

Reactivity and catalytic application of NHC stabilized stannylumylenes and stannylidenes

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Abstract

Tetryliumylidenes ($RE:^{+}$) are mono-substituted compounds with the central element E^{II} ($E = Si, Ge, Sn, Pb$) containing a lone pair of electrons and two vacant orbitals. Due to their unsaturated and ambiphilic nature, they are highly reactive and are of increasing interest for catalytic applications. To date, many tetryliumylidenes have been reported, however, the reactivity investigations and catalytic applications of stannylumylidenes are still scarce compared to Si and Ge analogues. This thesis comprises the isolation and characterization of the N-heterocyclic carbene (NHC)-stabilized stannylumylidenes, including three-coordinated and two-coordinated variants based on diverse coordination number by NHC. Their fascinating reactivities towards small molecules and catalytic applications are investigated. Additionally, an amido/terphenyl-stannylen–NHC adduct was isolated, which not only activates ketones and aldehydes in stoichiometric reactions but also catalyzes the hydrosilylation of these carbonyl compounds.

Kurzusammenfassung

Tetryliumylidene ($RE:^{+}$) sind monosubstituierte Verbindungen mit einem Element der Gruppe 14 in der Oxidationsstufe +2 ($E = Si, Ge, Sn, Pb$), das ein freies Elektronenpaar und zwei unbesetzte Orbitale besitzt. Aufgrund ihrer ambiphilen und ungesättigten Natur sind sie hochreaktiv und gewinnen zunehmend an Bedeutung in der Katalyse. Während zahlreiche Tetryliumylidene untersucht wurden, ist die Chemie der Stannylumylidene im Vergleich zu ihren Silicium- und Germanium-Analoga noch wenig erforscht. Diese Arbeit konzentriert sich auf die Isolierung und Charakterisierung von NHC-stabilisierten Stannylumylidenen, einschließlich drei- und zweifach koordinierten Spezies, die durch die NHC-Koordination beeinflusst werden. Ihre Reaktivität gegenüber kleinen Molekülen sowie ihre katalytischen Anwendungen. Zusätzlich wurde ein Amido/Terphenyl-Stannylen–NHC-Addukt isoliert, das nicht nur Ketone und Aldehyde in stöchiometrischen Reaktionen aktiviert, sondern auch als Katalysator für die Hydrosilylierung dieser Carbonylverbindungen dient.

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List of Abbreviations and Formulas

Alk	alkyl group
Ad	adamantly; C ₁₀ H ₁₅
BArF ₄	B{3,5-(CF ₃) ₂ -C ₆ H ₃ } ₄
CAAC	cyclic (alkyl)(amino)carbenes
Cat.	catalyst
cDAC	Cyclic diamidocarbene
CO	Carbon monoxide
Cp	Cyclopentadiene; C ₅ H ₅
Cp*	1,2,3,4,5-pentamethyl-cyclopentadiene; C ₅ Me ₅
Cy	Cyclohexyl
DIBAL	diisobutylaluminum hydride
Dipp	2,6-di-isopropyl-phenyl; 2,6- <i>i</i> Pr ₂ C ₆ H ₃
DMAP	4-dimethylamidopyridine
DippTer	1,3-bis-diisopropylphenyl-benzene
DFT	Density Functional Theory
e.g.	Latin (exempli gratia): “for example”
Eind	1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl
HOMO	highest occupied molecular orbital
HBpin	Pinacolborane; (CH ₃) ₄ C ₂ O ₂ BH
IAd	1,3-di(adamantly)imidazole-2-ylidene
i.e.	Latin (id est): “that is”
IDipp	1,3-bis(2,6-diisopropylphenyl)imidazoline-2-ylidene (C[N-(2,6- <i>i</i> Pr ₂ C ₆ H ₃)CH])
IMe ₄	1,3,4,5-tetramethyl-imidazol-2-ylidene
IMes	1,3,4,5-tetramethylimidazolin-2-ylidene
<i>i</i> Pr	<i>iso</i> -propyl; C ₃ H ₇
ItBu	1,3- <i>tert</i> -butyl-2-ylidene (C[(N- <i>t</i> Bu)CH])

L	ligand
LB	Lewis base
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
Nacnac	β -diketiminatate ligand
Naph	Naphthalenide; $C_{10}H_8^-$
Np	Neopentyl
NHBO	N-heterocyclic boryloxy
NHC	N-heterocyclic carbene
NHCP	N-heterocyclic carbene-phosphinidene
NHI	N-heterocyclic imine
Nuc	nucleophile
PA	proton affinities
PEt ₃	triethylphosphine
Ph	Phenyl; C_6H_5
PVC	Polyvinyl chloride
red	reduction / reducing agent
SIMes	1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene
<i>t</i> Bu	<i>tert</i> -butyl; $C(CH_3)_3$
Tipp	2,4,6-tri-isopropylphenyl; 2,4,6- <i>i</i> Pr ₂ C ₆ H ₃
TMS	Trimethylsilyl
TMSCN	Trimethylsilyl cyanide
THF	Tetrahydrofuran
^{Tipp} Ter	1,3-bis-triisopropylphenyl-benzene
X	halide
SC-XRD	single-crystal X-ray diffractometry

ΔE_{ST}

singlet-triplet gap energy

Publication List

1. **D. Niu**, A. Kostenko, J. A. Kelly, D. Sarkar, H. Xu, S. Inoue*, CO₂ Hydrosilylation Catalyzed by an N-Heterocyclic Carbene (NHC)-Stabilized Stannylumylidene, Chemical Science, 10.1039/d4sc07116f.
2. **D. Niu**, J. A. Kelly, F. J. Kiefer, A. Kostenko, S. Inoue, Terphenyl Amido Stannylene-NHC Adduct: A Catalyst for the Hydrosilylation of Aldehydes and Ketones, Z. Anorg. Allg. Chem., **2024**, e202400143.

Conference Contributions

CO₂ Hydrosilylation Catalyzed by an N-Heterocyclic Carbene (NHC)-Stabilized Stannylumylidene

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1 Introduction

Tin (Sn), a soft, silvery-white metal, has played a significant role in human history.¹ It is one of the earliest known metals, valued for its versatility and unique properties. Since around 3500 BC, tin has been a key additive in alloy production, including bronze and pewter. Following the Industrial Revolution, its demand surged due to applications in iron and steel coatings, food preservation, and other industries.^{2, 3}

In nature, tin is primarily found as cassiterite (SnO_2) (Figure 2, (a)). The ore is extracted through dredging, open-cast mining, or gravel-washing, where high-pressure water jets separate it from deposits. The extracted ore is then concentrated by gravity separation, leveraging its higher density compared to sand. Subsequently, it undergoes roasting to remove arsenic and sulfur and to convert metal sulfides into oxides before being reduced by smelting in reverberatory, rotary, or electric furnaces (Figure 1).⁴

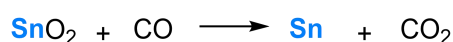


Figure 1. Reduction of SnO_2 with CO.

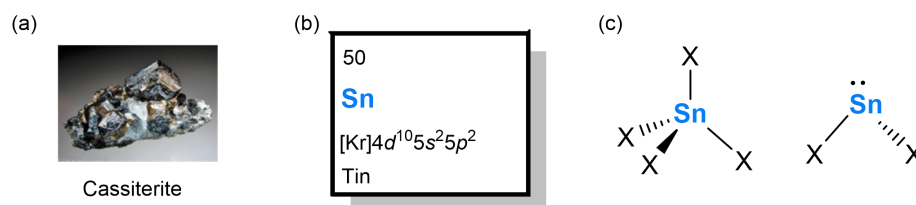


Figure 2. (a) Photograph of cassiterite crystals; (b) the electronic configuration of Sn; (c) Typical geometry of Sn(II) and Sn(IV) complexes.

Tin (Sn) belongs to Group 14 of the Periodic Table and has the electronic configuration $[\text{Kr}] 4d^{10}5s^25p^2$ (Figure 2, (b)).² It primarily exhibits two valence states, Sn(IV) and Sn(II) . In the Sn(IV) state, tin typically forms tetrahedral compounds (e.g., SnX_4 , X = halide) (Figure 2, (c)). In contrast, Sn(II) compounds (e.g. SnX_2) generally adopt a bent geometry due to the presence of a lone pair of electrons (Figure 2, (c)). The lone pair of electrons significantly affects the electronic and steric properties of Sn(II) complexes, making their structures more flexible than their Sn(IV) counterparts. Additionally, both Sn(IV) and Sn(II) can adopt higher coordination numbers beyond their typical tetrahedral and bent geometries due to electrostatic and steric effects. Trigonal pyramidal (Sn(II)) occurs in three-coordinate species with a lone pair, while distorted see-saw (Sn(II)) structures arise when Sn(II) coordinates to

additional ligands. A square planar (Sn(IV)) is found in certain ligand-stabilized complexes, such as tetracyanostannate(IV) $[\text{Sn}(\text{CN})_4]^{2-}$. Trigonal bipyramidal (Sn(IV)) and octahedral (Sn(IV)) geometries appear in hypercoordinate tin species with strong donor ligands. The stannyl radical was found to have a trigonal planar structure like the corresponding cation.

The first organotin compound is diethyltin diiodide $(\text{CH}_3\text{CH}_2)_2\text{SnI}_2$, discovered by Edward Frankland in 1849 via tin reacted with iodoethane in temperatures regions of 150 to 200 °C. The area grew rapidly after the discovery of the Grignard reagents, which are useful for producing Sn-C bonds. The first application of organotin compounds came in about 1943 when they were used for stabilizing polyvinyl chloride (PVC) against heat during processing. In this regard, dibutyltin dilaurate (DBTDL) is a typical additive to improve PVC's heat and light stability, making the polymer more durable and suitable for industrial applications. Afterward, various industrial and biological applications were developed.⁵ Tin oxide (SnO_2), one of the most common inorganic tin compounds, has been used in glass coatings, catalysis, sensors, semiconductors, cognitive remediation, and lithium-ion batteries.^{6, 7} Additionally, tin has gained attention as a promising alternative to lead in organic-inorganic halide perovskite solar cells (PSCs), offering lower toxicity while achieving high power conversion efficiency (PCE).^{8, 9}

2 Tetrylenes and Tetryliumylidenes

2.1 N-Heterocyclic Carbenes (NHCs)

The classical N-heterocyclic carbenes (NHCs) are a class of stable singlet carbenes with a neutral divalent carbon atom directly attached to two nitrogen atoms within a heterocyclic scaffold (Figure 3, (a)).¹⁰ The cyclic (alkyl)(amino)carbenes (cAACs), the replacement of one of the electronegative and π -donating amino substituents of NHCs by a strong σ -donor alkyl group, exhibit enhanced amphiphilicity compared to NHCs (Figure 3, (b)).¹¹ Additionally, mesoionic carbenes (iMICs) are a subclass of the family of NHCs with the carbonic carbon atom at the unusual C4 (or C5) position, which are stronger σ -donors than classical NHCs (Figure 3, (c)).¹²⁻¹⁵ However, a profound discussion of iMICs would exceed the scope of this introduction.

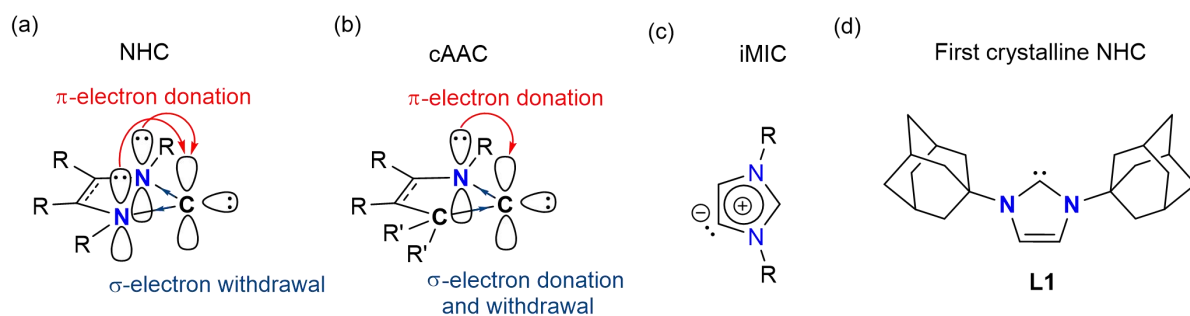


Figure 3. Schematic representation of electronic effects in (a) NHCs (b) CAACs, and (c) first NHC.

Since the first crystalline NHC, 1,3-di(adamantyl)imidazole-2-ylidene (IAd) (Figure 3(d), **L1**), which was isolated and identified in 1991 by Arduengo et al.,¹⁶ NHCs have garnered significant academic interest as one of the most powerful tools in organometallic chemistry, demonstrating substantial commercial utility.

The primary application of NHCs is their use as ligands for coordination to transition metals. Due to their strong σ -donor ability and weak π -acceptor properties, NHCs are comparable to phosphines and were initially seen as an alternative.¹⁷ However, NHCs have several advantages over phosphines, such as a stronger σ -donor ability that leads to stronger metal-ligand bonds, making NHC-metal bonds generally more stable.¹⁸ The steric and electronic properties of NHCs can also be easily varied, allowing them to compete with phosphines as supporting ligands in organometallic chemistry.

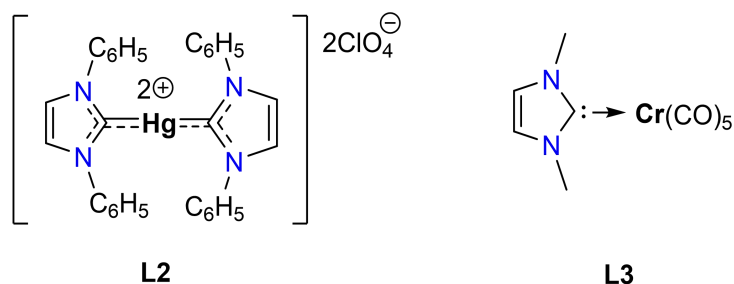


Figure 4. Selected early carbene transition-metal complexes.

Twenty years before the isolation of free carbene, NHC transition metal complexes had been reported. In 1968, Wanzlick synthesized mercury salt-carbene complex by treating 1,3-dimethylimidazolium perchlorate with mercury (II) acetate (Figure 4, **L2**).¹⁹ In the same year, Öfele reported the synthesis of NHC chromium (0) complex (**L3**) via heating 1,3-dimethylimidazolium hydrogen pentacarbonylchromate under high vacuum at 120 °C.²⁰ Since then, numerous NHC-metal complexes have been synthesized, leading to a wide range of applications, especially in homogeneous catalysis. One of the most extensively

studied classes of catalytic reactions is ruthenium-based catalysts for olefin metathesis. Notably, Grubbs catalysts demonstrate how ligand exchange can improve catalytic activity. Grubbs' second-generation catalyst (**L5**) with NHC ligand shows greater stability and higher activity in olefin metathesis compared to first-generation catalyst (**L4**) featuring two PCy₃ (Cy = cyclohexyl) ligands bound to ruthenium. Mechanistic studies reveal that the **L5** binds alkenes much more effectively than **L4**, due to the more electron-rich metal center, improving catalytic performance by a factor of 10,000.²¹

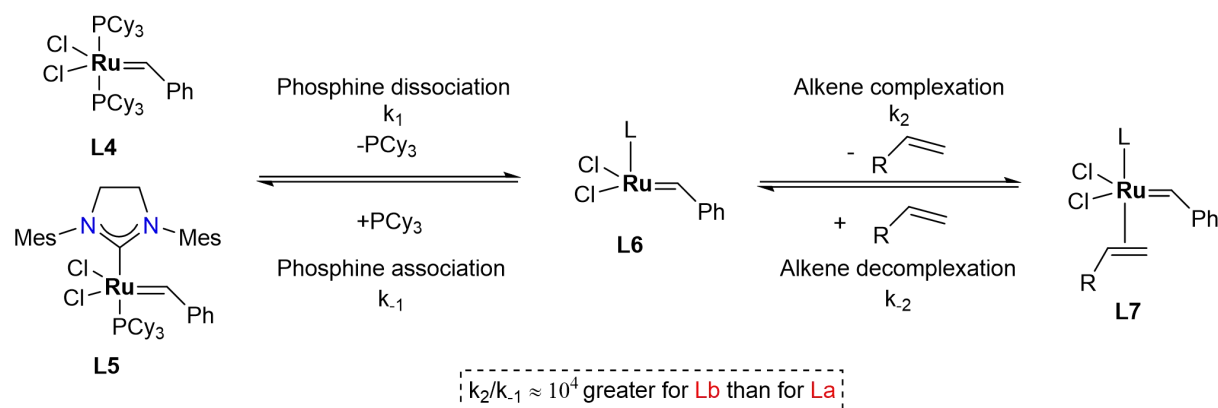


Figure 5. Structures of First-generation Grubb's catalyst **L4** and Second-generation Grubb's catalyst **L5**, as well as a proposed mechanism of transition-metal alkene metathesis. (Cy = cyclohexyl)

As excellent ligands for transition metals, it has also been demonstrated that NHCs can effectively stabilize main group compounds in low oxidation states. The key feature of the carbene-main group element bond is the σ -donation of the carbene into an empty σ -accepting orbital of the low-valent p-block element. Pioneering work in this area was done by Robinson and colleagues in 2008, who demonstrated that NHCs could stabilize a silicon(0) species (Figure 6, **L8**) and a phosphorus(0) species (**L9**).^{22, 23} Braunschweig et al. stabilized a boron-boron triple bond (**L10**) with carbenes.²⁴ NHCs have also been used to stabilize elemental carbon species (**L11**), described as a 'bent allene' with an electronic structure featuring two lone pairs at the central carbon.²⁵ NHCs have also proven to be highly useful in synthesizing parent systems, which contain hydrogen substituents instead of bulky groups and are crucial for understanding low-valent main group compounds. A notable example is the parent borylene (**L12**) from Bertrand et al., stabilized by cAACs.²⁶ These examples highlight the versatility of NHCs in stabilizing various main group element compounds.

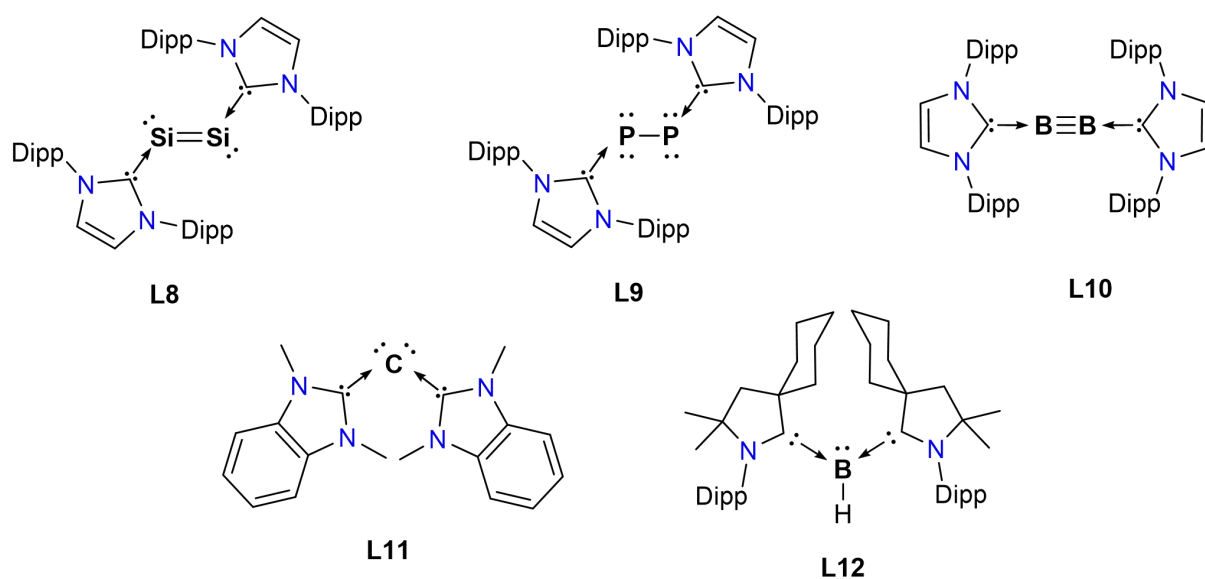


Figure 6. Stabilization of p-block species by NHCs.

2.1.1 NHCs in Small Molecule Activation

With the lone pair of carbene electrons, both NHCs and cAAC behave as nucleophiles and can activate CO_2 to form imidazolium carboxylates (Figure 7, **L13-L15**)²⁷⁻²⁹, which has been proved to be an important intermediate in the CO_2 hydrosilylation reaction catalyzed by NHCs.

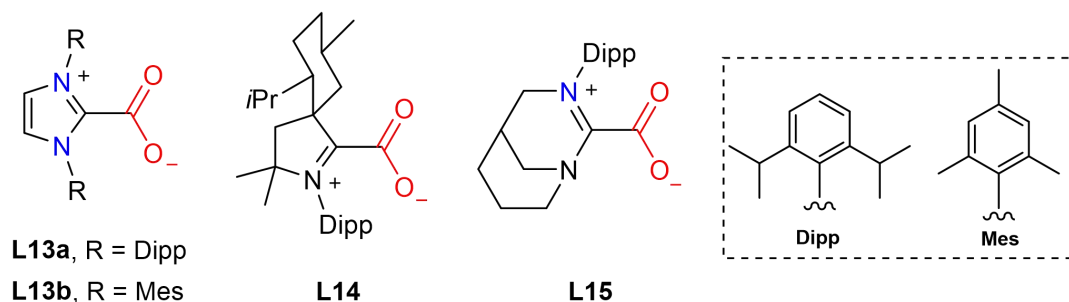


Figure 7. Selected examples of CO_2 activation by NHCs.

Carbon monoxide (CO) activation by NHCs has attracted attention since the 1990s. However, during the first decade, the existence of an isolated NHC-ketene complex remained a subject of debate.³⁰⁻³² This uncertainty was finally resolved in 2006 when Guy Bertrand and colleagues reported the reaction of stable alkyl amino carbenes (**L16**) with CO, yielding stable ketenes (**L17**) (Figure 8, (a)).³³ Later, in 2009, a study by the Bielawski group demonstrated that a cyclic diamidocarbene (cDAC) (**L18**) could capture CO molecules (Figure 8, (b)), leading to the first example of a diamidoketene (**L19**).³⁴ This process was

found to be thermally reversible, with equilibrium parameters of $K_{eq} = 2.62 \text{ M}^{-1}$ at 30°C , $\Delta H = -35.33 \text{ kJ mol}^{-1}$, and $\Delta S = -109.5 \text{ J mol}^{-1} \text{ K}^{-1}$. Comparing these findings, a ferrocene-based NHC (**L20**) was also shown to activate CO, forming a zwitterionic product (**L21**) (Figure 8, (c)).³⁵ A similar reaction model was observed by Guy Bertrand in 2013 (Figure 8, (d)), where an anti-Bredt carbene (**L22**) facilitated the preparation and isolation of oxyallyl radical cations (**L23**).³⁶

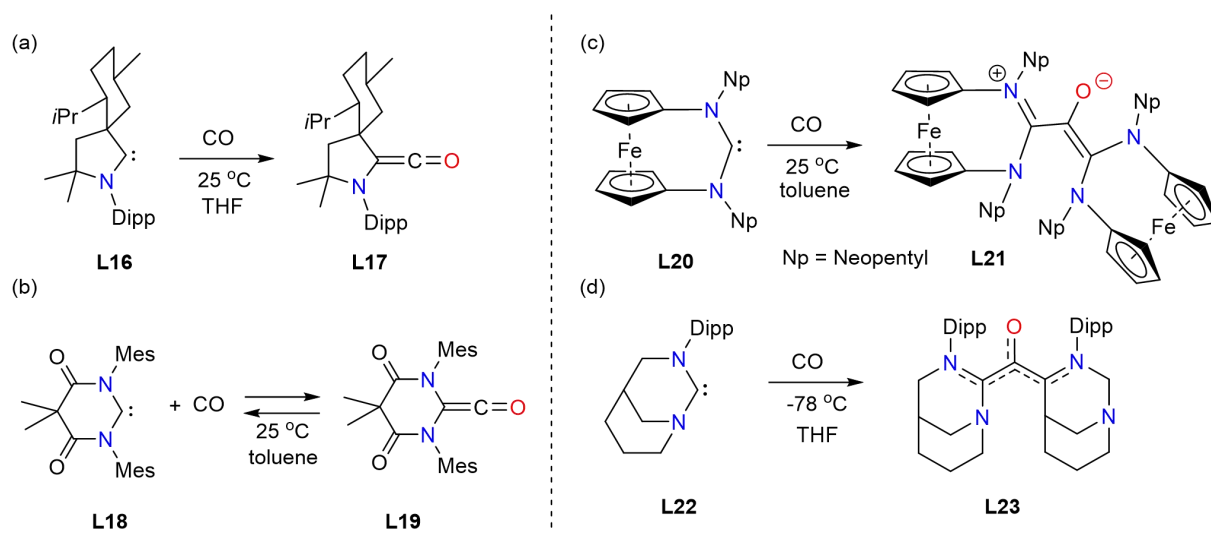


Figure 8. Examples of CO activation by NHCs.

NHCs are able to capture N_2O to give stable adducts under ambient conditions (Figure 9, (a)), which display a bent N_2O group, bonded to the heterocycle through the N atom (**L25**).^{28, 37} **L25** is stable at room temperature but decomposes to urea (**L26**) upon heating. **L27** underwent alkylation with MeI to induce a rupture of the N-N bond (**L27**). Similar to N_2O , NHCs have been confirmed as a potential candidate to fix nitric oxide (NO), an important small radical molecule.³² Eunsung Lee and colleagues (2015) reported the preparation of NHC nitric oxide (**L28**) by direct addition of nitric oxide to NHC in toluene (Figure 9, (b)).³⁸ **L28** can be thermally transformed to another N-heterocyclic carbene, forming urea (**L26**) with the release of NO and N_2O .

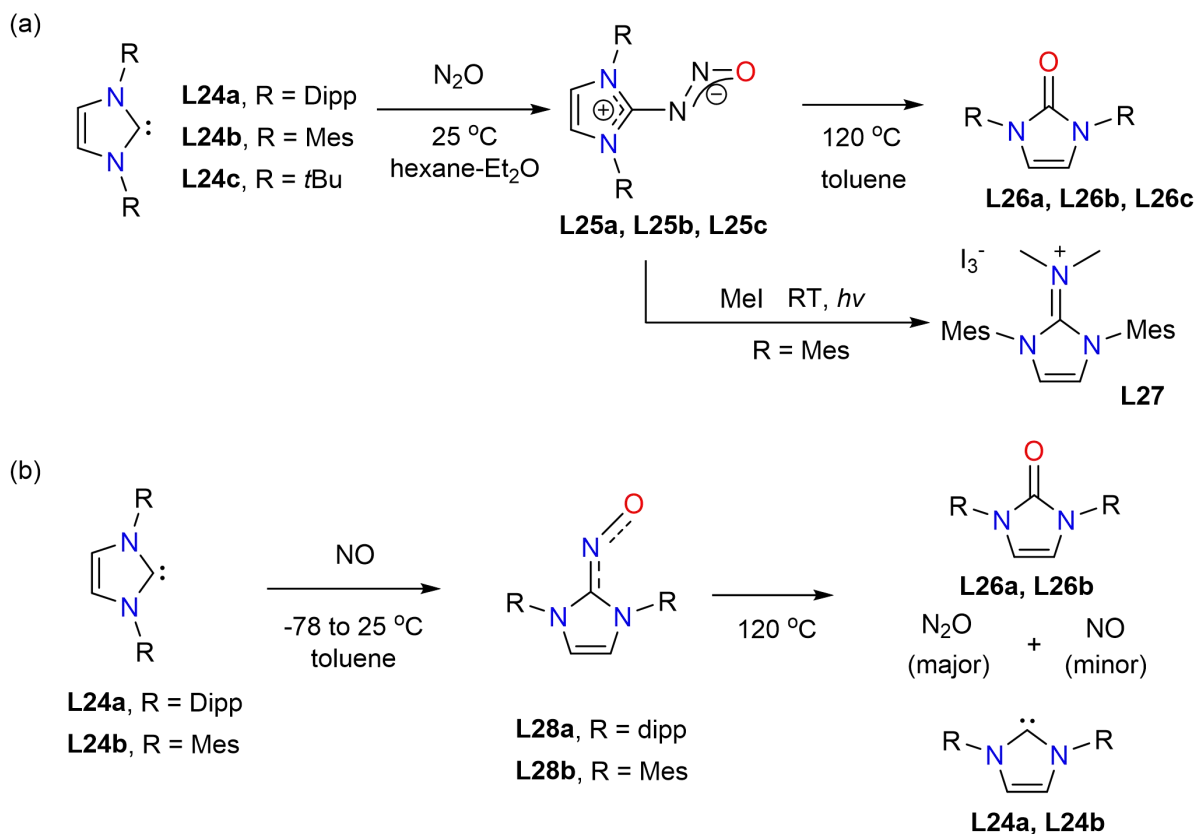


Figure 9. Examples of N_2O or NO activation by NHCs.

As shown in Figure 10, the nucleophilic behaviours allow some carbene to activate ammonia by splitting the N-H bond. The first example of ammonia activation was reported by the Bertrand group in 2007 (**L29**).³⁹ Later, the synthesis of *N,N'*-dimesityl-4,6-diketo-5,5-dimethylpyrimidin-2-ylidene was reported by Bielawski (2010), which activates NH_3 to afford **L30**.⁴⁰ Additionally, a typical NHC 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene (SIMes) (**L31**), was found to be an organic reagent to reversibly activate ammonia (Figure 10, (b)).⁴¹

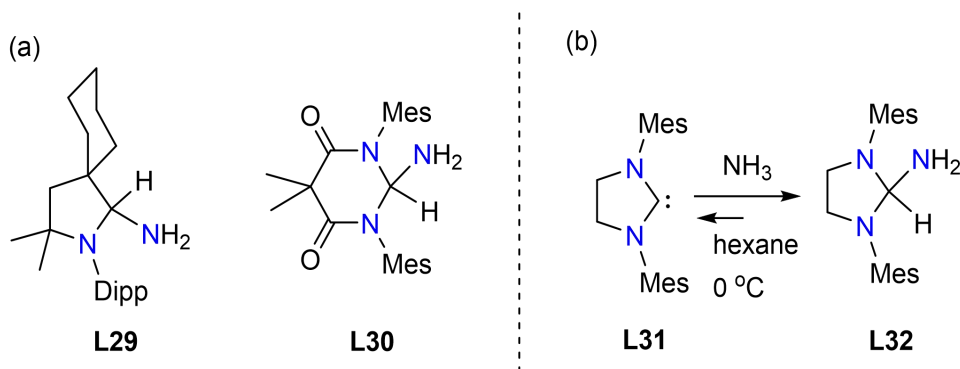


Figure 10. (a) Selected products from activation of NH_3 by NHCs; (b) reversible activation of NH_3 by SIMes.

In addition, a rare example of NHC-mediated H_2 activation was reported by the Bertrand group in 2007 as shown in Figure 11.³⁹ More nucleophilic and electrophilic (alkyl)(amino)carbenes (**L16**) were found to split the $H-H$ bond under mild conditions, whereas typical cyclic bis(amino)carbenes remained inert toward dihydrogen. The proposed mechanism involves the lone pair of the NHC interacting with the antibonding orbital of H_2 , facilitating bond cleavage.

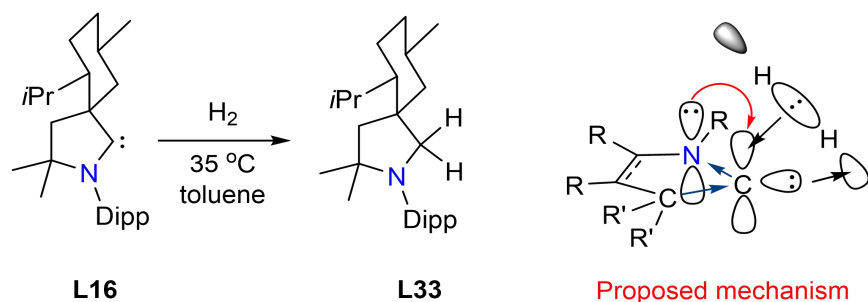


Figure 11. H_2 activation by NHCs and its proposed mechanism.

Until now, N_2 fixation using NHCs has remained largely limited to theoretical investigations. Studies suggest that N_2 activation at a carbon center could be achieved through the design of either thermodynamically stable ambiphilic amino carbenes or amino carbenes capable of one-electron reduction. These strategies could provide a promising entry point for non-metal-based nitrogen fixation systems.

2.1.2 Catalytic Applications of NHCs

Free NHCs are highly valuable as nucleophilic organic catalysts, and the isolation of NHC activation products provides key insights into their reaction mechanisms.²⁹ The use of NHCs as catalysts for the hydrosilylation of CO_2 was first reported by Zhang, Ying, and coworkers.⁴² Subsequent experimental and theoretical studies revealed that the NHC- CO_2 adduct (**L13a**) serves as the active catalytic species in CO_2 hydrosilylation, where the $Si-H$ bond is activated through coordination with the oxygen atom of the NHC- CO_2 adduct (**L34**) as shown in Figure 12.^{43, 44}

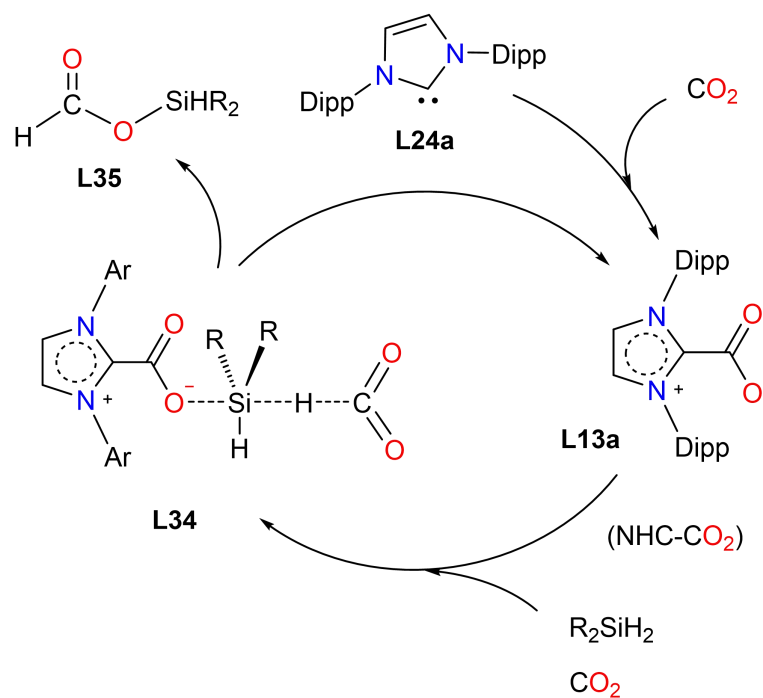


Figure 12. The mechanism of NHC-catalyzed CO_2 hydrosilylation.

The second major application of NHCs, organocatalysis, stems from their nucleophilicity toward carbonyl groups in organic compounds.⁴⁵ Organocatalysis is often associated with high selectivity and environmental compatibility. Most NHC-organocatalyzed reactions involve the attack of NHCs on aldehydes. As early as 1943, Ukai et al. reported that thiazolium salts could catalyze benzoin condensation, though the mechanism remained unclear.⁴⁶ In 1958, Breslow and colleagues proposed that a carbene species (Figure 13(a), **L36**) serves as the catalyst, initially attacking the aldehyde to form a zwitterionic intermediate (**L37**).⁴⁷ Due to the electron-withdrawing effect of the cationic azolium group, the aldehydic proton becomes significantly more acidic, facilitating the formation of the Breslow intermediate (**L38**) via a 1,2-proton shift. In 2012, Berkessel and colleagues successfully isolated this intermediate.⁴⁸ This process achieves an inversion of reactivity, allowing the previously electrophilic carbonyl carbon to react with electrophiles. In benzoin condensation, the Breslow intermediate reacts with a second aldehyde molecule, forming intermediate (**L39**), which subsequently eliminates benzoin and regenerates the catalyst (**L36**).

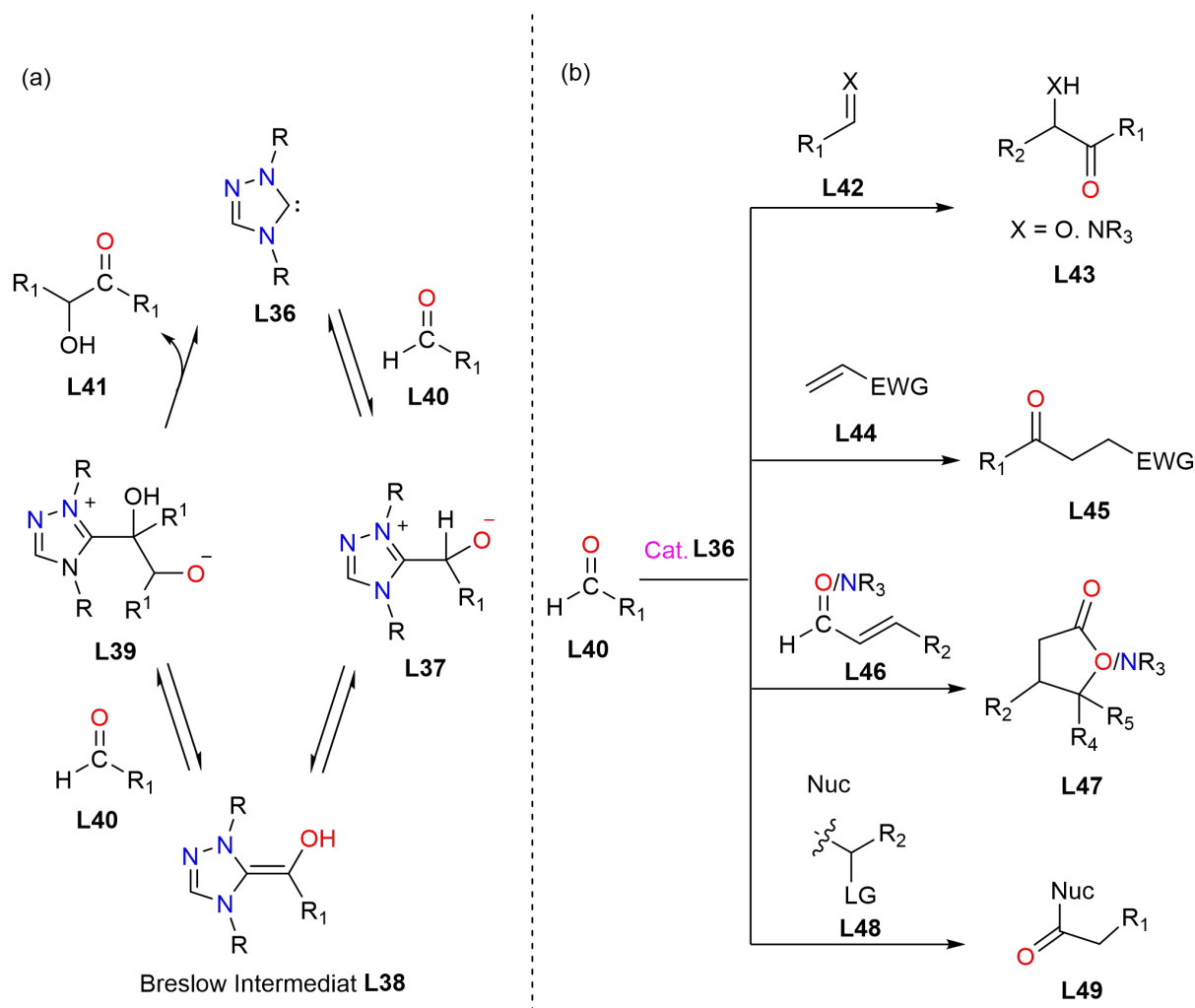


Figure 13. (a) The mechanism of carbene-catalyzed benzoin condensation; (b) Examples of carbene-catalyzed reactions with aldehydes.

Due to the reversibility of benzoin condensation, other electrophiles, such as activated alkenes, can also participate in the reaction, as seen in Figure 13 (b).⁴⁹ NHCs also play a catalytic role in cyclization reactions involving α,β-unsaturated aldehydes and in azolium substitution when a leaving group is present at the α-position.⁵⁰⁻⁵²

2.2 Heavier Tetrylenes

Heavier tetrylenes (R₂E:, E = Si, Ge, Sn, Pb) are singlet species of divalent silicon, germanium, tin, or lead, characterized by a non-bonding electron pair in the ground state and a vacant p-orbital. Unlike carbon, heavier Group 14 elements have a lower tendency to form hybrid orbitals and favor an (ns)²(np)² valence electron configuration in their divalent state.⁵³ This trend is supported by theoretical calculations of the singlet-triplet energy

difference ($\Delta E_{\text{ST}} = E(\text{triplet}) - E(\text{singlet})$). While methylene ($\text{H}_2\text{C}:$) is a triplet species with $\Delta E_{\text{ST}} = -14.0$ kcal/mol, heavier tetrylenes exhibit singlet ground states with increasing stability: 16.7 kcal/mol (Si), 21.8 kcal/mol (Ge), 24.8 kcal/mol (Sn), and 34.8 kcal/mol (Pb).⁵⁴ However, without steric or electronic stabilization, tetrylenes are thermally unstable and readily undergo reactions leading to tetravalent compounds or elemental metal deposition, even for plumbylenes. This high reactivity stems from their vacant p-orbitals and the electron deficiency relative to the octet rule. These characteristics make tetrylenes promising candidates for small-molecule activation, catalytic applications, and materials science.

To isolate tetrylenes, appropriate thermodynamic and/or kinetic stabilization strategies are required to protect their highly reactive vacant p-orbitals.⁵⁵ Thermodynamic stabilization generally involves intra- or intermolecular electron donation, which partially compensates for the electron deficiency through coordination or mesomeric effects. Kinetic stabilization, on the other hand, employs sterically demanding groups to shield the vacant p-orbital, preventing self-oligomerization or nucleophilic attack. A variety of isolable tetrylenes have been synthesized by incorporating bulky substituents and heteroatoms such as N, O, P, or other Lewis bases for additional stabilization. Figure 14 illustrates their typical primary synthesis routes: (a) Utilizing a photo-reduction approach from $\text{R}_2\text{E}(\text{SiR}'_3)_2$. (b) Implementing a reduction method, either photochemically or thermally, from three-membered metalliranes or metallirenes. (c) Reducing dihalides (R_2EX_2) using a reducing agent such as KC_8 , NaNaph , or alkali metals. Depending on the compound, this can yield either the tetrylene or its respective dimeric dimetallene. (d) Splitting dimetallene through photochemical or thermal means or by introducing an additional Lewis base, such as IMe_4 or dioxane. (e) Conducting substitution reactions from a halide-salt EX_2 ($\text{E} = \text{Si, Ge, Sn, Pb}$; $\text{X} = \text{Cl, Br, I}$) with an organometallic nucleophile, such as RLi or RMgBr .

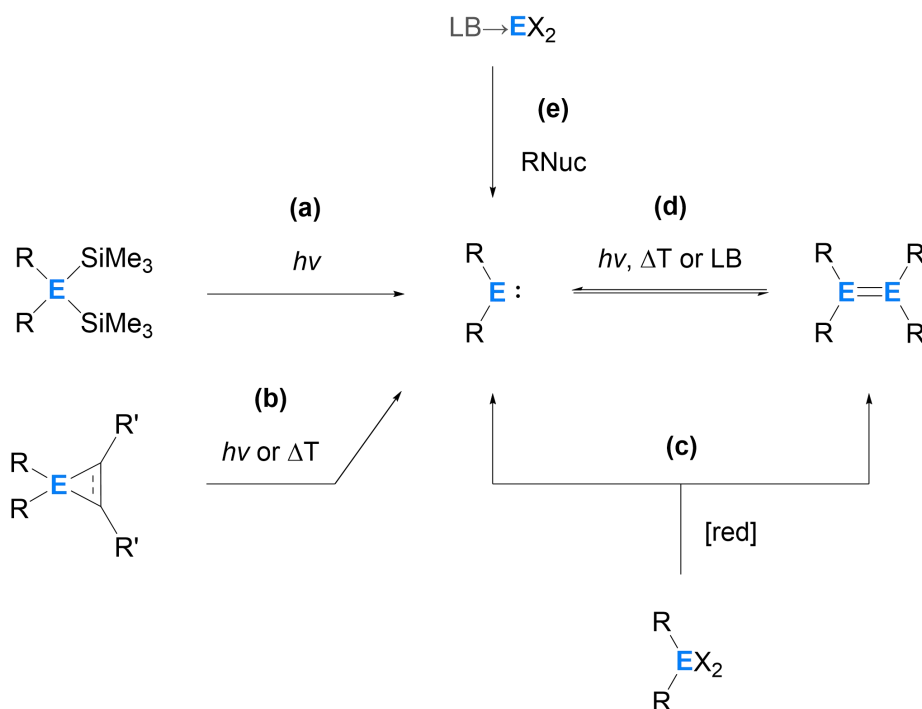


Figure 14. Common synthetic routes to generate stable tetrylenes ([red] = reducing agent (e.g. KC_8 , NaNaph , alkali metals), LB = Lewis base (e.g. polar solvent, NHC, dioxane, etc.), Nuc = Li, MgBr, SiMe_3 , $\text{X} = \text{Cl, Br, I}$).

Tetrylenes have been extensively investigated due to their unique electronic structures and reactivity, which systematically down Group 14. Seminal contributions by the Lappert group, diamino ligand tetrylenes $[(\text{TMS})_2\text{N}]_2\text{E}$: (Figure 15(a), **L50**) and $[(\text{TMS})(\text{CMe}_3)\text{N}]_2\text{E}$: (**L51**) were isolated.⁵⁶ In terms of silicon, West found that $[(\text{TMS})_2\text{N}]_2\text{Sn}$: (**L50a**) was only stable at low temperatures in solution.⁵⁷ In 1986, the first acyclic silylene Cp^*_2Si : (**L52a**) was reported by Jutzi via the reduction of dichloro(bis-pentamethylcyclopentadienyl)silane with alkali metal naphthalenides.⁵⁸ This stabilized system was also extended to heavier tetrylenes (Ge, Sn, Pb) (**L52b-c**).^{59, 60} It was shown that heavier germylenes, stannylenes, and plumbylenes are more stable in the +II state. Further notable developments include cyclic tetrylenes (**L54**) reported by Veith,^{61, 62} as well as Kira's dialkyl-substituted carbocyclic tetrylenes (**L53**),⁶³ and Lappert's pioneering NHSi species (**L55a**) containing conjugated π -frameworks.⁶⁴

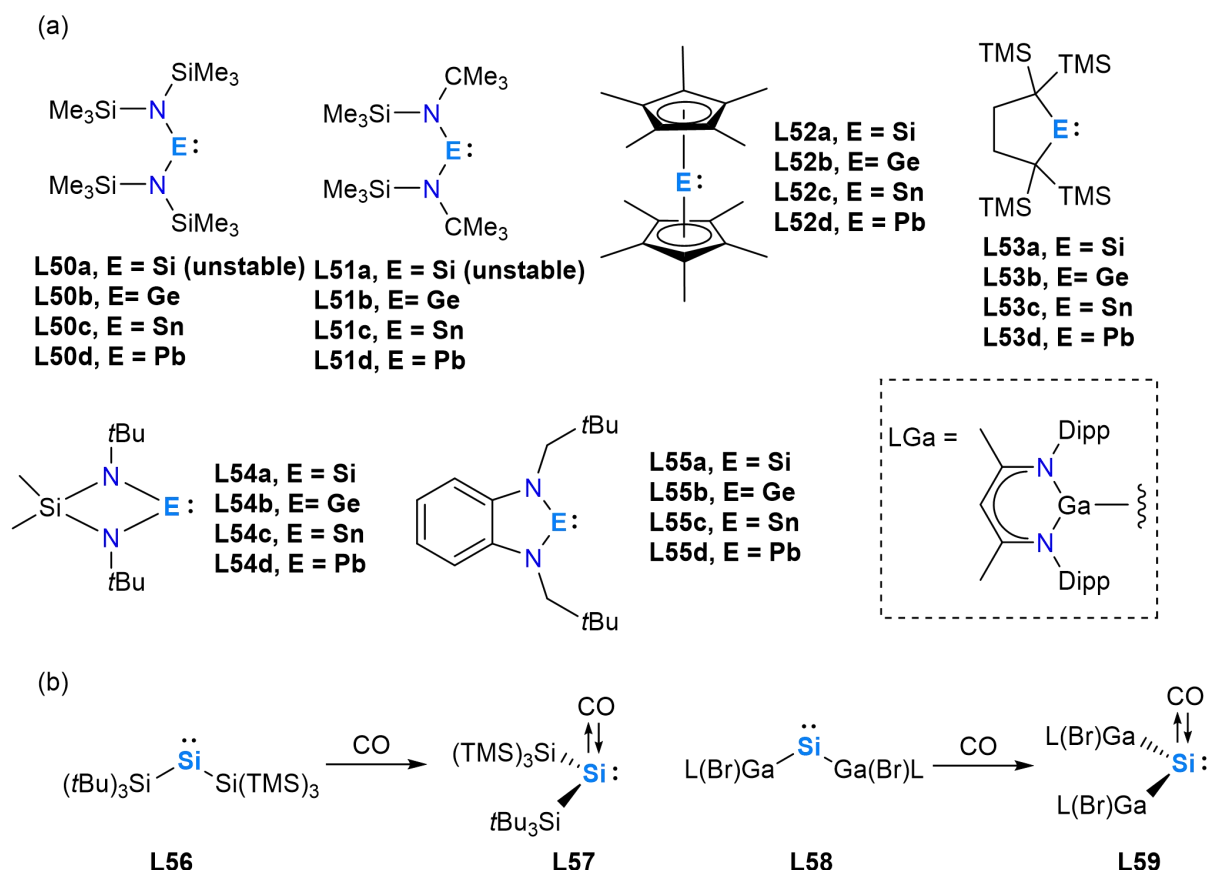


Figure 15. (a) Literature known examples of tetrylenes; (b) Reported CO silylene complexes reported by Inoue and Schulz.

Reactivity studies have shown tetrylenes can activate substrates such as CO_2 , N_2O , alkenes, and alkynes. Notably, heavier congeners such as germynes and stannynes favor insertion or rearrangement reactions to preserve the +II state, exemplified by CO_2 insertion into Ge–H bonds⁶⁵ and Sn–C bonds.^{66, 67} Their reactivity mimics transition metal-like behaviour in three-membered ring formation with olefins and C–H/C–C activation of alkynes.^{68–71} The examples of CO coordination to Group 14 centers are rare, which are limited to silylene-CO complexes (Figure 15(b), **L57** and **L59**) reported by the Inoue group and the Schulz group in 2020.^{72, 73}

The following section will explore stannynes' structural diversity, bonding features, and applications in detail.

2.2.1 Stannylene

Stannynes, as part of the tetrylene family (divalent group 14 elements), exhibit unique chemical behavior due to the heavier atomic nature of tin. Their lone pair of electrons and empty p-orbital render them a fascinating subject of studies for understanding bonding,

reactivity, and applications in catalysis. Since the milestone reports on stable acyclic stannylene (Figure 15, **L50c**) prepared by Lappert group in 1974,⁵⁶ several ligands tailored with appropriate electronic and steric attributes, such as the N-heterocyclic analogues, bulky aryl ligands, and heteroatom-substituted ligands, have been devised and utilized for stannylenes stabilization. To better understand the diversity of stannylenes, we categorize them into cyclic and acyclic stannylenes.

Figure 16 summarises a selection of reported cyclic stannylenes. Veith sets the first milestone in regard to stable cyclic stannylene (**L54c**) with the structure of four silicon-nitrogen rings.⁷⁴ In the wake of this, a multitude of four-membered cyclic stannylenes emerged with various structural characters, such as the use of bulky nitrogen-bound substituents or a silicon entity substituted by alternate heteroatoms. Rivard's group reported the new bis(amido) chelates bearing very hindered flanking groups at nitrogen, $[\text{NSiN}]^{\text{Dipp}}$ and $[\text{NSiN}]^{\text{SiPh}_3}$, to use to access tetrylenes (**L60a**, **L60b**).⁷⁵ Subsequently, a similar tetrylene (**L60c**) was reported by the Zheng group, in which the isopropyl group of silicon substituents was replaced by a methyl group.⁷⁶ The novel stannylenes (**L60d**) were isolated from the reactions of alkali metal bis(imino)phosphides and SnCl_2 , in which the silicon entity was substituted by phosphorus compared to **L54c**.⁷⁷ In addition, both five-membered and six-membered stannylenes have been reported. Rivard (2012) reported a bis(amido)disilyl ($[\text{NSiSiN}]$) stannylene (**L61**).⁷⁸ The Aldridge group has synthesized five- (**L62**) and six-membered (**L63**) stannylenes, featuring the diazaborolyl group as the N-bound substituents.⁷⁹ The reaction of the 1,2-diaminobenzenes with one equivalent of $[(\text{TMS})_2\text{N}]_2\text{Sn}$: (**L50c**) (TMS = trimethylsilyl) gave the benzannulated stannylenes (**L64**). The steric bulk of N,N'-substituents determines the mode of aggregation of stannylenes in the solid state.⁸⁰

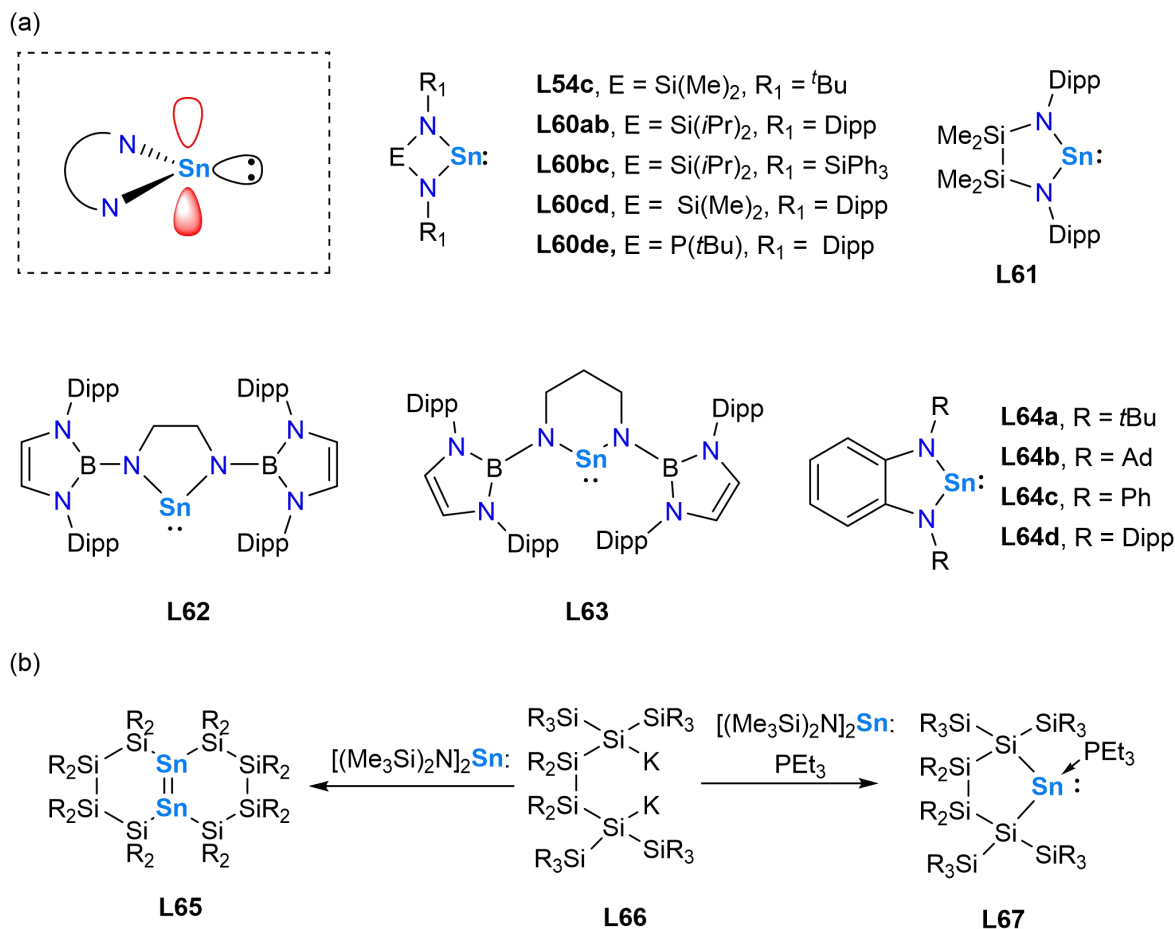


Figure 16. (a) Selected examples of cyclic stannylenes; (b) The effect of Lewis base for the synthesis of stannylene.

As shown in Figure 16(b), Müller undertook a series of efforts to synthesize cyclic disilylated stannylenes and discovered that, in the presence of the Lewis base triethylphosphine (PEt_3), a stannylene- PEt_3 adduct (**L67**) was formed. In contrast, an endocyclic distannene (**L65**) was obtained in the absence of PEt_3 .⁸¹

Like cyclic stannylenes, amino ligands are also efficient tools for preparing acyclic stannylenes as shown in Figure 17. Lappert and coworkers reported several bis-amides substituted stannylenes such as $[(\text{TMS})_2\text{N}]_2\text{Sn}$: (**L50c**),⁵⁶ and $\text{Sn}[\text{NC}(\text{Me})_2(\text{CH}_2)_3\text{CMe}_2]_2$ (**L68**).⁸² An extremely bulky boryl-amide ligand was utilized in the preparation of acyclic diiminostannylene (**L69**).⁸³ In 2012, Aldridge introduced an (amido)(boryl)stannylene (**L70**) by the reaction of lithium $(\text{thf})_2\text{Li}\{\text{B}(\text{NDippCH}_2)_2\}$ and $[\text{Sn}\{\text{N}(\text{SiMe}_3)\text{Dipp}\}(\mu\text{-Cl})]$.⁸⁴ Use of extremely bulky amido substituents could minimize another substituent to a simple hydrogen atom, yielding stannylene hydride (**L71**).^{85, 86} Jones reported the first example of two coordinated amido/alkyl stannylenes (**L72**), which used amido-/hydrido-stannylene as precursors (**L71**) for reaction with unactivated cyclic and acyclic alkenes, and one internal

alkyne.⁸⁷ In 2022, the Aldridge group described a series of amido terphenyl stannylenes bearing different silyl substituents (**L73**).⁸⁸ The Inoue group has reported several cases of cyclic N-heterocyclic imine (NHI)-stannylenes, including aryl(imino)stannylene $^{\text{Mes}}\text{Ter}[\text{N}(\text{IDipp})]\text{Sn}$ (See Figure 14, **L74**) ($^{\text{Mes}}\text{Ter}$ = 2,6-Mes₂C₆H₃, IDipp = C[N-(2,6-*i*Pr₂C₆H₃)CH]), amino(imino)stannylene (TMS₂N)(*It*BuN)Sn (**L75**) (*It*Bu = C[(N-*t*Bu)CH]), and the homoleptic NHI-stabilized stannylene (*It*BuN)₂Sn (**L76**).

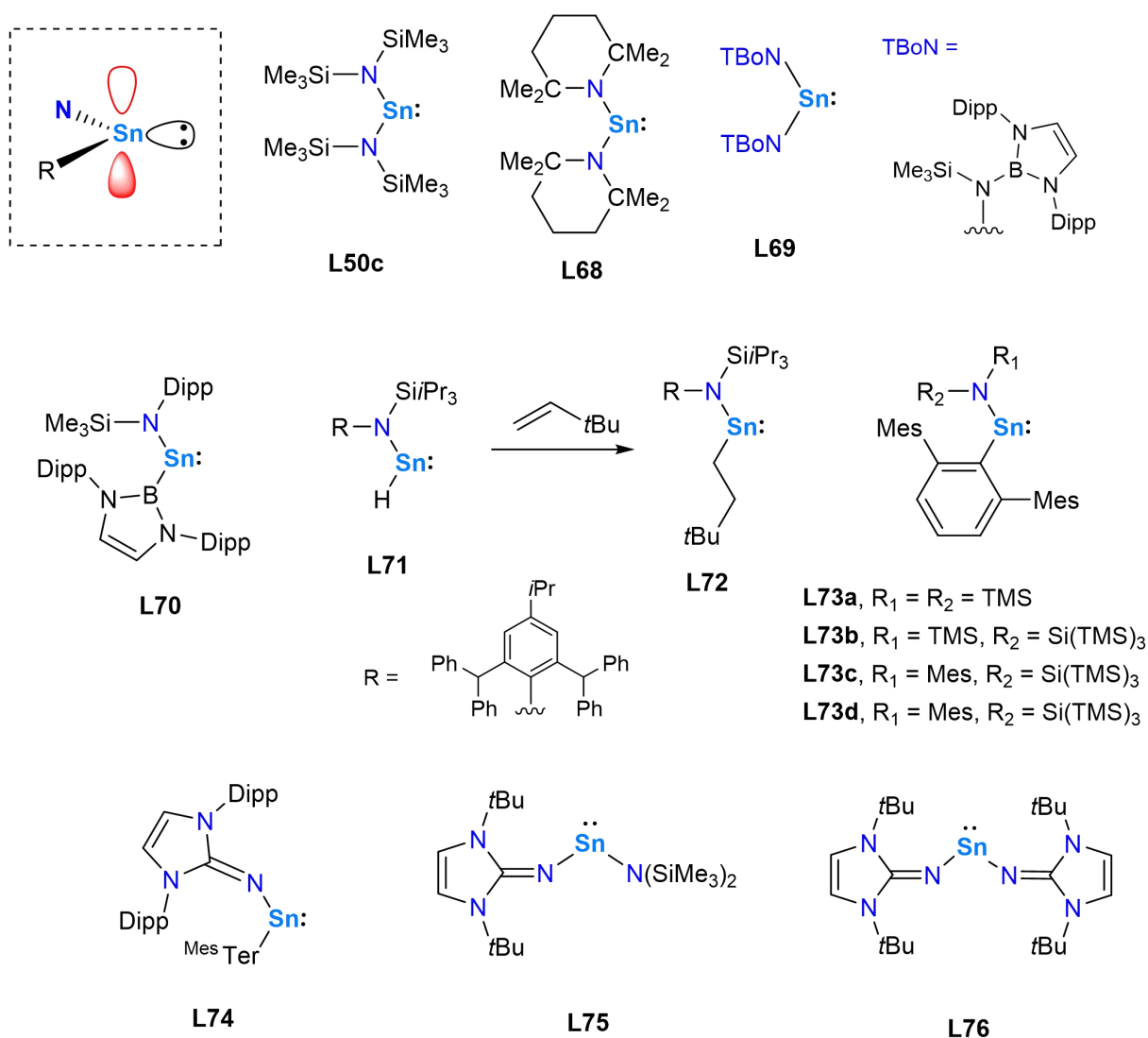


Figure 17. Selected examples of acyclic stannylenes reported.

Acyclic aryl or alkyl stannylenes have been extensively developed. Less bulky C-substituted stannylenes were stabilized by intramolecular contacts between the tin atom and neighboring fluorine atom or were dimeric in the solid state. In contrast, the use of more sterically hindered substituents can lead to the formation of stable stannylenes. Some notable examples of aryl stannylenes are shown in Figure 18. The first diarylstannylene

monomeric (**L77**) in the solid state was isolated by the reaction **L50c** with lithiated ligand precursor by Weidenbruch and co-workers in 1994.⁸⁹ In the wake of this, Power embarked on comprehensive studies on terphenyl-substituted stannylenes, such as diaryl stannylenes (**L79**),⁹⁰ heterolepic stannylenes (**L78**)⁹¹. A noteworthy example of Sn(II) hydride, [ArSn(μ -H)]₂ (**L80**), was reported by Power, by the reaction of chloride stannylene (2,6-Trip₂C₆H₃SnCl) with diisobutylaluminum hydride (DIBAL). Sn(II) hydrides [ArSn(μ -H)]₂ can be used as precursors to readily generate the alkyl-/alkenyl-substituted stannylenes by the reactions with norbornene (NB) or norbornadiene (NBD)⁹², or diphenyl acetylene.⁹³

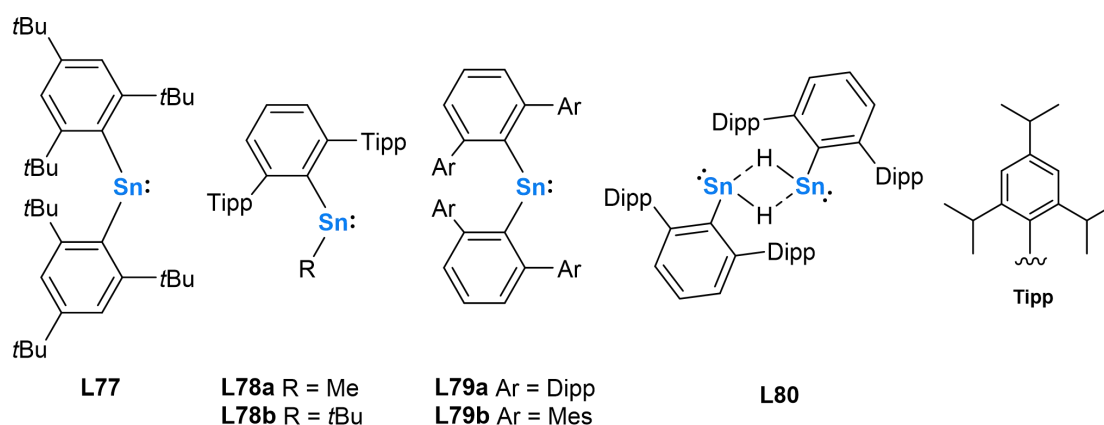


Figure 18. Selected examples of aryl substituted stannylenes.

Some heteroatoms-substituted stannylenes have been reported (Figure 19), which possess several unusual features. For example, an extensive series of acyclic, monomeric dichalcogenolate stannylenes (**L81**), which incorporate an array of bulky terphenyl ligands.⁹⁴ Izod later synthesized a P-substituted stannylene (**L82**). The structure was crystallographically authenticated, revealing a P=Sn bond resulting from the P-Sn π interaction between the lone pair of the planar P center and the vacant p orbital at the Sn center.⁹⁵ N-heterocyclic boryloxy (NHBO) ligands have been used to stabilize the corresponding stannylene (**L83**) by the Aldridge group.⁹⁶ Notably, Aldridge developed an N-heterocyclic boryl stannylene (**L84**) by employing strong σ -donating boryl ancillary ligands.⁹⁷ The Inoue group reported silyl supported stannylenes (**L85**) which enable activation of white phosphorus under mild conditions.⁹⁸

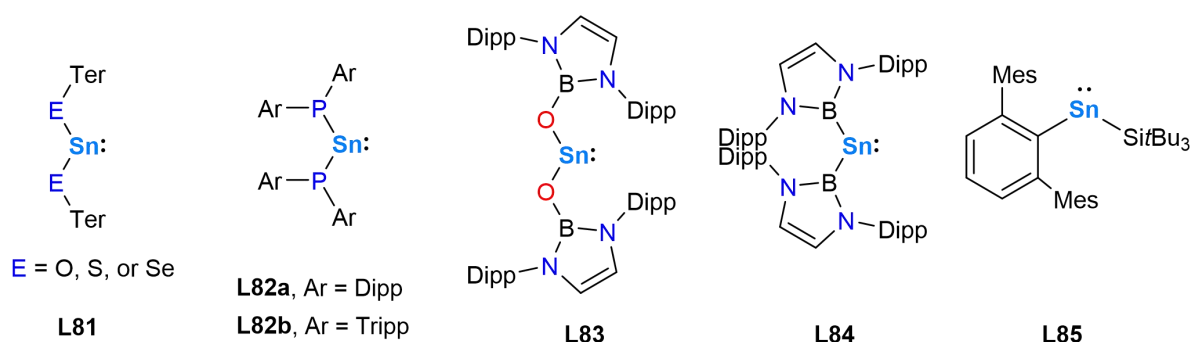


Figure 19. Selected examples of heteroatom-substituted stannylenes.

2.2.2 Reactivities and Catalytic Applications of Stannylenes

With the development of various stannylenes, their unique reactivity has been explored, including interactions with gaseous compound small molecules (CO_2 , H_2 , NH_3 , etc.), organic molecules (alkenes, alkynes, and aromatic compounds), and their catalytic applications, particularly in hydroboration, hydrosilylation, and cyanosilylation reactions.^{55, 99}

Treatment of the stannylenes (**L79a**) with H_2 under mild conditions (1 atm, 65 °C) afforded the product $[\text{ArSn}(\mu\text{-H})]_2$ (**L80**) with arene (Ar-H) elimination (Figure 20, (a)).^{90, 100} In contrast, less crowded stannylenes, **L50c** (See Figure 17) and **L79b** (See Figure 18), remained unreacted towards H_2 . The difference between their reactivity was attributed to the enhanced triplet character of **L79a**. Both **L79a** and **L79b** could undergo the reaction with NH_3 , giving the Sn(II) amide $[\text{ArSn}(\mu\text{-NH}_2)]_2$ (**L86**, **L87**) featuring symmetrically bridged NH_2 moieties.¹⁰¹

A systematic study on taming stannaimines ($\text{R}_2\text{Sn}=\text{NR}$) (**L88**) is reported by identifying a suitable supporting ligand framework for stannylenes in combination with organic azides (Figure 21).⁸⁸

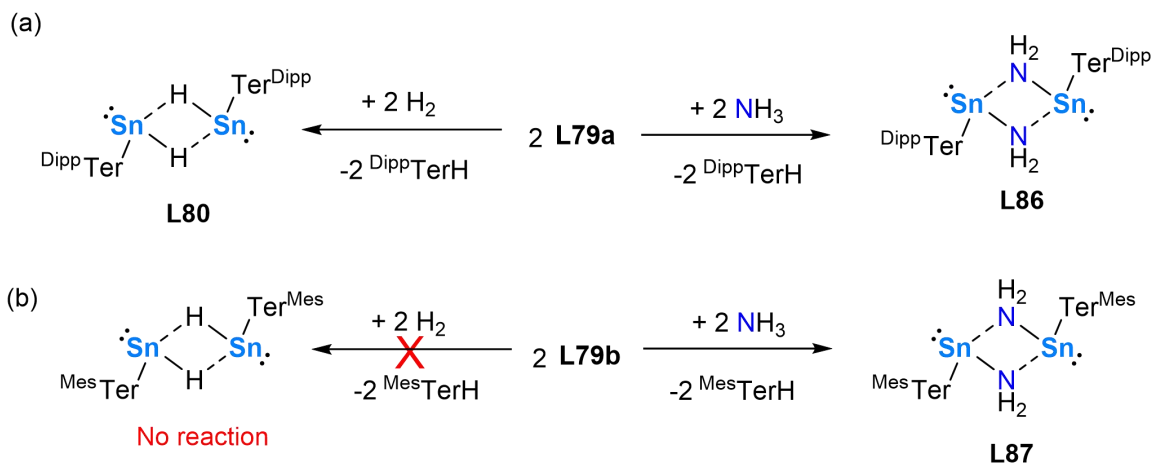


Figure 20. Reactivities of diaryl stannylenes with hydrogen and ammonia.

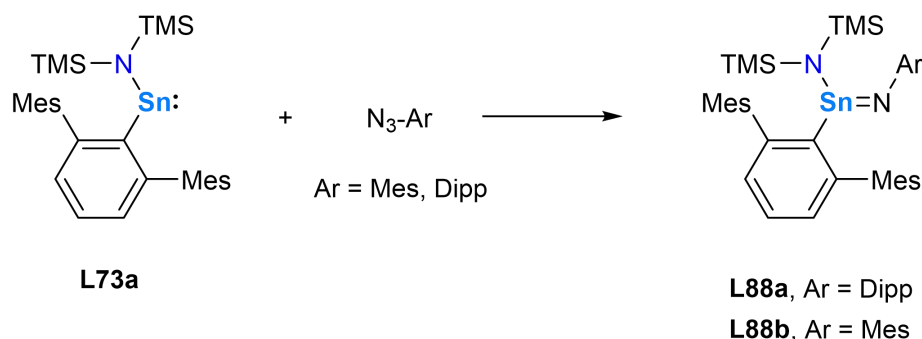


Figure 21. The synthesis of a Sn=N bond containing compound.

The bis-borylstannylenes **L84** (See Figure 19) exhibit good reactivities towards various small molecules (Figure 22). For example, it can undergo the oxidative addition reaction with H_2 , generating $(\text{boryl})_2\text{SnH}_2$ (**L89**), which was achieved for the first time by a single site Sn(II) (Figure 19, (a)).⁹⁷ Similar chemistry has been achieved for hydridic H-E bonds (E = H, Si, O, B, and N) (Figure 22, (a)). **L84** underwent alkyne insertions yielding divinyl-stannylenes (**L90**) (Figure 22, (b)).⁷¹ The reactions of both CO_2 and N_2O were demonstrated by the Aldridge group (Figure 22, (c), (d)), which resulted in Sn-B insertion products, retaining the formal Sn(II) oxidation state.⁶⁷ In the presence of CO_2 , sequential insertion into the Sn-B bonds produced hetero- (**L91**) and homolepic- (**L92**) Tin(II) borylcarboxylate compounds. Compound **L91** was thermally unstable in the absence of excess CO_2 and then generated boryl borylcarboxylate ester (**L93**). With N_2O , the insertion of an oxygen atom into one of the Sn-B bonds of **L84** produced heterolepic boryl(boryloxy)stannylene **L94**, which would undergo slow ligand redistribution to lead to the N-heterocyclic boryloxyl stannylenes (**L83**) and **L84**.

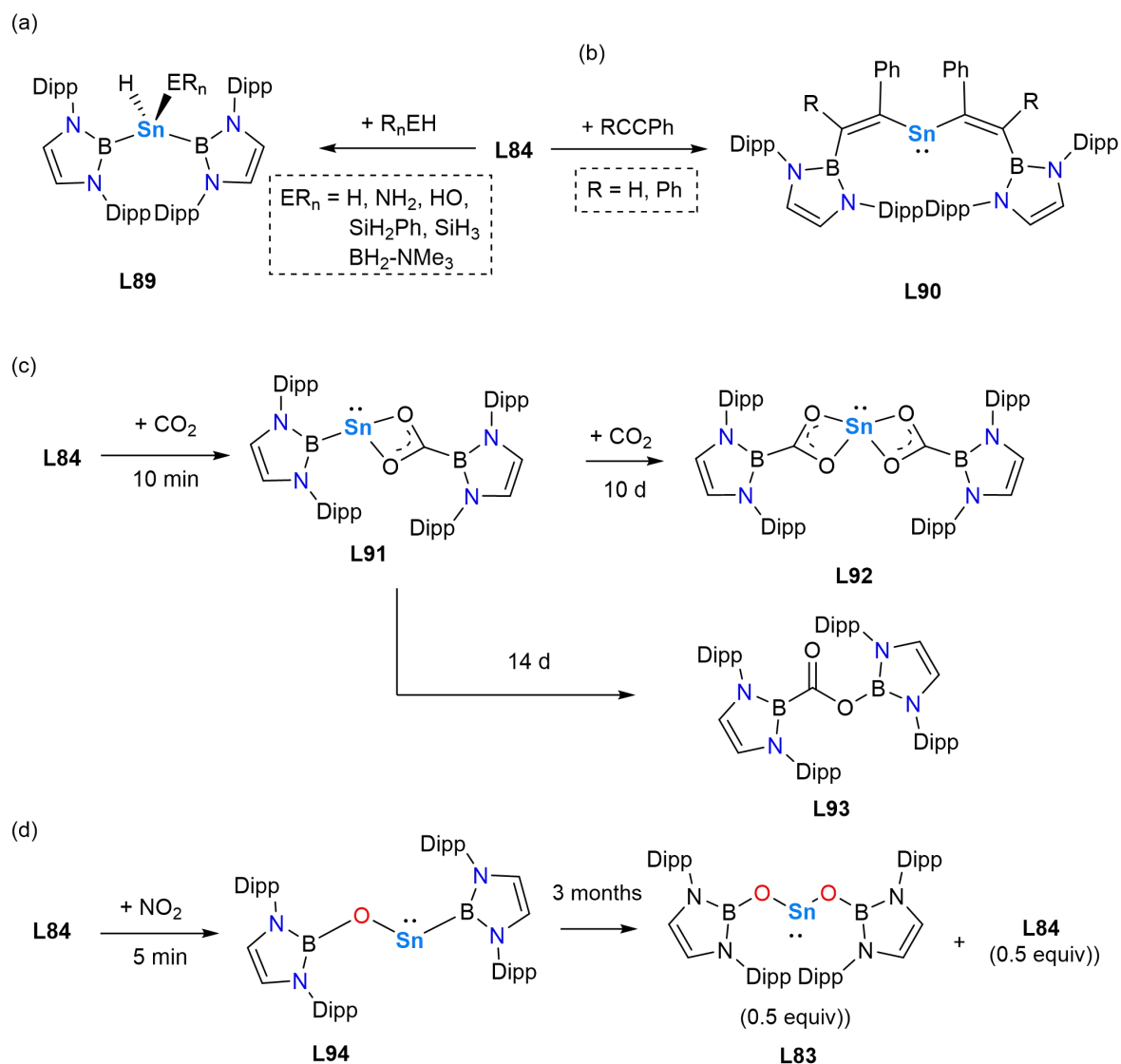


Figure 22. Reactivities of bis-borylstannylene with various *E-H* bonds, phenylacetylenes, CO_2 , and N_2O .

The two homoleptic NHI-stabilized stannylene **L76** undergo the insertion of CO_2 into each of the Sn-N bonds, forming the doubly $\kappa^2\text{O,O'}$ coordinated bis-carbamate (**L95**) (Figure 23, (a)).¹⁰² Furthermore, the reactivity of **L76** towards N_2O was also demonstrated, which results in partial oxidation to form stannylene dimer (**L96**). In comparison to **L76**, the aryl(imino)stannylene (**L74**) undergoes the insertion of one molecule of CO_2 into Sn-N bond to give a tin carboxylate (**L97**) (Figure 23, (b)).⁶⁶ Theoretical calculations and experimental study revealed that **L97** was the resting state and rate-determining step during hydrosilylation of CO_2 by **L74**.

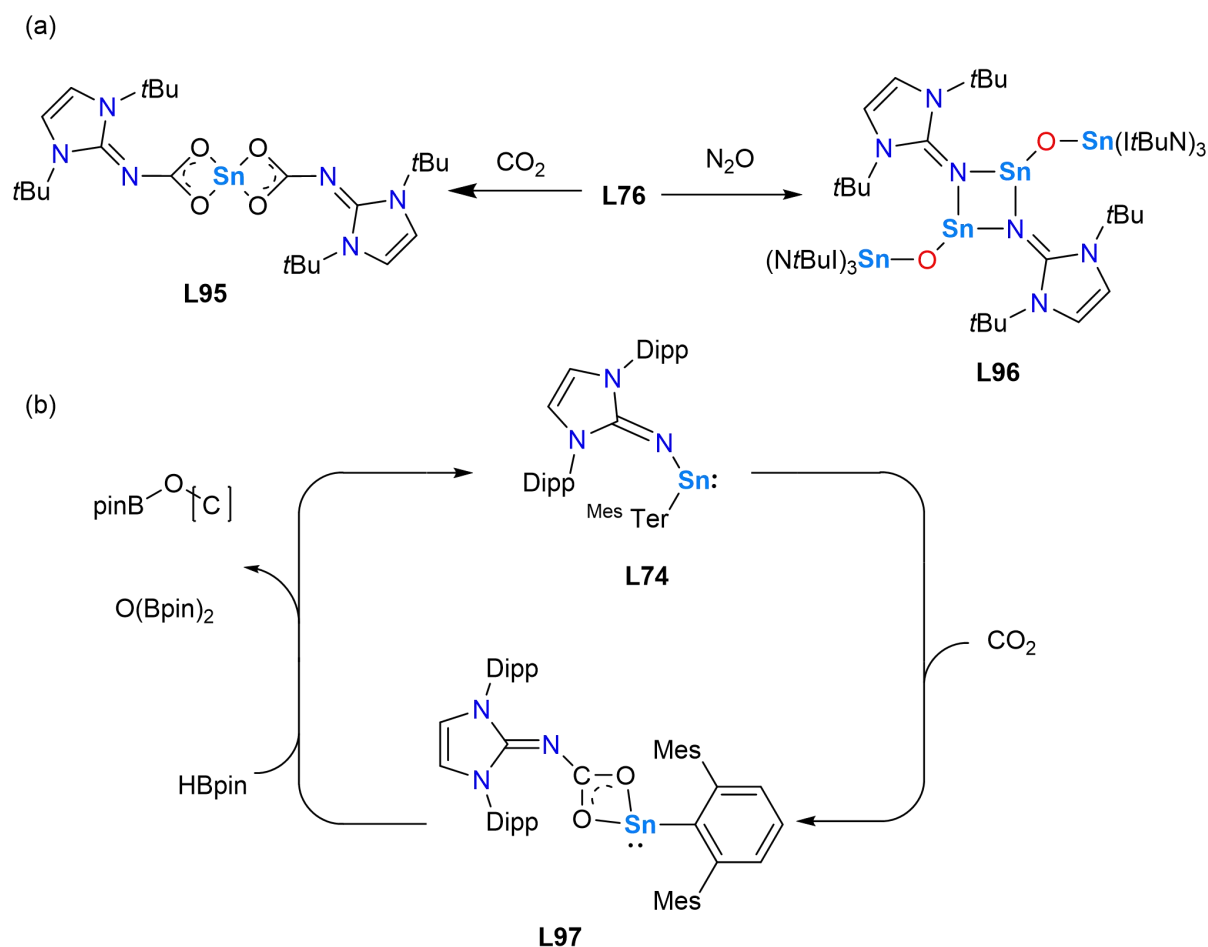


Figure 23. Reactivities towards CO_2 and N_2O of NHI-stabilized stannylene ; (b) CO_2 activation, and catalytic hydroboration activity of NHI-stabilized stannylene.

A notable example of a catalytic application is the hydroboration of aldehydes and ketones using bulky amido-substituted two-coordinated tin hydrides (**L71**), as reported by Jones and coworkers.⁸⁵ The proposed mechanism is shown in Figure 24. The pre-catalyst, stannylene alkoxide (**L98**), generates **L71** in situ in the presence of HBpin. **L71** facilitates the insertion of the aldehyde or ketone moiety into the Sn–H bond, forming alkoxide intermediates (**L100**). Kinetic experiments and theoretical studies suggest that **L100** serves as the resting state in the hydroboration of aldehydes and ketones. Furthermore, **L71** has been confirmed as an effective and selective catalyst for the reduction of CO_2 to methanol equivalent (MeOBR_2), using HBpin or HBcat as the hydrogen source.¹⁰³

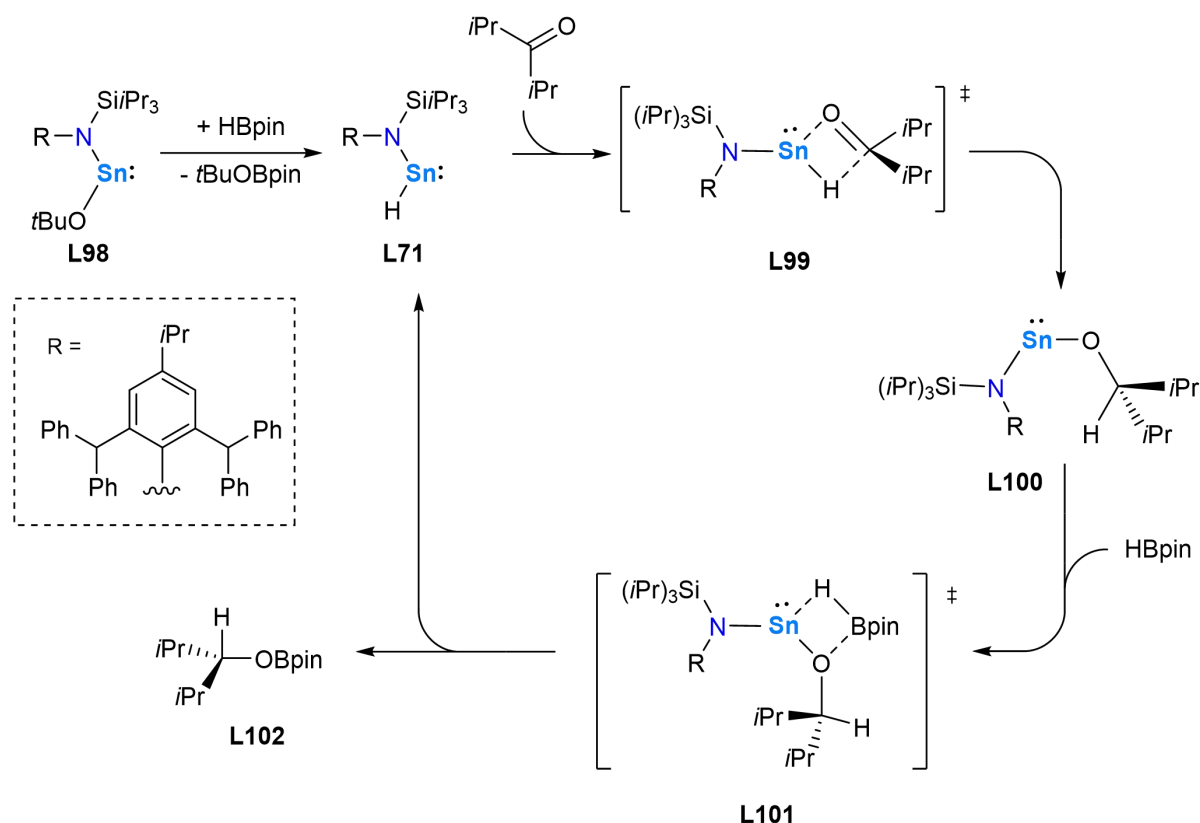


Figure 24. Proposed mechanism for the catalytic hydroboration of ketone with **L51** and HBpin.

The Power group reported the catalytic dehydrocoupling of boranes and amines using terphenyl tin(II) methoxides (Figure 25, **L103a** and **L103b**) as pre-catalysts, forming aminoborane.¹⁰⁴

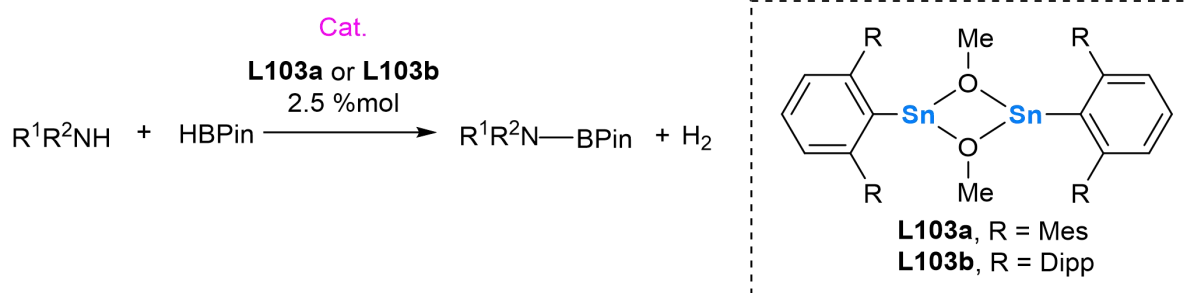


Figure 25. Dehydrocoupling of boranes and amines by **L103**.

Aldehydes and ketones were hydroborated by an intramolecular stannylene Lewis pairs (Figure 26, **L104**).¹⁰⁵ During the catalysis, **L104** forms a reactive tin hydride, which can act as an active catalyst in this transformation. A monomeric stannylene-phosphinidene compound (**L105**) was achieved by taking advantage of NHC coordination to the low-valent phosphorus center, which can be utilized for the hydroboration of aromatic ketones and aldehydes with HBpin under mild conditions.¹⁰⁶ A three-coordinated stannylene chloride

(**L106**), supported by an N',N'-di-tert-butyliminophosphoamide, can act as an efficient pre-catalyst for the hydroboration of a wide variety of aldehydes, ketones, and imines.¹⁰⁷ In 2021, Sen and co-workers reported the hypersilylstannylene (**L107**), which can catalyze the hydroboration of aldehyde, ketones, alkenes, and alkynes.¹⁰⁸

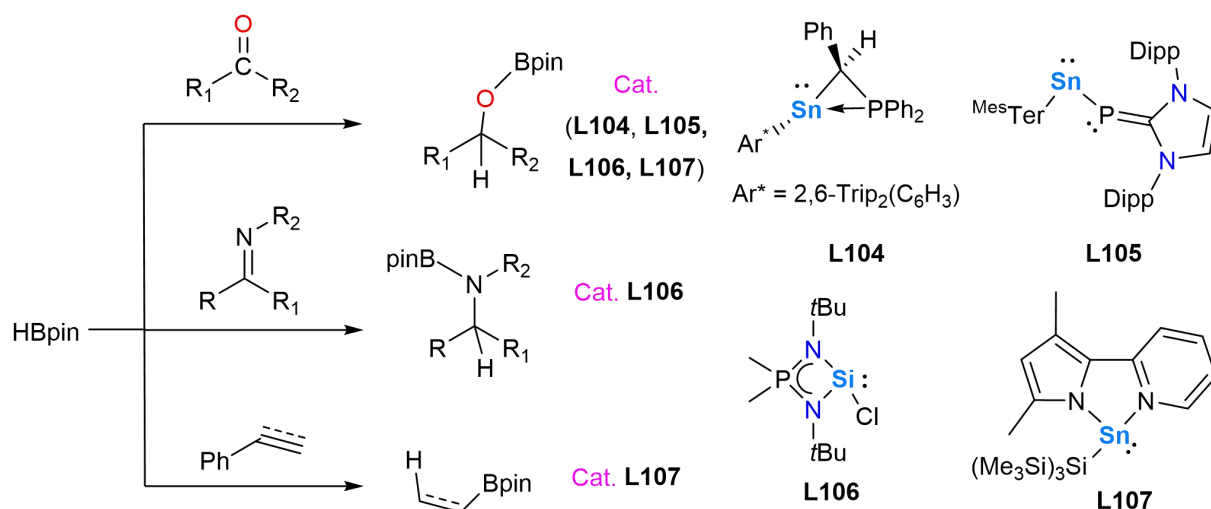


Figure 26. Selected stannylene catalysts for hydroboration.

Nagendran and co-workers introduced benzannulated N-heterocyclic stannylene (**L108**) and stannylene cyanide (**L109**), using them for the cyanosilylation of aldehydes (Figure 27).^{109, 110} Stoichiometric reactions of **L109** with aldehydes led to the isolation of the corresponding cyanostannylated product (**L110**), considered as intermediates in the cyanosilylation cycle.

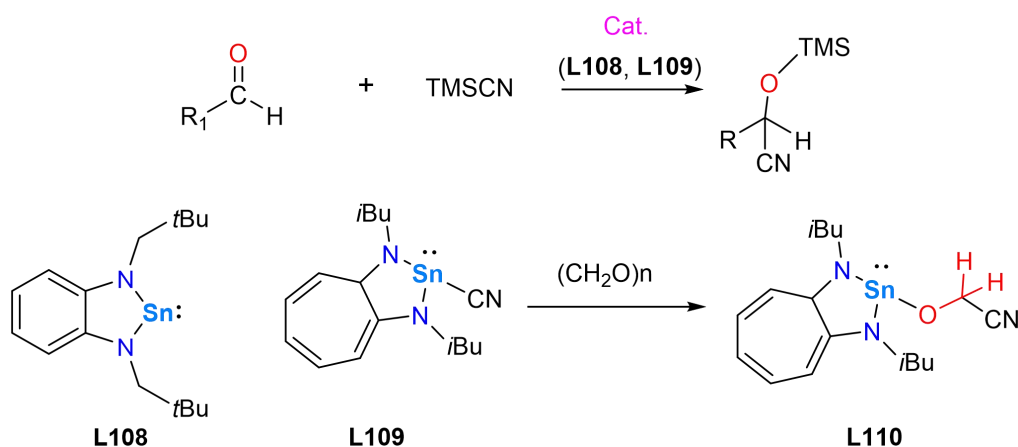


Figure 27. Selected stannylene catalysts for cyanosilylation of carbonyls.

2.3 Tetryliumylidene

Tetryliumylidenes ($\text{RE}^+:$) represent a class of low-valent Group 14 compounds characterized by a lone pair of electrons, two unoccupied orbitals, and a formal positive charge as shown in Figure 28.^{55, 99, 111} As a result, they combine the high electrophilicity of tetrylium cations with the Lewis ambiphilicity of tetrylenes. Due to these unique electronic properties, tetryliumylidenes have garnered significant interest in fundamental research, particularly for their potential in small molecule activation and catalytic applications.

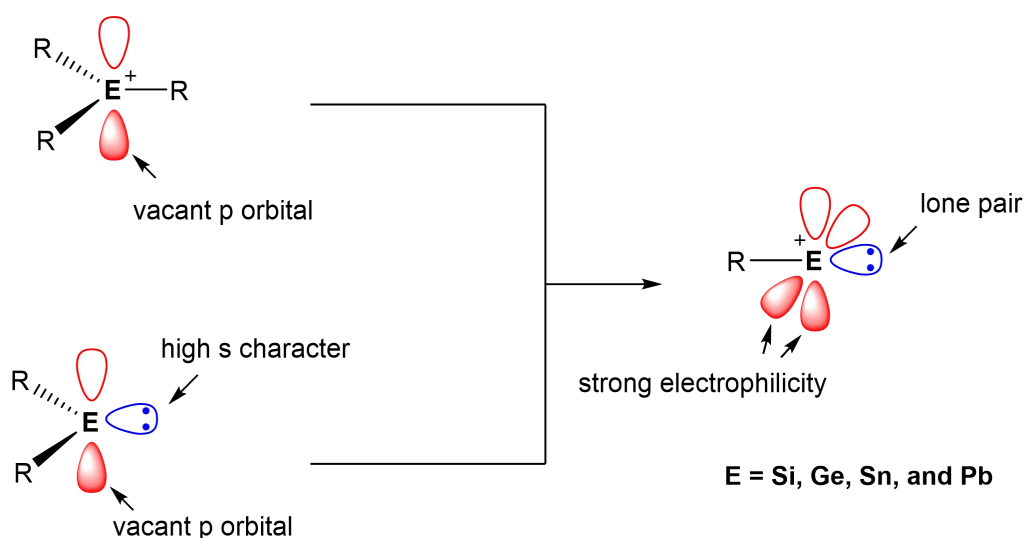


Figure 28. Electronic features of tetryliumylidenes.

2.3.1 Silyliumylidene

The first example of a silyliumylidene, $(\text{Me}_5\text{C}_5)\text{Si}^+[\text{B}(\text{C}_6\text{F}_5)_4]$ (Figure 29, **L112**), was reported by Jutzi and colleagues. It was obtained via the reaction of decamethylsilicocene (**L111**), $(\text{Me}_5\text{C}_5)_2\text{Si}:$, with a proton-transfer reagent $[(\text{Me}_5\text{C}_5\text{H}_2)^+[\text{B}(\text{C}_6\text{F}_5)_4]^-]$.¹¹² This compound was stabilized via a cationic π complex with an η^5 -pentamethylcyclopentadienyl ligand bound to a bare silicon center. Later, Jutzi et al. also reported a derivative penta-*iso*-propylcyclopentadienylsilicon(II) cation, $i\text{Pr}_5\text{C}_5\text{Si}^+$ by the reaction of mixed silicocene $(i\text{Pr}_5\text{C}_5)(\text{Me}_5\text{C}_5)\text{Si}$ with $\text{H}(\text{OEt}_2)_2^+\text{Al}[\text{OC}(\text{CF}_3)_3]_4^-$.¹¹³ A superior alternative route was reported by Filippou group (2018), via the selective protonolysis of SiCp^*_2 ($\text{Cp}^* = \text{C}_5\text{Me}_5$) with $[\text{H}(\text{Et}_2\text{O})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ facile to $[\text{Si}(\eta^5\text{-Cp}^*)][\text{B}(\text{C}_6\text{F}_5)_4]$ in multigram scale and high yield.¹¹⁴

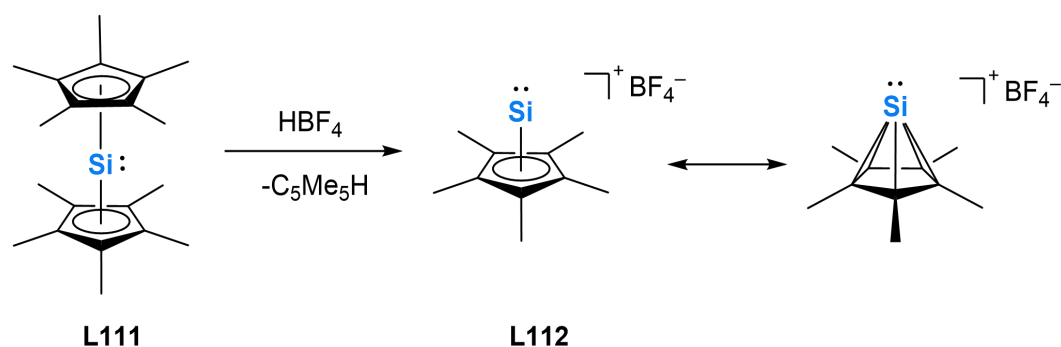


Figure 29. The first example of silyliumylidene cation.

A notable example of quasi-mono-coordinated silyliumylidene (**L114**) was found by Hinz in 2020 (Figure 30).¹¹⁵ It was prepared by halide abstraction from an iodosilylene (**L113**) with an extremely bulky carbamoyl substituent, with $\text{Ag}[\text{Al}(\text{OC}\{\text{CF}_3\})_4]$. The XRD structure revealed that it bears no other σ -donors except for the carbazoyl substituent and an interaction between the Si atom and the arena with a stabilization energy of 181.2 KJ/mol.

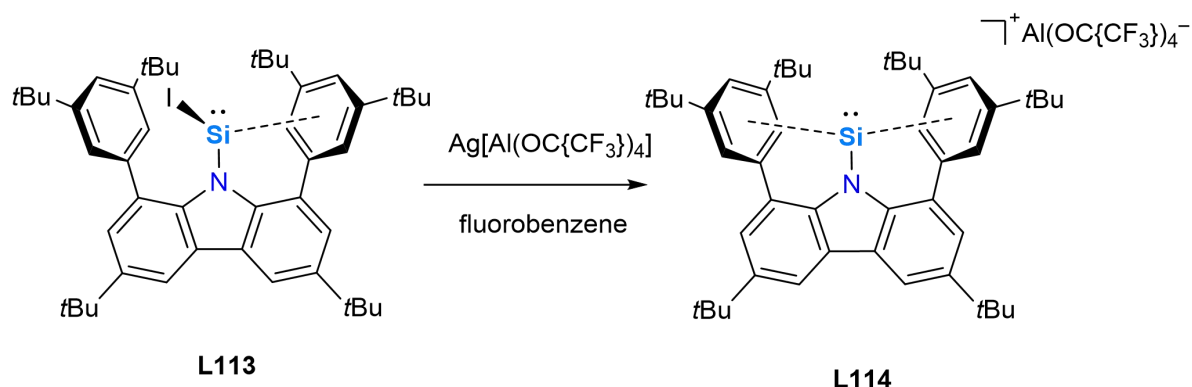


Figure 30. The synthesis of quasi-coordinated silyliumylidene.

Some two-coordinated silyliumylidenes are shown in Figure 31. The application of sterically encumbered β -diketiminate ligands by Driess and colleagues enabled the isolation of the first two-coordinate silyliumylidene (Figure 31, **L115a**), obtained via the electrophilic attack of a silylene by Jutzi's oxonium acid $[\text{H}(\text{Et}_2\text{O})_2][\text{B}(\text{C}_6\text{F}_5)_4]$.¹¹⁶ Similarly, in 2020, β -diketiminate ligands featuring a backbone NMe_4 group were employed to access a silyliumylidene (**L115b**).¹¹⁷ Notably, the introduction of transition metals has emerged as an effective strategy for stabilizing two-coordinate silyliumylidenes, where the metal can act as a Lewis base or substituent. For instance, the carbonylation of a silylidyne complex leads to the formation of a four-legged piano-stool complex cation (**L116**), in which the Si–Cr bond is a single bond (bond length: 2.393 Å, Wiberg Bond Index: 0.50).¹¹⁸ Furthermore, in 2022 Kato and colleagues reported the synthesis of a silyliumylidene cation complex (**L117**) stabilized

by a Ni(0)-based donating ligand.¹¹⁹ Experimental and theoretical studies indicate that the highly electrophilic Si(II) center is stabilized by a dative Ni→Si σ -interaction and π -donation from both the amino and Ni-moieties.

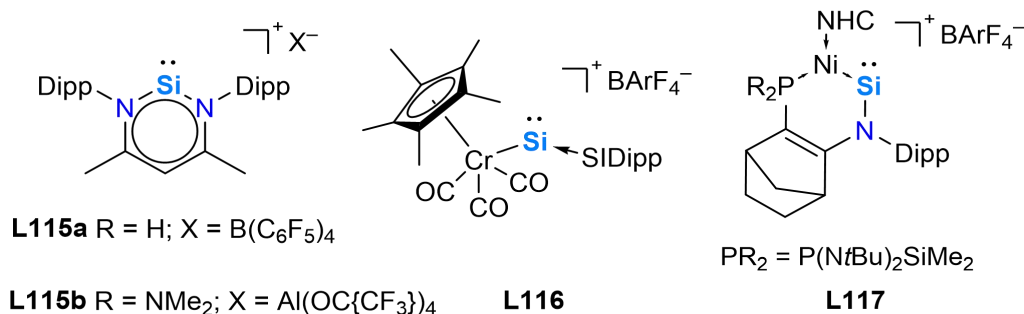


Figure 31. Selected two-coordinated silyliumylidenes.

Most of the reported silyliumylidene ions are three-coordinated, both stabilized kinetically, via sterically demanding ligands, and thermodynamically, via electron donation to the silicon center by Lewis bases (Figure 32). In this regard, NHCs play an important role in the stabilization of these low-valent silicon cations. An exchange of a sterically more demanding NHC (IiPr) to NHC stabilized SiI₂ led to the first example by Filippou in 2013 (**L118**).¹²⁰ The Inoue group utilized dichloroarylsilanes or dichlorosilylsilanes and three equivalents of NHCs in a facile one-pot reaction to the corresponding silyliumylidene ions (**L120**, **L121**).^{121, 122} It is an important strategy to synthesize silyliumylidene directly from Si(IV) precursors. The group of Tokitoh treated dibromodisilenes with an excess of NHCs to afford the bis-NHCs adduct [ArSi(NHC)₂][Br] (**L119**), which involves two steps: 1) formation of NHC-aryl bromosilylene adducts; 2) the second NHC replaces bromide to attach Si center.¹²³ In a similar approach, Masto reported another three coordinated silyliumylidene, bearing a fused-ring bulky E_{ind} substituent (**L123**).¹²⁴

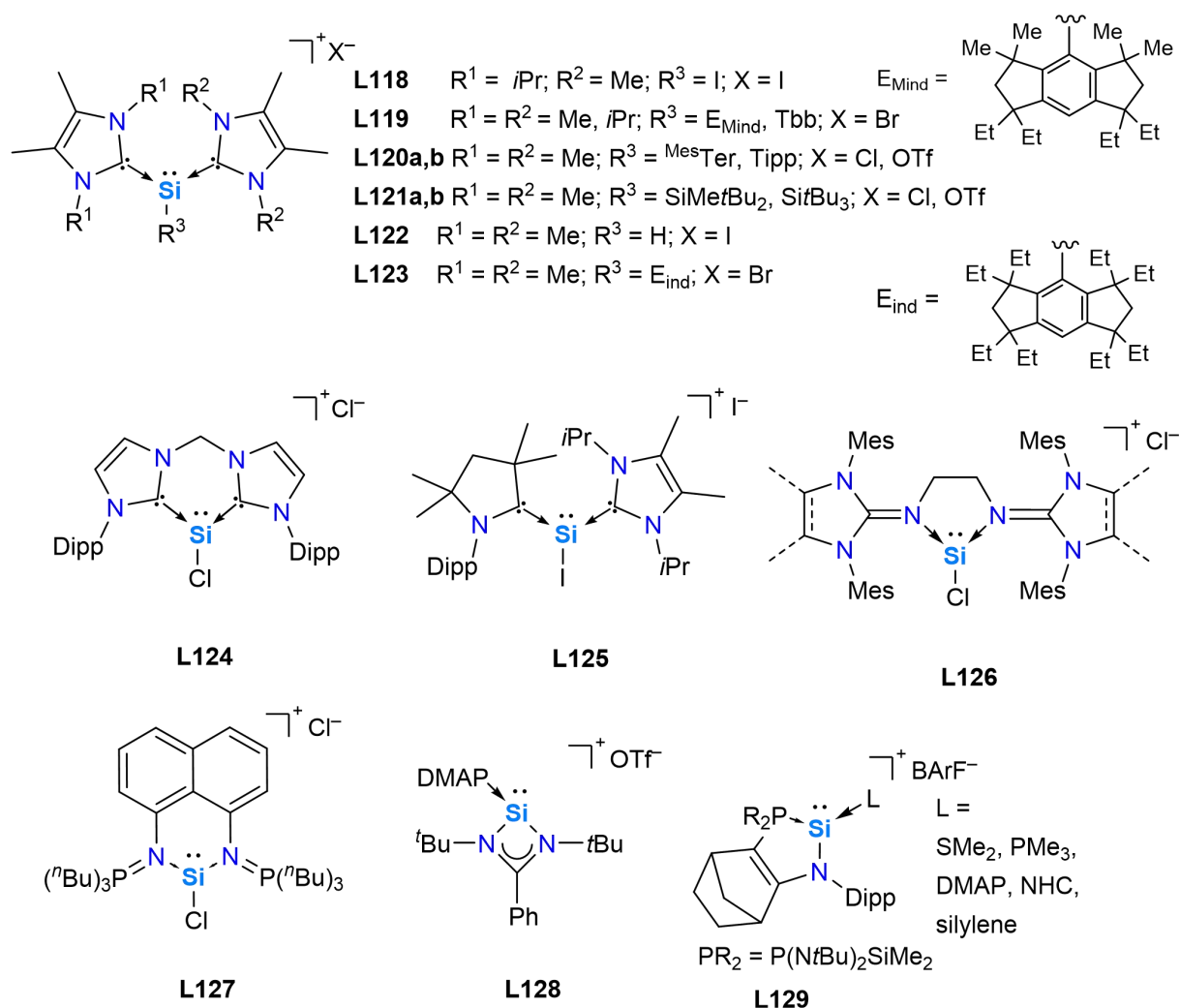


Figure 32. Selected three-coordinated silyliumylidenes (E_{Mind} = 1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-s-hydrindacen-4-yl; E_{ind} = 1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl).

In addition, cAAC, bis-NHC ligand (**L124**), bis-NHI, and bis(iminophosphorane) have been reported as powerful systems to stabilize the three coordinated stannylumylidenes (Figure 32). Treatment of cAAC-diiodosilylene with one equivalent of the *i*Pr afforded NHC-cAAC-silyliumylidene (**L125**) reported by the So group in 2016.¹²⁵ Bis-NHI silyliumylidene (**L126**) chloride was prepared by the reaction of the neutral bis-NHI ligand (1,2-(^{Mes}NHI)₂-C₂H₄ (^{Mes}NHI=1,3-bis(mesityl)-imidazolin-2-imine, mesityl=2,4,6-trimethylphenyl) with an equimolar amount of IDipp-stabilized dichloro-silylene (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene).^{122, 126} A silyliumylidene cation (**L128**) stabilized by an amidinate ligand and 4-dimethylamidopyridine (DMAP) was described by So et. al in 2013.¹²⁷ The chlorosilyliumylidene salt (**L127**) with a three-coordinate silicon(II) atom is accessible through ligand exchange between NHCSiCl₂ and bis(iminophosphorane) chelate ligand.¹²⁸ In addition, the same group reported the first NHC-parent-silyliumylidene cation ([Ime₄SiH]⁺[I]⁻),

L122) by the reaction *i*Pr–iodosilicon(I) dimer [*i*Pr(I)Si:]₂ with 4 equiv different NHC, IMe₄, which proceeded through the formation of a silicon(I) radical intermediate.¹²⁹ Very recently, Kato group synthesized various base-stabilized silyliumylidene ions (**L129**) with different ligands, such as SMe₂, PMes₃, and DMAP, and even a silylene.¹³⁰

2.3.2 Reactivities and Catalytic Applications of Silyliumylidenes

The ambiphilic behavior of silyliumylidenes was applied to activate small molecules, wherein they undergo salt-metathesis reaction with metal salts, coordinate with transition metals, and thereby accelerate the catalytic process. The first isolable silyliumylidene (**L112**) undergoes reaction with metal salts, leading to silylenes (Figure 33). Reaction of **L112** with lithium bis(trimethylsilyl)amide performed at –78°C afforded the silylene (Me₅C₅)SiN(TMS)₂ (**L132**), which is in dynamic equilibrium with the disilene (**L131**), because of the low energy barrier between silylene and disilene.¹¹² The first aryl-substituted monomeric silicon (II) species (**L134**) was isolated by Jutzi in 2009 through the reaction of **L112** with the lithium salt **L133**.¹³¹ The Inoue group reported the bulky imino-substituted acyclic silylene (**L136**) from the reaction of Li[NC{N(Dipp)CH}₂]₂ and **L112**.¹³²

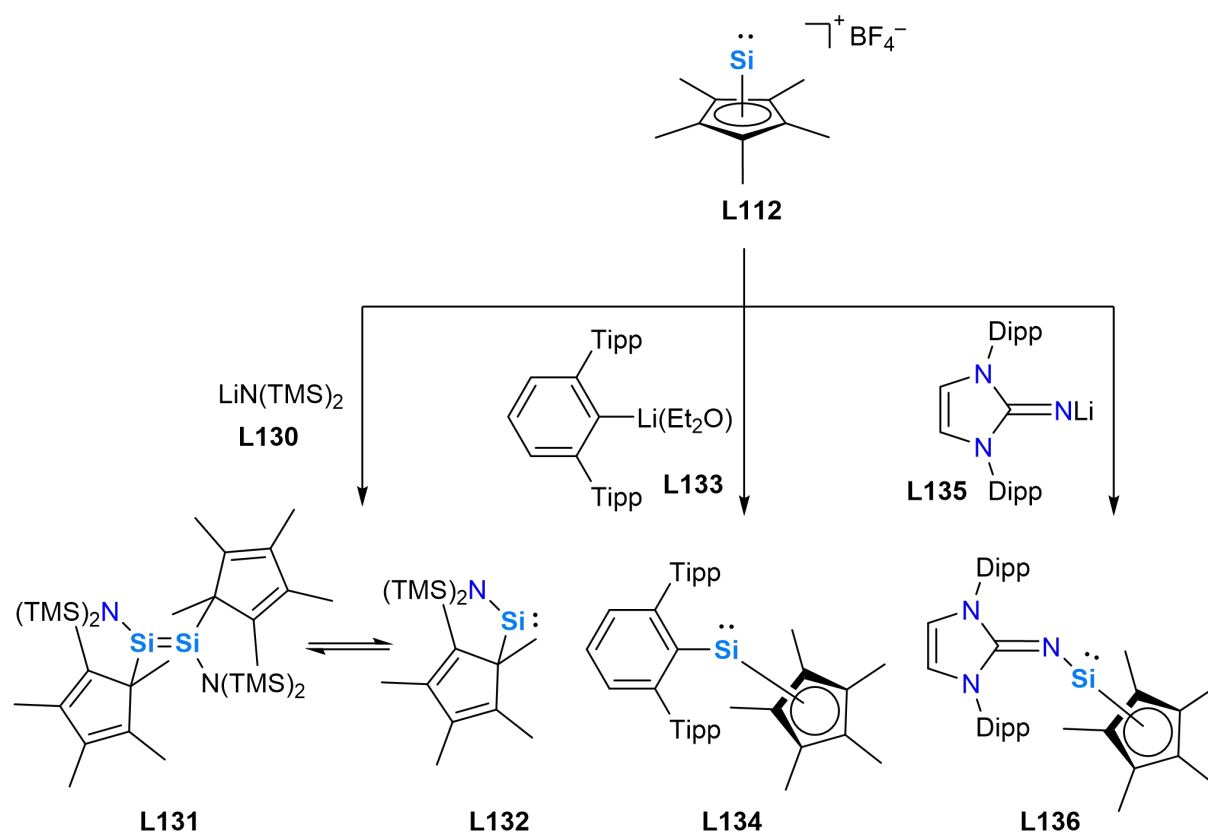


Figure 33. Silyliumylidene **L112** as a precursor to low valent silicon compounds (TMS = SiMe₃).

Despite the bulkiness of the carbazolyl moiety, the silyliumylidene cation (**L114**) retains high reactivity. **L114** was shown to react with an amine to form three bonds at the silicon atom in one reaction, which conforms with the notion of a “supersilylene”.¹¹⁵

Three coordinate aryl-, silyl-, or amido-substituted silyliumylidenes showed a plethora of reactivities, such as gaseous compound small molecules (CO_2 , N_2O , H_2S), chalcogen, E-H bond ($\text{E} = \text{H}, \text{C}, \text{N}, \text{Si}, \text{B}, \text{P}$), and transition metal adducts.¹¹¹ Some examples of silyliumylidene activation towards various molecules are illustrated in Figure 34. The activation of CO_2 with aryl-, silyl substituted silyliumylidenes **L116**, **L121** and **L129** to give a silicon-oxygen double bonds of the general structure $\text{R}^+\text{Si}=\text{O}$ (**L137**, **L138**, **L139**), the heavier analogues of ketones.^{133, 134} **L120**, **L121** and **L126** show the formation of the heavier silaacylium ions with sulphur, selenium, and tellurium via chalcogen-atom transfer.^{126, 135} **L126** can activate sulphur via the same reaction mode.¹²⁸ Interestingly, **L120** and **L121** can undergo S-H bond activation in hydrogen sulfide to form the thiosilaaldehyde (**L143**),¹³⁶ while it reacted with water in the presence of GaCl_3 , leading to the first donor-acceptor complex of a silaaldehyde (**L144**).¹³⁷

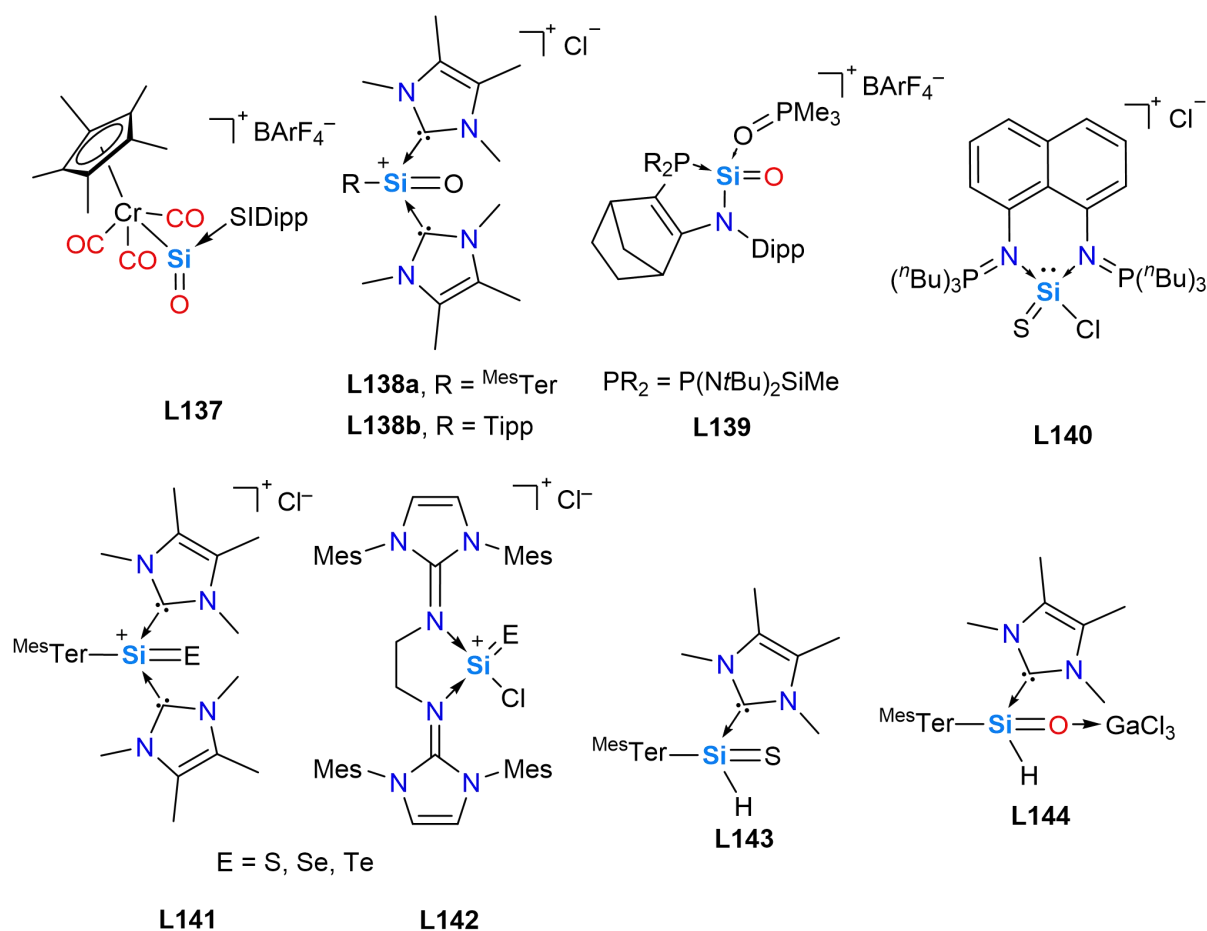


Figure 34. Selected silyliumylidenes reaction with CO₂; N₂O and chalcogen.

Some silyliumylidenes exhibit a typical silylene character in reaction with alkenes, alkynes, and dienes (Figure 35). Both **L117** and **L129** show abilities for the activation of diphenylacetylene and 2,3-dimethyl-1,3-butadiene, which gave the cycloaddition products (**L145-L148**).^{119, 130} **L129** can undergo the [1+2] cycloaddition with ethylene at the silicon centre to form the silacyclopropyl cation (**L149**). In a noticeable example by the Inoue group, **L120a** activates C-H bond of phenyl acetylene to yield 1-alkenyl-1,1-dialkynylsilane (**L150**).¹²¹

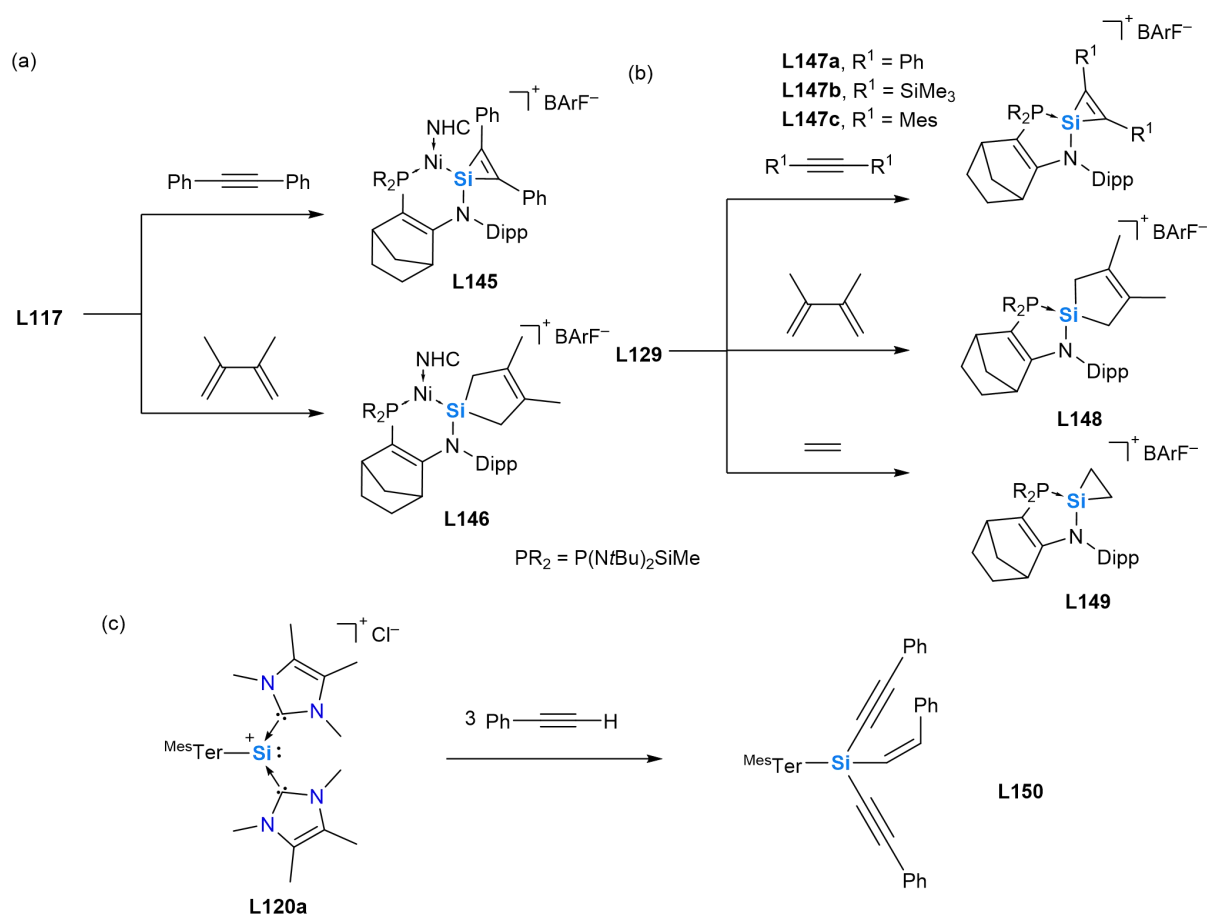


Figure 35. Activation of olefines by silyliumylidenes.

Owing to the presence of a lone pair of electrons, these silyliumylidenes react with coinage metals (copper, silver, and gold), or transition metal carbonyls (Cr, Mo, W, Fe) to form general silyliumylidene adducts (**L151**, **L152**, and **L153**) as shown in Figure 36.^{126, 138, 139} Bis-NHC stabilized silyliumylidene undergoes a consecutive reaction with PPh₃AuCl and K₂Fe(CO)₄, which gives rise to the heterobimetallic gold-iron complex (**L154**).¹²⁶ For Ru and Rh chloride adducts, **L120** and **L121** undergo an insertion of the Si^{III} cation into M-Cl bond with 1,2-migration of silicon-bound NHC moiety to metal (**L155**), through an initially formed silyliumylidene transition metal complex observed at low temperature.

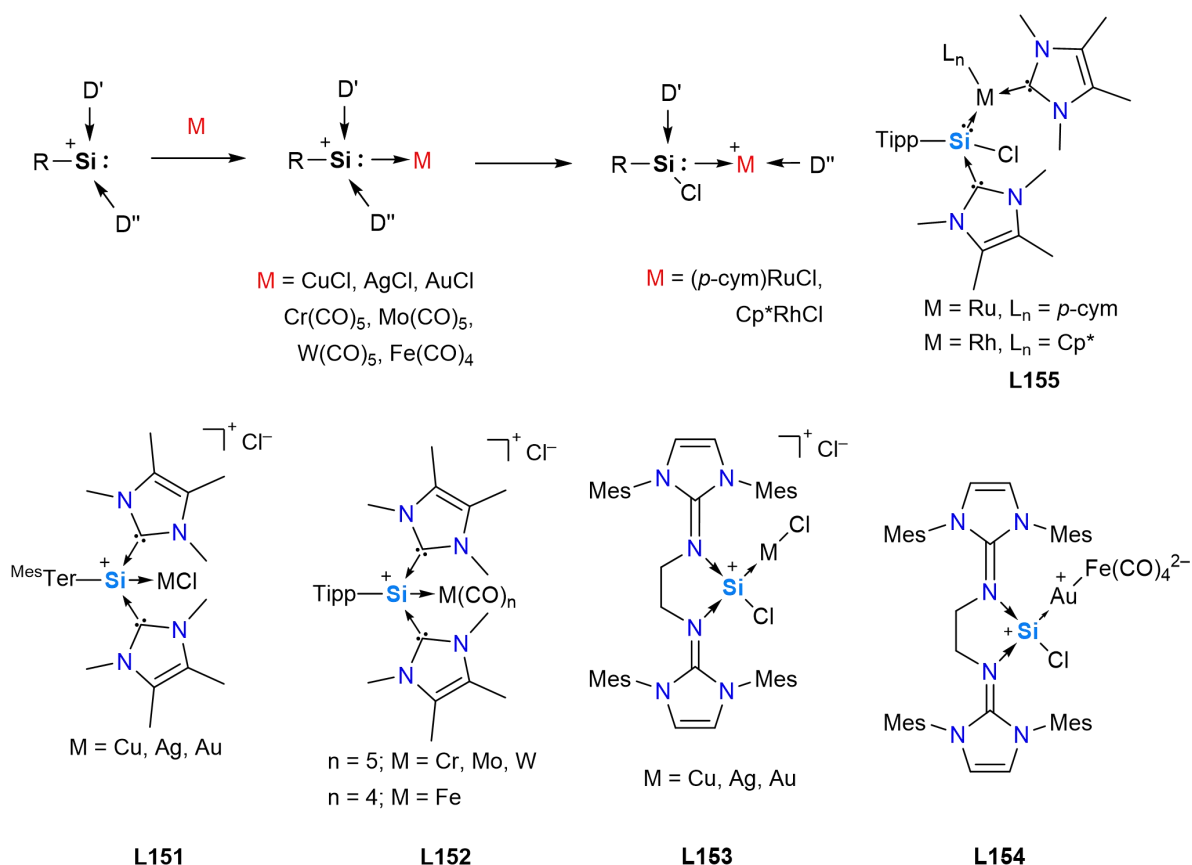


Figure 36. Silyliumylidene transition metal complexes.

Halido-substituted silyliumylidenes could be used as precursors for forming silylone and silaallene as shown in Figure 37. The chelating bis(carbene) stabilized silyliumylidene (**L124**) underwent dichlorination with sodium naphthalenide ($\text{NaC}_{10}\text{H}_8$) to give a silylone (**L156**) (Figure 37, (a)). As a comparison of **L125**, mixed NHC-cAAC stabilized silyliumylidene (**L112**) reacted with KC_8 to furnish a bent silaallene (Figure 37(b), **L157**) with a perturbed electronic structure, owing to the remarkably different electronic properties of cAAC (stronger σ -donor and better π -acceptor) in comparison with NHC (stronger σ -donor and weaker π -acceptor).¹²⁵

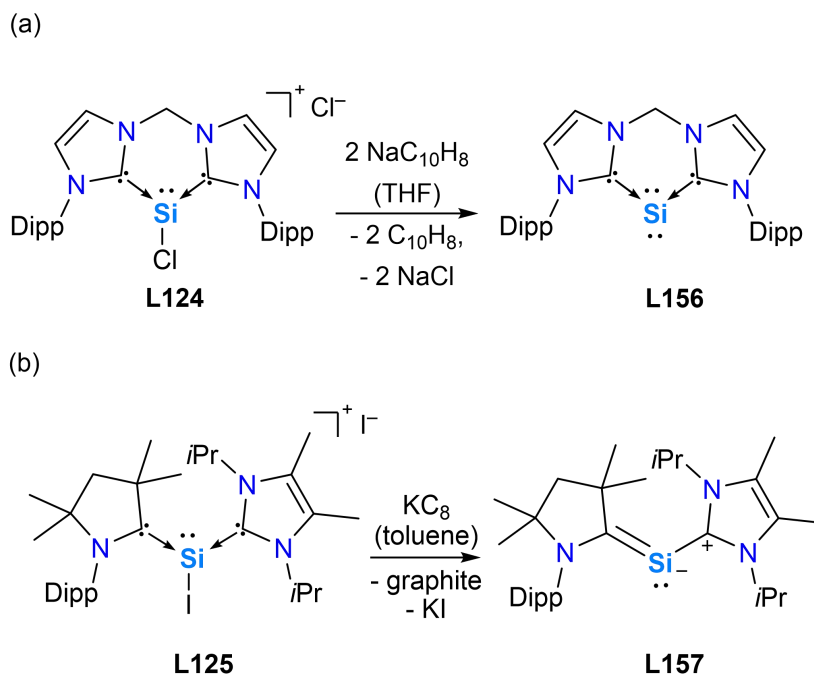


Figure 37. Formation of silylone (a) and silaallene (b) from different silyliumylidenes.

To date, there are only a few examples of silyliumylidenes used as catalysts. The first example of a silyliumylidene being employed in an organic transformation was reported by Jutzi and co-workers in 2011, where Cp^*Si^+ (**L112**) served as a catalyst for the specific degradation of oligo(ethyleneglycol) diethers.¹⁴⁰ In addition, **L112** was proved to be a very efficient non-metallic catalyst for the hydrosilylation of olefins at low catalyst amounts of <0.01 mol% (Figure 38). The proposed mechanism proceeds through initial coordination of the Si-H bond to the Lewis acidic Si center (**L158**) in **L112**, forming a hydrogen-bridged complex, followed by the insertion of alkene/alkyne (**L159**) and release of the product.¹⁴¹

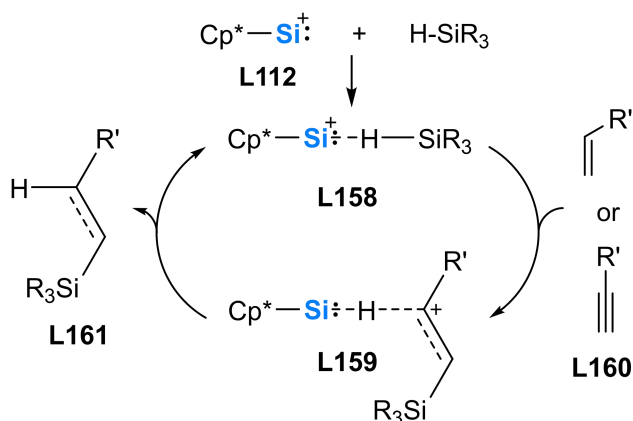


Figure 38. Hydrosilylation of alkenes and alkynes by silyliumylidene **L112**.

Another noticeable example of catalytic application was reported by So and co-workers (Figure 39). The NHC-parent-silyliumylidene cation ($[(\text{IME}_4)_2\text{SiH}]^+\text{I}^-$, **L122**) can catalyze hydroboration of CO_2 , aldehydes, ketones, and pyridines with a catalyst loading of 10 mol%, as well as isocyanates with a catalyst loading of 1 mol% (Figure 39, (a)). Additionally, **L122** was confirmed as a catalyst for the chemoselective *N*-formylation of primary and secondary amines using CO_2 and PhSiH_3 under mild conditions to afford the corresponding formamides (Figure 39, (b)). Mechanistic studies show **L122** sequentially activates CO_2 , PhSiH_3 , and amines (**L167**), which proceeds via a dihydrogen elimination mechanism, to form formamides, siloxanes, and dihydrogen gas.¹²⁹

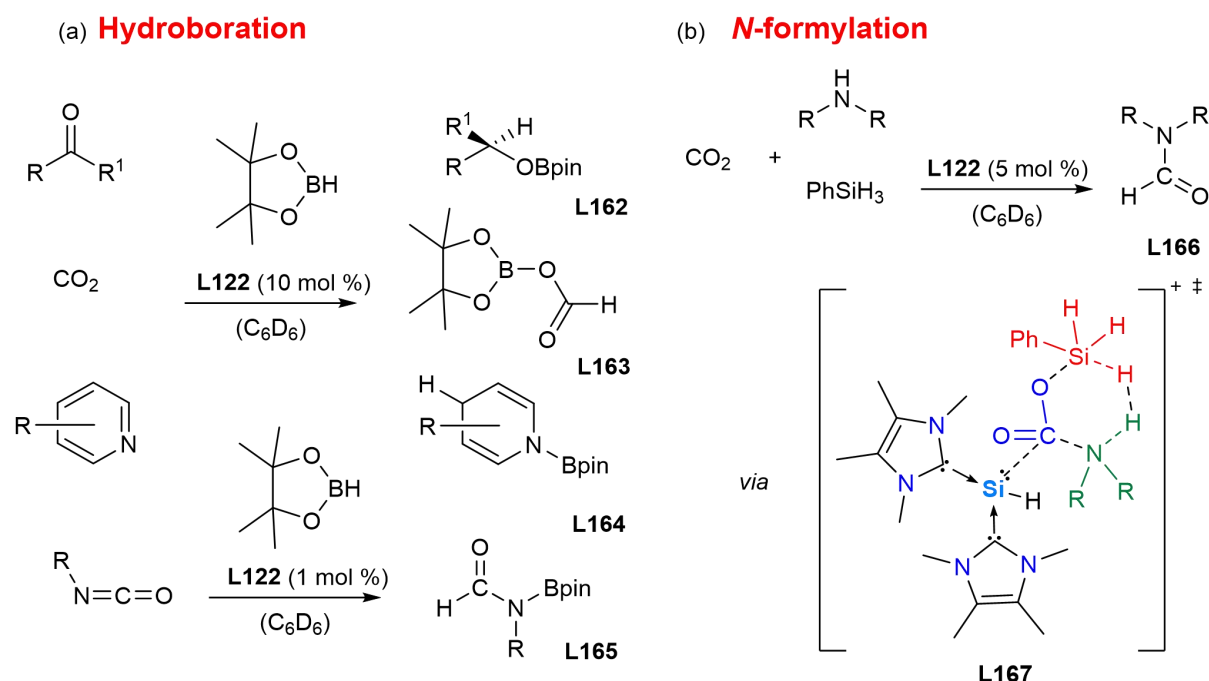
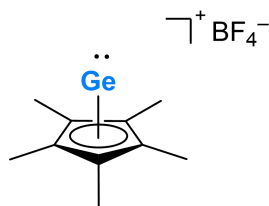


Figure 39. Multiple reactions catalyzed by silyliumylidene (**L122**) (a) hydroboration of aldehydes, ketones, CO_2 , pyridines, and isocyanates with pinacolborane (HBpin). (b) *N*-formylation of amines using CO_2 and phenylsilane.

2.3.3 Germyliumylidene

Among them, germyliumylidenes have the richest examples reported. In the 1980s, the first reported germyliumylidene $[(\text{n}^5\text{-C}_5\text{Me}_5)\text{Ge}]^+[\text{BF}_4]^-$ (Figure 40, **L168**) was isolated by reaction of decamethylgermanocene $(\text{Cp}^*)_2\text{Ge}$: with HBF_4 .⁵⁹ Following this seminal work, there have been a growing number of reports of these compounds. Synthetic routes involve halide abstraction, methyl abstraction, protonation, and metal-assisted approaches. The synergistic effect of thermodynamic and kinetic stabilization can achieve the purpose of stabilizing these compounds. Many types of donor ligands have been utilized in the preparation of germyliumylidene, such as carbenes, weak coordinating arenes, and N-donor ligands.¹¹¹



L168

Figure 40. The first example of germylumylidene.

NHCs have been extensively used to stabilize germylumylidene as shown in Figure 41. A chlorogermylumylidene (**L169**) was prepared by the Driess group in 2013 by employing the chelate dicarbene.¹⁴² Subsequently, the same group reported the first germylumylidene hydride (**L170**) through two steps, the formation of bis(NHC)borate-stabilized chlorogermylumylidene, following by Cl/H exchange reaction using potassium trisec.-butylborohydride ($\text{K}[\text{HB}(\text{s-Bu})_3]$) as a hydride source.¹⁴³ A single NHC together with the substituent can be used to isolate the two coordinated germylumylidenes. Aldrige and colleagues (2015) isolated the two coordinated germylumylidene (**L172a**) bearing a silyl group substituent, stabilized by a dipp-substituted NHC (dipp = 2,6-diisopropylphenyl), which lacks π -donor stabilization of the metal center and consequently has a very small HOMO–LUMO gap (187 kJ mol^{-1}).¹⁴⁴ In 2021, they reported the synthesis of the same model germylumylidene (**L172b, c, d**), but bearing a larger terphenyl-substituent.¹⁴⁵ An extremely bulky NHC featuring a sterically shielding umbrella-shaped trityl (CPh_3) group has been confirmed to be a powerful ligand to prepare single chloride-substituted germylumylidene (**L171**) via a metal-assisted approach.¹⁴⁶ By the addition of two equivalents of IMe_4 to an aryl chloro-germylene, the Inoue group isolated the corresponding three-coordinated germylumylidene (**L173**).¹⁴⁷

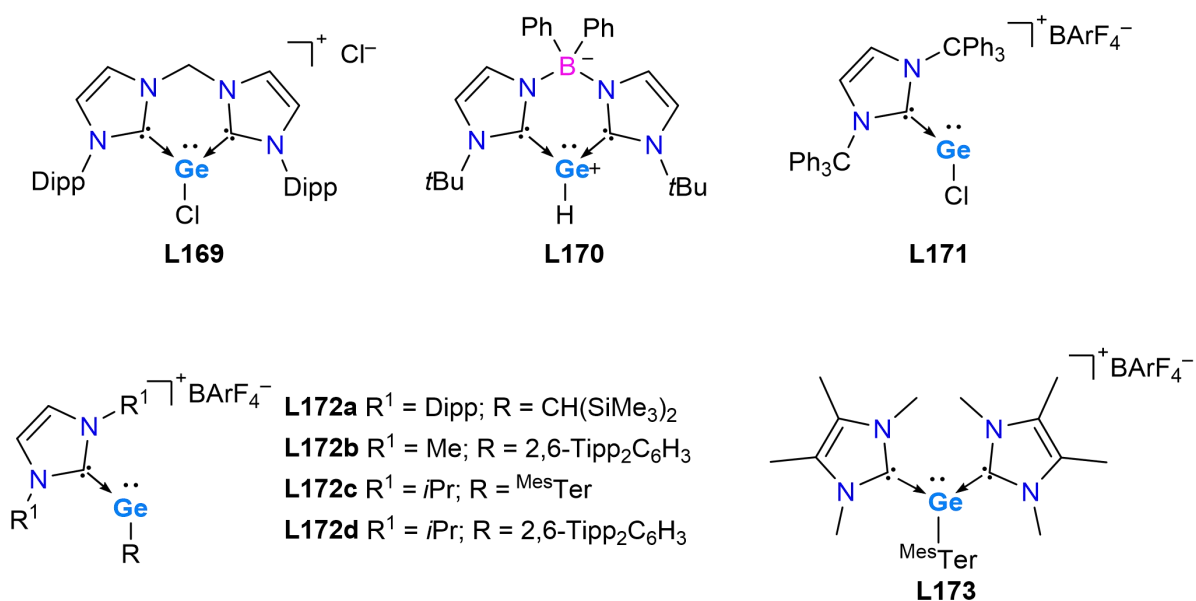


Figure 41. Various NHCs stabilization of germyliumylidenes.

The combination of a single carbene and an imino group as stabilization systems has also been utilized to prepare germyliumylidenes (Figure 42). In 2014, Kinjo et al. reported the autoionization of a germanium dichloride/dioxane complex with an imino-N-heterocyclic carbene ligand, yielding a chlorogermyliumylidene ion (**L174a**).¹⁴⁸ Additionally, the Kinjo group demonstrated the preparation of a methyl-substituted Ge(II) cation (**L174b**) via the reaction of germylone with one equivalent of MeOTf.¹⁴⁹ In a study by Glorius and Hahn in 2017, intramolecularly NHC-stabilized three-coordinated chlorogermylene underwent a chloride abstraction with NaBARF to give rise to cyclic two-coordinate germyliumylidene (**L175**).¹⁵⁰ A bisimino-carbene was utilised by Nikonov et al. to prepare **L176** by a metal-assisted approach, which involves the form of the zinc salt, followed by transmetalation with GeCl_2 -dioxane.¹⁵¹ Deprotonation of 1-mesityl-4,5-diphenyl-2-imidazole with $n\text{-BuLi}$, followed by salt metathesis reaction with GeCl_2 -dioxane complex, led to the formation of the chlorogermyliumylidene (**L177**) bearing two Ge–Cl units.¹⁵² The experimental data in conjunction with DFT calculations suggest that the positive charge mainly resides on the Ge atom between two nitrogen atoms.

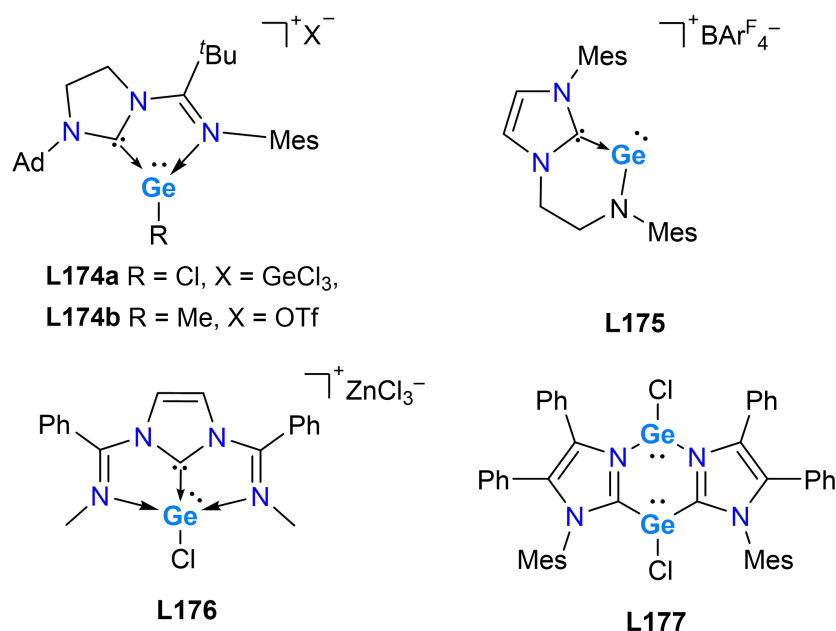


Figure 42. NHC-amido and NHC-imino ligands stabilization of germyliumylidenes.

N-donor ligand is the largest group to stabilize the germyliumylidene, which consists of amidinates, β -diketiminates, N-heterocyclic imines, cryptands, bipyridines, imine-substituted pyridines or other substituents. Some selected N-substituted ligand-stabilized germyliumylidenes are shown in Figure 43. Aminotroponimate ligand was used by Dias group in 1997 to stabilize the first example of cyclic two coordinated germyliumylidene (Figure 43(a), **L178a**) without halide substituent.¹⁵³ Similar compounds were reported by Nagendran group in 2019 (**L178b**).¹⁵⁴ Compared to the case of silyliumylidene, the β -diketiminato ligand (Nacnac) was earlier found to be suitable for the stabilizing Germyliumylidene. A two coordinated germyliumylidene cation was prepared by Power et al. by reaction of Ge(Cl)Dipp₂nacnac (Dipp₂nacnac = {N(C₆H₃-2,6-*i*Pr₂)C(Me)}₂CH) with B(C₆F₅)₃ in the presence of H₂O (**L179a**).¹⁵⁵ Recently, the β -diketiminato ligands featuring backbone NMe₂ groups have been exploited by the Aldridge group to access Ge(II) cations of the same type (**L179b**).¹⁵⁶ Müller reported the same fashion of germyliumylidene (**L180**), which is stabilized by an intramolecular interaction with a distant imido group.¹⁵⁷

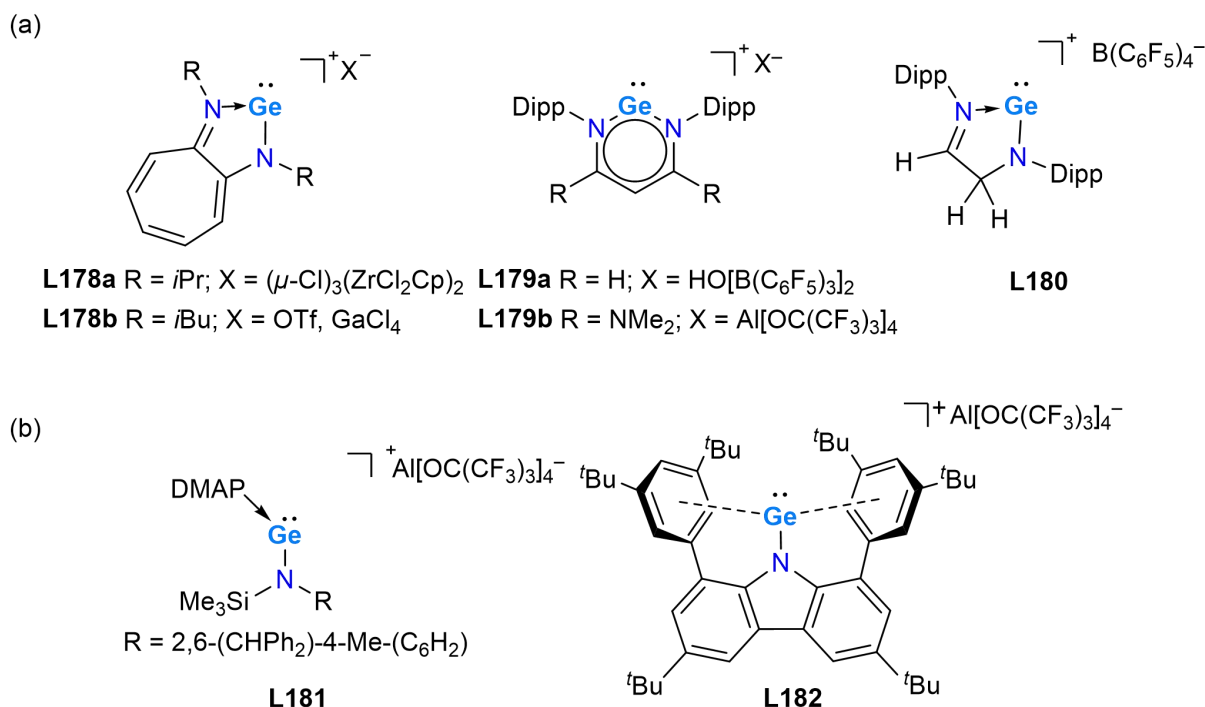


Figure 43. Selected examples of amido ligand stabilized germyliumylidenes: (a) cyclic species; (b) acyclic species.

Extremely bulky amido ligands have been confirmed to be a good candidate for stabilizing mono-coordinated germyliumylidene. A report by Jones and Krossing in 2012, mono Ge(II) cation was stabilized by an extremely bulky amido ligand and a very weakly coordinating anion. The Ge center exhibited weak intramolecular η^2 -arene interactions, and the interaction could be broken by the addition of one equivalent of DMAP, leading to a two-coordinated germyliumylidene (Figure 43(b), **L181**).¹⁵⁸ Recently, the chlorogermylene bearing bulky carbamoyl substituent was subjected to halide abstraction reactions, affording the corresponding germylium salts (**L182**) stabilized by arene coordination, consistent with silicon analogy.¹⁵⁹

Inoue group reported a variety of NHI stabilized germyliumylidene (Figure 44). The amino(imino)germylene reacted with B(C $_6$ F $_5$) $_3$ to afford the borate salt **L183** in a methyl-abstraction and ring-closing reaction.¹⁶⁰ One year later, another four-membered amino(imino)germyliumylidene (**L184**) was isolated by the reaction of amino(imino)germylene with BF $_3$ ·OEt $_2$ in a ring-closing reaction.¹⁶¹ The synthesis of neutral bis-NHI (NHI = *N*-heterocyclic imine) ligands and their application for the stabilization of chlorogermlyliumylidenes (**L185**) were reported by the Inoue group in 2020 and 2022.^{162, 163} The ligands' scaffold consists of either saturated or methylated imidazoline backbones, and the bridge is either flexible ethylene or more rigid *o*-phenylene.

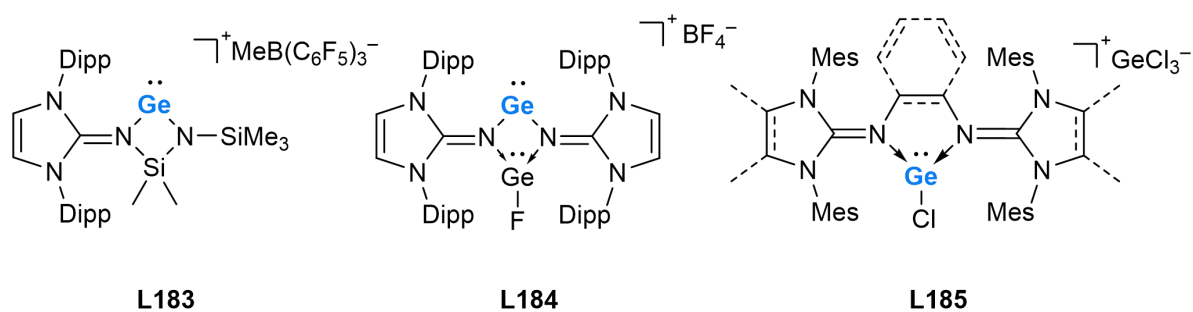
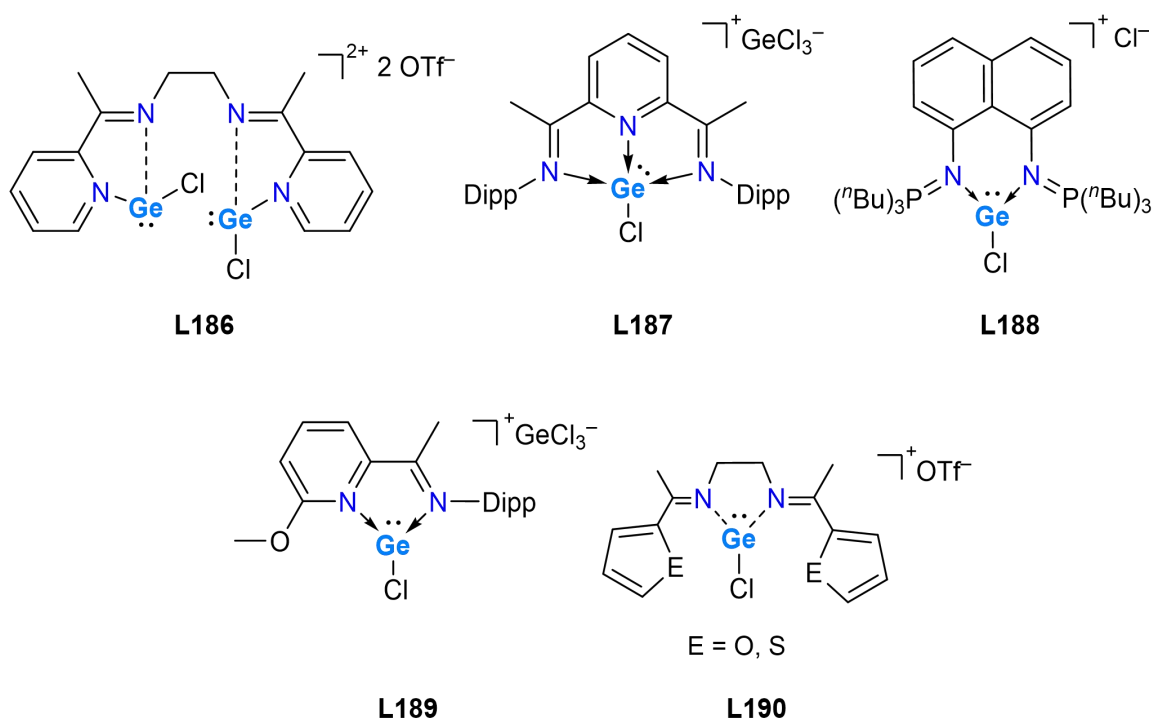


Figure 44. NHI stabilization of germyliumylidenes.

The germyliumylidenes bearing halide substituents are a notable class of compounds formed by halide abstraction of starting neutral complexes Lewis's base stabilized GeX_2 ($\text{X} =$ halide) in an amido ligand system. Some typical examples are provided in Figure 45. Bis(chlorogermlyumylidene) (**L186**) has been obtained by the reaction of 2,7-bis(2-pyridyl)-3,6-diazaocta-2,6-diene germylene with one equivalent of GeCl_2 -dioxane.¹⁶⁴ In 2012, Roesky and Stalke groups treated the substituted Schiff base as Lewis base (LB) with GeCl_2 -dioxane to give the germyliumylidene **L187**.¹⁶⁵ The Ge analogue (**L188**) of chlorosilyliumylidene salt (**L127**) was isolated by Driess group (2012) from the reaction of 1,8-bis(tri-*n*-butylphosphanzenyl)naphthalene) with GeCl_2 -dioxane.¹⁶⁶ In a report by Jambor group (2013), treatment of the neutral 2-[$\text{C}(\text{CH}_3)=\text{N}(\text{C}_6\text{H}_3-2,6\text{-}i\text{Pr}_2)$]-6-($\text{CH}_3\text{O})\text{C}_6\text{H}_3\text{N}$] ligand GeCl_2 provided the ionic germanium(II) complexes $[\text{LGe}^{\text{II}}\text{Cl}]^+[\text{Ge}^{\text{II}}\text{Cl}_3]^-$ (**L189**).¹⁶⁷ The chlorogermlyumylidenes (**L190**) have been stabilized by the two imino nitrogen coordinating sites, featuring acyclic flexible diiminodi(furan) and diiminodi(thiophene) ligands.¹⁶⁸



re 45. Selected N-ligand stabilized chlorogermylumylidenes.

Figu

2.3.4 Reactivities and Catalytic Applications of Germylumylidene

Several examples of the reactivity of germylumylidene ions have been reported, as well as a few catalytic applications that are known (Figure 46). **L188** underwent an oxidation reaction with elemental sulfur to afford germathionium [ClGe=S]⁺ cation (**L191**) containing species (Figure 46, (a)).¹⁶⁶ **L172a** can undergo a variety of facile oxidative bond-forming reactions, oxidative addition of dichloromethane (**L192**), [2+1] cycloaddition with phenylacetylene (**L193**), and formation of multiple bonds (**L194**) by reacting with Me₃SiN₃ or Me₃SiCHN₂ (Figure 46, (b)).¹⁴⁴ **L173** can react with N₂O to the germa-acylium (**L195**) (2020, Inoue), an efficient catalyst in CO₂ hydrosilylation and reduction N-functionalization of amines using CO₂ as a C1 source.¹⁴⁷

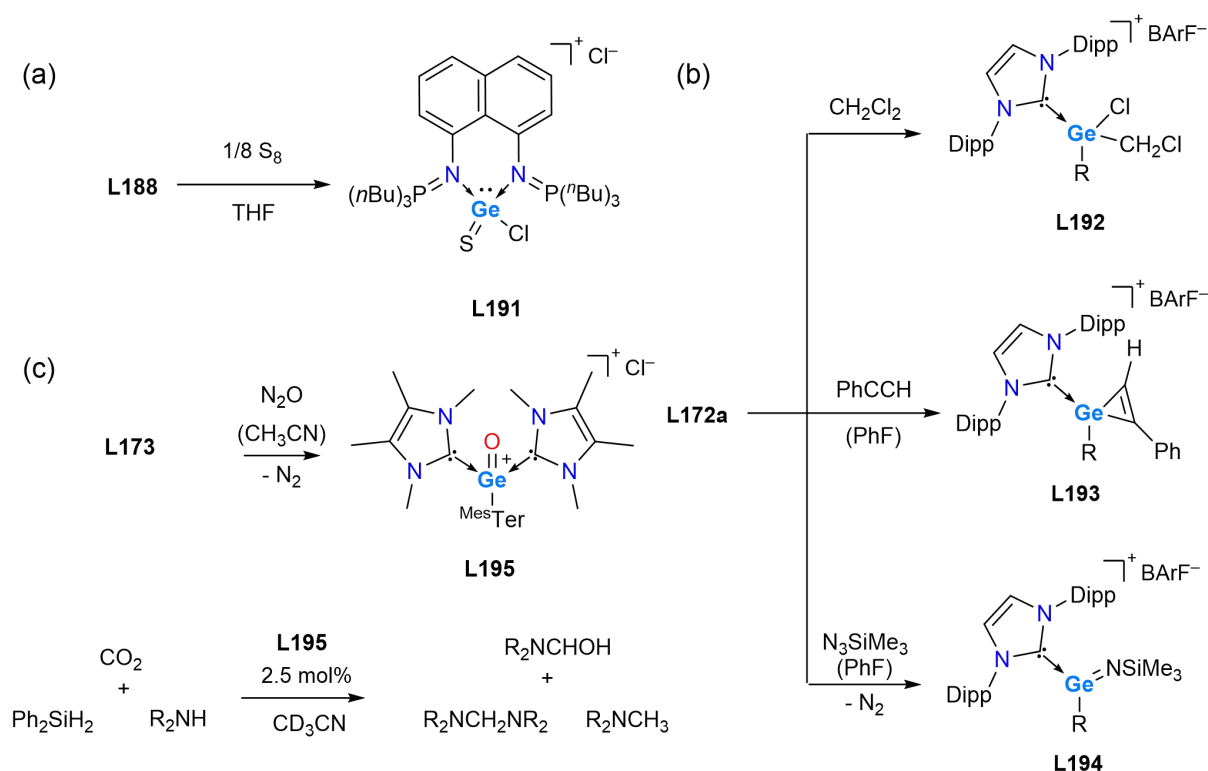


Figure 46. Oxidation reactions of germyliumylidenes.

Chlorogermayliumylidenes can undergo further reduction to yield germylone (Figure 47, (a)). Dechlorination of **L169** with sodium naphthalenide furnished the first isolable germylone (**L196**) coordinated by the bis-carbene chelate ligand.¹⁴² Its character was confirmed by DFT calculation with two proton affinities (PA), PA(1) 279.6 kcal/mol and PA(2) 175.0 kcal/mol. Reduction of the chlorogermayliumylidene ion (**L174a**) with potassium graphite also produced the corresponding germylone (**L197**).¹⁶⁹ The germylone dimNHCGe (**L198**, dimNHC = diimino N-heterocyclic carbene) was successfully prepared via the reduction of **L176** with KC_8 .¹⁷⁰

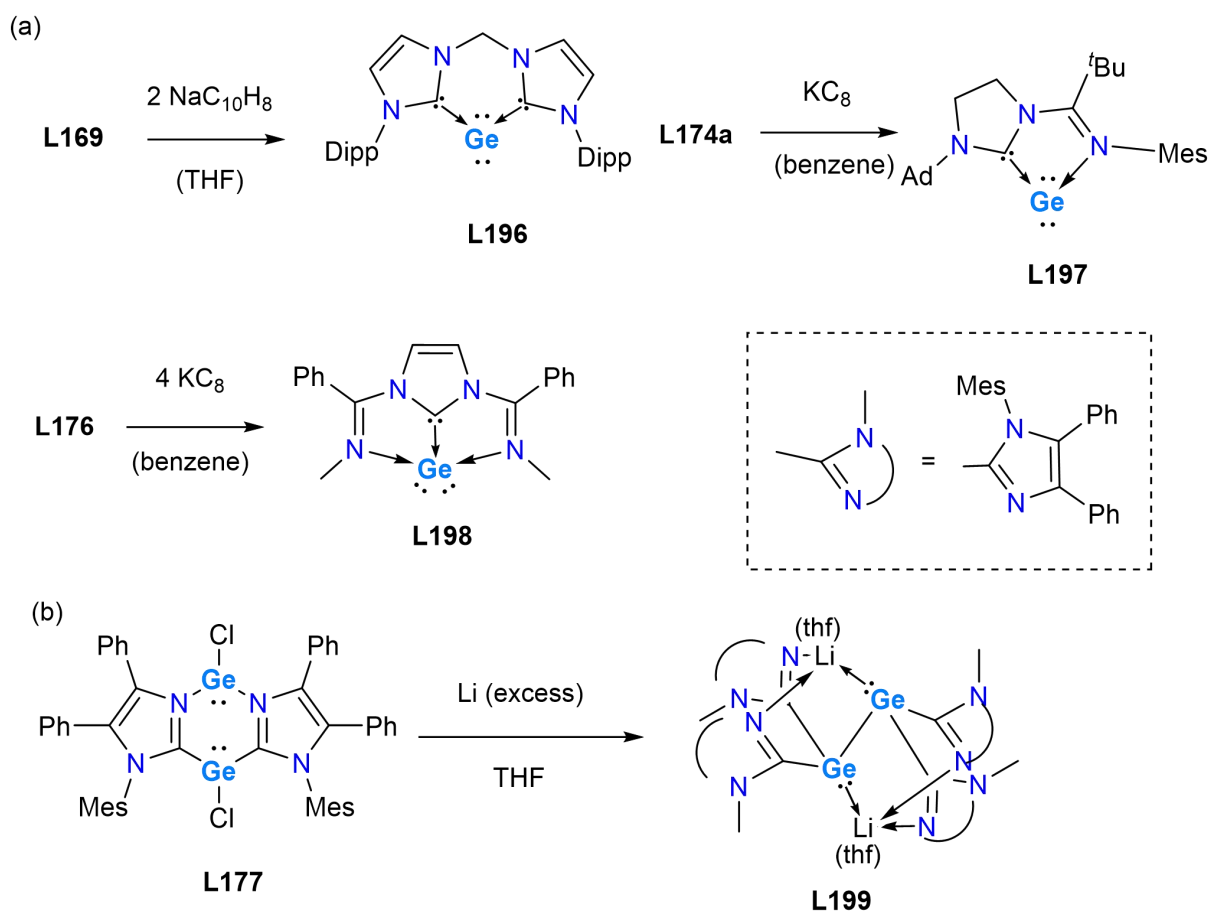


Figure 47. Reduction of germyliumylidenes (a) the formation of germylones (b) the formation of Ge–Ge bond.

Additionally, reduction of **L177** with an excess amount of lithium metal resulted in Ge–Ge bond formation concomitant with elimination of one of the Ge atoms of **L177**, to give rise to the digermenedilithium compound (Figure 47(b), **L199**) involving intramolecular coordination of the imines and the lone pairs to the Li atoms.¹⁵²

Compared to its Si analogue, the reaction of β -diketiminate stabilized germyliumylidene (**L179b**) and $t\text{BuNH}_2$ led to a simple adduct formation (Figure 48(a), **L200**).¹¹⁷ In comparison to **L179b**, two coordinate amido/NHC- (**L201**) or amido/phosphine (**L203**) stabilized germyliumylidenes can undergo a facile cleavage of N–H bonds in 1,2-fashion (Figure 48, (b)): the products resulting from reactions with carbazole feature a tethered secondary amine donor bound to a three-coordinate carbazoyl-Ge(II) center (**L202** and **L204**).¹⁷¹

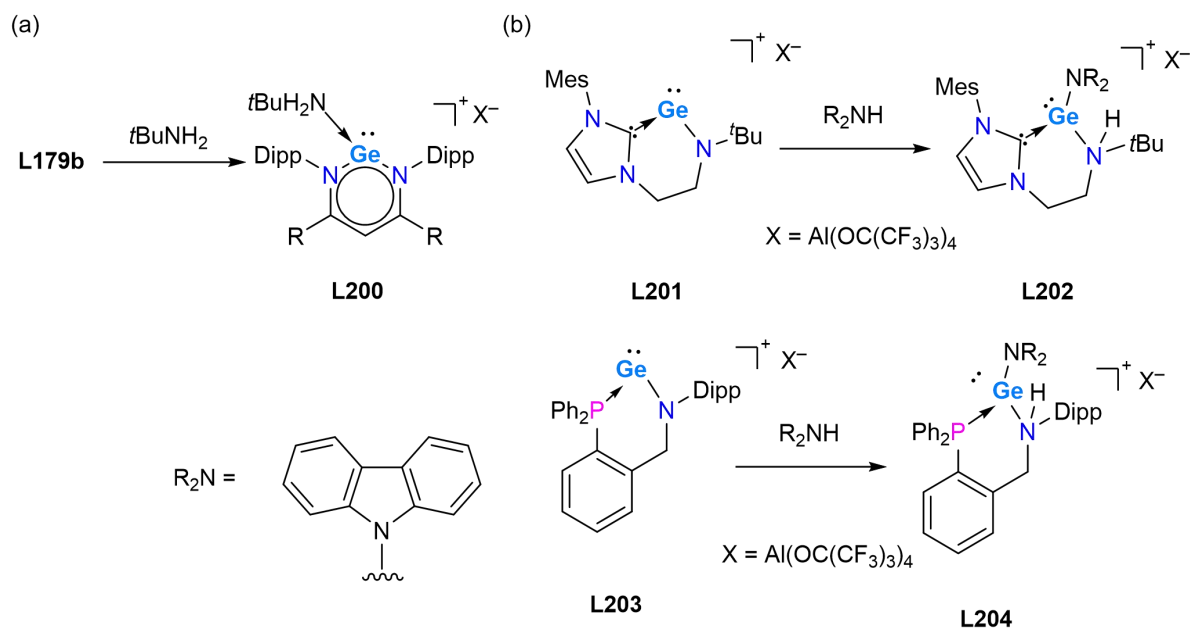


Figure 48. Cooperative N-H bond activation by germyliumylidenes.

Bis-NHI stabilized chlorogermylumylidene was found to undergo transmetalation as shown in Figure 49. Reaction of **L185** with NaBH_4 led to the formation of a push-pull-stabilized hydrogermyliumylidene complex (**L205**) by Cl/H exchange while reaction with LiAlH_4 afforded the transmetalation product (**L206**).¹⁶³

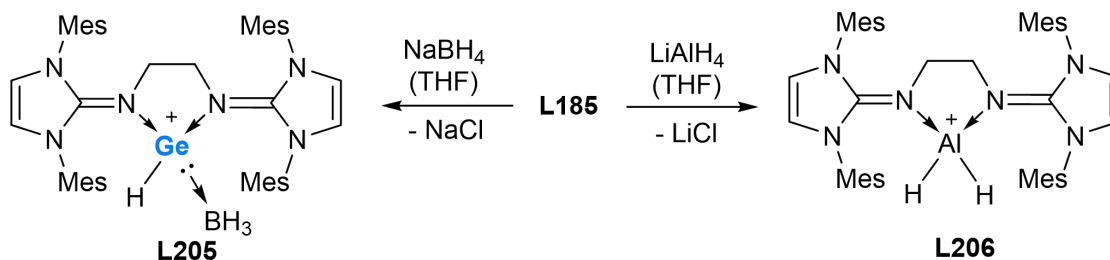


Figure 49. Reactivities of Bis-NHI germyliumylidene.

Despite the unique electronic features and reactivities of germyliumylidenes, their catalytic applications have only rarely been reported. Rivard and co-workers demonstrated the two-coordinated germyliumylidene (**L207**) promoted catalytic hydroborylation of sterically hindered ketones under mild conditions (Figure 50).¹⁷² This is the first example of catalysis using a germyliumylidene, but the authors didn't discuss a proposed mechanism.

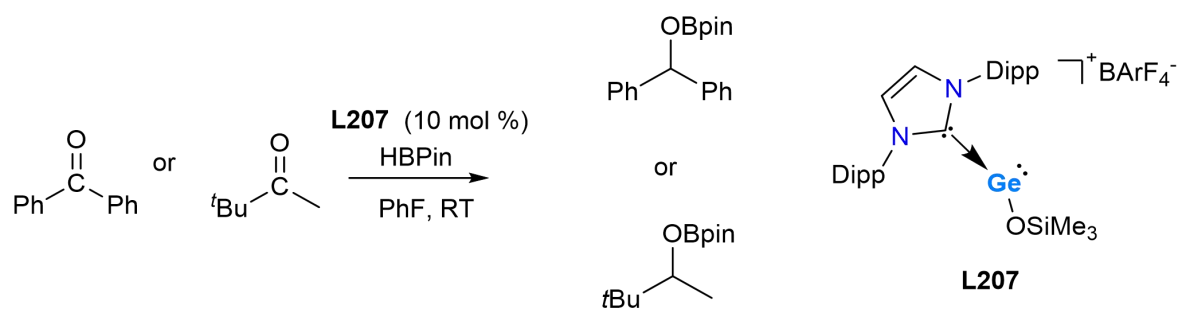


Figure 50. Hydroborylation of ketones by **L207**.

In 2019, Nagendran et al. reported that **L178b** catalyzed the hydroboration of various aldehydes and ketones (Figure 51).¹⁷³ In the proposed mechanism, **L178b** is a pre-catalyst and its reaction with HBpin produces an intermediate hydridogermylene (**L208**) as an active catalytic species. Then **L208** reacts with the carbonyl substrate to give the germylene alkoxide intermediate **L210** through a four-membered heterocyclic transition state (**L209**). Subsequent reaction with HBpin through σ -bond metathesis leads to the formation of hydroboration product (**L212**) and regeneration of the catalyst.

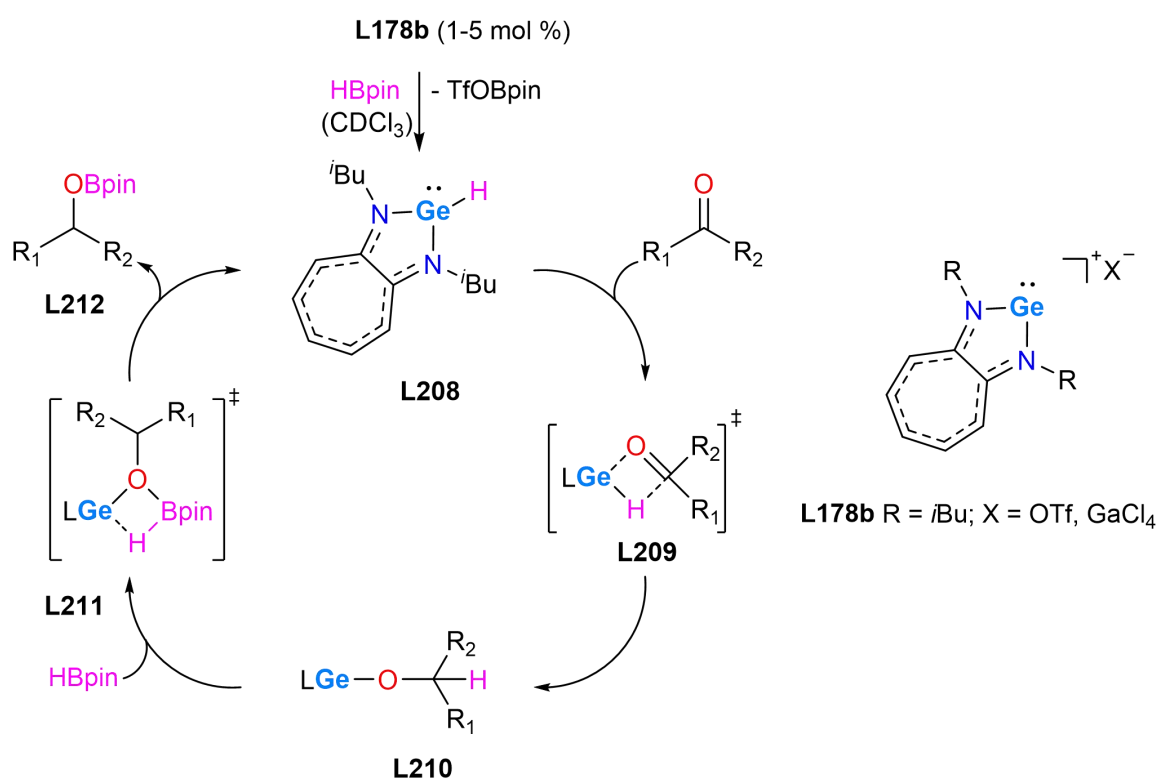
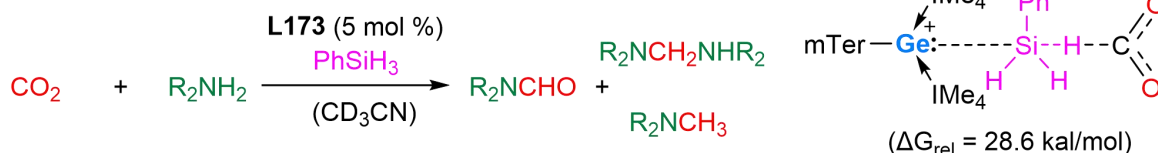


Figure 51. Proposed mechanism of hydroboration of carbonyls catalysed by **L178b**.

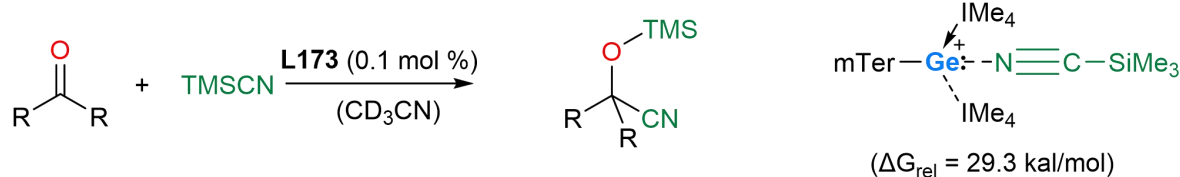
L173 can catalyse the reduction of CO₂ with amines and phenylsilane, the cyanosilylation of carbonyls with Trimethylsilyl cyanide (TMSCN), and the hydrosilylation of aldehydes with

HBPin (Figure 52).¹⁷⁴ DFT studies revealed that **L173** acts as Lewis base towards silane due to the presence of a lone pair on the germanium atom (**L213**) in N-methylation, while **L173** exhibits its electrophilic nature due to the accessible Ge-C^{NHC} σ* orbital in cyanosilylation (**L214**) and hydroboration (**L215**) reactions.

N-Methylation:



Cyanosilylation:



Hydroboration:

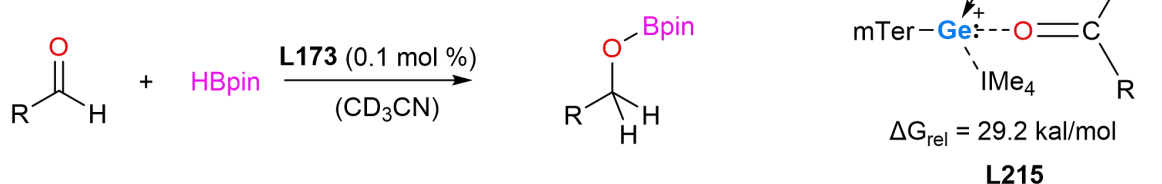


Figure 52. Selected reactions catalysed by germyliumylidene **L173**.

2.3.5 Stannylumylidene

Since the seminal work on the half-sandwich stannylumylidene (Figure 53, **L216**), several examples of these compounds have been reported.^{59, 112, 175-177} Similar to germanium, monoanionic bulky *N*-donor and neutral chelating ligands with nitrogen atoms or phosphine have been applied to stabilize the stannylumylidenes featuring cyclic structure (See Figure 53), such as aminotroponimate (**L217**),¹⁷⁸ bidentate β-diketiminato ligands (**L218**),^{156, 179} *N*-heterocyclic imine (NHI) (**L219**, **L220**),^{163, 180} iminopyridine (**L221**),¹⁶⁷ bisiminopyridine (**L222**),¹⁶⁵ and bis(α-iminopyridine) (**L223**),¹⁸¹ Bisphosphinidene (**L224**),¹⁸² *N*-heterocyclic carbene-phosphindene (NHCP) (**L225**).¹⁸³

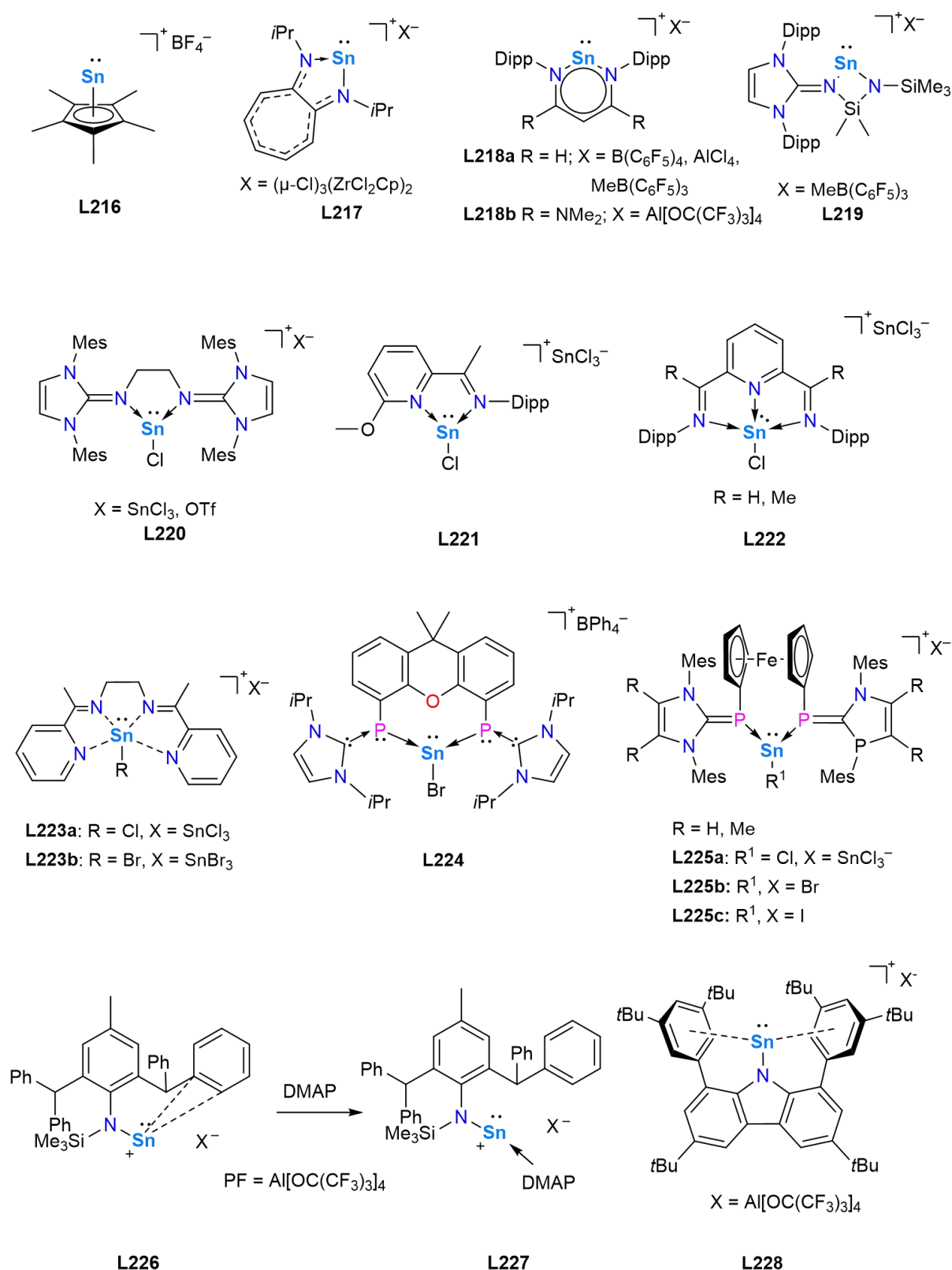


Figure 53. Selected examples of stannylumidenes.

There are still a few examples reported featuring acyclic structures, compared to germylumidenes. A noteworthy example from the Jones and Krossing groups is the first

quasi mono-coordinate Sn(II) cation (Figure 53, **L226**), [SnN(Ar*)(SiMe₃)]⁺[PF]⁻ (Ar* = (2,6-CHPh₂-4-MeC₆H₂), PF = Al[OC(CF₃)₃]₄)⁻, using an extremely bulky amido ligand, in which an intramolecular *n*² arene interaction to the Sn center was present. The addition of 4-dimethylaminopyridine (DMAP) led to the displacement of C^{arene}-Sn interaction, forming two-coordinated stannylumylidene (**L227**).^{66, 184} Another example of pseudo-one-coordinate stannylumylidenes (**L228**) was prepared by the reaction of a bulky carbamoyl substituent chlorostanylene with Li[Al[OC(CF₃)₃]₄].¹⁵⁹

2.3.6 Reactivities and Catalytic Applications of Stannylumylidene

The reactivity of stannylumylidenes is scarcely reported, and only a few examples of transmetalation, coordination of *t*BuNH₂, and activation towards elemental sulphur are known. The organo-phosphane oxide substituted stannylumylidene (Figure 54(a), **L229**) can activate elemental sulphur to form the four-membered-ring species (**L230**) containing a dinuclear dication, through the formation of intermediate [R-(DMAP)Sn=S]⁺.¹⁸⁵ Similar to its Ge analogue, the reaction of β-diketiminate stabilized stannylumylidene (**L218b**) with NH₂*t*Bu and led to a simple adduct formation (**L231**) (Figure 54, (b)).¹¹⁷

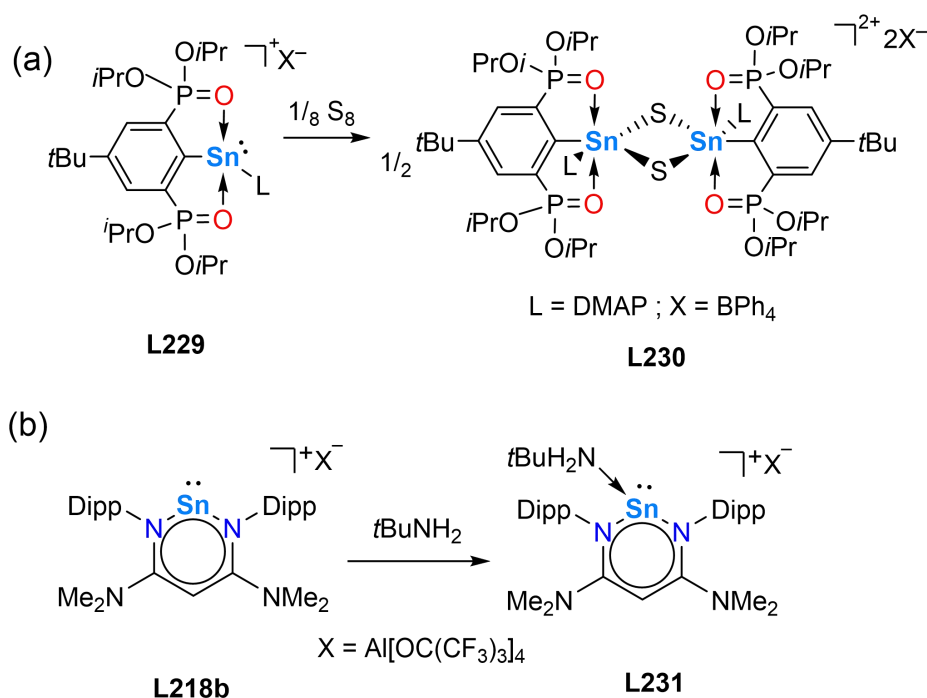


Figure 54 Reactions of stannylumylidene with S₈ (a) or *t*BuNH₂ (b).

The Inoue group has reported some reactivities of bis-NHI-stabilized chlorostannylumylidene as shown in Figure 55, including transmetalation of the Sn centre with other elements and ligand exchange.^{186, 187} Reaction of **L220** with NaBH₄ led to

transmetalation, yielding the corresponding dihydroboronium complex (**L231**). Also, the reaction with LiAlH_4 afforded the transmetalation product (**L232**). The transmetalation of **L220** with GeCl_2 -dioxane in acetonitrile at room temperature led to a germyliumylidene (**L233**). Two new bidentate ferrocene-bridged bis(*N*-heterocyclic carbene–phospinidenes) (bis-NHCPs) stannylumylidene (**L225a**) can undergo a transmetalation to a CuCl complex (**L234**) and ligand exchange with bis-NHI ligand to form **L220**.

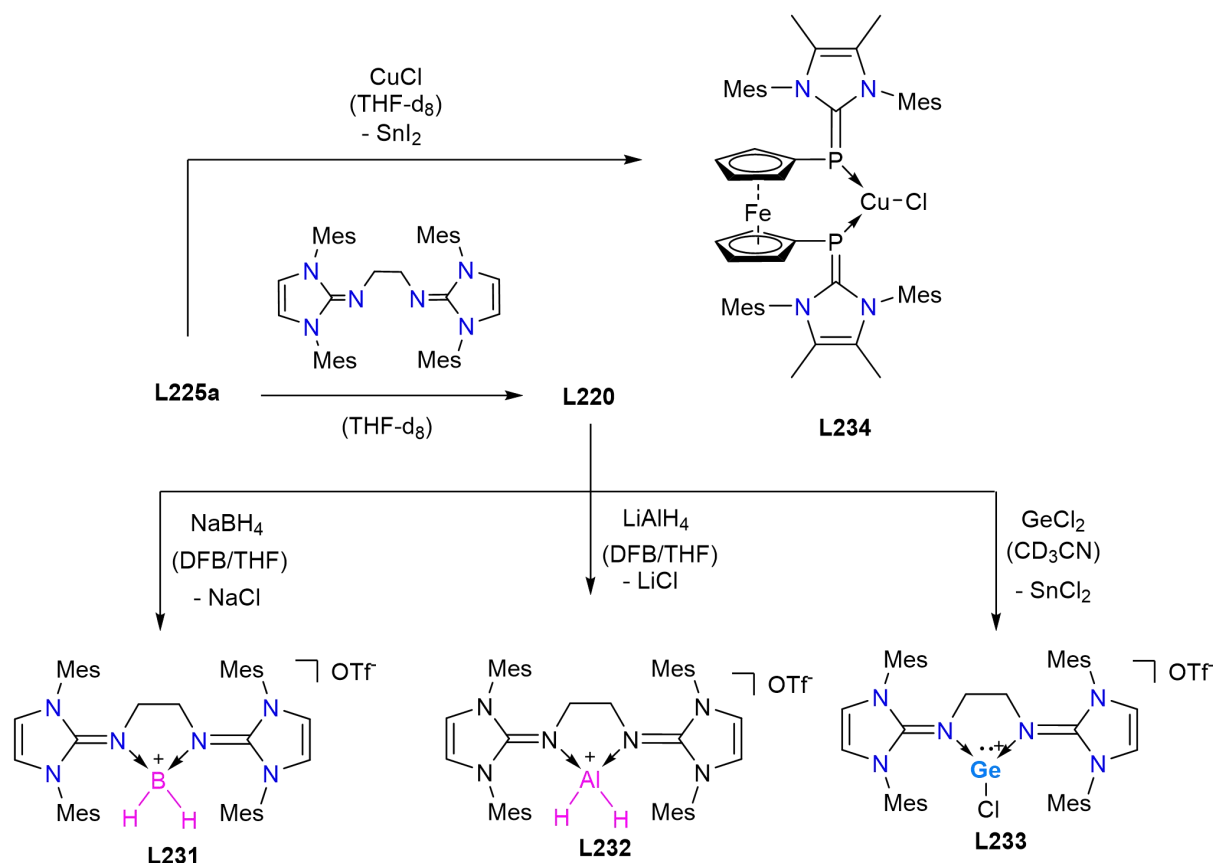


Figure 55. The reactivities of bis-NHI stannylumylidenes.

In comparison with silyliumylidene and germyliumylidene, catalytic applications of stannylumylidene are limited to two examples of hydroboration of carbonyl compounds (Figure 56). A tin(II) cation ($[\text{L}^+\text{Sn}(\text{II})][\text{OTf}]$, L = aminotroponate) (**L235**) is reported as an efficient catalyst for the hydroboration of aldehydes and ketones.¹⁸⁸ A DFT analysis revealed that hydridostannylenes (**L236**) is the active catalytic species and the H atom transfer from the Sn-H bond to the carbonyl carbon is the rate-determining step. The Inoue group reported **L237** tin cation, which could catalyze the hydroboration of ketones and aldehydes in the presence of HBpin .

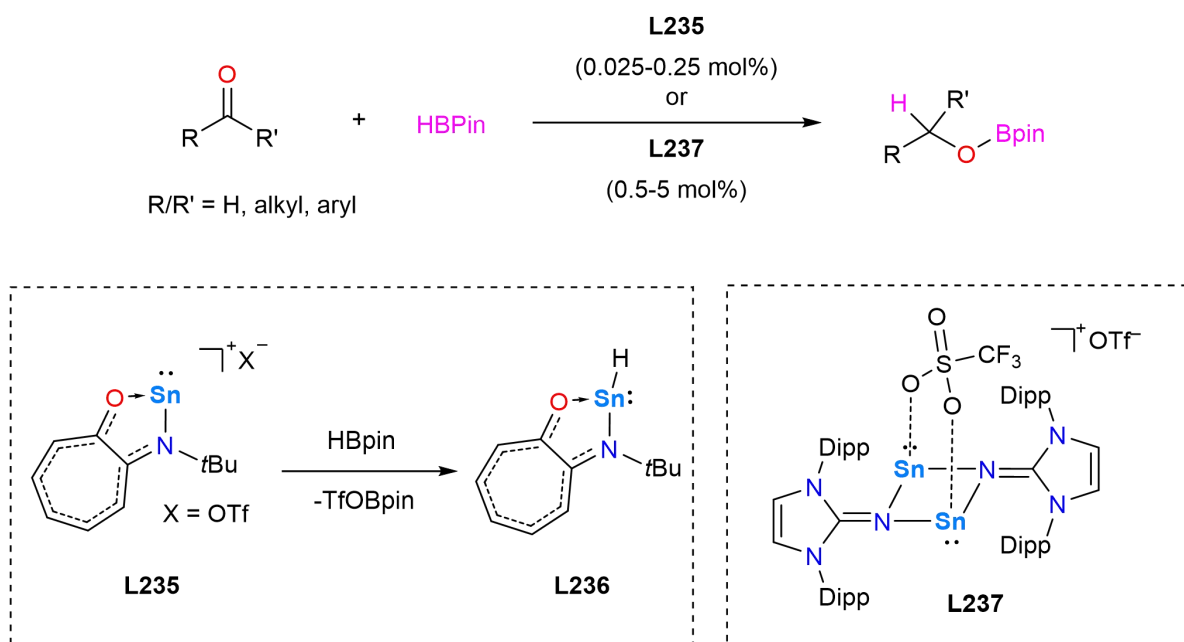


Figure 56. Hydroboration of aldehydes and ketones by stannylidumidenes.

2.3.7 Plumbilyumylidenes and Catalytic Applications

Isolable plumbilyumylidenes remain rare, particularly for the heaviest congeners. Similar to their lighter analogues, the first example of a stabilized plumbilyumylidene (Figure 57, **L238**) was reported by Jutzi's group, featuring stabilization by a pentamethylcyclopentadienyl ligand.¹⁸⁹ In 2004, the Power group reported a quasi-one-coordinate lead cation (**L239**) bound to the 2,6-Trip₂C₆H₃ moiety and weakly solvated by toluene, generated via demethylation of [PbMe(2,6-Trip₂C₆H₃)] (Trip = 2,4,6-iPr₃C₆H₂) with tris(perfluorophenyl)borane in toluene.¹⁹⁰ A three-coordinate Pb complex (**L240**) featuring an N₂S(alkanethiolate) ligand was later isolated by Godwin in 2006.¹⁹¹ The bulky β-diketimate ligand has proven to be a powerful tool for stabilizing plumbilyumylidenes (**L241**), facilitating their isolation via both halide abstraction and methyl group abstraction. Additionally, the bulky carbamoyl substituent, previously employed for Si, Ge, and Sn analogues, was successfully applied to stabilize the corresponding plumbilyumylidene (**L242**).¹⁵⁹ The incorporation of an electron-rich transition metal enabled by Braunschweig to isolate a dimeric plumbilyumylidene complex (**L243**).¹⁹² However, these compounds have exhibited limited reactivity to date.

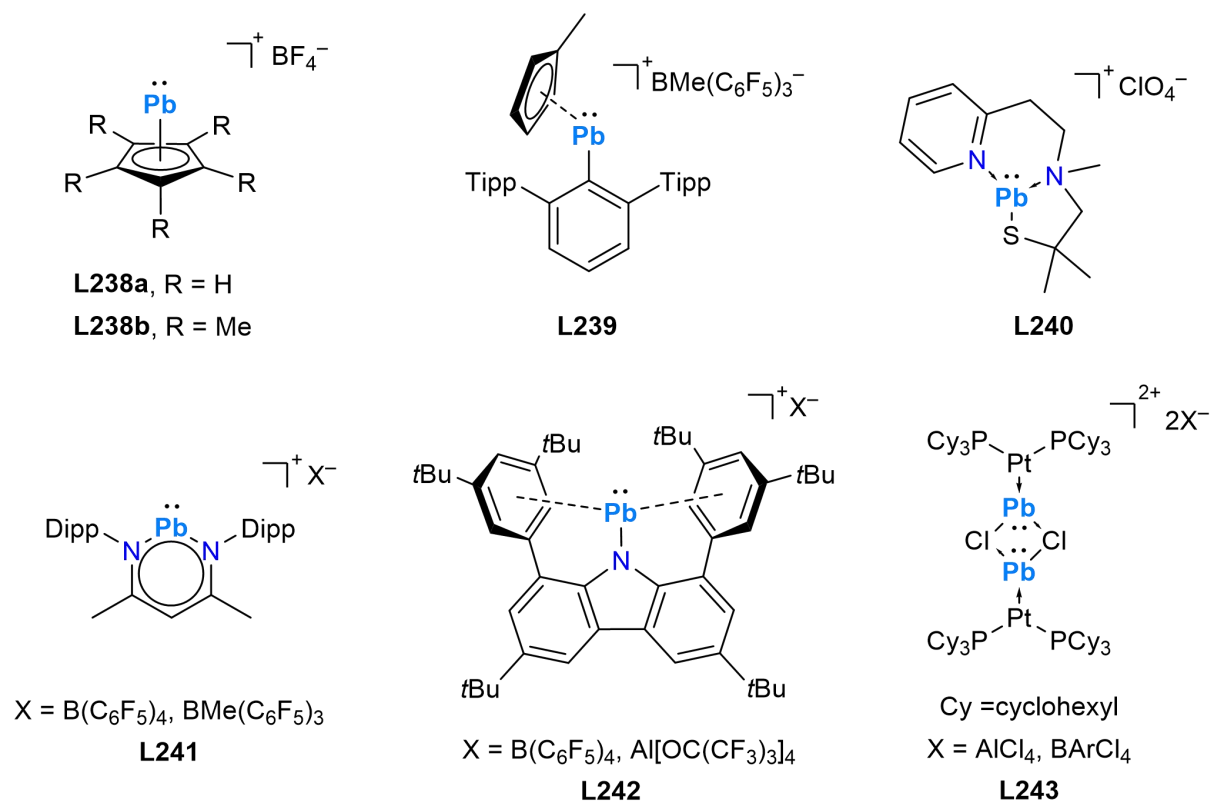


Figure 57. Selected examples of plumbyliumylidenes.

In 2022, Nakata synthesized the N,N'-di-tert-butyl-iminophosphonamide ligand-stabilized plumbyliumylidene (Figure 58, **L244**) by reacting the corresponding chloroplumbylene with NaBArF.¹⁹³ **L244** functions as a Lewis acid catalyst for the hydroboration of benzophenone and benzaldehyde, exhibiting high efficiency with catalyst loadings as low as 0.1 mol% under ambient conditions. In the proposed mechanism, **L244** captures a carbonyl compound, forming the plumbyliumylidene complex intermediate **L245**. Subsequently, **L245** reacts with HBpin, leading to the formation of a boronate ester (**L247**) and regenerating **L244** via a four-membered intermediate, **L246**.

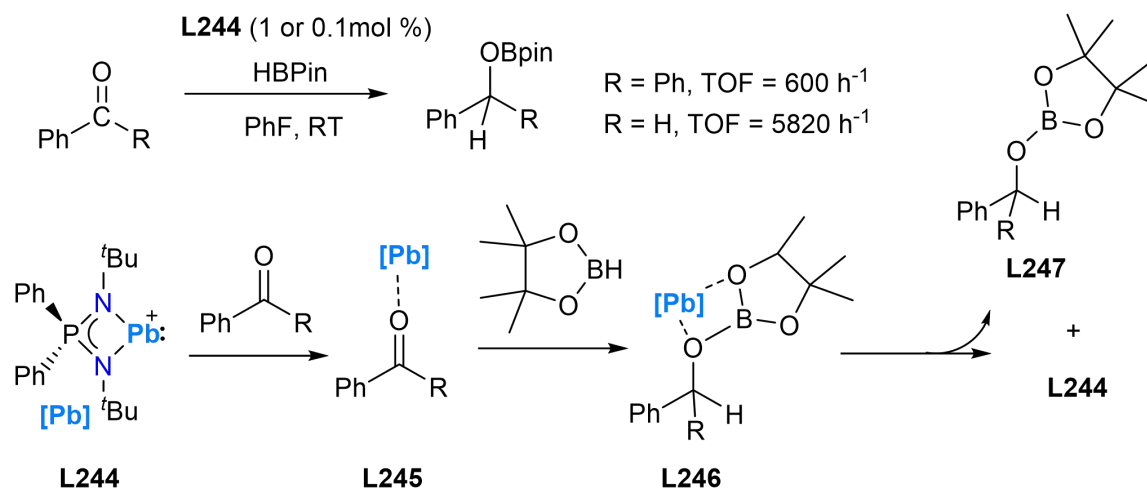


Figure 58. Plumbyliumylidene-catalysed hydroboration of benzaldehydes.

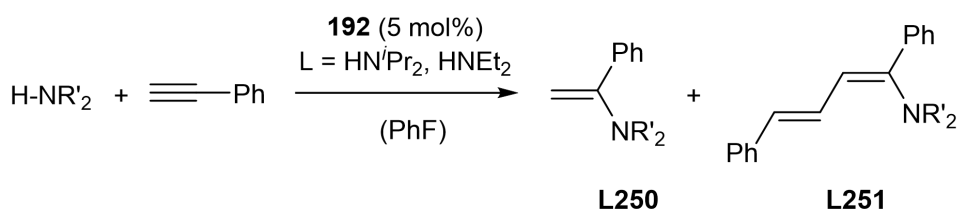
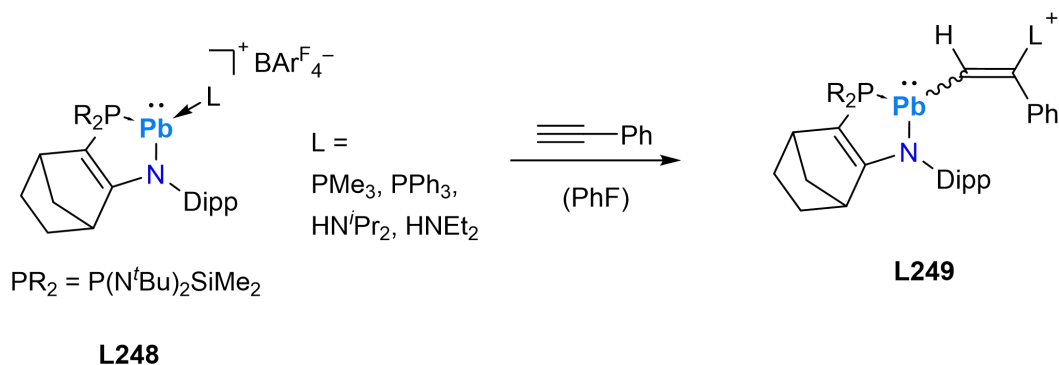


Figure 59. Reaction of **L120** with phenylacetylene and catalytic hydroamination of phenylacetylene.

Phosphine-stabilized Pb(II) cations (Figure 59, **L248**)¹⁹⁴ generated via chloride abstraction from chloroplumbylene, readily react with Lewis bases, such as phosphines and amines, to form the corresponding donor–acceptor complexes. These complexes (**L248**) undergo alkyne insertion into the Pb–L bond upon reaction with phenylacetylene, yielding the corresponding vinylplumbylenes (**L249**). Notably, the secondary amine adduct **L248** serves as an effective catalyst for the hydroamination of phenylacetylene.

3 Scope of this work

Heavier tetryliumylidenes (RE:^+) are a class of low-valent Group 14 compounds, which are characterized by the presence of a lone pair of electrons, two unoccupied orbitals, and a positive charge.¹¹¹ They combine the characteristics of highly electrophilic tetrylium cations and Lewis ambiphilicity of tetrylenes and have been attractive targets for fundamental research for small molecule activation and catalytic applications. As elaborated in the previous chapter, lighter tetryliumylidenes – e.g. silyliumylidenes and germyliumylidenes – have demonstrated various reactivities and catalytic applications. In comparison, a heavier tetryliumylidene analogue, stannylumylidene cations, are also an emerging class of low valent Sn species that may have the potential for molecular activations and catalysis applications. However, examples of utilization of stannylumylidene in the activation of small-molecule reactions are rare. This limitation may stem from the restricted structural diversity of stannylumylidenes. Nearly all isolable stannylumylidenes are stabilized through N-substitution, which provides π -donor stabilization to the Sn center, and they predominantly adopt cyclic structures. Thus, a major focus of this thesis concerns the isolation of acyclic stannylumylidenes which lack π -stabilization, followed by the investigation into their activities and catalytic application.

Recently, our group has successfully isolated di-NHCs-stabilized bulky aryl-substituted silyliumylidenes and germyliumylidenes, which have shown remarkable capabilities in small molecule activation and catalysis. Building on this work, we aimed to develop the Sn analogue, featuring one bulky aryl substituent and two NHC ligands coordinated to the Sn center. Following a similar synthetic approach to that which was used for the Ge analogue, we reacted chlorostannylene ($^{\text{Mes}}\text{TerSnCl}$) (**A**) with two equivalents of NHC in toluene, followed by the addition of one equivalent of Na[BARF] (BARF = (3,5-(CF_3)₂-C₆H₃)₄B) in a one-pot procedure as shown in Figure 60(a). This yielded the di-NHC-stabilized stannylumylidene (**B**). Inspired by the activation of CO₂ by stannylumylidenes and the catalytic hydrosilylation of CO₂ by germyliumylidenes, we explored the catalytic potential of **B** in the same reaction. A notable finding was that the reaction products (**C**, **D**) derived from **B** and CO₂ function as active catalytic species in the catalytic hydrosilylation of CO₂ (Figure 60, (b)).

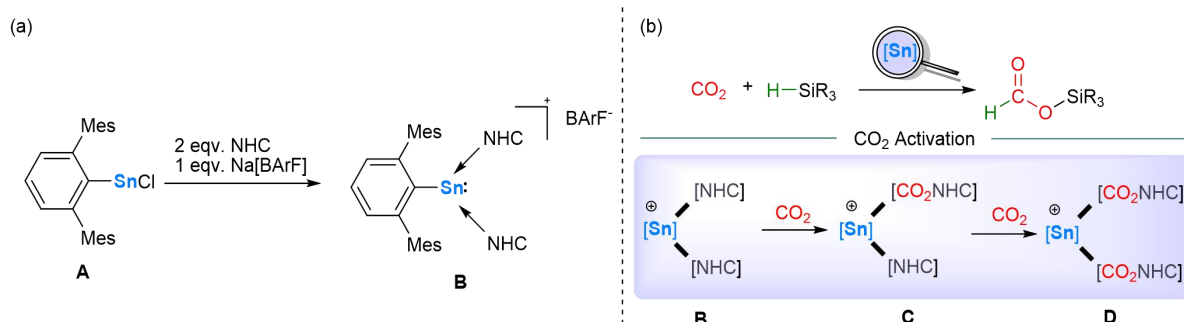


Figure 60. (a) Synthesis of di-NHCs stannylumylidene; (b) Activation CO_2 and hydrosilylation of CO_2 by di-NHCs stannylumylidene.

To further access a single Lewis base-supported stannylumylidene, the reaction of **A** with one equivalent of NHC was conducted, followed by the addition of NaBarF (Figure 61). This species is expected to have enhanced reactivity due to the presence of one vacant p -orbital. Following the successful synthesis of two-coordinated stannylumylidene, a detailed reactivity study will be performed towards small molecules, such as H_2 , NH_3 , N_2O , CO_2 , TMS-N_3 , and transition metal ($\text{Ni}(0)$).

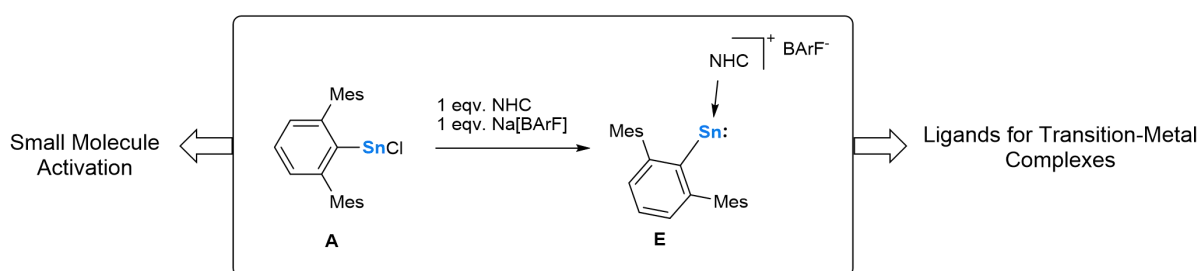


Figure 61. Synthesis of mono-NHC coordinated stannylumylidene.

NHC has been confirmed to be a powerful tool to prepare the stannylumylidene. To expand its application in low-valent tin chemistry, an amido/terphenyl stannylene supported by NHC was isolated and its reactivity towards ketones and aldehydes was explored (Figure 62).

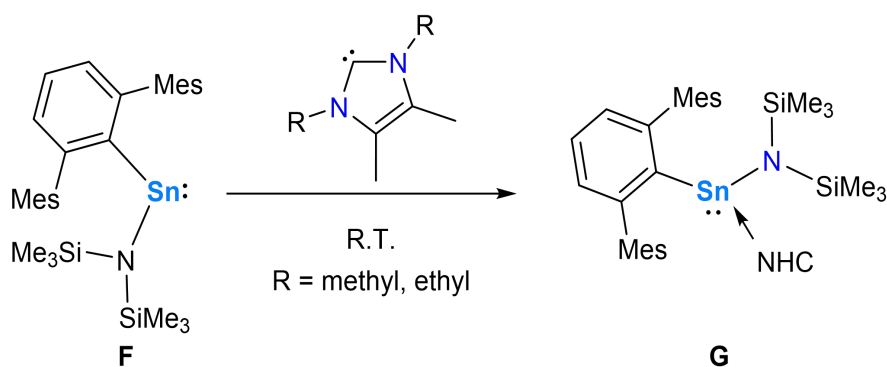


Figure 62. Synthesis of amido/terphenyl stannylene-NHC adducts.

Overall, this thesis aims to study the isolation of novel NHC-supported low valent tin(II) compounds, especially stannylumylenes, and gain a deeper understanding of their chemistry. It seeks to reveal the fundamental differences and/or similarities between tin and its lighter congeners—carbon, silicon, and germanium. The knowledge obtained from this project could open new avenues for developing novel catalytic processes and small molecule activation using these low-valent tin compounds.

4. CO₂ Hydrosilylation Catalyzed by an N-Heterocyclic Carbene (NHC)-Stabilized Stannylumylidene

Title: CO₂ Hydrosilylation Catalyzed by an N-Heterocyclic Carbene (NHC)-Stabilized Stannylumylidene

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Author: Dechuang Niu, Arseni Kostenko, John A. Kelly, Deotra Sarkar, Huihui Xu, and Shigeyoshi Inoue*

Content: The di-N-heterocyclic carbene (NHCs) stabilized stannylumylidene, $[\text{Mes}^{\text{Ter}}\text{Sn}(\text{IMe}_4)_2][\text{BArF}]$, (Mes^{Ter} = 2,6-Mes₂C₆H₃, Mes = 2,4,6-Me₃-C₆H₂, IMe₄ = 1,3,4,5-tetramethylimidazol-2-ylidene, BArF = (3,5-(CF₃)₂-C₆H₅)₄B), was isolated from the reaction of (Mes^{Ter})SnCl with two equivalents of IMe₄, followed by one equivalent of Na[BArF]. This stannylumylidene acts as a precatalyst for the homogeneous hydrosilylation of CO₂. Experimental mechanistic studies and quantum chemical calculations have been conducted to elucidate the catalytically active species and the mechanism for the transformation, revealing the stannylumylidene $[\text{Mes}^{\text{Ter}}\text{Sn}(\text{CO}_2\text{IMe}_4)_2][\text{BArF}]$, which is formed in the presence of CO₂, as the catalytically active species.

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CO₂ hydrosilylation catalyzed by an N-heterocyclic carbene (NHC)-stabilized stannylumidene†

Dechuang Niu,[†] Arseni Kostenko,[†] John A. Kelly,[†] Debotra Sarkar,[†] Huihui Xu[†] and Shigeyoshi Inoue[†]*

The di-N-heterocyclic carbene (NHCs) stabilized stannylumidene, $[\text{Mes}^{\text{Ter}}\text{Sn}(\text{IME}_4)_2][\text{BARf}]$, ($\text{Mes}^{\text{Ter}} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$, $\text{Mes} = 2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$, $\text{IME}_4 = 1,3,4,5\text{-tetramethylimidazol-2-ylidene}$, $\text{BARf} = (3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4\text{B}$), was isolated from the reaction of $(\text{Mes}^{\text{Ter}}\text{SnCl})$ with two equivalents of IME_4 , followed by one equivalent of $\text{Na}[\text{BARf}]$. This stannylumidene acts as a precatalyst for the homogeneous hydrosilylation of CO_2 . Experimental mechanistic studies and quantum chemical calculations have been conducted to elucidate the catalytically active species and the mechanism for the transformation, revealing the stannylumidene $[\text{Mes}^{\text{Ter}}\text{Sn}(\text{CO}_2\text{IME}_4)_2][\text{BARf}]$, which is formed in the presence of CO_2 , as the catalytically active species.

Introduction

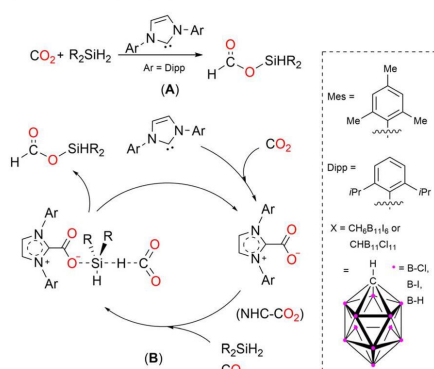
A major goal in contemporary chemical research is the utilization of carbon dioxide in the creation of fine chemicals, due to its high production/abundance and its status as a greenhouse gas. Recent advances in main group chemistry have seen the successful isolation of highly reactive compounds with unprecedented oxidation states and bonding modes, which in turn have demonstrated the remarkable capability of activating CO_2 .^{1–5} For example, silylenes can react with CO_2 yielding the corresponding silicon^{IV} carbonates $[\text{C}(\text{=O})(\text{O}-)]_2$.^{6,7} Germylene and stannylene species tend to afford E^{II} ($\text{E} = \text{Ge}$ and Sn) carboxylate compounds, owing to the weak nucleophilicity of their lone pair of electrons.^{8,9}

While main group-mediated CO_2 activation is becoming more commonplace, the catalytic transformation of carbon dioxide is still rare, especially when it comes to hydrosilylation reactions. Main-group catalysis has attracted tremendous attention recently, due to the higher abundance and lower toxicity of such elements. Currently, the most potent catalysts for the hydrosilylation of CO_2 using main group compounds are: Lewis bases (LBs), Lewis acids (LAs), and frustrated Lewis pairs (FLPs).¹ The use of N-heterocyclic carbenes (NHCs) as catalysts for the hydrosilylation of CO_2 was first reported by Zhang, Ying and coworkers (Fig. 1, A).¹⁰ Later, experimental and theoretical studies showed that the NHC-CO_2 adduct acts as the active catalytic species in the hydrosilylation of CO_2 , wherein

the Si-H bond is activated *via* coordination of the oxygen atom of the NHC-CO_2 adduct (Fig. 1, B).^{11,12}

Main-group Lewis acids have been shown to be capable of the catalytic hydrosilylation of CO_2 , examples include the silylium cation, C^{+3} and two-coordinate group 13 cations D, E, and F

(1) NHC catalyzed CO_2 hydrosilylation



(2) LA system for CO_2 hydrosilylation

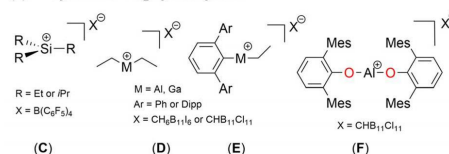


Fig. 1 (1) Proposed mechanism for NHC-catalyzed hydrosilylation of CO_2 ; (2) LA systems effective in CO_2 hydrosilylation.

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† Electronic supplementary information (ESI) available. CCDC 2255434, 2255353 and 2255355. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4sc07116f>



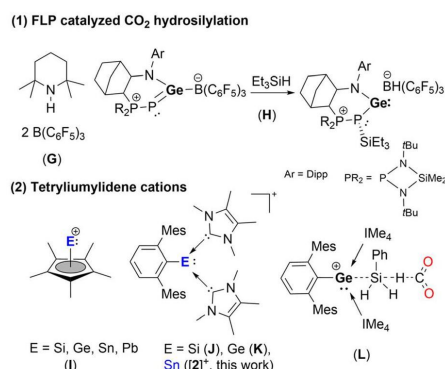


Fig. 2 (1) FLP systems; (2) heavier tetrelumylidene cations and K catalyzed CO₂.

(Fig. 1(2)).^{14–16} Okuda and coworkers found BPh₃ could catalyze the hydrosilylation of CO₂ to form silyl formate, but only in highly polar, aprotic solvents, such as acetonitrile.¹⁷ They posit the mechanism involves weak/dynamic coordination of BPh₃ to CO₂, as well as to the Si–H moiety, generating two partially polarized transient species.

Another pertinent contribution to main-group based catalysis was reported in 2009 by the Piers group, in which amine/borane FLP (Fig. 2, G) was effective in the hydrosilylation of CO₂.¹⁸ Since then, a multitude of various FLP catalytic systems have been reported, such as {[Tism^{Pribenz}]M} [HB(C₆F₅)₃] (M = Zn, Mg; Tism^{Pribenz} = tri[(1-isopropylbenzimidazol-2-yl)-dimethylsilyl]methyl)^{19,20} and [(^{Dipp}PPnacnac)Ga(Ad)] [HB(C₆F₅)₃] (^{Dipp}PPnacnac = [(N(Dipp)CMe)₂CH][−], Dipp = 2,6-diisopropylphenyl, Ad = 1-adamantyl).²¹ A noteworthy example from the Kato group is an N,P-heterocyclic germylene/B(C₆F₅)₃ Lewis pair that can be used as a catalyst for the selective CO₂ hydrosilylation to H₂C(OSiEt₃)₂, through Si–H bond activation to give the highly reactive cationic (amino)(phosphino) germylene with HB(C₆F₅)₃[−] as a counter anion, followed by activation of CO₂ (Fig. 2, H).²²

An emerging class of compounds that is of high interest to main group chemists, from the point of view of their catalytic capabilities, are the tetrelumylidenes. Tetrelumylidenes (RE⁺), are mono-substituted E^{II} (E = Si, Ge, Sn, Pb) atoms with a lone pair of electrons and two vacant orbitals, that exhibit high reactivity due to their unsaturated and amphiphilic nature.^{4,23,24} There has been a growing number of reports of these compounds ever since the first was reported by Jutzi and coworkers,^{23,25} whereby they used pentamethyl-cyclopentadienyl to stabilize the heavier tetrelumylidenes (Fig. 2, I, Cp⁺E⁺, E = Si,²⁶ Ge,²⁷ Sn,²⁷ Pb;²⁸ Cp⁺ = Me₅C₅). These were shown to be able to activate small molecules (e.g., CO₂, H₂, N₂O, alkenes, ketones, etc.).²⁴ Silyliumylidene ions stabilized by Lewis bases (e.g., N-heterocyclic carbene (NHC) (J),²⁹ PMe₃) could reduce CO₂, resulting in the silylacylium ions, [RSi(O)(IME₄)₂]Cl (R = ^{Mes}Ter or Tipp, ^{Mes}Ter = 2,6-Mes₂-C₆H₃, Mes = 2,4,6-Me₃-C₆H₃, Tipp =

2,4,6-iPr₃-C₆H₂, IME₄ = 1,3,4,5-tetramethylimidazol-2-ylidene),^{30,31} via the initial coordination of the C atom to the Si center. We reported on the CO₂ insertion into the Si–C^{NHC} bond of the dicationic silicon^{IV} compound [^{Mes}Ter(IME₄)₂SiH][OTf]₂ (OTf = CF₃SO₃[−]).³²

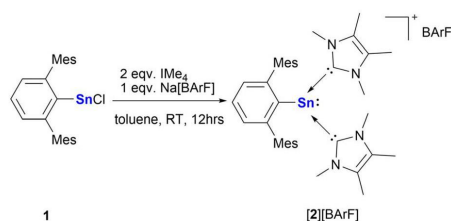
Recently, our group has isolated the germyliumylidene ion (K, Fig. 2), which was shown to react with N₂O to produce a germa-acylium ion [(^{Mes}Ter)Ge(O)(IME₄)₂]X (X = Cl or BARF, BARF = (3,5-(CF₃)₂C₆H₃)₄B).³³ This germa-acylium ion could then be utilized in the catalytic functionalization of CO₂, forming the catalytically active germylene, (^{Mes}Ter)Ge(OSiHPh₂)(IME₄). It is also worth noting that K catalyzes the reduction of CO₂ with silane via a three-component transition state (Fig. 2, L).³⁴ The mechanism is analogous to the cooperative silane/CO₂ mechanism for the hydrosilylation of CO₂ catalyzed by NHC (Fig. 1, B).¹²

The heavier tetrelumylidene analogues, i.e. stannylumylidene cations, are also an emerging class of low valent main group species that may have the potential to be used in catalysis. However, examples of the utilization of stannylumylidene in the activation of small molecules are rare. Herein, we present the first substantiated example of stannylumylidene acting as a catalyst for CO₂ hydrosilylation. We report the synthesis of the NHC-stabilized stannylumylidene [2]⁺ – the tin analogue of J and K, which reacts with CO₂ to form the catalytically active stannylumylidene [4]⁺. We present the mechanism of conversion of [2]⁺ to the catalytically active stannylumylidene species, isolating and fully describing the reactive intermediates of this process, as well as the catalytically active species. Additionally, we examine the catalytic performance of the stannylumylidene species in the catalytic hydrosilylation CO₂ using various silanes and conditions. Based on these studies and quantum chemical calculations we propose a mechanism for the catalytic reaction.

Results and discussion

Synthesis of stannylumylidene

NHC-stabilized stannylumylidene [^{Mes}TerSn(IME₄)₂][BARF] ([2][BARF]) was obtained by the reaction of chlorostannylene, ^{Mes}TerSnCl (1) with two equivalents of IME₄ in toluene, followed by adding one equivalent of Na[BARF] in a one-pot procedure (Scheme 1). It was isolated as a colorless crystalline solid in



Scheme 1 Synthesis of NHC-stabilized stannylumylidene ion [2][BARF].

a 72% yield. $[2][\text{BarF}]$ has poor solubility in nonpolar organic solvents, *e.g.*, benzene and toluene, but it is soluble in fluorobenzene and THF. In acetonitrile, substitution occurs between the Ime_4 and solvent molecules leading to a mixture of coordination compounds. This is in stark contrast to silyliumylidene (Fig. 2, J) and germyliumylidene ions (Fig. 2, K), where ligand substitution does not occur.^{29,33} In the $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum, one sharp signal was observed at $\delta = -235.72$ ppm in THF-d_8 , similar to the cationic stannylene, $[\text{Tip}^{\text{pp}}\text{TerSn}(\text{Ime}_2)_2][\text{HB}(\text{C}_6\text{F}_5)_3][\text{Tip}^{\text{pp}}\text{Ter} = 2,6\text{-Tip}_2\text{-C}_6\text{H}_3]$ ($\delta = -234$ ppm), reported by the Wesemann group.³⁵ The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum displays a resonance at $\delta = 170.18$ ppm for the carbon of Ime_4 , which is downshifted compared to that of the germyliumylidene (K) ($\delta = 164$ ppm) and the silyliumylidene (J) ($\delta = 160$ ppm).^{29,33}

X-ray quality crystals of $[2][\text{BarF}]$ were obtained from a toluene/fluorobenzene ($\text{C}_6\text{H}_5\text{F}$) solution stored at -35°C . Single crystal X-ray diffraction (SC-XRD) analysis revealed that the Sn central is tricoordinate with two Ime_4 moieties and one Mes^{Ter} -substituent (Fig. 3). The sum of the bond angles around the Sn1 atom is 300.4° . The Sn1–B1 distance is $8.587\text{ \AA}$, indicating no interaction between the cation and anion. Additionally, we found the shortest distance between the Sn atom and a fluorine atom at $4.032\text{ \AA}$. This also indicates there is no Sn–F interaction as the sum of the van der Waals radii of these atoms amounts to $3.56\text{ \AA}$ ($2.16\text{ \AA}$ for Sn and $1.40\text{ \AA}$ for F). The Sn–C^{NHC} bond distances are Sn1–C25 = $2.339(4)\text{ \AA}$ and Sn1–C32 = $2.308(4)\text{ \AA}$. They are similar to that found in $\text{IPr}_{\text{Me}}\text{SnCl}_2$ ($2.290(5)\text{ \AA}$) ($\text{IPr}_{\text{Me}} = 1,3\text{-diisopropyl-4,5-dimethylimidazol-2-ylidene}$).³⁶ $\text{IPr}_{\text{Me}}\text{Sn}[\text{C}(\text{Cl})\text{PMes}^*]_2$ ($\text{Mes}^* = 2,4,6\text{-tri-}t\text{-butylphenyl}$) ($2.316(2)\text{ \AA}$)³⁷ and slightly longer than $(\text{Dipp}^{\text{pp}}\text{Ter})\text{Sn}(\text{Ime}_4)\text{CH}_2\text{P}(\text{CH}_3)_2 = \text{P}^{\text{Mes}^{\text{Ter}}}$ ($2.274(3)\text{ \AA}$) ($\text{Dipp}^{\text{pp}}\text{Ter} = 2,6\text{-Dipp}_2\text{-C}_6\text{H}_3$, $\text{Dipp} = 2,6\text{-iPr}_2\text{-C}_6\text{H}_3$).³⁸ As expected, they are longer than the observed distances in the NHC-stabilized silyliumylidene ion (J) ($1.948(19)\text{ \AA}$, $1.966(19)\text{ \AA}$) and NHC-stabilized germyliumylidene ion (K) ($2.063(3)\text{ \AA}$, $2.093(3)\text{ \AA}$).

To gain further insight into the electronic structure of $[2]^+$, as well as to analyze the thermodynamics and kinetics in the processes involving this species, quantum chemical

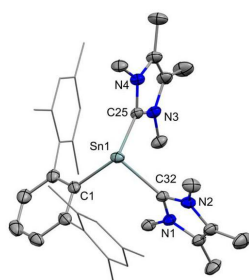


Fig. 3 The molecular structure of $[2]^+$. Ellipsoids are set at the 30% probability level; hydrogen atoms and $[\text{BarF}]^-$ anion are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1–C1 $2.244(4)$, Sn1–C32 $2.308(4)$, Sn1–C25 $2.339(4)$, C1–Sn1–C25 $107.7(1)$, C1–Sn1–C32 $96.7(1)$, C25–Sn1–C32 $96.0(1)$.

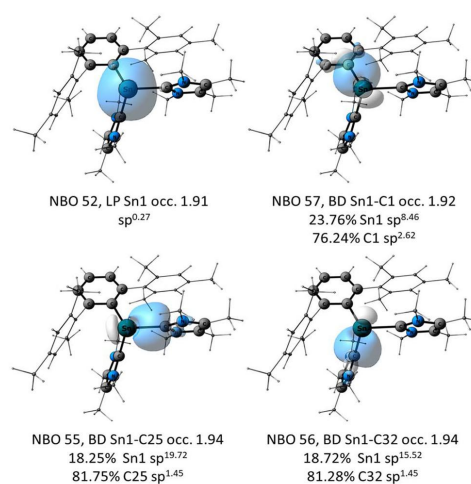
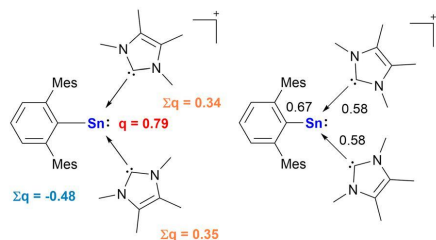
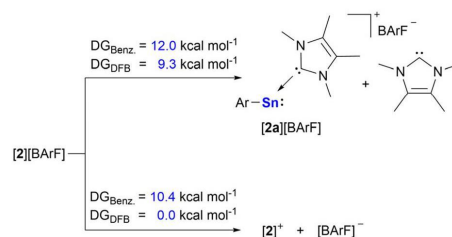


Fig. 4 NBOs of $[2]^+$ (iso = 0.04) at the PBE0/def2-TZVP//r2SCAN-3c level of theory. The mesityl substituents and the methyl substituents are shown as wireframes for clarity.

calculations were carried out. For details regarding the computational methods see the ESI† Natural Bond Orbital (NBO) analysis of the optimized structure of $[2]^+$ (Fig. 4) shows that the stannylumylidene cation exhibits the expected bonding situation around the tin center with a σ -type lone pair of electrons at Sn (NBO 55), and a polarized Sn–C^{ar} bond (NBO 57) with Wiberg Bond Index (WBI) of 0.67. The bonding between the Sn1 and C25 (of Ime_4) where the WBI = 0.58, indicates a very polarized bonding interaction with electron density of 18.25% on Sn and 81.75% on C (NBO 55). This type of polarization, as well as the $\text{sp}^{1.45}$ hybridization of the carbon, which interacts with the almost pure p orbital of Sn ($\text{sp}^{19.72}$), can be interpreted as carbene coordination to the empty p-orbital of the Sn center. The situation is almost identical to that of the second carbene (Sn1–C32, NBO 56), in terms of bond polarization, hybridization of the interacting orbitals and the WBI (0.58) (Fig. 5). The Sn center of $[2]^+$ is positively charged by 0.79 el. The aryl moiety of $[2]^+$ withdraws substantial electron density being negatively charged with -0.48 el., while the Sn center is compensated by the donation from the NHC moieties with the sum of NPA charges of $+0.34$ and $+0.35$ el. In addition to the $[2]^+$ representation as a bis(NHC)-stabilized stannylumylidene – with dative bonds between the NHC ligands and the Sn atom – the NBO depiction may also hint at the stannyl anion character of the Sn center. In this case, the ionic representation of $[2]^+$, where the negative charge is located on the Sn atom to which the two positively charged NHC moieties are bound covalently, should be considered. A detailed discussion of such stannyl-anion-type species is given in the ESI (Fig. S55 and S56†).

The frontier orbitals of $[2]^+$ are presented in Fig. 6. According to the NBO analysis of the canonical MOs, the HOMO has 52%

Fig. 5 NPA charges and WBIs in $[2]^+$.Scheme 2 Calculated free energies for anion-cation interaction and for NHC dissociation in $[2][BArF]$.

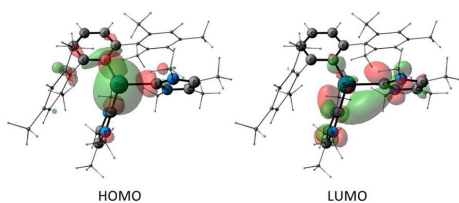
non-bonding and 43% bonding character and consists mostly of the non-bonding lone pair of electrons at Sn (51%). Additional important contributions arise from the Sn-Ar and Sn- IMe_4 bonding interactions (Sn-C1 (16%) and Sn-C25 (7%)). The LUMO is 73% anti-bonding and 19% non-bonding with the most significant contributions from $\pi^*(N3-C25)$ 25%, $\pi^*(N1-C32)$ 21%, $\sigma^*(Sn1-C1)$ 11%, $\sigma^*(Sn1-C32)$ 7%.

Calculations at the PW6B95-D4/def2-QZVPP(CPCM)/ r^2 SCAN-3c level of theory show that the anion-cation interaction in $[2][BArF]$ is weak, and only 10.4 and 0.0 kcal mol $^{-1}$ are required to fully separate the ions in benzene and difluorobenzene, respectively (Scheme 2). The charge transfer in $[2][BArF]$ between $[2]^+$ cation ($\Sigma q_{NPA} = +0.98$ el.) and the $[BArF]^-$ anion ($\Sigma q_{NPA} = -0.98$ el.) is negligible. The Sn- IMe_4 bonding is also quite labile, with a dissociation free energy for $[2][BArF]$ to form $[2a][BArF]$ and free NHC of 12.0 and 9.3 kcal mol $^{-1}$ in benzene and difluorobenzene, respectively (Scheme 2). This bond lability may imply that $[2][BArF]$ may be capable of reacting as a two coordinated stannylumylidene, upon dissociation of an IMe_4 ligand in solution.

Hydrosilylation of CO $_2$ by stannylumylidene

Inspired by the successful hydrosilylation of CO $_2$ catalyzed by germyliumylidene (**K**),³⁴ we attempted to investigate the catalytic potential of $[2][BArF]$ in the same reaction.

We found the optimal conditions for the catalytic reaction of CO $_2$ and diphenylsilane at room temperature in the presence of 5 mol% $[2][BArF]$ in the C $_6$ D $_6$:C $_6$ H $_5$ F (4:1) solvent mixture. According to the 1 H NMR spectrum, the consumption of the

Fig. 6 Frontier molecular orbitals of $[2]^+$ (iso = 0.04) at the PBE0/def2-TZVP// r^2 SCAN-3c level of theory. The mesityl substituents and the methyl substituents are shown as wireframes for clarity.

majority (94%) of the Ph $_2$ SiH $_2$ was observed within 25 hours, resulting in silyl formate, Ph $_2$ SiH(OCHO), which is then transformed into silylated methanol (Table 1, Entry 1) (Fig. S35†). The catalyst $[2][BArF]$ exhibited poor solubility in benzene, which led to lower catalytic efficiency (Table, Entry 2). To further investigate the impact of polar solvents on the CO $_2$ hydrosilylation catalyzed by $[2][BArF]$, 1,2-difluorobenzene (C $_6$ H $_4$ F $_2$) (Table 1, Entry 4) in different ratios with C $_6$ D $_6$ (Table 1, Entry 5) were selected as reaction solvents. The results indicated that polar solvents did not participate in the hydrosilylation reaction mechanism; their role was limited to enhancing the solubility of $[2][BArF]$. In comparison to fluorobenzene, the use of THF, a donor solvent, resulted in lower conversion (Table 1, Entry 3). Elevated temperature accelerated the catalytic rate, achieving 64% conversion in 2 hours (Table 1, Entry 6). However, the catalyst decomposed rapidly under these conditions (Fig. S40†).

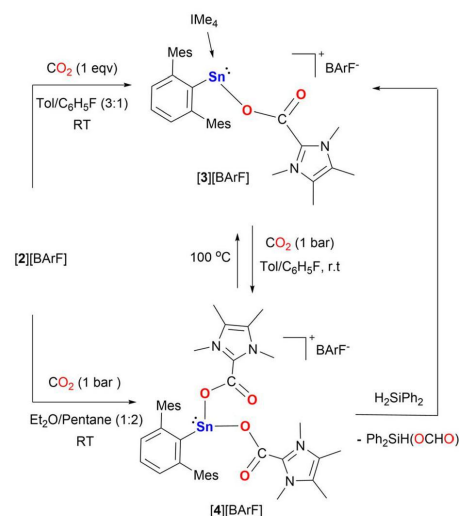
Scheme 3 Reactions of NHC-stabilized stannylumylidene ion $[2][BArF]$ with CO $_2$.



Table 1 Screening of the conditions for the hydrosilylation (H_2SiPh_2) of CO_2

$\text{CO}_2 + \text{H}_2\text{SiPh}_2 \xrightarrow[25 \text{ hours}]{\text{Cat. [2][BArF]}} \text{H}-\text{C}(=\text{O})-\text{O}-\text{SiHPh}_2$		
Entry	Deviation from the standard conditions ^a	Conversion ^b (%)
1	None	94
2	C_6D_6	78
3	THF-d_8	75
4	$\text{C}_6\text{D}_6/\text{C}_6\text{H}_5\text{F}$ (4 : 1)	97
5	$\text{C}_6\text{D}_6/\text{C}_6\text{H}_5\text{F}$ (1 : 1)	94
6	50 °C	64 (2 hours)
7	0.5 mol%	4
8	1 mol%	11
9	2.5 mol%	74
10	$[\text{2}][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$	70
11	$[\text{3}][\text{BArF}]^c$	92
12	$[\text{4}][\text{BArF}]^c$	93
13	IME_4 (10 mol%)	51
14	$\text{IME}_4\text{-CO}_2$ (10 mol%), $\text{C}_6\text{D}_6/\text{C}_6\text{H}_5\text{F}$ (1 : 1)	51
15	Hg^d	89

^a Standard reaction conditions: H_2SiPh_2 (80 μmol), 1,3,5-trimethoxybenzene (8 μmol , internal standard), and 5 mol% $[\text{2}][\text{BArF}]$ catalysis in C_6D_6 (0.32 mL) and $\text{C}_6\text{H}_5\text{F}$ (0.08 mL) under 1 bar CO_2 at RT for 25 hours. ^b NMR yield was monitored by ^1H NMR with methoxybenzene as an internal standard. ^c Refer to Scheme 3 for the synthesis of $[\text{3}][\text{BArF}]$ and $[\text{4}][\text{BArF}]$. ^d Hg to catalyst ratio 250 : 1.

Furthermore, to examine the effect the counter anion has on the conversion we performed this reaction under the same conditions with $[\text{2}][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$, and a decrease in activity was observed (Table 1, Entry 10). This decrease in catalytic activity could indicate that the very weak coordination strength between $\text{Al}(\text{ORf})_4^-$ and the Sn atom increases the electrophilicity of the Sn center, which suppresses NHC dissociation from Sn center, compared to BArF^- .³⁹ Furthermore, the hydrosilylation of CO_2 , catalyzed by the $[\text{2}][\text{BArF}]$, exhibited minimal perturbation in

the presence of excess mercury (Hg), strongly suggesting the nature of the catalytic cycle is homogeneous (Table 1, Entry 15).

In addition to diphenylsilane we tested the catalytic performance of $[\text{2}][\text{BArF}]$ toward a few other silanes (Table 2). In the case of HSiMe_2Ph (Table 2, Entry 2), the corresponding silyl formate is formed with a 47% conversion within 25 hours. The catalyst deactivated after consumption of 71% of phenylsilane within 12 hours (Entry 5). The more sterically demanding silanes, HSiPh_3 and HSiEt_3 , were less effective in the hydrosilylation of CO_2 even at elevated temperatures (Table 2, Entries 4 and 5).

$[\text{2}][\text{BArF}]$ demonstrated superior performance in CO_2 hydrosilylation compared to certain Lewis acids, such as $[\text{Et}_3\text{Al}]^+$ and $[\text{Et}_3\text{Si}]^+$.¹⁴ However, it was slightly less effective than $[(2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{O})_2\text{Al}]^+$, $[2,6\text{-Ph}_2\text{C}_6\text{H}_3\text{AlEt}]^+$, and $[(2,6\text{-Dipp}_2\text{C}_6\text{H}_3)\text{GaEt}]^+$ at elevated temperatures, which produced methane, toluene, and diphenylmethane as products.^{15,16} $[\text{2}][\text{BArF}]$ was less effective than some FLP catalytic systems, such as the N,P-heterocyclic germylene/B(C_6F_5)₃ pair (**H**),²² and $[\text{TismPriBenz}]\text{M}[\text{HB}(\text{C}_6\text{F}_5)_3]$ ($\text{M} = \text{Zn}, \text{Mg}$),¹⁹ which selectively produced bis(silyl)acetals or methane. Its performance was comparable to that of germa-acylium ions and germilyumylidene (**L**), which yielded silyl formate, bis(silyl)acetal, and silylated methanol.^{33,34}

Although $[\text{2}][\text{BArF}]$ exhibits moderate catalytic ability for CO_2 hydrosilylation, its ability to selectively reduce CO_2 to silyl formate in a one-step process is valuable for studying the mechanism of CO_2 hydrosilylation.

Mechanistic studies

To study the mechanism of the hydrosilylation of CO_2 catalyzed by $[\text{2}][\text{BArF}]$, stoichiometric reactivity studies were conducted. Exposing $[\text{2}][\text{BArF}]$ to 1 equivalent of CO_2 in toluene: $\text{C}_6\text{H}_5\text{F}$ (3 : 1) at room temperature, afforded the mono-insertion product $[\text{Mes-TerSn}(\text{CO}_2\text{IME}_4)\text{IME}_4][\text{BArF}]$, $[\text{3}][\text{BArF}]$, after 4 hours. It bears one CO_2 molecule inserted between the Sn center and one of the IME_4 ligands. It has increased solubility in nonpolar organic solvents such as benzene and toluene compared to $[\text{2}][\text{BArF}]$. The $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of $[\text{3}][\text{BArF}]$ shows a resonance at $\delta = -10.61$ ppm, which is downfield shifted compared to $[\text{2}][\text{BArF}]$, due to the Sn being bound to the more electro-negative oxygen atom. The $^{13}\text{C}\{^1\text{H}\}$ resonance of the corresponding carboxylate ($\text{IME}_4\text{-C}(\text{O})\text{OSn}$) appears at $\delta = 157.48$ ppm (THF-d_8), which is comparable to the reported NHC- CO_2 adducts, *i.e.*, IPrCO_2 ($\text{IPr} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazole-2-ylidene}$) ($\delta = 152.3$ ppm, CD_2Cl_2), IMECO_2 ($\text{IME} = 1,3\text{-dimethylimidazolium}$) ($\delta = 158$ ppm, D_2O),⁴⁰ ItBuCO_2 ($\text{ItBu} = 1,3\text{-di-tert-butyl-4,5-dimethylimidazolin-2-ylidene}$) ($\delta = 160$ ppm, CD_2Cl_2), IME_4CO_2 ($\delta = 155.9$ ppm, CD_2Cl_2).⁴¹

The SC-XRD analysis of $[\text{3}][\text{BArF}]$ revealed that the central Sn is tricoordinate with an IME_4 ligand, a terphenyl substituent, and an imidazolium carboxylate (Fig. 7(a)). The Sn1-O1 bond length of 2.231(2) Å is longer than that of the reported Gibson's ($^{\text{Dipp}}\text{nacnac}$) $\text{SnO}(\text{iPr})$, (2.000(5) Å),⁴² tin-carbamate complex ($^{\text{Dipp}}\text{nacnac}$) $\text{SnOC}(\text{O})\text{N}(\text{iPr}_2)$ (2.1346(16) Å)⁴³ and shorter than ($\text{Ar}^{\text{NET}_2}\text{Ge})(\mu\text{-}k^1(\text{C})\text{-}k^2(\text{O},\text{O}')\text{-CO}_2)(\text{SnAr}^{\text{NET}_2})$ (2.301(3), 2.336(3) Å),

Table 2 Screening of the silanes for the hydrosilylation of CO_2

$\text{CO}_2 + \text{HSiR}_3 \xrightarrow[\text{C}_6\text{D}_6 / \text{C}_6\text{H}_5\text{F}, \text{RT}]{\text{Cat. [2][BArF]}} \text{H}-\text{C}(=\text{O})-\text{O}-\text{SiR}_3$				
Entry	Silanes ^a	T (°C)	Time (h)	Conversion ^b (%)
1	H_2SiPh_2	RT	25	94
2	HSiMe_2Ph	RT	25	47
3	H_3SiPh	RT	12 ^c	71
4	HSiEt_3	60	25	29
5	HSiPh_3	80	— ^d	—

^a Standard reaction conditions: H_2SiPh_2 (80 μmol), 1,3,5-trimethoxybenzene (8 μmol , internal standard), and 5 mol% $[\text{2}][\text{BArF}]$ catalysis in C_6D_6 (0.32 mL) and $\text{C}_6\text{H}_5\text{F}$ (0.08 mL) under 1 bar CO_2 at RT for 25 hours. ^b NMR yield was monitored by ^1H NMR with methoxybenzene as an internal standard. ^c Refer to Scheme 3 for the synthesis of $[\text{3}][\text{BArF}]$ and $[\text{4}][\text{BArF}]$. ^d Hg to catalyst ratio 250 : 1.

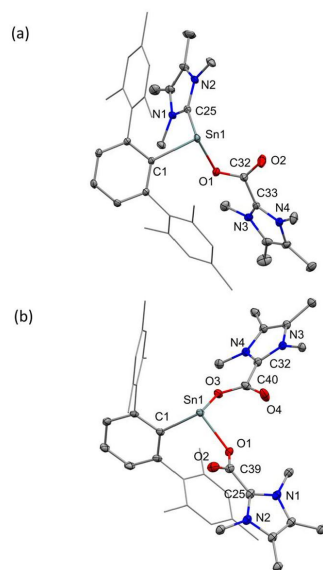


Fig. 7 Molecular structures of $[3]^+$ (a) and $[4]^+$ (b) in the solid state. Ellipsoids are set at the 30% probability level; hydrogen atoms and counterions are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: $[3]^+$ C1–Sn1 2.237(3), C25–Sn1 2.283(3), O1–Sn1 2.231(2), O1–C32 1.263(4), C32–O2 1.211(4), C32–C33 1.508(5), C1–Sn1–C25 96.3(1), C1–Sn1–O1 93.38(9), C25–Sn1–O1 86.39(9). $[4]^+$ C1–Sn1 2.231(2), Sn1–O1 2.168(2), O1–C39 1.270(3), O2–C39 1.223(3), C39–C25 1.450(1), Sn1–O3 2.230(2), O3–C40 1.279(2), C40–O4 1.220(3), C40–C32 1.522(5), C1–Sn1–O1 96.41(7), C1–Sn1–O3 90.89(7), O1–Sn1–O3 90.12(6).

(Ar^{NET2} = [2,6-(Et₂NCH₂)₂C₆H₃]).⁴⁴ The C–O bond lengths (C39–O1 = 1.263(4), C39–O2 = 1.211(4) Å) with the C–O moiety bound to the Sn center being the longer of the two, are longer than those in free CO₂ (1.16 Å). This is also in the same range as other imidazolium carboxylates,⁴⁵ IPrCO₂ (1.221(4) and 1.225(4) Å)⁴⁶ and ItBuMe₃-CO₂-B(C₆F₅)₃ (ItBuMe₃ = 1,3-di-*tert*-butyl-4,5-dimethylimidazolin-2-ylidene) (1.302(3) and 1.211(3) Å).⁴⁶ The C–C bond length between the IMe₄ and CO₂ is 1.508(5) Å in $[3]$ [BArF], which is close to the reported imidazolium carboxylates,^{41,45,46} IPrCO₂ (1.511(4) Å), IMe₄CO₂ (1.521 Å) and IEtMe₃CO₂ (IEtMe₃ = 1,3-diethyl-4,5-methyl-imidazolium) (1.535(15) Å). In addition, the carboxylic carbon atoms exhibit a trigonal-planar coordination environment, with the bond angles of 126.5(3)° for O1–C32–O2, 116.3(3)° for C33–C32–O2 and 117.0(3)° for C33–C32–O1.

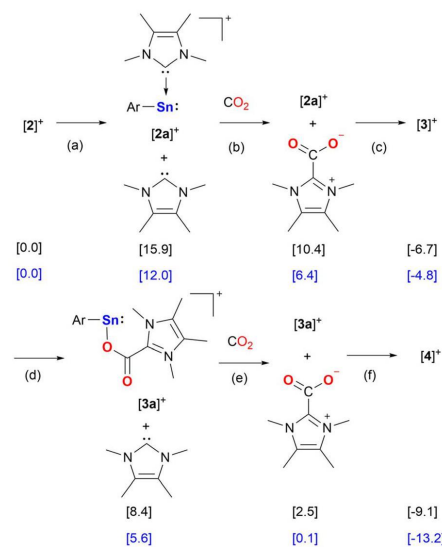
The addition of excess CO₂ (1 bar) to a solution of $[2]$ [BArF] in Et₂O and pentane at room temperature results in the doubly CO₂ inserted product [Me₃TerSn(CO₂IMe₄)₂] [BArF], $[4]$ [BArF], after 21 hours. Yellow crystals suitable for SC-XRD were obtained from an Et₂O/pentane (1 : 2) solution stored at –35 °C under a CO₂ atmosphere. The ¹¹⁹Sn{¹H} NMR spectrum of $[4]$ [BArF], shows a sharp singlet signal at δ = 55.9 ppm, which is

shifted downfield compared to $[2]$ [BArF] and $[3]$ [BArF], due to the Sn center now being bound to two electronegative O atoms. The resonance of the carboxyl carbon atom appears at δ = 157.48 ppm in the ¹³C{¹H} NMR spectrum, which is consistent with $[3]$ [BArF]. The SC-XRD of $[4]$ [BArF] (Fig. 7(b)) shows that the bond lengths of Sn1–O1 and Sn1–O3 are 2.168(2) Å and 2.230(2) Å, respectively. The C–O bond lengths are as follows: C39–O1 (1.270(3) Å), C40–O3 (1.279(2) Å) and C39–O2 (1.223(3) Å), C40–O4 (1.220(3) Å). The lengths of C–C bonds between the IMe₄ carbon and the CO₂ group C39–C25 (1.450(1) Å) and C40–C32 (1.522(5) Å) are different compared to $[3]$ [BArF] (1.508(5) Å), but comparable to imidazolium carboxylates.^{41,45,46}

The isolation of large quantities of pure solid $[4]$ [BArF] is not possible as it decomposes to $[3]$ [BArF] under reduced pressure *via* the release of one molecule of CO₂.

To study the stability of $[4]$ [BArF] in solution, ¹H NMR-monitoring experiments were conducted in a toluene-*d*₈/C₆H₅F solution under a CO₂ atmosphere (Fig. S29†). At 100 °C, $[4]$ [BArF] slowly converts to $[3]$ [BArF], releasing one equivalent of CO₂. Leaving the sample at ambient temperature for 15 hours resulted in the reformation of $[4]$ [BArF].

Calculations at the PW6B95-D4/def2-QZVPP(CPCM)/r²SCAN-3c level of theory show that the likely scenario for the formation of $[3]$ [BArF] and $[4]$ [BArF] is a stepwise reaction, in which the consecutive dissociation of a IMe₄ ligands from the Sn center of $[2]$ [BArF] occurs (Scheme 4). The IMe₄ ligands react with carbon dioxide to form the imidazolium carboxylates and reassociate with the Sn complex (Scheme 4). The IMe₄ dissociation from $[2]$



Scheme 4 Calculated pathway and relative Gibbs energies for the reaction of $[2]^+$ with CO₂ to give $[3]^+$ and $[4]^+$ (black). Gibbs energies for the reactions including the counter anion, relative to $[2]$ [BArF] are shown in blue.

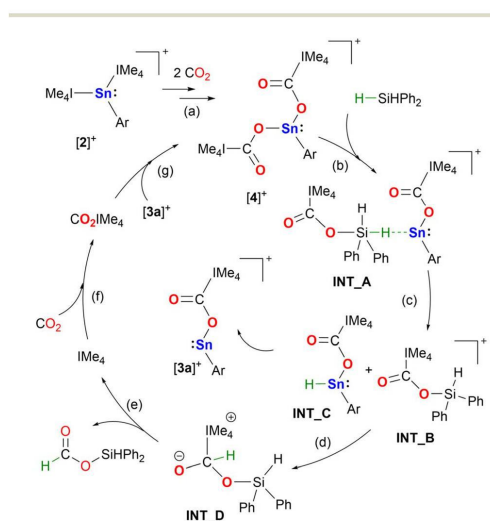
[BARF] is endergonic by 12.0 kcal mol⁻¹ and proceeds without a barrier yielding [2a][BARF] and free IMe₄ (Scheme 4, path (a)). The IMe₄ reacts with a molecule of CO₂ to form the IMe₄-CO₂ imidazolium carboxylate at 6.4 kcal mol⁻¹ (Scheme 4, path (b)). The barrier for the reaction of IMe₄ with CO₂ is only 9.3 kcal mol⁻¹. [3][BARF] forms upon barrierless association of IMe₄-CO₂ with [2a][BARF] at -4.8 kcal mol⁻¹ (Scheme 4, path (c)). We also considered a mechanism in which [2][BARF] reacts with CO₂ concertedly, without IMe₄ dissociation, to give [3][BARF]. However, this scenario requires overcoming a barrier of 29.6 kcal mol⁻¹ (Fig. S57†). The formation of [4][BARF] proceeds *via* similar steps from [3][BARF], *i.e.* dissociation of the IMe₄ from [3][BARF] giving [3a][BARF] + IMe₄ at 5.6 kcal mol⁻¹ (Scheme 4, path (d)), followed by the formation of the imidazolium carboxylate at 0.1 kcal mol⁻¹ (Scheme 4, path (e)), and finally association of [3a][BARF] with IMe₄-CO₂ to give [4][BARF] at -13.2 kcal mol⁻¹ (Scheme 4, path (f)).

Notably, comparison of the spectroscopic data indicated the formation of [3][BARF] and [4][BARF] during the [2][BARF] catalyzed hydrosilylation of CO₂ (Fig. S35†). Furthermore, [4][BARF] could be converted to [3][BARF] by adding Ph₂SiH₂ under an argon atmosphere, with the simultaneous formation of silyl formate (Fig. S31†). DFT calculations for the proposed mechanism of this transformation were performed (see Fig. S58†). Conversely, [3][BARF] decomposed to unidentified compounds when treated with Ph₂SiH₂ at room temperature. Both [3][BARF] and [4][BARF] are efficient catalysts for CO₂ hydrosilylation (Table 1, Entries 11 and 12), comparable to the performance of [2][BARF]. Thus, we propose [4][BARF] as the resting state of the active cycle. Furthermore, control experiments using IMe₄ and IMe₄-CO₂ as catalysts both show lower conversion (Table 1,

Entries 13 and 14), suggesting that these compounds are not the catalytically active species.

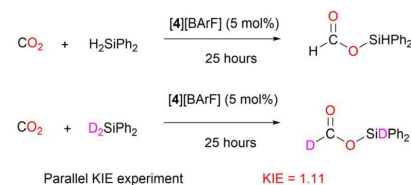
Based on our reactivity studies and the quantum chemical calculations (Scheme 4, Fig. S57 and S58†) a mechanism for the catalytic hydrosilylation of CO₂ using [2][BARF] is proposed (Scheme 5). Under catalytic conditions, the stannylumylidene [2]⁺ reacts with two equivalents of carbon dioxide to form the double insertion product, [4]⁺, *via* [3]⁺, as described above (Scheme 5, step (a)). Compound [4]⁺ reacts with a molecule of diphenylsilane to form intermediate INT_A (Scheme 5, step (b)), which dissociates to the ((silylcarbonyl)oxy)imidazolium intermediate (INT_B) and the stannyl hydride (INT_C). The former can abstract a hydride from the stannyl hydride, releasing the tin complex [3a]⁺ and forming a zwitterionic adduct, INT_D (Scheme 5, step (d)). This type of adduct is well known in NHC organocatalysis, as similar species can form upon the reaction of NHC with an aldehyde, which can later convert to amino enols, known as Breslow intermediates.⁴⁷ In this case the reverse reaction of the zwitterionic adduct releasing the diphenylsilyl formate product, and the NHC (Scheme 5, step (e)). The NHC reacts with an additional equivalent of CO₂ forming the imidazolium carboxylate (Scheme 5, step (f)), which reassociates with tin complex [3a]⁺ to regenerate the starting compound [4]⁺ (Scheme 5, step (g)).

In addition to the isolation of the two key intermediates of the catalytic cycle ([3][BARF] and [4][BARF]) and the quantum chemical calculations, we carried out additional experiments (Scheme 6), using deuterated silanes (D₂SiPh₂), to support the reaction mechanism proposed. Under standard conditions, the rate of the reactions with H₂SiPh₂ and D₂SiPh₂ were compared, giving a kinetic isotope effect (KIE) of 1.11 (Scheme 6, (a)). This value indicates a secondary isotope effect, which is consistent with the rate-determining transition state TS4 in the proposed mechanism (Fig. S58†), in which the H/D atom is a substituent on carbon from which the NHC moiety is dissociated.⁴⁸

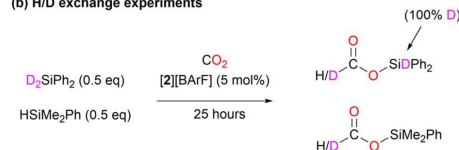


Scheme 5 Proposed catalytic cycle of hydrosilylation of carbon dioxide by diphenylsilane in the presence of stannylumylidene [2]⁺.

(a) Kinetic isotope effect (KIE)



(b) H/D exchange experiments



Scheme 6 Mechanistic studies.





Furthermore, CO₂ hydrosilylation catalyzed by [2][BARF] was performed in the presence of 1:1 mixture of D₂SiPh₂ and HSiMe₂Ph (Scheme 6, (b)). H/D exchange was observed at the carbon center, supporting the formation of the tin-hydride intermediate INT_C (Scheme 5) in the proposed catalytic cycle.⁴⁹ This intermediate can form either *via* deuterium abstraction from D₂SiPh₂ or *via* hydrogen abstraction from HSiMe₂Ph. Subsequently, INT_C, whether D/H-substituted, can transfer deuterium or hydrogen to the ((silylcarbonyl)oxy)imidazolium INT_B, which can also form in the previous step from either D₂SiPh₂ or HSiMe₂Ph. The H/D transfer from INT_C to INT_B will ultimately produce Ph₂SiD(OCDO), Ph₂SiD(OCHO), Me₂PhSi(OCDO), and Me₂PhSi(OCHO).

Conclusions

In summary, we reported on the synthesis of a di-NHCs-stabilized stannylidene [2][BARF], which can act as an efficient carbon dioxide hydrosilylation catalyst under ambient conditions. Both experimental and computational studies have been performed to elucidate the reaction mechanism, revealing it to be distinct from those previously proposed for the lighter germlylidenes.³⁴ In the latter case, [Me^{ter}Ge(IME₄)₂]⁺ (K, Fig. 2) was identified as the active catalytic species, with the Si-H bond activation occurring through coordination with the germanium lone pair (L, Fig. 2), which constitutes the rate-determining step. In comparison to K, [2][BARF] captures CO₂ *via* dissociation of NHC, followed by reassociation of the NHC-CO₂ moiety to the Sn center, forming the catalytically active species, [4][BARF]. This divergent mechanism is another example of how the lighter and heavier congeners can behave differently and is something we hope to exploit in our further studies in applying tetrylidenes to catalytic transformations.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

D. N. and D. S. carried out the synthetic and reaction studies, and D. N. wrote the original draft. A. K. carried out the computational studies. J. A. K. conducted the crystallographic studies. A. K., J. A. K., H. X., and D. S. reviewed and edited the draft. S. I. managed the project.

Conflicts of interest

There are no conflicts to declare.

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5. Terphenyl Amido Stannylene-NHC Adduct: A Catalyst for the Hydrosilylation of Aldehydes and Ketones

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Author: Dechuang Niu, John A. Kelly, Fiona J. Kiefer, Arseni Kostenko, and Shigeyoshi Inoue*

Content: The terphenyl amido stannylene-NHC adducts, $\text{HMDS}^{(\text{MesTer})}\text{Sn}(\text{NHC})$, (MesTer = 2,6-Mes₂C₆H₃, Mes = 2,4,6-Me₃-C₆H₂, HMDS = N(SiMe₃)₂, NHC = IMe₄, IEt, IMe₄ = 1,3,4,5-tetramethylimidazol-2-ylidene, IEt = 1,3-diethyl-4,5-dimethylimidazol-2-ylidene), were reacted with benzaldehyde resulting forming $\text{HMDS}^{(\text{MesTer})}\text{Sn}(\text{OCH}(\text{Ph})\text{NHC})$. In the presence of acetophenone, deprotonation occurs to afford the tin enolate, $(\text{MesTer})\text{Sn}(\text{NHC})(\text{OPhC}=\text{CH}_2)$, via the release of hexamethyldisilamine. This stannylene-NHC adduct is a catalyst for the homogeneous hydrosilylation of aldehydes and ketones under ambient conditions.

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ARTICLE

Terphenyl Amido Stannylene-NHC Adduct: A Catalyst for the Hydrosilylation of Aldehydes and Ketones

Dechuang Niu, John A. Kelly, Fiona J. Kiefer, Arseni Kostenko, and Shigeyoshi Inoue*

Dedicated to Professor Hubert Schmidbaur on the occasion of his 90th birthday

Abstract: The terphenyl amido stannylene-NHC adducts, HMDS^(MesTer)Sn(NHC), (^{MesTer} = 2,6-Mes₂C₆H₃, Mes = 2,4,6-Me₃-C₆H₂, HMDS = N(SiMe₃)₂, NHC = IMe₄, IEt, IMe₄ = 1,3,4,5-tetramethylimidazol-2-ylidene, IEt = 1,3-diethyl-4,5-dimethylimidazol-2-ylidene), were reacted with benzaldehyde resulting forming HMDS^(MesTer)Sn(OCH(Ph)NHC). In the presence of acetophenone, deprotonation occurs to afford the tin enolate, (^{MesTer}Sn(NHC)(OPhC=CH₂), via the release of hexamethyldisilamine. This stannylene-NHC adduct is a catalyst for the homogeneous hydrosilylation of aldehydes and ketones under ambient conditions.

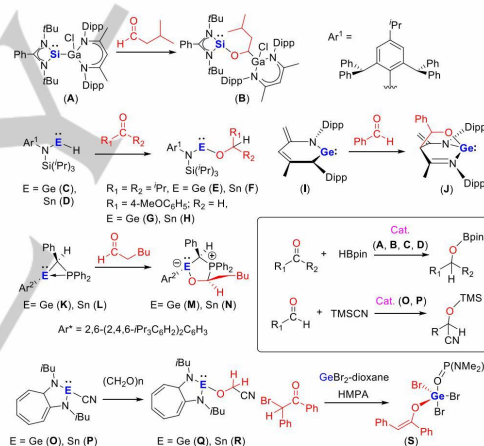
Introduction

The activation of small molecules and subsequent catalytic transformations utilizing main-group-element compounds has seen significant growth in the past half century.^[1] The oxidative addition of small molecules is a crucial step in catalytic cycles, and studying this process can offer deeper insights into catalytic mechanisms.^[2] Low oxidation state group 14 compounds have shown such reactivity, for example, various silylenes have been shown to activate ketones and aldehydes, yielding diverse products depending on the structures of silylenes and ketone substrates.^[3] Recently, an acyclic metallasilylene L*(Cl)GaSiL (A), L* = HCl[C(Me)NDipp]₂, Dipp = 2,6-*i*-Pr₂C₆H₃; L = PhC(N^tBu)₂, reacted with isovaleraldehyde to produce the alkoxysilylene, LSIOCH[Ga(Cl)L*]CH₂CHMe₂ (B), which was shown to be an active hydroboration catalyst.^[4]

The activation of aldehydes and ketones by germynes and stannylenes, have also been reported. A notable example of such reactivity is the bulky amido-substituted two-coordinate germanium (C) and tin hydrides (D) reported by Jones and coworkers. These compounds undergo insertion of the aldehyde/ketone moiety into the E-H bond, producing alkoxides (E, F, G, H).^[5] Kinetic experiments and theoretical studies suggested that the alkoxide intermediate is the resting state in the

hydroboration of aldehydes and ketones.^[6] The reaction of *N*-heterocyclic ylide-like germylene (I) with benzaldehyde yielded the [4+2] cycloaddition product (J), proposed as a crucial intermediate in the catalytic hydroboration of aldehydes.^[7] Germylene, K and stannylene, L reacted with hexanal yields cyclic addition products (M, N) stabilized by the intramolecular phosphine moiety.^[8]

1) Selected reactions of tetrelenes with ketones and aldehydes and catalytic reactions



2) Hydrosilylation of ketones and aldehydes by NHC stabilized stannylene (This work)

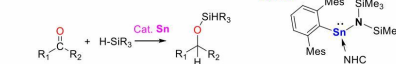


Figure 1. Selected tetrelenes activation towards ketones and aldehydes.

Nagendran and co-workers introduced germylene, O^[9] and stannylene, P^[10] cyanides, using them for the cyanosilylation of aldehydes. Stoichiometric reactions of O/P with aldehydes led to the isolation of the corresponding cyanogermylated (Q) and cyanostannylated (R) products, considered intermediates in the cyanosilylation cycle. Gerny enolate, S was isolated from the treatment of α,β-unsaturated or α-bromo ketones with germanium (II) salts, serving as an intermediate in the aldol reaction.^[11]

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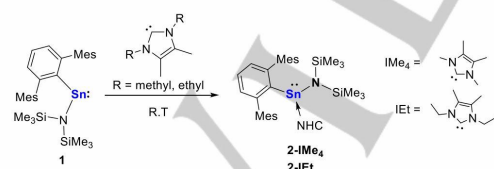
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ARTICLE

The hydrosilylation of carbonyl groups is an industrially significant synthetic transformation that yields alkoxy silane products. These products serve as valuable synthetic intermediates and monomers for organosilane polymers and materials. Despite its importance, catalytic hydrosilylation reactions of carbonyl compounds using tetrylenes remain rare. Herein, we present the synthesis of terphenyl/amido stannylene-NHC adducts, HMDS(^{Mes}Ter)Sn(NHC) (^{Mes}Ter = 2,6-Mes₂C₆H₃, Mes = 2,4,6-Me₃-C₆H₂ (^{Mes}Ter = 2,6-Mes₂C₆H₃, Mes = 2,4,6-Me₃-C₆H₂, HMDS = N(SiMe₃)₂, NHC = IMe₄, IEt, IMe₄ = 1,3,4,5-tetramethylimidazol-2-ylidene, IEt = 1,3-diethyl-4,5-dimethylimidazol-2-ylidene), and its reactivity towards aldehydes and ketones. Subsequently, the catalytic activity of this stannylene-NHC adduct for the hydrosilylation of aldehydes and ketones was also demonstrated.

Results and Discussion

Addition of NHC to amido/terphenyl stannylene, HMDS(^{Mes}Ter)Sn (**1**)^[12] forms the stannylene-NHC adducts, HMDS(^{Mes}Ter)Sn(NHC), **2-IMe₄**, and **2-IEt** (Scheme 1). Notably, the choice of NHC significantly affects the stability of the target product. **2-IMe₄** is unstable in solution and decomposes to an intractable mixture of products after 4 hours at room temperature. In the ¹¹⁹Sn {¹H} NMR spectrum, one sharp signal was observed at δ = -15.5 ppm for **2-IMe₄** and δ = -0.1 ppm for **2-IEt**, which significantly upshifted compared to **1** (1192.8 ppm) and HMDS(^{Dipp}Ter)Sn (1196.8 ppm) reported by Power and co-workers (^{Dipp}Ter = 2,6-Dipp₂C₆H₃).^[13] Single crystals X-ray diffraction (SC-XRD) analysis of **2-IMe₄** revealed a tricoordinate stannylene structure, where the tin atom is bonded a ^{Mes}Ter substituent, amido ligand, and an IMe₄. The Sn-N bond length of 2.204(2) Å is slightly longer than that in compound **1** (2.097(3) Å) and HMDS(^{Dipp}Ter)Sn (2.094(5) Å).^[13] The Sn1-C1 distance 2.282(1) Å is comparable to those in **1** (2.246(3) Å) and HMDS(^{Dipp}Ter)Sn (2.225(5) Å). The Sn-C^{NHC} bond distances (Sn1-C25 = 2.328(1) Å) is similar to that found in IPrSnCl₂ (2.290(5) Å) (IPr = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene),^[14] and IPrSn[C(Ci)PMes*]₂ (2.316(2) Å) (Mes* = 2,4,6-tri-*tert*-butylphenyl).^[15]



Scheme 1. Synthesis of terphenyl/amido-stannylene-NHC adducts.

The reaction of **2-IEt** with benzaldehyde at room temperature yielded the insertion products, HMDS(^{Mes}Ter)Sn(OCH(Ph)IEt) (**3-IEt**) (Scheme 2). However, we could not isolate the corresponding product in the case of **2-IMe₄**. The ¹³C{¹H} and ¹H NMR spectra of

3-IEt showed signals at δ = 68.65 and 4.09 ppm for SnOCH, respectively, consistent with other aldehyde insertion products.^[3], 4, 8, 16] The ¹¹⁹Sn signal of **3-IEt** appeared at 148.7 ppm, significantly downshifted compared to **2-IEt** (0.06 ppm), due to the Sn being bound to the more electronegative oxygen atom. The solid-state structure of **3-IEt** revealed a pyramidal geometry at the Sn centre, with a sum of angles: 295°, suggesting the presence of a lone pair of electrons at the tin atom (Figure 3). The C-O bond length of 1.393(2) Å is much longer than a C=O double bond (1.2 Å), and within a similar range to C-O single bond (1.41 Å).^[16] The Sn-O bond is 2.136(1) Å, which is close to the cyclic stannylene addition product, **N** (*vide supra*) (Sn-O, 2.104 Å).^[8]

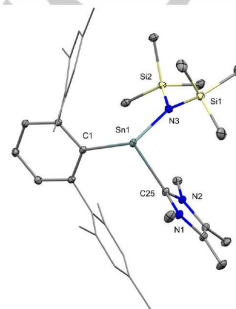
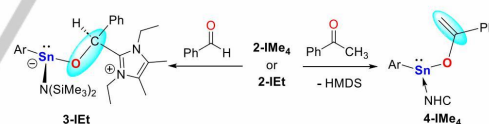


Figure 2. Molecular structures of **2-IMe₄** in the solid state.^[17] Ellipsoids are set at the 30% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1-C1 2.282(1), Sn1-N3 2.204(2), Sn1-C25 2.328(1), N3-Si1 1.735(1), N3-Si2 1.722(2), C1-Sn1-C25 102.65(2), C1-Sn1-N3 108.38(5), C25-Sn1-N3 90.37(5).



Scheme 2. The reactions of **2-IMe₄**/**2-IEt** with benzaldehyde and acetophenone.

When **2-IMe₄** was treated with acetophenone, it yielded the tin(II) enolate, ^{Mes}TerSn(IMe₄)(OPhC=CH₂) (**4-IMe₄**) via the release of hexamethyldisilamine (Scheme 2). The multinuclear NMR spectra and SC-XRD analysis of **4-IMe₄** confirmed the O-bound enolate structure. In the ¹H NMR spectrum, the terminal methylene group displayed two singlets at δ = 3.71 and 3.31 ppm, indicating their vinyl nature. The corresponding ¹³C{¹H} NMR resonance appears at δ = 81.1 ppm. In the ¹¹⁹Sn{¹H} NMR spectrum of **4-IMe₄**, a sharp signal as a singlet is observed at δ = -41 ppm.

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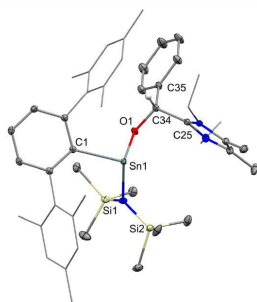


Figure 3. The molecular structure of **3-IEt** in the solid state. Ellipsoids are set at the 30% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1-O1 2.136(1), Sn1-N3 2.160(1), Sn-C1 2.286(2), C34-O1 1.393(2), C34-C35 1.529(2), Si-N3 1.719(1), Si2-N3 1.719(1), O1-Sn1-N3 91.38(4), O1-Sn1-C1 99.47(4), N3-Sn1-C1 104.18(5).

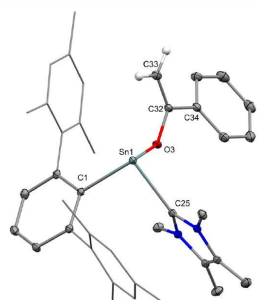


Figure 4. The molecular structure of **4-IME4** in the solid state. Ellipsoids are set at 30% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1-O3 2.096, C32-O3 1.344, C32-C33 1.345, C32-C34 1.493, C33-C32-O3 125.76, C33-C32-C34 121.20, C34-C32-O3 113.04.

The solid-state molecular structure of **4-IME4** revealed a tri-coordinated stannylene bonded to an IME_4 , an alkoxide, and a Mes^{Ter} ligand (Figure 4). The Sn-O bond distance, 2.093(2) Å, is slightly shorter than that in **3-IEt** (2.136(1) Å) and tin-carbamate complex ($[(\text{Dipp}^{\text{Ter}}\text{nacnac})\text{SnOC}(\text{O})\text{N}(\text{iPr}_2)]$) (2.1346(16) Å), $\text{Dipp}^{\text{Ter}}\text{nacnac} = [\text{N}(\text{Dipp})\text{CMe}_2\text{CH}]$.^[18] It is close to the aldehyde inserted stannylene, **N** (2.104(4) Å)^[8] and slightly longer than those in the bulky amido-substituted alkoxide stannylenes (**F** 1.998(4), **H** 2.020(5) Å).^[5] The olefinic C-C bond length of 1.338(5) Å is close to the standard C=C bond length (1.34 Å).^[19] The C-O bond distance of 1.345(3) Å is between the typical values for C-O (1.43 Å) and C=O (1.20 Å), suggesting partial delocalization of the π electrons.^[19] The reaction of **2-IEt** with acetophenone produced the tin(II) enolate, $\text{Mes}^{\text{Ter}}\text{Sn}(\text{IEt})(\text{OPhC}=\text{CH}_2)$ (**4-IEt**), which is

consistent with the outcome observed when **2-IME4** was reacted with acetophenone.

The reactivity of **2-IEt** towards aldehyde and ketones prompted us to investigate its use in catalytic transformations, particularly hydrosilylation. In the presence of diphenylsilane (H_2SiPh_2), **2-IEt** could effectively convert benzaldehyde into the corresponding alkoxy silane product. We tested the reaction by varying the concentration of **2-IEt** (5, 2.5, 1, 0.5, and 0.1 mol%). Complete conversion was achieved with 1 mol% of **2-IEt** at ambient temperature within 1 hour (Entry 1-5, Table 1). Using 0.5 mol% of **2-IEt** at 50 °C (Entry 6, Table 1) also resulted in complete consumption of benzaldehyde within 1 hour. Solvent screening showed that THF- d_8 resulted in lower turnover, while CD_3CN was comparable to C_6D_6 (Entry 7-8, Table 1). After optimization, we determined that 1 mol% of **2-IEt** at room temperature in C_6D_6 provided suitable reaction conditions.

Table 1. Selected hydrosilylation of aldehydes and ketones under the different reaction conditions.^{a)}

Entry	R	Catalyst (mol%)	Solvent	T (°C)	Conversion/% ^{b)}
1	H	2-IEt (0.1)	C_6D_6	25	11.2
2	H	2-IEt (0.5)	C_6D_6	25	90.0
3	H	2-IEt (1)	C_6D_6	25	100
4	H	2-IEt (2.5)	C_6D_6	25	100
5	H	2-IEt (5)	C_6D_6	25	100
6	H	2-IEt (0.5)	C_6D_6	50	100
7	H	2-IEt (1)	THF- d_8	25	64.4
8	H	2-IEt (1)	CD_3CN	25	100
9	H	1 (1)	C_6D_6	25	100
10	H	3-IEt (1)	C_6D_6	25	87.4
11	H	IEt (5)	C_6D_6	25	- ^{c)}
12	CH_3	IEt (5)	C_6D_6	25	- ^{c)}
13	CH_3	2-IEt (1)	C_6D_6	25	90.1
14	CH_3	1 (1)	C_6D_6	25	90.6 ^{d)}
15	CH_3	4-IME4 (1)	C_6D_6	25	53.3 ^{d)}
16	CH_3	4-IEt (1)	C_6D_6	25	52.8 ^{d)}

a) Benzaldehyde (or acetophenone) (0.080 mmol), H_2SiPh_2 (1 eq.), trimethoxylbenzene (0.1 eq, internal standard), and catalyst in 0.4 ml deuterated solvent for 1 hour (24 hours for acetophenone). b) NMR yield was monitored by ^1H NMR with methoxybenzene as an internal standard. c) No reaction. d) reaction time for 24 hours.

Control experiments with **IEt** under optimized conditions showed that neither benzaldehyde (Entry 11, Table 1) nor acetophenone

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(Entry 12, Table 1) underwent hydrosilylation. Notably, using 1 mol% HMDS(^{Mes}Ter)Sn (**1**) resulted in excellent yields for the hydrosilylation of benzaldehyde (100% yield in 1 hour) (Entry 9, Table 1). Compound **1** also effectively catalyzed the hydrosilylation of acetophenone (Entry 13, Table 1), comparably to **2-IEt**. Compound **3-IEt** showed lower catalytic activity for benzaldehyde hydrosilylation compared to **2-IEt** (1 hour, 87.4%) (Entry 10 vs 3, Table 1). Similarly, both **4-IME₄** and **4-IEt** exhibited lower catalytic turnover for acetophenone hydrosilylation, reaching 50.0% conversion in 24 hours (Entry 13 vs. Entries 15 and 16, Table 1). This indicates that **3-IEt** and **4-IEt** (or **4-IME₄**) are not the intermediates in their respective catalytic cycles.

In C₆D₆ with 1 mol% **2-IEt** catalyst loading, the hydrosilylation of various aldehydes with diphenylsilane was explored under mild conditions (Table 2). The hydrosilylation of benzaldehyde was completed at room temperature, yielding the benzyloxysilane in high yields (Entry 1, Table 2). Electron withdrawing and -donating groups showed a negative impact on the reactivity (Entry 2 and Entry 3, Table 2). However, the incorporation of two or three MeO-groups in the aryl position of benzaldehyde resulted in a high reaction rate (Entry 4 and Entry 5, Table 2). Isobutyraldehyde demonstrated lower rates of hydrosilylation compared to benzaldehyde (Entry 1 vs Entry 6, Table 2). Bulky mesitaldehyde resulted in negligible turnover after 24 hours under the standard reaction conditions (Entry 7, Table 2). The tin-NHC adduct (**2-IEt**) demonstrated significantly superior performance in the hydrosilylation of benzaldehyde compared to most traditional transition metal catalytic systems under the same conditions, such as [MesDPB^{Ph}Ni]^[20] (MesDPB^{Ph} = MesB(*o*-Ph₂PC₆H₄)₂), [L₂CoBr][PF₆] (L = phosphinoquinoline),^[21] Fe(N(SiMe₃)₂)₂,^[22] and Pt(Ph₃)₃.^[23] Its efficacy was on par with that of Et₂OFe(CAT-POP)^[24] (CAT-POP = porous organic catecholate ligand) and [K³-Tptm]ZnH (K³-Tptm = tris(2-pyridylthio)methyl),^[25] but slightly less effective than [(DPB)Fe]₂ and [DPB]Co(N₂).^[26]

Table 2. Hydrosilylation of aldehydes and ketones under the catalysis of **2-IEt**.

a)

Entry	R ₁	R ₂	Time/hour	Conversion/% ^{b)}
1	C ₆ H ₅	H	1	100
2	4-Br-C ₆ H ₄	H	9	100
3	4-OCH ₃ -C ₆ H ₄	H	24	97.6
4	3,5-OCH ₃ -C ₆ H ₄	H	1	100
5	2,4,6-OCH ₃ -C ₆ H ₄	H	1	100
6	(CH ₃) ₂ CH	H	6	100
7	2,4,6-CH ₃ -C ₆ H ₄	H	24	- ^{c)}
8	C ₆ H ₅	CH ₃	24	90.1
9	4-F-C ₆ H ₄	CH ₃	24	86.4
10	4-OCH ₃ -C ₆ H ₄	CH ₃	24	100

11	C ₆ H ₅	C ₆ H ₅	24	52.1
12	(CH ₃) ₃ C	CH ₃	24	14.6
13	C ₆ H ₅	(CH ₃) ₃ C	24	- ^{c)}

a) Standard reaction conditions: substrate (0.080 mmol), H₂SiPh₂ (1 eq.), trimethoxybenzene (0.1 eq, internal standard), and 1 mol% **2-IEt** in 0.4 ml C₆D₆ at r.t for 1 hour. b) NMR yield was monitored by ¹H NMR with methoxybenzene as an internal standard. c) No reaction.

We next focused on the hydrosilylation of ketones. In contrast to its performance with aldehydes, the tin-NHC complex (**2-IEt**) did not exhibit significant activity towards ketones when compared to transition-metal catalysts.^[22, 24-25, 27] Using 1 mol% of **2-IEt** in C₆D₆ at room temperature, the ketone substrate scope is shown in Table 2 (Entries 8-13). The hydrosilylation of acetophenone yielded 90.1% conversion within 24 hours (Entry 8, Table 2). Introducing electron-donating groups, such as methoxy (OMe), at the 4-position of the acetophenone increased the yield compared to electron-withdrawing groups, like fluorine (F) (Entries 10 and 9, Table 2). More sterically demanding ketones, such as benzophenone, showed a decreased rate of forming the corresponding silyl ethers (Entry 11, Table 2). Dialkyl ketones exhibited lower reactivity for hydrosilylation (Entry 12, Table 2). The non-enolizable ketones, such as 2,2-dimethylpropiophenone, produced negligible amounts of the hydrosilylated product (Entry 13, Table 2).

Conclusions

In summary, we have synthesized stannylene-NHC adduct (**2-IEt**), which act as a catalyst for the hydrosilylation of aldehydes and ketones under ambient conditions. Treating **2-IEt** with one equivalent of benzaldehyde produced the insertion product **3-IEt**. Reacting **2-IME₄** or **2-IEt** with acetophenone yielded the tin enolate **4-IME₄**/**4-IEt**, respectively. However, in both cases, using them as hydrosilylation catalysts leads to lower catalytic turnover compared to their precursor (**2-IEt**), indicating they aren't involved in the catalytic cycle. Studies aimed at revealing the mechanism of the stannylene catalyzed hydrosilylation of aldehydes and ketones are currently ongoing.

Experimental Section

General Considerations

All experiments and manipulations were carried out under a dry oxygen-free argon atmosphere using standard Schlenk techniques or in a glovebox. All glass junctions were coated with PTFE-based grease Merkels Triboflon III. Solvents were dried by standard methods (withdrawn from MBraun Solvent Purification System (SPS) and stored over molecular (3 Å) or distilled from sodium/benzophenone or CaH₂ under argon atmosphere and degassed via freeze-pump-thaw cycling). The ¹H, ¹³C{¹H}, ¹¹⁹Sn{¹H}, and ²⁹Si{¹H} NMR spectra of the compounds were measured on a Bruker 400 MHz spectrometer. Chemical shifts are referenced to (residual) solvent signals (¹H and ¹³C{¹H} NMR). Deuterated solvents

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benzene (C₆D₆) and deuterated tetrahydrofuran (THF-d₈) were obtained from Sigma-Aldrich Deutero Chemie GmbH, stored over 4 Å molecular sieves in the glovebox. Unless otherwise stated, all reagents were purchased from commercial sources and used as received. Abbreviations: s = singlet, br = broadened, d = doublet, t = triplet, m = multiplet, dec = decompose. Some NMR spectra include resonances for silicone grease (C₆D₆: δ(¹H) = 0.29 ppm, δ(¹³C) = 1.4 ppm; δ = THF-d₈: δ(¹H) = 0.11 ppm, δ(¹³C) = 1.2 ppm). Liquid Injection Field Desorption Ionization Mass Spectrometry (LIFDI-MS) was measured directly from an inert atmosphere glovebox with a Thermo Fisher Scientific Exactive Plus Orbitrap equipped with an ion source from Linden CMS. Melting Points (m.p.) were determined in sealed glass capillaries under inter gas by a Büchi M-540. IMe₄ (1,3,4,5-tetramethylimidazool-2-ylidene), IET (1,3-diethyl-4,5-dimethylimidazool-2-ylidene),^[28] and Chlorogermylene (^{Mes}Ter)SnCl^[29] were synthesized according to the literature procedures.

Synthesis of HMDS(^{Mes}Ter)Sn (1)

The HMDS(^{Mes}Ter)Sn was synthesized via a modified route compared to the literature procedure reported by Aldridge group.^[12] A solution of potassium hexamethyldisilazane (KHMDs) (1.00 eq, 213.3 mg, 1.07 mmol) in toluene (10 mL) was added via dropping funnel to a suspension of (^{Mes}Ter)SnCl (1.00 eq, 500.0 mg, 1.07 mmol) in toluene (10 mL). The resulting brown-red suspension was stirred for 1 hour at room temperature followed by cannula filtration of the supernatant. All volatile components were removed under vacuum and **1** was obtained as a brown solid. Yield: 627.3 mg (1.06 mmol, 99.0%).

¹H NMR (400 MHz, 298 K, C₆D₆): δ[ppm] = −0.02 (s, 18 H, N(Si(CH₃)₃)₂), 2.15 (s, 6 H, 2xC⁴-CH₃, Mes), 2.32 (s, 12 H, 2xC^{2,6}-CH₃, Mes), 6.83 (s, 4H, 2xC^{3,5}-H, Mes), 7.03–7.05 (d, ³J_{H-H} = 8 Hz, 2 H, C^{3,5}-H, C₆H₃), 7.23–7.26 (t, ³J_{H-H} = 8 Hz, 1 H, C⁴-H, C₆H₃).

¹³C{¹H} NMR (101 MHz, 298 K, C₆D₆): δ[ppm] = 6.08 (N(Si(CH₃)₃)₂), 21.02 (C⁴-CH₃, Mes), 22.12 (C^{2,6}-CH₃, Mes), 128.01 (CH_{Ar}), 129.92 (CH_{Ar}), 130.44 (CH_{Ar}), 136.81 (C_{q, Ar}), 137.19 (C_{q, Ar}), 137.80 (C_{q, Ar}), 146.14 (C_{q, Ar}), 184.87 (Sn-C, C₆H₃).

¹¹⁹Sn{¹H} NMR (150 MHz, 298 K, C₆D₆): δ[ppm] = 1192.83 (Sn).

²⁹Si{¹H} NMR (80 MHz, 298 K, C₆D₆): δ[ppm] = −0.49 (SiMe₃).

LIFDI-MS m/z C₃₀H₄₃NSi₂Sn (M)⁺ calcd: 593.1956; m/z found: 593.1952.

Synthesis of HMDS(^{Mes}Ter)Sn(IMe₄) (2-IMe₄)

C₆D₆ was added to a mixture of solid **1** (1.00 eq, 20.0 mg, 0.0337 μmol) and IMe₄ (1.00 eq, 4.2 mg, 33.7 μmol) in a J-Young NMR tube. The reaction solution's colour changed from brown to light yellow immediately and **2-IMe₄** was confirmed by ¹H, ¹³C{¹H}, ¹¹⁹Sn{¹H} NMR spectroscopy, and LIFDI-MS.

¹H NMR (400 MHz, 298 K, C₆D₆): δ[ppm] = 0.24 (s, 18 H, N(Si(CH₃)₃)₂), 1.26 (s, 6 H, 2xC-CH₃, NHC), 2.05 (s, 6 H, 2xC-CH₃, NHC), 2.27, 2.50 (s, 6 H, 2xC⁴-CH₃, Mes), 3.23 (s, 6 H, 4xN-CH₃, NHC), 6.52, 6.73 (br, 4 H, 2xC^{3,5}-H, Mes), 7.05 (d, ³J_{H-H} = 8 Hz, 2 H, C^{3,5}-H, C₆H₃), 7.26 (t, ³J_{H-H} = 8 Hz, 1 H, C⁴-H, C₆H₃).

¹³C{¹H} NMR (101 MHz, 298 K, C₆D₆): δ[ppm] = 7.35 (N(Si(CH₃)₃)₂), 8.33 (2xC^{4,5}-CH₃, NHC), 21.26 (C⁴-CH₃, Mes), 23.00, 23.44 (C^{2,6}-CH₃, Mes),

35.55 (4xN-CH₃, NHC), 124.22 (C^{4,5}-CH₃, NHC), 127.12 (CH_{Ar}), 128.09, 128.45 (CH_{Ar}), 129.15 (CH_{Ar}), 135.84 (C_{q, Ar}), 135.93 (C_{q, Ar}), 137.23 (C_{q, Ar}), 143.44 (C_{q, Ar}), 149.52 (C_{q, Ar}), 169.82 (Sn-C, C₆H₃), 180.03 (Sn-C, NHC).

¹¹⁹Sn{¹H} NMR (150 MHz, 298 K, C₆D₆): δ[ppm] = −15.52.

²⁹Si{¹H} NMR (80 MHz, 298 K, C₆D₆): δ[ppm] = −2.51.

LIFDI-MS m/z C₃₇H₅₅N₃Si₂Sn (M)⁺ calcd: 717.2957; m/z found: 717.2968.

Synthesis of HMDS(^{Mes}Ter)Sn(IET) (2-IET)

In a Glove Box, a solution of IET (1 eq, 128.0 mg, 844 μmol) in toluene (2 mL) was added via syringe to a solution of HMDS(^{Mes}Ter)Sn (**1**) (1.00 eq, 500.0 mg, 844 μmol) in toluene (6 mL). The color changed from red brown to yellow after stirring for one hour at room temperature followed by all volatiles removed under vacuum to afford **2-IET** as a yellow solid. Yield: 584.5 mg (785 μmol, 93%).

¹H NMR (400 MHz, 298 K, C₆D₆): δ[ppm] = 0.31 (s, 18 H, N(Si(CH₃)₃)₂), 1.04 (t, ³J_{H-H} = 7 Hz, 6 H, CH₂CH₃, NHC), 1.38 (s, 6 H, 2xC-CH₃, NHC), 2.09 (s, 6 H, 2xC⁴-CH₃, Mes), 2.15 (br, 12 H, 2xC^{2,6}-CH₃, Mes), 3.84 (br, 4 H, CH₂CH₃, NHC), 6.55 (br, 4 H, 2xC^{3,5}-H, Mes), 7.01 (d, ³J_{H-H} = 8 Hz, 2H, C^{3,5}-H, C₆H₃), 7.26 (t, ³J_{H-H} = 8 Hz, 1 H, C⁴-H, C₆H₃).

¹³C{¹H} NMR (101 MHz, 298 K, C₆D₆): δ[ppm] = 7.70 (N(Si(CH₃)₃)₂), 8.69 (2xC^{4,5}-CH₃, NHC), 16.42 (CH₂CH₃, NHC), 21.44 (C⁴-CH₃, Mes), 23.44 (C^{2,6}-CH₃, Mes), 43.19 (CH₂CH₃, NHC), 124.60 (C^{4,5}-CH₃, NHC), 127.30 (CH_{Ar}), 128.43 (CH_{Ar}), 129.41 (CH_{Ar}), 135.75 (C_{q, Ar}), 136.59, 136.52 (C_{q, Ar}), 143.24 (C_{q, Ar}), 150.00 (C_{q, Ar}), 170.23 (Sn-C, C₆H₃).

¹¹⁹Sn{¹H} NMR (150 MHz, 298 K, C₆D₆): δ[ppm] = −0.09 (Sn).

²⁹Si{¹H} NMR (80 MHz, 298 K, C₆D₆): δ[ppm] = −2.03 (SiMe₃).

LIFDI-MS m/z C₃₉H₅₉N₃Si₂Sn (M)⁺ calcd: 745.3270; m/z found: 745.3268.

Synthesis of HMDS(^{Mes}Ter)Sn(OCH(Ph)IET) (3-IET)

In a Glove Box, **2-IET** (1.00 eq, 200.0 mg, 268 μmol) was dissolved in toluene (4 mL), and then benzaldehyde (1.00 eq, 28.5 mg, 268 μmol) was added via a pipette at room temperature. The reaction solution was stirred for 18 hours, and the light-yellow solution formed was concentrated to 2 mL, followed by storage at −35 °C. **3-IET** was obtained as light-yellow block crystals, and they were suitable for single-crystal X-ray diffraction. Yield: 173.0 mg (206 μmol, 77.2%).

¹H NMR (400 MHz, 298 K, C₆D₆): δ[ppm] = −0.2–0.92 (24 H, N(Si(CH₃)₃)₂, CH₂CH₃), 1.24 (s, 6 H, 2xC-CH₃, NHC), 2.18 2.09 (s, 6 H, 2xC⁴-CH₃, Mes), 2.57, 2.58 (s, 12 H, 2xC^{2,6}-CH₃, Mes), 4.09 (s, 1 H, OCH), 3.26, 4.09, 4.81 (br, 4 H, CH₂CH₃, NHC), 6.45, 6.89 (s, 4 H, 2xC^{3,5}-H, Mes), 7.00 (d, ³J_{H-H} = 8 Hz, 2 H, C^{3,5}-H, C₆H₃), 7.05–7.14, 7.25–7.30 (m, 6 H, CH_{Ar}).

¹³C{¹H} NMR (101 MHz, 298 K, C₆D₆): δ[ppm] = 7.58 (N(Si(CH₃)₃)₂), 21.36 (C⁴-CH₃, Mes), 23.09, 23.25 (C^{2,6}-CH₃, Mes), 68.65 (OCH), 126.05 (CH_{Ar}), 126.26 (CH_{Ar}), 126.85 (CH_{Ar}), 127.84 (CH_{Ar}), 128.35 (CH_{Ar}), 128.78 (CH_{Ar}), 129.35 (CH_{Ar}), 130.00 (CH_{Ar}), 134.32 (C_{q, Ar}), 135.83 (C_{q, Ar}), 136.97 (C_{q, Ar}), 144.76 (C_{q, Ar}), 146.97 (C_{q, Ar}), 148.04 (C_{q, Ar}), 151.92 (OCC, NHC), 175.84 (Sn-C, C₆H₃).

¹¹⁹Sn{¹H} NMR (150 MHz, 298 K, C₆D₆): δ[ppm] = −149.31 (Sn).

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$^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, 298 K, C_6D_6): no signal.

LIFDI-MS m/z $\text{C}_{46}\text{H}_{65}\text{N}_3\text{OSi}_2\text{Sn}$ (M)⁺ calcd: 851.3688; m/z found: 851.3698.

Synthesis of $(^{\text{Mes}}\text{Ter})\text{Sn}(\text{IME}_4)(\text{OPhC}=\text{CH}_2)$ (**4-IME₄**)

A solution of IME_4 (1.00 eq, 41.9 mg, 338 μmol) in toluene (1 mL) was added to the solution of $\text{HMDS}(\text{Mes})\text{Sn}$ (**1**) (1.00 eq, 200.0 mg, 338 μmol) in toluene (4 mL). The resulting yellow solution was stirred for 1 hour at room temperature followed by the addition of acetophenone (1.20 eq, 48.6 mg, 405 μmol). The reaction solution was stirred for one day, resulting in a light-yellow suspension. After filtration, the precipitate was dried to yield the white solid target product. The filtrate was then placed in the freezer at -30°C , producing colorless crystals after three days as an additional batch of the product. Yield: 198.0 mg (294 μmol , 87.0%).

^1H NMR (400 MHz, 298 K, THF-d_8): $\delta[\text{ppm}]$ = 1.98, 2.15, 2.20 (s, 18 H, $2\times\text{C}^{2,4,6}\text{-CH}_3$, Mes), 2.02 (s, 6 H, $2\times\text{C-CH}_3$, NHC), 3.31 (s, 1 H, OCCHH), 3.32 (6 H, $2\times\text{N-CH}_3$, NHC), 3.71 (s, 1 H, OCCHH), 6.66, 6.71 (s, 4 H, $2\times\text{C}^{3,5}\text{-H}$, Mes), 6.80 (d, 2 H, $\text{C}^{3,5}\text{-H}$, C_6H_3 , $^3J_{\text{H-H}}$ = 8), 7.03–7.21 (6 H, (1 H, $\text{C}^4\text{-H}$, C_6H_3), (5 H, Ph)).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 298 K, THF-d_8): $\delta[\text{ppm}]$ = 8.44 ($\text{C}^{4,5}\text{-CH}_3$, NHC), 21.29, 21.48, 21.99 ($\text{C}^{2,4,6}\text{-CH}_3$, Mes), 34.66 (s, $2\times\text{N-CH}_3$, NHC), 81.11 ($\text{OC}=\text{CH}_2$), 125.85 ($\text{C}^{4,5}\text{-CH}_3$, NHC), 126.65, 127.18, 127.40 (CH_{ArYl}), 128.58, 128.79 (CH_{ArYl}), 129.34 (CH_{ArYl}), 135.83, 135.92, 136.80, 142.60 ($\text{C}_{\text{q, ArYl}}$), 143.93 ($\text{C}_{\text{q, ArYl}}$), 149.63 ($\text{C}_{\text{q, ArYl}}$), 165.12 ($\text{OC}=\text{CH}_2$), 166.64 (Sn–C, C_6H_3), 178.28 (Sn–C, NHC).

$^{119}\text{Sn}\{^1\text{H}\}$ NMR (150 MHz, 298 K, THF-d_8): $\delta[\text{ppm}]$ = –41.08 (Sn).

LIFDI-MS m/z $\text{C}_{39}\text{H}_{44}\text{N}_2\text{OSn}$ (M)⁺ calcd: 676.2476; m/z found: 676.2498.

Synthesis of $(^{\text{Mes}}\text{Ter})\text{Sn}(\text{IET})(\text{OPhC}=\text{CH}_2)$ (**4-IET**)

In a Glove Box, **2-IET** (1.00 eq, 150.8 mg, 202 μmol) was dissolved in toluene (4 mL), and then acetophenone (1.20 eq, 29.2 mg, 243 μmol) was added via a pipette at room temperature. The reaction solution was stirred for 18 hours. The resulting light-yellow solution was concentrated to 1 mL, followed by the addition of 3 mL of hexane. After storing the solution at -35°C for one day, **4-IET** were obtained as light-yellow block-formed crystals. Yield: 77.3 mg (109 μmol , 55.4%).

^1H NMR (400 MHz, 298 K, C_6D_6): $\delta[\text{ppm}]$ = 0.89 (t, $^3J_{\text{H-H}}$ = 8 Hz, 6 H, CH_2CH_3 , NHC), 1.36 (s, 6 H, $2\times\text{C-CH}_3$, NHC), 2.15 (s, 6 H, $2\times\text{C}^4\text{-CH}_3$, Mes), 2.18, 2.41 (s, 12 H, $2\times\text{C}^{2,6}\text{-CH}_3$, Mes), 3.45, 3.66 (br, 4 H, CH_2CH_3 , NHC), 4.07, 4.49 (s, 2 H, $\text{OC}=\text{CH}_2$), 6.65, 6.79 (s, 4 H, $2\times\text{C}^{3,5}\text{-H}$, Mes), 7.02 (d, $^3J_{\text{H-H}}$ = 8 Hz, 2 H, $\text{C}^{3,5}\text{-H}$, C_6H_3), 7.16–7.19, 7.23–7.30, 7.60–7.62 (6 H, CH_{ArYl}).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 298 K, C_6D_6): $\delta[\text{ppm}]$ = 7.96 ($2\times\text{C}^{4,5}\text{-CH}_3$, NHC), 16.05 (CH_2CH_3 , NHC), 21.30 ($\text{C}^4\text{-CH}_3$, Mes), 21.75, 22.08 ($\text{C}^{2,6}\text{-CH}_3$, Mes), 42.64 (CH_2CH_3 , NHC), 83.06 ($\text{OC}=\text{CH}_2$), 124.33 ($\text{C}^{4,5}\text{-CH}_3$, NHC), 126.71 (CH_{ArYl}), 126.82 (CH_{ArYl}), 127.30 (CH_{ArYl}), 127.41 (CH_{ArYl}), 128.26 (CH_{ArYl}), 128.35 (CH_{ArYl}), 128.69 (CH_{ArYl}), 128.87 (CH_{ArYl}), 135.27 ($\text{C}_{\text{q, ArYl}}$), 135.78 ($\text{C}_{\text{q, ArYl}}$), 136.52 ($\text{C}_{\text{q, ArYl}}$), 142.49 ($\text{C}_{\text{q, ArYl}}$), 143.45 ($\text{C}_{\text{q, ArYl}}$), 149.32 ($\text{C}_{\text{q, ArYl}}$), 165.85 ($\text{OC}=\text{CH}_2$), 166.56 (Sn–C, C_6H_3), 177.70 (Sn–C, NHC).

$^{119}\text{Sn}\{^1\text{H}\}$ NMR (150 MHz, 298 K, C_6D_6): $\delta[\text{ppm}]$ = –24.97 (Sn).

LIFDI-MS m/z $\text{C}_{41}\text{H}_{48}\text{N}_2\text{OSn}$ (M)⁺ calcd: 704.2789; m/z found: 704.2811.

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Keywords: stannylene • carbonyl compounds • hydrosilylation • carbenes

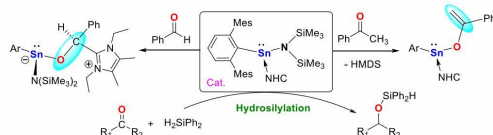
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FULL PAPER



We report on a stannylene-NHC adduct, $\text{HMDS}^{(\text{MesTer})}\text{Sn}(\text{NHC})$, that is a catalyst for hydrosilylation of aldehydes and ketones, forming silyl ethers at room temperature. When $\text{HMDS}^{(\text{MesTer})}\text{Sn}(\text{NHC})$ reacts with benzaldehyde, it forms the insertion product, $\text{HMDS}^{(\text{MesTer})}\text{Sn}(\text{OCH}(\text{Ph})\text{NHC})$. In contrast, with acetophenone, it undergoes deprotonation to form tin enolate, $(\text{MesTer})\text{Sn}(\text{NHC})(\text{OPhC}=\text{CH}_2)$.

Dechuang Niu, John A. Kelly, Fiona J. Kiefer, Arseni Kostenko, and Shigeyoshi Inoue*

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Terphenyl Amido Stannylene-NHC Adducts: A Catalyst for the Hydrosilylation of Aldehydes and Ketones

6. Summary and Outlook

Tetryliumylidenes combine the characteristics of highly electrophilic tetrylium cation and Lewis ambiphilicity of tetrylenes and have been attractive targets for fundamental research for small molecule activation and catalytic applications. N-heterocyclic carbenes (NHCs) proved to be an effective tool for the stabilization of low-coordinate elements in different oxidation states in main group elements and transition-metal chemistry. In previous studies by our group, aryl-substituted silyliumylidene and germiumylidene supported by di-NHCs coordination were isolated, and they could undergo various reactivities, including small molecules activation, transition-metal coordination, and catalytic applications. This PhD thesis started with the initial goal to isolate the di-NHCs stabilized stannylumylidene, a tin analogue of silyliumylidene and germiumylidene.

A di-N-heterocyclic carbene (NHCs) stabilized stannylumylidene, $[\text{MesTerSn}(\text{IMe}_4)_2][\text{BArF}]$ ($[\mathbf{2}][\text{BArF}]$), ($\text{MesTer} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$, $\text{Mes} = 2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$, $\text{IMe}_4 = 1,3,4,5\text{-tetramethylimidazol-2-ylidene}$, $\text{BArF} = (3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4\text{B}$), was isolated from the reaction of $(\text{MesTer})\text{SnCl}$ ($\mathbf{1}$) with two equivalents of IMe_4 , followed by one equivalent of $\text{Na}[\text{BArF}]$ (Figure 63). DFT calculations indicate that the anion-cation interaction in $[\mathbf{2}][\text{BArF}]$ is weak, requiring only $10.4 \text{ kcal mol}^{-1}$ and $0.0 \text{ kcal mol}^{-1}$ to fully separate the ions in benzene and 1,2-difluorobenzene, respectively (Figure 63). The Sn-IMe_4 bonding is also quite labile, with a dissociation free energy of 12.0 and $9.3 \text{ kcal mol}^{-1}$ in benzene and difluorobenzene, respectively for the conversion of $[\mathbf{2}][\text{BArF}]$ to form $[\mathbf{2a}][\text{BArF}]$ and free NHC (Figure 63). This bond lability may imply that $[\mathbf{2}][\text{BArF}]$ may react as a two coordinated stannylumylidene, upon dissociation of an IMe_4 ligand in solution. This stannylumylidene $[\mathbf{2}][\text{BArF}]$ acts as a pre-catalyst for the homogeneous hydrosilylation of CO_2 .

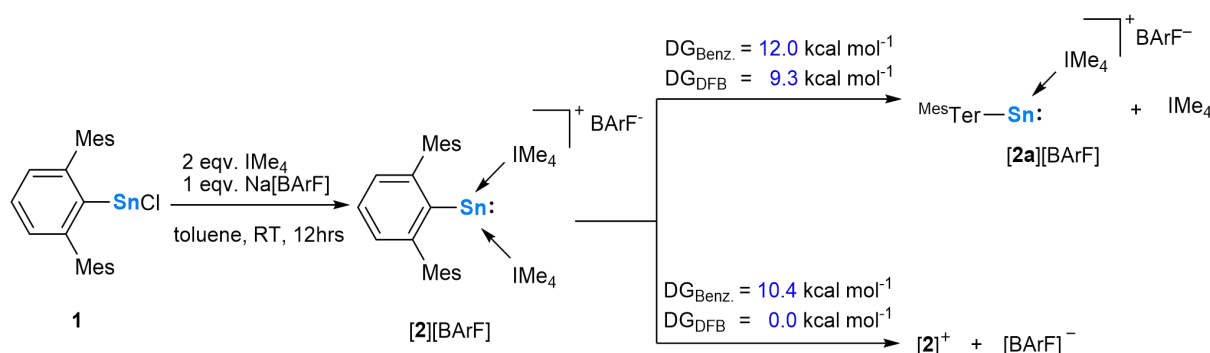


Figure 63. Synthesis of di-NHCs stabilized stannylumylidenes $[\mathbf{2}][\text{BArF}]$ and calculated free energies for anion cation interaction and NHC dissociation in $[\mathbf{2}][\text{BArF}]$.

To study the mechanism of the hydrosilylation of CO₂ catalyzed by **[2][BArF]**, stoichiometric reactivity studies were conducted (Figure 64). In the presence of excess CO₂, sequential insertion into Sn-C (NHC) bonds produced mono-insertion product **[^{Mes}TerSn(CO₂IMe₄)IMe₄][BArF]** (**[3][BArF]**) and doubly CO₂ inserted product **[^{Mes}TerSn(CO₂IMe₄)₂][BArF]** (**[4][BArF]**). The activation mode for CO₂ by **[2][BArF]** differs from that of its silicon and germanium analogues. It indicates that the Sn center exhibits a stronger Lewis base character and an inert lone pair of electrons, which is consistent with the increased singlet-triplet energy difference of Sn(II).

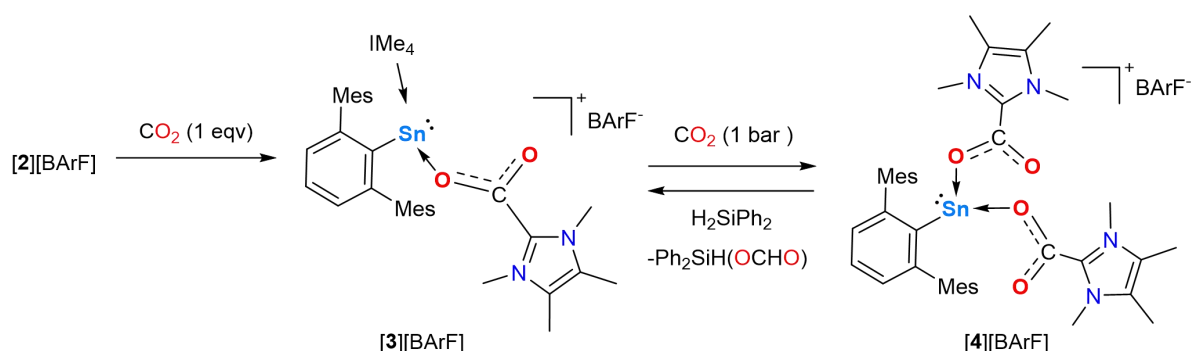


Figure 64. Reactions of di-NHCs stabilized stannylidene **[2][BArF]** with CO₂.

Notably, a comparison of the ¹H NMR spectroscopic data of **[3][BArF]** and **[4][BArF]** with the ¹H NMR of the catalytic progress indicated that **[3][BArF]** and **[4][BArF]** formed during the **[2][BArF]** catalyzed hydrosilylation of CO₂. Furthermore, **[4][BArF]** could be converted to **[3][BArF]** by adding Ph₂SiH₂ under an argon atmosphere, with the simultaneous formation of silyl formate (Ph₂SiH(OCHO)) (Figure 64). Based on experimental mechanistic studies and quantum chemical calculations, we confirmed that **[4][BArF]** is the catalytically active species for CO₂ hydrosilylation, which is distinct from those previously proposed for the lighter germlylidenes.

A rare two-coordinate aryl-substituted stannylidene supported by a single NHC was successfully isolated (Figure 65), by the reaction of (^{Mes}Ter)SnCl (**1**) with one equivalent of NHC *i*Pr (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene), followed by one equivalent of NaBArF. It is found to undergo various activities owing to the presence of both one vacant orbital and a lone pair of electrons, including coordination, splitting the N-H bond of NH₃, and activation of N₂O and TMS-N₃. Treating a solution of **[5][BArF]** with H₂ (1 bar) resulted in no reaction, even when conducted at elevated temperatures (80 °C). Notably, **[5][BArF]** does not react with CO₂ and cannot catalyze CO₂ hydrosilylation at room temperature, which shows obvious differences with di-NHCs stabilized stannylidene (**[2][BrF]**). This stannylidene undergoes a reaction with bis(cyclooctadiene)nickel(0), Ni(COD)₂, yielding

the stannylumylidene-Ni complex (Figure 65, **[10][BArF]**) via the replacement of 1,5-cyclooctadiene (1,5-COD) from Ni center and migration of *i*Pr from Sn to Ni atom.

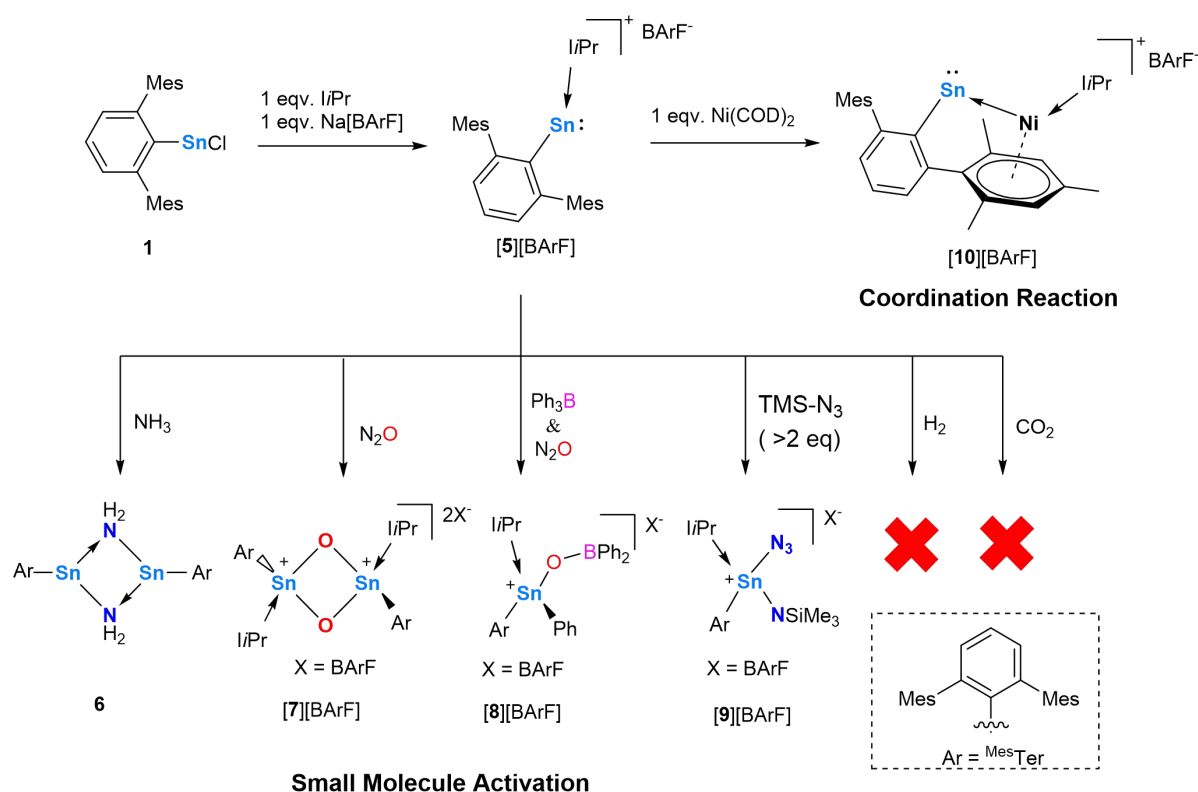


Figure 65. (a) Synthesis of mono-NHC stabilized stannylumylidenes (**[5][BArF]**) and its reactivities.

The terphenyl amido stannylene-NHC adducts (Figure 66, **11-IMe₄**, **11-IEt**), HMDS(^{Mes}Ter)Sn(NHC), (^{Mes}Ter = 2,6-Mes₂C₆H₃, Mes = 2,4,6-Me₃-C₆H₂, HMDS = N(SiMe₃)₂, NHC = IMe₄, IEt, IMe₄ = 1,3,4,5-tetramethylimidazol-2-ylidene, IEt = 1,3-diethyl-4,5-dimethylimidazol-2-ylidene), were reacted with benzaldehyde forming HMDS(^{Mes}Ter)Sn(OCH(Ph)NHC) (**12-IEt**). In the presence of acetophenone, deprotonation occurs to afford the tin enolate, (^{Mes}Ter)Sn(NHC)(OPhC=CH₂) (**11-IMe₄**, **11-IEt**), via the release of hexamethyldisilamine (HMDS). This stannylene-NHC adduct also acts as a catalyst for the homogeneous hydrosilylation of aldehydes and ketones under ambient conditions.

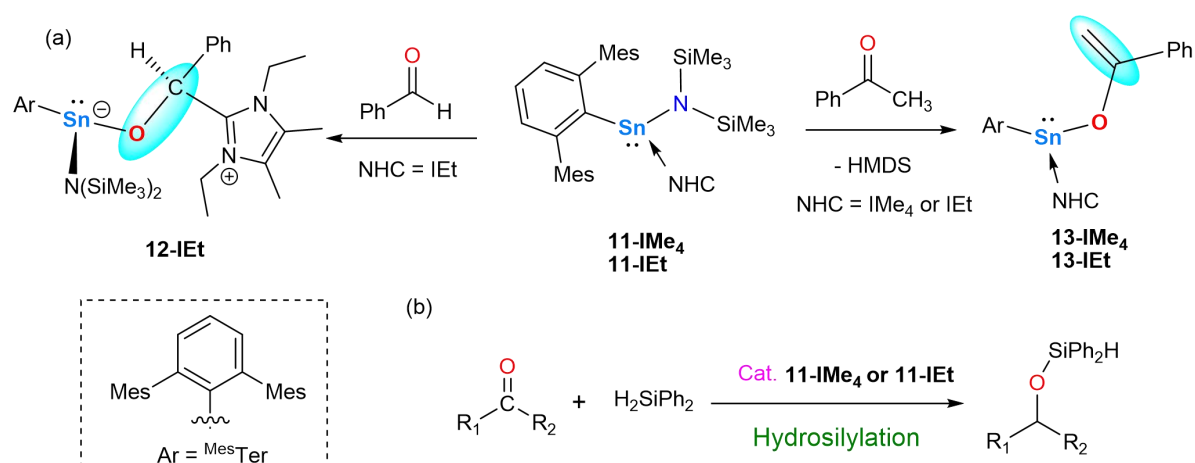


Figure 66. (a) The reactivity of **11-*IMe*₄/11-IET** with benzaldehyde and acetophenone; (b) **11-*IMe*₄/11-IET** catalyzed hydrosilylation of carbonyls.

As a conclusion, this thesis describes a systematic and detailed research on synthesis, characterization, and reactivities of low valent tin compounds, stannylumidenes and stannylene-NHC adduct, through experimental work and theoretical calculation and significantly extends the scope of catalytic applications of molecular tin compounds, as well as our general understanding of tin chemistry.

7. Appendix

7.1 Supporting Information for Chapter 4

Supplementary Information (SI) for Chemical Science.
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Supporting Information

CO₂ Hydrosilylation Catalyzed by an N-Heterocyclic Carbene (NHC)-stabilized stannylumylidene

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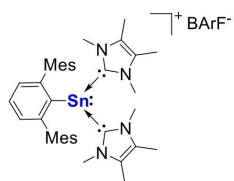
1. Experimental Details

1.1 General Methods and Instrumentation

All experiments and manipulations were carried out under a dry oxygen-free argon atmosphere using standard Schlenk techniques or in a glovebox. All glass junctions were coated with PTFE-based grease Merckel Triboflon III. Solvents were dried by standard methods (withdrawn from MBraun Solvent Purification System (SPS) over molecular (3 Å) or distilled from sodium/benzophenone or CaH_2 under argon atmosphere and degassed via freeze-pump-thaw cycling). The ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{119}\text{Sn}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of the compounds were measured on Bruker 400 MHz and 300 MHz spectrometer. Chemical shifts are referenced to (residual) solvent signals (^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR). Deuterated benzene (C_6D_6), deuterated toluene (toluene- d_8) and deuterated tetrahydrofuran (THF- d_8) were obtained from Sigma-Aldrich Deutero Chemie GmbH, stored over 4 Å molecular sieves in the glovebox. Carbon dioxide (5.0) was purchased from Westfalen AG and used as received. Unless otherwise stated, all reagents were purchased from commercial sources and used as received. Abbreviations: s = singlet, br = broadened, d = doublet, t = triplet, m = multiplet, dec = decompose. Some NMR spectra include resonances for silicone grease (C_6D_6 : $\delta(^1\text{H}) = 0.29$ ppm, $\delta(^{13}\text{C}) = 1.4$ ppm; $\delta = \text{THF-}d_8$: $\delta(^1\text{H}) = 0.11$ ppm, $\delta(^{13}\text{C}) = 1.2$ ppm). Liquid Injection Field Desorption Ionization Mass Spectrometry (LIFDI-MS) were measured directly from an inert atmosphere glovebox with a Thermo Fisher Scientific Exactive Plus Orbitrap equipped with an ion source from Linden CMS. The UV-vis spectra were taken on a *Agilent Cary 50* spectrophotometer with a *Schlenk* quartz cuvette as the Central Analytic Department at the TUM Catalysis Research Center. Quantitative elemental analyses (EA) were carried out using an EURO EA (HEKA tech) instrument equipped with a CHNS combustion analyzer at the Laboratory for Microanalysis at the TUM Catalysis Research Center. For fluoride determination, the sample is digested in an alkaline medium. Fluoride content is then measured directly by potentiometry using a Titrand 904 (Metrohm). For tin determination, the sample is acid digested. Measurements are conducted at a wavelength of 235.5 nm in an acetylene/nitrous oxide flame using atomic absorption spectroscopy (Agilent 280 FS-AA). Melting Points (m.p.) were determined in sealed glass capillaries under inter gas by a Büchi M-540. IMe_4 (1,3,4,5-tetramethylimidazolid-2-ylidene), Chlorostannylene [$^{\text{Mes}}\text{TerSnCl}$] (**1**), Sodium tetrakis [3,5-bis(trifluoromethyl)phenyl] borate (NaBArF), and $\text{Li}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ were synthesized according to the literature procedures.^{S1}

1.2 Synthesis of Stannyliumylidene [**2**]⁺

1.2.1 Synthesis of [**2**][BArF]



[2][BArF]: A solution of IMe_4 (2.00 eq, 531.0 mg, 4.28 mmol) in toluene (3 mL) was added dropwise to [$^{\text{Mes}}\text{TerSnCl}$] (1.00 eq, 1.00 g, 2.14 mmol) dissolved in toluene (10 mL) at room temperature. After stirring for 10 minutes, NaBArF [BArF] = 1,3-bis(trifluoromethyl)-boron (1.00 eq, 1.90 g, 2.14 mmol) was introduced, resulting in the immediate formation of a brown precipitate. Following this, fluorobenzene ($\text{C}_6\text{H}_5\text{F}$) (3 mL) was

added, and the reaction was allowed to stir overnight at room temperature. The mixture was then filtered, and the filtrate was concentrated to a volume of 5 mL. After 2 days at $-35\text{ }^{\circ}\text{C}$, colourless crystals suitable for XRD analysis were obtained. Yield: 2.65 g (1.72 mmol, 80.4%).

^1H NMR (400 MHz, 298 K, THF- d_8): δ [ppm] = 2.08 (s, 12 H, 4xC-CH₃, NHC), 2.09 (s, 6 H, 2xC⁴-CH₃, Mes), 2.15 (s, 12H, 2xC^{2,6}-CH₃, Mes), 3.41 (s, 12 H, 4xN-CH₃, NHC), 6.69 (s, 4 H, 2xC^{3,5}-H, Mes), 7.04 (d, $^3J_{\text{H-H}} = 8\text{ Hz}$, 2 H, C^{3,5}-H, C₆H₃), 7.38 (t, $^3J_{\text{H-H}} = 8\text{ Hz}$, 1 H, C⁴-H, C₆H₃), 7.59, 7.79 (s, 12 H, 4xC^{2,4,6}, 4C₆H₃(CF₃)₂).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 298 K, THF- d_8): δ [ppm] = 8.68 (2xC^{4,5}-CH₃, NHC), 20.99 (C⁴-CH₃, Mes), 21.81 (C^{2,6}-CH₃, Mes), 36.38 (4xN-CH₃, NHC), 118.13 (*p*-CH_{B-Ar}), 121.52, 124.22, 126.93 (C, BArF), 128.01 (C^{4,5}-CH₃, NHC), 128.50 (C⁴-H, C₆H₃), 128.56 (4xC^{3,5}-H, Mes), 129.61 (C^{3,5}-H, C₆H₃), 129.95-130.54 (m-C_{B-Ar}), 135.66 (o-CH_{B-Ar}), 136.52 (2xC¹-Mes), 137.22 (2xC⁴-Mes), 141.73 (2xC^{2,6}-Mes), 150.00 (2xC^{2,6}-C₆H₃), 159.66 (Sn-C, C₆H₃), 159.66-163.62 (ipso-CB-Ar), 170.18 (Sn-C, NHC).

$^{119}\text{Sn}\{^1\text{H}\}$ NMR (150 MHz, 298 K, THF- d_8): δ [ppm] = -235.72 (Sn).

$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, 298 K, THF- d_8): δ [ppm] = -6.52 (B, BArF).

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, 298 K, THF- d_8): δ [ppm] = -63.45 (CF₃, BArF).

LIFDI-MS *m/z* C₃₈H₄₉N₄Sn calcd: 681.2979; found: 681.2932.

Elemental analysis (%) calcd for C₇₀H₆₁BF₂₄N₄Sn: C 54.46, H 3.98, N 3.63, F 29.54, Sn 7.69; found: C 54.42, H 4.25, N 3.72, F 26.5, Sn 7.3.

m.p.: 126 $^{\circ}\text{C}$.

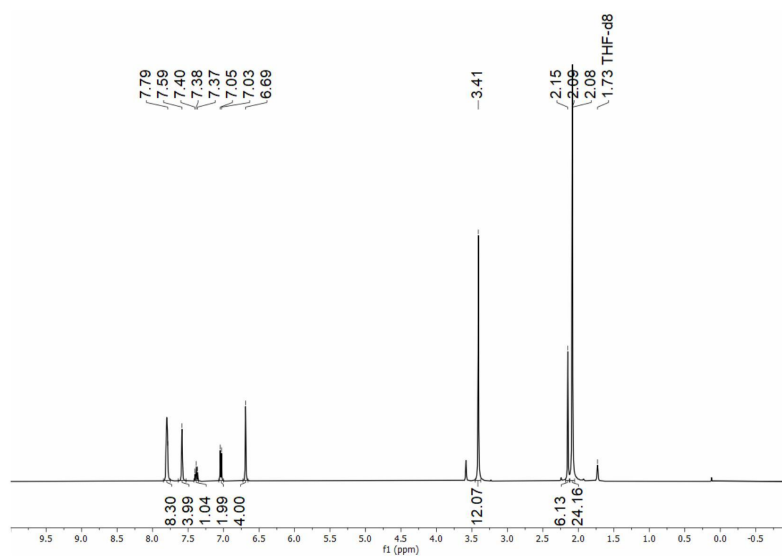


Figure S1. ¹H NMR spectrum of [2][BArF] in THF-d₈ at 298 K.

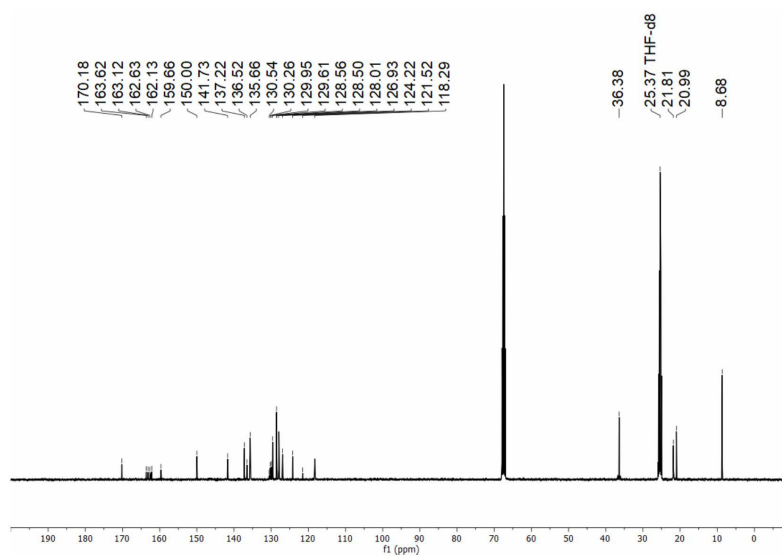


Figure S2. ¹³C{¹H} NMR spectrum of [2][BArF] in THF-d₈ at 298 K.



Figure S3. $^1\text{H}/^{13}\text{C}$ NMR HSQC spectrum of $[2][\text{BArF}]$ in THF-d_8 at 298 K.

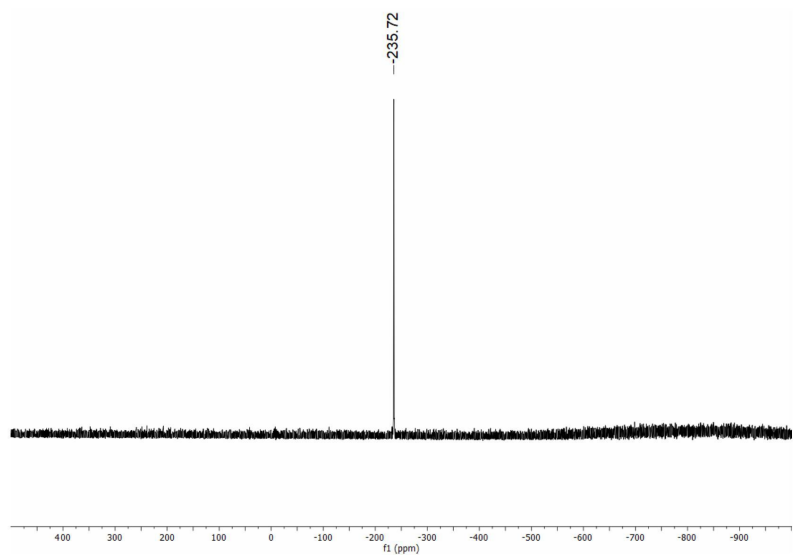


Figure S4. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of $[2][\text{BArF}]$ in THF-d_8 at 298 K.

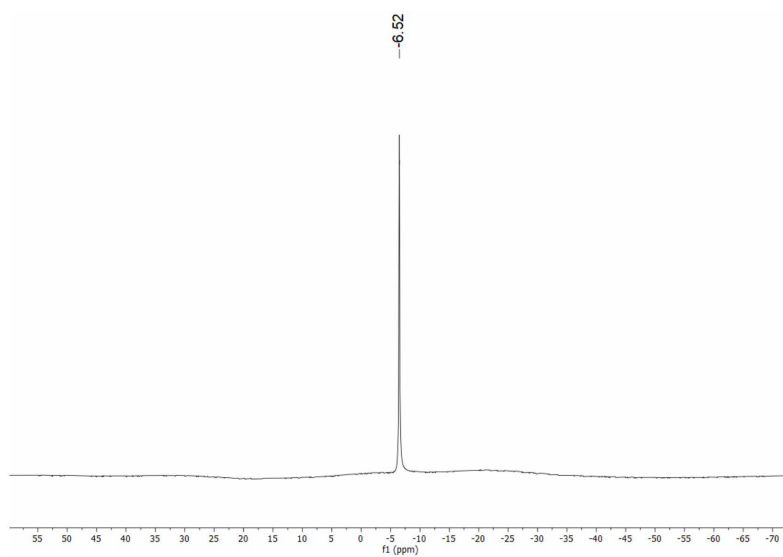


Figure S5. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **[2][BArF]** in THF- d_8 at 298 K.

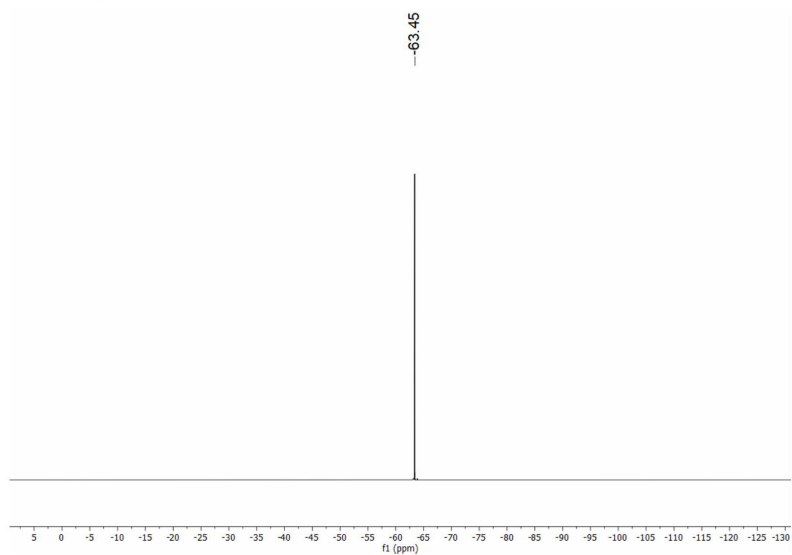


Figure S6. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **[2][BArF]** in THF- d_8 at 298 K.

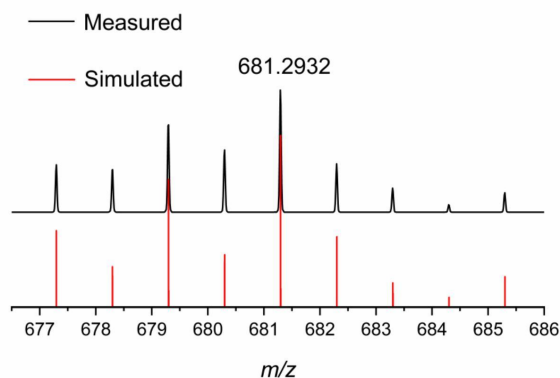
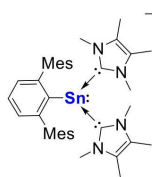


Figure S7. LIFDI-MS spectrum (detail view) of $[2]^+$ in $[2][BArF]$ (measured spectrum: top; simulated spectrum: bottom).

1.2.2 Synthesis of $[2][Al(OC(CF_3)_3)_4]$



$[2][Al(OC(CF_3)_3)_4]$: A solution of IMe_4 (2.00 eq, 53.1 mg, 0.43 mmol) in toluene (2 mL) was added dropwise to $[Mes^+TerSnCl]$ (1.00 eq, 100.0 mg, 0.21 mmol) dissolved in toluene (3 mL) at room temperature. After stirring for 10 minutes, $Li[Al(OC(CF_3)_3)_4]$ (1.00 eq, 229.9 mg, 0.21 mmol) was introduced, leading to the immediate formation of a brown precipitate. Subsequently, fluorobenzene (1 mL) was added, and the reaction was stirred overnight at room temperature, producing a colorless suspension. The mixture was filtered, and the filtrate was concentrated and stored at $-35^\circ C$. After 2 days, colorless crystals formed. Yield: 281.0 mg (0.18 mmol, 86.3%).

1H NMR (400 MHz, 298 K, THF- d_8): δ [ppm] = 2.08 (s, 12 H, $2xC^4-CH_3$, Mes), 2.09 (s, 12 H, $4xC-CH_3$, NHC), 2.15 (s, 6 H, $2xC^{2,6}-CH_3$, Mes), 3.41 (s, 12 H, $4xN-CH_3$, NHC), 6.69 (s, 4 H, $2xC^{3,5}-H$, Mes), 7.03 (d, $^3J_{H-H}=8$ Hz, 2 H, $C^{3,5}-H$, C_6H_3), 7.38 (t, $^3J_{H-H}=4$ Hz, 1 H, C^4-H , C_6H_3).

$^{13}C\{^1H\}$ NMR (101 MHz, 298 K, THF- d_8): δ [ppm] = 8.79 ($2xC^{4,5}-CH_3$, NHC), 21.10 (C^4-CH_3 , Mes), 21.92 ($C^{2,6}-CH_3$, Mes), 36.49 ($4xN-CH_3$, NHC), 120.99, 123.90 (C,

Al(OC(CF₃)₃)₄), 128.07 (C^{4,5}-CH₃, NHC), 128.60 (C⁴-H, C₆H₃), 128.68 (4xC^{3,5}-H, Mes), 129.72 (C^{3,5}-H, C₆H₃), 136.63 (2xC¹-Mes), 137.35 (2xC⁴-Mes), 141.85 (2xC^{2,6}-Mes), 150.12 (2xC^{2,6}-C₆H₃), 159.79 (Sn-C, C₆H₃), 170.30 (Sn-C, NHC).

¹¹⁹Sn{¹H} NMR (149 MHz, 298 K, THF-d₈): δ[ppm] = -235.31 (Sn).

¹⁹F{¹H} NMR (376 MHz, 298 K, THF-d₈): δ[ppm] = -75.89 (CF₃, Al(OC(CF₃)₃)₄).

LIFDI-MS m/z C₃₈H₄₉N₄Sn calcd: 681.2979; m/z found: 681.2949.

m.p.: 148 °C

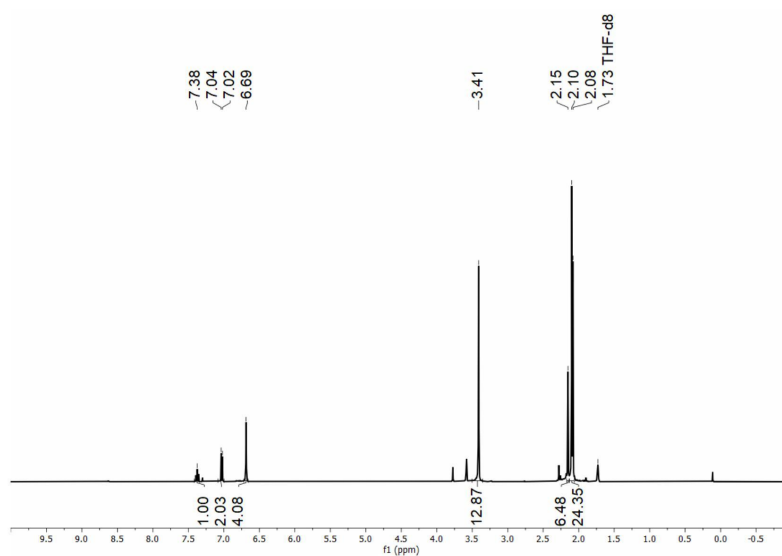


Figure S8. ¹H NMR spectrum of [2][Al(OC(CF₃)₃)₄] in THF-d₈ at 298 K.

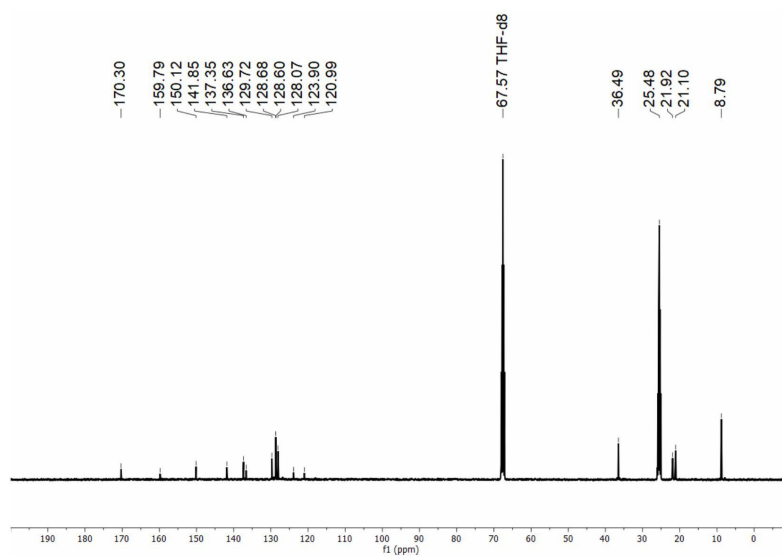


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\mathbf{2}][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ in THF-d_8 at 298 K.

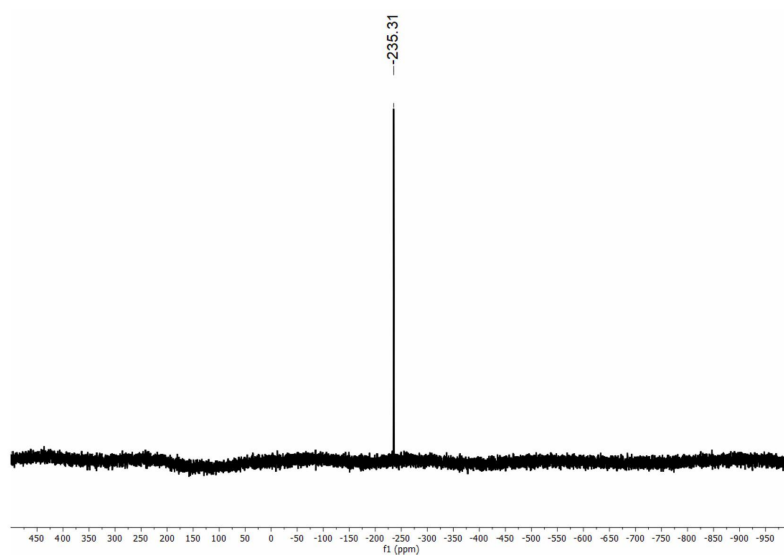


Figure S10. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of $[\mathbf{2}][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ in THF-d_8 at 298 K.

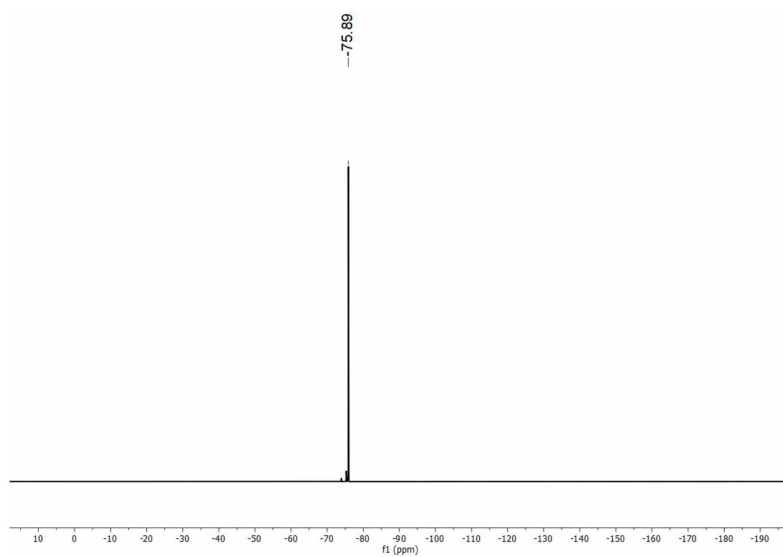


Figure S11. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $[2][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ in THF-d_8 at 298 K.

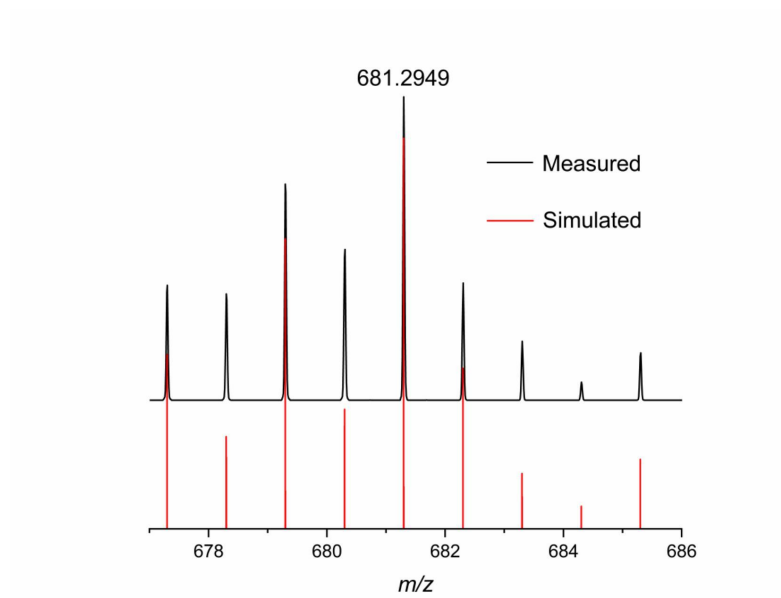
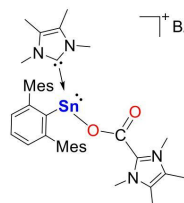


Figure S12. LIFDI-MS spectrum (detail view) of $[2]^+$ in $[2][Al(OC(CF_3)_3)_4]$ (measured spectrum: top; simulated spectrum: bottom).

1.3 Synthesis of $[3][BArF]$



$[2][BArF]$ (1.00 eq, 200.0 mg, 0.13 mmol) was dissolved in a mixture of toluene (3 mL) and fluorobenzene (1 mL). CO_2 (1.1 eq, 3.20 mL, 1 bar) was then added via a syringe at room temperature. After stirring for 4 hours, the solution changed from colorless to pale yellow. The mixture was filtered, and the filtrate was concentrated to 3 mL before being stored at $-35^\circ C$. After 2 days, yellow crystals suitable for XRD analysis were obtained after. Yield: 126.0 mg (0.080 mmol, 61.3%).

1H NMR (400 MHz, 298 K, THF- d_8): δ [ppm] = 1.94, 2.21 (s, 12 H, $2xC^{2,6}-CH_3$, Mes), 2.10 (s, 6 H, $2xC^4-CH_3$, Mes), 2.11 (s, 12 H, $2xC-CH_3$, NHC), 2.28 (s, 6 H, $2xC-CH_3$, NHC-COO), 3.36 (s, 6 H, $2xN-CH_3$, NHC), 3.74 (s, 6 H, $2xN-CH_3$, NHC-COO), 6.69, 6.77 (s, 4H, $2xC^{3,5}-H$, Mes), 6.91 (d, $^3J_{H-H}$ = 7.5 Hz, 2 H, $C^{3,5}-H$, C_6H_3), 7.30 (t, $^3J_{H-H}$ = 8 Hz, 1 H, C^4-H , C_6H_3), 7.59, 7.80 (s, 12 H, $4xC^{2,4,6}$, $4C_6H_3(CF_3)_2$).

$^{13}C\{^1H\}$ NMR (101 MHz, 298 K, THF- d_8): δ [ppm] = 8.32 ($C^{4,5}-CH_3$, NHC-COO), 8.39 ($C^{4,5}-Me$, NHC), 20.96 (C^4-CH_3 , Mes), 21.60, 21.03 ($C^{2,6}-CH_3$, Mes), 34.34 ($2xN-CH_3$, NHC-COO), 35.65 ($2xN-CH_3$, NHC), 118.26 ($p-CH_{B-Ar}$), 121.52, 124.23, 126.93, 127.11 (C , BArF), 128.06 (C^4-H , C_6H_3), 128.81 ($C^{4,5}-CH_3$, NHC-COO), 128.87 ($C^{4,5}-CH_3$, NHC), 128.95 ($4xC^{3,5}-H$, Mes), 129.64 ($2xC^{2,6}-Mes$), 129.82 ($C^{3,5}-H$, C_6H_3), 129.95-130.55 ($m-C_{B-Ar}$), 135.67 ($o-CH_{B-Ar}$), 136.64 ($2xC^4-Mes$), 136.69 (N_2C , NHC), 137.28 ($2xC^{2,6}-Mes$), 140.98 ($2xC^4-Mes$), 148.86 ($2xC^{2,6}-C_6H_3$), 157.48 (CCO_2), 162.13-163.62 (ipso- C_{B-Ar}), 164.94 (Sn-C, C_6H_3), 177.70 (Sn-C, NHC).

$^{119}Sn\{^1H\}$ NMR (149 MHz, 298 K, THF- d_8): δ [ppm] = -10.61 (Sn).

$^{11}B\{^1H\}$ NMR (128 MHz, 298 K, THF- d_8): δ [ppm] = -6.47 (B, BArF).

$^{19}F\{^1H\}$ NMR (376 MHz, 298 K, THF- d_8): δ [ppm] = -63.36 (CF_3 , BArF).

LIFDI-MS m/z $C_{39}H_{49}N_4O_2Sn$ calcd: 725.2878; m/z found: 725.2868.

Elemental analysis (%) calcd for $C_{71}H_{61}BF_{24}N_4O_2Sn$: C 53.71, H 3.87, N 3.53, F 28.72, Sn 7.48; found: C 51.96, H 3.88, N 3.43, F 25.5, Sn 7.7.

m.p.: 128.9 $^\circ C$.

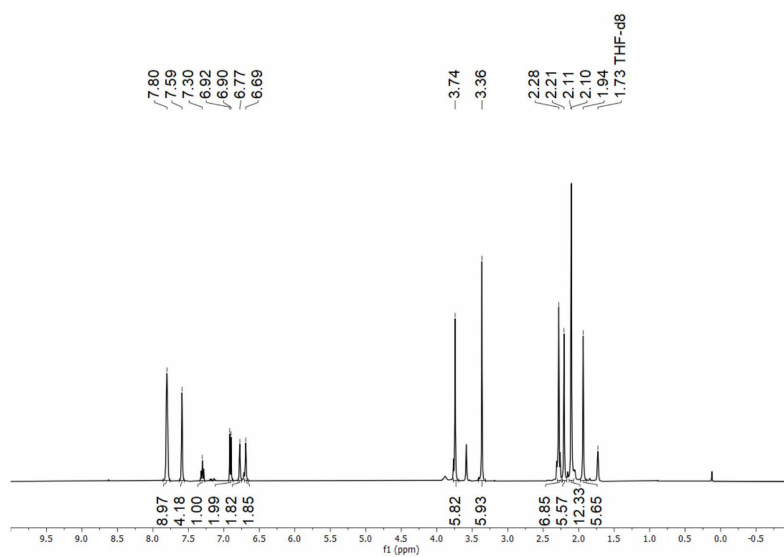


Figure S13. ¹H NMR spectrum of [3][BArF] in THF-d₈ at 298 K.

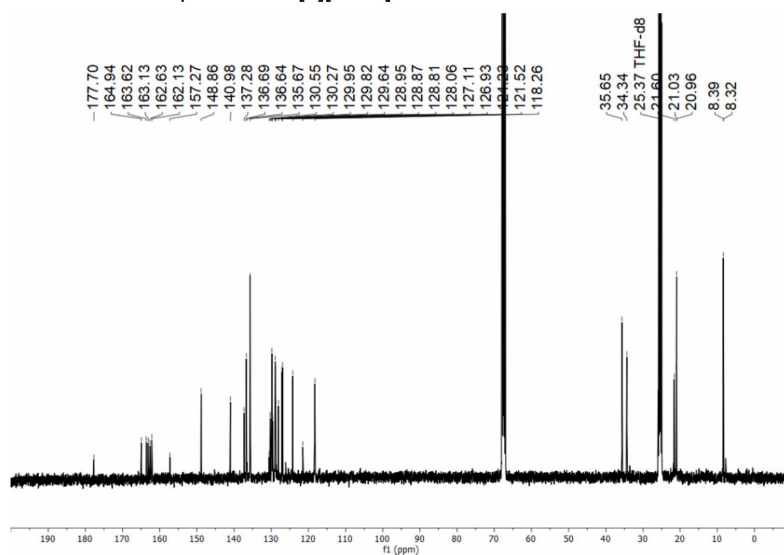


Figure S14. ¹³C{¹H} NMR spectrum of [3][BArF] in THF-d₈ at 298 K.



Figure S15. $^1\text{H}/^{13}\text{C}$ NMR HSQC spectrum of $[3][\text{BArF}]$ in THF-d_8 at 298 K.

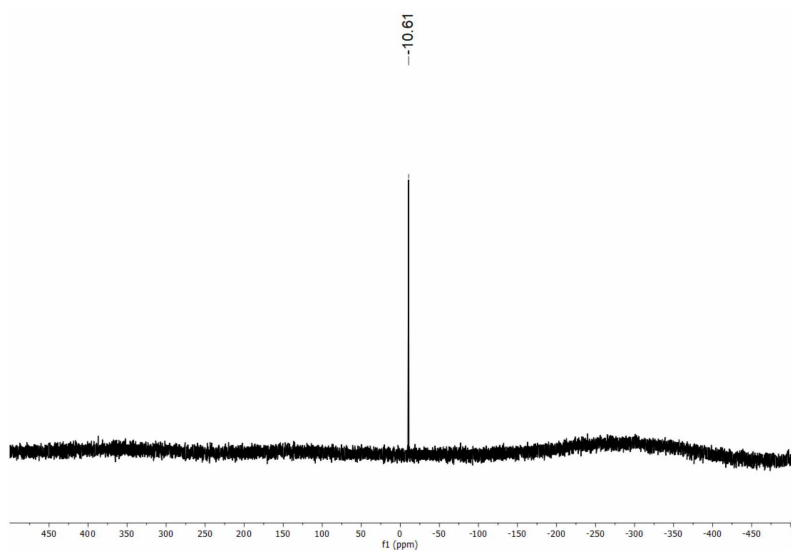


Figure S16. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of $[3][\text{BArF}]$ in THF-d_8 at 298 K.

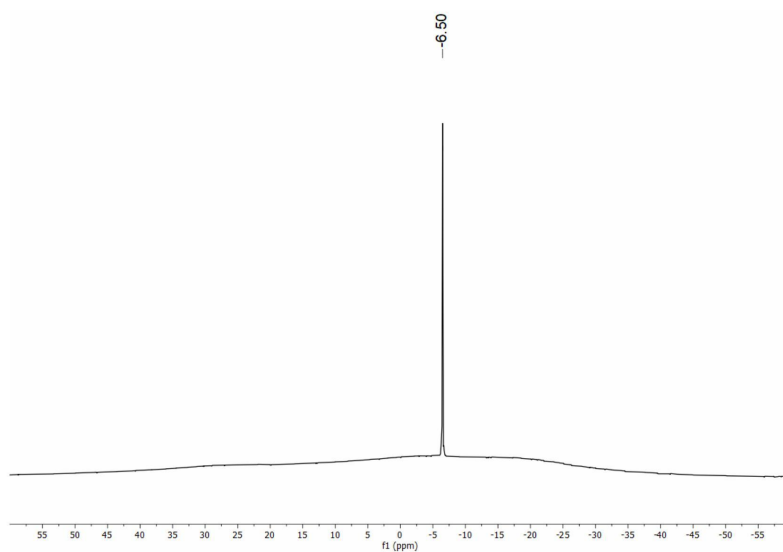


Figure S17. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of $[\mathbf{3}][\text{BArF}]$ in THF-d_8 at 298 K.

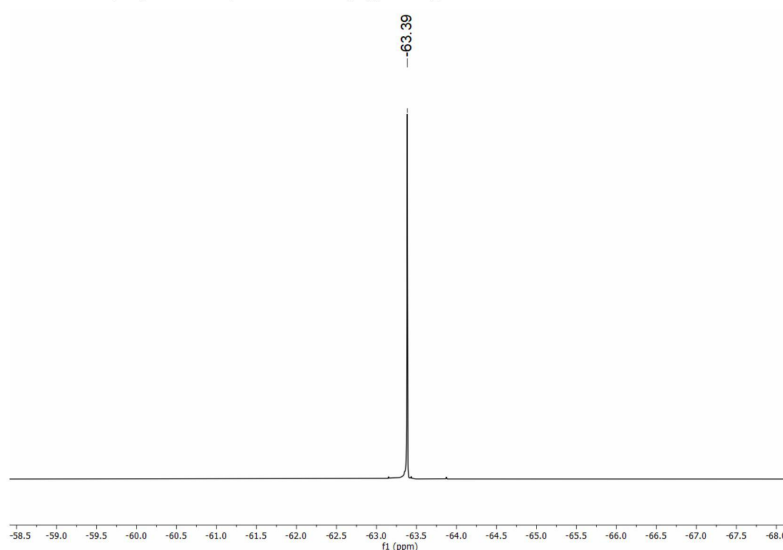


Figure S18. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $[\mathbf{3}][\text{BArF}]$ in THF-d_8 at 298 K.

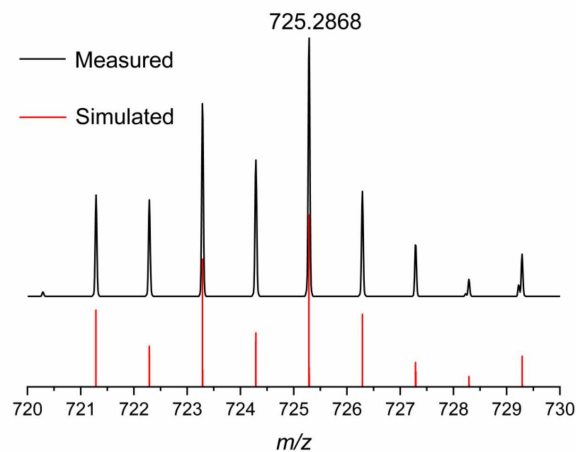
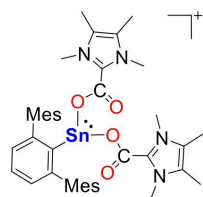


Figure S19. LIFDI-MS spectrum (detail view) of $[3]^+$ in $[3][\text{BArF}]$ (measured spectrum: top; simulated spectrum: bottom).

1.4 Synthesis of $[4][\text{BArF}]$



1.4.1 NMR Reaction

$[2][\text{BArF}]$ (16.2 μmol , 25.0 mg) was dissolved in THF-d_8 (0.4 mL) in a J-Young NMR tube. The solution was degassed using a freeze-pump-thaw cycle and then pressurized with 1 bar of CO_2 at room temperature. The reaction to form $[4][\text{BArF}]$ was completed after 21 hours, as confirmed by ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{119}\text{Sn}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopys.

1.4.2 Crystallisation of $[4][\text{BArF}]$

$[2][\text{BArF}]$ (32.4 μmol , 50.0 mg) was dissolved in Et_2O (1 mL) and pentane (2 mL). The solution was degassed freeze-pump-thaw cycle, followed by the addition of 1 bar of CO_2 at room temperature. After stirring for 24 hours, the solution's color changed from colorless to light yellow. The reaction solution was then stored at -35°C under the CO_2 atmosphere. After an additional 24 hours, light-yellow crystals suitable for single-crystal X-ray analysis were obtained.

Note: It was not possible to obtain solid samples of pure [4][BArF] in large quantities due to decomposition when placed under vacuum.

¹H NMR (400 MHz, 298 K, THF-d₈): δ[ppm] = 2.07 (s, 12 H, 2xC^{2,6}-CH₃, Mes), 2.11 (s, 6 H, 2xC⁴-CH₃, Mes), 2.30 (s, 12 H, 4xC-CH₃, NHC), 3.92 (s, 12 H, 4xN-CH₃, NHC), 6.70 (s, 4 H, 2xC^{3,5}-H, Mes), 6.87 (d, ³J_{H-H} = 8 Hz, 2 H, C^{3,5}-H, C₆H₃), 7.29 (t, ³J_{H-H} = 8 Hz, 1 H, C⁴-H, C₆H₃), 7.60, 7.81 (s, 12 H, 4xC^{2,4,6}, 4C₆H₃(CF₃)₂).

¹³C{¹H} NMR (101 MHz, 298 K, THF-d₈): δ[ppm] = 8.36 (2xC^{4,5}-CH₃, NHC), 21.14 (C⁴-CH₃, Mes), 21.88 (C^{2,6}-CH₃, Mes), 34.37 (4xN-CH₃, NHC), 118.27 (*p*-CH_{B-Ar}), 121.54, 124.24, 126.95 (C, BArF), 125.94 (CO₂ (aq)), 128.05 (4xC^{3,5}-H, Mes), 128.67 (C⁴-H, C₆H₃), 129.04 (C^{3,5}-H, C₆H₃), 129.11 (C^{4,5}-CH₃, NHC), 129.65-130.59 (*m*-C_{B-Ar}), 135.68 (*o*-CH_{B-Ar}), 136.41 (2xC⁴-Mes), 136.94 (N₂C, NHC), 137.77 (2xC¹-Mes), 141.74 (2xC^{2,6}-Mes), 149.45 (2xC^{2,6}-C₆H₃), 157.48 (CCO₂), 159.66-163.62 (ipso-CB-Ar), 172.98 (Sn-C, C₆H₃).

¹¹⁹Sn{¹H} NMR (149 MHz, 298 K, THF-d₈): δ[ppm] = 46.41 (Sn).

¹¹B{¹H} NMR (128 MHz, 298 K, THF-d₈): δ[ppm] = -6.47 (B, BArF).

¹⁹F{¹H} NMR (376 MHz, 298 K, THF-d₈): δ[ppm] = -63.36 (CF₃, BArF).

LIFDI-MS *m/z* C₄₀H₄₉N₄O₄Sn calcd: 769.2776; *m/z* found: 769.2777.

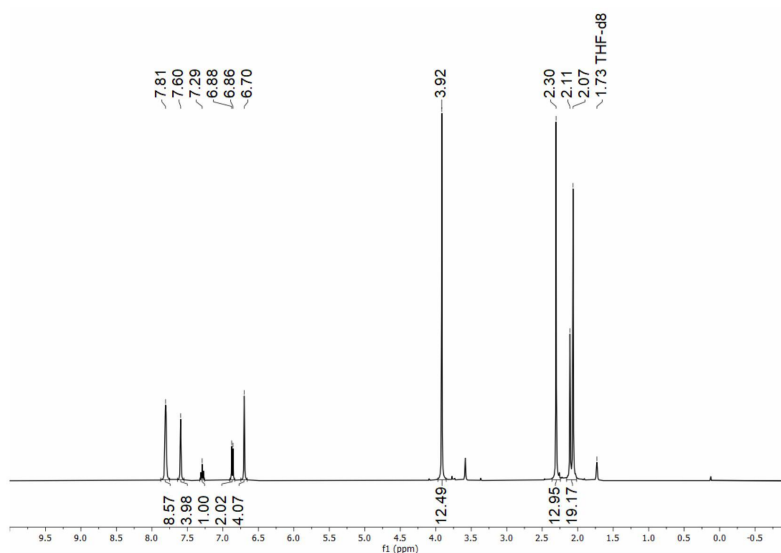


Figure S20. ¹H NMR spectrum of [4][BArF] in THF-d₈ at 298 K.

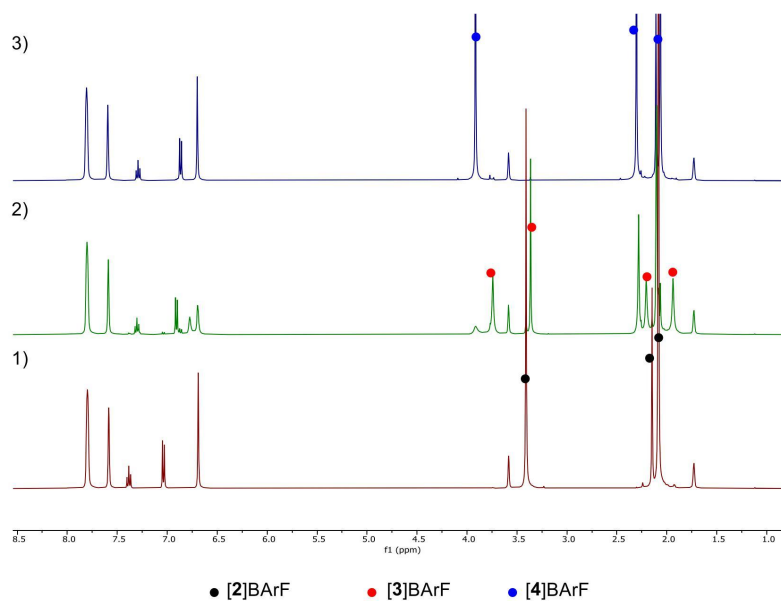


Figure S21. Stacked ^1H NMR spectra of the reaction of $[2][\text{BArF}]$ with CO_2 (1 bar): 1) $[2][\text{BArF}]$; 2) $[2][\text{BArF}] + \text{CO}_2$, RT 6 hours; 3) $[2][\text{BArF}] + \text{CO}_2$, RT 21 hours.

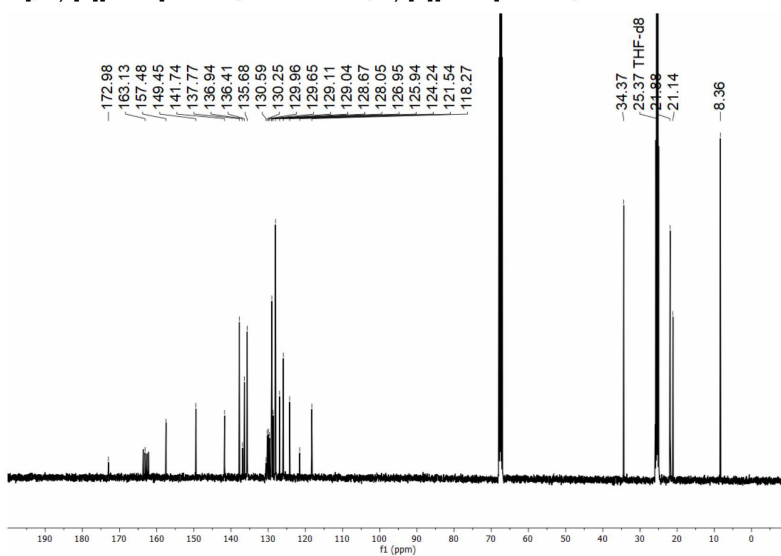


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **[4][BArF]** in THF- d_8 at 298 K.

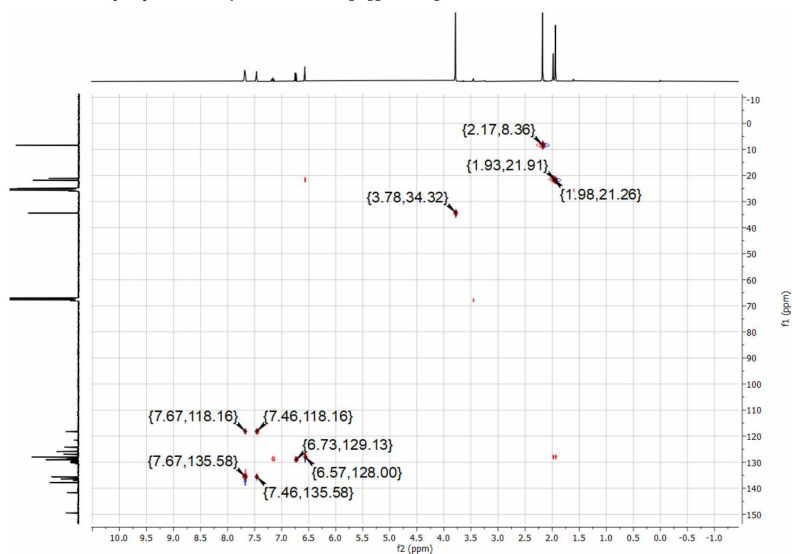


Figure S23. $^1\text{H}/^{13}\text{C}$ NMR HSQC spectrum of **[4][BArF]** in THF- d_8 at 298 K.

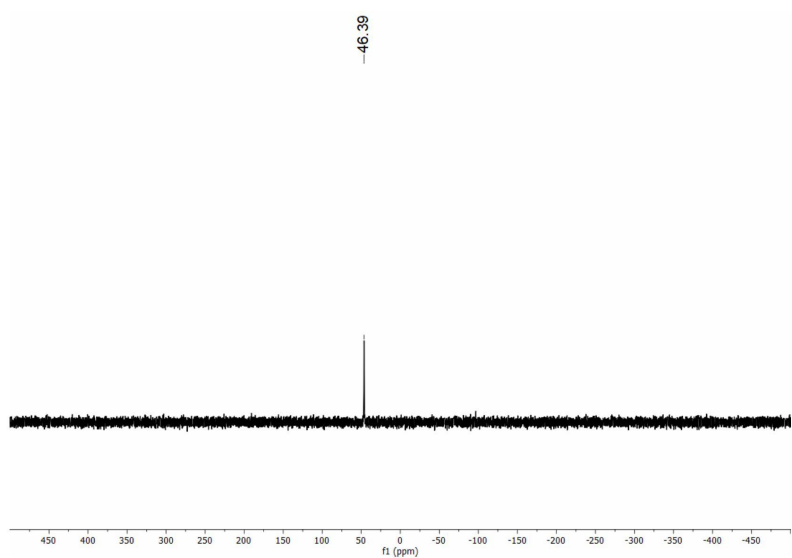


Figure S24. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **[4][BArF]** in THF- d_8 at 298 K.

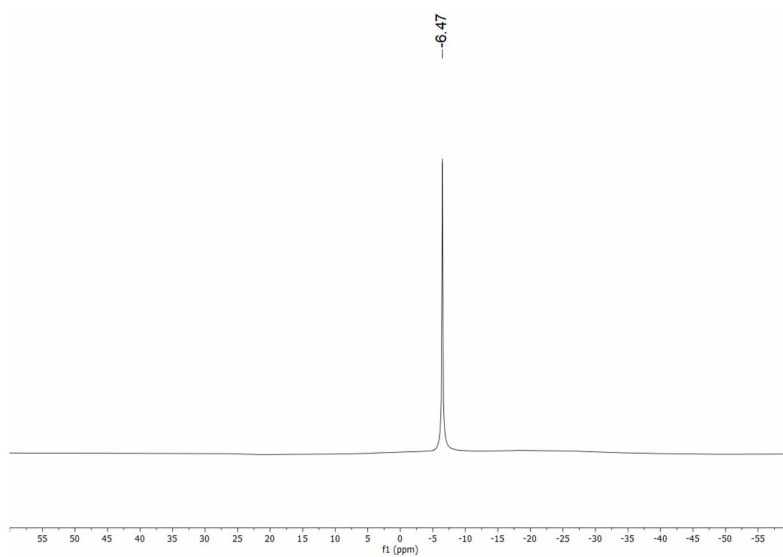


Figure S25. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **[4][BArF]** in THF-d_8 at 298 K.

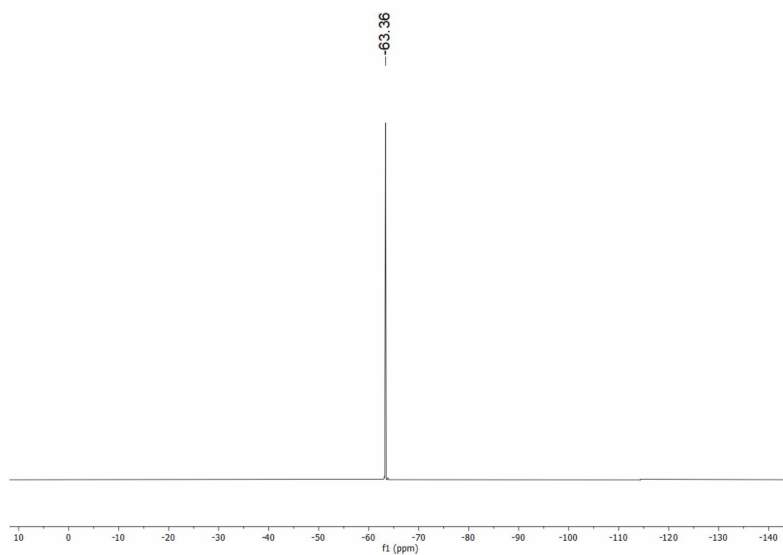


Figure S26. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **[4][BArF]** in THF-d_8 at 298 K.

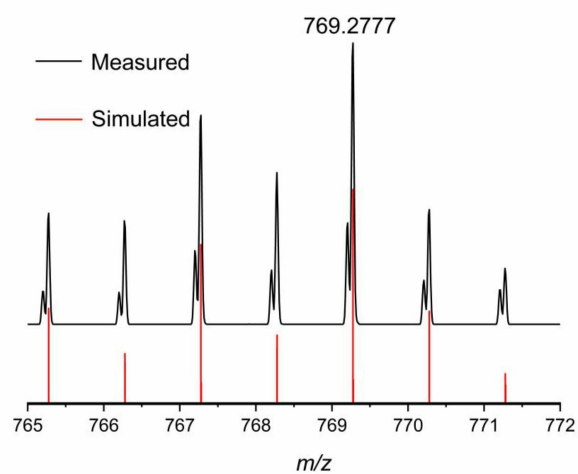


Figure S27. LIFDI-MS spectrum (detail view) of $[4]^+$ in $[4][\text{BArF}]$ (measured spectrum: top; simulated spectrum: bottom).

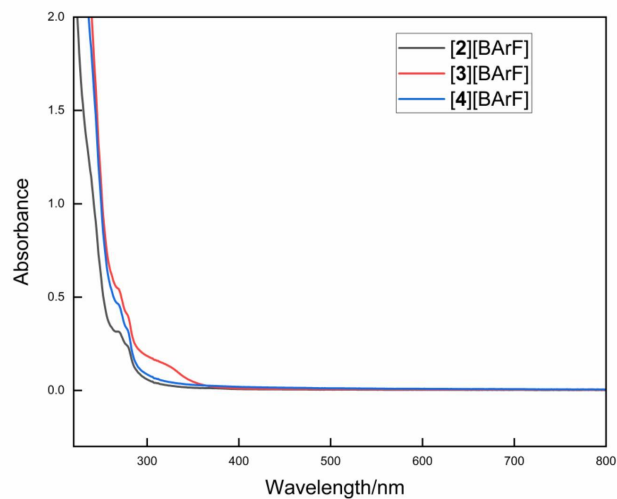
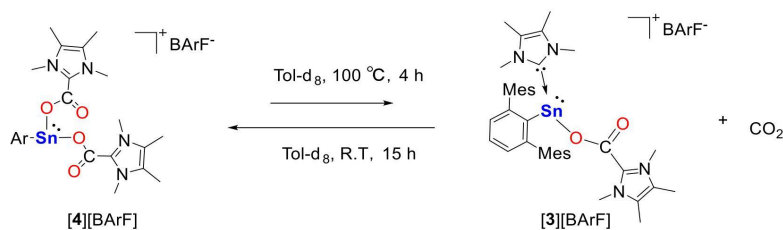


Figure S28. UV-vis spectrums of **[2][BArF]**, **[3][BArF]**, and **[4][BArF]** (r.t., THF, concentration: 3.125×10^{-5} M). No abstraction signal is observed in the UV spectra of **[2][BArF]**, **[3][BArF]**, and **[4][BArF]**.

1.5 NMR Experiments

1.5.1 The thermal stability of **[4][BArF]**



To test the reversibility of **[4][BArF]**, a solution of **[4][BArF]** in toluene- d_8 (0.2 mL) and fluorobenzene (0.2 mL) was heated to 100 °C under CO_2 or argon atmosphere in a J-Young NMR tube and monitored by 1H NMR.

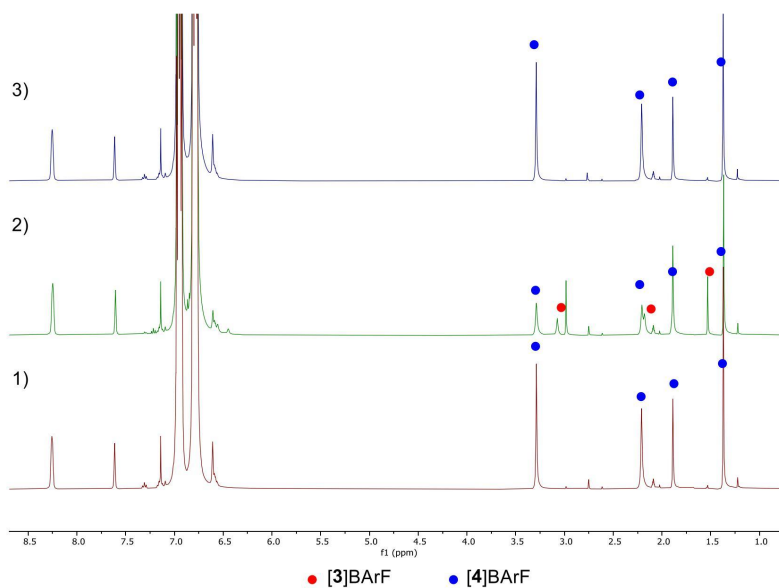


Figure S29. Stacked ^1H NMR spectra showing reversibility of [4]BArF under CO_2 atmosphere. 1) [4]BArF; 2) [4]BArF heating 4 hours at 100°C ; 3) cool to rt for 15 hours.

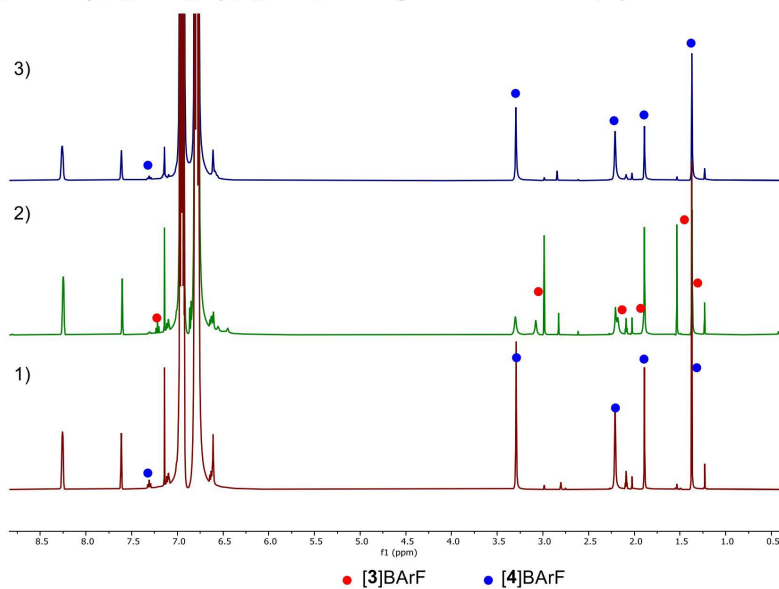


Figure S30. Stacked ^1H NMR spectra showing reversibility of [4][BArF] under argon atmosphere. 1) [4][BArF]; 2) [4][BArF] heating 4 hours at 100 °C; 3) cool to room temperature for 15 hours.

1.5.2 [4][BArF] reaction with Ph_2SiH_2

[2][BArF] (1.00 eq, 16.2 μmol , 25.0 mg) was dissolved in C_6D_6 (0.2 mL) and fluorobenzene (0.2 mL) in a J-Young NMR tube. The solution was then freeze-pump-thaw degassed and was then pressurised with 1 bar of CO_2 at room temperature. After 21 hours (when [4][BArF] was completely formed) the excess CO_2 was removed and H_2SiPh_2 (1.00 eq, 16.2 μmol , 2.43 μL) was added. The reaction progress was monitored by ^1H NMR spectroscopy.

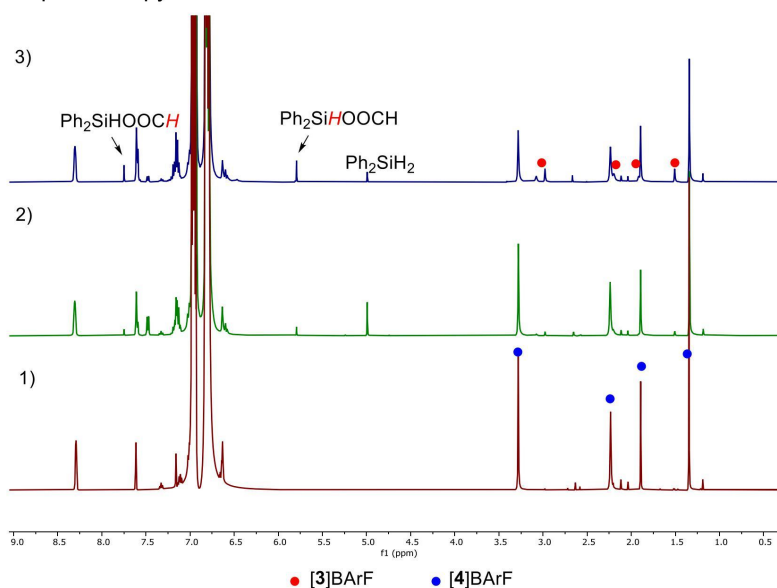


Figure S31. Stacked ^1H NMR spectra showing [4][BArF] reaction with Ph_2SiH_2 : 1) the formation of [4][BArF]; 2) [4][BArF] + H_2SiPh_2 , RT 1 hour; 3) [4][BArF] + H_2SiPh_2 , RT 5 hours.

1.6 Catalytic Experiments

General Procedure for Hydrosilylation of CO_2 : Silane (80.0 μmol , 14.9 μL), 1,3,5-trimethoxybenzene (0.10 eq of the silane, as an internal standard),* and catalyst were dissolved in a mixture of $\text{C}_6\text{D}_6/\text{C}_6\text{H}_5\text{F}$ in a J-Young NMR tube under an argon atmosphere. An initial ^1H NMR spectrum was measured to determine the concentration of silane (by comparison to the internal standard). Subsequently, the solution was rapidly degassed using a Schlenk line and then refilled with 1 bar of CO_2 . The progression of reaction was monitored via ^1H NMR spectroscopy by the consumption of silane alongside the

emergence of the respective hydrosilylation products resonances. After 25 hours, the conversion of silane was determined by comparing integrals of the unreacted silane resonances to the integrals of the internal standard. The yield was determined by comparing integrals of the $R_2SiH(OCHO)$ or $R_3Si(OCHO)$ resonances of the hydrosilylation product to the integral of the internal standard. The summary of the results was shown in **Table S1**.

* = 1,3,5-trimethoxybenzene was selected as the internal standard, setting its concentration to 10 mol% of the added silane. This equivalent exhibits a strong signal-to-noise ratio, and the signal of internal standard is comparable to that of silane.

Mercury Test Experiment

[2][BArF] (5 mol%, 4.00 μ mol, 80.0 μ L, 0.05 M in C_6H_5F), H_2SiPh_2 (80.0 μ mol, 14.9 μ L), and 1,3,5-trimethoxybenzene (0.10 eq of the Ph_2SiH_2) as an internal standard were dissolved in C_6D_6 (0.32 mL) in a J-Young NMR tube. Then mercury (13.5 mg) was added to the solution. The solution was rapidly degassed using a Schlenk line and then refilled with 1 bar of CO_2 at room temperature. The progression of reaction was monitored via 1H NMR spectroscopy. The results are shown in Table S1 (Entry 11).

Catalytic reduction of CO_2 with Ph_2SiH_2 by [4][BArF]

[2][BArF] (5 mol%, 4.00 μ mol, 80.0 μ L, 0.05 M in C_6H_5F) and 1,3,5-trimethoxybenzene (0.10 eq, 8.0 μ mol) were introduced into 0.32 mL of C_6D_6 within a J-Young NMR tube. The solution was degassed and refilled with 1 bar of CO_2 at room temperature. The solution of [4][BArF] was obtained after 21 hours and excess CO_2 was removed, then H_2SiPh_2 (1.0 eq, 80.0 μ mol, 14.9 μ L) was added in gloves box. The solution was degassed again and then pressurised with 1 bar of CO_2 at room temperature. The reaction was monitored via 1H NMR spectroscopy.

Table S1. Hydrosilylation of CO₂

Entry	Catalysis (mol%)	Solvent	T /°C	Silane	Conversion/% (time)	NMR Yield/% [R ₃ Si(OCHO)]	TOF /h ⁻¹	¹ H NMR Number
1	[2][BArF] (0.5)	C ₆ D ₆ :C ₆ H ₅ F (4:1)	25	H ₂ SiPh ₂	4	<1	0.35	Figure S32
2	[2][BArF] (1)	C ₆ D ₆ :C ₆ H ₅ F (4:1)	25	H ₂ SiPh ₂	11	4	0.45	Figure S33
3	[2][BArF] (2.5)	C ₆ D ₆ :C ₆ H ₅ F (4:1)	25	H ₂ SiPh ₂	74	63	1.18	Figure S34
4	[2][BArF] (5)	C ₆ D ₆ :C ₆ H ₅ F (4:1)	25	H ₂ SiPh ₂	94	81	0.75	Figure S35
5	[2][BArF] (5)	C ₆ D ₆	25	H ₂ SiPh ₂	78	71	0.62	Figure S36
6	[2][BArF] (5)	THF-d ₈	25	H ₂ SiPh ₂	75	54	0.60	Figure S37
7	[2][BArF] (5)	C ₆ D ₆ :C ₆ H ₄ F ₂ (4:1)	25	H ₂ SiPh ₂	97	77	0.77	Figure S38
8	[2][BArF] (5)	C ₆ D ₆ :C ₆ H ₄ F ₂ (1:1)	25	H ₂ SiPh ₂	94	81	0.75	Figure S39
9	[2][BArF] (5)	C ₆ D ₆ :C ₆ H ₅ F (4:1)	50	H ₂ SiPh ₂	64 (2 hours)	64	0.79	Figure S40
10	[2][Al(OC(CF ₃) ₃) ₃] (5)	C ₆ D ₆ :C ₆ H ₅ F (4:1)	25	H ₂ SiPh ₂	70	60	0.56	Figure S41
11	[2][BArF] (5)+Hg	C ₆ D ₆ :C ₆ H ₅ F (4:1)	25	H ₂ SiPh ₂	89	69	0.71	Figure S42
12	[3][BArF] (5)	C ₆ D ₆ :C ₆ H ₅ F (4:1)	25	H ₂ SiPh ₂	92	83	0.74	Figure S43
13	[4][BArF] (5)	C ₆ D ₆ :C ₆ H ₅ F (4:1)	25	H ₂ SiPh ₂	93	93	0.74	Figure S44
14	IMe ₄ (10)	C ₆ D ₆ :C ₆ H ₅ F (4:1)	25	H ₂ SiPh ₂	51	< 1	0.39	Figure S45
15	IMe ₄ -CO ₂ (10)	C ₆ D ₆ :C ₆ H ₄ F ₂ (1:1)	25	H ₂ SiPh ₂	51	9	0.41	Figure S46
16	[2][BArF] (5)	C ₆ D ₆ :C ₆ H ₅ F (4:1)	25	Me ₂ PhSiH	47	46	0.37	Figure S47
17	[2][BArF] (5)	C ₆ D ₆ :C ₆ H ₅ F (4:1)	25	H ₃ SiPh	48 (2 hours) 71 (12 hours)	39 <1	4.8 1.18	Figure S48

18	[2][BArF] (5)	C ₆ D ₆ :C ₆ H ₅ F (4:1)	60	HSiEt ₃	29	27	0.23	Figure S49
19	[2][BArF] (5)	C ₆ D ₆ :C ₆ H ₅ F (4:1)	80	HSiPh ₃	No reaction	-	-	Figure S50

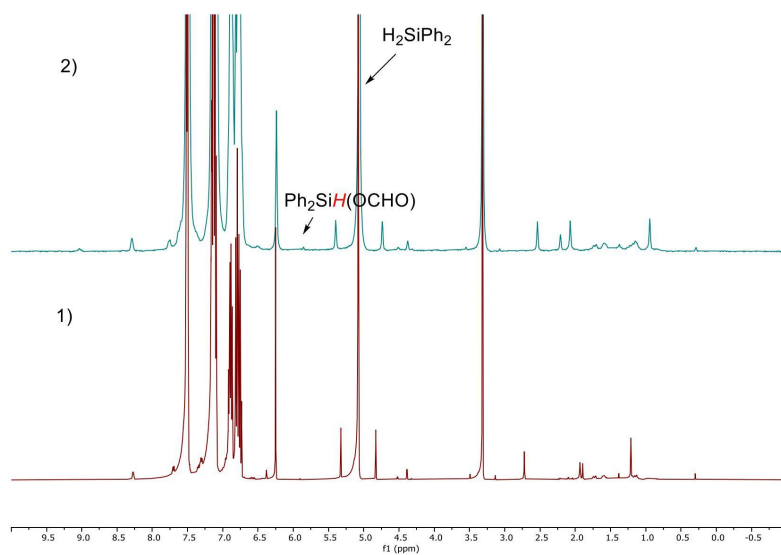


Figure S32. Stacked ¹H NMR spectra of hydrosilylation of CO₂ with H₂SiPh₂ by [2][BArF] (0.5 mol%) in C₆D₆/C₆H₅F (4:1): 1) [2][BArF] (0.5 mol%) + H₂SiPh₂; 2) [2][BArF] (0.5 mol%) + H₂SiPh₂ + CO₂, RT 25 hours.

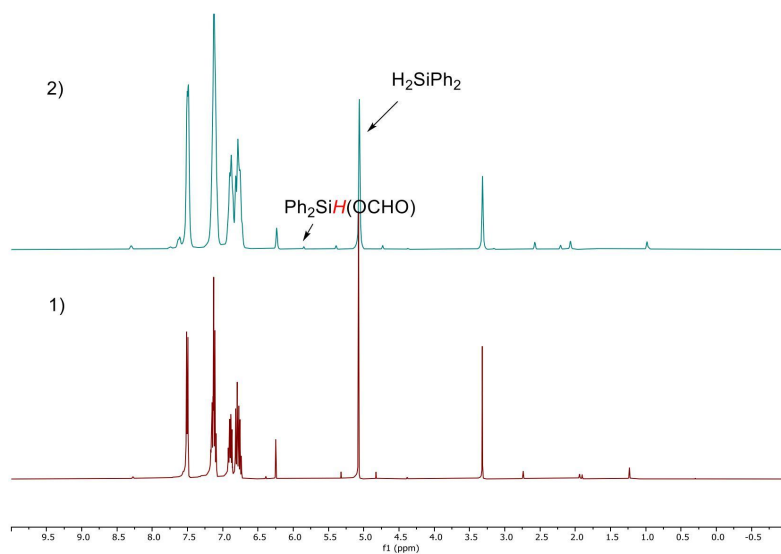


Figure S33. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with H_2SiPh_2 by $[\mathbf{2}][\text{BArF}]$ (1 mol%) in $\text{C}_6\text{D}_6/\text{C}_6\text{H}_5\text{F}$ (4:1): 1) $[\mathbf{2}][\text{BArF}]$ (1 mol%) + H_2SiPh_2 ; 2) $[\mathbf{2}][\text{BArF}]$ (1 mol%) + H_2SiPh_2 + CO_2 , RT 25 hours.

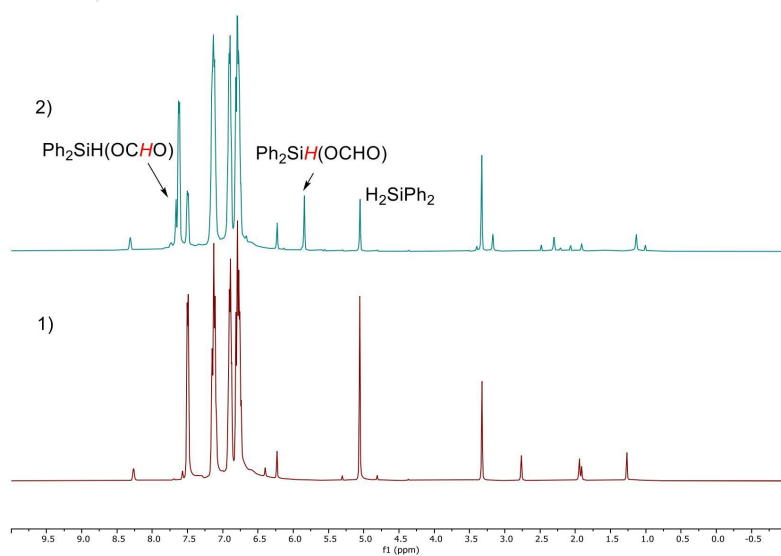


Figure S34. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with H_2SiPh_2 by **[2]**[BArF] (2.5 mol%) in $\text{C}_6\text{D}_6/\text{C}_6\text{H}_5\text{F}$ (4:1): 1) **[2]**[BArF] (2.5 mol%) + H_2SiPh_2 ; 2) **[2]**[BArF] (2.5 mol%) + H_2SiPh_2 + CO_2 , RT 25 hours.

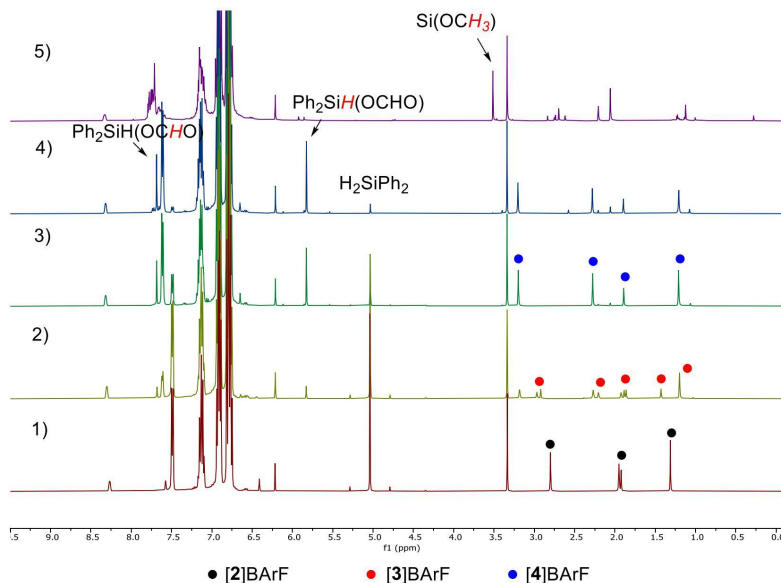


Figure S35. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with H_2SiPh_2 by **[2]**[BArF]: 1) **[2]**[BArF] (5 mol%) + H_2SiPh_2 ; 2) **[2]**[BArF] (5 mol%) + H_2SiPh_2 + CO_2 , RT 2 hours; 3) **[2]**[BArF] (5 mol%) + H_2SiPh_2 + CO_2 , RT 12 hours; 4) **[2]**[BArF] (5 mol%) + H_2SiPh_2 + CO_2 , RT 25 hours; 5) **[2]**[BArF] (5 mol%) + H_2SiPh_2 + CO_2 , RT 72 hours.

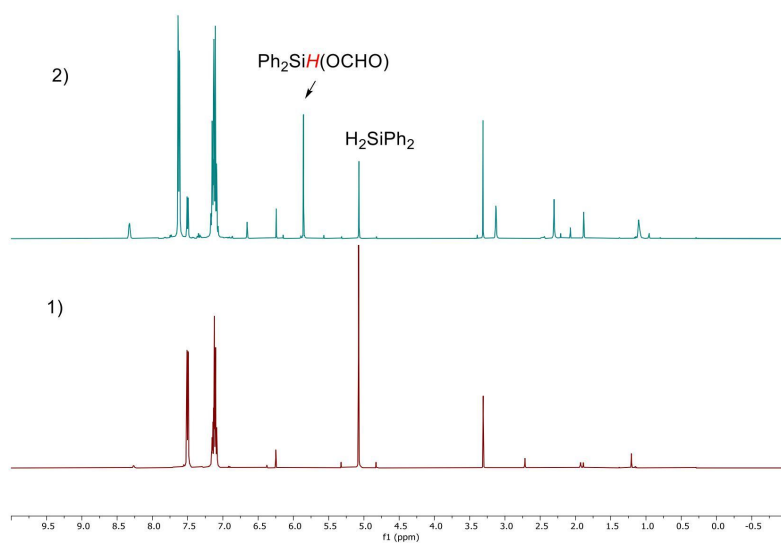


Figure S36. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with H_2SiPh_2 by $[\mathbf{2}][\text{BArF}]$ in C_6D_6 : 1) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_2SiPh_2 ; 2) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_2SiPh_2 + CO_2 , RT 25 hours.

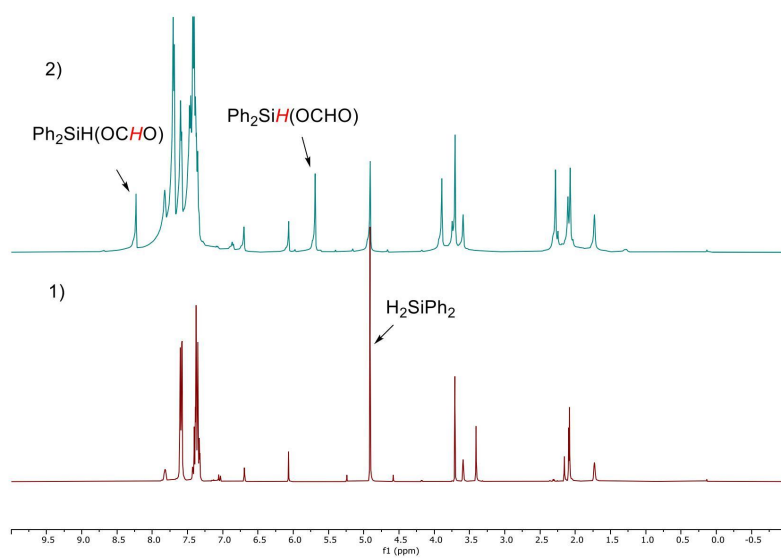


Figure S37. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with H_2SiPh_2 by $[\mathbf{2}][\text{BArF}]$ in THF-d_8 : 1) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_2SiPh_2 ; 2) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_2SiPh_2 + CO_2 , RT 25 hours.

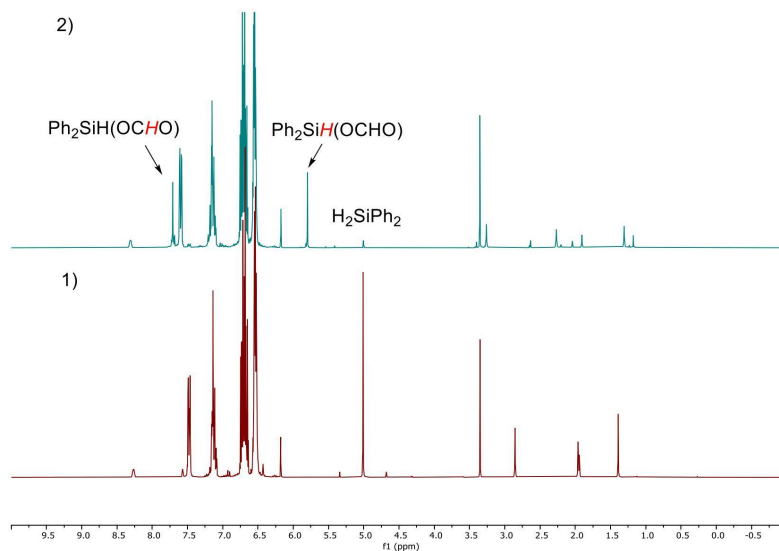


Figure S38. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with H_2SiPh_2 by $[\mathbf{2}][\text{BArF}]$ in $\text{C}_6\text{D}_6/\text{C}_6\text{H}_4\text{F}_2$ (4:1): 1) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_2SiPh_2 ; 2) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_2SiPh_2 + CO_2 , RT 25 hours.

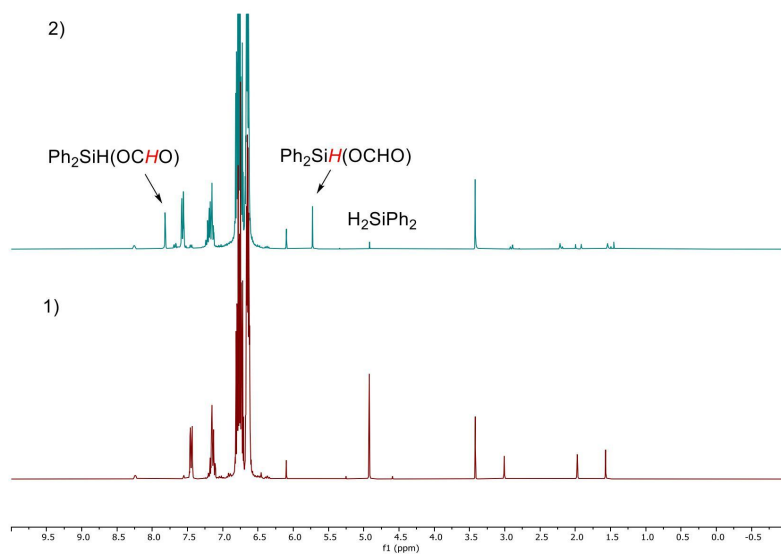


Figure S39. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with H_2SiPh_2 by $[\mathbf{2}][\text{BArF}]$ in $\text{C}_6\text{D}_6/\text{C}_6\text{H}_4\text{F}_2$ (1:1): 1) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_2SiPh_2 ; 2) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_2SiPh_2 + CO_2 , RT 25 hours.

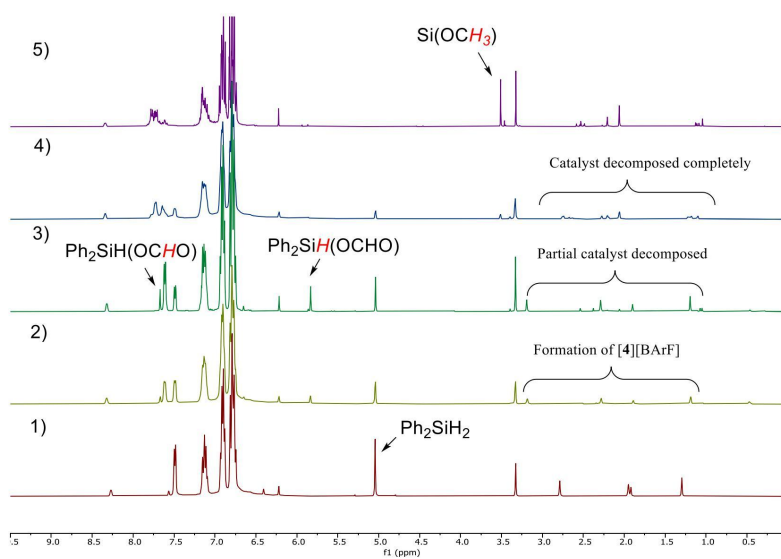


Figure S40. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with H_2SiPh_2 by $[\mathbf{2}][\text{BArF}]$ in $\text{C}_6\text{D}_6/\text{C}_6\text{H}_5\text{F}$ (4:1) at 50°C : 1) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_2SiPh_2 ; 2) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_2SiPh_2 + CO_2 , 50°C 1 hour; 3) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_2SiPh_2 + CO_2 , 50°C 2 hours; 4) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_2SiPh_2 + CO_2 , 50°C 7 hours; 5) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_2SiPh_2 + CO_2 , 50°C 25 hours.

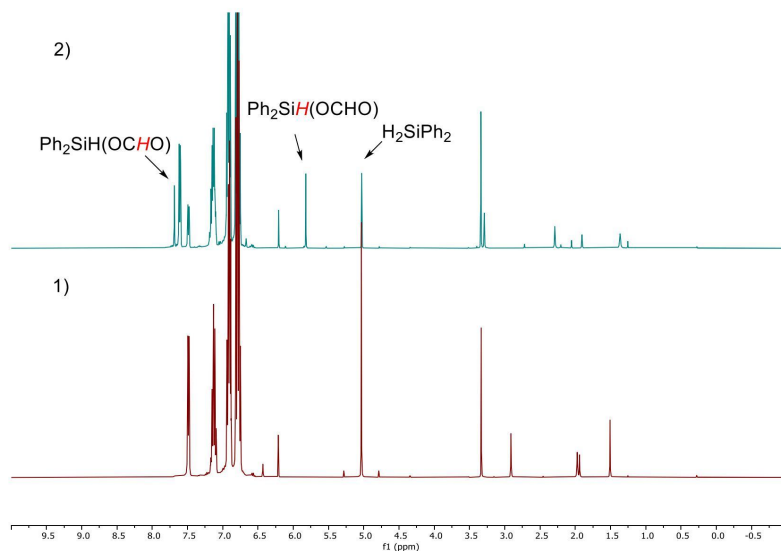


Figure S41 Stacked ^1H NMR spectra of hydrosilylation of CO_2 with H_2SiPh_2 by $[\mathbf{2}][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ in $\text{C}_6\text{D}_6/\text{C}_6\text{H}_5\text{F}$ (4:1): 1) $[\mathbf{2}][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ (5 mol%); 2) $[\mathbf{2}][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ (5 mol%) + H_2SiPh_2 + CO_2 , RT 25 hours.

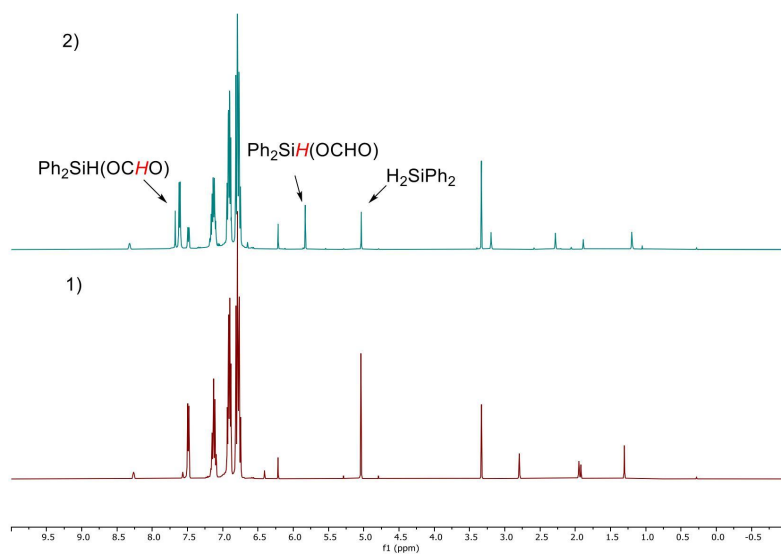


Figure S42. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with H_2SiPh_2 by $[\mathbf{2}][\text{BArF}]$ in $\text{C}_6\text{D}_6/\text{C}_6\text{H}_5\text{F}$ (4:1) in the presence of Hg: 1) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_2SiPh_2 ; 2) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_2SiPh_2 + CO_2 , RT 25 hours.

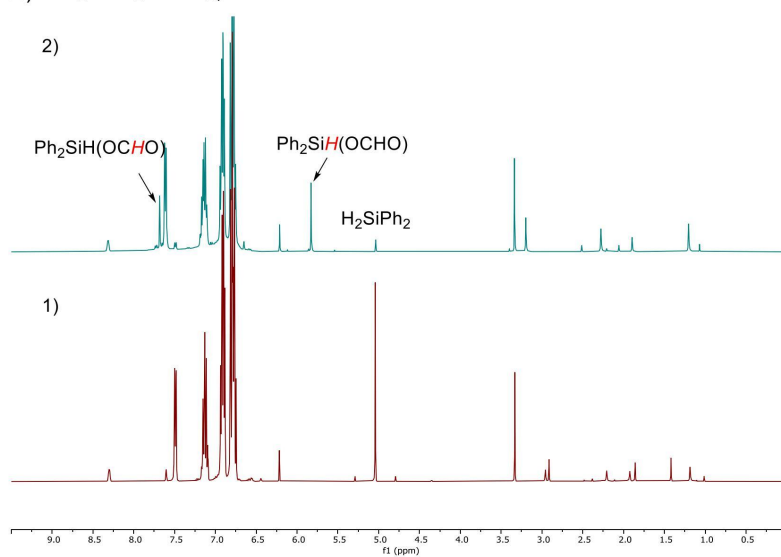


Figure S43. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with H_2SiPh_2 by **[3]**[BArF]:
 1) **[3]**[BArF] (5 mol%) + H_2SiPh_2 ; 2) **[3]**[BArF] (5 mol%) + H_2SiPh_2 + CO_2 , RT 25 hours.

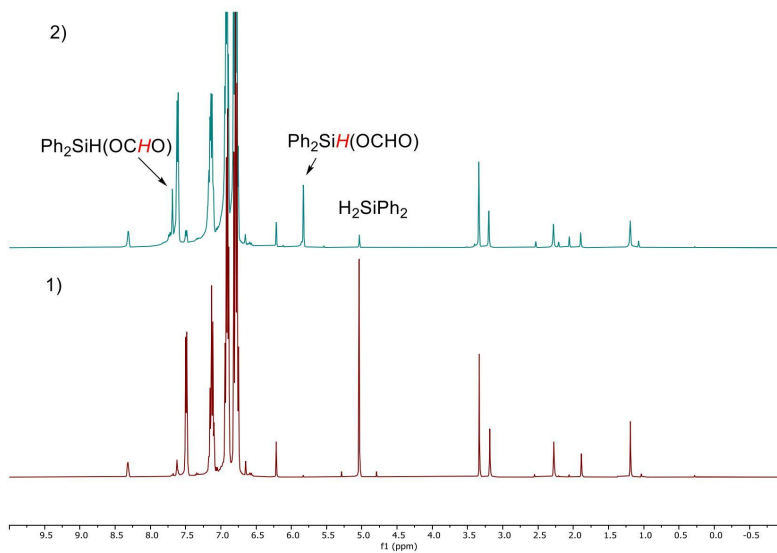


Figure S44. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with H_2SiPh_2 by **[4]**[BArF]:
 1) **[4]**[BArF] (5 mol%) + H_2SiPh_2 ; 2) **[4]**[BArF] (5 mol%) + H_2SiPh_2 + CO_2 , RT 25 hours.

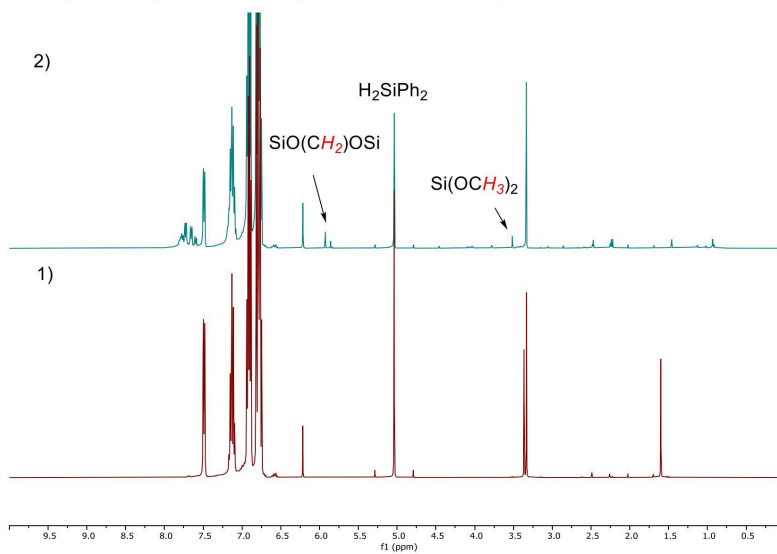


Figure S45. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with H_2SiPh_2 by IMe4: 1) IMe4 (10 mol%) + H_2SiPh_2 ; 2) IMe4 + H_2SiPh_2 + CO_2 , after 25 hours.

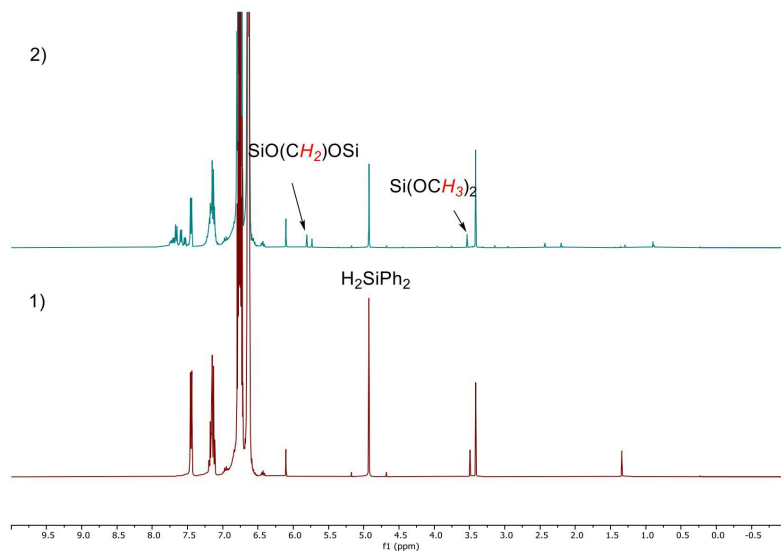


Figure S46. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with H_2SiPh_2 by IMe4- CO_2 : 1) IMe4- CO_2 (10 mol%) + H_2SiPh_2 ; 2) IMe4- CO_2 + H_2SiPh_2 + CO_2 , RT 25 hours.

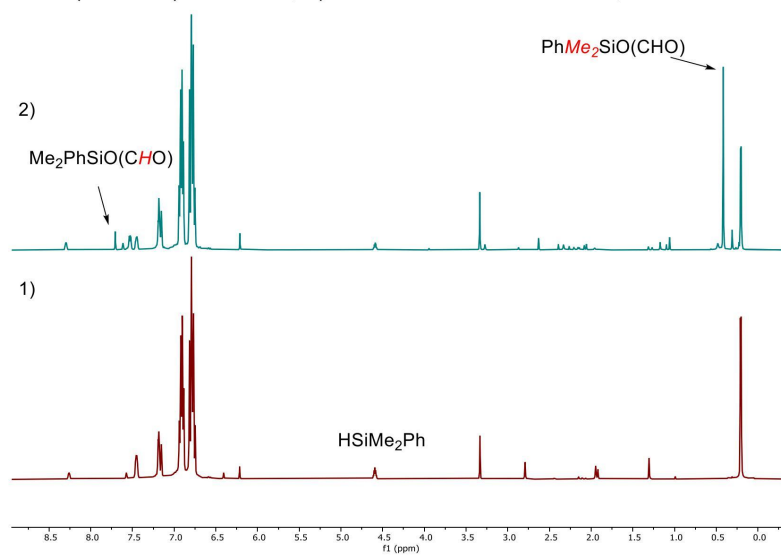


Figure S47. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with HSiMe_2Ph by $[\mathbf{2}][\text{BArF}]$: 1) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + HSiMe_2Ph ; 2) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + HSiMe_2Ph + CO_2 , RT 25 hours.

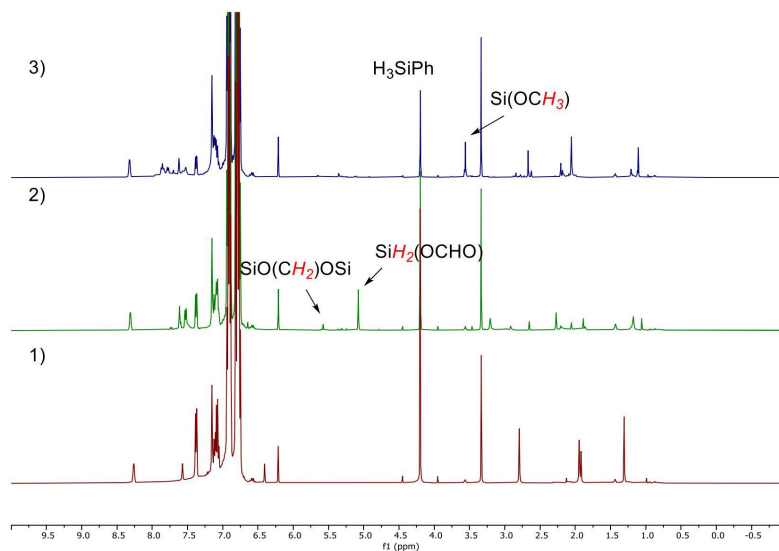


Figure S48. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with H_3SiPh by $[\mathbf{2}][\text{BArF}]$: 1) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_3SiPh ; 2) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_3SiPh + CO_2 , RT 2 hours; $[\mathbf{2}][\text{BArF}]$ (5 mol%) + H_3SiPh + CO_2 , RT 12 hours.

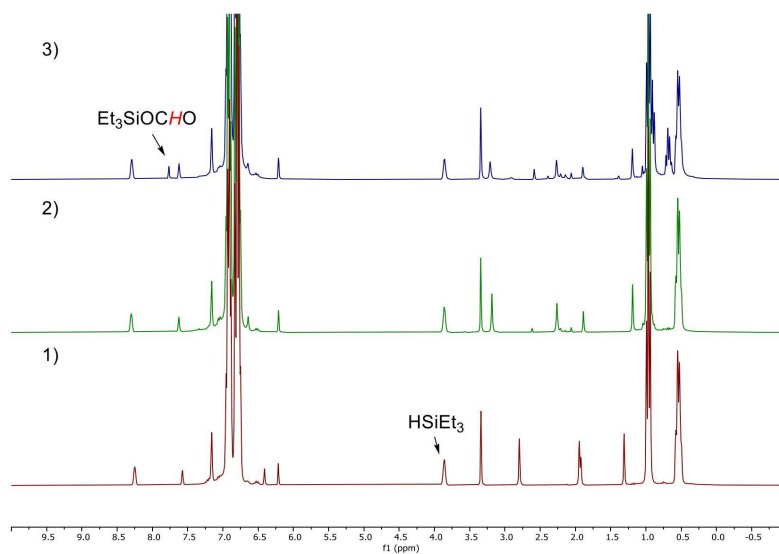


Figure S49. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with HSiEt_3 by $[\mathbf{2}][\text{BArF}]$: 1) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + HSiEt_3 ; 2) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + HSiEt_3 + CO_2 , RT 21 hours; $[\mathbf{2}][\text{BArF}]$ (5 mol%) + HSiEt_3 + CO_2 , RT 21 hours + 60 °C 25 hours.

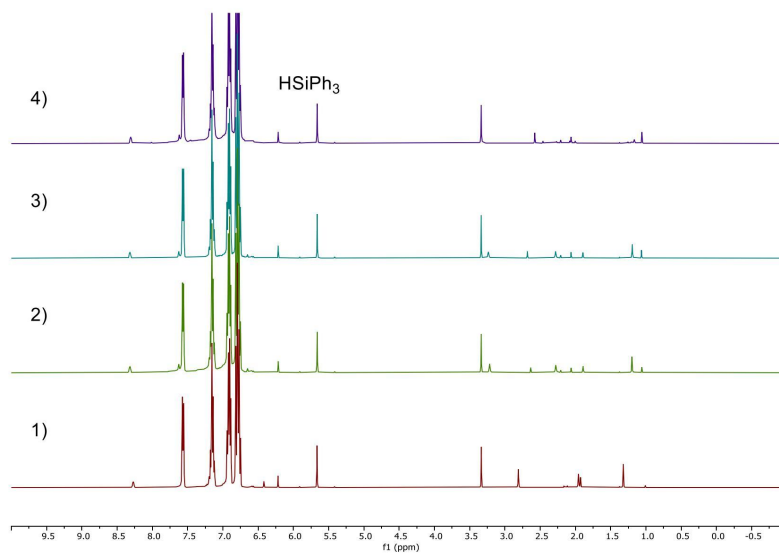
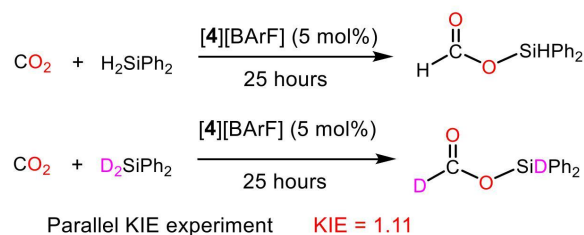


Figure S50. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with HSiPh_3 by **[2][BArF]**: 1) **[2][BArF]** (5 mol%) + HSiPh_3 ; 2) **[2][BArF]** (5 mol%) + HSiPh_3 + CO_2 , RT 17 hours + 60 °C 18 hours + 80 °C 18 hours.

2. Mechanistic Studies

2.1 Kinetic Isotope Experiments



[2][BArF] (5 mol%, 4.00 μmol , 80.0 μL , 0.05 M in $\text{C}_6\text{H}_5\text{F}$) and 1,3,5-trimethoxybenzene (0.10 eq, 8.0 μmol) were introduced into 0.32 mL of C_6D_6 within a J-Young NMR tube. The solution was degassed and refilled with 1 bar of CO_2 at room temperature. The solution of **[4][BArF]** was obtained after 21 hours and excess CO_2 was removed, then H_2SiPh_2 (1.0 eq, 80.0 μmol , 14.9 μL) (or D_2SiPh_2 (1.0 eq, 80.0 μmol , 14.7 μL)) was added in gloves box. The solution was degassed again and then pressurised with 1 bar of CO_2 at room temperature. The reaction progression was monitored via ^1H NMR spectroscopy by the consumption of silane alongside the emergence of the respective hydrosilylation products resonances. After 25 hours, the conversion of silane was determined by comparing integrals of the unreacted silane resonances to the integrals of the internal standard.

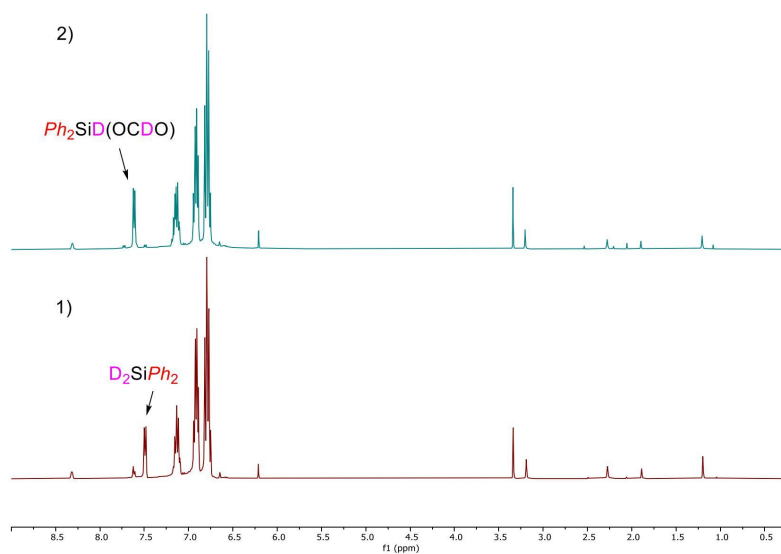


Figure S51. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with D_2SiPh_2 by $[4][\text{BArF}]$: 1) $[4][\text{BArF}]$ (5 mol%) + D_2SiPh_2 ; 2) $[4][\text{BArF}]$ (5 mol%) + $\text{H}_2\text{SiPh}_2 + \text{CO}_2$, RT 25 hours.

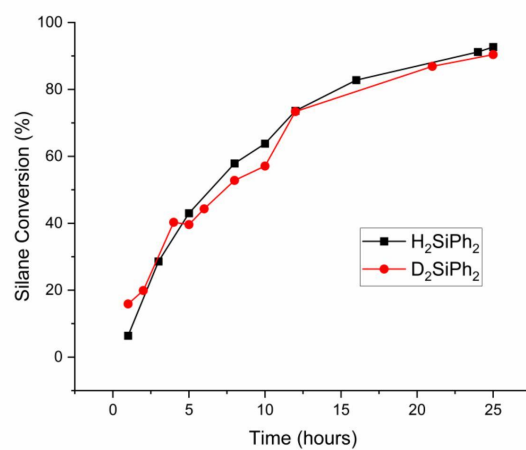


Figure S52. Kinetic isotope effect experiments.

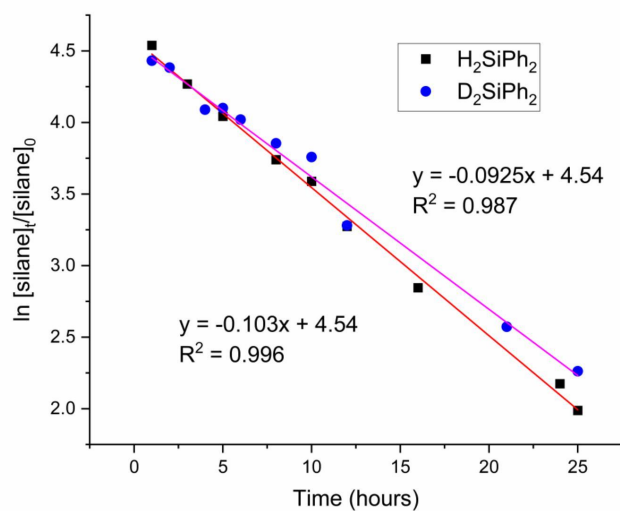
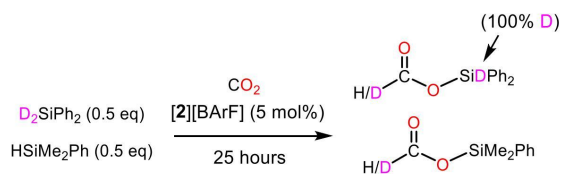


Figure S53. Kinetic isotope effect experiments.

2.2 H/D Exchange Experiments



[2][BARF] (5 mol%, 4.00 μmol , 80.0 μL , 0.05 M in $\text{C}_6\text{H}_5\text{F}$), D_2SiPh_2 (0.5 eq, 40.0 μmol , 8.35 μL), HSiMe_2Ph (0.5 eq, 40.0 μmol , 6.13 μL), and 1,3,5-trimethoxybenzene (0.10 eq of the H_2SiPh_2) as an internal standard were dissolved in C_6D_6 (0.32 mL) in a J-Young NMR tube. The solution was rapidly degassed using a Schlenk line and then refilled with 1 bar of CO_2 at room temperature. The progression of reaction was monitored via ^1H NMR spectroscopy.

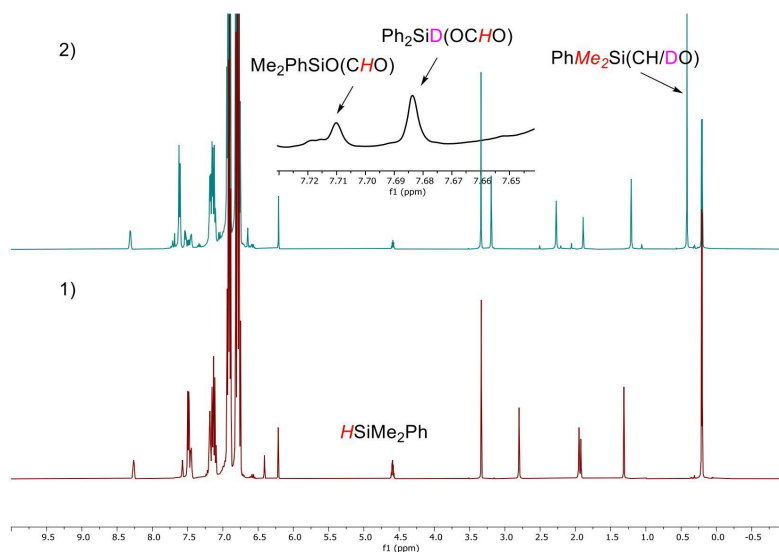


Figure S54. Stacked ^1H NMR spectra of hydrosilylation of CO_2 with $\text{D}_2\text{SiPh}_2/\text{HSiMe}_2\text{Ph}$ by $[\mathbf{2}][\text{BArF}]$: 1) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + D_2SiPh_2 + HSiMe_2Ph ; 2) $[\mathbf{2}][\text{BArF}]$ (5 mol%) + D_2SiPh_2 + HSiMe_2Ph + CO_2 , RT 25 hours.

3. X-Ray Crystallographic Details

General considerations

Single crystals diffraction data were recorded on a Bruker Photon D8 Venture DUO IMS system equipped with a Helios optic monochromator and a Mo IMS microsource ($\lambda = 0.71073 \text{ \AA}$) and an Atlas SuperNova system equipped with a mirror monochromator and a Cu micro-focus sealed X-ray tube ($\lambda = 1.54178 \text{ \AA}$). The data collection was performed, using the APEX IV software package^{S4} and CrysAlisPro^{S5} on single crystals coated with Fomblin®Y as perfluorinated ether. The single crystal was picked on a micro sampler, transferred to the diffractometer, and measured frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorentz 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 $\text{Uiso}(\text{H}) = 1.2 \text{ Ueq}(\text{C})$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Fullmatrix least-squares refinements were carried

out by minimizing $\Sigma w(F_o - F_c)^2$ 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 CCDC numbers 2255434, 2255353 and 2255355 contain the supplementary crystallographic data for the structures [2][BArF], [3][BArF] and [4][BArF], respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>.

Table S2. Crystallographic details

Compound #	[2][BArF]	[3][BArF]	[4][BArF]
CCDC-Number	2255434	2255353	2255355
Empirical formula	C ₇₀ H ₆₁ BF ₂₄ N ₄ Sn	C ₇₉ H ₈₀ N ₅ O ₂ B ₅ F ₂₄ Sn	C ₇₂ H ₆₁ N ₄ O ₄ BF ₂₄ Sn
Formula weight	1543.84	1760.22	1631.74
Temperature/K	100.00	100.00	100.00
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	13.4232(4)	15.2450(13)	10.4739(5)
b/Å	17.0569(6)	17.2704(13)	16.0890(8)
c/Å	18.5469(7)	17.6243(14)	23.3384(11)
α /°	102.535(3)	92.495(3)	109.831(2)
β /°	101.839(3)	102.397(3)	92.107(2)
γ /°	109.969(3)	112.807(2)	102.860(2)
Volume/Å ³	3711.1(2)	4136.1(6)	3579.7(3)
Z	2	2	2
ρ_{calc} /g/cm ³	1.382	1.413	1.514
μ /mm ⁻¹	3.644	0.411	0.471
F(000)	1560.0	1792.0	1648.0
Crystal size/mm ³	0.1 × 0.07 × 0.05	0.382 × 0.287 × 0.198	0.347 × 0.26 × 0.106
Radiation	CuK α (λ = 1.54184)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	5.124 to 147.842	4.684 to 50.7	3.864 to 50.7
Index ranges	-16 ≤ h ≤ 11, -20 ≤ k ≤ 21, -23 ≤ l ≤ 22	-18 ≤ h ≤ 18, -20 ≤ k ≤ 20, -21 ≤ l ≤ 21	-12 ≤ h ≤ 12, -19 ≤ k ≤ 19, -27 ≤ l ≤ 28
Reflections collected	26916	93421	66144
Independent reflections	14585 [R _{int} = 0.0442, R _{sigma} = 0.0593]	15133 [R _{int} = 0.0264, R _{sigma} = 0.0179]	13105 [R _{int} = 0.0252, R _{sigma} = 0.0179]
Data/restraints/parameters	14585/9/969	15133/272/1069	13105/737/1206
Goodness-of-fit on F ²	1.032	1.067	1.029
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0484, wR ₂ = 0.1198	R ₁ = 0.0418, wR ₂ = 0.1026	R ₁ = 0.0299, wR ₂ = 0.0702
Final R indexes [all data]	R ₁ = 0.0649, wR ₂ = 0.1323	R ₁ = 0.0457, wR ₂ = 0.1061	R ₁ = 0.0325, wR ₂ = 0.0719
Largest diff. peak/hole / e Å ⁻³	0.78/-0.96	1.24/-0.81	0.75/-0.52

4. Quantum chemical calculations

Calculations were carried out using ORCA 5.0.4 software.^{S12}

Geometry optimizations were carried using the r^2 SCAN-3c composite method, utilizing the regularized and restored SCAN functional,^{S13-14} geometrical counterpoise correction gCP,^{S15} the atom-pairwise dispersion correction based on tight binding partial charges (D4),^{S16-18} the def2-mTZVPP basis set and def2-mTZVPP/J auxiliary basis set.^{S19} Effective core potential def2-ECP was used for Sn (ECP parameters for Sn have been obtained from TURBOMOLE (7.0.2)).^{S20} The optimized geometries were verified as minima or transition states by analytical frequency calculations. The transition states were additionally verified by IRC calculations. Single point calculations of the optimized geometries were carried out at the r^2 SCAN-3c level using the SMD solvation module^{S21} to obtain electrostatic contribution and the cavity term in order to account for the solvent effects. To get more accurate electronic energies for the mechanistic investigations, single point calculations of the r^2 SCAN-3c optimized geometries were carried using the PW6B95^{S22} functional, with D4 dispersion correction, the def2-QZVPP^{S23} basis set and def2/J^{S24} and def2-QZVPP/C^{S25} auxiliary basis sets. def2-ECP was used for Sn. The method is denoted as PW6B95-D4(SMD)/def2-QZVPP// r^2 SCAN-3c. The summary of the thermochemistry results is presented in Table S2. The NBO analysis was done using the NBO7 software,^{S26} at the PBE0^{S27}/def2-TZVP^{S28}/ r^2 SCAN-3c level of theory.

Table S3. Calculated energies (Eh). E_{PW6B95} - electronic energy at the PW6B95-D4/def2-QZVPP// r^2 SCAN-3c level; $G-E_{el}$ - Gibbs energy minus the electronic energy at the r^2 SCAN-3c// r^2 SCAN-3c level; G_{cfs} (cavity term) and G_{enp} (electrostatic contribution) at r^2 SCAN-3c (SMD=Benzene)// r^2 SCAN-3c level; G_{conc} - concentration-induced free-energy shift ($G_{conc} = RT\ln(24.5)$); G - free energy at the PW6B95-D4(SMD)/def2-QZVPP// r^2 SCAN-3c level, $G = E_{PW6B95} + [G-E_{el}] + G_{cfs} + G_{enp} + G_{conc}$. Thermochemistry at 298.15 K.

Compound	ID	E_{PW6B95}	$G-E_{el}$	G_{cfs}	G_{enp}	G_{conc}	G
[2] ⁺	3525538	-1913.90390	0.70795	-0.04503	-0.02061	0.00302	-1913.25857
[2][BArF]	3536119	-5567.93743	1.05894	-0.03668	-0.01860	0.00302	-5566.93074
[2a] ⁺	3531069	-1529.73254	0.53363	-0.04332	-0.01812	0.00302	-1529.25733
[2a][BArF]	3539097	-5183.77457	0.88298	-0.03103	-0.01624	0.00302	-5182.93584
[3] ⁺	3525578	-2102.82456	0.71945	-0.04727	-0.02122	0.00302	-2102.17058
[3][BArF]	3746351	-5756.86611	1.07621	-0.03610	-0.01667	0.00302	-5755.83965
[3a] ⁺	3529038	-1718.65656	0.54497	-0.04506	-0.01757	0.00302	-1718.17119
[3a][BArF]	3690093	-5372.69690	0.89536	-0.03274	-0.01600	0.00302	-5371.84726
[4] ⁺	3525581	-2291.73103	0.72772	-0.05029	-0.02500	0.00302	-2291.07558
[4][BArF]	3748659	-5945.78061	1.08218	-0.03854	-0.02036	0.00302	-5944.75431
TS(2_3)	3527035	-2102.76624	0.71701	-0.04662	-0.01985	0.00302	-2102.11268
TS(3_4)	3529058	-2291.69025	0.72861	-0.04819	-0.02048	0.00302	-2291.02728
TS1	4191715	-3046.84610	0.91624	-0.05369	-0.02890	0.00302	-3046.00943
INT_A	3685470	-3046.84678	0.91442	-0.05369	-0.03156	0.00302	-3046.01460

TS2	3969171	-3046.84872	0.91828	-0.05673	-0.02918	0.00302	-3046.01333
INT_B	597622	-1327.40280	0.33756	-0.04675	-0.01672	0.00302	-1327.12569
INT_C	3549415	-1719.40308	0.54938	-0.02562	-0.01758	0.00302	-1718.89388
TS3	3607573	-3046.84986	0.91654	-0.05162	-0.02707	0.00302	-3046.00898
INT_D	612540	-1328.16718	0.34679	-0.01659	-0.01457	0.00302	-1327.84852
TS4	3734923	-1328.15477	0.34547	-0.01265	-0.01423	0.00302	-1327.83316
IMe ₄	592934	-384.10329	0.14625	-0.01132	-0.01048	0.00302	-383.97582
IMe ₄ CO ₂	592935	-573.02057	0.15737	-0.01695	-0.00877	0.00302	-572.88590
H ₂ SiPh ₂	3543195	-755.11620	0.16050	-0.00590	-0.00935	0.00302	-754.96794
HCO ₂ SiHPh ₂	3614592	-944.04318	0.17260	-0.00777	-0.00900	0.00302	-943.88432
[BArF] ⁻	3536159	-3653.94294	0.31746	-0.03055	-0.00259	0.00302	-3653.65559
CO ₂	592933	-188.89490	-0.00901	-0.00094	0.00057	0.00302	-188.90126

According to the request by one of the referees, in addition to the Lewis structure of **[2]⁺** presented in the main text, also shown in **Figure S55** **[2]⁺_a**, here we additionally discuss the ionic representation, i.e. **[2]⁺_b**. The dative form, **[2]⁺_a** is a bis(NHC) stabilized stannylumylidene in which the interactions between the NHC units and the Sn centre are depicted as dative bonds. In **[2]⁺_b** the negative charge is located on the Sn atom to which the two positively charged NHC moieties are bound covalently **[2]⁺_b**, which results a stannyl-anion-type species.

As discussed in the main text, the NBO depiction of bonding between the NHCs and the low valent Sn centre in **[2]⁺** is that of polarized bonds between the carbons and the tin. This may hint to the stannyl anion character of **[2]⁺**, which is why **[2]⁺_b** is considered.

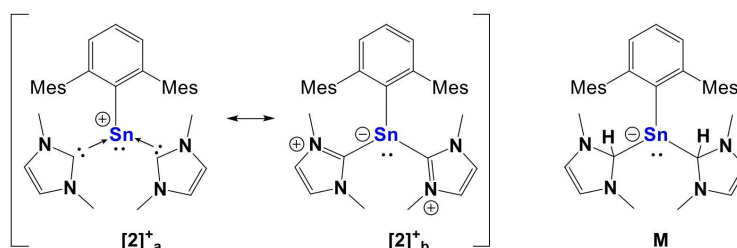


Figure S55. Resonance structures of donor stabilized stannylumylidene **[2]⁺** and the related model system stannyl anion **M**.

In the main text, we depicted **[2]⁺** as **[2]⁺_a** because we accounted for the following considerations. In general, it is a common situation in the NBO analysis for a dative bond to be shown as a bonding orbital polarized toward the donor atom, reflecting that the electron pair is largely provided by the donor. Additionally, it is also worth looking at the

Wiberg bond index and Mayer bond order. In this case, the bond is strongly polarized toward carbon and the Wiberg bond index is low for each Sn-C bond (0.58 for both). The Mayer bond orders are also quite low (0.48, 0.42). In **[2]⁺** the charge distribution is such that the NPA charge on Sn centre is +0.79. Additionally, the NHC-Sn bonds are longer 2.34 and 2.33 Å in comparison to the covalent Sn-C^{Ar} bond (2.24 Å). Furthermore, the reactivity of the complex, where NHC behaves as a donor ligand, which can readily dissociate from the metal centre, intuitively leads to the dative bond representation being more plausible.

In order to distinguish between the electronic properties of donor stabilized stannylumylidene and stannyl anion we carried out additional calculation of compound **M**, which is obtained by substituting the carbenic carbons with H⁻ (**Figure S55, S56**).

As in **[2]⁺**, in **M** the NPA charge on the Sn centre is positive (+0.74 el.). However, the Sn-C Wiberg bond indexes of 0.63 and 0.65 are somewhat higher than those in **[2]⁺** (0.58 and 0.58). The Mayer bond orders in the more covalent bonds Sn-C of **M** are also higher than in **[2]⁺**: 0.73 and 0.75 vs 0.48 and 0.42.

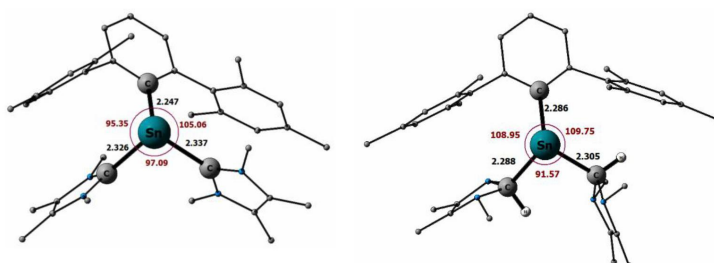


Figure S56. Optimized geometries of **[2]⁺** and **M**.

In term of geometries, the optimized structure of **M** exhibits a substantial shortening of the Sn-C bonds by 0.038 and 0.031 Å (**Figure S56**), which would be typical for more covalent bonds. Also, the geometry of the Sn centre in **M** is less pyramidalized than in **[2]⁺** $\Sigma\alpha=310.27^\circ$ vs $\Sigma\alpha=305.46^\circ$, respectively, which would be typical for a stannyl anion.

According to the NBO analysis in **M** the Sn-C bonds are slightly less polarized than in **[2]⁺**: Sn(22.54%)-C(77.46%) and Sn(21.12%)-C(78.88%) in **M** vs Sn(18.25%)-C(81.75%) and Sn(18.72%)-C(81.28%).

The very important difference in the electronic structure between the two species is in the hybridization of the orbitals that constitute the Sn-C interaction. In **M**, in comparison to **[2]⁺**, there is significant increase of the s character of the Sn hybrid orbitals and a significant increase in the p character of the C hybrid orbitals in comparison to **[2]⁺**: Sn(sp^{9.11})-C(sp^{2.61}) and Sn(sp^{9.91})-C(sp^{2.50}) in **M** vs Sn(sp^{19.72})-C(sp^{1.45}) and Sn(sp^{15.52})-

C(sp^{1.45}) in **[2]**⁺. And this is the distinction between the formal C(sp²)→Sn(p) interaction between a donor and stannylumylidene, and the C(sp³)-Sn(sp³) interaction expected in a stannyl anion.

In general, we are not strictly in favour of either dative or ionic representations. We think that both annotations could be correct, and each case should be looked at separately. In this case, when comparing **[2]**⁺_a with **[2]**⁺_b, we think that the representation of **[2]**⁺_a with dative bonds between the Sn-centre and the NHCs is the more intuitive and reflects better the electronic properties and the reactivity of **[2]**⁺.

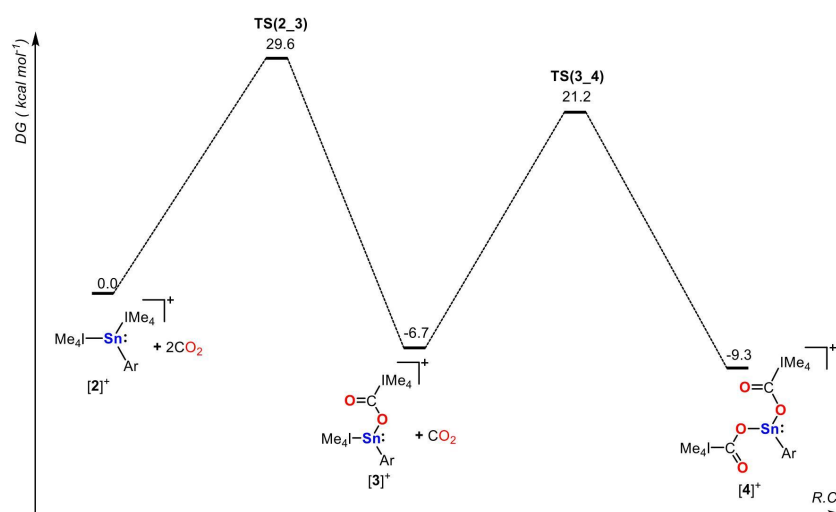


Figure S57. Calculated reaction coordinate diagram for the concerted reactions of **[2]**⁺ with CO₂ to form **[3]**⁺ and **[4]**⁺.

In addition to the reaction of **[2]**⁺ to form **[3]**⁺ and **[4]**⁺ via the stepwise dissociation of IMe₄ described in Scheme 4, we also considered a mechanism in which **[2]**⁺ and **[3]**⁺ react with CO₂ concertedly (Scheme S57). In this case, the barrier for the first reaction is 29.6 kcal mol⁻¹ (TS(2_3)). For the second reaction the barrier (TS(3_4)) (at 21.2 kcal mol⁻¹) is 27.9 kcal mol⁻¹ (TS(3_4)). This makes this mechanism kinetically less preferable to the one which involves the IMe₄ dissociation, presented in Scheme 4 in the main text.

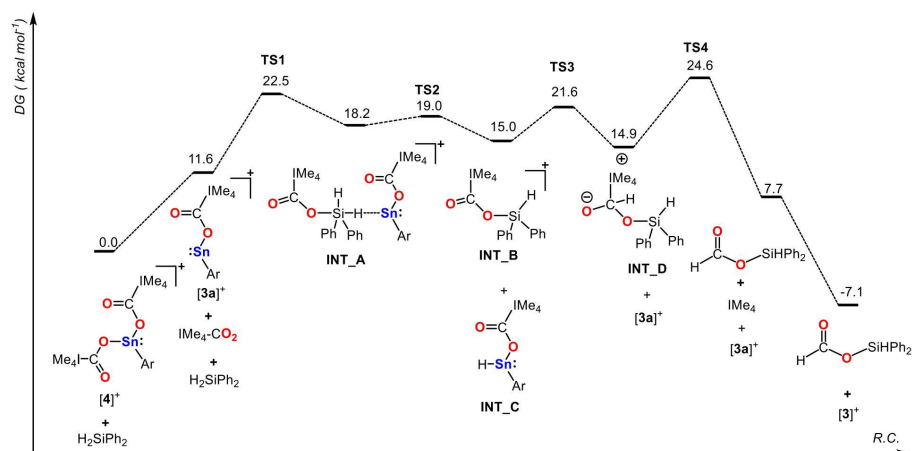


Figure S58. Calculated reaction coordinate diagram for the reaction of $[4]^+$ with H_2SiPh_2 .

The proposed mechanism for the reaction of $[4]^+$ with H_2SiPh_2 to form the CO_2 hydrosilylation product $Ph_2SiH(OCHO)$ and $[3]^+$ as observed experimentally (Scheme 3) is presented in Figure S58. Drawings of the geometries of key intermediates and transition states are shown in Figure S59. In the first step of the proposed mechanism, compound $[4]^+$ dissociates to the imidazolium carboxylate and $[3a]^+$ at 11.6 kcal mol⁻¹. The Si-H bond in Ph_2SiH_2 is activated by the stannylum center of $[3a]^+$ via a **TS1** at 22.5 kcal mol⁻¹ to generate intermediate **INT_A** at 18.2 kcal mol⁻¹. This is followed by the hydride transfer from the hyper-coordinate silane to the stannylum center, generating ((silylcarbonyl)oxy)imidazolium intermediate (**INT_B**) and the stannyl hydride (**INT_C**) at 15.0 kcal mol⁻¹. The next step is a hydride abstraction from **INT_C** by **INT_B**, releasing $[3a]^+$ and forming a zwitterionic adduct **INT_D**. In the last step, **INT_D** releases diphenylformoxysilane ($Ph_2SiH(OCHO)$) and free IMe_4 , which then bonds to the Sn center of $[3a]^+$ to generate the $[3]^+$.

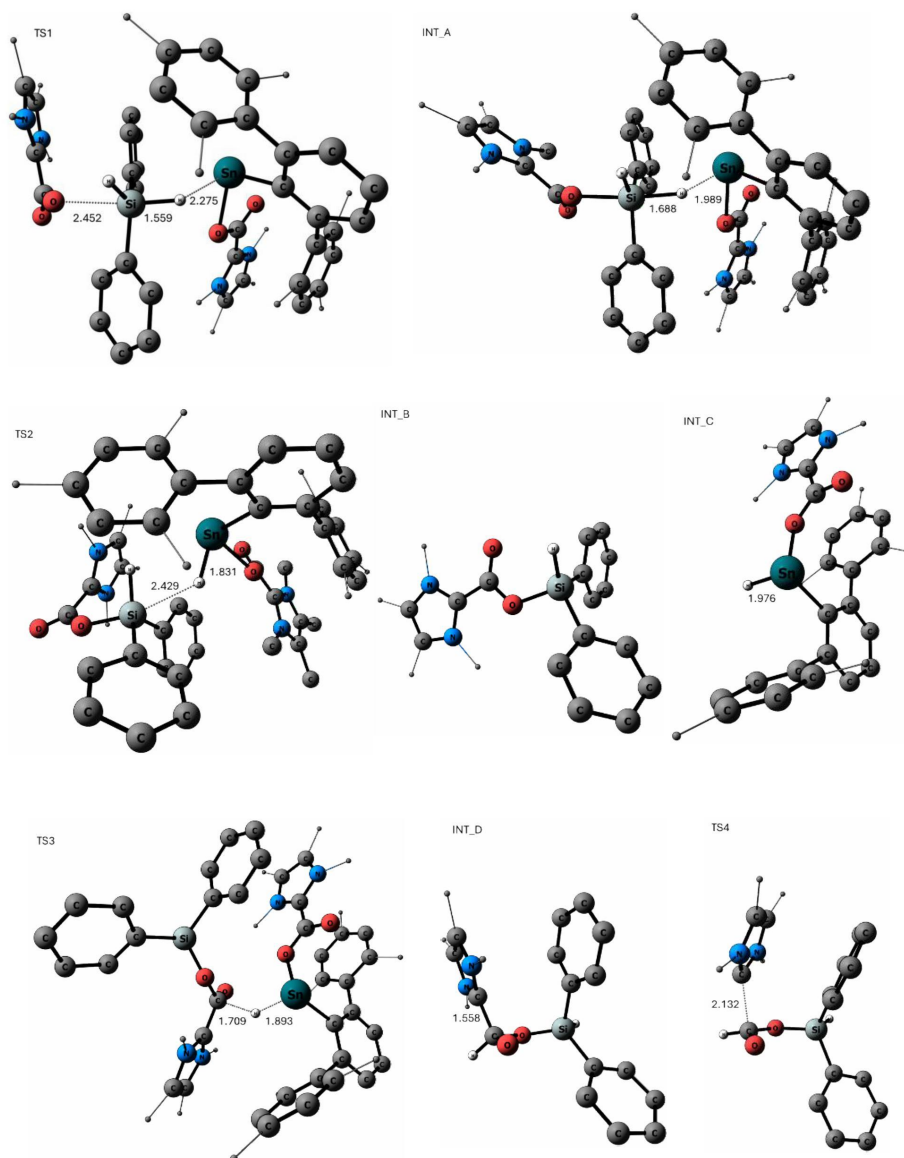


Figure S59. Geometries of key intermediates and transition states.

Cartesian coordinates and energies of the optimized geometries at the r²SCAN-3c level

Calculated energies and coordinates of [2] ⁺				C	4.330321	11.321519	0.782078
Electronic energy				H	3.233513	11.270839	0.739239
Total Enthalpy				H	4.704469	11.176218	-0.234479
Final Gibbs free energy				H	4.592096	12.330119	1.113917
CARTESIAN COORDINATES (ANGSTROEM)				C	-3.806499	10.374076	2.241519
Sn	1.871044	9.948868	3.058533	H	-3.779305	11.268632	1.608158
N	-1.118512	10.207896	4.729189	H	-4.708940	10.428146	2.853060
N	2.696946	7.297550	4.680012	H	-3.904845	9.502593	1.584141
N	2.796556	8.836635	6.166870	C	5.931691	8.089060	1.983710
N	-1.310525	10.271967	2.600358	C	-3.509119	10.250868	5.536790
C	-0.384233	10.244358	3.593601	H	-3.405656	9.399182	6.218243
C	-0.548118	10.140676	6.062437	H	-4.508921	10.205382	5.101284
H	-0.413238	9.100421	6.382225	H	-3.446553	11.171351	6.131064
H	-1.198793	10.660855	6.768573	C	3.765175	7.650288	8.172238
H	0.411173	10.651365	6.041013	H	4.638195	8.297576	8.318838
C	2.425454	8.612786	4.879415	H	4.055911	6.635387	8.448273
C	3.232073	6.705182	5.816781	H	2.988380	7.976260	8.873118
C	2.739055	10.115617	6.861134	C	5.381772	9.084402	1.174432
H	2.601099	10.907065	6.122225	H	5.343794	8.933559	0.097146
H	3.679255	10.290695	7.389561	C	-3.401484	13.856146	4.527637
H	1.924928	10.124815	7.594302	H	-3.698622	14.721230	3.925488
C	2.900219	11.791546	3.829720	H	-3.757103	14.018718	5.548642
C	4.303630	11.707444	3.683588	H	-3.929039	12.984257	4.119616
C	-2.482386	10.233915	4.465463	C	6.454051	6.814186	1.379986
C	2.348401	13.004503	4.289694	H	7.358050	7.004461	0.790096
C	0.874714	13.224023	4.380692	H	5.720350	6.363423	0.703041
C	3.287508	7.682067	6.766564	H	6.710915	6.080862	2.149543
C	0.130137	13.371672	3.189565	Calculated energies and coordinates of [2][BArF]			
C	0.227812	13.360676	5.617078	Electronic energy			
C	2.552142	6.574842	3.419231	Total Enthalpy			
H	2.060577	7.223436	2.692108	Final Gibbs free energy			
H	1.954777	5.671254	3.570664	CARTESIAN COORDINATES (ANGSTROEM)			
H	3.540606	6.305930	3.031370	Sn	1.831134	9.677246	3.045045
C	5.123036	12.781455	4.038995	F	-1.429303	-3.143716	7.834758
H	6.199902	12.691545	3.915606	F	1.661373	-2.003442	1.296276
C	-2.604482	10.285565	3.109043	F	-0.210833	-3.036877	6.031564
C	-1.242961	13.577646	3.261829	F	0.575682	-2.298085	7.919080
H	-1.808148	13.713712	2.340435	F	2.095163	-0.304976	0.011166
C	0.972292	13.353212	6.928594	F	0.573854	-1.750208	-0.574505
H	1.988769	12.967985	6.831960	F	3.970498	3.549019	1.733213
H	0.436429	12.768424	7.684810	F	-3.795816	2.014004	0.517970
H	1.057134	14.373398	7.321996	F	5.480192	1.058728	7.343180
C	4.928654	10.475521	3.102948	F	3.568238	0.208003	7.948186
C	4.567935	13.958676	4.524832	N	-1.017001	10.183730	4.881356
H	5.206761	14.794804	4.794268	N	2.506524	7.158114	4.925875
C	5.565462	9.524805	3.917852	F	-1.884278	7.367920	6.991424
C	-1.912859	13.651349	4.485738	F	-4.461092	0.545034	1.975717
C	-1.027668	10.399607	1.175767	N	2.826758	8.841472	6.213399
H	-1.210618	11.426655	0.842614	N	-1.382452	10.056532	2.777060
H	-1.664271	9.716453	0.607379	F	3.994614	2.306764	8.333013
H	0.018679	10.143139	0.994690	C	-0.442598	1.206872	3.091818
C	-1.159262	13.552326	5.648221	C	-0.533924	3.527784	4.477973
H	-1.652323	13.656602	6.614115	C	-0.847669	1.104121	5.645884
C	6.029309	8.335217	3.349510	C	1.550421	2.003177	4.740413
H	6.510553	7.598706	3.991968	C	-0.557088	4.272264	5.667695
C	5.836833	9.780569	5.375628	H	-0.290628	3.782607	6.602568
H	6.877598	10.101286	5.508708	C	-1.096450	-1.002997	6.860135
H	5.703089	8.869582	5.968459	C	0.448037	0.411652	2.365197
H	5.207353	10.576310	5.775311	H	1.477052	0.306859	2.702047
C	3.188471	14.070363	4.636419	C	0.056112	-0.266960	1.209662
H	2.743794	15.000092	4.984050	C	2.171433	1.615059	5.930417
C	4.887469	10.272478	1.705446	H	1.567897	1.232840	6.750149
C	0.816243	13.377877	1.849347	C	-0.379008	10.094626	3.691309
H	1.680276	14.050449	1.855178	C	-1.999615	1.543793	6.303733
H	0.130096	13.703316	1.062802	H	-2.396577	2.535283	6.097401
H	1.205814	12.390361	1.572060	C	-1.760012	1.259695	2.611760
C	3.636389	5.277056	5.860675	H	-2.505662	1.831798	3.162139
H	2.787864	4.607397	5.680120	F	5.627633	2.328914	2.447170
H	4.050109	5.031722	6.840131	C	2.391537	2.517701	3.736260
H	4.402378	5.053642	5.109411	H	1.951914	2.859050	2.801899

C	-0.429613	-0.203864	5.937910	H	6.897654	9.533571	5.146898
H	0.436793	-0.614405	5.422051	H	5.536513	8.508923	5.606049
C	-0.883911	4.217650	3.309426	H	5.319358	10.269550	5.413805
H	-0.881481	3.689641	2.360086	C	-3.566528	0.753856	0.980522
F	-4.842615	1.665024	6.988063	C	3.341566	13.871831	4.284044
C	-2.675395	0.742437	7.225922	H	2.947569	14.835571	4.599223
C	-1.244241	-0.176599	0.732548	C	4.649751	3.174993	2.837654
H	-1.547245	-0.698079	-0.167098	C	4.762126	9.992946	1.387272
C	-0.955044	5.608239	5.695491	C	0.783374	12.994521	1.651898
C	3.558321	1.684428	6.095557	H	1.724239	13.546468	1.564177
F	-1.322061	5.540404	8.035196	H	0.093722	13.351471	0.881658
C	-0.549820	-2.369476	7.159343	H	1.022190	11.947540	1.426677
C	-0.334377	10.258999	6.162116	C	3.238303	5.201281	6.329781
H	-0.135465	9.260942	6.563290	H	2.317772	4.621940	6.190289
H	-0.946540	10.823541	6.868563	H	3.598545	5.015362	7.342828
H	0.597892	10.797094	6.008493	H	3.979251	4.802102	5.629851
C	-1.265813	5.558189	3.332760	C	4.165954	11.062913	0.514362
C	-2.151347	0.594645	1.454684	H	3.071437	11.077470	0.603657
C	2.383233	8.508485	4.971737	H	4.410049	10.884115	-0.535911
C	1.085293	-1.083574	0.483858	H	4.521383	12.058882	0.795870
F	5.285621	4.300048	3.300860	C	-3.896801	10.188935	2.612684
C	3.014300	6.648614	6.112130	H	-3.918507	11.043345	1.925207
C	2.939638	10.186352	6.754217	H	-4.746121	10.286113	3.291569
H	2.820259	10.902643	5.939740	H	-4.045379	9.278672	2.022175
H	3.928967	10.323575	7.199241	C	5.770438	7.783778	1.577624
H	2.185226	10.359561	7.530086	C	-3.334784	10.355671	5.868999
C	-2.228322	-0.536733	7.524636	H	-3.177945	9.576125	6.621402
H	-2.749175	-1.158354	8.242641	H	-4.366120	10.276690	5.519753
C	2.932132	11.564228	3.614549	H	-3.221471	11.331315	6.359328
C	4.152710	1.302169	7.420095	C	3.715533	7.790815	8.328214
C	4.374310	2.155965	5.079714	H	4.659947	8.344881	8.395538
H	5.451683	2.201080	5.202087	H	3.893387	6.784848	8.712074
F	-3.879445	-0.093987	-0.024332	H	2.993032	8.277650	8.993565
C	-1.312320	6.272478	4.525286	C	5.211561	8.809407	0.812386
H	-1.643876	7.306332	4.543905	H	5.123390	8.680303	-0.264760
B	-0.066451	1.959058	4.493464	C	-3.260041	13.856490	4.491553
C	3.769246	2.588108	3.898423	H	-3.591329	14.628053	3.788519
C	4.321477	11.427746	3.390832	H	-3.550331	14.167708	5.498851
F	0.216756	6.895649	7.314241	H	-3.812986	12.939715	4.249030
C	-2.397407	10.217507	4.726397	C	6.204042	6.498001	0.930451
F	-3.601683	2.432532	8.598649	H	6.713405	6.688327	-0.019636
C	2.448429	12.821189	4.035581	H	5.339306	5.859361	0.714413
C	0.989578	13.105546	4.179646	H	6.876437	5.929493	1.577521
C	3.212959	7.717760	6.933390	F	-2.637165	7.142325	2.221190
C	0.182189	13.157443	3.022002	F	-1.966568	5.420241	1.069681
C	0.415095	13.389342	5.427982	F	-0.559219	6.996253	1.586277
F	-4.473190	0.441386	8.752374				
C	2.229799	6.306986	3.769419				
H	1.682969	6.880737	3.020558				
H	1.627507	5.448268	4.078720				
H	3.172532	5.957688	3.334257				
C	5.196096	12.484717	3.655657				
H	6.260560	12.349014	3.477037				
C	-2.629008	10.147356	3.384394				
C	-1.179199	13.413226	3.145776				
H	-1.791574	13.466260	2.246253				
C	1.229703	13.475691	6.694413				
H	2.198927	12.982928	6.601825				
H	0.686655	13.040999	7.540881				
H	1.430869	14.523412	6.949541				
C	4.870409	10.170186	2.785223				
C	-3.895031	1.307394	7.892025				
C	4.709479	13.702243	4.115695				
H	5.390439	14.525234	4.314035				
C	5.505947	9.183209	3.555312				
C	-1.778008	13.626115	4.389055				
C	-1.213559	10.045622	1.329249				
H	-1.386458	11.047877	0.921770				
H	-1.916452	9.340841	0.880063				
H	-0.196782	9.725174	1.091386				
C	-0.995208	6.336925	7.003714				
C	-1.611605	6.259303	2.055467				
C	-0.962244	13.625271	5.513517				
H	-1.399263	13.831641	6.489890				
C	5.920774	7.995890	2.943747				
H	6.396010	7.228504	3.553148				
C	5.818745	9.386511	5.013723				

Calculated energies and coordinates of [2a] ⁺			
Electronic energy	...	-1526.98783236 Eh	
Total Enthalpy	...	-1526.35173142 Eh	
Final Gibbs free energy	...	-1526.45419801 Eh	
CARTESIAN COORDINATES (ANGSTROM)			
Sn	-1.475789	9.810765	2.693709
N	-0.793559	12.664716	4.335156
N	-2.512344	11.669422	5.145700
C	-0.720087	10.999834	0.995815
C	-1.650132	11.882307	0.433843
C	-1.324536	12.606490	-0.712650
H	-2.045262	13.290540	-1.153874
C	-0.074173	12.427506	-1.300126
H	0.180427	12.977653	-2.201315
C	0.848728	11.539175	-0.752048
H	1.817336	11.400704	-1.226236
C	0.533179	10.814882	0.401394
C	-2.958553	11.966623	1.140832
C	-3.319249	13.120010	1.865953
C	-4.474042	13.099966	2.643220
H	-4.744082	13.994269	3.202804
C	-5.290212	11.969235	2.735513
C	-4.930750	10.840088	2.010300
H	-5.572820	9.961200	2.033601
C	-3.792341	10.820053	1.187797
C	-2.478869	14.366912	1.820695
H	-1.417729	14.132948	1.706942
H	-2.624232	14.965530	2.724474
H	-2.755870	14.993332	0.964424

C	-6.552435	11.996877	3.552803	C	1.971225	-3.654871	-0.186644
H	-6.461929	12.666805	4.413662	H	2.682038	-3.500902	-0.995154
H	-6.825989	10.999611	3.909478	C	1.364161	-4.904085	-0.068507
H	-7.390091	12.365790	2.949142	C	1.054608	0.954733	-0.753001
C	-3.639446	9.674797	0.210004	H	1.236032	1.545676	0.139591
H	-3.939156	8.721924	0.655953	C	-2.823906	0.081904	-1.252278
H	-2.627553	9.582890	-0.187782	C	4.732348	-2.137485	0.537308
H	-4.303446	9.856781	-0.643971	H	4.349440	-2.839291	1.276391
C	1.477062	9.854596	1.041961	C	0.877720	-2.929870	1.793915
C	2.623381	10.307261	1.724475	H	0.677434	-2.182557	2.555639
C	3.402537	9.386076	2.423088	F	-0.339784	-0.624837	-5.254271
H	4.285469	9.740396	2.952694	C	1.203169	-1.075537	-1.980843
C	3.098531	8.025284	2.444580	H	1.490624	-2.118719	-2.075820
C	2.000890	7.586494	1.708157	C	4.424421	-0.324702	-0.972556
H	1.783706	6.521455	1.659525	H	3.799869	0.428622	-1.447899
C	1.189183	8.473000	0.998274	C	0.947523	0.208384	2.306717
C	3.079476	11.743521	1.667009	H	0.050583	-0.001140	1.729114
H	3.535693	12.049640	2.613581	F	6.463998	-4.490592	0.644244
H	2.273088	12.436137	1.416869	C	6.080184	-2.201090	0.190629
H	3.845699	11.863030	0.891261	C	0.495168	-5.180983	0.981231
C	3.947179	7.062468	3.226975	H	0.020840	-6.151677	1.073069
H	3.736512	7.141612	4.300183	C	3.173241	0.803882	3.812116
H	5.012510	7.271498	3.089729	C	0.454547	1.566776	-1.851827
C	3.759148	6.028607	2.927125	F	5.204947	0.042640	4.754379
C	0.086857	7.924137	0.125941	C	6.284248	0.574920	-2.355889
H	-0.884607	7.885093	0.638616	C	-1.839759	-1.645515	0.266593
H	0.320903	6.899772	-0.175385	H	-2.306235	-2.593469	0.545015
H	-0.047155	8.528706	-0.775130	H	-2.051051	-0.921363	1.055667
C	-1.560832	11.559915	4.187226	H	-0.759797	-1.788203	0.172351
C	-1.259981	13.470276	5.364610	C	0.810278	0.874081	3.521029
C	-2.360229	12.839930	5.875692	C	0.275025	-4.180230	1.921082
C	0.440758	12.921909	3.602119	C	1.599870	-5.933463	-1.136218
H	1.308091	12.728682	4.242219	F	0.017243	-2.482274	-4.168783
H	0.469797	13.960283	3.262043	C	6.618631	-1.326910	-0.747314
H	0.473187	12.261925	2.734553	H	7.665399	-1.378122	-1.020694
C	-0.601038	14.745729	5.742290	C	-4.733469	2.635061	-0.234039
H	0.447761	14.590890	6.019304	C	-0.027133	2.979096	-1.781786
H	-1.107040	15.195137	6.598215	C	0.240641	0.873695	-3.039767
H	-0.625327	15.471691	4.921238	H	-0.195238	1.365461	-3.902808
C	-3.282650	13.223684	6.973860	F	0.088988	-4.967904	4.151002
H	-2.983272	14.182371	7.399851	C	1.928052	1.184754	4.291698
H	-3.281394	12.484739	7.782963	H	1.827959	1.699405	5.240150
H	-4.314037	13.325688	6.616790	B	2.304454	-1.096618	0.444863
C	-3.553526	10.686212	5.430619	C	0.625261	-0.457708	-3.089664
H	-3.419248	10.282830	6.439218	C	-5.800018	1.828893	0.189886
H	-3.488561	9.871222	4.708178	F	5.173629	2.057424	3.938359
H	-4.540775	11.147280	5.349780	C	-2.491882	-1.979284	-2.121164
				F	6.974175	-3.064119	2.203168
				C	-4.998355	3.912620	-0.751493
				C	-3.875973	4.809035	-1.147953
				C	-3.040579	5.358322	-0.152821
				C	-3.635031	5.106622	-2.500489
				F	8.216904	-3.216146	0.420379
				C	-7.119256	2.262421	0.056712
				H	-7.935319	1.626230	0.391773
				C	-3.006724	-1.191823	-3.113292
				C	-1.946807	6.131219	-0.535432
				H	-1.304832	6.552673	0.236288
				C	-4.549672	4.638509	-3.605200
				H	-5.171819	3.792610	-3.305160
				H	-3.974489	4.360522	-4.494628
				H	-5.233311	5.442704	-3.904578
				C	-5.469448	0.513408	0.813267
				C	6.938734	-3.237077	0.858014
				C	-7.377748	3.517948	-0.484235
				H	-8.401897	3.867070	-0.581590
				C	-5.691970	-0.687554	0.104107
				C	-1.657737	6.385503	-1.875484
				C	-3.674770	1.226295	-3.289320
				H	-2.899443	1.592548	-3.970807
				H	-3.926353	2.011288	-2.574920
				H	-4.567547	0.966400	-3.865611
				C	4.420239	1.131986	4.584446
				C	-0.550349	1.286500	3.992281
				C	-2.524664	5.880968	-2.839842
				H	-2.331233	6.091011	-3.890451
				C	-5.355018	-1.898167	0.696237

Calculated energies and coordinates of [2a][BArF]
 Electronic energy ... -5174.89548763 Eh
 Total Enthalpy ... -5173.80705990 Eh
 Final Gibbs free energy ... -5174.01250912 Eh
 CARTESIAN COORDINATES (ANGSTROM)

Sn	-2.758607	1.755398	0.310386
F	5.986825	1.860066	-2.036746
F	1.316993	-7.187328	-0.720350
F	7.623358	0.504508	-2.518411
F	5.723919	0.344825	-3.572538
F	2.872156	-5.928611	-1.582083
F	0.805252	-5.695846	-2.222838
F	1.688890	-1.367739	-4.993973
F	-1.583282	-5.352068	2.813323
F	-1.423522	3.002643	-1.774686
F	0.326231	3.711825	-2.855300
N	-2.389849	-1.171813	-0.998717
F	4.152290	1.628982	5.813774
F	-1.218474	-3.334380	3.555063
N	-3.198825	0.064530	-2.551610
F	0.364365	3.634461	-0.681874
C	1.711991	-2.608813	0.714484
C	2.195264	-0.208633	1.813764
C	3.863231	-1.199125	-0.035854
C	1.449278	-0.393504	-0.781102
C	3.302754	0.119504	2.601803
H	4.297982	-0.169279	2.272739
C	5.772734	-0.386259	-1.322460

H	-5.531132	-2.821455	0.145472
C	-6.296942	-0.671791	-1.273899
H	-5.988121	0.213057	-1.836154
H	-7.392062	-0.644584	-1.220713
H	-6.013217	-1.568920	-1.832165
C	-0.602214	-4.458673	3.105779
C	-6.325449	4.338372	-0.878086
H	-6.527452	5.329485	-1.277644
C	0.498996	-1.228551	-4.371329
C	-4.913203	0.466323	2.111918
C	-3.331029	5.182317	1.317757
H	-2.984627	6.056176	1.876736
H	-2.812735	4.313140	1.746075
H	-4.400183	5.052876	1.505366
C	-4.828080	1.685544	2.999366
H	-5.682245	1.686459	3.687872
H	-4.867289	2.622176	2.440072
H	-3.918001	1.669385	3.606010
C	-3.368640	-1.505098	-4.518368
H	-2.987544	-2.490823	-4.791078
H	-2.937378	-0.781803	-5.217049
H	-4.456492	-1.509695	-4.661925
C	-4.797724	-1.966742	1.978320
C	-2.085012	-3.406227	-2.104075
H	-2.164996	-3.836851	-3.103011
H	-2.715535	-3.996076	-1.427654
H	-1.045568	-3.521786	-1.775964
C	-4.568563	-0.779082	2.659914
H	-4.140888	-0.808698	3.659870
C	-0.436344	7.173121	-2.259544
H	-0.504096	7.541276	-3.286755
H	0.462300	6.548368	-2.188422
C	-0.290427	8.029926	-1.594360
C	-4.485619	-3.297962	2.601492
H	-5.411600	-3.814974	2.880272
H	-3.875293	-3.190085	3.500081
H	-3.950725	-3.955161	1.907378
F	-0.916680	2.508103	3.513023
F	-0.634635	1.361976	5.337589
F	-1.518474	0.416526	3.584352

Calculated energies and coordinates of [3]⁺
 Electronic energy ... -2098.97915889 Eh
 Total Enthalpy ... -2098.13057677 Eh
 Final Gibbs free energy ... -2098.25970783 Eh
 CARTESIAN COORDINATES (ANGSTROEM)

Sn	-1.421963	9.642426	3.138694
O	0.638493	9.427200	4.079652
C	0.986204	8.193509	4.174196
O	0.344996	7.196885	3.851221
N	-0.770639	12.619960	4.605180
N	-2.651882	11.819946	5.237642
N	3.213466	8.903305	5.222179
N	2.953730	6.774601	4.882305
C	-0.681758	10.808159	1.348066
C	-1.658530	11.655387	0.781464
C	-1.420342	12.334429	-0.415504
H	-2.197323	12.973869	-0.828372
C	-0.213104	12.176151	-1.082956
H	-0.032260	12.692365	-2.021346
C	0.750640	11.330218	-0.553223
H	1.687210	11.174848	-1.084080
C	0.528659	10.641112	0.646863
C	-2.992247	11.833645	1.435469
C	-3.303596	13.043598	2.086343
C	-4.549417	13.196250	2.692185
H	-4.780255	14.135895	3.192591
C	-5.511471	12.187042	2.656676
C	-5.200501	11.006939	1.987828
H	-5.946585	10.216311	1.925321
C	-3.967136	10.818119	1.358241
C	-2.336183	14.197224	2.104544
H	-1.298930	13.856426	2.091419
H	-2.502416	14.828652	2.982564
H	-2.469882	14.826510	1.216117
C	-6.862866	12.382129	3.289172

H	-6.837283	13.153625	4.064828
H	-7.237320	11.454202	3.732880
H	-7.597979	12.700227	2.540348
C	-3.770199	9.577847	0.523109
H	-4.195031	8.698467	1.015968
H	-2.720087	9.382461	0.299765
H	-4.287518	9.699936	-0.436788
C	1.615632	9.712444	1.083350
C	2.853889	10.224164	1.515306
C	3.882329	9.343218	1.854388
H	4.838427	9.749721	2.184269
C	3.735620	7.962962	1.725690
C	2.514779	7.474972	1.267530
H	2.388478	6.403187	1.122017
C	1.450979	8.321407	0.949574
C	3.126541	11.706729	1.567421
H	3.860244	11.947972	2.344367
H	2.219301	12.291420	1.731685
H	3.548420	12.053683	0.616348
C	4.889609	7.033390	1.990710
H	4.546139	6.052397	2.336666
H	5.577485	7.445642	2.736069
H	5.466766	6.863131	1.073889
C	0.171416	7.718769	0.435773
H	-0.526853	7.508748	1.257527
H	0.370023	6.765543	-0.062210
H	-0.332143	8.384187	-0.269810
C	-1.574876	11.540412	4.468320
C	-1.340906	13.580500	5.433793
C	-2.542586	13.071789	5.832374
C	0.535434	12.758573	3.980947
H	1.317938	12.816390	4.745795
H	0.575642	13.664825	3.368379
H	0.704373	11.888046	3.347441
C	-0.678999	14.876847	5.725857
C	0.299137	14.737782	6.200538
H	-1.293828	15.471845	6.403454
H	-0.524692	15.464580	4.812875
C	-3.606504	13.638512	6.698927
H	-3.322322	14.633083	7.046912
H	-3.789191	13.015484	7.581823
H	-4.554289	13.731626	6.155748
C	-3.798846	10.940188	5.440460
H	-3.872540	10.657052	6.495516
H	-3.669034	10.042324	4.833581
H	-4.716368	11.444098	5.126112
C	2.353452	7.975868	4.755008
C	4.379901	8.287622	5.637665
C	4.213636	6.942061	5.425996
C	2.979172	10.348676	5.255140
H	2.086136	10.566068	5.843185
H	2.832327	10.711599	4.236744
H	3.849405	10.825745	5.705831
C	5.540032	9.030079	6.194113
H	6.339380	8.332778	6.447475
H	5.276606	9.574138	7.107861
H	5.946065	9.747852	5.472677
C	5.145165	5.814963	5.685037
H	4.711407	5.077718	6.369012
H	6.062222	6.188275	6.142186
H	5.423809	5.300954	4.758227
C	2.387697	5.479160	4.483315
H	1.505265	5.253652	5.083910
H	3.151789	4.716591	4.632537
H	2.086816	5.520183	3.436308

Calculated energies and coordinates of [3][BArF]
 Electronic energy ... -5746.88680094 Eh
 Total Enthalpy ... -5745.58602844 Eh
 Final Gibbs free energy ... -5745.81592677 Eh
 CARTESIAN COORDINATES (ANGSTROEM)

Sn	-2.865784	-0.624782	-0.004643
O	-1.415617	-2.256964	-0.671147
C	-0.687717	-2.561844	0.341950
O	-0.800680	-2.121438	1.485101
N	-3.192692	-0.941812	-3.357695

N	-2.716948	1.064572	-2.786159
N	0.569378	-4.415602	-0.924000
N	1.315941	-3.906454	1.049099
C	-4.728598	-1.921435	-0.117229
C	-5.896263	-1.160525	-0.334105
C	-7.154620	-1.764155	-0.401020
H	-8.033402	-1.144834	-0.567833
C	-7.281310	-3.136817	-0.233767
H	-8.259128	-3.608573	-0.276398
C	-6.148562	-3.897207	0.023000
H	-6.239277	-4.967477	0.197239
C	-4.878663	-3.307328	0.090429
C	-5.815127	0.328016	-0.454941
C	-5.966206	0.958847	-1.701512
C	-5.854067	2.348221	-1.782672
H	-5.962160	2.828922	-2.754493
C	-5.621686	3.131625	-0.654828
C	-5.536188	2.495878	0.583336
H	-5.390994	3.095050	1.479270
C	-5.635940	1.111380	0.706484
H	-6.291285	0.173834	-2.944504
H	-5.918695	-0.850627	-2.883042
H	-5.870681	0.655384	-3.832960
H	-7.377779	0.110102	-3.084615
C	-5.454073	4.622346	-0.759030
H	-5.744975	4.991496	-1.746667
H	-4.410361	4.910378	-0.580271
H	-6.055855	5.142692	-0.006922
C	-5.594467	0.482719	2.074757
H	-4.619737	0.024455	2.284978
H	-6.345297	-0.307499	2.170582
H	-5.771270	1.235824	2.846703
C	-3.747366	-4.207556	0.471142
C	-3.296633	-5.225310	-0.387812
C	-2.280957	-6.084923	0.040384
H	-1.947738	-6.880015	-0.627473
C	-1.715115	-5.978839	1.307740
C	-2.197404	-4.986849	2.158996
H	-1.787445	-4.896589	3.163539
C	-3.206233	-4.107858	1.769160
C	-3.888537	-5.451582	-1.757539
H	-4.371985	-6.434345	-1.808867
H	-3.111415	-5.439556	-2.532060
H	-4.640604	-4.703331	-2.010440
C	-0.662723	-6.948211	1.776498
H	0.031720	-6.472084	2.476610
H	-0.084360	-7.352874	0.939552
H	-1.119110	-7.796381	2.301493
C	-3.714090	-3.092282	2.754149
H	-3.238952	-2.117952	2.594591
H	-3.475949	-3.395430	3.776711
H	-4.795034	-2.952643	2.664578
C	-2.930665	-0.170577	-2.278552
C	-3.150815	-0.203242	-4.533128
C	-2.851609	1.076666	-4.168200
C	-3.456171	-2.369700	-3.304143
H	-4.460675	-2.591465	-3.681858
H	-3.389441	-2.692630	-2.265940
H	-2.719973	-2.910869	-3.907987
C	-3.382222	-0.812566	-5.866196
H	-3.325715	-0.049220	-6.644460
H	-4.369485	-1.285709	-5.930482
H	-2.628833	-1.576493	-6.093895
C	-2.632341	2.300475	-4.978340
H	-1.596379	2.649972	-4.901681
H	-3.281834	3.121753	-4.654230
H	-2.842542	2.100155	-6.030665
C	-2.355799	2.247215	-2.010975
H	-1.397606	2.641844	-2.359129
H	-2.271132	1.975662	-0.956536
H	-3.128465	3.015160	-2.112300
C	0.392827	-3.578042	0.118523
C	1.599757	-5.290929	-0.647708
C	2.071901	-4.970345	0.598507
C	-0.195892	-4.463645	-2.167199
H	-0.585764	-5.475793	-2.303715
H	0.458141	-4.201393	-3.003999
H	-1.010256	-3.747092	-2.099732
C	2.022039	-6.341897	-1.605113
H	2.284294	-5.911646	-2.577489
H	1.231446	-7.084828	-1.765537
H	2.903058	-6.861960	-1.227367
C	3.140587	-5.611773	1.404350
H	3.581891	-6.435364	0.841095
H	2.740233	-6.020089	2.339336
H	3.944448	-4.912838	1.651616
C	1.547819	-3.215101	2.325498
H	1.602932	-2.139908	2.153466
H	2.492553	-3.569886	2.737284
H	0.725149	-3.412077	3.015743
B	2.126787	1.327969	0.665634
F	-2.775187	3.818338	1.572214
F	-1.310868	4.844404	2.811311
F	-2.241310	5.884516	1.137946
F	-0.088939	4.446043	-3.674403
F	2.040294	4.619189	-3.252376
F	0.688456	6.243775	-2.726873
F	4.702486	-3.155413	0.080794
F	5.545443	-2.320991	-1.739832
F	4.173103	-4.002253	-1.860490
F	-0.339672	-1.760731	-3.815732
F	1.417459	-1.138225	-4.925984
F	0.111698	0.358713	-4.035059
F	7.171226	0.988062	-1.382782
F	6.256979	2.512636	-2.633513
F	7.895364	3.041232	-1.297980
C	5.315360	4.779615	2.695817
F	6.630428	4.915633	2.990982
F	4.671724	4.503349	3.852069
F	4.880872	6.001616	2.288656
F	4.977481	0.023598	4.865431
F	4.342872	-2.030308	4.523917
F	3.653393	-0.957569	6.289580
C	-1.001536	-0.527445	4.380510
F	-1.202916	-1.865824	4.543022
F	-1.983974	-0.067059	3.581653
F	-1.192374	0.027715	5.605815
C	1.105229	2.535910	0.235833
C	0.111681	3.094098	1.043317
H	-0.078494	2.686894	2.032165
C	-0.642926	4.198522	0.631731
C	-0.421380	4.802598	-0.595287
H	-0.993627	5.669959	-0.905467
C	0.583975	4.277047	-1.408406
C	1.321735	3.173115	-1.002638
H	2.118252	2.812518	-1.649135
C	-1.731240	4.695553	1.536528
C	0.822689	4.899129	-2.752201
C	2.125767	0.108010	-0.432413
C	3.082677	-0.912983	-0.314883
H	3.740610	-0.923136	0.551719
C	3.265397	-1.874444	-1.305495
C	2.486775	-1.864027	-2.459344
H	2.673333	-2.569017	-3.263133
C	1.500184	-0.891124	-2.573175
C	1.310580	0.060807	-1.569878
H	0.542645	0.816750	-1.704735
C	4.415026	-2.831392	-1.204973
C	0.680019	-0.848032	-3.827250
C	3.598154	2.061816	0.649643
C	4.576650	1.865647	-0.325630
H	4.415165	1.141081	-1.120900
C	5.779990	2.577398	-0.317109
C	6.047469	3.514630	0.667706
H	6.983391	4.060785	0.681716
C	5.077300	3.731143	1.646781
C	3.879821	3.028282	1.630759
H	3.141881	3.227726	2.404939
C	6.778269	2.288791	-1.399461
C	1.854976	0.667747	2.137019
C	0.569212	0.347118	2.606843
H	-0.299296	0.533370	1.981896
C	0.372932	-0.234771	3.856141
C	1.451433	-0.587582	4.663356

H	1.292730	-1.045986	5.634257
C	2.731610	-0.335060	4.191595
C	2.925608	0.299491	2.964201
H	3.942616	0.520511	2.650340
C	3.921088	-0.807084	4.973460

Calculated energies and coordinates of [3a]⁺
 Electronic energy ... -1715.59126734 Eh
 Total Enthalpy ... -1714.93782488 Eh
 Final Gibbs free energy ... -1715.04629365 Eh

CARTESIAN COORDINATES (ANGSTROEM)

Sn	-1.358324	9.548407	3.279070
O	0.772151	9.531429	4.314947
C	0.941687	8.327618	3.967919
O	0.111723	7.690510	3.258428
N	3.144948	8.156018	5.180262
N	2.496821	6.352110	4.146399
C	-0.596171	10.369707	1.363533
C	-1.643965	11.094498	0.752705
C	-1.472481	11.726212	-0.476205
H	-2.298878	12.276335	-0.919561
C	-0.244905	11.646710	-1.122435
H	-0.098347	12.135266	-2.081554
C	0.798421	10.939781	-0.537399
H	1.760824	10.877333	-1.040932
C	0.642163	10.298658	0.698041
C	-2.953767	11.168649	1.467513
C	-3.183346	12.196137	2.403593
C	-4.370064	12.188541	3.136145
H	-4.546700	12.979135	3.862592
C	-5.336708	11.198560	2.957596
C	-5.101723	10.206369	2.006562
H	-5.853366	9.436726	1.844230
C	-3.928517	10.175881	1.251655
C	-2.178678	13.301203	2.598058
H	-1.159319	12.916659	2.715494
H	-2.427235	13.907824	3.471974
H	-2.155562	13.961012	1.722750
C	-6.590963	11.192561	3.785698
H	-6.921418	12.209723	4.014075
H	-6.420337	10.681351	4.740901
H	-7.404570	10.671784	3.274065
C	-3.725276	9.107997	0.209294
H	-4.477911	8.321535	0.301770
H	-2.730735	8.652482	0.273414
H	-3.801040	9.532329	-0.798839
C	1.853088	9.579924	1.203458
C	2.819060	10.277820	1.947514
C	4.023468	9.645063	2.264124
H	4.784871	10.202678	2.808533
C	4.298820	8.341918	1.851175
C	3.318709	7.659902	1.130876
H	3.522961	6.648686	0.780466
C	2.102686	8.259252	0.794510
C	2.573199	11.697581	2.378975
H	3.436399	12.104682	2.912836
H	1.695530	11.761688	3.032339
H	2.371463	12.343253	1.517711
C	5.644653	7.718300	2.106512
H	5.578770	6.628370	2.182266
H	6.103144	8.104079	3.022455
H	6.334096	7.941906	1.283495
C	1.085034	7.504832	-0.016455
H	0.141298	7.407075	0.532216
H	1.445303	6.504805	-0.273457
H	0.853240	8.031185	-0.948476
C	2.157444	7.627147	4.428297
C	4.132313	7.212240	5.364598
C	3.722511	6.071649	4.710867
C	3.185580	9.525843	5.708524
H	2.340098	9.691973	6.377988
H	3.129333	10.234879	4.881549
H	4.121054	9.653450	6.251560
C	5.371798	7.471596	6.139835
H	6.009390	6.587066	6.129954
H	5.153388	7.710381	7.186478

H	5.949050	8.299122	5.713259
C	4.395859	4.754564	4.582358
H	3.802647	3.949946	5.030520
H	5.359069	4.777218	5.092983
H	4.584120	4.497968	3.534150
C	1.705390	5.406461	3.348490
H	0.737932	5.236945	3.823749
H	2.257768	4.469961	3.284225
H	1.544636	5.819062	2.351641

Calculated energies and coordinates of [3a][BarF]
 Electronic energy ... -5363.49812873 Eh
 Total Enthalpy ... -5362.39235147 Eh
 Final Gibbs free energy ... -5362.60276821 Eh

CARTESIAN COORDINATES (ANGSTROEM)

Sn	-2.312789	2.433152	0.026458
F	6.074535	1.260299	-2.779122
F	1.278923	-6.749500	1.013093
F	7.629941	-0.264075	-2.846080
F	5.715696	-0.610758	-3.825564
F	2.668723	-5.754605	-0.336008
F	0.551081	-5.860423	-0.836596
F	1.351962	-1.789122	-5.006630
F	-2.162863	-3.874963	3.284502
F	-0.854358	3.329856	-3.053725
F	1.188502	3.488528	-3.777192
N	-2.401209	-2.362755	-1.638139
F	4.540105	2.942507	5.144741
F	-1.653347	-1.791089	3.667808
N	-3.322766	-1.315617	-3.307106
F	0.745179	3.909008	-1.688429
C	1.557976	-1.966675	1.044173
C	2.291327	0.553958	1.615043
C	3.814869	-0.955340	0.011923
C	1.468958	-0.111513	-0.884156
C	3.444615	0.897495	2.328536
H	4.389642	0.421198	2.080823
C	5.743836	-0.677453	-1.460424
C	1.838607	-3.225936	0.487336
H	2.608801	-3.312013	-0.274995
C	1.176432	-4.381677	0.897573
C	1.235709	1.239934	-1.185474
H	1.518048	2.002545	-0.466049
C	-2.764340	-1.144455	-2.088897
C	4.625031	-1.781260	0.804498
H	4.211248	-2.228700	1.706954
C	0.588356	-1.946927	2.056876
H	0.337502	-1.009094	2.541729
F	-0.771079	-1.328823	-4.943365
C	1.112114	-1.032918	-1.878165
H	1.292940	-2.091689	-1.713262
C	4.416089	-0.409875	-1.127218
H	3.840685	0.243612	-1.779099
C	1.115638	1.228629	1.986723
H	0.190729	1.015525	1.453476
F	6.175563	-4.180543	1.478193
C	5.951311	-2.050254	0.475397
C	0.205202	-4.334412	1.891429
H	-0.312043	-5.233386	2.210918
C	3.427600	1.836903	3.360062
C	0.669207	1.638514	-2.395924
F	5.345151	1.028463	4.484433
C	6.297893	-0.075888	-2.719305
C	-1.725590	-2.649072	-0.367566
H	-1.396037	-3.686937	-0.382972
H	-2.414247	-2.473356	0.461652
H	-0.861039	-1.995065	-0.256311
C	1.093776	2.163667	3.018844
C	-0.081389	-3.099735	2.463647
C	1.437554	-5.683184	0.199481
F	0.051235	-2.890135	-3.658794
C	6.528904	-1.503551	-0.665574
H	7.559174	-1.714393	-0.924846
C	-4.488299	2.694916	0.464460
C	0.446610	3.089693	-2.714923
C	0.325430	0.705573	-3.368581

H	-0.099665	1.021621	-4.316168
F	-0.636704	-3.378750	4.754481
C	2.253756	2.481031	3.721218
H	2.238507	3.205361	4.527216
B	2.280483	-0.606202	0.461740
C	0.558291	-0.637626	-3.095403
C	-5.533532	1.792519	0.717984
F	5.586064	2.794627	3.240015
C	-2.739408	-3.318446	-2.570083
F	6.801072	-2.456326	2.645130
C	-4.768859	4.075064	0.493697
C	-3.645511	5.002200	0.162470
C	-2.890004	5.589731	1.197092
C	-3.274890	5.199326	-1.183843
F	8.012599	-3.128108	0.963599
C	-6.807976	2.280638	1.030492
H	-7.606707	1.571102	1.236443
C	-3.321744	-2.657179	-3.623880
C	-1.759512	6.332469	0.867918
H	-1.160850	6.762473	1.668422
C	-4.111979	4.651900	-2.312451
H	-4.369148	3.598138	-2.165821
H	-3.587247	4.752470	-3.265685
H	-5.061152	5.196960	-2.382382
C	-5.362614	0.312436	0.629838
C	6.740716	-2.949169	1.382946
C	-7.061165	3.646804	1.079856
H	-8.056534	4.005322	1.327467
C	-5.792423	-0.356251	-0.528287
C	-1.356751	6.512841	-0.456514
C	-3.810143	-0.285845	-4.227557
H	-3.191770	-0.298405	-5.129853
H	-3.739329	0.685321	-3.744919
H	-4.848566	-0.502385	-4.491694
C	4.718653	2.151462	4.061770
C	-0.171112	2.891892	3.348263
C	-2.132186	5.952045	-1.466989
H	-1.835905	6.088507	-2.504449
C	-5.669422	-1.745134	-0.600060
H	-6.006293	-2.261535	-1.498764
C	-6.378788	0.408266	-1.685758
H	-5.714659	1.221217	-2.000668
H	-7.332819	0.873831	-1.415122
H	-6.560475	-0.254394	-2.537340
C	-1.123399	-3.029236	3.541766
C	-6.042487	4.550638	0.799037
H	-6.231802	5.621594	0.810796
C	0.305953	-1.655703	-4.165230
C	-4.823493	-0.416601	1.700797
C	-3.276753	5.385261	2.636655
H	-4.247411	5.844546	2.854812
H	-2.530321	5.817841	3.306379
H	-3.376402	4.320048	2.875995
C	-4.318666	0.275770	2.935614
H	-4.289538	-0.409939	3.786094
H	-4.933315	1.142113	3.195499
H	-3.294975	0.638642	2.782132
C	-3.826363	-3.162551	-4.923433
H	-3.741681	-4.249032	-4.962091
H	-3.245388	-2.751552	-5.757230
H	-4.878334	-2.900333	-5.081792
C	-5.154796	-2.487642	0.461968
C	-2.426038	-4.759080	-2.406047
H	-2.840290	-5.326203	-3.240830
H	-2.847880	-5.163943	-1.480635
H	-1.344071	-4.928714	-2.388061
C	-4.735663	-1.805687	1.602857
H	-4.328378	-2.367287	2.441939
C	-0.095321	7.265841	-0.773184
H	-0.035902	7.518629	-1.834880
H	0.784066	6.659763	-0.525555
H	-0.028936	8.190978	-0.191783
C	-5.084231	-3.989749	0.396854
H	-5.917639	-4.443100	0.946795
H	-4.161601	-4.368823	0.850839
H	-5.142044	-4.347049	-0.636413
F	-0.314324	4.025199	2.607125

F	-0.239687	3.266920	4.642201
F	-1.283919	2.138158	3.099001
O	-2.896221	1.219068	-1.899861
C	-2.642625	0.117600	-1.322580
O	-2.295717	0.047782	-0.114246

Calculated energies and coordinates of [4]⁺
 Electronic energy ... -2287.56604510 Eh
 Total Enthalpy ... -2286.70013232 Eh
 Final Gibbs free energy ... -2286.83832856 Eh

CARTESIAN COORDINATES (ANGSTROM)

Sn	3.390065	11.977764	8.063714
O	1.687531	13.180963	8.932262
O	3.036134	12.827292	10.687914
O	2.367100	12.437654	6.064367
O	0.381805	11.460423	6.567078
C	4.669595	13.767370	7.589197
C	4.521501	15.138350	7.867123
C	5.420372	16.066954	7.322798
H	5.286239	17.122409	7.551976
C	6.475505	15.660444	6.516820
H	7.163299	16.394599	6.106449
C	6.656454	14.307369	6.261881
H	7.494134	13.964630	5.658513
C	5.766921	13.373189	6.795319
C	3.479049	15.720228	8.771915
C	3.799358	15.958436	10.119061
C	2.879369	16.624735	10.932807
H	3.145978	16.833078	11.968406
C	1.651365	17.066716	10.444230
C	1.345791	16.808116	9.108775
H	0.399150	17.161406	8.700772
C	2.241127	16.146457	8.267314
C	5.116660	15.503730	10.684400
H	5.207671	14.413761	10.617267
H	5.220519	15.800971	11.731958
H	5.957095	15.926890	10.124566
C	0.712094	17.861061	11.311891
H	-0.335375	17.657653	11.065994
H	0.873056	18.937194	11.174209
H	0.865992	17.644517	12.373648
C	1.867332	15.871914	6.838569
H	0.953024	16.404715	6.559586
H	1.707630	14.795907	6.699606
H	2.669987	16.170567	6.155402
C	6.005755	11.918377	6.538455
C	5.669028	11.339597	5.303240
C	5.868076	9.971349	5.113275
H	5.598013	9.526492	4.156956
C	6.417979	9.166834	6.107392
C	6.782670	9.764419	7.314142
H	7.234233	9.154525	8.094353
C	6.585978	11.122644	7.548695
C	5.126885	12.177602	4.176450
H	5.944240	12.584267	3.567448
H	4.552950	13.022324	4.561005
H	4.488274	11.578281	3.518438
C	6.607470	7.689769	5.898361
H	6.553161	7.424886	4.838995
H	5.833003	7.120012	6.425872
H	7.574959	7.355841	6.285875
C	6.986266	11.720517	8.871545
H	7.480884	12.687748	8.741084
H	7.658464	11.048201	9.410548
H	6.113301	11.898351	9.515051
C	1.980334	13.224330	10.172318
C	1.224620	11.928924	5.804815
N	-0.336533	14.121186	10.687547
H	-0.484774	14.678290	8.666282
H	-1.999119	14.100927	9.432190
H	-0.707012	12.948963	8.973513
H	-1.763198	10.178856	1.804325
N	1.062407	14.105082	12.352313
H	3.135185	14.312393	12.602308
H	2.446351	12.853297	13.333330
H	2.154998	14.446934	14.093681
H	2.396401	14.038746	4.572468

C	0.921016	13.796409	11.048599
H	-1.433032	9.992702	4.749620
C	-0.998040	14.663477	11.773139
H	-2.532504	15.916538	10.948933
H	-2.690226	15.572935	12.672034
H	-3.101951	14.326942	11.493454
C	0.543397	14.208997	1.025549
C	-0.114758	14.652516	12.824659
H	0.395442	15.935863	14.468324
H	-0.117471	14.305576	14.943025
H	-1.305684	15.479352	14.374360
C	-0.922930	13.948469	9.351438
C	-0.742394	10.356818	1.450103
H	-0.807351	10.827628	0.468170
H	-0.255064	9.383885	1.318331
C	0.900644	13.179459	0.912992
H	1.958209	13.221379	0.628734
H	0.352825	12.724967	0.086516
C	1.994072	14.024045	3.561809
H	2.816568	14.066013	2.843342
H	1.327260	14.877698	3.404256
C	-2.402659	15.141637	11.712395
H	-0.461888	8.949875	3.666050
C	-0.288618	15.114988	14.225177
H	0.189508	9.485668	5.242257
C	2.280201	13.916938	13.149585
N	0.148837	10.945456	3.733036
N	1.246855	12.778519	3.370664
C	0.898104	11.894602	4.325971
C	0.014598	11.229793	2.382391
C	0.701273	12.392335	2.155398
C	-0.425821	9.765993	4.389533

Calculated energies and coordinates of [4][BArF]			
Electronic energy	...	-5935.48159210 Eh	
Total Enthalpy	...	-5934.16336500 Eh	
Final Gibbs free energy	...	-5934.39940847 Eh	
CARTESIAN COORDINATES (ANGSTROM)			
Sn	-4.367022	1.282271	0.664131
F	3.098727	-2.519958	4.977083
F	3.781768	-3.778354	3.334340
F	5.098295	-2.255087	4.160881
F	0.970859	2.159259	-5.352165
F	1.848459	0.273678	-5.998057
F	2.918803	2.142381	-6.324397
F	-1.494899	-5.792929	-0.745920
F	0.288733	-6.104515	-1.952200
F	0.476496	-5.789486	0.188495
F	-1.939046	0.146122	-2.830841
F	-2.708419	-1.749712	-3.667523
F	-3.248159	-1.071486	-1.577269
F	3.859541	-5.844031	-3.734189
F	5.848273	-5.470630	-4.541463
F	4.153153	-4.277432	-5.212334
O	-3.078969	-0.270524	1.580766
O	-4.789394	-1.619662	1.043502
O	-2.578556	2.648982	1.069414
O	-1.190994	1.367117	-0.182506
C	-5.255619	1.983057	2.618928
C	-5.194053	1.433388	3.912151
C	-5.814449	2.083990	4.987337
H	-5.750973	1.637745	5.978010
C	-6.507395	3.273372	4.802208
H	-6.983542	3.765469	5.646110
C	-6.599885	3.818076	3.527564
H	-7.156183	4.737700	3.357679
C	-5.987482	3.176592	2.449269
C	-4.513808	0.141157	4.235750
C	-3.168453	0.130138	4.635084
C	-2.579278	-1.071834	5.026429
H	-1.538896	-1.071828	5.350239
C	-3.297950	-2.267289	5.034792
C	-4.626874	-2.239729	4.617041
H	-5.205884	-3.162358	4.617072
C	-5.248651	-1.053633	4.219757
C	-2.361504	1.396966	4.600008

H	-1.357272	1.241075	5.004159
H	-2.849559	2.196636	5.168154
H	-2.269781	1.748823	3.565316
C	-2.671425	-3.540997	5.536988
H	-3.174903	-4.422320	5.126518
H	-2.744180	-3.605825	6.629698
H	-1.609255	-3.599394	5.277910
C	-6.683105	-1.066756	3.768017
H	-6.755351	-0.774123	2.714644
H	-7.288965	-0.357379	4.341697
H	-7.118549	-2.064008	3.875875
C	-6.137516	3.765219	1.081349
C	-7.113201	3.248969	0.205542
C	-7.227161	3.782190	-1.076234
H	-7.979494	3.377925	-1.751032
C	-6.397733	4.812683	-1.517756
C	-5.455029	5.326890	-0.631239
H	-4.810494	6.143364	-0.953190
C	-5.319055	4.827829	0.664899
C	-8.011867	2.120641	0.634149
H	-8.396969	2.277302	1.646431
H	-7.469977	1.164822	0.650395
H	-8.853310	2.010630	-0.054769
C	-6.507305	5.335539	-2.924112
H	-7.549867	5.370762	-3.254909
H	-5.965805	4.685916	-3.622669
H	-6.085117	6.340783	-3.010838
C	-4.321147	5.446474	1.605948
H	-4.800733	6.203293	2.239734
H	-3.516888	5.936438	1.047038
H	-3.887704	4.694008	2.267986
N	-1.395887	-2.477431	1.979643
N	-3.065944	-3.857382	1.840927
C	-2.715045	-2.560067	1.711923
C	-0.908746	-3.728244	2.302183
C	-1.962075	-4.600969	2.208444
C	-0.561543	-1.270687	1.932438
H	0.480526	-1.587185	1.922704
H	-0.766556	-0.648770	2.807504
H	-0.782164	-0.694046	1.034400
C	0.499758	-3.968415	2.699017
H	1.195346	-3.728354	1.888194
H	0.642725	-5.018147	2.957924
H	0.775701	-3.362462	3.569510
C	-2.030397	-6.062312	2.452096
H	-2.482709	-6.586977	1.604759
H	-2.615301	-6.295387	3.350270
H	-1.025647	-6.463731	2.588911
C	-4.397182	-4.436260	1.654052
H	-4.413327	-5.019620	0.727513
H	-5.122881	-3.627879	1.588443
H	-4.618321	-5.091722	2.500529
N	-0.328629	4.562766	1.125436
N	0.193417	3.800034	-0.836155
C	-0.585108	3.579143	0.241346
C	0.643208	5.406257	0.612604
C	0.962634	4.933169	-0.631457
C	-0.868395	4.687552	2.479592
H	-1.611133	3.908572	2.636240
H	-1.340763	5.667282	2.592172
H	-0.054980	4.584198	3.203712
C	1.185706	6.551139	1.384138
H	0.401942	7.267215	1.655574
H	1.932952	7.080222	0.791056
H	1.668590	6.212696	2.308223
C	1.893394	5.458634	-1.660693
H	2.582136	6.179009	-1.216580
H	1.352682	5.960116	-2.472802
H	2.491514	4.656357	-2.099943
C	0.239213	3.000449	-2.067067
H	-0.685191	2.437252	-2.174226
H	1.079383	2.299957	-2.020500
H	0.374716	3.672225	-2.916554
C	-3.627334	-1.412679	1.412693
C	-1.523015	2.406131	0.386886
C	2.833889	-0.865066	0.523848
C	2.300614	0.326486	1.028942

H	1.876098	1.054436	0.340413	C	-2.647032	1.112685	-1.787445
C	2.294311	0.610368	2.393849	C	-3.142369	2.279593	-1.172561
C	2.779677	-0.305295	3.319620	C	-4.369696	2.237988	-0.514259
H	2.769816	-0.088704	4.382022	H	-4.739117	3.143522	-0.034832
C	3.275562	-1.514763	2.839872	C	-5.139170	1.075883	-0.460089
C	3.312879	-1.781283	1.472869	C	-4.659376	-0.059334	-1.105701
H	3.727247	-2.727852	1.134419	H	-5.262300	-0.965778	-1.111329
C	1.694860	1.900358	2.852398	C	-3.439414	-0.059308	-1.789819
F	1.994236	2.205432	4.132549	C	-2.400116	3.587471	-1.236346
F	2.092976	2.954825	2.089383	H	-1.344479	3.447312	-1.472250
F	0.330916	1.875924	2.769417	H	-2.495204	4.135196	-0.293051
C	3.815136	-2.516385	3.820849	H	-2.820912	4.224599	-2.023847
C	3.002647	0.125976	-1.982692	C	-6.474371	1.063444	0.231978
C	2.508488	0.234755	-3.292877	H	-6.530819	1.827864	1.012749
H	1.888344	-0.560480	-3.698395	H	-6.686020	0.088125	0.680701
C	2.792647	1.335304	-4.097145	H	-7.279729	1.271855	-0.482426
C	3.607322	2.369315	-3.639948	C	-3.092646	-1.261877	-2.634344
H	3.836706	3.218911	-4.273451	H	-3.400569	-2.191242	-2.146463
C	4.129063	2.266262	-2.356536	H	-2.029901	-1.321810	-2.874928
C	3.830674	1.168887	-1.548687	H	-3.632942	-1.196970	-3.587186
H	4.266539	1.127672	-0.552823	C	2.124024	-0.557142	-2.065493
C	2.146089	1.464603	-5.445603	C	3.349149	0.046053	-1.726627
C	5.038793	3.325430	-1.806274	C	4.466814	-0.755599	-1.486488
F	4.592041	3.786148	-0.602430	H	5.417312	-0.276015	-1.255059
F	6.291273	2.866292	-1.598977	C	4.409729	-2.143519	-1.583469
F	5.136351	4.404116	-2.621168	C	3.184734	-2.726982	-1.900184
C	1.325256	-1.928323	-1.296903	H	3.125765	-3.808904	-2.008402
C	1.140662	-3.285740	-1.001124	C	2.046602	-1.962274	-2.156318
H	1.991236	-3.880447	-0.672251	C	3.509515	1.545022	-1.677278
C	-0.097953	-3.912716	-1.151234	H	4.314408	1.829511	-0.992240
C	-1.199185	-3.206384	-1.616918	H	2.588635	2.049282	-1.373885
H	-2.153960	-3.696620	-1.777197	H	3.771912	1.945873	-2.663387
C	-1.038830	-1.853607	-1.905288	C	5.644445	-2.987059	-1.422002
C	0.189005	-1.225005	-1.725873	H	5.415914	-3.953730	-0.961687
H	0.260507	-0.163325	-1.936214	H	6.405052	-2.483673	-0.818448
C	-0.206982	-5.389875	-0.917869	H	6.093677	-3.197396	-2.399978
C	-2.223901	-1.119691	-2.464623	C	0.795087	-2.655384	-2.627704
C	4.011227	-2.189520	-1.528900	H	0.017545	-2.691098	-1.852424
C	3.878392	-3.115855	-2.569852	H	1.012197	-3.686201	-2.919588
H	2.909405	-3.256133	-3.044885	H	0.357258	-2.137468	-3.486843
C	4.956816	-3.873437	-3.023582	C	-1.339028	1.108926	1.260214
C	6.219210	-3.730665	-2.460101	C	-1.315192	3.118527	2.303858
H	7.057103	-4.321225	-2.809715	C	-2.376411	2.411654	2.791133
C	6.375139	-2.799005	-1.439321	C	0.479447	2.701903	0.613683
C	5.295292	-2.043624	-0.988777	H	1.326330	2.869195	1.286860
H	5.465490	-1.318512	-0.194831	H	0.281812	3.628617	0.067724
C	4.714860	-4.863716	-4.125940	H	0.717153	1.916312	-0.105518
C	7.708539	-2.601771	-0.778263	C	-0.813508	4.477154	2.629094
F	7.692383	-3.029817	0.511880	H	0.209724	4.446414	3.020618
F	8.704528	-3.267994	-1.402154	H	-1.444197	4.938673	3.390516
F	8.062522	-1.293168	-0.742003	H	-0.816214	5.134224	1.751368
B	2.781131	-1.214606	-1.071541	C	-3.397957	2.761732	3.808907

Calculated energies and coordinates of **TS(2_3)**

Electronic energy ... -2098.92836904 Eh
Total Enthalpy ... -2098.08225296 Eh
Final Gibbs free energy ... -2098.21135727 Eh

CARTESIAN COORDINATES (ANGSTROM)

Sn	-0.956589	-0.755452	-0.022301
O	0.485229	-0.105657	3.701418
C	-0.095057	-0.985842	3.119054
O	-1.099869	-1.657148	3.128254
N	-0.700064	2.299405	1.366265
N	-2.365575	1.188691	2.136757
N	2.298955	-1.139440	1.729774
N	1.130081	-2.938469	1.559218
C	-0.248032	0.379242	-1.833361
C	-1.301484	1.097408	-2.440084
C	-1.120305	1.748631	-3.660182
H	-1.950874	2.290987	-4.106211
C	0.105974	1.679022	-4.309801
H	0.248399	2.174878	-5.265527
C	1.137543	0.940006	-3.747819
H	2.083394	0.843030	-4.275349
C	0.973969	0.280138	-2.520937

H -0.120931 -4.144507 0.374632

Calculated energies and coordinates of **TS(3_4)**
Electronic energy ... -2287.52986583 Eh
Total Enthalpy ... -2286.66645624 Eh
Final Gibbs free energy ... -2286.80125225 Eh
CARTESIAN COORDINATES (ANGSTROEM)

Sn 0.658985 -1.257593 0.201077
O -1.075959 0.156470 0.739824
O -0.005579 -0.533203 2.563227
O -3.396481 -1.245895 -0.922361
O -2.156917 -2.576732 0.481773
C 1.991910 0.479271 -0.337772
C 2.069562 1.794436 0.167137
C 3.114713 2.639315 -0.225070
H 3.149405 3.649788 0.176784
C 4.103161 2.205230 -1.098705
H 4.910448 2.872886 -1.386020
C 4.054414 0.909063 -1.591175
H 4.825346 0.544372 -2.266480
C 3.014635 0.056398 -1.213827
C 1.102834 2.390950 1.141197
C 1.356290 2.303465 2.520361
C 0.512033 2.971335 3.410165
H 0.727997 2.926740 4.476823
C -0.572817 3.727477 2.968041
C -0.805334 3.804189 1.595710
H -1.630808 4.412821 1.227297
C 0.025026 3.160015 0.677111
C 2.530253 1.518870 3.037292
H 2.428729 0.455486 2.794157
H 2.621659 1.615426 4.122559
H 3.465284 1.861847 2.582198
C -1.425535 4.498354 3.939935
H -1.049915 5.522081 4.056970
H -1.420954 4.037911 4.932900
H -2.462516 4.572412 3.596799
C -0.208583 3.333711 -0.798384
H 0.428859 4.132295 -1.198014
H -1.247112 3.607961 -1.010526
H 0.047087 2.424771 -1.348013
C 3.018101 -1.331185 -1.774371
C 2.538444 -1.554849 -3.075739
C 2.590086 -2.843123 -3.609848
H 2.242391 -3.005086 -4.628567
C 3.112706 -3.914735 -2.888230
C 3.606685 -3.669901 -1.605917
H 4.046531 -4.488986 -1.040148
C 3.582279 -2.395501 -1.041499
C 2.038506 -0.411274 -3.915397
H 2.869379 0.224439 -4.242919
H 1.359391 0.235823 -3.349983
H 1.527389 -0.781763 -4.807306
C 3.155291 -5.300284 -3.473392
H 2.976355 -5.285178 -4.552111
H 2.398541 -5.949839 -3.014639
H 4.126391 -5.773655 -3.298540
C 4.183522 -2.161305 0.317677
H 4.886330 -1.322050 0.297554
H 4.708288 -3.051860 0.670946
H 3.420677 -1.908214 1.067188
C -0.950960 0.059032 2.002268
C -2.494030 -1.880838 -0.439578
N -3.115483 1.308242 2.416067
H -3.612952 0.552558 0.508412
H -2.743991 2.109035 0.514340
H -4.461131 2.043728 1.006817
H -1.440123 -4.803181 -4.505886
N -2.015743 0.694134 4.191193
H -0.013510 0.514034 4.798400
H -0.970686 -0.970739 4.950768
H -1.237373 0.375475 6.097190
H -1.612970 0.708985 -1.597239
C -2.005722 0.671870 2.842083
H -0.860097 -5.071491 -2.044404
C -3.832368 1.754568 3.506914

H -4.975235 3.437091 2.824550
H -5.472563 2.775709 4.381905
H -5.885240 1.915172 2.897979
H -2.414244 -0.627394 -5.414676
C -3.138617 1.365048 4.628560
H -2.677879 2.159602 6.569516
H -3.567237 0.624039 6.597056
H -4.392912 2.120786 6.162769
C -3.509350 1.513833 1.016223
C -0.615317 -4.083935 -4.578518
H -0.545496 -3.764513 -5.620038
H 0.311731 -4.607630 -4.322974
C -1.369439 -0.940343 -5.301387
H -0.742246 -0.048861 -5.410807
H -1.134339 -1.619373 -6.122932
C -1.685906 0.434543 -2.649037
H -1.042019 1.089987 -3.244095
H -2.724788 0.541063 -2.977380
C -5.106568 2.508138 3.390126
H 0.685941 -4.289586 -1.587278
C -3.454303 1.574477 6.064344
H -0.760046 -4.098092 -0.553279
C -0.991424 0.114190 5.068510
N -0.791196 -2.994363 -2.320017
N -1.256905 -0.948779 -2.791846
C -1.055232 -1.785757 -1.733881
C -0.836487 -2.913498 -3.693436
C -1.145842 -1.608037 -3.995175
C -0.407104 -4.192328 -1.579876

Calculated energies and coordinates of **TS1**

Electronic energy ... -3041.42260597 Eh
Total Enthalpy ... -3040.34613708 Eh
Final Gibbs free energy ... -3040.50636656 Eh

CARTESIAN COORDINATES (ANGSTROEM)

Sn 1.670829 -0.103240 0.307410
O -0.123629 0.881114 1.353828
O 1.268136 -0.003426 2.850411
C 2.909428 1.756179 0.119703
C 3.119995 2.827005 1.005703
C 4.056846 3.820736 0.695533
H 4.202569 4.641514 1.394857
C 4.797960 3.766611 -0.477790
H 5.523017 4.544283 -0.701018
C 4.607596 2.711513 -1.360432
H 5.181660 2.651068 -2.282411
C 3.676302 1.716130 -1.064059
C 2.395806 2.985650 2.303153
C 2.967126 2.501650 3.489914
C 2.330200 2.759028 4.704752
H 2.796992 2.414217 5.626250
C 1.134065 3.471579 4.770051
C 0.574191 3.932463 3.577682
H -0.350662 4.508027 3.609246
C 1.197036 3.714378 2.346849
C 4.240332 1.703641 3.460373
H 4.080874 0.743831 2.952168
H 4.600285 1.496450 4.471422
H 5.027967 2.225786 2.909994
C 0.502098 3.786855 6.099529
H -0.585065 3.886297 6.017536
H 0.886270 4.733586 6.498067
H 0.727215 3.014173 6.842564
C 0.594196 4.249602 1.077448
H -0.287189 4.865135 1.280825
H 0.301628 3.422315 0.420651
H 1.316372 4.857183 0.521272
C 3.474715 0.597640 -2.035676
C 2.623180 0.781924 -3.138108
C 2.409537 -0.283651 -4.013572
H 1.744350 -0.136821 -4.862863
C 3.029103 -1.518307 -3.829597
C 3.895945 -1.673328 -2.748630
H 4.401807 -2.625115 -2.600982

C	4.140406	-0.631745	-1.855101
C	1.965236	2.110452	-3.387069
H	2.695373	2.845271	-3.748087
H	1.540727	2.522620	-2.465830
H	1.173941	2.020198	-4.136069
C	2.785639	-2.653718	-4.787667
H	2.613675	-3.596930	-4.256899
H	3.649164	-2.804962	-5.446449
H	1.918763	-2.445786	-5.421568
C	5.104363	-0.823528	-0.715139
H	5.803230	0.016301	-0.642588
H	5.673490	-1.747971	-0.837084
H	4.589628	-0.880304	0.253623
C	0.200536	0.566148	2.543067
N	-1.925802	1.577398	3.472577
H	-1.676180	2.846911	1.816226
H	-3.337761	2.728257	2.455155
H	-2.640933	1.402579	1.487021
N	-0.658902	0.548976	4.913770
H	1.383210	0.335526	5.349531
H	0.529211	-1.187633	5.029616
H	0.250059	-0.327305	6.571196
C	-0.777022	0.885534	3.612463
C	-2.538702	1.697225	4.703163
H	-3.740639	3.476009	4.641715
H	-4.123838	2.357129	5.950845
H	-4.628539	1.979425	4.302742
C	-1.739778	1.046028	5.613698
H	-1.092980	1.317538	7.639237
H	-1.978843	-0.194660	7.352470
H	-2.839510	1.344751	7.401661
C	-2.427763	2.175406	2.227661
C	-3.823562	2.415758	4.903926
C	-1.915946	0.864485	7.076754
C	0.449499	-0.209409	5.506566
H	0.268976	0.690370	-1.298555
Si	-0.985018	0.076500	-1.991628
H	-0.520913	0.173022	-3.391142
O	-2.755507	-0.946848	-3.345143
C	-3.429336	-1.961391	-3.027353
O	-4.460753	-2.059880	-2.347499
C	-0.953515	-1.665861	-1.297886
C	-1.722347	-2.059641	-0.197311
C	-0.088350	-2.607124	-1.875083
C	-1.626487	-3.352334	0.313693
H	-2.409288	-1.352856	0.262805
C	0.005112	-3.900030	-1.371524
H	0.543584	-2.316452	-2.713566
C	-0.763594	-4.274785	-0.271025
H	-2.230049	-3.641179	1.170395
H	0.691412	-4.610457	-1.825074
H	-0.680583	-5.279395	0.135641
C	-2.280381	1.307556	-1.427217
C	-1.878318	2.642633	-1.289235
C	-3.619216	0.985609	-1.160470
C	-2.777422	3.632823	-0.904802
H	-0.849130	2.920893	-1.502749
C	-4.514816	1.972420	-0.754295
H	-3.979814	-0.027782	-1.311760
C	-4.099879	3.296094	-0.628292
H	-2.447840	4.666337	-0.830841
H	-5.550761	1.706036	-0.563598
H	-4.810007	4.066406	-0.337606
C	-2.843700	-3.271376	-3.546626
C	-1.558466	-4.730658	-4.655312
C	-2.223221	-5.416905	-3.676262
N	-1.960820	-3.409127	-4.557752
N	-3.018465	-4.496917	-3.013957
C	-1.474248	-2.337005	-5.430997
H	-2.249306	-1.583676	-5.556790
H	-0.601120	-1.856039	-4.981546
H	-1.206968	-2.774402	-6.394814
C	-3.905945	-4.851059	-1.904023
H	-4.251387	-3.931580	-1.434459
H	-4.767053	-5.405209	-2.290292
H	-3.353287	-5.471169	-1.194185
C	-0.584441	-5.205098	-5.670141
H	0.352482	-4.639375	-5.625335
H	-0.349582	-6.257234	-5.497198
H	-0.978915	-5.118689	-6.688674
C	-2.168437	-6.846522	-3.281806
H	-1.743436	-6.965836	-2.277266
H	-3.163251	-7.304447	-3.280118
H	-1.544724	-7.408009	-3.978508

Calculated energies and coordinates of **INT_A**
 Electronic energy ... -3041.42447827 Eh
 Total Enthalpy ... -3040.34726393 Eh
 Final Gibbs free energy ... -3040.51006015 Eh
 CARTESIAN COORDINATES (ANGSTROM)

Sn	1.937681	-0.088136	0.465927
O	0.247046	0.763463	1.700263
O	1.191804	-0.384622	3.396922
C	2.915831	1.919460	0.160174
C	2.960801	3.047651	0.998234
C	3.737952	4.157653	0.641630
H	3.769703	5.015764	1.309926
C	4.484346	4.163477	-0.529694
H	5.087526	5.029460	-0.787610
C	4.472969	3.045320	-1.354615
H	5.070431	3.022867	-2.263537
C	3.704038	1.933647	-1.008243
C	2.260579	3.124848	2.316082
C	2.795575	2.469660	3.436567
C	2.188262	2.646015	4.682534
H	2.632608	2.165309	5.552972
C	1.056886	3.440953	4.844121
C	0.528259	4.070257	3.716127
H	-0.351734	4.704472	3.821580
C	1.122837	3.938131	2.461484
C	4.009069	1.587577	3.323531
H	3.724560	0.579893	2.992368
H	4.503731	1.480624	4.292905
H	4.728598	1.982033	2.600847
C	0.460705	3.666981	6.208029
H	-0.614274	3.867314	6.149593
H	0.927140	4.529894	6.698707
H	0.619683	2.803069	6.862791
C	0.547721	4.663357	1.274500
H	-0.437864	5.079633	1.505020
H	0.459976	3.993670	0.412620
H	1.194363	5.490521	0.961110
C	3.736019	0.718150	-1.879512
C	2.928978	0.645543	-3.026522
C	2.936240	-0.522588	-3.790760
H	2.300960	-0.578081	-4.672910
C	3.736914	-1.610945	-3.454958
C	4.562025	-1.507510	-2.335006
H	5.210054	-2.341197	-2.071037
C	4.584377	-0.358635	-1.546825
C	2.088895	1.819418	-3.446304
H	2.707732	2.585597	-3.929047
H	1.617304	2.298601	-2.583768
H	1.311982	1.518169	-4.153934
C	3.743340	-2.859667	-4.294809
H	2.884952	-2.888077	-4.972287
H	3.721080	-3.758514	-3.669647
H	4.651050	-2.914734	-4.907517
C	5.517440	-0.267937	-0.369103
H	6.130755	0.637732	-0.423937
H	6.178032	-1.137258	-0.328314
H	4.972342	-0.214943	0.582058
C	0.328527	0.346694	2.908229
N	-1.829993	1.594042	3.470743
H	-1.277111	2.753139	1.810540
H	-3.020768	2.743188	2.201753
H	-2.260599	1.336632	1.415785
N	-0.860391	0.572836	5.126543
H	1.099488	0.216605	5.789567
H	0.119934	-1.239627	5.578447
H	-0.202615	-0.153245	6.964294
C	-0.772581	0.827749	3.803876
C	-2.593152	1.839933	4.596011

H	-3.613894	3.699919	4.271912	C	4.131228	3.204732	-1.677467
H	-4.266063	2.704383	5.574435	H	4.525132	3.472247	-2.655697
H	-4.579884	2.261003	3.895429	C	3.243377	2.134632	-1.561272
C	-1.982725	1.192742	5.641521	C	2.583388	2.189435	2.187143
H	-1.608912	1.584399	7.718773	C	3.149071	1.159795	2.951190
H	-2.515897	0.090596	7.407127	C	2.691525	0.948918	4.254603
H	-3.302802	1.659446	7.234460	H	3.164362	0.175200	4.858191
C	-2.115852	2.140814	2.138470	C	1.681107	1.729456	4.811371
C	-3.825833	2.669120	4.577107	C	1.106033	2.727283	4.022818
C	-2.366388	1.123515	7.074702	H	0.315204	3.348629	4.442990
C	0.101253	-0.203136	5.918715	C	1.547204	2.972722	2.723449
H	0.559527	0.272872	-0.922382	C	4.222275	0.273867	2.381367
Si	-0.699003	-0.459054	-1.776066	H	3.783031	-0.492700	1.727115
H	0.153594	-0.368752	-2.979905	H	4.768073	-0.243387	3.175242
O	-1.985335	-1.372158	-2.995898	H	4.932460	0.842762	1.775472
C	-2.797875	-2.315300	-2.670741	C	1.263895	1.550761	6.247342
O	-3.507468	-2.429227	-1.679964	H	0.195189	1.751528	6.382425
C	-0.565991	-2.030398	-0.751847	H	1.808319	2.244625	6.899309
C	-1.171788	-2.166463	0.501210	H	1.480005	0.538717	6.605084
C	0.183292	-3.105545	-1.249077	C	0.904476	4.051498	1.893514
C	-1.030118	-3.337538	1.240267	H	0.069614	4.516807	2.426027
H	-1.767910	-1.349289	0.901719	H	0.542488	3.645802	0.940035
C	0.332580	-4.276366	-0.509845	H	1.620501	4.839277	1.636268
H	0.679912	-3.017218	-2.214743	C	2.843543	1.379632	-2.788385
C	-0.275450	-4.394407	0.737859	C	1.746979	1.821364	-3.550155
H	-1.508271	-3.426924	2.211934	C	1.379969	1.107741	-4.690258
H	0.936708	-5.091338	-0.900097	H	0.533272	1.461929	-5.274799
H	-0.153291	-5.303201	1.320661	C	2.088060	-0.018415	-5.106889
C	-1.861449	0.962797	-1.352193	C	3.174891	-0.441789	-4.342018
C	-1.343937	2.262009	-1.258230	H	3.750283	-1.308892	-4.664018
C	-3.243354	0.791014	-1.182233	C	3.568408	0.241880	-3.189553
C	-2.175203	3.356591	-1.040963	C	1.006128	3.070134	-3.163481
H	-0.272403	2.419512	-1.356405	H	1.633354	3.955458	-3.321892
C	-4.073440	1.881271	-0.930549	H	0.739653	3.054194	-2.101830
H	-3.674555	-0.203554	-1.245330	H	0.090441	3.185406	-3.748752
C	-3.544699	3.167885	-0.872688	C	1.721478	-0.726713	-6.382829
H	-1.753550	4.357344	-1.001030	H	2.097234	-1.754015	-6.397176
H	-5.140906	1.725067	-0.798077	H	2.157088	-0.216709	-7.250581
H	-4.196823	4.021069	-0.704605	H	0.637564	-0.744384	-6.535475
C	-2.826832	-3.452456	-3.658194	C	4.764831	-0.218324	-2.403134
C	-2.827150	-4.692440	-5.514165	H	5.540588	0.553829	-2.385963
C	-2.999719	-5.533497	-4.446167	H	5.193034	-1.127631	-2.832817
N	-2.711192	-3.410204	-4.998095	H	4.501550	-0.418220	-1.356625
N	-3.000007	-4.740088	-3.309035	C	0.302870	-0.657512	2.372343
C	-2.556424	-2.208202	-5.821066	N	-1.633949	0.629604	3.417461
H	-2.481470	-1.341394	-5.167225	H	-1.253042	2.284356	2.173033
H	-1.641495	-2.290614	-6.414339	H	-2.978750	1.846971	2.393471
H	-3.416684	-2.110780	-6.489438	H	-1.918227	0.865464	1.344355
C	-3.118174	-5.239274	-1.932309	N	-0.665225	-0.819862	4.709206
H	-2.467529	-4.661076	-1.274903	H	1.270410	-1.612261	4.810390
H	-4.150138	-5.141280	-1.586938	H	-0.019275	-2.822445	4.873925
C	-2.812397	-6.286171	-1.920947	H	0.289345	-1.777818	6.295466
C	-2.766518	-4.965442	-6.971901	C	-0.638878	-0.272560	3.480425
H	-1.811049	-4.645550	-7.402335	C	-2.296861	0.669564	4.632957
H	-2.874503	-6.034289	-7.160452	H	-3.165703	2.627564	4.738930
H	-3.567229	-4.448306	-7.512548	H	-3.761216	1.476707	5.938616
C	-3.155560	-7.009347	-4.398256	H	-4.301649	1.349451	4.264134
H	-2.303467	-7.492202	-3.906317	C	-1.683938	-0.246080	5.449821
H	-4.066038	-7.300393	-3.863937	H	-1.119389	-0.323192	7.518925
H	-3.221457	-7.409813	-5.410870	H	-2.127682	-1.680206	6.984298
Calculated energies and coordinates of TS2				H	-2.842795	-0.084563	7.221200
Electronic energy ... -3041.42230439 Eh				C	-1.967595	1.461622	2.256615
Total Enthalpy ... -3040.34637604 Eh				C	-3.440133	1.578231	4.900889
Final Gibbs free energy ... -3040.50402540 Eh				C	-1.952943	-0.606250	6.865082
CARTESIAN COORDINATES (ANGSTROM)				C	0.278425	-1.825272	5.206117
Sn	1.439176	-0.063164	-0.463597	H	-0.022670	0.829358	-1.109634
O	0.414277	0.263946	1.499414	Si	-1.621449	-0.310268	-2.539814
O	0.813342	-1.777153	2.416558	H	-0.233746	-0.711066	-2.778093
C	2.708083	1.760509	-0.315306	O	-2.440106	-1.264173	-3.777970
C	3.097182	2.491251	0.818285	C	-2.597034	-2.571490	-3.841638
C	3.993549	3.560038	0.692743	O	-3.371626	-3.135493	-4.576681
H	4.289265	4.108719	1.584709	C	-2.405168	-0.869539	-0.934916
C	4.511787	3.915958	-0.545890	C	-3.733554	-0.496812	-0.674048
H	5.210400	4.743512	-0.627841	C	-1.750280	-1.679278	0.004652
				C	-4.384189	-0.909978	0.485396
				H	-4.263740	0.136174	-1.383247
				C	-2.397797	-2.095373	1.165971

H	-0.714595	-1.973690	-0.159352
C	-3.715754	-1.710215	1.408877
H	-5.413039	-0.609848	0.665034
H	-1.860652	-2.705838	1.887590
H	-4.220982	-2.034830	2.315385
C	-2.181400	1.380404	-3.047317
C	-2.350105	2.395334	-2.096763
C	-2.405184	1.678181	-4.397616
C	-2.721464	3.677256	-2.485591
H	-2.178225	2.178562	-1.045505
C	-2.770011	2.961474	-4.788200
H	-2.303038	0.900661	-5.151369
C	-2.925651	3.963352	-3.833990
H	-2.847443	4.456244	-1.739459
H	-2.939251	3.179647	-5.838640
H	-3.209101	4.966132	-4.140166
C	-1.761245	-3.395201	-2.895400
C	-0.055955	-4.352313	-1.827117
C	-1.217951	-4.776163	-1.237221
N	-0.422320	-3.499167	-2.859361
N	-2.260977	-4.188378	-1.935886
C	0.518963	-2.949908	-3.840352
H	-0.022124	-2.332249	-4.558550
H	1.267991	-2.329206	-3.335453
H	1.005443	-3.776002	-4.367769
C	-3.673380	-4.285008	-1.564782
H	-4.280827	-3.855851	-2.360005
H	-3.942505	-5.337118	-1.440705
H	-3.839807	-3.740285	-0.630006
C	1.364604	-4.627818	-1.507789
H	1.881890	-3.701190	-1.227687
H	1.433050	-5.319526	-0.668924
H	1.892584	-5.077126	-2.358625
C	-1.450630	-5.666628	-0.073713
H	-2.059699	-5.170925	0.687147
H	-1.962177	-6.589222	-0.368431
H	-0.497257	-5.941157	0.383906

Calculated energies and coordinates of INT_B

Electronic energy	...	-1325.04745581 Eh
Total Enthalpy	...	-1324.63125306 Eh
Final Gibbs free energy	...	-1324.70989275 Eh

CARTESIAN COORDINATES (ANGSTROEM)

O	-0.049662	-0.314659	0.571652
O	-0.958281	1.548539	1.479133
C	-1.039511	0.516550	0.847425
H	-4.286104	-2.993418	-1.547206
H	-4.816142	1.792242	1.750204
H	-0.780887	-1.134571	-1.709116
H	-6.340921	0.149383	1.048389
C	-4.524030	-1.959354	-1.817960
H	-5.609771	-1.859948	-1.812296
H	-4.182454	-1.784291	-2.844198
C	-5.964918	0.331660	0.035625
H	-6.138542	1.384234	-0.211426
H	-6.561227	-0.270731	-0.650070
C	-3.745278	1.703711	1.572831
H	-3.228133	1.485591	2.507175
H	-3.350664	2.636626	1.165635
H	-1.096128	-2.433809	-0.541533
H	-2.049543	-2.338448	-2.047133
N	-2.568860	-0.917987	-0.611365
N	-3.528775	0.607874	0.614241
C	-2.337206	0.060352	0.293230
C	-3.923557	-0.991214	-0.865550
C	-4.529643	-0.027678	-0.088944
C	-1.556229	-1.760816	-1.267184
Si	1.605244	0.087067	0.993462
H	1.582022	0.343236	2.449586
C	2.103451	1.587615	0.032020
C	2.480326	-1.472026	0.499352
C	3.737297	-1.424481	-0.119825
C	1.924228	-2.728121	0.789761
C	2.597673	-3.898264	0.460565
C	3.842521	-3.832261	-0.161315

C	4.412660	-2.596226	-0.447774
H	4.195257	-0.464686	-0.347112
H	4.371057	-4.746346	-0.415498
H	5.386299	-2.543610	-0.925598
H	0.961682	-2.795289	1.293721
H	2.159090	-4.863474	0.696696
C	2.333026	1.514103	-1.351347
H	2.249991	0.559751	-1.868511
C	2.686855	2.648653	-2.071851
C	2.820166	3.872081	-1.419186
H	2.868206	2.579696	-3.140429
C	2.595437	3.961631	-0.048550
H	3.104361	4.757250	-1.980853
C	2.235918	2.828034	0.672058
H	2.702240	4.915611	0.459011
H	2.054104	2.908391	1.741054

Calculated energies and coordinates of INT_C

Electronic energy	...	-1716.33206638 Eh
Total Enthalpy	...	-1715.67322741 Eh
Final Gibbs free energy	...	-1715.78268516 Eh

CARTESIAN COORDINATES (ANGSTROEM)

Sn	3.829209	11.931927	8.576658
O	2.220643	13.128437	9.652846
O	3.104913	13.121067	11.748449
C	4.887783	13.734116	7.710236
C	4.773188	15.104639	7.996605
C	5.615824	16.038953	7.377439
H	5.498381	17.094159	7.618986
C	6.579862	15.637335	6.462553
H	7.225022	16.371424	5.987303
C	6.703485	14.286674	6.158508
H	7.445238	13.948066	5.437303
C	5.872245	13.351768	6.776432
C	3.754783	15.673470	8.931050
C	4.101457	15.966101	10.257928
C	3.177552	16.619933	11.076160
H	3.465940	16.874853	12.095326
C	1.912435	16.975721	10.613688
C	1.571082	16.641461	9.302921
H	0.585269	16.909957	8.922267
C	2.474443	15.998578	8.455058
C	5.439737	15.552500	10.803014
H	5.533700	14.460564	10.780021
H	5.563542	15.884695	11.837601
H	6.260066	15.957944	10.201676
C	0.963165	17.749837	11.490091
H	-0.082031	17.528746	11.248496
H	1.106439	18.830385	11.364331
H	1.127854	17.525733	12.550169
C	2.075951	15.626374	7.054256
H	1.080570	16.010562	6.809369
H	2.078731	14.534316	6.935543
H	2.790405	16.016859	6.321812
C	6.017394	11.907310	6.417725
C	5.272509	11.372359	5.352698
C	5.405685	10.017782	5.044017
H	4.821275	9.603669	4.224313
C	6.266112	9.187035	5.757285
C	7.014887	9.740198	6.795550
H	7.696110	9.104888	7.358946
C	6.905271	11.085952	7.137819
C	4.361854	12.252006	4.539800
H	4.940763	12.954847	3.928247
H	3.713308	12.846928	5.190034
H	3.734280	11.653587	3.873725
C	6.368015	7.719647	5.437964
H	6.022049	7.507807	4.422112
H	5.753468	7.128105	6.127770
H	7.398696	7.362989	5.532146
C	7.716684	11.653092	8.269736
H	8.347922	12.481815	7.930242
H	8.355505	10.886317	8.715881
H	7.062136	12.055253	9.052734
C	2.229983	13.325854	10.909616

N	-0.230318	14.010254	10.700241
H	0.154037	14.238759	8.645854
H	-1.499249	13.693150	9.079017
H	-0.108403	12.570523	9.164416
N	0.696246	14.413393	12.620991
H	2.623349	14.897736	13.286050
H	1.886425	13.525710	14.119092
H	1.298221	15.184719	14.460078
C	0.920887	13.904186	11.394155
C	-1.195003	14.608478	11.494015
H	-2.572684	15.558283	10.149834
H	-3.143301	15.386235	11.810856
H	-3.111042	13.977995	10.747786
C	-0.611227	14.860066	12.707105
H	-0.675519	16.453469	14.144035
H	-1.069750	14.854566	14.805101
H	-2.232170	15.704161	13.784468
C	-0.436642	13.600174	9.305467
C	-2.574360	14.893459	11.020980
C	-1.169875	15.499499	13.925454
C	1.689691	14.512764	13.694938
H	2.631239	11.961092	7.238805

Calculated energies and coordinates of **TS3**

Electronic energy ... -3041.42997837 Eh
 Total Enthalpy ... -3040.35489622 Eh
 Final Gibbs free energy ... -3040.51343766 Eh

CARTESIAN COORDINATES (ANGSTROM)

Sn	0.649834	1.221211	0.581754
O	-1.034665	-0.047720	1.298486
O	-2.083215	0.859373	-0.463813
C	1.568246	-0.315825	-0.754138
C	1.027355	-1.461615	-1.365736
C	1.777570	-2.170326	-2.314489
H	1.342638	-3.059819	-2.765636
C	3.055781	-1.765294	-2.673837
H	3.619778	-2.326821	-3.413255
C	3.608763	-0.643298	-2.070274
H	4.614516	-0.315760	-2.325595
C	2.872934	0.069942	-1.123374
C	-0.312623	-2.046461	-1.050813
C	-1.376636	-1.889053	-1.954337
C	-2.570943	-2.576628	-1.728560
H	-3.384541	-2.470524	-2.445240
C	-2.731203	-3.428139	-0.636630
C	-1.671457	-3.553130	0.260326
H	-1.770337	-4.226001	1.111060
C	-0.467294	-2.872163	0.074705
C	-1.241073	-0.982821	-3.147079
H	-0.471634	-1.341748	-3.838835
H	-0.945803	0.024113	-2.833120
H	-2.184019	-0.913344	-3.696772
C	-3.990918	-4.234188	-0.463825
H	-4.194901	-4.443882	0.591305
H	-3.907085	-5.200542	-0.975998
H	-4.859058	-3.718758	-0.887266
C	0.644184	-3.018908	1.076665
H	0.753445	-2.093903	1.657126
H	1.602376	-3.210185	0.581916
H	0.437878	-3.835446	1.775044
C	3.521464	1.241483	-0.457706
C	4.290194	1.032512	0.700450
C	4.934306	2.117355	1.295430
H	5.564738	1.938694	2.165182
C	4.828452	3.406580	0.774510
C	4.061292	3.594882	-0.374485
H	3.981362	4.591584	-0.803813
C	3.417399	2.532506	-1.008461
C	4.456716	-0.354044	1.261392
H	5.024394	-0.327422	2.196374
H	4.987933	-1.002864	0.555890
H	3.482686	-0.824203	1.442020
C	5.527683	4.568937	1.427200
H	5.875531	5.290819	0.682675
H	6.396355	4.239529	2.005818

H	4.855849	5.112048	2.105098
C	2.642717	2.759636	-2.276803
H	3.072472	2.185113	-3.104800
H	2.639913	3.816888	-2.551927
H	1.602410	2.427505	-2.175570
C	-2.051440	0.153658	0.548424
N	-3.534750	-1.301105	2.056319
H	-1.616470	-1.237333	2.915990
H	-2.461880	-2.799491	3.047056
H	-2.968648	-1.422252	4.066745
N	-4.477883	-0.454311	0.292284
H	-4.571488	1.347240	-0.794167
H	-5.718688	0.067683	-1.294571
H	-3.979669	-0.048093	-1.707598
C	-3.313742	-0.528353	0.973436
C	-4.849191	-1.721022	2.061392
H	-5.361661	-2.078462	4.110228
H	-4.840006	-3.519810	3.227417
H	-6.439915	-2.832141	2.928395
C	-5.446172	-1.187034	0.949231
H	-7.420730	-1.927357	1.160695
H	-6.898078	-1.786417	-0.517573
H	-7.340649	-0.335913	0.402447
C	-2.578355	-1.712637	3.087613
C	-5.399056	-2.581874	3.137015
C	-6.845529	-1.311133	0.468335
C	-4.702818	0.276427	-0.958980
H	1.398333	0.559841	2.189446
C	0.978669	0.286197	3.823654
O	0.508585	-0.843384	3.946180
O	0.228000	1.427700	3.987748
C	2.403708	0.551620	4.178619
Si	-1.194349	1.552992	4.888065
N	3.024947	1.742607	4.297228
N	3.284917	-0.403387	4.536225
H	-1.365704	0.329436	5.707785
C	-2.677670	1.821271	3.790853
C	-0.877575	3.041706	5.967527
C	4.315250	1.542804	4.764179
C	2.484514	3.050526	3.905288
C	3.048716	-1.851986	4.507523
C	4.482373	0.191910	4.909654
C	-2.586271	2.545445	2.595118
C	-3.939723	1.369454	4.201928
C	-1.556100	4.253574	5.791032
C	0.108547	2.967948	6.964622
C	5.243341	2.664248	5.056022
H	3.324634	3.728908	3.757672
H	1.939099	2.948863	2.966432
H	1.815602	3.437948	4.678928
H	2.375343	-2.145208	5.315462
H	2.592014	-2.131174	3.558050
H	4.010377	-2.352675	4.620773
C	5.662622	-0.584769	5.367022
H	-1.618015	2.897752	2.243595
C	-3.719261	2.804878	1.829979
C	-5.075146	1.624351	3.438202
H	-4.041506	0.819054	5.136421
C	-1.255008	5.360782	6.580616
H	-2.329936	4.332829	5.030709
C	0.410634	4.071043	7.754663
H	0.641874	2.032434	7.133179
H	4.810867	3.358838	5.784793
H	6.175238	2.280044	5.473118
H	5.492597	3.234851	4.154648
H	6.461977	0.096269	5.662000
H	5.426388	-1.214258	6.231817
H	6.057780	-1.230319	4.573946
C	-4.964456	2.344187	2.250886
H	-3.623868	3.364412	0.903813
H	-6.047299	1.273835	3.774509
C	-0.271578	5.271048	7.560402
H	-1.791197	6.293764	6.433071
H	1.168310	3.995954	8.529702
H	-5.852060	2.556955	1.660251
H	-0.040968	6.132999	8.179914

Calculated energies and coordinates of INT_D

Electronic energy ... -1325.80488896 Eh
Total Enthalpy ... -1325.38013281 Eh
Final Gibbs free energy ... -1325.45809480 Eh

CARTESIAN COORDINATES (ANGSTROEM)

O -0.348945 -1.388986 1.128033
O -0.615975 -1.355306 -1.191575
C 0.132839 -1.796623 -0.233560
H 5.315963 0.845862 -1.094996
H 1.314599 -2.577635 1.989112
H 2.062531 -0.046619 -3.198011
H 5.272229 -2.073875 1.267576
C 4.335495 0.752412 -1.565521
H 4.486288 0.405295 -2.594088
H 3.884375 1.750606 -1.613347
C 4.958862 -1.028289 1.168064
H 5.780372 -0.477621 0.706378
H 4.814489 -0.626215 2.177981
C 2.379695 -2.468470 1.786231
H 2.831463 -3.441045 1.561596
H 2.864136 -2.041543 2.668180
H 0.481581 -0.194467 -2.327451
H 1.482995 1.282997 -2.143277
N 2.157958 -0.428576 -1.139921
N 2.547990 -1.558691 0.655665
C 1.593297 -1.255291 -0.246945
C 3.480138 -0.177838 -0.787796
C 3.731394 -0.899312 0.342123
C 1.500821 0.199209 -2.291362
H 0.227779 -2.909380 -0.138563
Si -1.326980 -0.041046 1.101890
H -1.426252 0.275479 2.557643
C -3.108093 -0.147084 0.516001
C -0.445575 1.434877 0.320923
C -1.008955 2.189890 -0.715058
C 0.814769 1.819998 0.800275
C 1.495333 2.908159 0.259776
C 0.914545 3.648617 -0.768464
C -0.341646 3.287891 -1.251940
H -1.983885 1.907888 -1.106837
H 1.433963 4.508317 -1.184058
H -0.800507 3.864006 -2.051299
H 1.273151 1.257962 1.614127
H 2.469796 3.190322 0.652007
C -3.537290 -0.783297 -0.657848
H -2.799613 -1.298139 -1.266590
C -4.878819 -0.757225 -1.028932
C -5.816110 -0.090419 -0.244002
H -5.195125 -1.261057 -1.938844
C -5.408081 0.548196 0.923128
H -6.862351 -0.072138 -0.538343
C -4.068271 0.512991 1.298821
H -6.133696 1.066380 1.544593
H -3.765132 1.005100 2.221465

Calculated energies and coordinates of TS4

Electronic energy ... -1325.79283035 Eh
Total Enthalpy ... -1325.36937631 Eh
Final Gibbs free energy ... -1325.44736048 Eh

CARTESIAN COORDINATES (ANGSTROEM)

O -0.622189 -1.959877 0.565532
O -0.829826 -1.448482 -1.638875
C -0.328814 -2.182739 -0.777433
H 4.722426 1.565709 -1.110927
H 1.484087 -2.916572 1.511433
H 2.592682 -0.839122 -3.633664
H 4.939933 -0.758992 1.735414
C 3.974965 1.088881 -1.748858
H 4.491986 0.685500 -2.628045
H 3.284369 1.868364 -2.091285
C 4.277860 0.043587 1.387951
H 4.905797 0.871125 1.050684
H 3.701261 0.396335 2.251829
C 2.243707 -2.155688 1.684507

H 3.178854 -2.629060 2.003469
H 1.891645 -1.488413 2.480076
H 0.935843 -1.260975 -3.084551
H 1.452859 0.435661 -3.114218
N 2.241109 -0.737736 -1.561435
N 2.444483 -1.419224 0.446624
C 1.728690 -1.631947 -0.685115
C 3.256878 0.029774 -0.996457
C 3.386351 -0.404519 0.288461
C 1.783964 -0.593243 -2.936090
H -0.128321 -3.247795 -0.936268
Si -1.228550 -0.451686 0.999448
H -1.118868 -0.485546 2.483407
C -3.034688 -0.167754 0.594471
C -0.146051 0.983171 0.445744
C -0.261625 1.568161 -0.824072
C 0.762911 1.549223 1.349165
C 1.536443 2.655241 1.002609
C 1.403594 3.223356 -0.259388
C 0.502504 2.676519 -1.172226
H -0.957566 1.142396 -1.541752
H 1.992799 4.096061 -0.529691
H 0.386918 3.126258 -2.155528
H 0.857508 1.128973 2.349476
H 2.231517 3.080739 1.722083
C -3.650371 -0.524740 -0.614074
H -3.066675 -1.028061 -1.378751
C -4.994245 -0.239097 -0.837097
C -5.746905 0.413085 0.135699
H -5.456477 -0.527437 -1.777501
C -5.152052 0.775999 1.340337
H -6.795846 0.634489 -0.042606
C -3.810568 0.483575 1.565736
H -5.734379 1.280438 2.106656
H -3.362375 0.762348 2.518053

Calculated energies and coordinates of IMe₄

Electronic energy ... -383.32167062 Eh
Total Enthalpy ... -383.12957541 Eh
Final Gibbs free energy ... -383.17542336 Eh

CARTESIAN COORDINATES (ANGSTROEM)

N -1.058056 -0.708079 0.000141
N 1.058061 -0.708052 0.000183
C -2.436046 -1.163330 0.000211
H -2.969552 -0.811088 -0.890945
H -2.969696 -0.810324 0.890977
H -2.417824 -2.254157 0.000669
C -0.680794 0.636085 -0.000149
C 0.680765 0.636102 -0.000130
C 2.436062 -1.163268 0.000169
H 2.969862 -0.809906 0.890702
H 2.969400 -0.811355 -0.891220
H 2.417868 -2.254096 0.001036
C 1.659771 1.754891 -0.000212
H 2.308634 1.729860 0.884111
H 1.140485 2.716391 -0.001491
H 2.310166 1.728347 -0.883353
C -1.659828 1.754850 -0.000281
H -2.309997 1.728454 -0.883595
H -1.140566 2.716363 -0.001244
H -2.308916 1.729638 0.883870
C 0.000013 -1.571661 0.000375

Calculated energies and coordinates of IMe₄CO₂

Electronic energy ... -571.91928470 Eh
Total Enthalpy ... -571.70945168 Eh
Final Gibbs free energy ... -571.76191821 Eh

CARTESIAN COORDINATES (ANGSTROEM)

O 0.816022 9.338188 3.651725
C 0.954329 8.242167 4.219692
O 0.166653 7.314350 4.467501
N 3.303293 8.900886 5.122384
N 3.016385 6.780601 4.833655
C 2.405154 7.978151 4.718984
C 4.489562 8.284340 5.501059

C	4.312213	6.945027	5.307064
C	3.067951	10.342673	5.209336
H	3.080303	10.656068	6.258187
H	2.100108	10.545475	4.746631
H	3.853593	10.871922	4.662015
C	5.653529	9.051886	6.011723
H	6.467334	8.372963	6.272720
H	5.395554	9.625764	6.909222
H	6.032654	9.758594	5.264541
C	5.232370	5.797484	5.509878
H	4.847069	5.095549	6.258536
H	6.206268	6.150982	5.853122
H	5.388099	5.237642	4.580575
C	2.439033	5.487130	4.465849
H	2.521790	4.798675	5.312149
H	2.976623	5.073964	3.606336
H	1.385617	5.652868	4.232144

Calculated energies and coordinates of H_2SiPh_2
 Electronic energy ... -753.85890538 Eh
 Total Enthalpy ... -753.64849461 Eh
 Final Gibbs free energy ... -753.69840992 Eh
 CARTESIAN COORDINATES (ANGSTROM)
 H -1.106527 -0.496432 -1.322883
 Si -2.487240 0.033120 -1.149112
 H -2.424945 1.516897 -1.255968
 C -3.099338 -0.510000 0.538980
 C -3.637311 -0.587169 -2.495194
 C -4.166881 -1.884640 -2.441172
 C -3.979906 0.222875 -3.585777
 C -4.817272 -0.248071 -4.593424
 C -5.329714 -1.539948 -4.524639
 C -5.004228 -2.358218 -3.445629
 H -3.929165 -2.530029 -1.597634
 H -5.985505 -1.908306 -5.308709
 H -5.405963 -3.366001 -3.386457
 H -3.591552 1.237277 -3.647751
 H -5.073740 0.395218 -5.430624
 C -4.464947 -0.459228 0.854152
 H -5.180053 -0.125575 0.104551
 C -4.924203 -0.841284 2.110100
 C -4.023833 -1.284231 3.076017
 H -5.985977 -0.796153 2.336175
 C -2.665520 -1.345531 2.780335
 H -4.381866 -1.584998 4.056765
 C -2.209443 -0.962839 1.521783
 H -1.960746 -1.696087 3.529269
 H -1.145775 -1.021992 1.300936

Calculated energies and coordinates of $\text{HCO}_2\text{SiHPh}_2$
 Electronic energy ... -942.45802637 Eh
 Total Enthalpy ... -942.22813805 Eh
 Final Gibbs free energy ... -942.28542377 Eh
 CARTESIAN COORDINATES (ANGSTROM)
 H 1.018553 -3.616374 -1.699797
 C 1.127897 -2.897388 -0.870504
 O 0.071791 -2.076395 -0.805280
 O 2.076233 -2.862401 -0.125856
 Si 0.019559 -0.864238 0.409367
 H 0.198580 -1.530019 1.720426
 C -1.687323 -0.142756 0.206464
 C 1.335124 0.427517 0.144071
 C -2.035685 0.997364 0.946054
 C -2.647541 -0.701218 -0.646732
 C 2.601259 0.293130 0.731763
 C 1.081660 1.553957 -0.651713
 H -1.305352 1.459126 1.608797
 C -3.302929 1.559110 0.840411
 C -3.916101 -0.138161 -0.756029
 H -2.400299 -1.581477 -1.233405
 C 3.583419 1.256380 0.530019
 H 2.821195 -0.580656 1.339714
 C 2.065101 2.516055 -0.857117
 H 0.102647 1.683773 -1.108228
 C -4.245616 0.990658 -0.012599

H	-3.555321	2.441967	1.420874
H	-4.648861	-0.581814	-1.424283
C	3.316171	2.367893	-0.265118
H	4.560005	1.139288	0.991147
H	1.854892	3.383399	-1.476596
H	-5.235957	1.429163	-0.098293
H	4.084136	3.120331	-0.422633

Calculated energies and coordinates of $[\text{BArF}]^-$
 Electronic energy ... -3647.80715843 Eh
 Total Enthalpy ... -3647.35676866 Eh
 Final Gibbs free energy ... -3647.48969397 Eh
 CARTESIAN COORDINATES (ANGSTROM)
 F -1.545305 -2.882373 8.060532
 F 2.296378 -1.423679 0.829475
 F -2.358456 -3.056745 6.050870
 F -0.211089 -2.860052 6.337852
 F 2.457838 0.552458 -0.060054
 F 1.198431 -0.960557 -0.993260
 F 4.077953 4.211132 2.484189
 F -3.834863 1.023600 0.374767
 F 5.297659 0.611899 7.509212
 F 3.628913 -0.772215 7.296910
 F -1.134221 7.715542 6.558850
 F -4.154713 -0.246824 2.110469
 F 3.426082 0.985080 8.558907
 C -0.325027 1.144843 3.065756
 C -0.560775 3.514561 4.329508
 C -0.963181 1.179548 5.617332
 C 1.502361 1.974455 4.866879
 C -0.258899 4.417377 5.364372
 H 0.295684 4.061134 6.230187
 C -1.542259 -0.930768 6.711423
 C 0.696099 0.698234 2.223735
 H 1.733926 0.873948 2.497046
 C 0.426453 0.017011 1.033538
 C 2.063959 1.267468 5.930380
 H 1.428108 0.655457 6.656960
 C -1.851505 1.805413 6.494084
 H -2.001407 2.880814 6.431805
 C -1.638419 0.854485 2.656766
 H -2.468262 1.156431 3.292689
 F 5.740898 2.949611 3.108053
 C 2.387114 2.761555 4.104302
 H 1.992178 3.348094 3.278474
 C -0.839886 -0.215631 5.748382
 H -0.174390 -0.751798 5.075269
 C -1.252442 4.039543 3.235439
 H -1.501417 3.394546 2.395966
 F -4.516986 2.418949 7.650238
 C -2.567559 1.087673 7.456968
 C -0.877147 -0.245451 0.638621
 H -1.086891 -0.775366 -0.282851
 C -0.647708 5.751654 5.316929
 C 3.432914 1.325209 6.215011
 F -0.223169 6.051869 7.631344
 C -1.407199 -2.422518 6.790027
 C -1.636115 5.382487 3.179903
 C -1.910600 0.181002 1.470853
 C 1.583429 -0.451039 0.202129
 F 5.194361 4.688530 4.291811
 C -2.421645 -0.285460 7.580289
 H -2.971090 -0.842069 8.330466
 C 3.949903 0.543332 7.385523
 C 4.289667 2.093644 5.444717
 H 5.351447 2.137925 5.660957
 F -3.468595 -1.116652 0.234251
 C -1.341665 6.254388 4.217579
 H -1.644914 7.293898 4.178414
 B -0.086557 1.952956 4.470256
 C 3.746938 2.814464 4.379554
 F 0.961790 7.228840 6.238354
 F -2.880229 2.844176 9.014755
 F -4.085410 1.050445 9.288848
 C -3.507264 1.839918 8.351340
 C -0.267566 6.678303 6.433555

C	-2.359058	5.867375	1.958657
C	-3.334041	-0.043994	1.054866
C	4.674959	3.663026	3.562452
F	-2.815405	7.136950	2.088850
F	-3.430889	5.091203	1.661849
F	-1.559875	5.850989	0.859034

Calculated energies and coordinates of CO₂

Electronic energy	...	-188.57006287 Eh
Total Enthalpy	...	-188.55480755 Eh
Final Gibbs free energy	...	-188.57907474 Eh

CARTESIAN COORDINATES (ANGSTROM)

C	-3.264744	-2.136338	-0.259115
O	-4.428170	-2.136338	-0.259115
O	-2.101318	-2.136338	-0.259115

Calculated energies and coordinates of **M**

Electronic energy	...	-1911.69641591 Eh
Total Enthalpy	...	-1910.85136300 Eh
Final Gibbs free energy	...	-1910.97358793 Eh

CARTESIAN COORDINATES (ANGSTROM)

Sn	1.543211	10.468882	3.114231
N	-0.861915	10.094645	5.328656
N	2.498200	7.497353	3.449037
N	2.709940	8.455998	5.520237
N	-1.416580	9.960257	3.086467
C	-0.557349	10.733572	4.026461
C	-0.746674	11.007259	6.446001
H	-0.848506	10.471812	7.397806
H	-1.495807	11.824670	6.404200
H	0.243941	11.469559	6.421097
C	1.884838	8.543233	4.301141
C	3.050445	6.554756	4.351160
C	2.078893	9.008161	6.696754
H	1.907267	10.077883	6.533914
H	2.734950	8.897625	7.568016
H	1.097859	8.541106	6.917976
C	2.941988	12.090720	3.912440
C	4.341779	11.872344	3.873003
C	-2.103492	9.428061	5.175357
C	2.535605	13.437787	4.079961
C	1.098223	13.843848	4.064396
C	3.168490	7.113650	5.572368
C	0.431705	14.047587	2.843036
C	0.430356	14.108070	5.269280
C	1.588694	6.993608	2.437262
H	1.280457	7.825655	1.793162
H	0.672278	6.548322	2.879921
H	2.086700	6.241544	1.815092
C	5.255876	12.916855	4.047040
H	6.320878	12.690784	4.012770
C	-2.433099	9.359757	3.871360
C	-0.906554	14.439799	2.854348
H	-1.423890	14.571818	1.904955
C	1.152053	13.991958	6.586689
H	1.857856	13.155860	6.580630
H	0.443772	13.859924	7.411136
H	1.742960	14.894523	6.788363
C	4.940447	10.524856	3.620899
C	4.824227	14.222768	4.243204

H	5.539747	15.031591	4.370514
C	5.404510	9.758474	4.701385
C	-1.598377	14.657235	4.044534
C	-1.826042	10.742254	1.936083
H	-2.410436	11.642173	2.226626
H	-2.422478	10.132246	1.248128
H	-0.926132	11.075656	1.403921
C	-0.907873	14.504161	5.243000
H	-1.426377	14.679665	6.184975
C	6.023913	8.534108	4.457048
H	6.363645	7.934364	5.300734
C	5.288080	10.280346	6.107593
H	6.035449	11.062641	6.297721
H	5.442353	9.477456	6.834384
H	4.305848	10.725599	6.282253
C	3.458867	14.475209	4.251661
H	3.089441	15.491917	4.381533
C	5.142656	10.071835	2.307111
C	1.151282	13.862129	1.535486
H	2.091063	14.425346	1.521928
H	0.526966	14.190272	0.698704
H	1.412114	12.805131	1.380855
C	3.586309	5.266997	3.836496
H	2.790540	4.586111	3.504297
H	4.170297	4.746736	4.600986
H	4.239635	5.447853	2.970346
C	4.724052	10.908035	1.128933
H	3.627913	10.971154	1.072831
H	5.093266	10.473606	0.194567
H	5.102783	11.932605	1.216822
C	-3.513165	8.582704	3.204651
H	-4.210663	9.227611	2.653350
H	-4.096258	8.015023	3.934819
H	-3.085769	7.873824	2.480063
C	6.198365	8.052190	3.163499
C	-2.717527	8.746684	6.347559
H	-1.976466	8.107216	6.849604
H	-3.558016	8.118207	6.041111
H	-3.091415	9.458375	7.096052
C	3.867314	6.599229	6.780088
H	4.669740	7.281593	7.097461
H	4.317010	5.622480	6.580387
H	3.189714	6.482417	7.637152
C	5.752823	8.833544	2.101155
H	5.885203	8.475226	1.081074
C	-3.068765	14.975254	4.034749
H	-3.358011	15.504458	3.120886
H	-3.353278	15.590194	4.895106
H	-3.658618	14.049927	4.080280
C	6.890181	6.735798	2.922299
H	7.980993	6.858721	2.888207
H	6.579244	6.292850	1.970510
H	6.664221	6.021146	3.720693
H	0.843013	8.207319	4.564413
H	-0.921865	11.789807	4.053993

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Supporting Information

Terphenyl Amido Stannylene-NHC Adduct: A Catalyst for the Hydrosilylation of Aldehydes and Ketones

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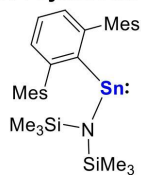
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1. Experimental Details

1.1 General Methods and Instrumentation

All experiments and manipulations were carried out under a dry oxygen-free argon atmosphere using standard Schlenk techniques or in a glovebox. All glass junctions were coated with PTFE-based grease Merckel Triboflon III. Solvents were dried by standard methods (withdrawn from MBraun Solvent Purification System (SPS) and stored over molecular sieve (3 Å)) or distilled from sodium / benzophenone or CaH₂ under argon atmosphere and degassed via freeze-pump-thaw cycling). The ¹H, ¹³C{¹H}, ¹¹⁹Sn{¹H}, and ²⁹Si{¹H} NMR spectra of the compounds were measured on a Bruker 400 MHz spectrometer. Chemical shifts are referenced to (residual) solvent signals (¹H and ¹³C{¹H} NMR). Deuterated solvents benzene (C₆D₆) and tetrahydrofuran (THF-d₈) were obtained from Sigma-Aldrich Deutero Chemie GmbH and stored over 4 Å molecular sieves in the glovebox. Unless otherwise stated, all reagents were purchased from commercial sources and used as received. Abbreviations: s = singlet, br = broadened, d = doublet, t = triplet, m = multiplet, dec = decompose. Some NMR spectra include resonances for silicone grease (C₆D₆: δ(¹H) = 0.29 ppm, δ(¹³C) = 1.4 ppm; δ = THF-d₈: δ(¹H) = 0.11 ppm, δ(¹³C) = 1.2 ppm). Liquid Injection Field Desorption Ionization Mass Spectrometry (LIFDI-MS) was measured directly from an inert atmosphere glovebox with a Thermo Fisher Scientific Exactive Plus Orbitrap equipped with an ion source from Linden CMS.^[1] Melting Points (m.p.) were determined in sealed glass capillaries under inter gas by a Büchi M-540. IMe₄ (1,3,4,5-tetramethylimidazoli-2-ylidene), IEt (1,3-diethyl-4,5-dimethylimidazoli-2-ylidene),^[2] and Chlorogermylene (^{Mes}Ter)SnCl^[3] were synthesized according to the literature procedures.

1.2 Synthesis of HMDS(^{Mes}Ter)Sn (1)



1
C₃₀H₄₃NSi₂Sn
M = 592,56 g/mol

HMDS(^{Mes}Ter)Sn was synthesized via a modified route compared to the literature procedure reported by the Aldridge group.^[4] A solution of potassium hexamethyldisilazide (KHMDs) (1.00 eq, 213.0 mg, 1.07 mmol) in 10 mL toluene was added via dropping funnel to a suspension of (^{Mes}Ter)SnCl (1.00 eq, 500.0 mg, 1.07 mmol) in toluene (10 mL). The resulting brown-red suspension was stirred for 1 hour at room temperature followed by cannula filtration of the supernatant. All volatile components were removed *in vacuo* and **1** was obtained as a brown solid. Yield: 627.0 mg (1.06 mmol, 99.0%).

¹H NMR (400 MHz, 298 K, C₆D₆): δ[ppm] = -0.02 (s, 18 H, N(Si(CH₃)₃)₂), 2.15 (s, 6 H, 2xC⁴-CH₃, Mes), 2.32 (s, 12 H, 2xC^{2,6}-CH₃, Mes), 6.83 (s, 4 H, 2xC^{3,5}-H, Mes), 7.03–7.05 (d, ³J_{H-H} = 8 Hz, 2 H, C^{3,5}-H, C₆H₃), 7.23–7.26 (t, ³J_{H-H} = 8 Hz, 1 H, C⁴-H, C₆H₃).

¹³C{¹H} NMR (101 MHz, 298 K, C₆D₆): δ[ppm] = 6.08 (N(Si(CH₃)₃)₂), 21.02 (C⁴-CH₃, Mes), 22.12 (C^{2,6}-CH₃, Mes), 128.01 (CH_{Aryl}), 129.92 (CH_{Aryl}), 130.44 (CH_{Aryl}), 136.81 (C_{q, Aryl}), 137.19 (C_{q, Aryl}), 137.80 (C_{q, Aryl}), 146.14 (C_{q, Aryl}), 184.87 (Sn-C, C₆H₃).

¹¹⁹Sn{¹H} NMR (150 MHz, 298 K, C₆D₆): δ[ppm] = 1192.83 (Sn).

²⁹Si{¹H} NMR (80 MHz, 298 K, C₆D₆): δ[ppm] = -0.49 (SiMe₃).

LIFDI-MS m/z C₃₀H₄₃NSi₂Sn (M)⁺ calcd: 593.1956; m/z found: 593.1952.

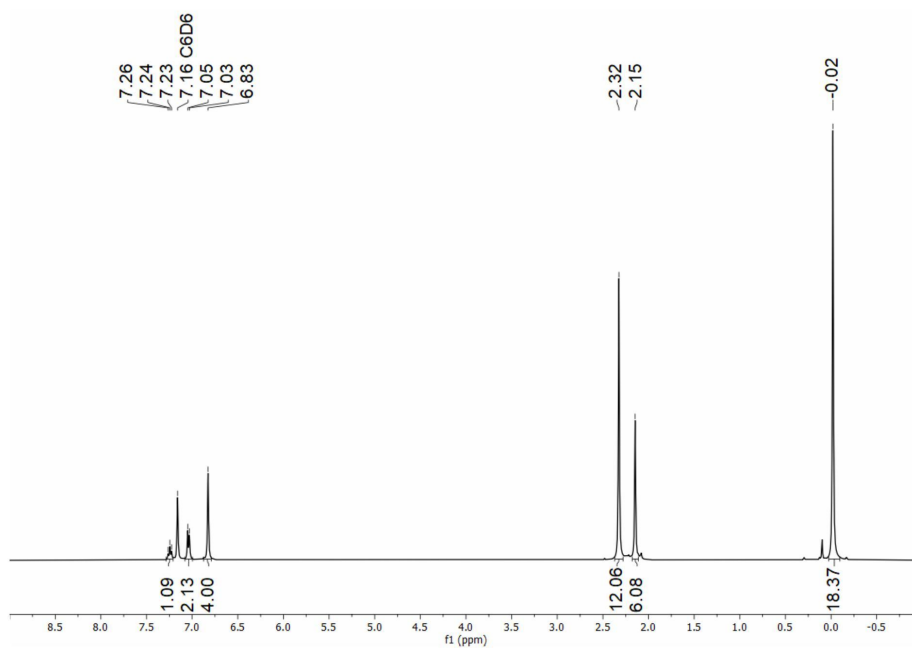


Figure S1. ¹H NMR spectrum of **1** in C₆D₆ at 298 K.

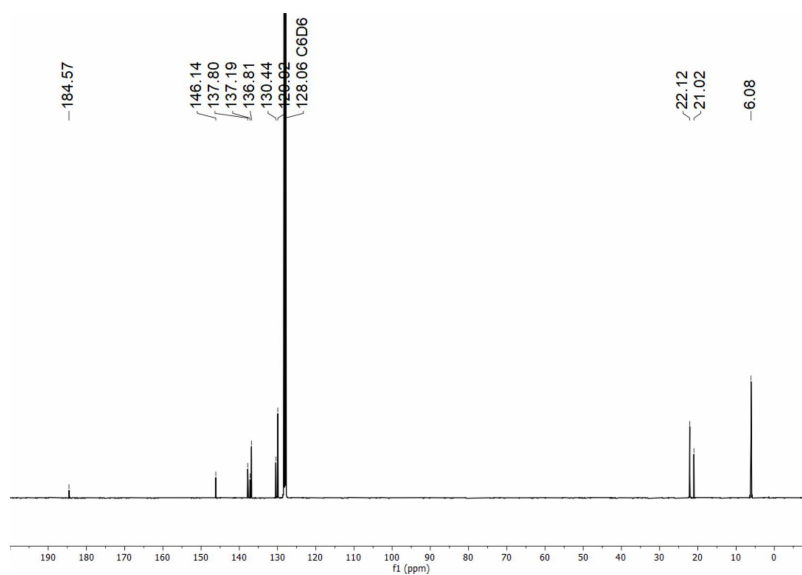


Figure S2. ¹³C{¹H} NMR spectrum of **1** in C₆D₆ at 298 K.

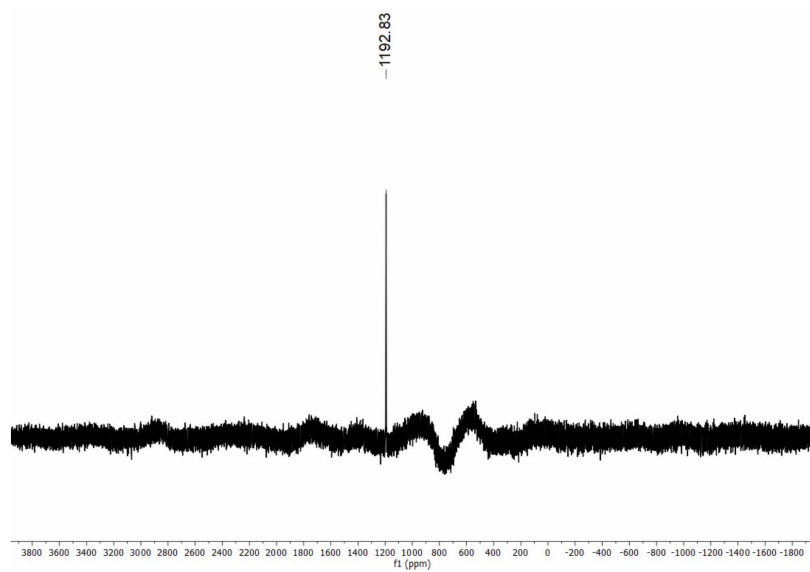


Figure S3. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **1** in C_6D_6 at 298 K.

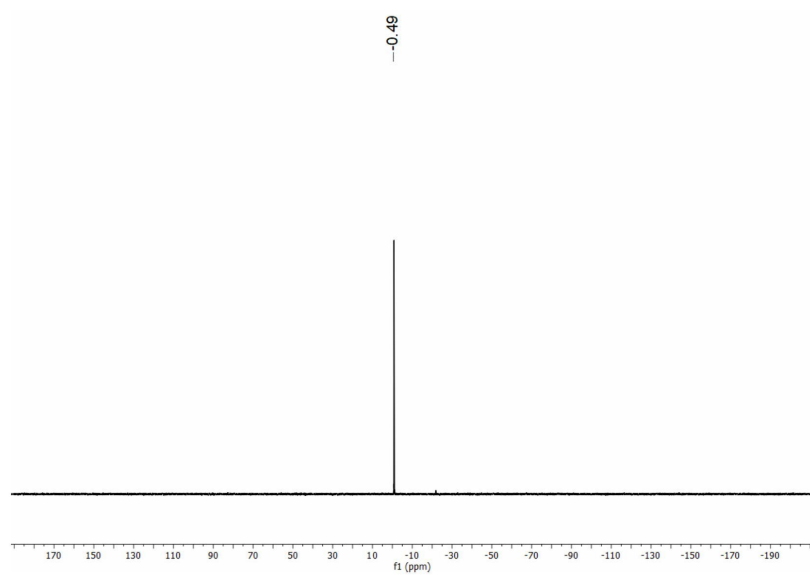


Figure S4. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **1** in C_6D_6 at 298 K.

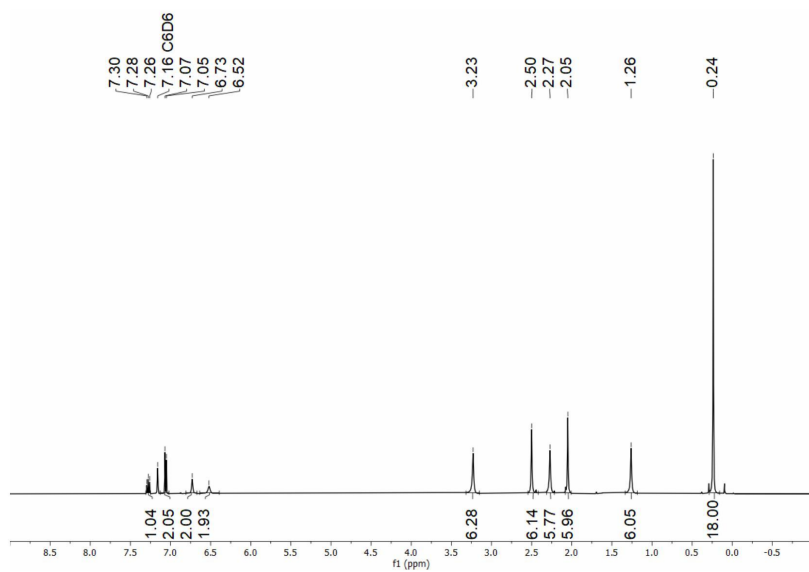


Figure S6. ¹H NMR spectrum of **2-Ime₄** in C₆D₆ at 298 K.

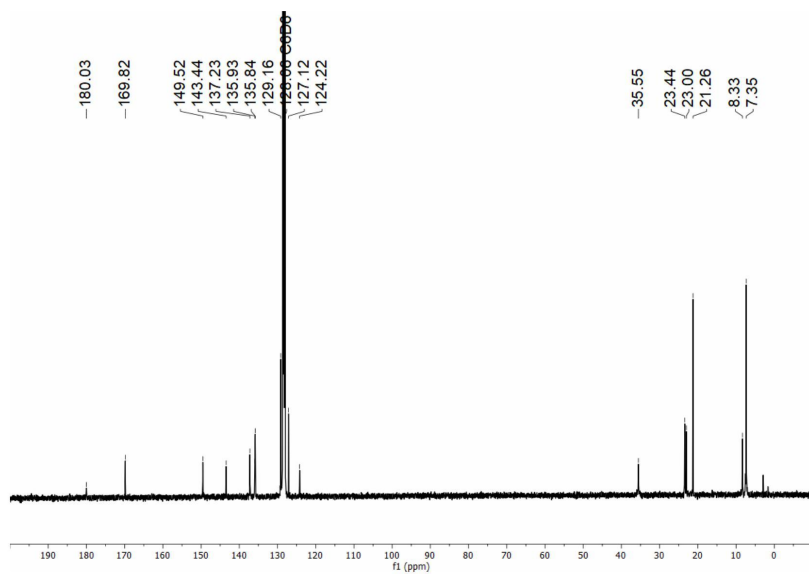


Figure S7. ¹³C{¹H} NMR spectrum of **2-Ime₄** in C₆D₆ at 298 K.

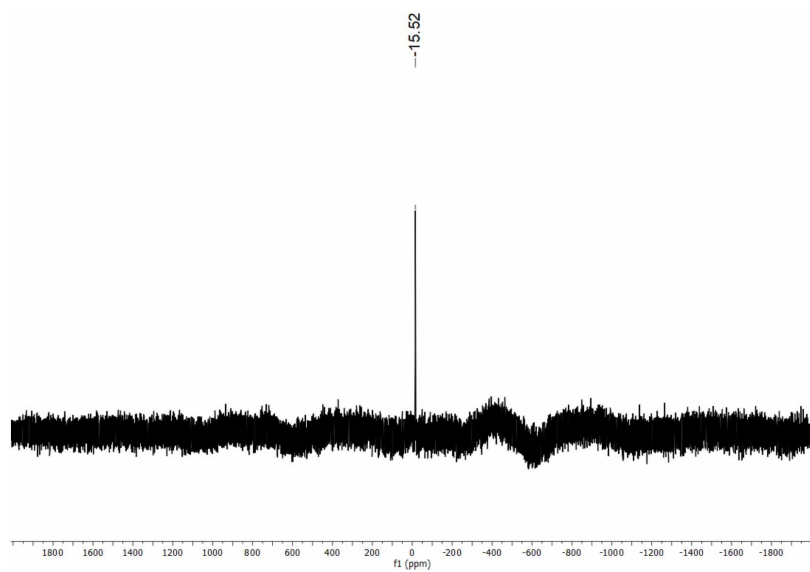


Figure S8. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **2-Ime₄** in C_6D_6 at 298 K.

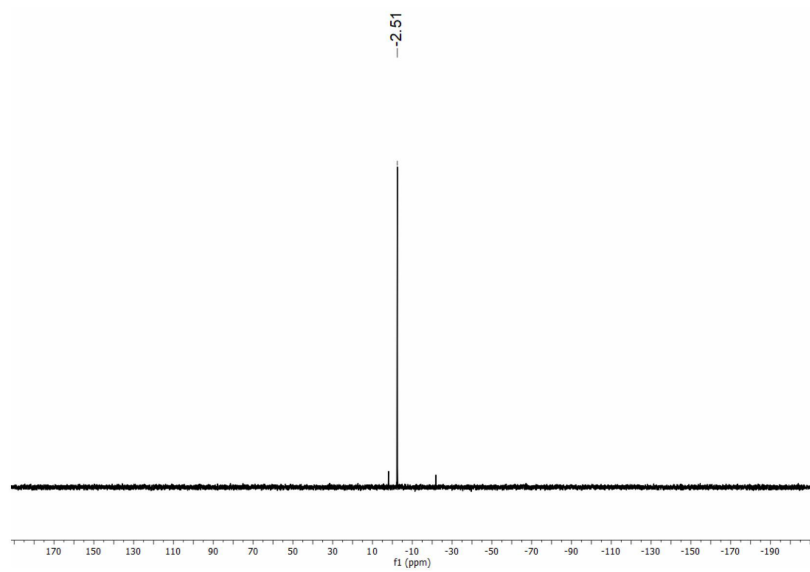


Figure S9. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2-Ime₄** in C_6D_6 at 298 K.

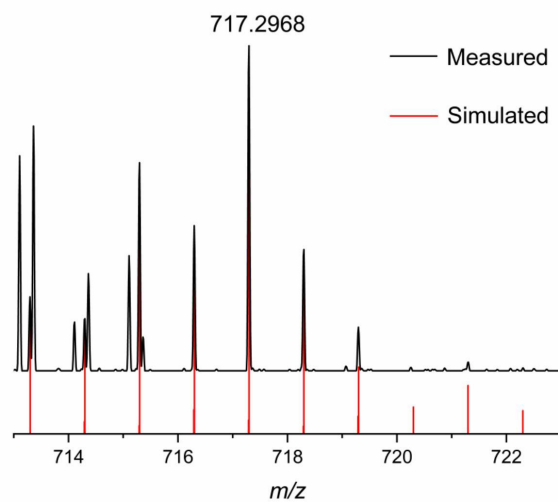


Figure S10. LIFDI-MS spectrum (detail view) of **2-Ime₄** (measured spectrum: top; simulated spectrum: bottom).

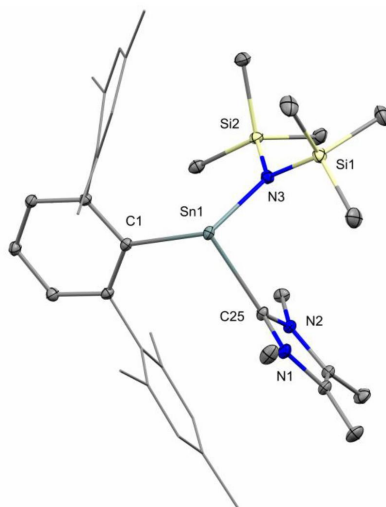
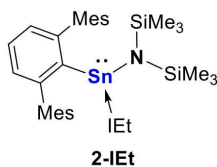


Figure S11. Molecular structures of **2-Ime₄** in the solid state. Ellipsoids are set at the 30% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1-C12.282(1), Sn1-N3 2.204(2), Sn1-C25 2.328(1), N3-Si1 1.735(1), N3-Si2 1.722(2), C1-Sn1-C25 102.65(2), C1-Sn1-N3 108.38(5), C25-Sn1-N3 90.37(5).

1.4 Synthesis of HMDS^(MesTer)Sn(IEt) (2-IEt)



$C_{39}H_{59}N_3Si_2Sn^{2+}$
744.80 g/mol

In a Glove Box, a solution of IEt (1.00 eq, 128.0 mg, 844 μ mol) in toluene (2 mL) was added via syringe to a solution of HMDS^(MesTer)Sn (**1**) (1.00 eq, 500.0 mg, 844 μ mol) in toluene (6 mL). The color changed from red brown to yellow after stirring for one hour at room temperature. All volatiles were removed *in vacuo* to afford **2-IEt** as a yellow solid. Yield: 584.0 mg (785 μ mol, 93.0%).

1H NMR (400 MHz, 298 K, C_6D_6): δ [ppm] = 0.31 (s, 18 H, $N(Si(CH_3)_3)_2$), 1.04 (t, $J_{HH} = 7$ Hz, 6 H, CH_2CH_3 , NHC), 1.38 (s, 6 H, $2 \times C-CH_3$, NHC), 2.09 (s, 6 H, $2 \times C^4-CH_3$, Mes), 2.15 (br, 12 H, $2 \times C^{2,6}-CH_3$, Mes), 3.84 (br, 4 H, CH_2CH_3 , NHC), 6.55 (br, 4 H, $2 \times C^{3,5}-H$, Mes), 7.01 (d, $^3J_{H-H} = 8$ Hz, 2 H, $C^{3,5}-H$, C_6H_3), 7.26 (t, $^3J_{H-H} = 8$ Hz, 1 H, C^4-H , C_6H_3).

$^{13}C\{^1H\}$ NMR (101 MHz, 298 K, C_6D_6): δ [ppm] = 7.70 ($N(Si(CH_3)_3)_2$), 8.69 ($2 \times C^{4,5}-CH_3$, NHC), 16.42 (CH_2CH_3 , NHC), 21.44 (C^4-CH_3 , Mes), 23.44 ($C^{2,6}-CH_3$, Mes), 43.19 (CH_2CH_3 , NHC), 124.60 ($C^{4,5}-CH_3$, NHC), 127.30 (CH_{Aryl}), 128.43 (CH_{Aryl}), 129.41 (CH_{Aryl}), 135.75 (C_q , Aryl), 136.59 (C_q , Aryl), 143.24 (C_q , Aryl), 150.00 (C_q , Aryl), 170.23 (Sn-C, C_6H_3).

$^{119}Sn\{^1H\}$ NMR (150 MHz, 298 K, C_6D_6): δ [ppm] = -0.09 (Sn).

$^{29}Si\{^1H\}$ NMR (80 MHz, 298 K, C_6D_6): δ [ppm] = -2.03 ($SiMe_3$).

LIFDI-MS m/z $C_{39}H_{59}N_3Si_2Sn$ (M)⁺ calcd: 745.3270; m/z found: 745.3268.

m.p.: 119 °C.

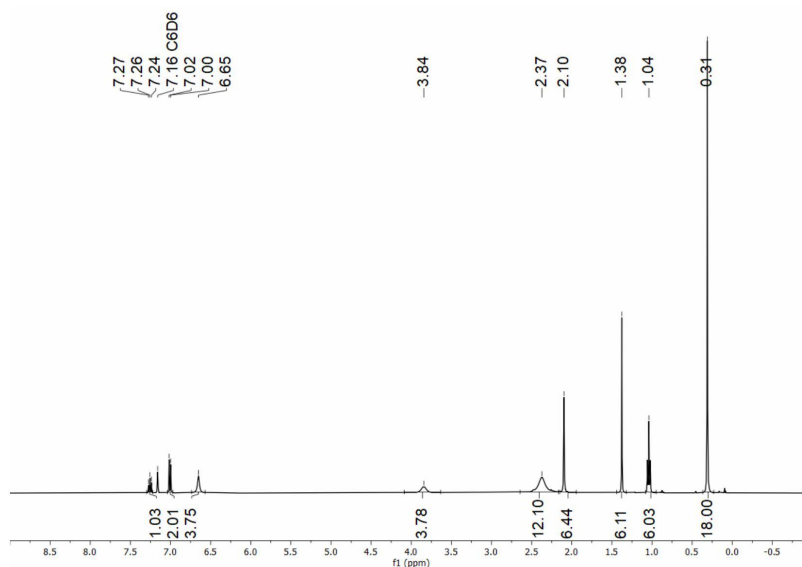


Figure S12. 1H NMR spectrum of **2-IEt** in C_6D_6 at 298 K.

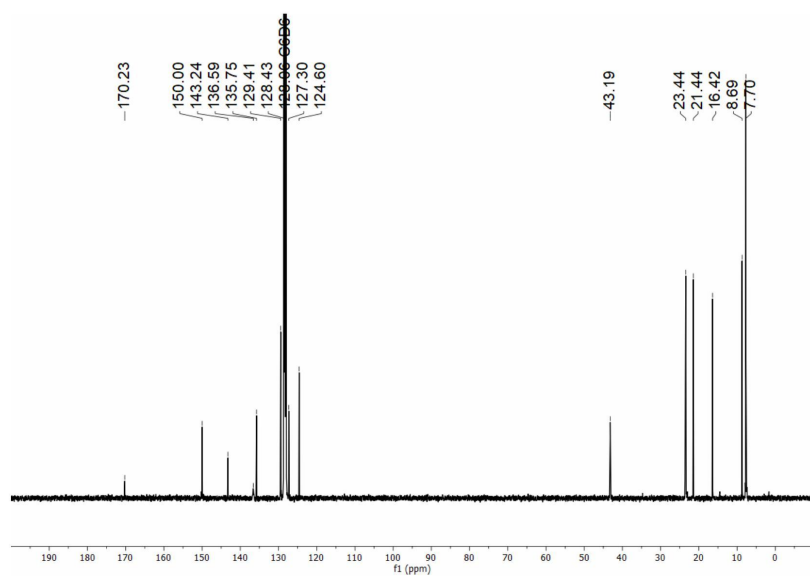


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-IEt** in C_6D_6 at 298 K.

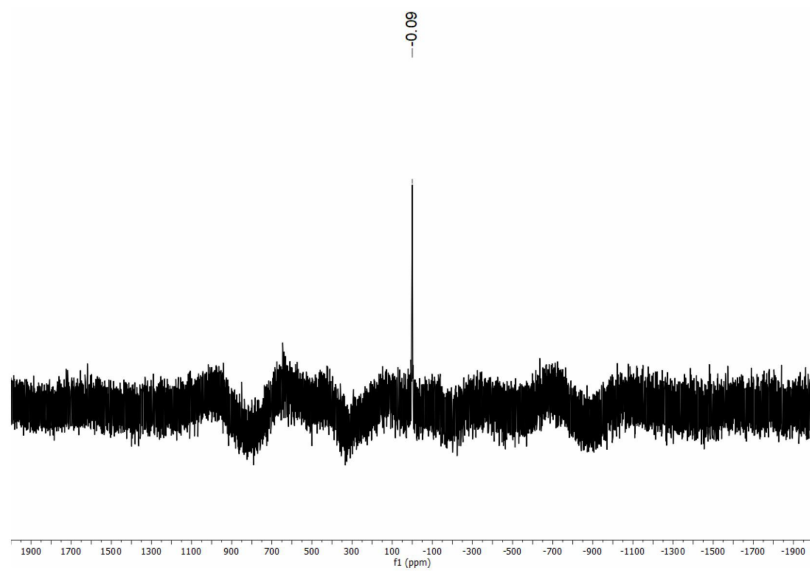


Figure S14. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **2-IEt** in C_6D_6 at 298 K.

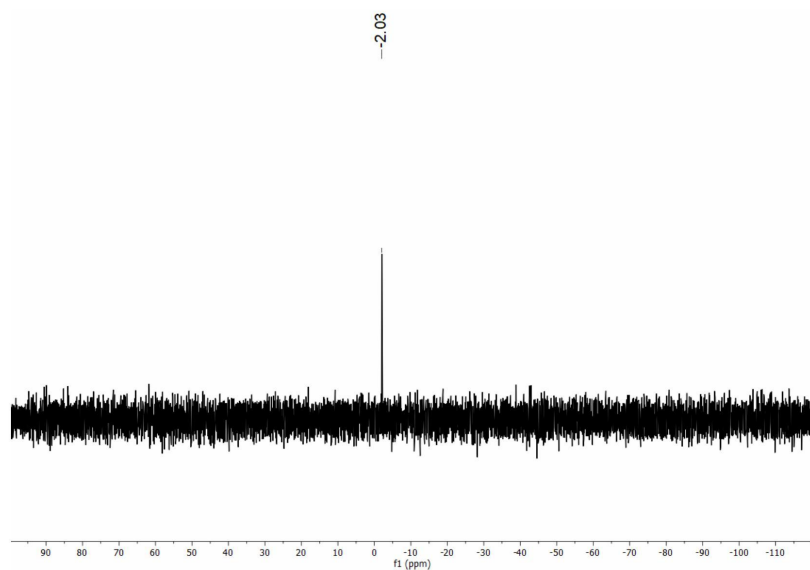


Figure S15. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2-IEt** in C_6D_6 at 298 K.

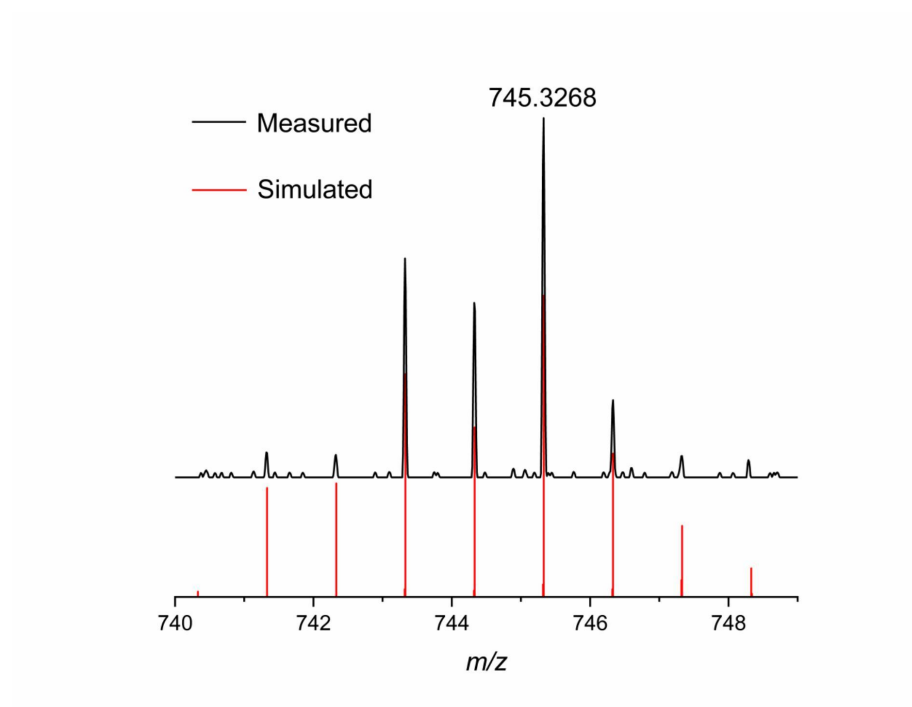
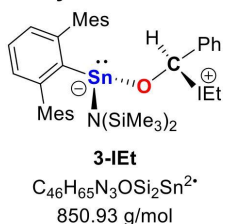


Figure S16. LIFDI-MS spectrum (detail view) of **2-IEt** (measured spectrum: top; simulated spectrum: bottom).

1.5 Synthesis of HMDS^(MesTer)Sn(OCH(Ph)IEt) (3-IEt)



In a Glove Box, **2-IEt** (1.00 eq, 200.0 mg, 268 μ mol) was dissolved in toluene (4 ml), and then benzaldehyde (1.00 eq, 28.5 mg, 268 μ mol) was added via a pipette at room temperature. The reaction solution was stirred for 18 hours. The resulting light-yellow solution was concentrated to 2 mL and stored at -35°C . **3-IEt** was obtained as light-yellow block-formed crystals, and they were suitable for single-crystal X-ray diffraction. Yield: 173.0 mg (206 μ mol, 77.0%).

^1H NMR (400 MHz, 298 K, C_6D_6): $\delta[\text{ppm}] = -0.2\text{--}0.92$ (24 H, (N(Si(CH₃)₃)₂, CH₂CH₃), 1.24 (s, 6 H, 2xC-CH₃, NHC), 2.18 2.09 (s, 6 H, 2xC⁴-CH₃, Mes), 2.57, 2.58 (s, 12 H, 2xC^{2,6}-CH₃, Mes), 4.09 (s, 1 H, OCH), 3.26, 4.09, 4.81 (br, 4 H, CH₂CH₃, NHC), 6.45, 6.89 (s, 4 H, 2xC^{3,5}-H, Mes), 7.00 (d, $^3J_{\text{H-H}} = 8$ Hz, 2 H, C^{3,5}-H, C₆H₃), 7.05–7.14, 7.25–7.30 (m, 6 H, CH_{Aryl}).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 298 K, C_6D_6): $\delta[\text{ppm}] = 7.58$ (N(Si(CH₃)₃)₂), 21.36 (C⁴-CH₃, Mes), 23.09, 23.25 (C^{2,6}-CH₃, Mes), 68.65 (OCH), 126.05 (CH_{Aryl}), 126.26 (CH_{Aryl}), 126.85 (CH_{Aryl}), 127.84 (CH_{Aryl}), 128.35 (CH_{Aryl}), 128.78 (CH_{Aryl}), 129.35 (CH_{Aryl}), 130.00 (CH_{Aryl}), 134.32 (C_q, Aryl), 135.83 (C_q, Aryl), 136.97 (C_q, Aryl), 144.76 (C_q, Aryl), 146.97 (C_q, Aryl), 148.04 (C_q, Aryl), 151.92 (OCC, NHC), 175.84 (Sn-C, C₆H₃).

$^{119}\text{Sn}\{^1\text{H}\}$ NMR (150 MHz, 298 K, C_6D_6): $\delta[\text{ppm}] = -149.31$ (Sn).

$^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, 298 K, C_6D_6): no signal.

LIFDI-MS m/z $C_{46}H_{65}N_3OSi_2Sn$ (M)⁺ calcd: 851.3688; m/z found: 851.3698.

m.p.: 115 $^\circ\text{C}$.

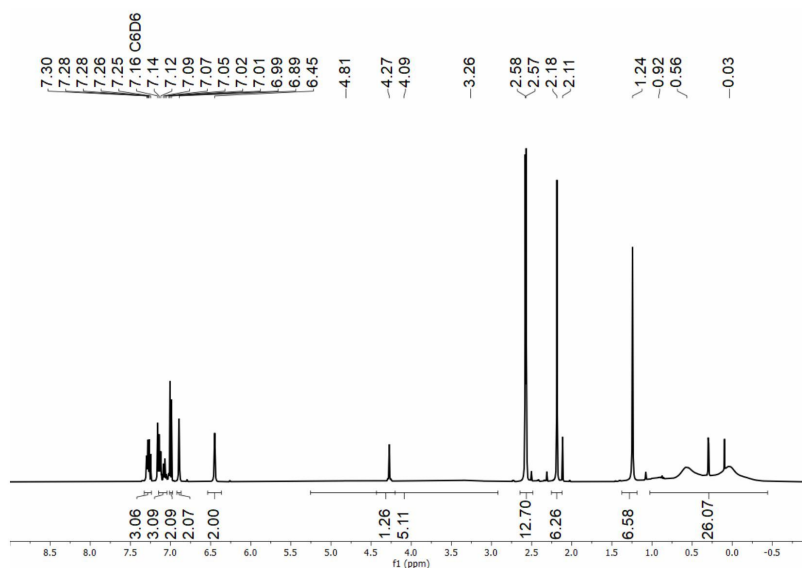


Figure S17. ^1H NMR spectrum of **3-IEt** in C_6D_6 at 298 K.

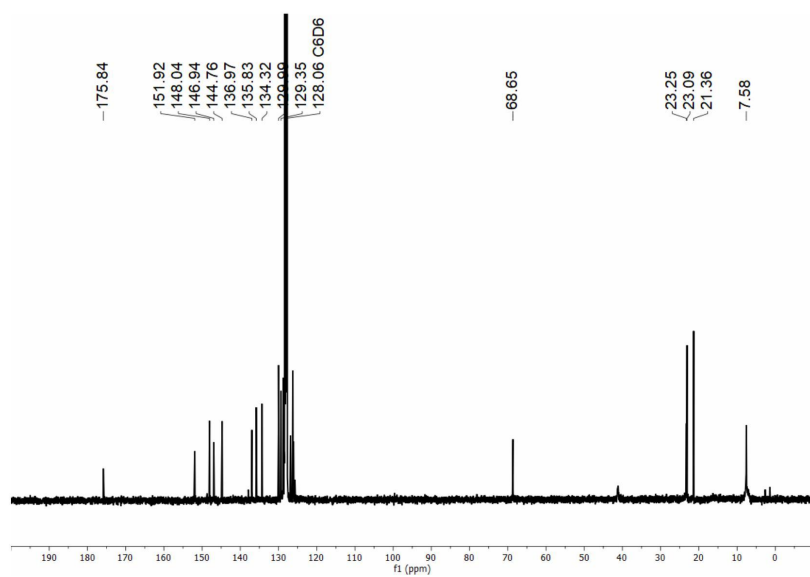


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3-Iet** in C_6D_6 at 298 K.

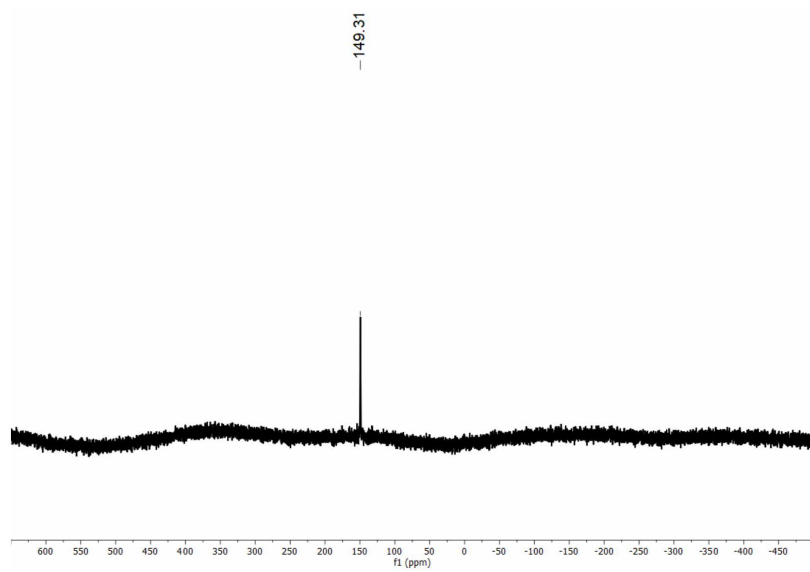


Figure S19. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **3-Iet** in C_6D_6 at 298 K.

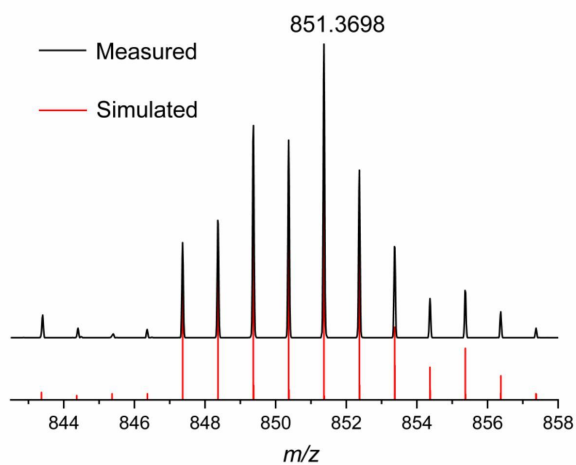


Figure S20. LIFDI-MS spectrum (detail view) of **3-IeT** (measured spectrum: top; simulated spectrum: bottom).

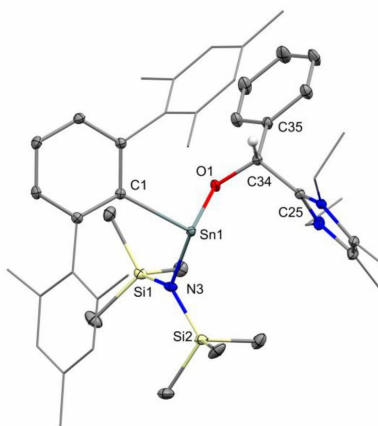
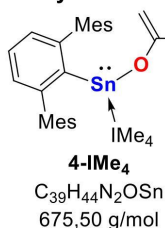


Figure S21. The molecular structure of **3-IeT** in the solid state. Ellipsoids are set at the 30% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1-O1 2.136(1), Sn1-N3 2.160(1), Sn-C1 2.286(2), C34-O1 1.393(2), C34-C35 1.529(2), Si-N3 1.719(1), Si2-N3 1.719(1), O1-Sn1-N3 91.38(4), O1-Sn1-C1 99.47(4), N3-Sn1-C1 104.18(5).

1.6 Synthesis of ^{(Mes)Ter}Sn(Ime₄)(OPhC=CH₂) (4-Ime₄)



A solution of Ime₄ (1.00 eq, 41.9 mg, 338 μmol) in toluene (1 mL) was added to the solution of HMDS^{(Mes)Ter}Sn (**1**) (1.00 eq, 200.0 mg, 338 μmol) in toluene (4 mL). The resulting yellow solution was stirred for 1 hour at room temperature followed by adding acetophenone (1.20 eq, 48.6 mg, 405 μmol) to the reaction solution. The reaction solution was stirred for one day, resulting in a light-yellow suspension. After filtration, the precipitate was dried to yield the white solid target product. The filtrate was then placed in the freezer at -30 °C, producing colorless crystals after three days as an additional batch of the product.

Yield: 198.0 mg (294 μmol, 87.0%).

¹H NMR (400 MHz, 298 K, THF-d₈): δ[ppm] = 1.98, 2.15, 2.20 (s, 18 H, 2xC^{2,4,6}-CH₃, Mes), 2.02 (s, 6 H, 2xC-CH₃, NHC), 3.31 (s, 1 H, OCCHH), 3.32 (6 H, 2xN-CH₃, NHC), 3.71 (s, 1 H, OCCHH), 6.66, 6.71 (s, 4 H, 2xC^{3,5}-H, Mes), 6.80 (d, 2 H, C^{3,5}-H, C₆H₃, ³J_{H-H} = 8), 7.03-7.21 (6 H, (1 H, C⁴-H, C₆H₃), (5 H, Ph)).

¹³C{¹H} NMR (101 MHz, 298 K, THF-d₈): δ[ppm] = 8.44 (C^{4,5}-CH₃, NHC), 21.29, 21.48, 21.99 (C^{2,4,6}-CH₃, Mes), 34.66 (2xN-CH₃, NHC), 81.11 (OC=CH₂), 125.85 (C^{4,5}-CH₃, NHC), 126.65, 127.18, 127.40 (CH_{Aryl}), 128.58, 128.79 (CH_{Aryl}), 129.34 (CH_{Aryl}), 135.83, 135.92, 136.80, 142.60 (C_q, Aryl), 143.93 (C_q, Aryl), 149.63 (C_q, Aryl), 165.12 (OC=CH₂), 166.64 (Sn-C, C₆H₃), 178.28 (Sn-C, NHC).

¹¹⁹Sn{¹H} NMR (150 MHz, 298 K, THF-d₈): δ[ppm] = -41.08.

LIFDI-MS m/z C₃₉H₄₄N₂OSn (M)⁺ calcd: 676.2476; m/z found: 676.2498.

m.p.: 147 °C.

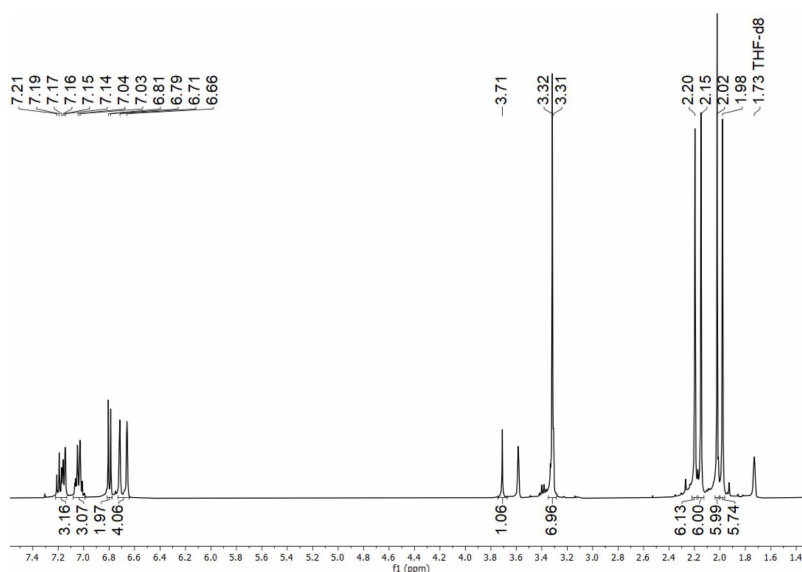


Figure S22. ¹H NMR spectrum of **4-Ime₄** in THF-d₈ at 298 K.

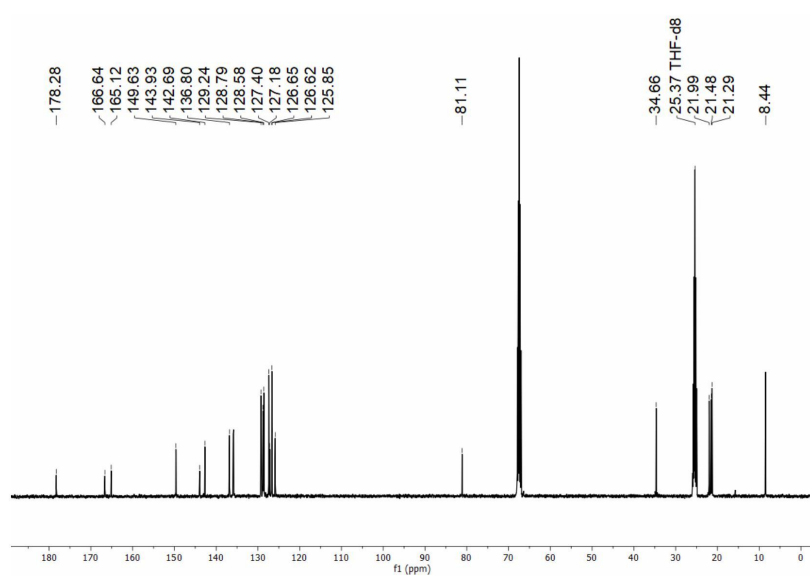


Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4-Ime₄** in THF- d_8 at 298 K.

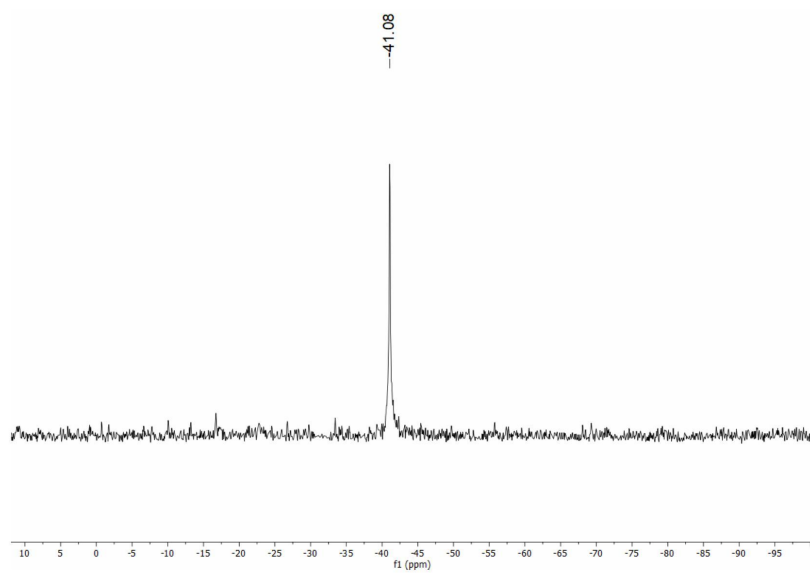
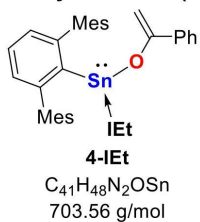


Figure S24. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **4-Ime₄** in THF- d_8 at 298 K.

1.7 Synthesis of ^{(Mes)Ter}Sn(IEt)(OPhC=CH₂) (**4-IEt**)



In a Glove Box, **2-IEt** (1.00 eq, 150.8 mg, 202.51 μmol) was dissolved in toluene (4 ml), and then acetophenone (1.20 eq, 29.2 mg, 243.01 μmol) was added via a pipette at room temperature. The reaction solution was stirred for 18 hours. The resulting light-yellow solution was concentrated to 1 ml, followed by the addition of hexane (3 ml). After storing the solution at -35 °C for one day, **4-IEt** were obtained as light-yellow block-formed crystals. Yield: 77.3 mg (109.87 μmol, 55.4%).

¹H NMR (400 MHz, 298 K, C₆D₆): δ[ppm] = 0.89 (t, ³J_{H-H} = 8 Hz, 6 H, CH₂CH₃, NHC), 1.36 (s, 6 H, 2xC-CH₃, NHC), 2.15 (s, 6 H, 2xC⁴-CH₃, Mes), 2.18, 2.41 (s, 12 H, 2xC^{2,6}-CH₃, Mes), 3.45, 3.66 (br, 4 H, CH₂CH₃, NHC), 4.07, 4.49 (s, 2 H, OC=CH₂), 6.65, 6.79 (s, 4 H, 2xC^{3,5}-H, Mes), 7.02 (d, ³J_{H-H} = 8 Hz, 2 H, C^{3,5}-H, C₆H₃), 7.16-7.19, 7.23-7.30, 7.60-7.62 (6 H, CH_{Aryl}).

¹³C{¹H} NMR (101 MHz, 298 K, C₆D₆): δ[ppm] = 7.96 (2xC^{4,5}-CH₃, NHC), 16.05 (CH₂CH₃, NHC), 21.30 (C⁴-CH₃, Mes), 21.75, 22.08 (C^{2,6}-CH₃, Mes), 42.64 (CH₂CH₃, NHC), 83.06 (OC=CH₂), 124.33 (C^{4,5}-CH₃, NHC), 126.71 (CH_{Aryl}), 126.82 (CH_{Aryl}), 127.30 (CH_{Aryl}), 127.41 (CH_{Aryl}), 128.26 (CH_{Aryl}), 128.35 (CH_{Aryl}), 128.69 (CH_{Aryl}), 128.87 (CH_{Aryl}), 135.27 (C_q, Aryl), 135.78 (C_q, Aryl), 136.52 (C_q, Aryl), 142.49 (C_q, Aryl), 143.45 (C_q, Aryl), 149.32 (C_q, Aryl), 165.85 (OC=CH₂), 166.56 (Sn-C, C₆H₃), 177.70 (Sn-C, NHC).

¹¹⁹Sn{¹H} NMR (150 MHz, 298 K, C₆D₆): δ[ppm] = -24.97 (Sn).

LIFDI-MS m/z C₄₁H₄₈N₂OSn (M)⁺ calcd: 704.2789; m/z found: 704.2811.

m.p.: 118 °C.

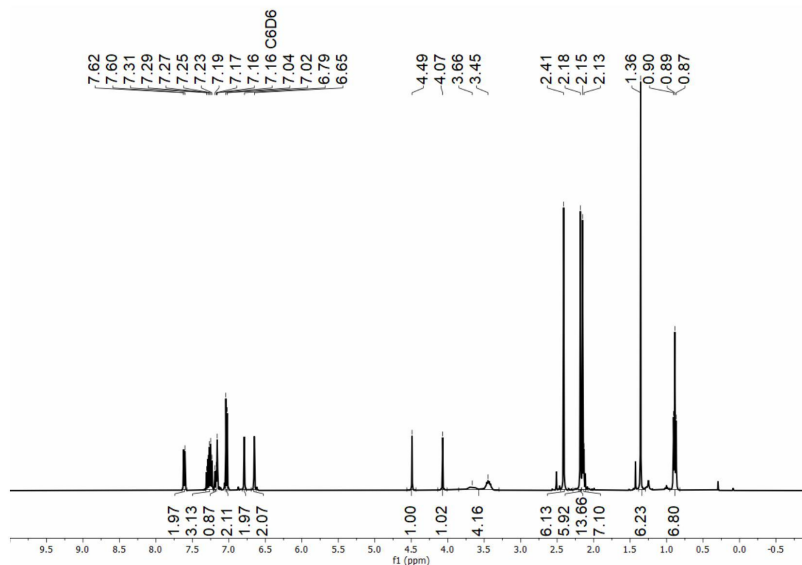


Figure S27. ¹H NMR spectrum of **4-IEt** in C₆D₆ at 298 K.

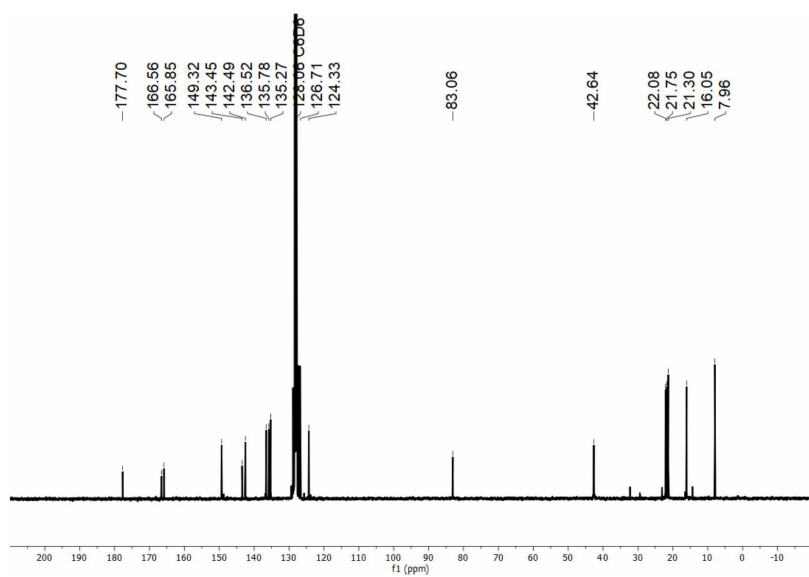


Figure S28. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4-Iet** in C_6D_6 at 298 K.

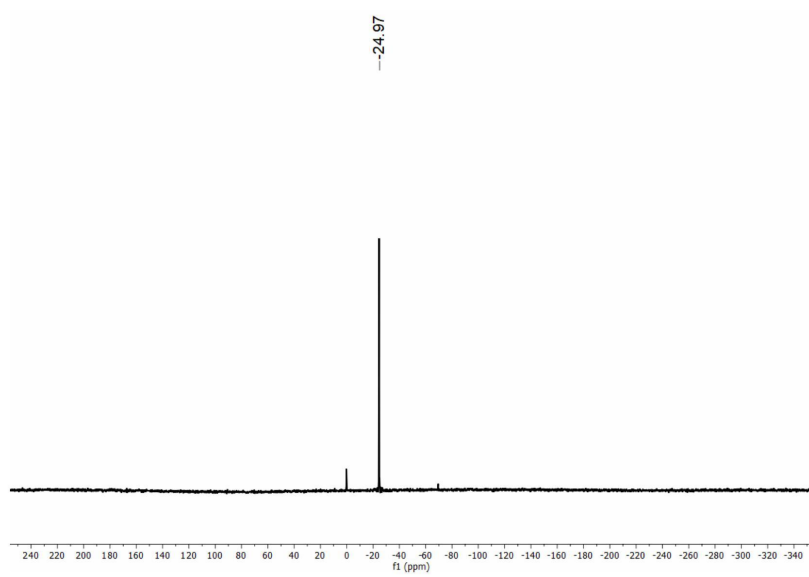


Figure S29. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **4-Iet** in C_6D_6 at 298 K.

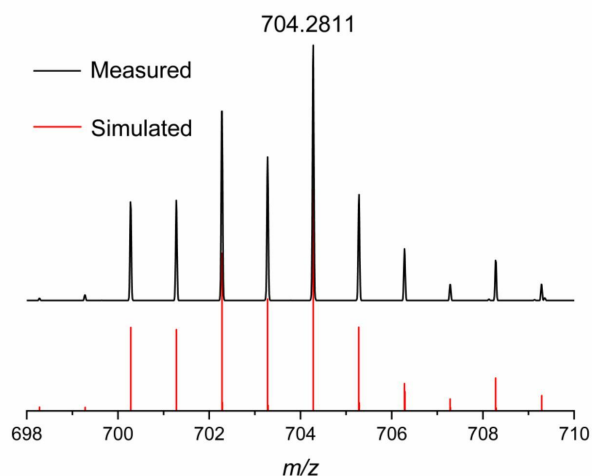


Figure S30. LIFDI-MS spectrum (detail view) of **4-IEt** (measured spectrum: top; simulated spectrum: bottom).

1.7 Catalytic Experiments

General Procedure for Hydrosilylation of Carbonyl Compounds (Aldehydes and Ketones): Diphenylsilane (H_2SiPh_2) (1.00 eq, 80.0 μmol , 14.85 μL), aldehyde (or ketone) (1.00 eq, 80.0 μmol), and 1,3,5-trimethoxybenzene (0.10 eq of H_2SiPh_2 , as an internal standard) were dissolved in a deuterated solvent (C_6D_6 , THF-d_8 , or MeCN-d_3) in a J-Young NMR tube under an argon atmosphere. An initial ^1H NMR spectrum was measured to determine the concentration of silane (by comparison to the internal standard). The catalyst was then added to the reaction solution. The reaction progress was monitored via ^1H NMR spectroscopy by analyzing the consumption of carbonyl compounds. After the completed reaction, the conversion of the carbonyl compound was determined by comparing integrals of the unreacted carbonyl compound resonances to the integrals of the internal standard. The summary of the results is shown in **Table S1**.

Mercury Test Experiment^[5]

H_2SiPh_2 (1.00 eq, 80.0 μmol , 14.85 μL), Benzaldehyde (or acetophenone) (1.00 eq, 80.0 μmol), and 1, 3, 5-trimethoxybenzene (0.10 eq of the Ph_2SiH_2) as an internal standard were dissolved in C_6D_6 in a J-Young NMR tube. Then mercury (12.6 eq, 203.0 mg, 1.01 mmol) was added to the solution, followed by the addition of a catalyst (1 mol%). The progression of reaction was monitored via ^1H NMR spectroscopy. The results are shown in **Table S1**. The hydrosilylation of benzaldehyde catalyzed by **2-IEt** showed minimal changes in the presence of excess mercury (Hg), suggesting that the catalytic cycle is homogeneous. This observation was consistent in the hydrosilylation of acetophenone as well.

Table S1. Hydrosilylation of aldehydes and ketones.

Entry	R ₁	R ₂	Catalyst (mol%)	Solvent	T (°C)	Conversion (%) (time)
1	Ph	H	2-IEt (0.1)	C ₆ D ₆	25	11.2 (1 h)
2	Ph	H	2-IEt (0.5)	C ₆ D ₆	25	90 (1 h)
3	Ph	H	2-IEt (1)	C ₆ D ₆	25	100 (1 h)
4	Ph	H	2-IEt (2.5)	C ₆ D ₆	25	100 (1 h)
5	Ph	H	2-IEt (5)	C ₆ D ₆	25	100 (1 h)
6	Ph	H	2-IEt (0.5)	C ₆ D ₆	50	100 (1 h)
7	Ph	H	2-IEt (1)	THF-d ₈	25	64.4 (1 h)
8	Ph	H	2-IEt (1)	CD ₃ CN	25	100 (1 h)
9	Ph	H	2-IEt (1) + Hg	C ₆ D ₆	25	100 (1 h)
10	Ph	H	1 (1)	C ₆ D ₆	25	100 (1 h)
11	Ph	H	3-IEt (1)	C ₆ D ₆	25	87.4 (1 h)
12	Ph	H	IEt (5)	C ₆ D ₆	25	-
13	Ph	Me	2-IEt (1)	C ₆ D ₆	25	90.1 (24 h)
14	Ph	Me	IEt (5)	C ₆ D ₆	25	-
15	Ph	Me	1 (1)	C ₆ D ₆	25	90.6 (24 h)
16	Ph	Me	4-IMe₄ (1)	C ₆ D ₆	25	53.3 (24 h)
17	Ph	Me	4-IEt (1)	C ₆ D ₆	25	52.8 (24 h)
18	Ph	Me	2-IEt (1) + Hg	C ₆ D ₆	25	89.1 (24 h)

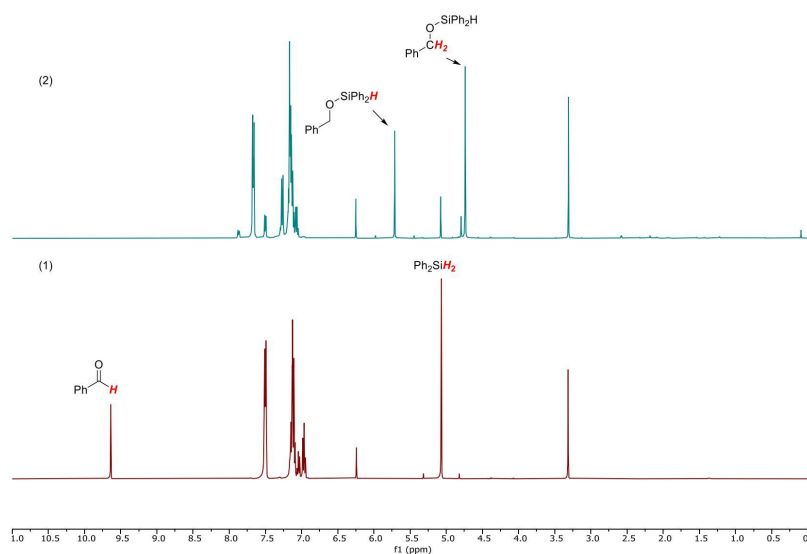


Figure S31. Stacked ^1H NMR spectra of hydrosilylation of benzaldehyde with H_2SiPh_2 by **2-IEt** (1 mol%) in C_6D_6 : (1) benzaldehyde + H_2SiPh_2 ; (2) benzaldehyde + H_2SiPh_2 + **2-IEt** (1 mol%), RT 1 hour.

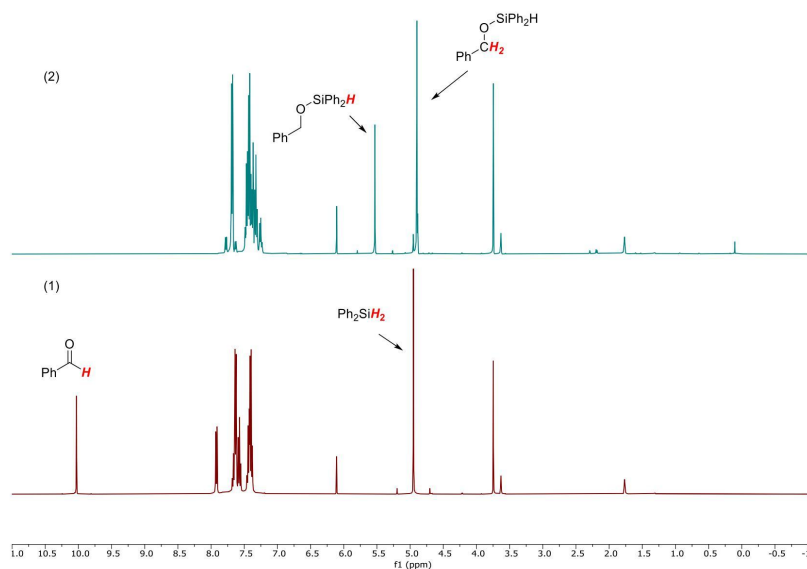


Figure S32. Stacked ^1H NMR spectra of hydrosilylation of benzaldehyde with H_2SiPh_2 by **2-IEt** (1 mol%) in THF-d_8 : 1) benzaldehyde + H_2SiPh_2 ; 2) benzaldehyde + H_2SiPh_2 + **2-IEt** (1 mol%), RT 3 hours.

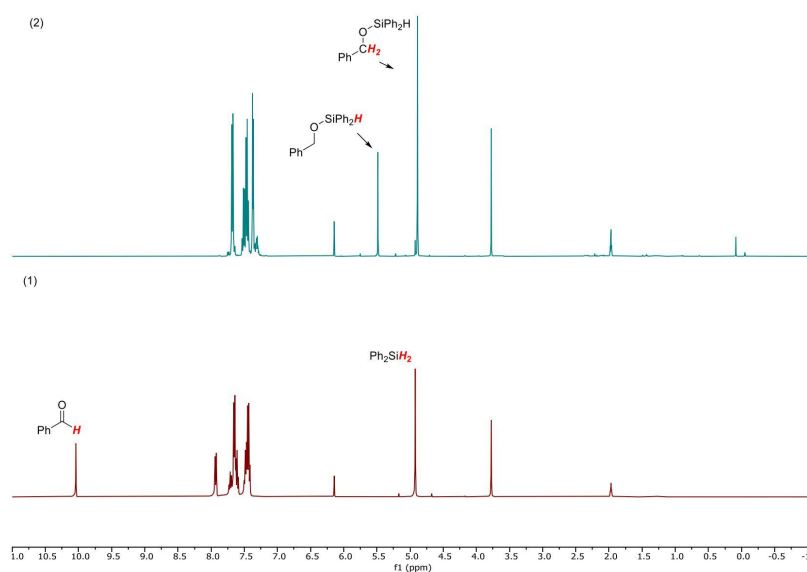


Figure S33. Stacked ^1H NMR spectra of hydrosilylation of benzaldehyde with H_2SiPh_2 by **2-IEt** (1 mol%) in CD_3CN : 1) benzaldehyde + H_2SiPh_2 ; 2) benzaldehyde + H_2SiPh_2 + **2-IEt** (1 mol%), RT 1 hour.

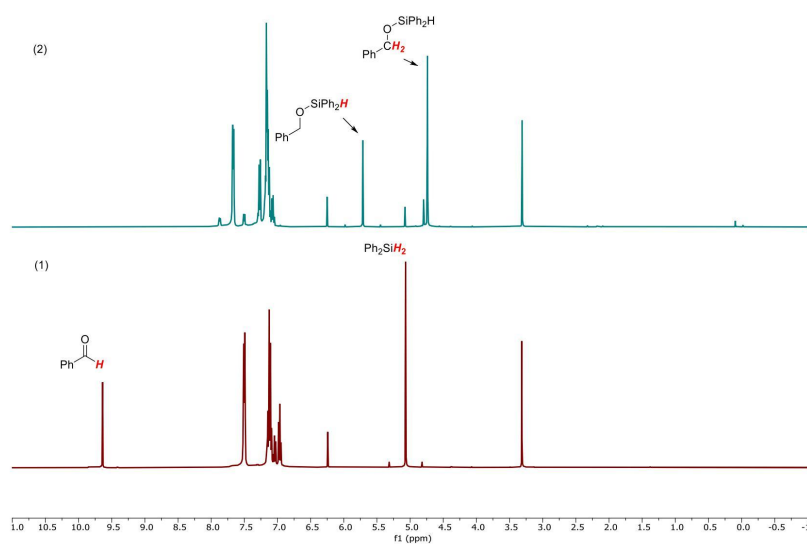


Figure S34. Stacked ^1H NMR spectra of hydrosilylation of benzaldehyde with H_2SiPh_2 by **2-IEt** (0.5 mol%) in C_6D_6 : 1) benzaldehyde + H_2SiPh_2 ; 2) benzaldehyde + H_2SiPh_2 + **2-IEt** (0.5 mol%), 50°C 1 hour.

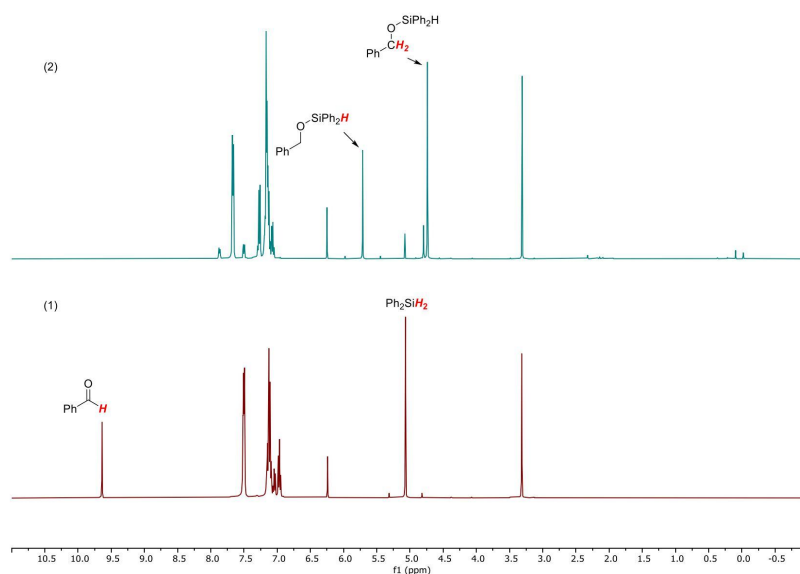


Figure S35. Stacked ^1H NMR spectra of hydrosilylation of benzaldehyde with H_2SiPh_2 by **1** (1 mol%) in C_6D_6 : 1) benzaldehyde + H_2SiPh_2 ; 2) benzaldehyde + H_2SiPh_2 + **1** (1 mol%), RT 1 hour.

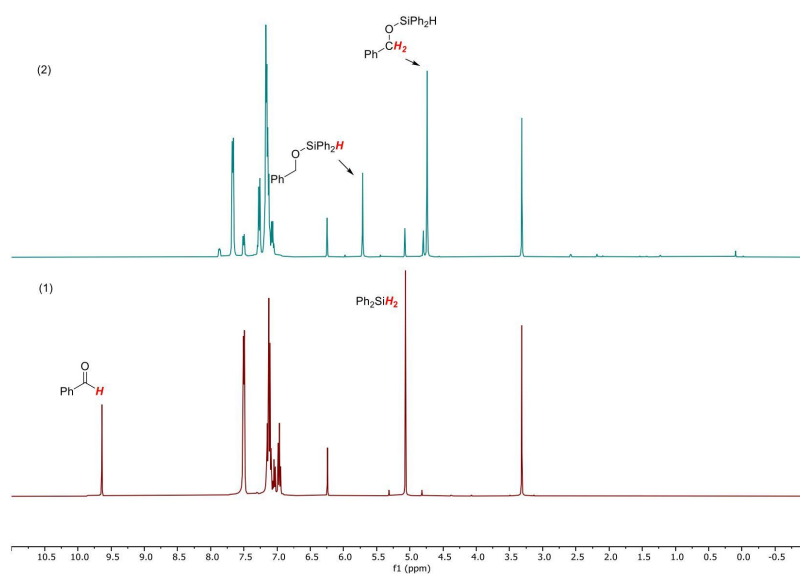


Figure S36. Stacked ^1H NMR spectra of hydrosilylation of benzaldehyde with H_2SiPh_2 by **2-IEt** (1 mol%) in C_6D_6 in the presence of Hg: 1) benzaldehyde + H_2SiPh_2 ; 2) benzaldehyde + H_2SiPh_2 + Hg + **2-IEt** (1 mol%), RT 1 hour.

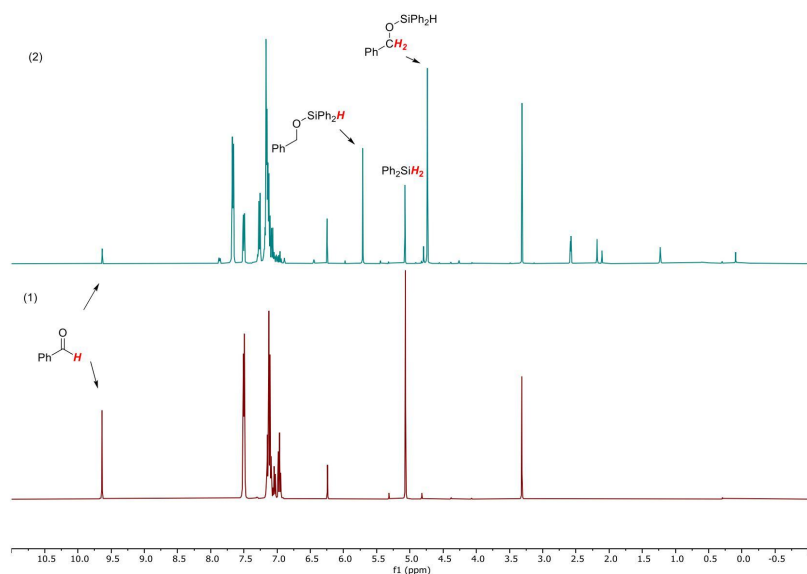


Figure S37. Stacked ^1H NMR spectra of hydrosilylation of benzaldehyde with H_2SiPh_2 by **3-IEt** (1 mol%) in C_6D_6 : 1) benzaldehyde + H_2SiPh_2 ; 2) benzaldehyde + H_2SiPh_2 + **3-IEt** (1 mol%), RT 1 hour.

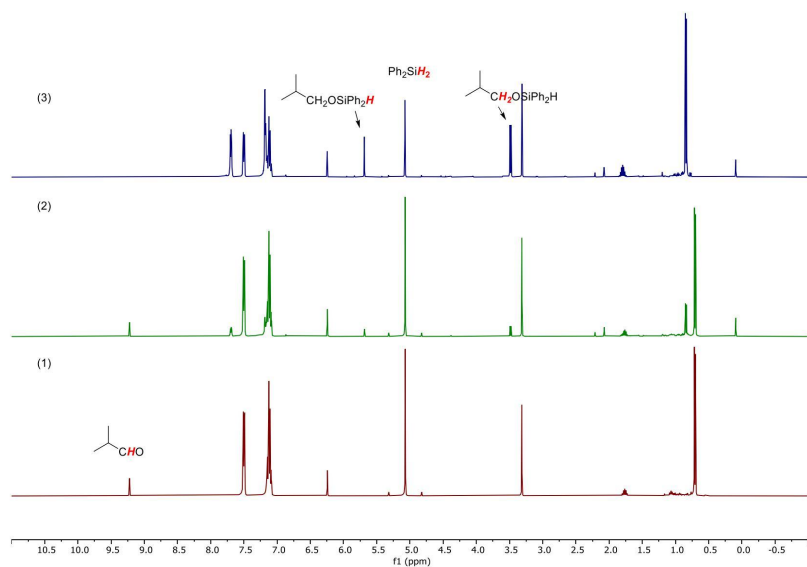


Figure S38. Stacked ^1H NMR spectra of hydrosilylation of isobutyraldehyde with H_2SiPh_2 by **2-IEt** (1 mol%) in C_6D_6 : 1) isobutyraldehyde + H_2SiPh_2 ; 2) isobutyraldehyde + H_2SiPh_2 + **2-IEt** (1 mol%), RT 1 hours; isobutyraldehyde + H_2SiPh_2 + **2-IEt** (1 mol%), RT 6 hours.

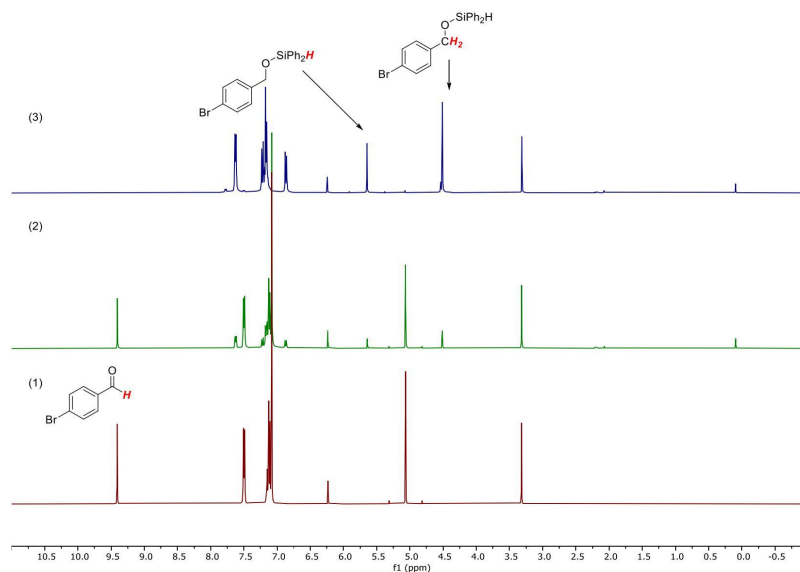


Figure S39. Stacked ^1H NMR spectra of hydrosilylation of 4-bromobenzaldehyde with H_2SiPh_2 by **2-IEt** (1 mol%) in C_6D_6 : 1) 4-bromobenzaldehyde + H_2SiPh_2 ; 2) 4-bromobenzaldehyde + H_2SiPh_2 + **2-IEt** (1 mol%), RT 1 hours; 3) 4-bromobenzaldehyde + H_2SiPh_2 + **2-IEt** (1 mol%), RT 9 hours.

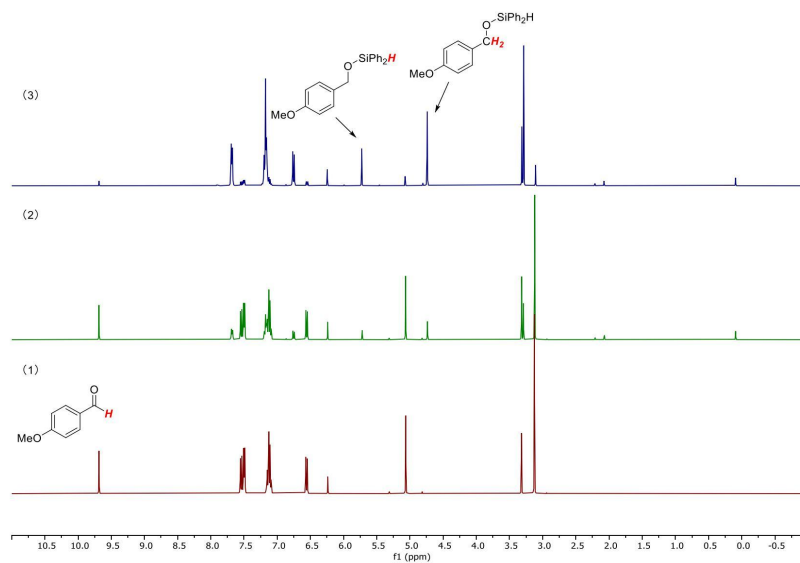


Figure S40. Stacked ^1H NMR spectra of hydrosilylation of 4-methoxybenzaldehyde with H_2SiPh_2 by **2-IEt** (1 mol%) in C_6D_6 : (1) 4-methoxybenzaldehyde + H_2SiPh_2 ; 2) 4-methoxybenzaldehyde + H_2SiPh_2 + **2-IEt** (1 mol%), RT 1 hours; 3) 4-methoxybenzaldehyde + H_2SiPh_2 + **2-IEt** (1 mol%), RT 12 hours.

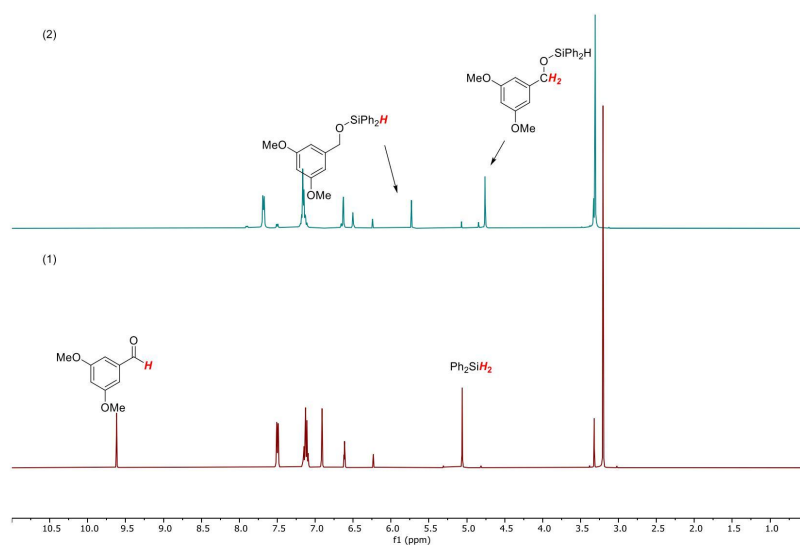


Figure S41. Stacked ^1H NMR spectra of hydrosilylation of 3,5-dimethoxybenzaldehyde with H_2SiPh_2 by **2-IEt** (1 mol%) in C_6D_6 : 1) 3,5-dimethoxybenzaldehyde + H_2SiPh_2 ; 2) 3,5-dimethoxybenzaldehyde + H_2SiPh_2 + **2-IEt** (1 mol%), RT 1 hour.

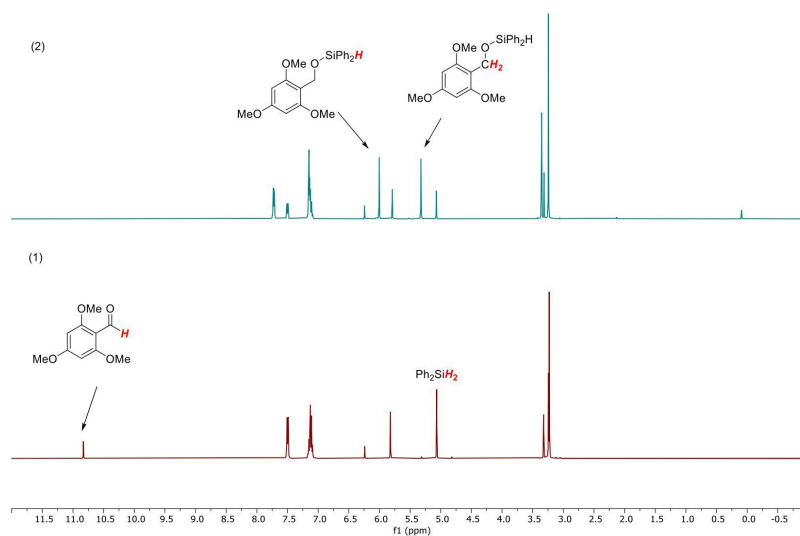


Figure S42. Stacked ^1H NMR spectra of hydrosilylation of 2,4,6-trimethoxybenzaldehyde with H_2SiPh_2 by **2-IEt** (1 mol%) in C_6D_6 : 1) 2,4,6-trimethoxybenzaldehyde + H_2SiPh_2 ; 2) 2,4,6-trimethoxybenzaldehyde + H_2SiPh_2 + **2-IEt** (1 mol%), RT 1 hour.

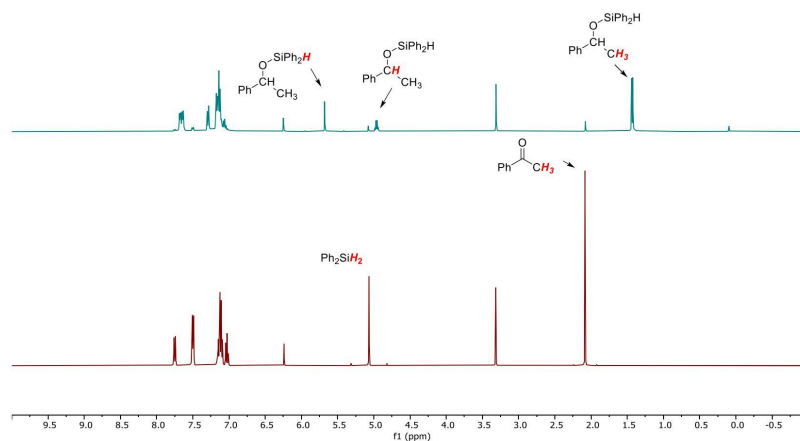


Figure S43. Stacked ^1H NMR spectra of hydrosilylation of acetophenone with H_2SiPh_2 by **2-IEt** (1 mol%) in C_6D_6 : 1) acetophenone + H_2SiPh_2 ; 2) acetophenone + H_2SiPh_2 + **2-IEt** (1 mol%), RT 24 hours.

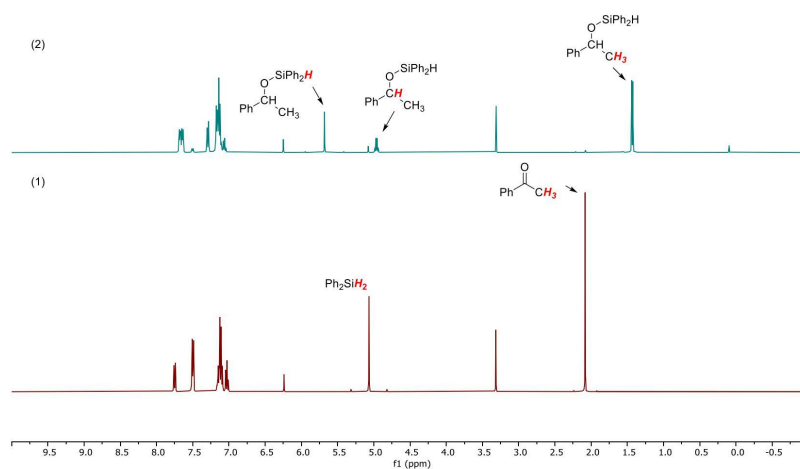


Figure S44. Stacked ^1H NMR spectra of hydrosilylation of acetophenone with H_2SiPh_2 by **1** (1 mol%) in C_6D_6 : 1) acetophenone + H_2SiPh_2 ; 2) acetophenone + H_2SiPh_2 + **1** (1 mol%), RT 24 hours.

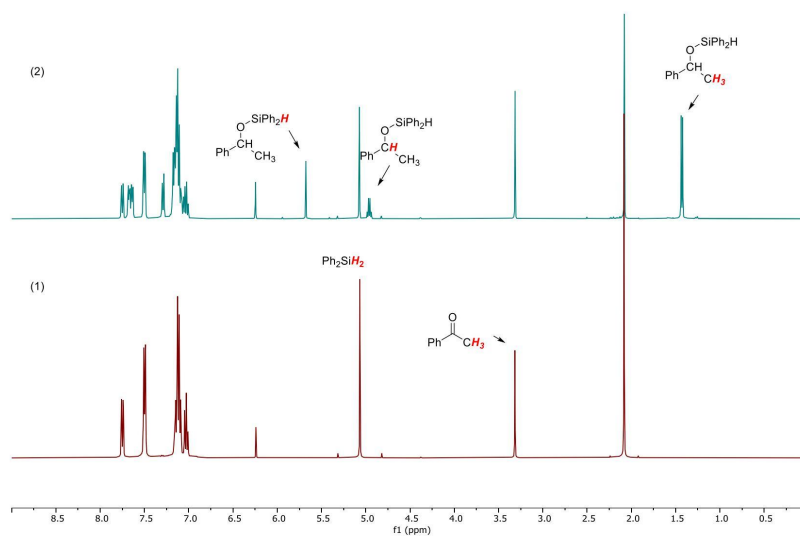


Figure S45. Stacked ^1H NMR spectra of hydrosilylation of acetophenone with H_2SiPh_2 by **4-Ime₄** (1 mol%) in C_6D_6 : 1) acetophenone + H_2SiPh_2 ; 2) acetophenone + H_2SiPh_2 + **4-Ime₄** (1 mol%), RT 24 hours.

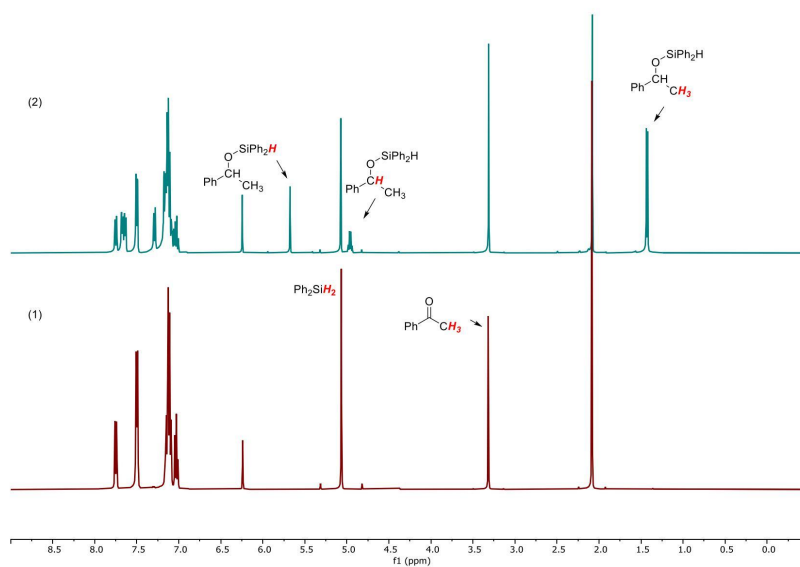


Figure S46. Stacked ^1H NMR spectra of hydrosilylation of acetophenone with H_2SiPh_2 by **4-Iet** (1 mol%) in C_6D_6 : 1) acetophenone + H_2SiPh_2 ; 2) acetophenone + H_2SiPh_2 + **4-Iet** (1 mol%), RT 24 hours.

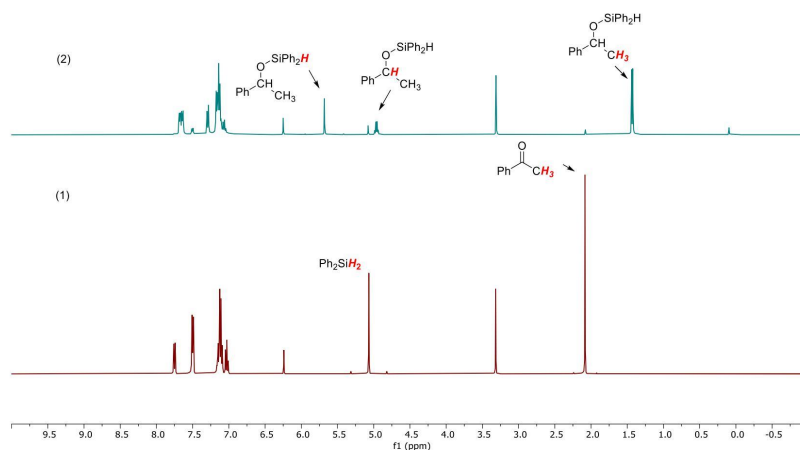


Figure S47. Stacked ^1H NMR spectra of hydrosilylation of acetophenone with H_2SiPh_2 by **2-IEt** (1 mol%) in C_6D_6 in the presence of Hg: 1) acetophenone + H_2SiPh_2 ; 2) acetophenone + H_2SiPh_2 + Hg + **2-IEt** (1 mol%), RT 24 hours.

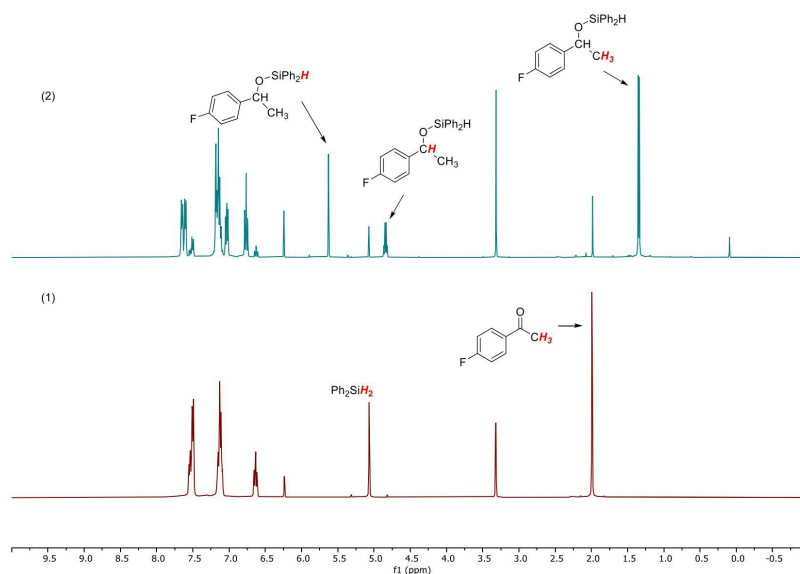


Figure S48. Stacked ^1H NMR spectra of hydrosilylation of 4'-fluoroacetophenone with H_2SiPh_2 by **2-IEt** (1 mol%) in C_6D_6 : 1) 4'-fluoroacetophenone + H_2SiPh_2 ; 2) 4'-fluoroacetophenone + H_2SiPh_2 + **2-IEt** (1 mol%), RT 24 hours.

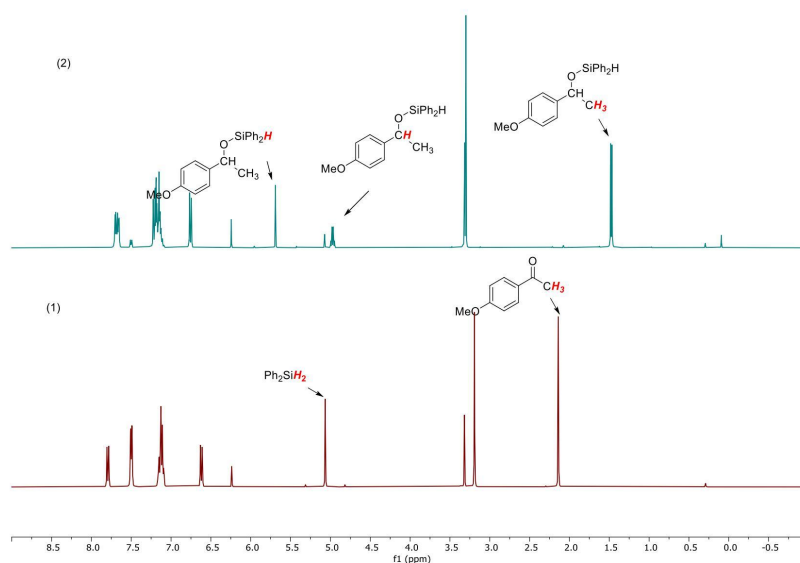


Figure S49. Stacked ^1H NMR spectra of hydrosilylation of 4'-methoxyacetophenone with H_2SiPh_2 by **2-IEt** (1 mol%) in C_6D_6 : 1) 4'-methoxyacetophenone + H_2SiPh_2 ; 2) 4'-methoxyacetophenone + H_2SiPh_2 + **2-IEt** (1 mol%), RT 24 hours.

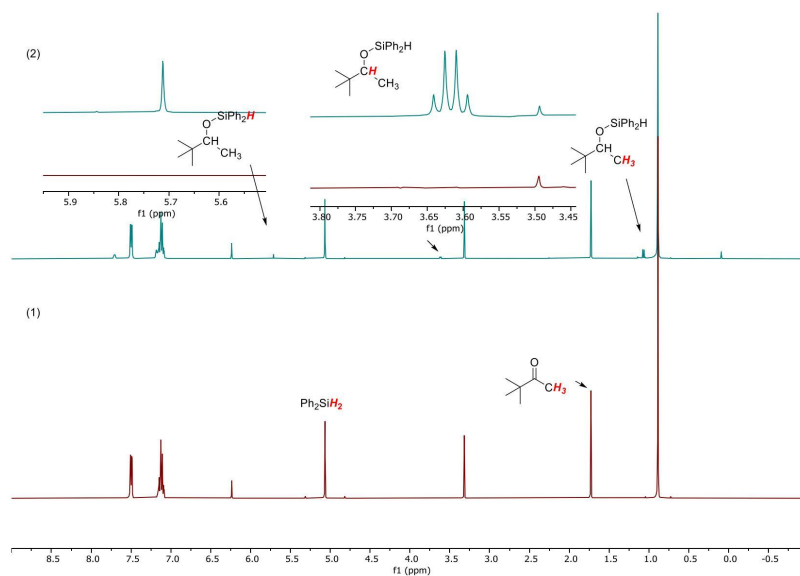


Figure S50. Stacked ^1H NMR spectra of hydrosilylation of 3,3-dimethyl-2-butanone with H_2SiPh_2 by **2-IEt** (1 mol%) in C_6D_6 : 1) 3,3-dimethyl-2-butanone + H_2SiPh_2 ; 2) 3,3-dimethyl-2-butanone + H_2SiPh_2 + **2-IEt** (1 mol%), RT 24 hours.

2. Single crystal X-Ray diffraction

2.1 General considerations

Single crystal X-ray diffraction data for all compounds were collected on an X-ray single crystal diffractometer equipped with a CMOS detector (*Bruker Photon-100*), a rotating anode (*Bruker IMS*) with MoK α radiation ($\lambda = 0.71073$ Å) and a *Helios* mirror optic by using the *APEX III* software package.^[6] The measurement was performed on a single crystal coated with the perfluorinated ether *Fomblin*[®] Y. The crystal was picked on a micro sampler, fixed on the top of a micro sampler, transferred to the diffractometer, and frozen under a stream of cold nitrogen (100 K). The data collection was performed, using the *APEX IV* software package.^[7] A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorentz and polarization effects, scan speed, and background using *SAINT*.^[8] Absorption corrections, including odd and even ordered spherical harmonics were performed using *SADABS*.^[4] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. The structure was solved by direct methods with the aid of successive difference Fourier maps, and was refined against all data using the *APEX III* software in conjunction with *SHELXL-2014*^[9] and *SHELXLE*^[10] or *OLEX2*^[11]. For **2-IMe₄**, the symmetry was corrected from P-1 to P2₁/n via ADDSYM function in *Platon*.^[12] For refinement of **3-IEt**, the rotational disorder of SiMe₃ (Si2) was modeled with an occupancy of 17.11% (Si2). All H atoms (except Si–H) 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 $U_{iso}(H) = 1.2 \cdot U_{eq}(C)$. Fourier maps and were allowed to refine freely. Full-matrix least-squares refinements were carried out by minimizing $\Delta w(F_o^2 - F_c^2)$ ^[8] with *SHELXL-97* weighting scheme.^[9] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.^[13] The images of the crystal structures were generated by *Mercury*.^[14] The CCDC numbers 2370672, 2370673, and 2255354 contain the supplementary crystallographic data for the structures **2-IMe₄**, **3-IEt**, and **4-IMe₄**. The 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 Structural Refinement Parameters

	2-IMe₄	3-IEt	4-IMe₄
CCDC Number	2370672	2370673	2255354
Crystal Data			
Chemical formula	C ₃₇ H ₅₅ N ₃ Si ₂ Sn	C ₄₆ H ₆₅ N ₃ O ₂ Si ₂ Sn	C ₃₉ H ₄₄ N ₂ O ₂ Sn
<i>M_r</i>	716.73	850.88	675.45
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Triclinic, <i>P</i> -1
Temperature (K)	100	100	100.00
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.592 (4), 21.087 (7), 16.871 (7)	11.2073 (8), 20.9116 (17), 19.5884 (16)	10.8816 (10), 12.4913 (11), 13.1177 (12)
α , β , γ (°)	90.00, 100.609 (14), 90.00	90.00, 101.580 (3), 90.00	109.058(3), 96.959(4), 98.201(10)
<i>V</i> (Å ³)	3704 (2)	4497.3 (6)	1641.0(3)
<i>Z</i>	4	4	2
<i>F</i> (000)	1504	1792	700.0
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
No. of reflections for cell measurement	7357	9588	9913
θ range (°) for cell measurement	2.75– 34.97	2.69– 26.38	2.85– 25.36

μ (mm ⁻¹)	0.78	0.66	0.81
Crystal shape	fragment	block	block
Colour	colorless	yellow	colorless
Crystal size (mm)	0.31 × 0.29 × 0.21	0.31 × 0.25 × 0.20	0.05 × 0.04 × 0.01
Data Collection			
Diffractometer	Bruker Photon CMOS IMS microsource	Bruker Photon CMOS IMS microsource	Bruker Photon CMOS IMS microsource
Radiation source	fine-focus sealed tube	fine-focus sealed tube	fine-focus sealed tube
Detector resolution (p mm ⁻¹)	16	16	16
Scan method	phi- and omega- rotation scans	phi- and omega- rotation scans	phi- and omega- rotation scans
Absorption correction	Multi-scan	Multi-scan	Multi-scan
$T_{\min}$, $T_{\max}$	0.652, 0.747	0.699, 0.745	0.654, 0.745
No. of measured, independent and observed [$I > 2s(I)$] reflections	124338, 14702, 11884	194982, 9231, 8949	56011, 5893, 5656
R_{int}	0.061	0.028	0.047
θ values (°)	$\theta_{\max} = 37.37$, $\theta_{\min} = 1.93$	$\theta_{\max} = 26.44$, $\theta_{\min} = 1.95$	$\theta_{\max} = 50.72$, $\theta_{\min} = 3.84$
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	0.854	0.626	0.603
Range of h , k , l	$h = -15 \rightarrow 16$, $k = -35 \rightarrow 30$, $l = -28 \rightarrow 24$	$h = -14 \rightarrow 14$, $k = -26 \rightarrow 26$, $l = -24 \rightarrow 24$	$h = -13 \rightarrow 13$, $k = -15 \rightarrow 15$, $l = -15 \rightarrow 15$
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.034, 0.066, 1.03	0.020, 0.050, 1.05	0.030, 0.083, 1.20
No. of reflections	14702	9231	5893
No. of parameters	404	525	398
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$\omega = 1/[\sigma^2(F_o^2) + (0.0202P)^2 + 2.5940P]$ where $P = (F_o^2 + 2F_c^2)/3$	$\omega = 1/[\sigma^2(F_o^2) + (0.0202P)^2 + 3.5133P]$ where $P = (F_o^2 + 2F_c^2)/3$	$\omega = 1/[\sigma^2(F_o^2) + 4.5191P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	1.06, -1.72	0.60, -0.38	1.13, -0.65

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