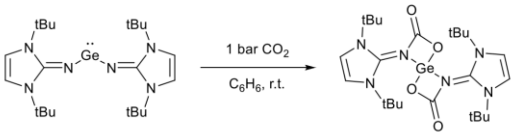


Figure S13: $^{13}C\{^{1}H\}$ NMR spectrum of compound **4** in CD_3CN at 298 K.

1.6 Synthesis of $(I^{t}BuN\text{-}CO_2)_2Ge$: (5)



10 mg of $^{tBu}NHI_2Ge$ (1.0 eq., 0.022 mmol) were dissolved in 0.4 ml C_6H_6 in a *J-Young* NMR tube. After freeze-pump-thaw degassing the bright yellow solution two times, 1 bar of CO_2 was added, resulting in rapid loss of color followed by formation of a crystalline precipitate after about 10 minutes. The suspension was treated with 1 ml of pentane in order to preticipate all product. The residue was isolated and washed three more times with 0.5 ml of pentane and dried *in vacuo*, giving 12.1 mg (0.019 mmol, 86 %) of a colorless solid. Due to poor solubility of the product in C_6H_6 and THF, NMR characterization was carried out in CD_3CN. SC-XRD characterization could be performed directly from the initially obtained crystalline precipitate in Benzene.

^{1}H-NMR (400MHz, CD_3CN): δ (ppm) = 7.02 (s, 4H, NC***H***), 1.61 (s, 36H, C(C***H***$_3$)$_3$).

^{13}C{^{1}H} NMR (101 MHz, 298 K,CD_3CN): δ (ppm) = 125.81 (N***C***N), 114.61 (N***CC***N), 60.15 (***C***(CH$_3$)$_3$), 29.62 (C(***C***H$_3$)$_3$).

Anal. Calcd. [%] for $C_{27}H_{43}GeN_6O_4$ (5*$^1/_2$ C_6D_6): C 55.12, H 7.37, N 14.29. Found: C 54.80, H 7.50, N 13.29.

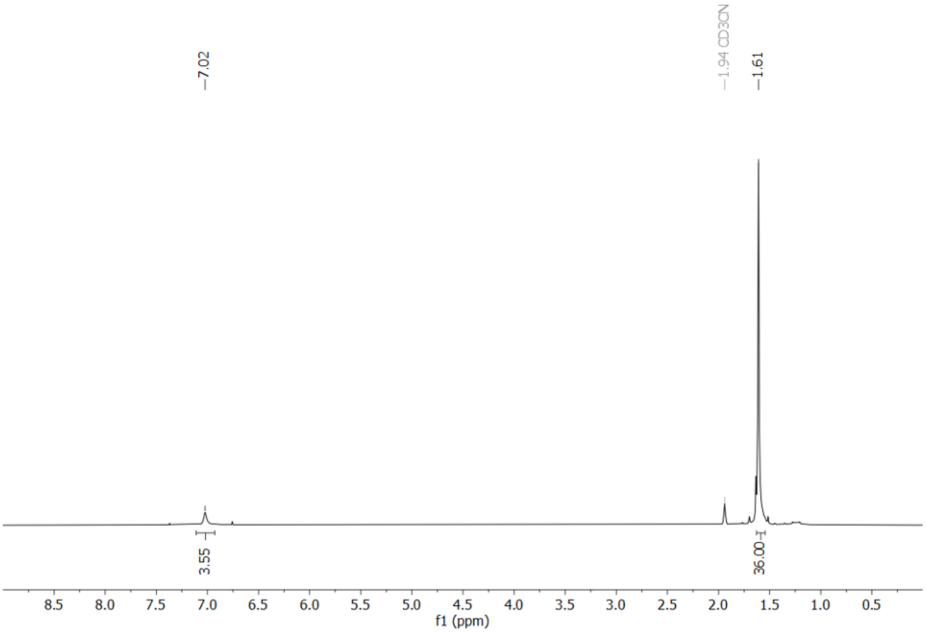


Figure S14: ^{1}H NMR spectrum of compound **5** in CD_3CN at 298 K.

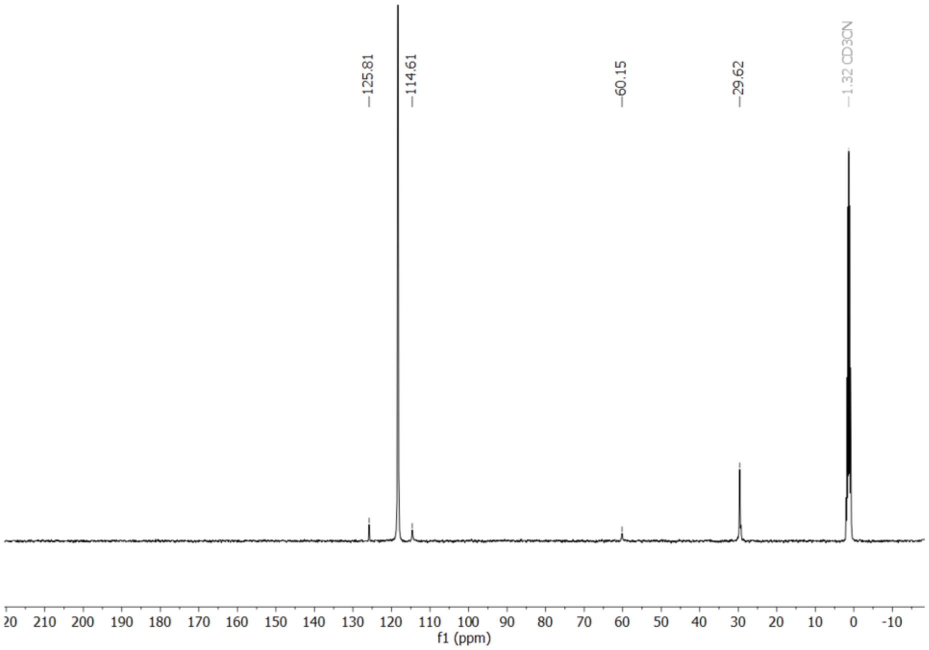
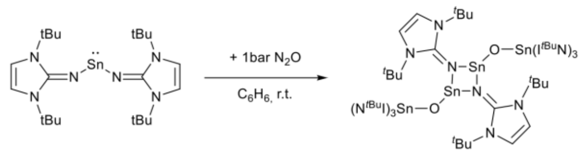


Figure S15: $^{13}C\{^1H\}$ NMR spectrum of compound **5** in CD_3CN at 298 K.

1.7 Synthesis of [((I^{t}BuN)$_3$SnO)(I^{t}BuN)Sn:]$_2$ (6)



10 mg of ^{tBu}NHI$_2$Sn (1.0 eq., 0.019 mmol) were dissolved in 0.4 ml C_6H_6 in a *J-Young* NMR tube. After freeze-pump-thaw degassing the solution two times, 1 bar of N_2O was added, resulting in loss of color during the span of about 10 minutes. The solution was dried *in vacuo* followed by recrystallization in a minimal amount of pentane, resulting in crystals suitable for SC-XRD characterization.

^{1}H-NMR (400MHz, C_6D_6) δ (ppm) = 6.22 (s, 4H, bridging-NC***H***), 6.15 (s, 12H, terminal-NC***H***), 1.70 (s, 36H, bridging-C(C***H***$_3$)$_3$), 1.67 (s, 108H, terminal-C(C***H***$_3$)$_3$).

^{13}C{^{1}H} NMR (101 MHz, 298 K,C_6D_6): δ (ppm) = 147.95 (N***C***N), 107.43 (N***CC***N), 106.98 (N***CC***N), 55.19 (***C***(CH$_3$)$_3$), 54.85 (***C***(CH$_3$)$_3$), 29.46 (C(***C***H$_3$)$_3$), 29.36 (C(***C***H$_3$)$_3$).

Anal. Calcd. [%] for $C_{88}H_{160}N_{24}O_2Sn_4$: C 51.28, H 7.82, N 16.31. Found: C 51.29, H 8.28, N 15.83.

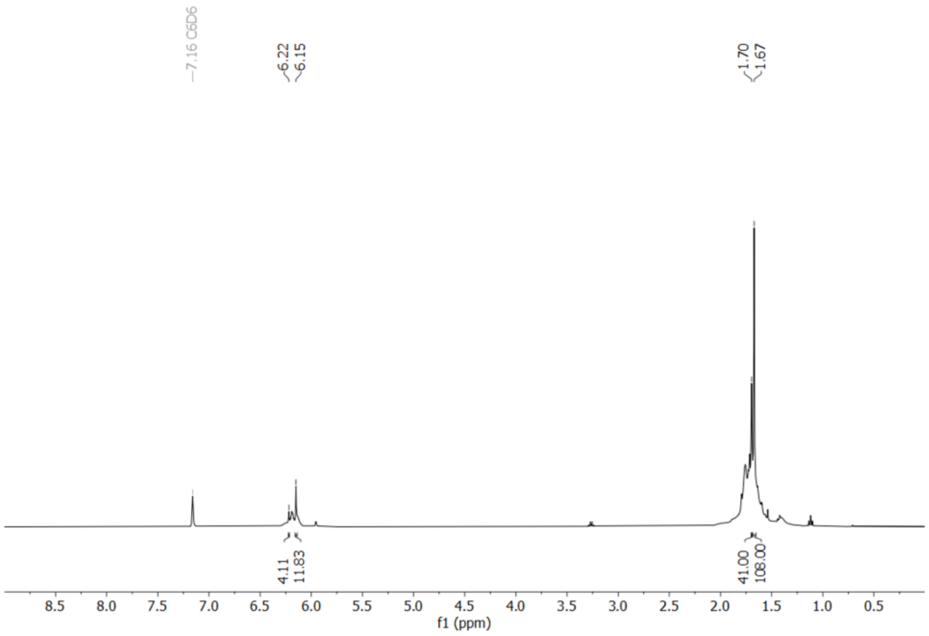


Figure S16: ^{1}H NMR spectrum of compound **6** in C_6D_6 at 298 K.

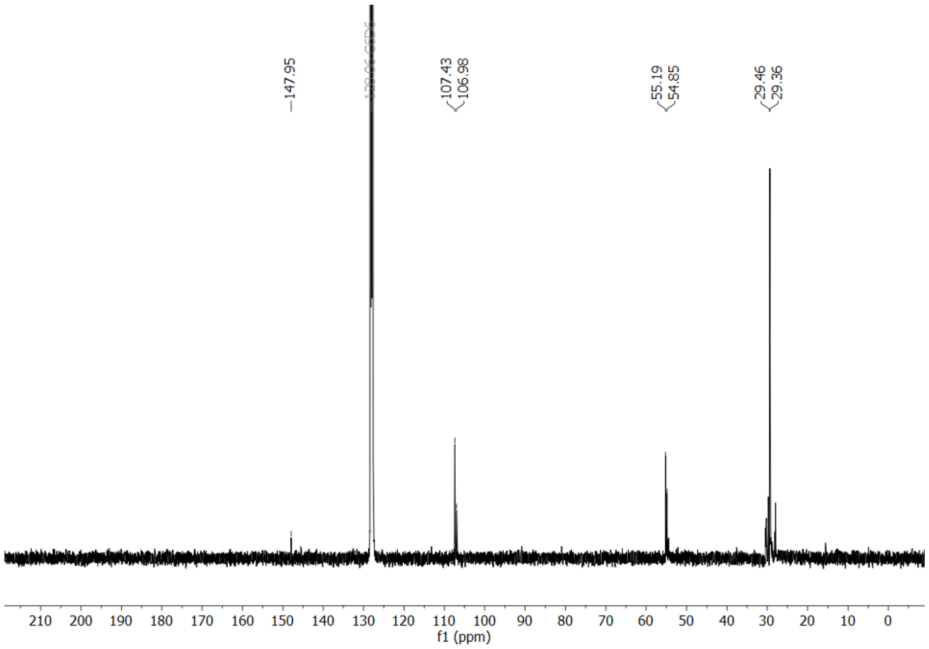


Figure S17: $^{13}C\{^{1}H\}$ NMR spectrum of compound **6** in C_6D_6 at 298 K.

2. VT-NMR Experiment of (I^{t}BuN)$_2$Sn: (2)

A saturated solution of (I^{t}BuN)$_2$Sn: (**2**) in toluene-d$_8$ was cooled down to -80 °C and then gradually warmed to room temperature with ^{1}H-NMR spectra being taken at -80 °C, -60 °C, -40 °C, -20 °C and 0 °C as well as ^{119}Sn-NMR spectra being taken at -80 °C, -60 °C, -20 °C and 0 °C.

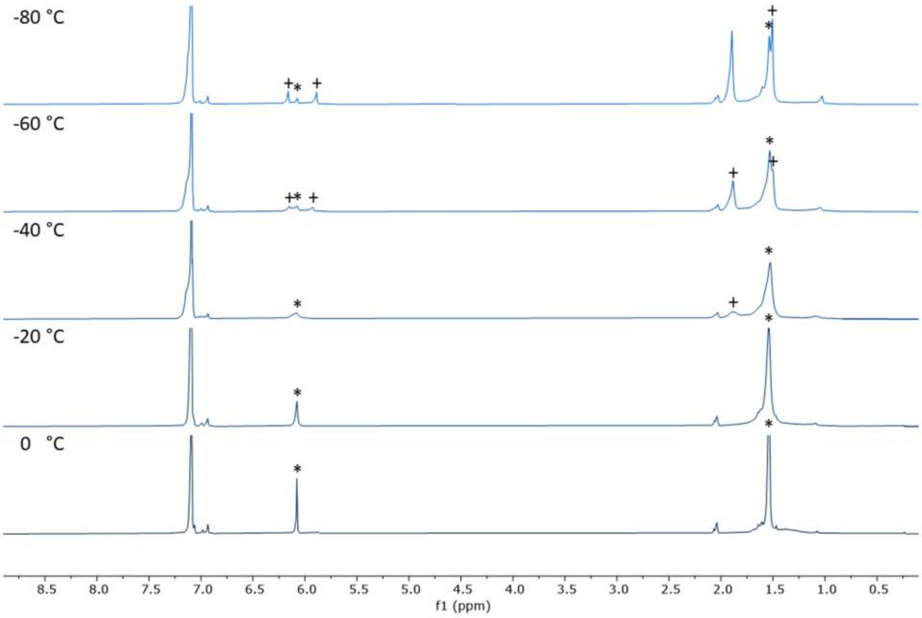


Figure S 18: Variable temperature ^{1}H NMR spectrum of stannylene **2** in Toluene-d$_8$ at -80 °C, -60 °C, -40 °C, -20 °C and 0 °C respectively. (* = signals corresponding to monomeric stannylene, + = signals corresponding to di-stannylene).

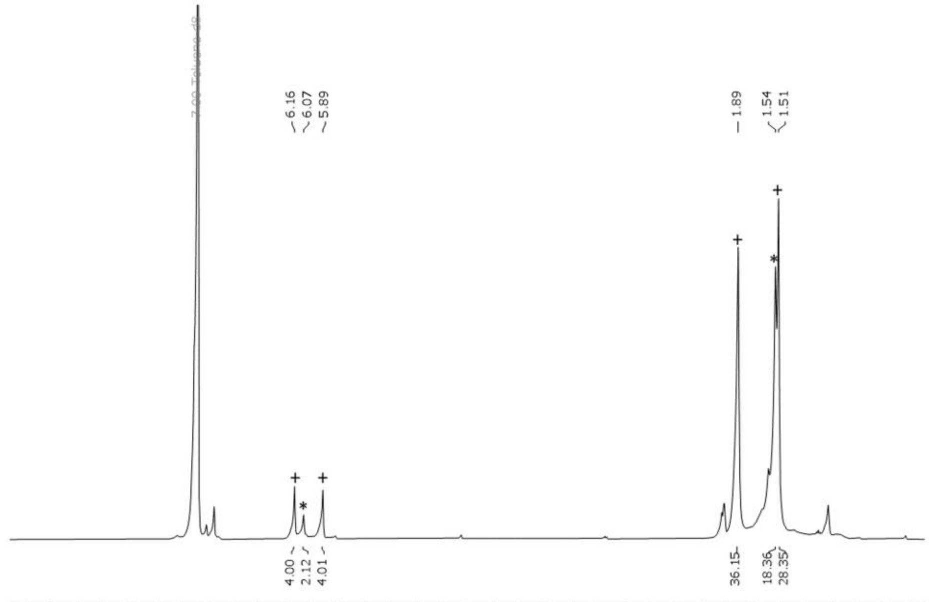


Figure S 19: Variable temperature ^{1}H NMR spectrum of stannylene **2** in Toluene-d_8 at -80 °C. (* = signals corresponding to monomeric stannylene, + = signals corresponding to di-stannylene).

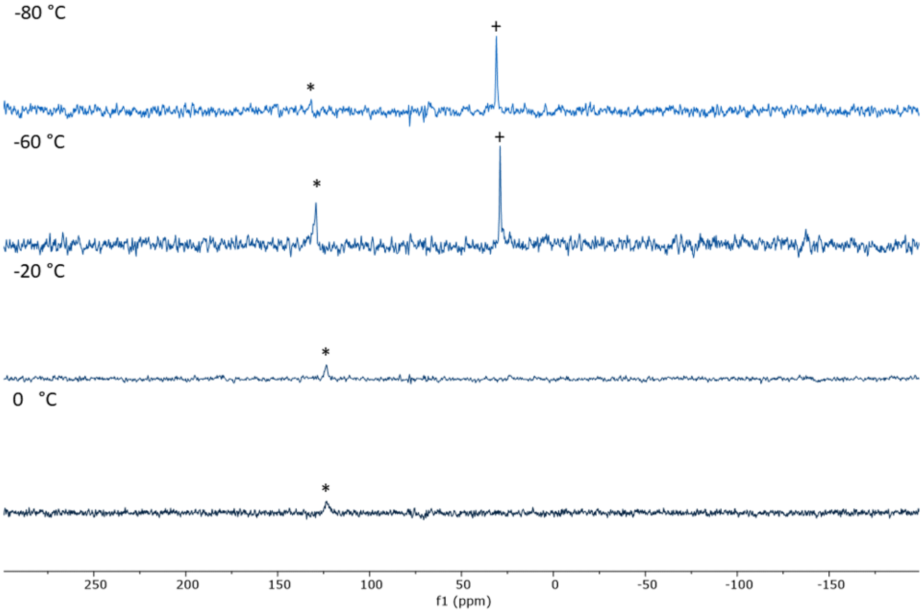


Figure S 20: Variable temperature ^{119}Sn NMR spectrum of stannylene **2** in Toluene-d_8 at -80 °C, -60 °C, -20 °C and 0 °C. (* = signals corresponding to monomeric stannylene, + = signals corresponding to di-stannylene).

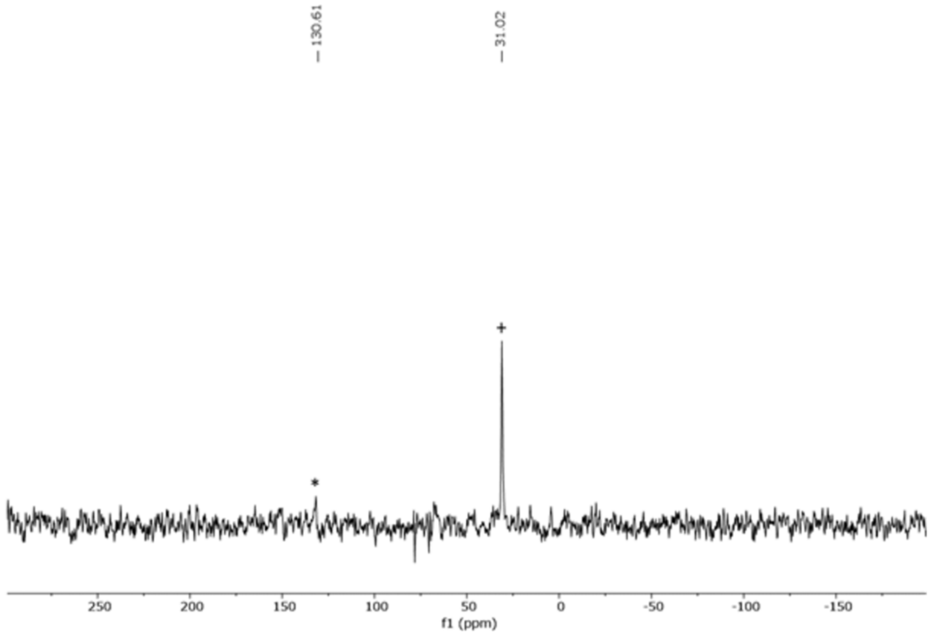


Figure S 21: Variable temperature ^{119}Sn NMR spectrum of stannylene **2** in Toluene-d$_8$ at -80 °C.

3. Proposed Mechanism for the Formation of [((I^{t}BuN)$_3$SnO)(I^{t}BuN)Sn:]$_2$ (6)

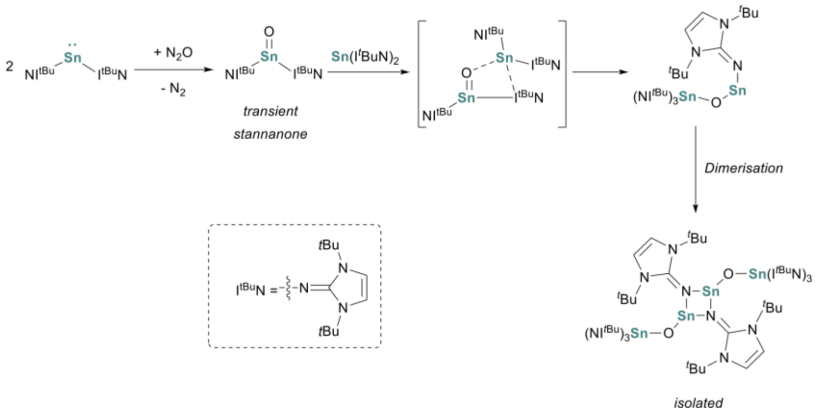


Figure S 22: Suggested Mechanism for the Formation of [((I^{t}BuN)$_3$SnO)(I^{t}BuN)Sn:]$_2$ (**6**) upon activation of N$_2$O by **2**. A transient stannanone is formed, which reacts with another stannylene, followed by dimerization.

4. X-Ray Crystallography

4.1 General Information

Single crystal diffraction data were recorded on a Bruker Photon D8 Venture DUO IMS system equipped with a Helios optic monochromator and a Mo IMS microsource (I = 0.71073 Å) The data collection was performed, using the APEX III & IV software package[S5] on single crystals coated with Fomblin®Y as perfluorinated ether. The single crystals were picked on a micro sampler, transferred to the diffractometer, and measured frozen under a stream of cold nitrogen (100 K). A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT.[S6] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[S6] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined against all data using the APEX IV software in conjunction with SHELXL-2014[S7] and SHELXLE.[S8] H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 and 0.95 Å, respectively, and $U_{iso}(H) = 1.2\cdot U_{eq(C)}$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma_w(Fo^2-Fc^2)^2$ with the SHELXL weighting scheme.[S9] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.[S10] The images of the crystal structures were generated by Mercury.[S11] The data (CCDC numbers 2302960-2302965) can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

4.2 Crystal Data and Structure Refinement for Compounds 1-6

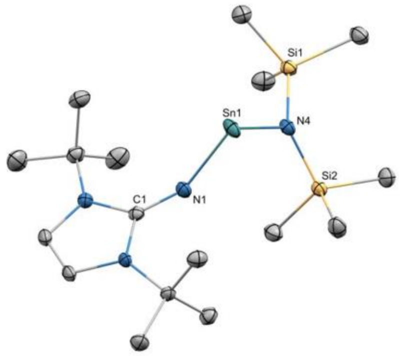


Figure S 23: Molecular structures of compound **1** in the solid state. Ellipsoids are set at 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1-N1 1.9891(15), Sn1-N4 2.1115(16), N1-C1 1.289(2), N4-Si1 1.7177(16), N4-Si2 1.7231(18), N1-Sn1-N4 97.37(6).

	1	2	3
CCDC Number	2302960	2302962	2302961
Empirical formula	$C_{17}H_{38}N_4Si_2Sn$	$C_{22}H_{40}N_6Sn$	$C_{22}H_{40}GeN_6$
Formula weight	473.4	507.29	461.19
Temperature/K	100	100	100.15
Crystal system	triclinic	monoclinic	cubic
Space group	P-1	$P2_1/n$	Im-3
a/Å	9.5891(4)	12.1212(5)	15.657(5)
b/Å	11.3820(5)	13.6549(5)	15.657(5)
c/Å	12.0183(5)	15.3306(6)	15.657(5)
α/°	87.537(2)	90	90
β/°	67.803(2)	103.9420(10)	90
γ/°	78.202(2)	90	90
Volume/Å^3	1188.00(9)	2462.67(17)	3838(4)
Z	2	4	6
ρ_{calc}g/cm^3	1.323	1.368	1.197
μ/mm^{-1}	1.183	1.057	1.216
F(000)	492	1056	1476
Crystal size/mm^3	0.137 × 0.112 × 0.107	0.8 × 0.7 × 0.4	0.09 × 0.05 × 0.04
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.68 to 50.7	3.862 to 51.402	3.678 to 51.47
Index ranges	$-11 \le h \le 11$, $-13 \le k \le 13$, $-14 \le l \le 14$	$-14 \le h \le 14$, $-16 \le k \le 16$, $-18 \le l \le 18$	$-19 \le h \le 19$, $-19 \le k \le 19$, $-19 \le l \le 19$
Reflections collected	39646	82900	88048
Independent reflections	4350 [R_{int} = 0.0485, R_{sigma} = 0.0216]	4690 [R_{int} = 0.0649, R_{sigma} = 0.0198]	693 [R_{int} = 0.0964, R_{sigma} = 0.0093]
Data/restraints/parameters	4350/0/229	4690/0/274	693/0/47
Goodness-of-fit on F^2	1.059	1.036	1.083
Final R indexes [I>=2σ (I)]	R_1 = 0.0192, wR_2 = 0.0396	R_1 = 0.0201, wR_2 = 0.0480	R_1 = 0.0266, wR_2 = 0.0690
Final R indexes [all data]	R_1 = 0.0218, wR_2 = 0.0404	R_1 = 0.0251, wR_2 = 0.0500	R_1 = 0.0298, wR_2 = 0.0705
Largest diff. peak/hole / e Å^{-3}	0.32/-0.36	0.35/-0.39	0.20/-0.30

Table S 1. Crystal data and structure refinement for compounds **1**, **2** and **3**.

	4	**5**	**6**
CCDC Number	2302965	2302964	2302963
Empirical formula	$C_{33}H_{49}N_6O_4Sn$	$C_{24}H_{40}GeN_6O_4$	$C_{100}H_{172}N_{24}O_2Sn_4$
Formula weight	712.49	1156.18	2217.37
Temperature/K	100	100	100
Crystal system	orthorhombic	orthorhombic	triclinic
Space group	Pbca	Pbcn	P-1
a/Å	16.6756(4)	14.050(6)	12.7150(17)
b/Å	15.4221(5)	19.077(7)	13.4081(17)
c/Å	27.4766(8)	11.887(4)	17.434(2)
α/°	90	90	83.374(4)
β/°	90	90	72.764(3)
γ/°	90	90	72.614(3)
Volume/Å^3	7066.2(4)	3186(2)	2707.9(6)
Z	8	4	1
ρ_{calc}g/cm^3	1.339	2.41	1.36
μ/mm^{-1}	0.766	9.346	0.969
F(000)	2968	2160	1156
Crystal size/mm^3	1 × 0.8 × 0.6	0.04 × 0.03 × 0.02	0.07 × 0.03 × 0.01
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.84 to 51.46	5.476 to 54.862	3.958 to 51.716
Index ranges	-20 ≤ h ≤ 20, -18 ≤ k ≤ 18, -33 ≤ l ≤ 33	-18 ≤ h ≤ 18, -24 ≤ k ≤ 24, -15 ≤ l ≤ 15	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -21 ≤ l ≤ 21
Reflections collected	367722	156984	100824
Independent reflections	6743 [R_{int} = 0.0285, R_{sigma} = 0.0063]	3632 [R_{int} = 0.0550, R_{sigma} = 0.0122]	10381 [R_{int} = 0.2088, R_{sigma} = 0.1162]
Data/restraints/parameters	6743/0/409	3632/6/153	10381/0/592
Goodness-of-fit on F^2	0.957	1.177	1.113
Final R indexes [I>=2σ (I)]	R_1 = 0.0261, wR_2 = 0.0889	R_1 = 0.1129, wR_2 = 0.2355	R_1 = 0.0880, wR_2 = 0.1670
Final R indexes [all data]	R_1 = 0.0268, wR_2 = 0.0896	R_1 = 0.1137, wR_2 = 0.2358	R_1 = 0.1228, wR_2 = 0.1811
Largest diff. peak/hole / e Å^{-3}	0.34/-0.85	2.26/-1.52	1.07/-2.30

Table S 2. Crystal data and structure refinement for compounds **4**, **5** and **6**.

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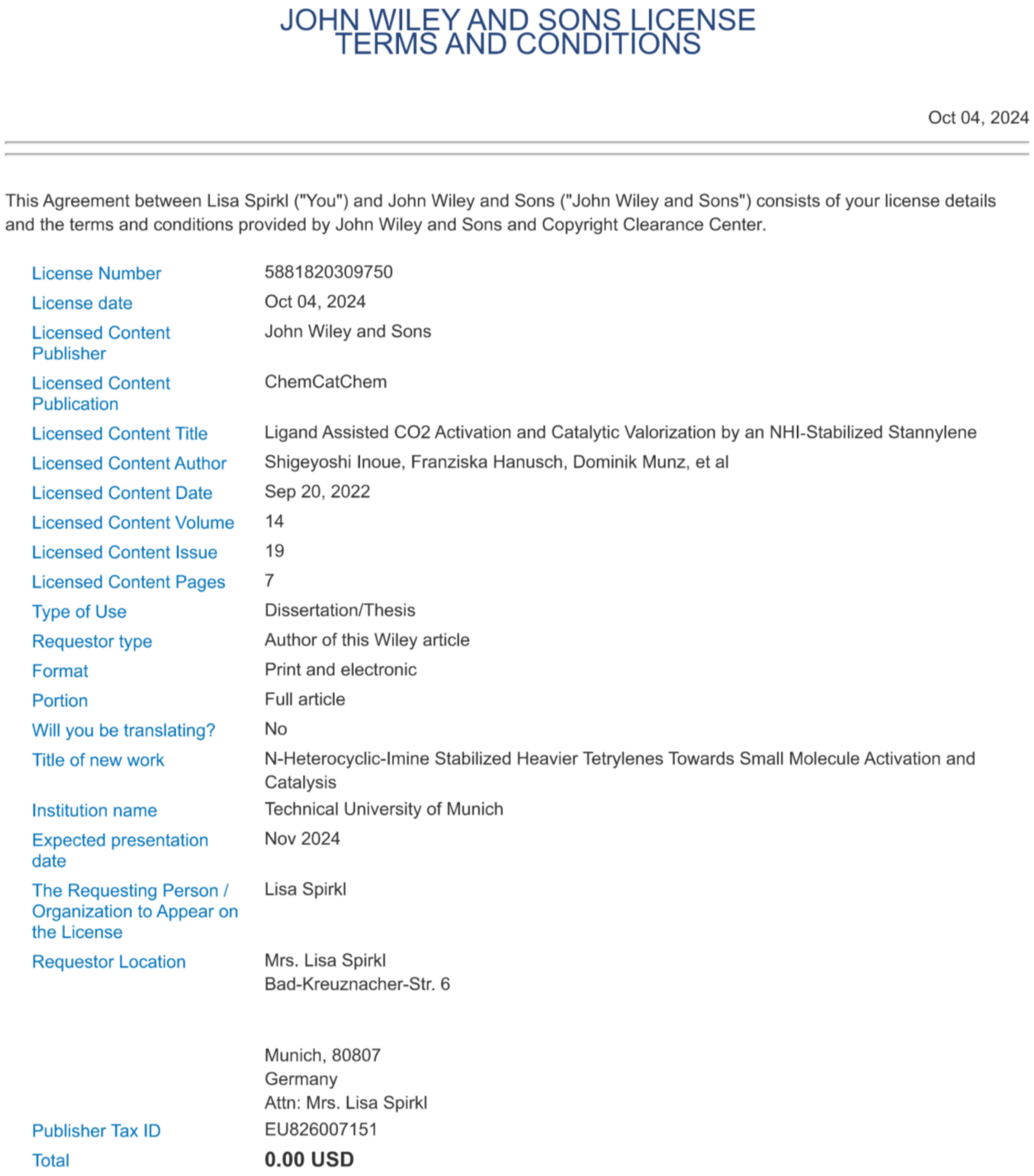

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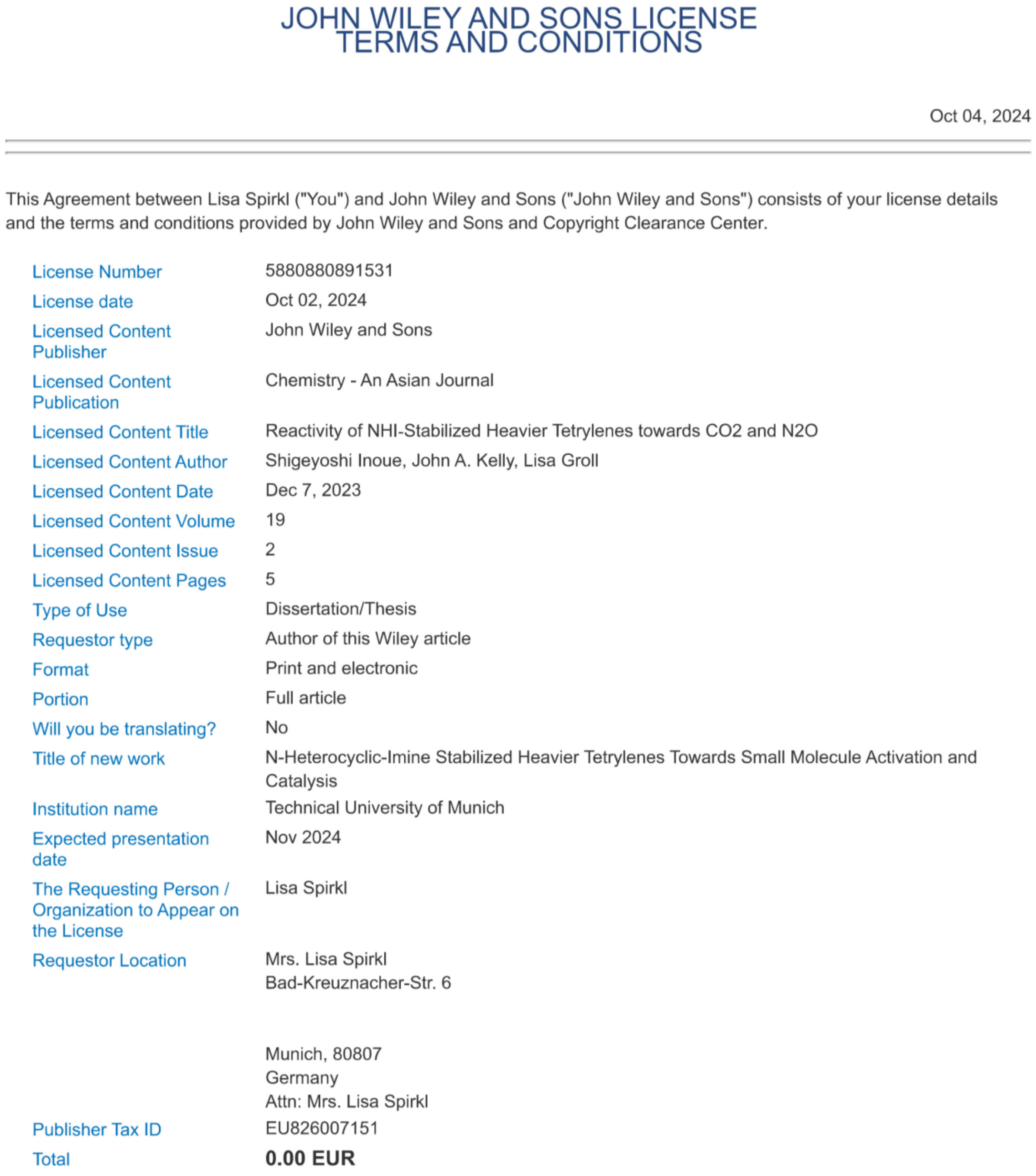

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