Anukul Jana

Unprecedented Synthetic and Reactivity Studies of Compounds with Low Valent Group 14 Elements

Unprecedented Synthetic and Reactivity Studies of Compounds with Low Valent Group 14 Elements

Dissertation

zur Erlangung des Doktorgrades

der Mathematisch–Naturwissenschaftlichen Fakultäten

der Georg–August–Universität zu Göttingen

vorgelegt von

Anukul Jana

aus Krishnakhayratibar

(Indien)

Göttingen 2009

D 7

Referent: Prof. Dr. Dr. h. c. mult. H. W. Roesky

Korreferent: Prof. Dr. Dietmar Stalke

Tag der mündlichen Prüfung: 22.10.2009

Dedicated to my parents for

their love and affection

Acknowledgement

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Abbreviations

δ	chemical shift
λ	wavelength
μ	bridging
$\tilde{\nu}$	wave number
av	average
C	Celsius
calcd.	calculated
Cp	cyclopentadienyl
Cp*	pentamethylcyclopetadienyl
EI	electron impact ionization
eqv.	equivalents
eV	electron volt
g	grams
h	hours
Hz	Hertz
IR	infrared
J	coupling constant
K	Kelvin
L	ligand
M	metal
m/*z*	mass/charge
Mp	melting point
M^+	molecular ion
Me	methyl
Et	ethyl
*i*Pr	*iso*-propyl
*t*Bu	*tert*-butyl
Ph	phenyl
Ar	aryl
Fc	ferrocenyl
MS	mass spectrometry, mass spectra

NMR	nuclear magnetic resonance
ppm	parts per million
q	quartet
R	organic substituents
s	singlet
d	doublet
t	triplet
sept	septet
m	multiplet
b	broad
THF	tetrahydrofuran

Chapter 1

Introduction

This section of the thesis gives the background and an overview of the area in several sections of the present work.

1.1. *β*-Diketiminate ligands

The *β*-diketiminate class, generally denoted as "nacnac", or [{ArNC(R)}$_2$CH]$^-$ (where Ar = aryl and R = Me or another group), occupies a rightful place alongside a narrow list of popular ancillary supports, given its ability to stabilize or generate unique coordination environments and to support reactive organometallic reagents or catalysts.[1-7] The "nacnac" ligand skeleton is analogous to the "acac" (acetylacetonate) ligand, but the oxygen atoms are exchanged for nitrogen-based moieties such as NR (R = alkyl, silyl, Ar) (Scheme 1.1). As a result, the substituent at the nitrogen donor atom can allow for steric protection at the metal center unlike "acac" could offer. When small moieties such as H, Me, or the SiMe$_3$ on the nitrogen the substance easily forms dimers and allows higher coordination to the metal center, whereas bulky aryl groups on nitrogen usually lead to the isolation of monomeric species with low coordination numbers at the metal.

The first documented cases of *β*-diketiminate metal complexes were reported by McGeachin,[8] Parks, and Holm[9] in 1968. The explosion in popularity of "nacnac" amongst synthetic chemists is driven, in part, by the monoanionic nature of the *β*-diketiminate group, the chelating nature but also variable mode of hapticity, the ease in preparation, and the versatility to tune both electronic and steric parameters. Till to date the N-aryl substituted "nacnac" ligands [HN(Ar)C(Me)CHC(Me)N(Ar)][10] and [HN(Ar)C(*t*Bu)CHC(*t*Bu)N(Ar)][11] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) showed to be the best for stabilization of low coordinate metal sites.

Scheme 1.1. Schematic diagram of (a) "acac", (b) "nacnac", and (c) "cyclopentadienyl" ligands

The major breakthrough in this area was achieved in the mid 1990's, when *β*-diketiminate ligands were used as spectator ligands, thus offering strong metal-ligand bonds like cyclopentadienyls (Scheme 1.1). In contrast to the latter, *β*-diketiminate ligands offer a possibility of subtle tuning of their electronic and steric properties by simple variation of the substituents on nitrogen and adjacent carbon atoms.

The chemistry of the *β*-diketiminate ligand since its initial recognition as an ancillary ligand and the effective stabilization of lower oxidation states and lower coordination numbers has experienced a burgeoning due to the steric and electronic properties and a variety of coordination modes. The ligand can be regarded as a bidentate and monoanionic ligand and can be prepared by direct condensation of 2,4-pentanedion, 2,6-diisopropylaniline, and HCl in boiling ethanol and subsequent neutralization of the generated ligand hydrochloride with Na_2CO_3 to obtain free LH (Scheme 1.2).[12]

Scheme 1.2. Preparation of ligand LH

Recently, a great deal of unique and fascinating results reflect the *β*-diketiminate ligand stabilizing properties with main group elements. Thus the isolation and structural characterization of a monomeric aluminum(I) compound LAl[13] and magnesium(I) compound LMgMgL with Mg-Mg bonds[14] were reported.

In this thesis we are describing the utility of bidentate and monoanionic properties of *β*-diketiminate ligand with group 14 elements. By using this ligand we are for the first time reporting here the synthesis and reactivity of the very pure monomeric germanium(II) and tin(II)-hydride. Moreover herein we also report the synthesis and reactivity of novel heteroleptic germanium(II) and tin(II) compounds including terminal tin(II) hydroxide.

It has been well established that the *β*- diketiminate ancillary framework has vulnerable sites, especially in the context of early transition metal or main group organometallic chemistry. Of

the many different modes of transformation involving the β-diketiminate ligand, perhaps the most common pathway is intramolecular C-H bond activation of peripheral groups stemming from the R-nitrogen atoms.[15-19] Other reactions of this ligand type include electrophilic activation at the γ-carbon due to delocalization of charge about the NCCCN ring,[20-27] as well as deprotonation of the β-methyl group composing the NCCCN ring.[28-33] The ability of the β-diketiminate's β-methyl hydrogens to tautomerize in [{ArNC(Me)}$_2$CH]$^-$ (Ar = 2,6-iPr$_2$C$_6$H$_3$) allows for facile deprotonation to form the N,N′-chelating, bis-anilide ligand [ArNC(Me)CHC(CH$_2$)NAr]$^{2-}$ (Scheme 1.3). Lewis acid coordination to the methylene moiety of [ArNC(Me)CHC(CH$_2$)NAr]$^{2-}$ can yield charge-separated species.[34] Even though the β-diketiminate ligand can readily undergo deprotonation of the β-methyl group, such a transformation can be avoided by incorporating a tBu group.[35]
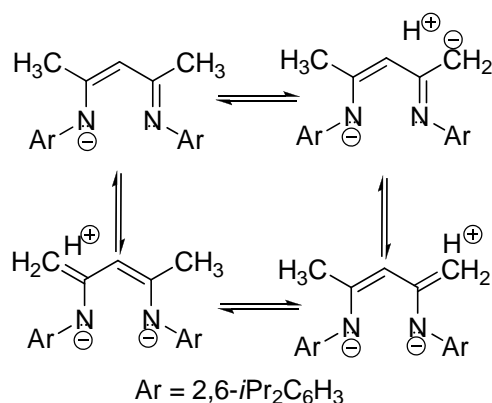
Scheme 1.3. Schematic diagram of bis-anilide ligand [ArNC(Me)CHC(CH$_2$)-NAr]$^{2-}$

The utility of bidentate and dianionic properties of bis-anilide ligand ([ArNC(Me)CHC(CH$_2$)-NAr]$^{2-}$ = L′; Ar = 2,6-iPr$_2$C$_6$H$_3$) offers the formation of heterocyclic compounds. *Driess et al.* reported the synthesis and reactivity of six-membered N-heterocyclic silylene, L′Si[36] and germylene L′Ge.[37] In this thesis we independently describe the utility of bidentate and dianionic properties of bis-anilide ligand [ArNC(Me)CHC(CH$_2$)NAr]$^{2-}$ for the synthesis of six-membered N-heterocyclic germylene and silylene systems.

1.2. Halides of Germanium(II) and Tin(II)

Halides of group 14 elements are important precursors for a variety of new reactions. Dihalogermylenes, GeX$_2$ (X = F, Cl, Br, I) were the first known divalent species that had

been studied and reviewed as starting materials and intermediates in organogermanium chemistry in 1973.[38] Cp*GeCl was the first example of a monohalide with the general composition RMX (M = Ge, Sn; R = organic group; X = halide) prepared in 1987,[39] followed by the tin analogue RSnCl (R = C(SiMe$_3$)$_2$C$_5$H$_4$N-2) in 1988.[40] After that in 2006 our group reported the synthesis and structure of the first monomeric chloro silylene [{PhC(NtBu)$_2$}SiCl].[41] In this year our group reported on the synthesis of the first stable "*bottleable*" Lewis base (NHC) stabilised dichloro silylene,[42] which has the potential for further reactions and may have the same impact like GeCl$_2$·di-oxane. *Filippou et al.* published the N-heterocyclic carbene adduct of dibromosilylene.[43] Moreover there were a variety of monohalide compounds prepared and their chemistry showed that it is an interesting class of compounds.[10, 44] The fluoro compounds are of interest and expected to have a different reactivity due to the strong electron withdrawing effect of fluorine compared to the other halides. Moreover, organometallic fluorides of group 14 elements are important because of their industrial application, synthetic methodology, and theoretical implications.[45-50] In the literature only two dimeric Sn(II) fluorides were reported as stable molecules,[51] and one Ge(II) fluoride, PhGeF, was studied as a reactive intermediate,[52] also the preparation of Ge(II) fluoride using the *β*-diketiminate ligand was reported by our group.[28] The parent low valent tin(II)difluoride (SnF$_2$) is not soluble in any organic solvents and only poorly soluble in water. SnF$_2$ is widely used in toothpaste, as a source of fluoride to harden dental enamel.[53] In the enamel it converts apatite into fluoroapatite, which is more resistant to attack by acids generated by bacteria. In the solid state SnF$_2$ exists as a tetramer containing a puckered eight-membered ring in which Sn and F atoms are alternately arranged. Four additional F atoms which are bound to the four tin atoms, provide weaker interactions with Sn atoms of the adjacent rings.[54] The most characteristic feature of the SnF$_2$ compound is the tendency to interact via Sn-F-Sn bridges and as a result of this, it is only poorly or not soluble in common organic solvents, even at higher temperatures in the gas phase it forms preferentially ring compounds. These difficulties are overcome by the use of a bulky and intramolecularly coordinating ligand. By applying this technique some monomeric organotin(IV)fluoride compounds were recently reported.[55-58] This development of Sn(IV) fluorides encouraged us to synthesize Sn(II) fluorides.

1.3. Hydrides of Germanium(II) and Tin(II)

Metal hydrides and their complexes are considered valuable synthons in chemistry. It was demonstrated that main-group and transition-metal hydrides are important intermediates in some industrial processes and also function as catalysts.[59-67] Furthermore, in the quest for alternative energy sources, metal hydrides have been considered as potential feedstocks for hydrogen storage.[68-71] In recent years the chemistry of metal hydrides has drawn great attention.[72, 73] The hydrides of group 14 elements are important and their chemistry and applications are very rich.[74-78] Group 14 hydrides such as R_3SiH, R_3GeH, and R_3SnH are important reagents for some key reactions in organic synthesis. However, almost all such compounds reported to date involve the central element in the +4 oxidation state. In recent years our group[28, 79] and *Power et al.*[80-82] first reported only on the synthesis of germanium(II) and tin(II) hydrides of a divalent group 14 element, although the existence of MH_2 (M = Si to Pb) has been anticipated by theoretical calculations.[83] Also the parent SnH_2 has been prepared and characterised in an argon matrix.[84] At elevated temperature SnH_2 changed to an insoluble solid of unknown structure.

Until now no reaction has been reported based on these hydrides. This is mainly due to the synthetic difficulties as well as stability for further reactions. Most of these hydrides of group 14 elements based on +4 oxidation state are performing the reaction in the presence of a metal catalyst or in the presence of a radical initiator such as azobis(isobutyronitrile) (AIBN). Comparison of hydrides of group 14 elements based on +4 oxidation state with those of the +2 oxidation state resulted in more reactive species, because the ionic radii of species with +2 oxidation state are larger when compared with those of the +4 oxidation state.[85] Herein we explore the reactivity studies of hydrides of group 14 elements based on +2 oxidation state towards unsaturated molecules.

1.4. Divalent Germanium(II) and Tin(II) Compounds of the Type LMR

Within the resurgence of interest in stable N-heterocyclic carbenes over the years,[86] the chemistry of their heavier analogues, silylenes, germylenes, stannylenes, and plumbylenes, has also attracted considerable interest. Studies showed that compounds of divalent germanium bonded to small alkyl substituents (such as Me, Et, Bu) are highly reactive, and therefore exist only as intermediates.[87, 88] However, the divalent germanium compounds can be stabilized with bulky ligands. *Jutzi et al.* reported the first example of such compounds by

oxidative addition of MeI, but failed to characterize these compounds by structural analysis.[89] Therefore it is important to explore the properties of alkylated germanium(II) compounds containing bulky ligands. Recently our group reported the synthesis and structure of LGeMe [L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$].[29] There has been considerable interest over the past three decades in the chemistry of dialkyl and diaryl Sn(II) compounds.[90-94] But remarkably little is known about the chemistry of simpler heteroleptic derivatives such as L′SnR (L′ = chelating ligand or bulky aryl ligand, and R a small substituent). It is of interest to further develop the chemistry of such compounds. *Power et al*. reported on the reaction of 2,6-Trip$_2$C$_6$H$_3$Sn(II)Cl (Trip = 2,4,6-iPr$_3$C$_6$H$_2$) with MeLi. They obtained 2,6-Trip$_2$C$_6$H$_3$Sn(II)-Sn(IV)(Me)$_2$-2,6-Trip$_2$C$_6$H$_3$ instead of 2,6-Trip$_2$C$_6$H$_3$Sn(II)Me.[95] Moreover it is mentioned that the dimethylstannylene (SnMe$_2$) is a transient species at room temperature, which is generated in situ under special experimental conditions from a variety of substrates and some aspects of its chemistry in solution and gas phase have been reported.[96-98]

1.5. Six-Membered N-Heterocyclic Silicon(II) and Germanium(II) Compounds

Silylenes are of considerable current interest owing to their fundamental interest and potential applications in transition metal catalysis.[99] Since the first stable N-heterocyclic silylene was reported by *West et al.* in 1994,[100] several other cyclic silylenes have been synthesized and fully characterized by Lappert,[101] Kira,[102] and others.[103, 104] Since the pioneering work on the synthesis of isolable germylenes (R$_2$Ge) reported by *Lappert et al.*[105] remarkable progress has been made in tuning the reactivity of the low coordinate Ge atom in germylenes through the presence of bulky and/or *p*-donor substituents R.[106-109] Sterically demanding amido or alkoxo substituents at the two coordinate Ge atom lead to derivatives which can serve as ligands with different donor-acceptor abilities for coordination compounds.[110-114] Herein we explored the reactivity studies of six-membered N-heterocyclic silicon(II) and germanium(II) compounds.

1.6. Hydroxides of Tin(II) Compounds

The compounds containing the hydroxy group are considered as potential building block in synthetic chemistry. In recent years we were interested in the synthesis of organometallic hydroxides. We reported on the preparation and structural characterization of unusual

compounds such as $[(Me_3Si)_3CSnO(OH)]_3$,[115] $[(CpZr)_6(\mu_4\text{-}O)(\mu\text{-}O)_4(\mu\text{-}OH)_8]$,[116] $[Cp_2*MMe(OH)]$ (M = Zr and Hf)[117, 118] $[LAl(OH)_2]$,[119] $[LAlR(OH)]$ (R = Me, Et, and Ph),[120-122] $[LGa(OH)_2]$,[123] $[LGaMe(OH)]$,[124] $[LMOH]$, (M = Ca and Sr)[125, 126] and $[LGeOH]$[127] where L = $HC(CMeNAr)_2$; Ar = $2,6\text{-}i\text{Pr}_2C_6H_3$, and their reactions generating heterobimetallic systems.[5, 128-130] Interestingly, only a few examples of well-characterized tin(IV) hydroxides are known in literature,[131] and one dimeric compound based on tin(II) has been reported.[132] This hydroxide was prepared from Ar′SnSnAr′ [Ar′ = $2,6\{(2,6\text{-}i\text{Pr}_2C_6H_3)_2\}C_6H_3$] and 2,2,6,6-tetramethylpiperidine-N-oxide (TEMPO) or nitrous oxide (N_2O) by serendipity. To the best of our knowledge there is presently no report available on a well-designed synthesis and structural characterization of any monomeric tin(II) hydroxide.

1.7. Amides of Germanium(II) and Tin(II) Compounds

Stable low-valent amide derivatives of heavier group 14 elements have been known for almost 3 decades. They have the general formula $M(NR_2)_2$, (M = Ge, Sn, and Pb) where the nitrogen substituents can be varied by bulky silyl, aryl, or alkyl groups.[133-136] In 2005 *Power et al.* reported the use of very crowding terphenyl ligands that enable the synthesis and stabilization of Ge(II), Sn(II), and Pb(II) amides of formula $(Ar*MNH_2)_2$ (M = Ge, Sn, or Pb) or $(Ar′GeNH_2)_2$, where Ar* = $2,6\{(2,4,6\text{-}i\text{Pr}_3C_6H_2)_2\}C_6H_3$ and Ar′ = $2,6\{(2,6\text{-}i\text{Pr}_2C_6H_3)_2\}C_6H_3$ with divalent group 14 element amides featuring the parent $-NH_2$ group.[137] To date, however, no examples of monomeric stable divalent group 14 element amides featuring the parent $-NH_2$ group have been reported. A number of stable $-NH_2$ derivatives of silicon(IV) are known,[138-142] and there are also a few stable $-NH_2$ derivatives of germanium(IV) reported.[139, 143, 144] These M(IV) compounds were obtained with the use of bulky coligands which prevent self-association by elimination of NH_3. However these results have not been expanded so much to divalent derivatives. In recent years, we were successful in the preparation of compounds with the parent $-NH_2$ group of group 13 elements such as $LAl(NH_2)_2$,[145] $LGa(NH_2)_2$[123] where L = $HC(CMeNAr)_2$; Ar = $2,6\text{-}i\text{Pr}_2C_6H_3$. Like tetravalent species, the scarcity of divalent $-NH_2$ derivatives is mainly due to their tendency to condense with elimination of ammonia. This process is especially feasible in divalent compounds where the group 14 elements can carry only one other substituent which renders steric protection more difficult.

1.8. Direction of the Thesis Work

The Sections 1.2-1.7 describe the importance of compounds with low valent group 14 elements silicon, germanium, and tin. The work described herein was aimed at achieving a facile and easy synthetic route for the preparation of compounds with low valent group 14 elements silicon, germanium, and tin starting from easily accessible precursor that is supported by the sterically encumbered *β*-diketiminate ligand. Based on these facts the objectives of the present work are

1. to synthesize divalent germanium and tin halides, especially tin(II) fluorides.
2. to develop methodologies for the synthesis of germanium(II) and tin(II) hydrides.
3. to explore the reactivity of the H functionality on the germanium(II) and tin(II) hydride compounds for the reaction with unsaturated compounds.
4. to explore the reactivity of *β*-diketiminate ligands for the preparation of germanium(II) and tin(II) organocompounds and their reactivity towards unsaturated molecules.
5. to develop the new method for the synthesis of six-membered N-heterocyclic germylene.
6. to develop a new synthetic strategy for the preparation of mononuclear molecular hydroxides of tin(II) via an aqueous route.
7. to synthesize monomeric germanium(II) and tin(II)-amides bearing the parent -NH$_2$ group.
8. to study the germanium(II) and tin(II) hydrides for the exchange of hydrogen towards fluorine.

Chapter 2

Syntheses and Characterization of the Germanium(II) and Tin(II) Halides

From the experience of the synthesis of LGeCl,[146] LSnCl,[146] and LGeF[28] we reacted the *β*-diketiminate lithium salt LLi(OEt$_2$)[146] [L = HC(CMeNAr)$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$] with SnF$_2$ or LSnCl with Me$_3$SnF.[147] From the first reaction we cannot get the desired product, and in the second case there is no complete conversion to the target product, even under different conditions. Thus LSnF (**1**) was prepared from the reaction of LSnMe and LSnN(SiMe$_3$)$_2$ respectively with Me$_3$SnF in toluene. The reaction of one equiv of *β*-diketiminate lithium salt LLi(OEt$_2$) [L = HC(CMeNAr)$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$] with either GeBr$_2$, SnBr$_2$, or SnI$_2$ in diethyl ether affords the synthetically useful monomeric *β*-diketiminate-metal halides LGeBr (**2**), LSnBr (**3**), and LSnI (**4**) respectively.

2.1. Synthesis of Tin(II) Fluoride

Generally organotin(IV) fluorides are prepared by the substitution of chloride with KF in the presence of a phase transfer catalyst.[55-58] Therefore the known compound LSnCl was used as a precursor. Compound LSnCl is soluble in common organic solvents. A complete reaction of LSnCl with Me$_3$SnF in toluene even after refluxing for several days was not observed, although LGeF was obtained by the reaction of LGeCl with Me$_3$SnF.[28] Consequently we changed the method for the preparation of compound LSnF. It is well known that Me$_4$Sn and Cl$_4$Sn dependent on the molecular ratio and temperature show metathesis and give in high yield Me$_3$SnCl, Me$_2$SnCl$_2$, and MeSnCl$_3$ respectively.[148, 149] The question was whether it is possible to apply this type of reaction to Me–Sn(II) and F–Sn(IV) species. It was therefore reasonable to prepare LSnMe from LSnCl with MeLi. Furthermore we prepared LSnN(SiMe$_3$)$_2$ and studied the reaction with Me$_3$SnF. Treatment of LSnMe with Me$_3$SnF in toluene at room temperature, refluxing the suspension for 3 h afforded the corresponding fluoride LSnF (**1**) in high yield (85 %) (Scheme 2.1).
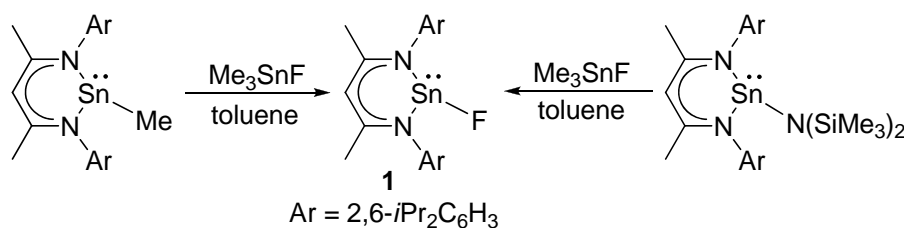
Scheme 2.1. Preparation of compound **1**

Compound **1** is thermally stable. No decomposition was observed at temperature below the corresponding melting point (130 $^{\circ}$C) under an inert atmosphere. Compound **1** is also obtained by treating LSnN(SiMe$_3$)$_2$ with Me$_3$SnF under the same conditions (Scheme 2.1). Compound **1** is a white solid that is soluble in benzene, toluene, *n*-hexane, and THF, in contrast to the fluorinating agent Me$_3$SnF, which is only slightly soluble in these solvents. **1** was characterized by multinuclear NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The ^{1}H NMR spectrum of compound **1** shows a singlet (δ 4.99 ppm) for the γ-CH proton and two septets (δ 3.84 and 3.09 ppm) corresponding to the two different types of C*H* protons of the *i*Pr moieties. Also, the complete disappearance of the resonance arising from Sn–C*H*$_3$ (δ 0.59 ppm) in LSnMe and the resonance arising from Sn–N(Si(C*H*$_3$)$_3$)$_2$ (δ 0.46 and 0.24 ppm) in LSnN(SiMe$_3$)$_2$ clearly indicates the formation of compound **1**. The ^{19}F NMR spectrum of **1** shows a singlet at -125.29 ppm, which is comparable with the analogues terminal ^{19}F NMR resonance for LGeF (δ -113 ppm).[28] Also the ^{119}Sn NMR spectrum exhibits a doublet resonance (δ -371.52 ppm). This value is very much different from the precursor LSnMe (δ 192.65 ppm), but this was expected when compared with that of compound LSnCl (δ -224 ppm). The Sn–F coupling constant of $J(^{119}\text{Sn}{-}^{19}\text{F}) = 3100$ Hz, is quite large, when compared with the previously reported Sn–F coupling constant.[51] EI-MS of **1** gave the corresponding monomeric molecular ion peak M$^+$.
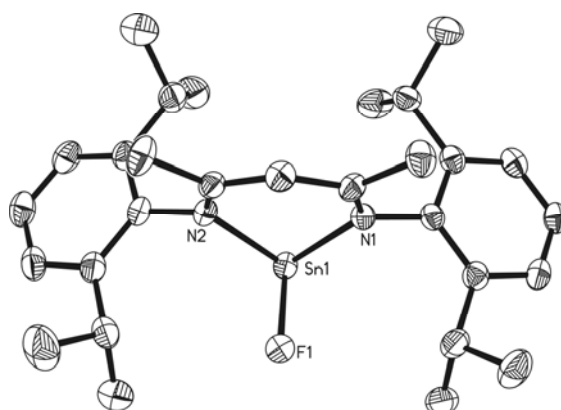
Figure 2.1. Molecular structure of **1**. Selected bond lengths [Å] and angles [°]; anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity: Sn1–F1 1.988(2), Sn1–N1 2.178(3), N1–C13 1.333(4); N1–Sn1–F1 90.26(9), N2–Sn1–F1 90.20(9), N1–Sn1–N2 86.22(10).

The molecular structure of **1** has been determined by single crystal X-ray diffraction analysis (Figure 2.1) which demonstrates that the complex exists as a monomer. Colorless crystals of **1** suitable for single crystal X-ray analysis were obtained from a *n*-hexane solution at -30 $^{\circ}$C after one day. Compound **1** crystallizes in the monoclinic space group *P*2$_1$/*c*, with one monomer in the asymmetric unit. The coordination polyhedron around the tin atom features a distorted tetrahedral geometry with one lone pair. The sum of angles around the tin atom is 266.68°. The terminal Sn–F bond distance (1.988 Å) in **1** is quite short when compared with that of the bridging one of Sn–F–Sn (2.156 Å).[51]

2.2. Synthesis of Germanium(II) and Tin(II) Bromides

Reaction of the *β*-diketiminato lithium salt LLi(OEt$_2$) with GeBr$_2$ and SnBr$_2$ in diethyl ether provided the monomeric compounds LMBr (M = Ge, (**2**); M = Sn, (**3**)) with three-coordinate metal centers (Scheme 2.2).

$$\text{M=Ge, X=Br (\textbf{2})}$$
$$\text{M=Sn, X=Br (\textbf{3})}$$
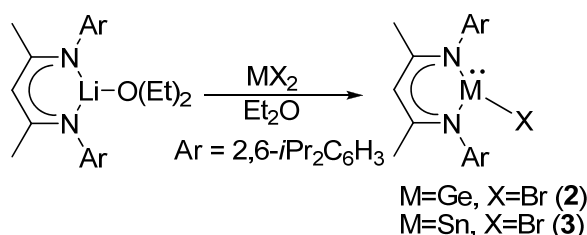
Scheme 2.2. Preparation of compounds **2** and **3**

2 and **3** are well soluble in common organic solvents, including benzene, THF, *n*-hexane, and *n*-pentane. **2** and **3** are characterized by NMR spectroscopy, EI-mass spectrometry, and elemental analysis. The ^{119}Sn NMR of **3** exhibits a singlet at -180.47 ppm (see Table 2.1).

The molecular structures of **2** and **3** are shown in Figures 2.2 and 2.3. The X-ray single-crystal structures of **2** and **3** show that all compounds are monomeric. The metal centers adopt similar three-coordinate sites and reside in a distorted-tetrahedral environment with one vertex occupied by a electron lone pair. The structural feature of compounds **2** and **3** is similar to the corresponding chloro derivative.[146] In compounds **2** and **3** the backbone of the chelating ligand is essentially planar and the metal atom is arranged out of the plane (23.5° in **2** and 23.7° in **3**). However the bond angle of N(1)–Ge(1)–N(2) (90.80(6)$^{\circ}$) in **2** is larger than the corresponding angle in **3** (N(1)–Sn(1)–N(2) 85.33(5)$^{\circ}$), and the bond length of N–Ge (1.9824(14) and 1.9934(14) Å) in **2** is slightly shorter than the corresponging N–Sn bond length in **3** (2.1758(13) and 2.1883(13) Å), as expected. This indicates that the ionic

interactions of the central metal atom with the ligand decrease from Ge to Sn due to the difference of the atomic radii (Ge(II) 0.93 Å, Sn(II) 1.12 Å).
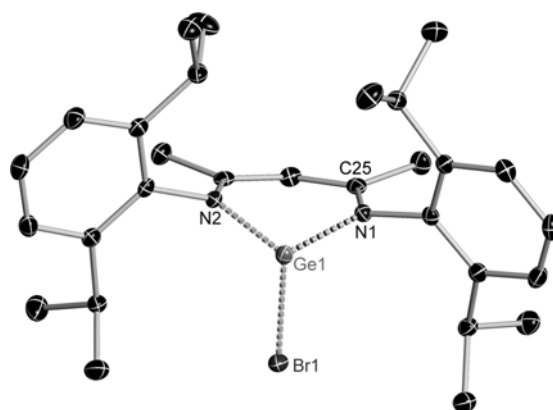
Figure 2.2. Molecular structure of **2**. Anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–Br1 2.5064(3), Ge1–N1 1.9934(14), N1–C25 1.326(2); N1–Ge1–N2 90.80(6), N1–Ge1–Br1 92.58(4), Ge1–N1–C25 124.91(11).
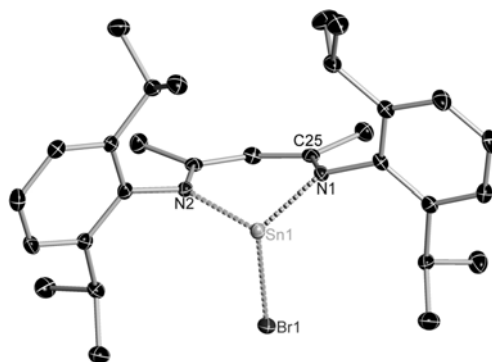
Figure 2.3. Molecular structure of **3**. Anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–Br1 2.6373(2), Sn1–N1 2.1758(13), N1–C25 1.337(2); N1–Sn1–N2 85.33(5), N1–Sn1–Br1 93.35(3), Sn1–N1–C25 123.82(10).

2.3. Synthesis of Tin(II) Iodide

The reaction of the β-diketiminato lithium salt LLi(OEt$_2$) with SnI$_2$ in diethyl ether provided the monomeric complex LSnI (**4**), (Scheme 2.3). Maintaing a diethyl ether solution of **4** for one day at -32 °C resulted in colorless crystals suitable for X-ray structural analysis. Compound **4** crystallizes in the triclinic space group *P*-1, with one monomer in the asymmetric unit. The coordination environment of the central Sn atom exhibits a distorted tetrahedral geometry.
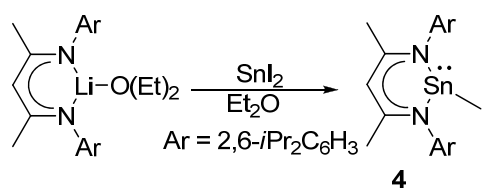
Scheme 2.3. Preparation of compound **4**

For **4**, two separate domains in the diffraction pattern were identified and integrated. The structure was refined as non-merohedrally twinned (BASF = 0.228). Therefore a discussion of selected bond lengths or angles is not carried out.
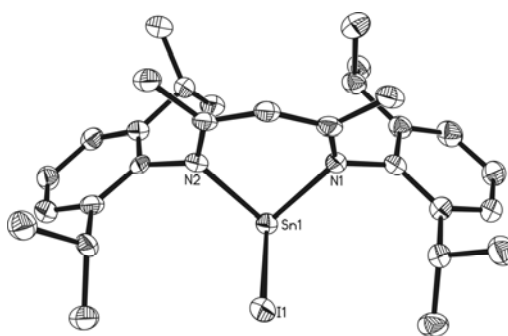
Figure 2.4. Molecular structure of **4**

In the ^{119}Sn NMR spectrum the resonance of compound **4** arises at δ -107.33 ppm, which is very different from that of the terphenyl tin(II)iodide 2,6-Trip$_2$C$_6$H$_3$SnI, Trip = 2,4,6-iPr$_3$C$_6$H$_2$; (δ 1140 ppm).[150] The different chemical shifts might be due to the different coordination environment around both the tin(II) atoms. In Table 2.1 we summarise the ^{119}Sn NMR data of all four halogen derivatives of tin(II) compounds with the same β-diketiminate ligand. These data are in the expected range for the high field fluorine compound and low field iodine derivative.

Table 2.1. ^{119}Sn NMR data of Sn(II) compounds

Compound*	^{119}Sn NMR (δ, ppm)
LSnF (**1**)	-371.52
LSnCl	-224
LSnBr (**3**)	-180.47
LSnI (**4**)	-107.33

* L = HC(CMeNAr)$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Chapter 3

Germanium(II) Hydride an Effective Reagent for Hydrogermylation Reactions

Metal hydrides and their complexes are considered valuable synthons in chemistry. It was demonstrated that main-group and transition-metal hydrides are important intermediates in some industrial processes and also function as catalysts.[59-67] Furthermore, in the quest for alternative energy sources, metal hydrides have been considered as potential feedstocks for hydrogen storage.[68-71] In recent years the chemistry of stable heteroleptic metal hydrides has attracted much attention due to their versatile reactivity.[72, 151, 152] In comparison with main group hydrides the chemistry of transition metal hydrides is well documented.[153] Organometallic hydrides of group 14 play an important role in various metathesis reactions and therefore the reactivity of hydrides like R_3SiH, R_3GeH, and R_3SnH are well studied.[154] Till now there is no reaction reported using germanium(II) hydride for hydrogenation reactions. The main reason for this imbalance is the synthetic difficulty and the stability of these low valent group 14 hydrides. In 2001 our group reported the first four coordinate monomeric germanium(II) hydride which exists as an adduct with the Lewis acid BH_3.[28] In 2003 *Power et al*. reported the first isomeric germanium(II) hydride with a bulky aryl ligand.[81] Recently, our group first published the molecular structure of the unique stable three coordinate germanium(II) hydride, LGeH, [L = HC(CMeNAr)$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$]; (**5**) with the bulky *β*-diketiminate ligand.[79] The corresponding carbon and silicon analogues are not reported yet. The unusual species LGeH (**5**) led us to explore the reactivity pattern of the germylene hydrogen bond. Herein, we report the first reaction of LGeH (**5**) with carbon dioxide, ketones, alkines, diazene, nitrous oxide, elemental sulfur, trimethylsilyl azide, and frustrated carbene borane Lewis pair respectively. To our surprise the formal oxidation state (II) at the germanium atom persists during the transfer of the hydrogen and germanium moiety from LGeH (**5**) to the corresponding carbon oxygen double bond and to the carbon carbon triple bond for the case of compounds with carbonyl group and alkine group respectively.

3.1. Germylene Hydride Starting Material

Initially we reported the synthesis of germanium(II) hydride, LGeH (**5**) from the reaction of the corresponding germanium(II) chloride, LGeCl[146] with one equiv of AlH$_3$·NMe$_3$[155] in toluene.[79] Preparation of **5** by using AlH$_3$·NMe$_3$ resulted in the formation of the expected product contaminated with small amounts of the starting material LGeCl. This slightly

impure LGeH (**5**) leads to products containing chlorine, when it was used in hydrogermylation reactions. Therefore the method of preparation had to be improved. Treatment of LGeCl with potassium trisecbutylborohydride (K[HB(*sec*Bu)$_3$]) in toluene at – 10 $^\circ$C afforded the germanium(II) hydride (**5**) in high yield (82 %) (Scheme 3.1). The crude reaction product was recrystallized from *n*-hexane and obtained as pure red crystals which were investigated by ^{1}H NMR spectroscopy and well matches with the previously reported data.[79]
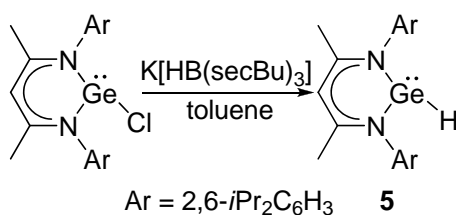
Scheme 3.1. Preparation of compound **5**

3.2. Reaction with Carbon Dioxide

Reactions of metal hydrides with carbon dioxide to generate the metal formates are quite well known for transition metal hydrides and alkali metal hydrides.[156] For group 14 metal hydrides there are only a few reports on the hydrogenation of carbon dioxide using silicon(IV) hydride and tin(IV) hydride, respectively.[157, 158] The reaction of carbon dioxide and silicon(IV) hydride requires a transition metal catalyst.[157(a)] To the best of our knowledge there are no reports on the hydrogenation of carbon dioxide using low valent group 14 metal hydrides. Herein, we report on the synthesis of the germylene ester of formic acid LGe–O–C(O)H (**6**) by the reaction of **5** with carbon dioxide at room temperature without any catalyst in quantitative yield (Scheme 3.2).
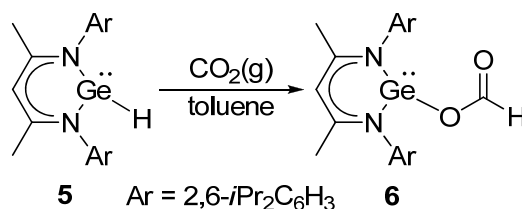
Scheme 3.2. Preparation of compound **6**

6 is a yellow solid, soluble in benzene, THF, *n*-hexane, and *n*-pentane and shows no decomposition on exposure to air. The compound was thoroughly characterized by ^{1}H NMR spectroscopy, IR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The ^{1}H NMR spectrum of **6** exhibits a singlet (δ 8.64 ppm) which can be assigned to the C*H* proton. Moreover, the ^{1}H NMR spectrum shows a singlet (δ 5.06 ppm) for the γ-C*H* proton and two septets (δ 3.53 and 3.08 ppm) corresponding to the two different C*H* protons of the *i*Pr moieties. The complete absence of the resonance (δ 8.08 ppm) arising from the hydride proton in LGeH (**5**) clearly indicates the formation of **6**. The IR spectrum shows two bands at 2854 and 1690 cm^{-1}, which are assigned to the C–H and C=O stretching frequencies.

Colorless crystals of **6** can be obtained after storage of a saturated *n*-hexane solution at –32 ^{o}C for one day. **6** crystallizes in the triclinic space group *P*-1 with one monomer in the asymmetric unit. The coordination polyhedron around the germanium atom features a distorted tetrahedral geometry with a stereochemical active lone pair (Figure 3.1).
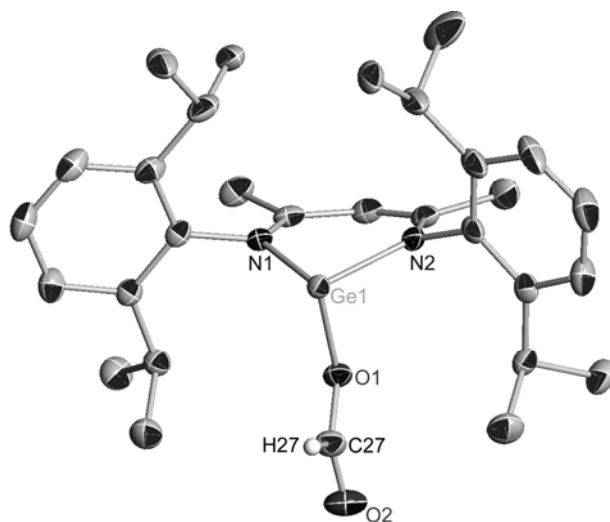
Figure 3.1. Anisotropic displacement parameters, depicted at the 50 % probability level of **6**. Hydrogen atoms except that for the C(O)H group are omitted for clarity. Two of the *i*Pr-groups are disordered. Selected bond lengths [Å] and angles [°]: Ge1–O1 1.9339(18), O1–C27 1.304(3), C27–O2 1.204(3), Ge1–N1 1.969(2), Ge1–N2 1.968(2); Ge1–O1–C27 120.07(17), O1–C27–O2 125.1(3), N2–Ge1–N2 91.34(9).

3.3. Reactions with Ketones

LGeH reacts with carbon dioxide, therefore we thought that it can react with other carbonyl compounds, which might generate the germanium(II)alkoxide by nucleophilic addition reaction to the carbon oxygen double bond. Although **5** displayed no reactivity toward

acetone or benzophenone at room temperature, it reacts cleanly with activated ketones namely 2,2,2-trifluoro acetophenone and 2,2,2-trifluoroacetothiophane. Treatment of **5** with 2,2,2-trifluoro acetophenone and 2,2,2-trifluoroacetothiophane leads quantitatively to the germylene alkoxides **7** and **8** respectively with a Ge(II)-O-CH framework that is formed by nucleophilic hydride addition to the respective carbon of the carbonyl group (Scheme 3.3). Compounds **7** and **8** were monitored by ^{1}H NMR spectra. Sharp resonances in the ^{1}H NMR spectra of **7** and **8** gave the initial indication that the products have been formed in high yield. Compounds **7** and **8** have one CF_3 group each and both display an interesting NMR spectrum. The ^{1}H NMR spectra of **7** and **8** exhibit a quartet each (δ 4.73 and 5.04 ppm) which corresponds to the quaternary C*H* proton and its coupling with the three F-atoms
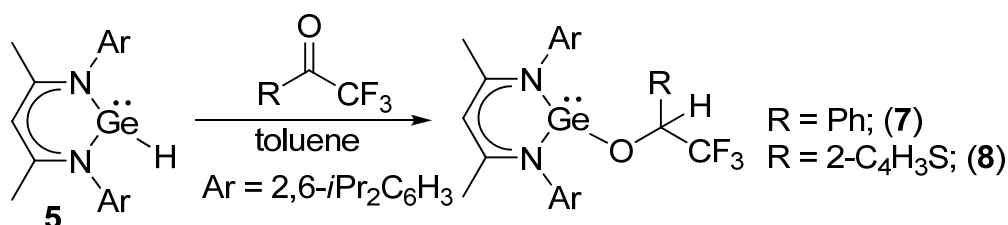
Scheme 3.3. Preparation of compounds **7** and **8**

of the CF_3 group ($^3J(^{19}$F-^{1}H) = 8 and 7 Hz respectively). The ^{19}F NMR resonance arises as a doublet (δ -75.76 (**7**) and -76.29 (**8**) ppm) with the same coupling constant of 8 and 7 Hz respectively. The four isopropyl groups of **7** and **8** are showing four different resonances, and even the two methyl groups in the backbone exhibit two different signals each in the ^{1}H NMR spectra.

Single crystals of **7** and **8** suitable for X-ray structural analysis were obtained from *n*-hexane solutions. **7** and **8** crystallize in the triclinic space group *P*-1 and monoclinic space group *P*2$_1$/*c* respectively. The molecular structures of **7** and **8** are shown in Figures 3.2 and 3.3. The asymmetric unit of **7** and **8** contains one formula unit of the compound, and there are two of the molecules in each unit cell. As predicted, based on the ^{1}H NMR spectrum and EI mass spectrum, compounds **7** and **8** contain a Ge(II)-O-CH core. The three coordinate germanium atom is surrounded by two N atoms of the *β*-diketiminato ligand, and an exocyclic O atom. The Ge-O bond lengths (1.862(3) Å, 1.855(2) Å) are shorter when compared with that of

compound **6**, LGeOC(O)H (1.9339(18) Å). The O-C bond distances of **7** and **8** are in a narrow range to each other (1.407 Å and 1.417 Å).
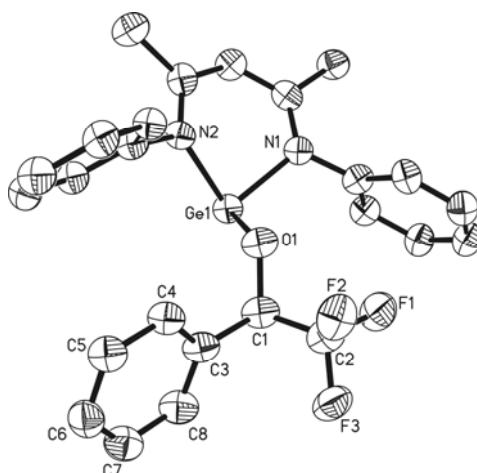
Figure 3.2. Molecular structure of **7**. Anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]; Ge1–O1 1.862(3), Ge1–N1 2.002(4), O1–C1 1.407(6); N1–Ge1–N2 88.77(15), N1–Ge1–O1 97.52(15), Ge1–O1–C1 112.8(3).
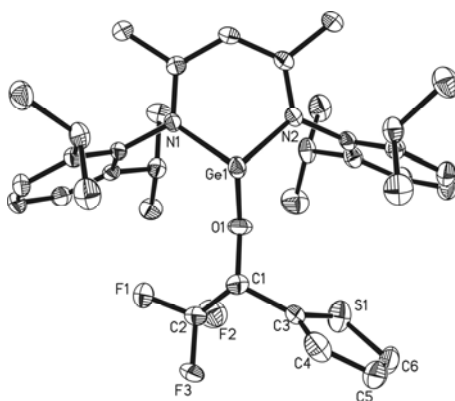
Figure 3.3. Molecular structure of **8**. Anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]; Ge1–O1 1.855(2), Ge1–N1 2.011(3), O1–C1 1.417(4); N1–Ge1–N2 88.45(11), N1–Ge1–O1 96.69(11), Ge1–O1–C1 112.8(2).

3.4. Reactions with Compounds Containing C≡C Triple Bonds

The hydrogenation of unsaturated hydrocarbon compounds with Ge(IV)–H reagents give a variety of acyclic and cyclic carbon-functionalized germanium compounds.[159] Due to the variable polarity of the Ge–H bond, various catalysts have been used in hydrogermane reactions to initiate different path ways.[160] Herein, we report hydrogermylation reactions of alkines using germanium(II) hydride without any catalyst. The germanium(II) hydride (**5**) reacts with the alkines HC≡CCO$_2$Me, HC≡CCO$_2$Et, MeO$_2$CC≡CCO$_2$Me, EtO$_2$CC≡CCO$_2$Et,

and tBuO$_2$CC≡CCO$_2$$t$Bu at room temperature to form germanium(II) substituted alkenes **9, 10, 11, 12,** and **13**. Compounds **9** and **10** are obtained by the 1,2-addition of germylene hydride (**5**) to the alkine methyl and ethyl propiolate and the result is the transfer of the hydrogen atom and germylene across the carbon carbon triple bond (Scheme 3.4), rather than the elimination of H$_2$ due to the different polarized Ge–H and C–H bonds.

$$R = H, R' = Me; (\mathbf{9})$$
$$R = H, R' = Et; (\mathbf{10})$$
$$R = CO_2Me, R' = Me; (\mathbf{11})$$
$$R = CO_2Et, R' = Et; (\mathbf{12})$$
$$R = CO_2tBu, R' = {}^tBu; (\mathbf{13})$$

Ar = 2,6-iPr$_2$C$_6$H$_3$

Scheme 3.4. Preparation of compounds **9, 10, 11, 12,** and **13**

The ^{1}H NMR spectra of **9** and **10** each exhibit two broad resonances (δ 6.20 and 5.82 ppm for **9** and δ 6.25 and 5.85 ppm for **10**) which corresponds to the two alkenyl protons. Moreover, the ^{1}H NMR spectrum of **10** shows a quartet and a triplet resonance (δ 4.07 and 0.87 ppm) corresponding to the two different types of CH protons of the ethyl moieties. The IR spectrum of **10** exhibits bands at 3379 and 1723 cm^{-1}, which are assigned to the C–H and C=O stretching frequencies.

Figure 3.4. Anisotropic displacement parameters, depicted at the 50 % probability level of **10**. Hydrogen atoms except that for the CH$_2$ group are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–C31 2.033(3), C30–C31 1.324(4), C31–C32 1.491(4), C32–O1 1.200(4), C32–O2 1.337(4), Ge1–N1 2.002(2), Ge1–N2 1.994(2); Ge1–C31–C32 130.5(2), C31–C32–O1 126.6(3), C31–C32–O2 111.2(2), N1–Ge1–N2 91.65(9).

Compound **10** crystallizes in the monoclinic space group *P*2$_1$/*c,* with one monomer in the asymmetric unit. Single crystals were obtained from a saturated *n*-hexane solution at −32 °C after two days. The coordination polyhedron around the germanium atom features a distorted tetrahedral geometry with a stereochemical active lone pair (Figure 3.4).

Furthermore we were interested in the selectivity of the addition across the carbon carbon triple bond. Therefore we selected the disubstituted alkines, dimethyl acetylenedicarboxylate, diethyl acetylenedicarboxylate, and ditertiarybutyl acetylenedicarboxylate. **5** reacts with dialkyl acetylenedicarboxylate, (RO$_2$CC≡CCO$_2$R, R = Me, Et, and *t*Bu) in toluene at room temperature to form only the isomer with *E*-germylene substituted alkene (Scheme 3.4). This was confirmed by ^{1}H NMR in solution. The ^{1}H NMR spectrum shows a singlet resonance (*δ* 6.64, 6.68, and 6.65 ppm) which corresponds to the alkenyl protons of the germylene substituted alkenes **11, 12,** and **13**, respectively. In addition these compounds exhibit a resonance at 4.89, 4.91, and 4.96 ppm for the *γ*-C*H* proton. Furthermore **11, 12,** and **13** were characterized by X-ray structural analysis (Figures 3.5, 3.6, and 3.7). **11** crystallizes in the monoclinic space group *P*2$_1$/*n,* with one monomer in the asymmetric unit from saturated *n*-hexane solution at −32 °C after one day (Figure 3.5). In the solid state also the *E*- form is the only isomer that was observed.

Figure 3.5. Anisotropic displacement parameters, depicted at the 50 % probability level of **11**. Hydrogen atoms except that for the CH group are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–C30 2.1093(14), C30–C31 1.340(2), C30–C34 1.4920(19), C34–O1 1.3415(17), C34–O2 1.2131(18), Ge1–N1 2.0060(12), Ge1–N2 2.0190(12); Ge1–C30–C31 122.99(11), Ge1–C30–C34 123.07(10), C30–C34–O1 112.53(12), C30–C34–O2 124.28(13), N1–Ge1–N2 90.78(5).

Compounds **12** and **13** crystallizes in the monoclinic space group $P2_1/c$ and $P2_1/n$ respectively (Figures 3.6 and 3.7). The coordination polyhedron around the germanium atom features a distorted tetrahedral geometry with one lone pair.

Figure 3.6. Molecular structure of **12**. Anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]; Ge1–C5 2.1083(18), Ge1–N1 2.0177(15), C4–C5 1.338(3); N1–Ge1–N2 91.07(6), N1–Ge1–C5 92.07(6), Ge1–C5–C4 122.03(14).

Figure 3.7. Anisotropic displacement parameters, depicted at the 50 % probability level of **13**. Hydrogen atoms except that for the CH group are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–C30 2.1060(16), C30–C31 1.340(2), C30–C37 1.500(2), C37–O3 1.2095(18), C37–O4 1.3491(18), Ge1–N1 2.0133(13), Ge1–N2 2.0175(13); Ge1–C30–C37 126.25(11), Ge1–C30–C31 121.37(11), C30–C37–O3 124.51(14), C30–C37–O4 110.68(12), N1–Ge1–N2 90.73(5).

3.5. Reactions with a Compound Containing a N=N Double Bond

Furthermore we performed the reaction of **5** with nitrogen nitrogen double bonded compound namely, diethyl azodicarboxylate (DEAD) to complete the reactivity pattern of LGeH (**5**) (Scheme 3.5). This reaction proceeds rapidly at room temperature under oxidative addition to give compound **14** in high yield.

Scheme 3.5. Preparation of compound **14**

Figure 3.8. Molecular structure of **14**. Thermal elipsoids are shown at 50% probability. H atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Ge1–N1 2.009(2), Ge1–N3 1.990(2), N3–N4 1.418(14), N1–Ge1–N2 90.94(9), N1–Ge1–N3 98.93(9).

Compound **14** crystallizes in the monoclinic space group $P2_1/n$, with one monomer in the asymmetric unit. Single crystals were obtained from a saturated *n*-hexane solution at −32 °C after three days (Figure 3.8). In the solid state the *E*- form is the only isomer that was observed. The IR spectrum exhibits bands at 3245 and 1752 cm^{-1}, which are assigned to the N–H and C=O stretching frequencies.

3.6. Reactions with Nitrous Oxide

Compounds with multiple bonds between elements of group 14 and group 16 are known.[161] They are generally formed by the reaction of compounds with low valent

group 14 elements with a chalcogen source. It is well known that nitrous oxide acts as a mono oxygen source. It can supply the oxygen to the low valent metal center or to the metal-metal bond to generate metal oxygen compounds.[162, 163] However there is no reaction known of group 14 metal hydride with nitrous oxide to form the metal hydroxide. Herein we describe the reaction of **5** with nitrous oxide with formation of LGeOH (**15**) in almost quantitative yield (Scheme 3.6). There is no indication of formation of LGe(O)H or LGe(O)OH even after a longer reaction time with nitrous oxide. Compound **15** was previously reported by our group by the reaction of LGeCl with water in the presence of 1,3-di(2,4,6-Me$_3$C$_6$H$_2$)-2-ylidene.[127]

Scheme 3.6. Preparation of compound **15**

3.7. Reactions with Elemental Sulfur

The insertion of elemental sulfur into the metal hydride bond or oxidative addition to a low valent metal center in the presence of transition metal catalysts is quite well known.[164] In contrast, there are no reactions reported where germanium hydrides were used for the formation of germanium thiols by insertion of elemental sulfur. However, there are some reports on the preparation of germanium thiol using other routes.[165] There are some additional reports of the synthesis of silane thiols by insertion of elemental sulfur into Si–H bonds.[166] The oxidative addition of elemental sulfur to germanium(II) atom is known.[167] Herein, we report the simultaneous insertion and addition of elemental sulfur into the germylene hydrogen bond and to the germylene atom, respectively, at room temperature without any catalyst. The resulting compound **16** is the germanium analogue of dithio carboxylic acid with a Ge(S)SH moiety. To the best of our knowledge, there are only five further crystal structures deposited in the *Cambridge Crystallographic Database*[168] with a Ge–S–H unit and only one derivative that contains a bridging Ge(S)SH moiety of composition [Dmp(Dep)Ge(μ-S)(μ-SH)Ru(PPh$_3$)]OTf.[169] Therefore compound **16** is the first example of a dithio carboxylic acid with a heavier group 14 element and a terminal SH bond.

The reaction of **5** in the presence of two equivalents of elemental sulfur at room temperature in toluene after 0.5 h leads to the white compound **16** in a moderate yield (60 %) (Scheme 3.7).

Scheme 3.7. Preparation of compound **16**

16 is a colorless solid soluble in benzene, THF, *n*-hexane, and *n*-pentane, respectively and shows no decomposition on exposure to dry air. **16** was characterized by ^{1}H NMR and IR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The ^{1}H NMR spectrum of **16** showed a singlet (δ –0.1 ppm) which can be assigned to the SH proton by comparison with the Al–SH analogue.[170] The IR spectrum exhibited a weak band at 2590 cm^{-1}, and it is lower in wave numbers than the literature data for H_2S(g) (2615 cm^{-1}).[171]

Maintaining a toluene solution of **16** for two days at –32 °C resulted in colorless single crystals suitable for X-ray structural analysis. **16** crystallizes in the monoclinic space group $P2_1/n$, with one molecule of **16** and one solvent molecule of toluene in the asymmetric unit. **16** exists as a monomer in the solid state (Figure 3.9). There are no intermolecular hydrogen bonds observed in the crystal lattice. The coordination polyhedron around the germanium atom comprises two nitrogen atoms from the supporting ligand, one mercapto group, and one sulfur atom, featuring a distorted tetrahedral geometry. The Ge–N bond lengths and N–Ge–N angle are 1.9110(10), 1.9157(10) Å, and 95.79(4)°, respectively. The comparisons of Ge–N bond lengths in **5-8, 10-15** with those of **16** are quite different due to the different oxidation states of the germanium atoms.

Figure 3.9. Anisotropic displacement parameters, depicted at the 50 % probability level of **16**. One toluene molecule and hydrogen atoms except that for the SH group are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–S1 2.2422(4), Ge1–S2 2.0641(4), Ge1–N1 1.9157(10), Ge1–N2 1.9111(10); S1–Ge1–S2 119.485(16), S1–Ge1–N1 100.66(3), S2–Ge1–N2 116.10(3).

No evidence was found for any tautomeric equilibrium of **16** and consequently the two Ge–S bond lengths are very different with 2.0641(4) and 2.2421(4) Å. The shorter one (Ge1–S2) shows a good agreement with the reported Ge=S bond lengths in [{HC(CMeNAr)$_2$}Ge(S)X] (X = Cl, F,)[172] (2.053(6), and 2.050(9) Å respectively), and can therefore be assigned to a formal double bond. Also the Ge1–S1 bond length is comparable with that previously reported for the Ge–SH moiety.[173]

The formation of **16** requires the oxidation of germanium(II) to germanium(IV). Therefore the synthesis of **16** also involves an unprecedented oxidative addition-insertion of elemental sulfur into the Ge(II)–H bond, which leads to the formal conversion of the GeH hydride to a SH proton. We assume that the first step of the reaction necessitates the intermediate LGe(II)SH, which can result from an insertion of sulfur into the germanium(II) hydride bond. The next step is the oxidative addition of elemental sulfur to LGe(II)SH. That leads to a concomitant LGe(S)SH formation. Alternatively it may be possible that first an oxidative addition of elemental sulfur to LGe(II)H might occur with the formation of LGe(S)H. The insertion of sulfur into the Ge–H bond leads then to an oxidation of the hydride to a proton under reduction of the sulfur to sulfide. The recently isolated LGe(II)OH supports as a first step the insertion of sulfur rather than the oxidation of germanium. Surprisingly there is no

precedent reaction of group 14 known where sulfur is added and inserted simultaneously at the same element. We were not able to isolate any intermediate of this reaction.

3.8. Reaction with Trimethylsilyl Azide

In 2005 our group reported the first end-on azide insertion into an Al-C bond of an aluminacyclopropene and the formation of aluminaazacyclobutene.[174] Subsequently we became interested in studying the reactivity of **5** with trimethylsilyl azide. Therefore we expected that the azide might also insert end-on into the germanium-hydrogen bond of **5**. However the reaction of **5** with trimethylsilyl azide at room temperature afforded two products in a ratio of 3:1 (Scheme 3.8).

Scheme 3.8. Preparation of compounds **17** and **18**

One is the germanium(II) azide (**17**), and the other is the germanium(IV) diamide (**18**). Compound **17** was formed by metathesis reaction of **5** with Me_3SiN_3 under elimination of Me_3SiH. Silicon(IV) and tin(IV) azides have been reported to be versatile reagents in main-group element chemistry[175] and in organic synthesis.[176] In comparison, studies on germanium(IV) azides are still limited[177] and for germanium(II) azides are to our knowledge only two compounds are known,[178, 179] probably due to their propensity to decompose to germanium(IV) nitrides. These two germanium(II) azides are prepared by nucleophilic substitution reactions using NaN_3 and germanium(II) chloride precursors. Whereas **18** was formed by elimination of dinitrogen from azide, the resulting intermediate nitrene inserts into the germanium-hydrogen bond. The final oxidative addition of another nitrene is followed by simultaneous hydrogen transfer from one methyl group, which is attached to the heterocyclic ring backbone. A few reactions of group 14 compounds with divalent elements and organic azides have been reported.[180] The initial dinitrogen elimination from Me_3SiN_3 is generally accepted, and supported by experimental observations.[181, 182]

The formation of the imide LGe(F)NSiMe$_3$ was observed by elimination of dinitrogen from Me$_3$SiN$_3$ followed by oxidative addition to the germanium(II) center of LGeF,[28] whereas the LGeMe reacted with Me$_3$SiN$_3$ under dinitrogen elimination, oxidative addition, followed by intramolecular hydrogen transfer from one methyl group of the backbone to yield L′Ge(Me)NHSiMe$_3$.[29] Subsequently we propose a reasonable pathway for the formation of **16** (Scheme 3.9).

$$LGeH \xrightarrow[-N_2]{Me_3SiN_3} LGe(H)NSiMe_3 \underset{}{\overset{1,2\text{-H-shift}}{\rightleftharpoons}} LGeNHSiMe_3$$

L = HC(CMeNAr)$_2$; Ar = 2,6-iPr$_2$C$_6$H$_3$

L' = CH{(C=CH$_2$)(CMe)(NAr)$_2$}; Ar = 2,6-iPr$_2$C$_6$H$_3$
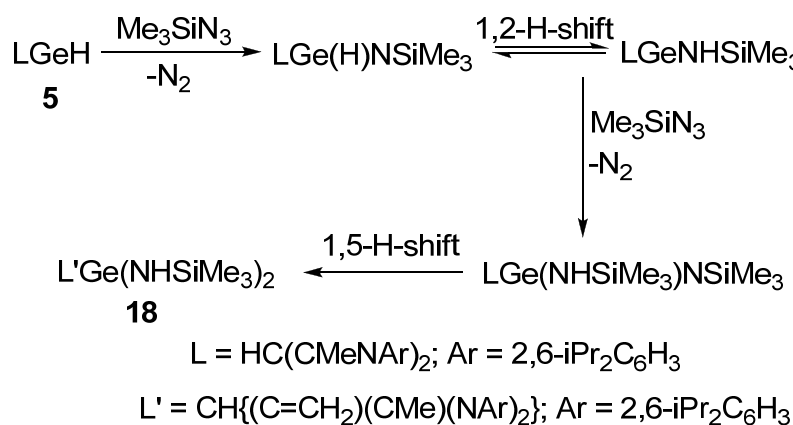
Scheme 3.9. Proposed pathway for the formation of **18**
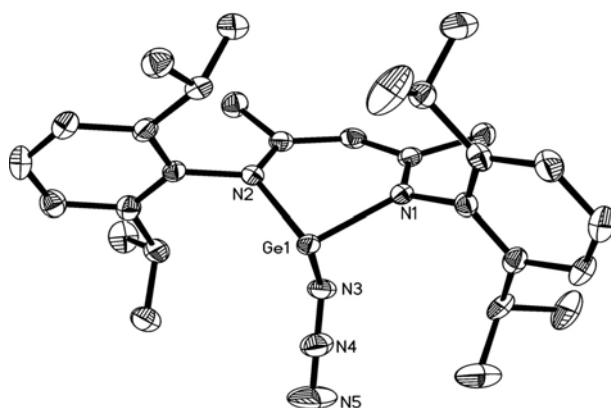
Figure 3.10. Molecular structure of **17**. Thermal ellipsoids are shown at 50% probability. H atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Ge1–N3 2.002(3), N3–N4 1.198(4), N4–N5 1.149(4), Ge1–N1 1.980(2), Ge1–N2 1.973(2); Ge1–N3–N4 121.5(3), N3–N4–N5 176.3(4), N1–Ge1–N2 90.69(11).

Compound **17** crystallizes in the triclinic space group *P*-1 from *n*-hexane. There are three independent molecules in the unit cell (Figure 3.10). The IR spectrum of **17** exhibits a band at 2068 cm^{-1}, which is assigned to the N$_3$ stretching frequency.

18 is a colorless solid soluble in benzene, THF, *n*-hexane, and *n*-pentane respectively and shows no decomposition on exposure to dry air. The ^{1}H NMR spectrum of **18** shows a singlet (δ 0.01 ppm), which can be assigned to the Si(CH_3)$_3$ protons. Maintaining an *n*-hexane solution of **18** for two days at –32 °C resulted in colorless single crystals suitable for X-ray structural analysis. **18** crystallizes in the monoclinic space group $P2_1/n$, with one molecule of **18** in the asymmetric unit. **18** exists as a monomer in the solid state (Figure 3.11). There are no intermolecular hydrogen bonds observed in the crystal lattice. The coordination polyhedron around the germanium atom comprises four nitrogen atoms, two from the supporting ligand, and two others from the amide groups, featuring a distorted tetrahedral geometry. The four Ge–N bond lengths are almost similar. The Ge–N bond lengths of **5** and **17** and those of **18** are quite different due to the non-equal oxidation states of the germanium atoms, and it is very much closer to the Ge–N bond lengths in compound **16**, due to the same oxidation state of the germanium atom.
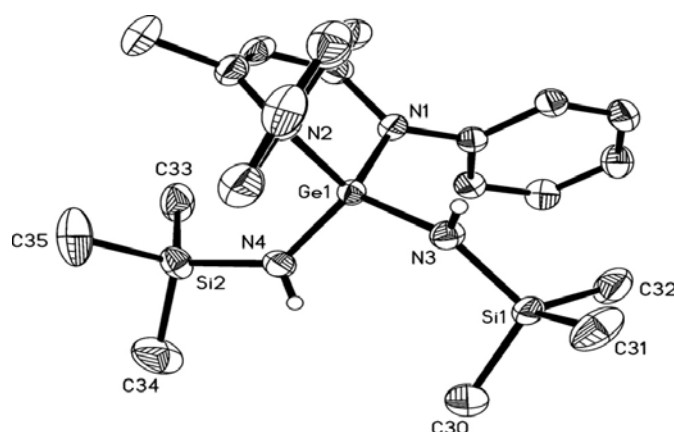
Figure 3.11. Molecular structure of **18**. Thermal ellipsoids are shown at 50% probability. H atoms except N3–H and N4–H and the *iso*-propyl groups are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.8416(14), Ge1–N2 1.8413(15), Ge1–N3 1.8011(14), Ge1–N4 1.8224(15); N1–Ge1–N2 101.59(6), N1–Ge1–N3 112.77(7), N3–Ge1–N4 111.24(8), N2–Ge1–N4 111.54(7).

The formation of **18** requires the oxidation of germanium(II) to germanium(IV). Therefore the synthesis of **18** also involves an unprecedented oxidative addition-insertion with nitrene (:NSiMe$_3$), which is formed in situ from trimethylsilyl azide by elimination of dinitrogen, and insertion into the Ge(II)–H bond, which leads to the formal conversion of the GeH hydride to a NH proton. Surprisingly there is no precedent reaction of group 14 known where nitrene is

added and inserted simultaneously at the same element. We were not able to isolate any intermediate of this reaction. No evidence was found for any tautomeric equilibrium of **18**.

3.9. Reactions with Frustrated Lewis Carbene-Borane Pair

The Lewis acid-base concept is fundamental for understanding numerous chemical reactions.[183] This principle is essential for main group elements as well as for transition metals.[53] In recent years, D. W. Stephan,[184] B. Rieger,[185] G. Erker,[186] and M. Tamm[187] were able to demonstrate that frustrated Lewis pairs of boranes, (in particular tris(pentafluorophenyl)borane, $B(C_6F_5)_3$),[188] in combination with sterically demanding phosphanes, amines, imines, and N-heterocyclic carbenes (NHCs), respectively, are excellent non-metallic systems for the activation of dihydrogen under mild conditions. NHCs and $B(C_6F_5)_3$ independently have also been employed for proton and hydride abstraction reactions.[145, 189] In compound **5**, the hydrogen atoms in the backbone methyl group are protonic hydrogen and the hydrogen atom at the germanium center are hydridic hydrogen. Therefore, it seemed possible that LGeH (**5**) might be dehydrogenated with a combination of Lewis NHC borane pair. In the literature dehydrogenation of alkanes is reported using transition metal catalyst.[190] Herein we report on the dehydrogenation of LGeH by a frustrated Lewis NHC borane pair under the formation of six-membered N-heterocyclic germylene L'Ge, [L' = CH{(C=CH_2)(CMe)(NAr)_2}; Ar = 2,6-*i*Pr_2C_6H_3]; (**19**).
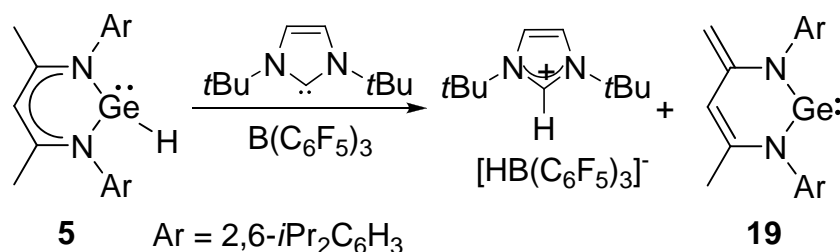
Scheme 3.10. Preparation of compoumd **19**

A toluene solution of equimolar amounts of **5** and of $B(C_6F_5)_3$ under stirring changed the color from red to colorless after a few minutes. To this reaction mixture we added an equivalent of 1,3-di-*tert*-butylimidazol-2-ylidene[191] and the reaction mixture immediately turned to brown-red with the formation of an insoluble white precipitate (Scheme 3.10). The latter was identified as imidazolium borate salt [(CHN*t*Bu)_2CH][HB(C_6F_5)_3][187] and was

recovered by filtration and dissolved in dichloromethane. The ^{1}H NMR spectrum indicates the formation of an imidazolium cation. The ^{11}B NMR resonance of borate salt at –25.3 ppm is identical with a previously reported imidazolium borate salt.[187] The soluble part of the reaction mixture was characterized to contain the heterocyclic germylene L′Ge (**19**), although there is no reaction between compound **5** and 1,3-di-*tert*-butylimidazol-2-ylidene.[191] Compound **19** was previously reported by *Driess et al.* by the reaction of LGeCl with LiN(SiMe$_3$)$_2$.[37]

Chapter 4

Hydrostannylation Reaction of LSnH with Unsaturated Molecules

In recent years the parent SnH_2 has been prepared and characterised in an argon matrix.[84] At elevated temperature SnH_2 changed to an insoluble solid of unknown structure. The terphenyl and β-diketiminate ligands have been used for the preparation of substituted tin(II) hydrides. The terphenyl derivatives show in the solid state dimeric structures,[80, 82] while the β-diketiminate moiety exhibits a terminal tin(II) hydride with very weak intermolecular interactions.[79] Until recently the reactions of organotin hydrides were based on tin(IV) precursor. Di- and triorganotin hydrides of composition R_2SnH_2 and R_3SnH with formal oxidation state of Sn(IV) show a rich variety of chemical transformations.[192] The preferred reagent of this class of compounds is the tributyltin hydride, and it is widely used as a reducing agent in organic and inorganic chemistry.[193] To the best of our knowledge there are no hydrostannylation reactions described using tin(II) hydride. Herein, we report the first hydrostannylation reactions of carbon dioxide, aldehydes, ketones, alkines, and carbodiimides with LSnH (**20**).

4.1. Stannylene Hydride Starting Material

Initially our group reported the synthesis of LSnH (**20**) from the reaction of the corresponding LSnCl,[146] with one equivalent of $AlH_3 \cdot NMe_3$[155] in toluene, just like the preparation of LGeH.[79] Preparation of **20** from $AlH_3 \cdot NMe_3$ resulted in the formation of the expected product contaminated with small amounts of the starting material LSnCl. This slightly impure LSnH leads to products containing chlorine, when it was used in hydrostannylation reactions. Furthermore this LSnH is unstable when contaminated with chlorine and decomposes in an inert glove box within four days. Therefore the method of preparation had to be changed. Treatment of LSnCl with potassium trisecbutylborohydride, (K[HB(*sec*Bu)₃]), in toluene at -10 °C afforded the tin(II) hydride LSnH (**20**) in high yield (Scheme 4.1).

Ar = 2,6-iPr$_2$C$_6$H$_3$ **20**
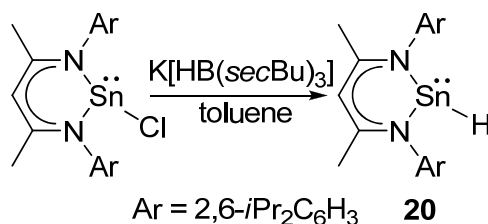
Scheme 4.1. Preparation of compound **20**

The crude reaction product was recrystallized from *n*-hexane and obtained as pure yellow crystals which were characterized by ^{1}H (δ 13.96 ppm) and ^{119}Sn (δ -4.45 ppm, $^1J(^{119}\text{Sn},^1\text{H}) =$ 64 Hz) NMR spectroscopy. The chemical shift for ^{119}Sn of **20** given in ref. [79] is that of LSnCl.

4.2. Reaction with Carbon Dioxide

Carbon dioxide is a readily accessible atmospheric gas that could be a useful feedstock for organic compounds.[194] The kinetic and thermodynamic stability of carbon dioxide present significant challenges in designing efficient chemical transformations. Herein, we report on the synthesis of a stannylene formate LSn–O–C(O)H (**21**), by the reaction of **20** with carbon dioxide at room temperature without any catalyst in quantitative yield (Scheme 4.2).
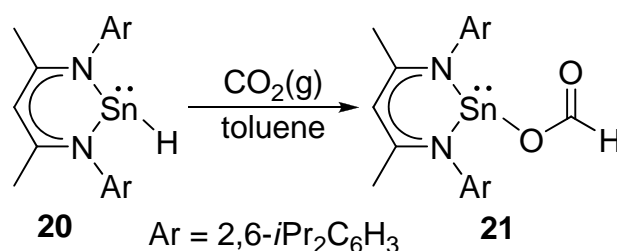
Scheme 4.2. Preparation of compound **21**

21 is a colorless solid, soluble in benzene, THF, *n*-hexane, and *n*-pentane and shows no decomposition on exposure to air. **21** was characterized by multinuclear NMR and IR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The ^{1}H NMR spectrum of **21** exhibits a singlet (δ 8.97 ppm) which can be assigned to the C*H* proton and is flanked by Sn satellite lines ($^3J(^{119}\text{Sn},^1\text{H}) = 52$ Hz). The ^{119}Sn NMR resonance of **21** arises at δ -360 ppm, which is very much different from the starting compound **20**. The IR spectrum shows two bands at 2700 and 1641 cm^{-1}, which are assigned to the C–H and C=O stretching frequencies.

Colorless compound **21** crystallizes in the triclinic space group *P*-1, with two monomers in the asymmetric unit from saturated *n*-hexane solution at -32 ^{o}C after two days. The coordination around the tin atom features a distorted tetrahedral geometry with one lone pair (Figure 4.1).
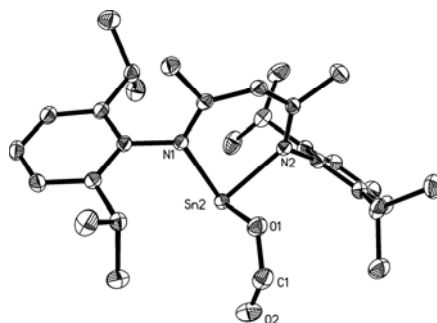
Figure 4.1. Molecular structure of **21**. Thermal elipsoids are shown at 50% probability. H atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Sn2–O1 2.1353(15), O1–C1 1.299(2), C1–O2 1.209(3), Sn2–N1 2.1655(17), Sn2–N2 2.1752(15); Sn2–O1–C1 116.40(13), O1–C1–O2 126.78(18), N1–Sn2–N1 86.42(6).

4.3. Reactions with Carbonyl Compounds

The carbonyl group and its transformation to other functional groups is very important in organic chemistry.[195] In literature there are numerous reports on hydrostannation reaction of compounds with carbonyl groups using tin(IV) hydride,[196] and carbonyl group insertion into the tin hydrogen bond of various complexes is well established.[197] Herein we demonstrate for the first time the hydrostannylation of a carbonyl group using tin(II) hydride. Examples are the reaction of ferrocene carbaldehyde, benzophenone, 2-benzoyl pyridine, di(2-pyridyl)ketone, and dicyclopropylketone with LSnH (**20**). Treatment of **20** with ferrocene carbaldehyde, benzophenone, 2-benzoyl pyridine, di(2-pyridyl)ketone, and dicyclopropylketone leads quantitatively to the stannylene alkoxides **22-26**, respectively with a Sn(II)-O-CH framework that is formed by nucleophilic hydride addition to the respective carbon of the carbonyl group (Scheme 4.3).

Compounds **22-26** were monitored by ^{1}H NMR spectra. Sharp resonances in the ^{1}H NMR of **22-26** gave the initial indication that the products have been formed in high yield. Ferrocene moieties are important in organometallic chemistry, with respect to electrochemistry[198] and material science, because bridging ferrocenophanes undergo polymerization and generate organometallic polymers with high molecular weight.[199] The reaction of **20** with ferrocene carbaldehyde generates bimetallic tin(II) alkoxide **22** (Scheme 4.3).
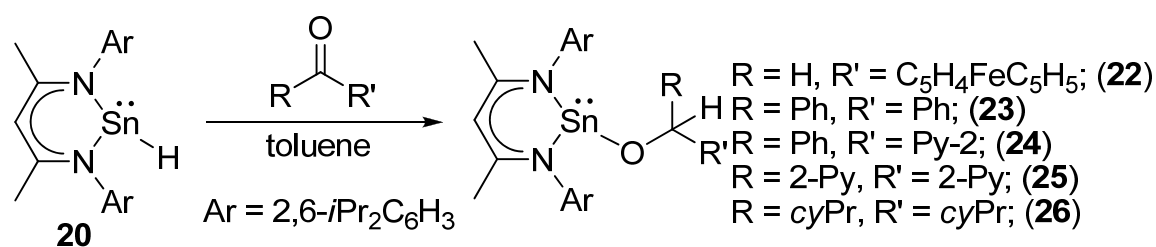
Scheme 4.3. Preparation of compounds **22**, **23**, **24**, **25**, and **26**

22 is an orange solid, soluble in benzene, THF, *n*-hexane, and *n*-pentane and shows no decomposition on exposure to air. **22** was characterized by multinuclear NMR and IR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis (Figure 4.2). The ^{1}H NMR spectrum of **22** exhibits a singlet (δ 4.81 ppm), which can be assigned to the C*H$_2$* protons and is flanked by Sn satellite lines ($^3J(^{119}$Sn,^{1}H) = 13.5 Hz). The ^{119}Sn NMR resonance of **22** arises at δ -262 ppm.
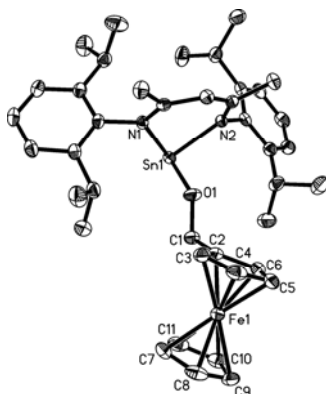
Figure 4.2. Molecular structure of **22**. Thermal elipsoids are shown at 50% probability. H atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Sn1–O1 2.0253(13), O1–C1 1.411(2), Sn1–N1 2.1834(14), Sn1–N2 2.1894(14); Sn1–O1–C1 129.13(11), N1–Sn1–O1 87.89(6), N1–Sn1–N2 85.10(5).

23, 24, and **25** were characterized by multinuclear NMR spectroscopy, EI mass spectrometry, elemental analysis. Furthermore compound **24** was characterised by X-ray structural analysis (Figure 4.3). The ^{1}H NMR spectra of **23, 24,** and **25** exhibit a singlet (δ 5.97, 6.28, and 6.59 ppm respectively) which can be assigned to the quaternary C*H* proton, and the complete disappearance of the proton resonance of Sn-*H* was observed. This indicates the conversion of the tin(II)-hydride to the corresponding tin(II)-alkoxide. The ^{119}Sn NMR exhibits resonances at -256, -286, and -324 ppm for compounds **5, 6,** and **7**. The three values are different due to the non identical electronic nature of the phenyl rings when compared with

those of the 2-pyridyl rings. In the EI mass spectra the molecular ion peaks were observed at *m/z* 719, 720, and 722 as the base peaks for **23, 24,** and **25**.

24 crystallizes in the triclinic space group *P*-1 with one monomer in the asymmetric unit (Figure 4.3). The Sn–O bond lengths (2.0414(15) Å) are comparable with the Sn–O bond lengths in compounds **21** (2.1353(15) Å), and **22 (**2.0253(13) Å).
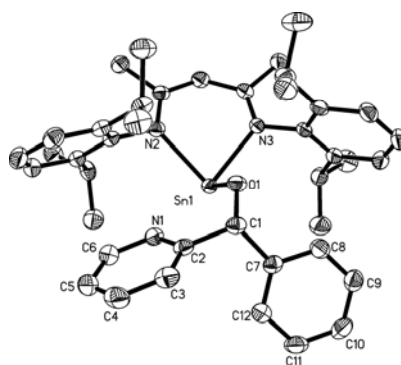
Figure 4.3. Molecular structure of **24**. Thermal elipsoids are shown at 50% probability. H atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Sn1–O1 2.0414(15), Sn1–N2 2.2420(16), Sn1–N3 2.2632(18); N2–Sn1–O1 99.99(6), N2–Sn1–N3 82.10(6).

At room temperature there is no reaction observed, when LSnH is treated with dicyclopropylketone in toluene. However after refluxing this mixture for 12 h compound **26** is formed in high yield. Compound **26** is composed of two cyclopropyl rings and to our surprise they were not decomposed during the reaction. The ^{1}H NMR spectrum of **10** exhibits a triplet (*δ* 2.47 ppm), which can be assigned to the quaternary C*H* proton which is coupled by two C-H protons from the two cyclopropyl rings with a coupling constant of 7.3 Hz. In the ^{1}H NMR spectrum of compound **26** the quaternary proton (*δ* 2.47 ppm) resonates upfield compared to the corresponding proton in compounds **23, 24,** and **25** (*δ* 5.97, 6.28, and 6.59 ppm respectively). This is mainly due to the different electronic nature of the two cyclopropyl rings in compound **26**. The other protons of the cyclopropyl rings show the expected resonances. The two quaternary C*H* protons of the two cyclopropyl rings exhibit a multiplet each at 0.75 ppm. The four C*H*$_2$ groups of the two cyclopropyl rings are not identical; they show four multiplets (*δ* 0.21, 0.02, -0.07, -0.25 ppm). Each multiplet is not consistent with each methylene group. It has been found that each multiplet corresponds to one proton from each of the two cyclopropyl rings.

Single crystal of **26** suitable for X-ray structural analysis was obtained from *n*-hexane solutions. **26** crystallizes in the triclinic space group *P*-1. The molecular structure of **26** is shown in Figure 4.4. The asymmetric unit of **26** contains one formula unit of the compound, and two of the molecules in each unit cell. As predicted, based on the ^{1}H NMR spectrum and EI mass spectrum, compounds **26** contains a Sn(II)-O-CH core with a two cyclopropyl groups.
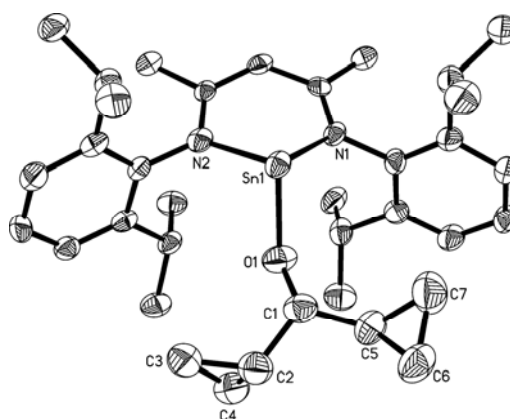
Figure 4.4. Molecular structure of **26**. Selected bond lengths [Å] and angles [°]; anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity: Sn1–O1 2.024(3), Sn1–N1 2.199(4), O1–C1 1.431(6); N1–Sn1–N2 82.79(14), N1–Sn1–O1 95.80(13), Sn1–O1–C1 117.5(3).

4.4. Reactions with Compounds Containing C≡C Triple Bonds

The hydrostannation of olefins and alkines is well known since nearly 50 years and follows a polar or a free radical pathway depending on substituents and conditions.[200] In contrast to this result the present hydrostannylation reaction of alkines with LSnH (**20**) proceeds without any catalyst although alkine insertion into transition metal hydride bonds is well established.[201] LSnH (**20**) reacts with the alkines HC≡CCO$_2$Me, HC≡CCO$_2$Et, MeC≡CCO$_2$Et, MeO$_2$CC≡CCO$_2$Me, EtO$_2$CC≡CCO$_2$Et, and *t*BuO$_2$CC≡CCO$_2$*t*Bu at room temperature to form tin(II) substituted alkenes **27, 28, 29, 30, 31,** and **32**. Compound **20** reacts with HC≡CCO$_2$Me and HC≡CCO$_2$Et respectively at room temperature to form the vinyl stannylenes **27** and **28** (Scheme 4.4).
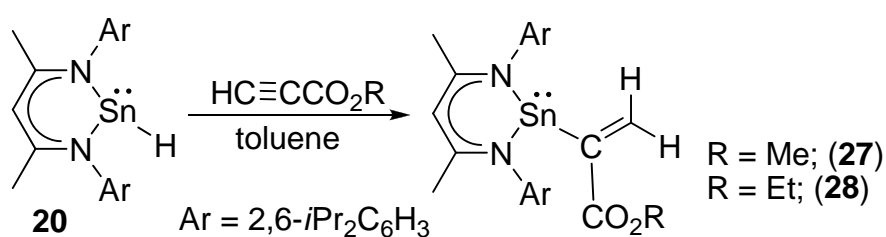
Scheme 4.4. Preparation of compounds **27** and **28**

27 and **28** are obtained by the 1,2-addition of stannylene hydride LSnH to the terminal alkines and the result is the transfer of the hydrogen atom and stannylene to the carbon carbon triple bond (Scheme 4.4), rather than the elimination of H_2 due to the different polarized Sn–H and C–H bonds.
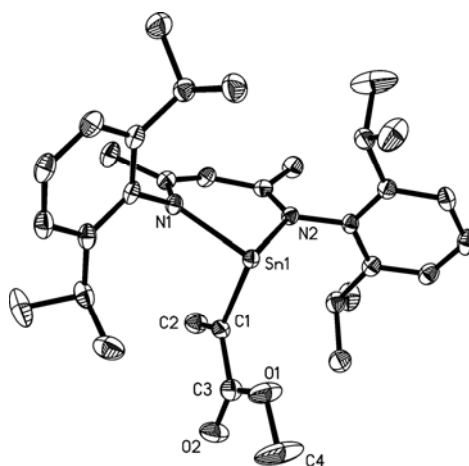
Figure 4.5. Molecular structure of **27**. Selected bond lengths [Å] and angles [°]; anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity: Sn1–C1 2.241(2), Sn1–N1 2.202(2), C1–C3 1.488(3); N1–Sn1–N2 85.64(7), N1–Sn1–C1 93.06(8), Sn1–C1–C3 116.79(17).

The ^{1}H NMR spectrum of **28** exhibits two broad resonances (δ 6.25 and 5.85 ppm) which correspond to the two alkenyl protons. Moreover, the ^{1}H NMR spectrum shows a quartet and a triplet resonance (δ 4.07 and 0.87 ppm) corresponding to the two different types of C*H* protons of the ethyl moieties. Compound **27** crystallizes in the triclinic space group *P*-1, with one monomer in the asymmetric unit, and with two molecules in each unit cell. Single crystals were obtained from a saturated *n*-hexane solution at –32 °C after two days. The coordination polyhedron around the tin atom features a distorted tetrahedral geometry with a stereochemically active lone pair (Figure 4.5).

Furthermore we were interested in the selectivity of the addition across the carbon carbon triple bond. Therefore we selected the disubstituted alkine, $MeC \equiv CCO_2Et$. Compound **20** reacts with $MeC \equiv CCO_2Et$ at room temperature to form stannylene **29** (Scheme 4.5). The ^1H NMR spectrum of **29** shows a broad resonance (δ 6.64 ppm) which can be tentatively assigned to the vinyl proton. The IR spectrum of this compound exhibits a strong band at 1686 cm^{-1}, which can be tentatively assigned to the carbonyl group.
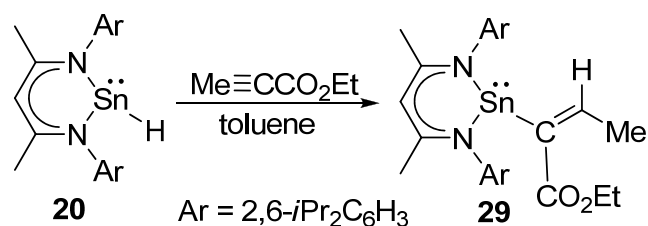
Scheme 4.5. Preparation of compound **29**

The crystal structure (Figure 4.6) of **29** reveals a *cis* orientation of the tin and hydrogen atom across the double bond and crystallizes in the triclinic space group *P*-1. Also in solution there is only one isomer observed. Therefore **29** is obtained by 1,2-*syn*-addition of **20** to the alkine and the result is the transfer of the hydrogen atom and stannylene across the carbon carbon triple bond.
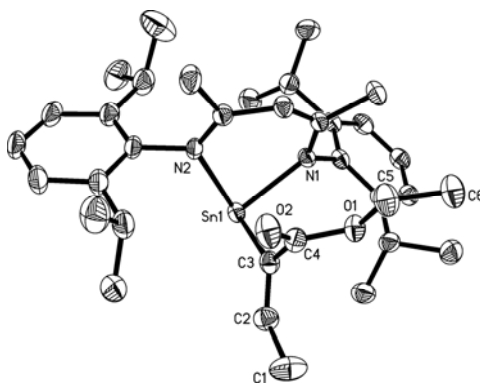
Figure 4.6. Molecular structure of **29**. Thermal elipsoids are shown at 50% probability. H atoms are omitted for clarity reasons.Selected bond lengths [Å] and angles [°]: Sn1–C3 2.242(3), C3–C2 1.335(4), C4–O2 1.2101(3), Sn1–N1 2.1990(19), Sn1–N2 2.199(2); Sn1–C3–C2 114.13(19), Sn1–C3–C4 127.37(13), N2–Sn1–N2 86.31(8).

Moreover we selected the symmetric disubstituted alkines, dimethyl acetylenedicarboxylate, diethyl acetylenedicarboxylate, and ditertiarybutyl acetylenedicarboxylate. **20** reacts with $RO_2CC\equiv CCO_2R$ (R = Me, Et, and *t*Bu) in toluene at room temperature to form the two isomers with *E*- and *Z*- stannylene substituted alkene in a different ratio (1:0.7 for **30**, 1.00:0.69 for **31**, and 1.00:1.52 for **32**) (Scheme 4.6). Each ^{1}H NMR spectrum of **30**, **31**, and **32** exhibits two singlets which are arranged between the tin satellites with two different coupling constants. The ^{119}Sn NMR resonances arises at δ -132 and -211 ppm, for *E*- and *Z*- isomers of **30**, δ -130 and -211 ppm, for *E*- and *Z*- isomers of **31**, and the resonance at δ -123 and -205 ppm for *E*- and *Z*- isomers of **32**.
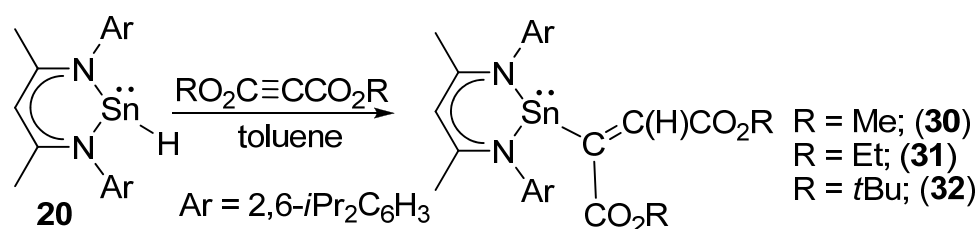
Scheme 4.6. Preparation of compounds **30**, **31**, and **32**
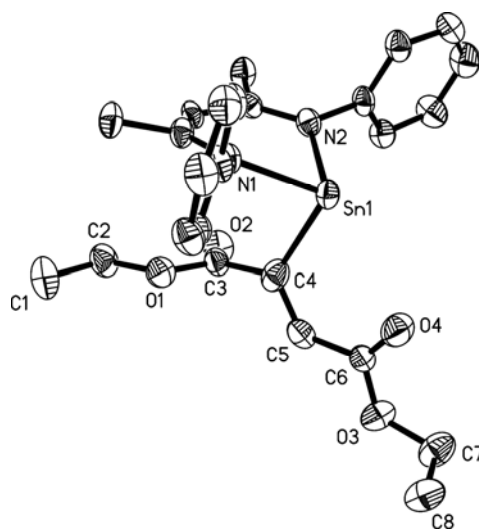
Figure 4.7. Molecular structure of **31**. Selected bond lengths [Å] and angles [°]; anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms and *iso*-propyl groups are omitted for clarity: Sn1–N1 2.207(5), Sn1–C4 2.330(8), C4–C5 1.331(9); N1–Sn1–N2 85.19(17), N1–Sn1–C4 92.3(2), Sn1–C4–C5 121.5(5).

31 crystallizes in the monoclinic space group *P2₁/c,* with one monomer in the asymmetric unit from saturated *n*-hexane solution at −32 °C after one day (Figure 4.7). In the crystalline state we were only able to isolate the *Z*- isomer.

4.5. Reactions with Compounds Containing C=N Double Bond

The reaction of **20** with compounds containing C–N multiple bonds was performed with dicyclohexyl carbodiimide (DCC), and diisopropyl carbodiimide (RN=C=NR, R = *i*Pr and Cy). This reaction proceeds rapidly and quantitatively at room temperature to give the spirocyclic compounds **33** and **34** containing the four- and six-membered heterocycles of composition C_3N_2Sn and CN_2Sn (Scheme 4.7).
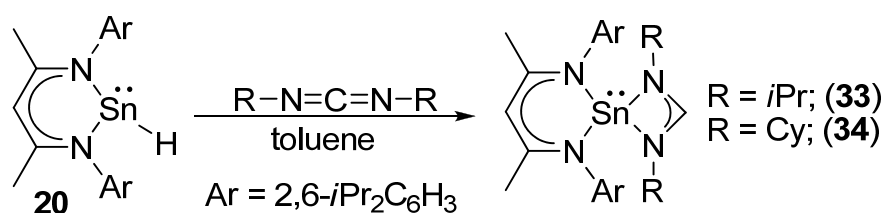
Scheme 4.7. Preparation of compounds **33** and **34**

Compoounds **33** and **34** were characterised by multinuclear NMR spectroscopy, EI mass spectroscopy, and elemental analysis. In the ^{1}H NMR spectra of **33** and **34** the C-*H* proton of the four-membered ring shows a singlet (δ 8.26 and 8.30 ppm) and other resonances as expected while the ^{119}Sn NMR resonance arises at δ -177.69 and -175 ppm respectively for **33** and **34**. In the EI mass spectra the molecular ion peaks were observed at *m/z* 664 and 744 as the base peaks for **33** and **34** respectively.

4.6. Reaction of LSnH with Fluorinated Carbonyl Compounds: Nucleophilic Addition Reaction *vs* Hydrogen for Fluorine Exchange in C-F Bonds

Fluorine's peculiar characteristics such as high electronegativity, low polarizability, and small covalent radius render fluorocarbons thermally stable, water repellent, and resistant to chemical degradation.[202] These unique properties, along with the great strength of the C-F bond (120-129 kcal/mol for aliphatic and olefinic C-F bonds, and up to 154 kcal/mol for C_6F_6),[203] make fluorocarbons valuable refrigerants, pesticides, and nonadhesive polymers but also very environmentally persistent. Therefore, methods for chemically manipulating fluorocarbons are sought to either degrade or add value to these materials. The hydrogen for fluorine exchange in fluorocarbons is a thermodynamically favorable reaction that does not occur in absence of a catalyst.[204] For example, passing a mixture of C_6F_6 and dihydrogen

over Pd/C or Pt/C at 300 °C gives a mixture of aromatic hydrofluorocarbons; Pt/C at 58% conversion gives C_6F_5H and mixed isomers of $C_6F_4H_2$ and $C_6F_3H_3$ in a 4:3:1 ratio.[205]

We have already discussed the nucleophilic addition reaction of LGeH (**5**) with compounds containing trifluoroacetyl group. There were no indications that the aliphatic C-F bonds can exchange with the Ge-H bond. We present here the reaction of LSnH (**20**) with fluorine substituted carbonyl compounds namely 2,2,2-trifluoro acetophenone, 2,2,2-trifluoro acetothiophane, pentafluoro benzophenone, perfluoro benzophenone, 4-fluoro benzophenone, and pentafluoro benzaldehyde.
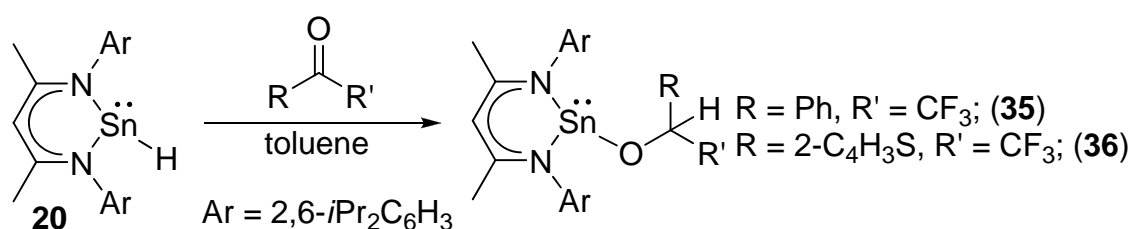
Scheme 4.8. Preparation of compounds **35** and **36**

The reaction of LSnH with 2,2,2-trifluoro acetophenone and 2,2,2-trifluoro acetothiophane leads to the tin(II) alkoxides **35** and **36** (Scheme 4.8). There are no indications that the C-F bonds of the CF_3 group are affected by the LSnH. Compounds **35** and **36** have one CF_3 group and display an interesting NMR spectrum.

^{1}H NMR spectra of **35** and **36** exhibit a quartet (δ 5.15 and 5.45 ppm respectively) which corresponds to the quaternary C*H* proton. The ^{19}F NMR resonance arises as a doublet (δ -76.29 and -77.38 ppm respectively) with a coupling constant of 6 and 7 Hz and is flanked by Sn satellite lines ($^4J(^{119}Sn,^1H)$ = 42 and 56 Hz). The four isopropyl groups of **35** and **36** are showing four different resonances and even the two methyl groups in the backbone exhibit two different signals in the proton NMR spectra.
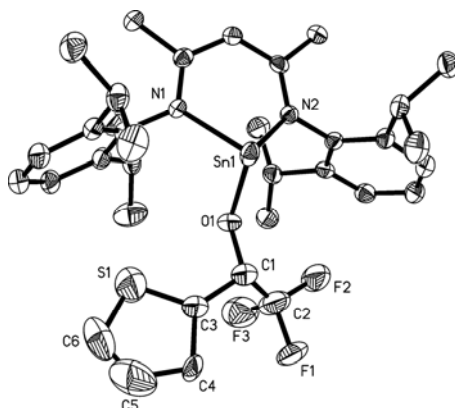
Figure 4.8. Molecular structure of **36**. Selected bond lengths [Å] and angles [°]; anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity: Sn1–O1 2.046(3), Sn1–N1 2.194(3), O1–C1 1.418(6); N1–Sn1–N2 83.30(11), N1–Sn1–O1 93.04(12), Sn1–O1–C1 114.5(4).

Single crystal of **36** suitable for X-ray structural analysis was obtained from *n*-hexane solution. **36** crystallizes in the triclinic space group *P*-1. The molecular structure of **36** is shown in Figure 4.8. The asymmetric unit of **36** contains one formula of the compound, and two of the molecules in each unit cell. As predicted, based on the ^{1}H NMR spectrum and EI mass spectrum, compound **36** contains a Sn(II)-O-CH core with a CF_3 group. The three coordinate tin atom is surrounded by two N atoms of the *β*-diketiminato ligand, and an exocyclic O atom.

When LSnH is treated separately with equivalent amounts of pentafluoro benzophenone ($PhCOC_6F_5$) and perfluoro benzophenone ($C_6F_5COC_6F_5$) in toluene at room temperature, the formation of two types of products occurs (Scheme 4.9). This is clearly shown from ^{119}Sn NMR spectra. One is the LSnF (**1**) and another one is the nucleophilic addition product tin(II) alkoxide $LSnOCH(C_6F_5)Ph$ (**37**), and $LSnOCH(C_6F_5)_2$ (**38**) respectively.
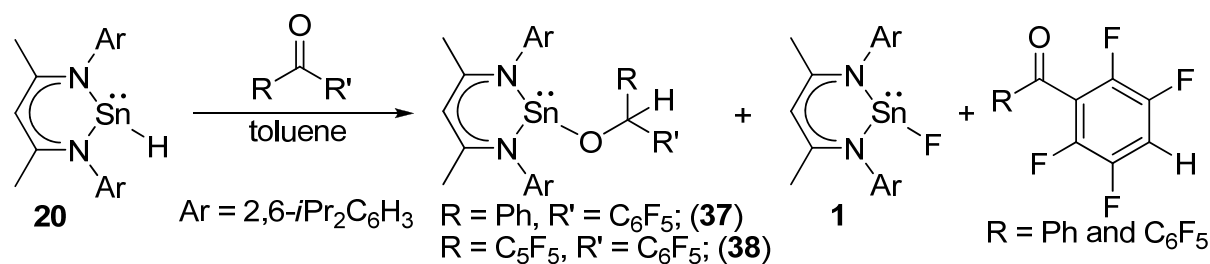
Scheme 4.9. Preparation of compounds **37** and **38**

There are no indications that in the alkoxide products containing fluorine exchange occurred at the aromatic group in either case. In the ^{1}H NMR spectrum the quaternary proton from the LSn-O-CH moiety is showing the singlet at δ 6.41 and 6.72 ppm respectively, which is comparable with those of analogous compounds. In the EI mass spectrum of **38** there is observed the molecular ion peak at *m/z* 900 as the base peak. The formation of LSnF (**1**) and the alkoxide product ratio are calculated by the integration of the resonances in the ^{1}H NMR spectrum. In the case of the reaction between LSnH and pentafluoro benzophenone, the product ratio is 0.6:1.0, and the ^{119}Sn NMR resonance arises at δ -217 ppm for compound LSnOCH(C$_6$F$_5$)Ph (**37**), and the other one is the doublet for LSnF (δ -363, -380 ppm, ^2J(Sn-F) = 3100 Hz). The latter signal matches well with that of LSnF. For the reaction of LSnH and perfluoro benzophenone, the product ratio is 0.8:1.0, and the ^{119}Sn NMR resonance arises at δ -252 ppm for LSnOCH(C$_6$F$_5$)$_2$ (**38**). The ^{1}H NMR spectrum of compound **38** shows a singlet (δ 4.77 ppm) for the γ-CH protons and two septets (δ 3.46 and 3.02 ppm) corresponding to the two different types of C*H* protons of the *i*Pr moieties. The other signals are as expected. The fate of the pentafluoro benzophenone and perfluoro benzophenone after fluorine exchange are products containing symmetric substituted fluorine atoms, due to *para* fluorine exchange. In ^{1}H NMR spectrum is present a triplet of triplets at δ 6.18 and 6.08 ppm, respectively. The coupling constants are ^3J(F-H) = 9.652 Hz, ^4J(F-H) =7.302 Hz, and ^3J(F-H) = 9.564 Hz, ^4J(F-H) =7.452 Hz respectively. These values are matching well with those of previously reported compounds. Therefore we can say that the selective exchange of hydrogen for fluorine in the para position is observed under formation of two new compounds PhCOC(4-C$_6$F$_4$H) and C$_6$F$_5$CO(4-C$_6$F$_4$H).

The reaction of LSnH (**20**) with 4-fluoro benzophenone leads to the exclusively nucleophilic addition product LSnOCHPh(4-C$_6$H$_4$F) (**39**) (Scheme 4.10). There are no indications that the *para* fluorine is affected. The ^{1}H NMR spectra of **39** exhibits a singlet (δ 5.15 ppm) which corresponds to the quaternary C*H* proton and the other signals are as expected. The ^{19}F NMR resonance arises at δ -112.3 ppm as a multiplet, also in the the ^{119}Sn NMR resonance of **39** arises a singlet at δ -212 ppm, which is similar to that of compound LSnOCHPh$_2$ (**23**) (δ -218 ppm) (see Table 4.1). In the EI mass spectrum the molecular ion peak was observed at *m/z* 737 with 90 % intensity and the base peak arises at *m/z* 652 for [M-C$_6$H$_4$F]$^+$ with 100 %.

Treatment of LSnH with pentafluoro benzaldehyde leads quantitatively to the stannylene alkoxide LSnOCH$_2$C$_6$F$_5$ (**40**), with a Sn(II)-O-CH$_2$ framework that is formed by nucleophilic hydride addition to the carbon of the carbonyl group (Scheme 4.10).
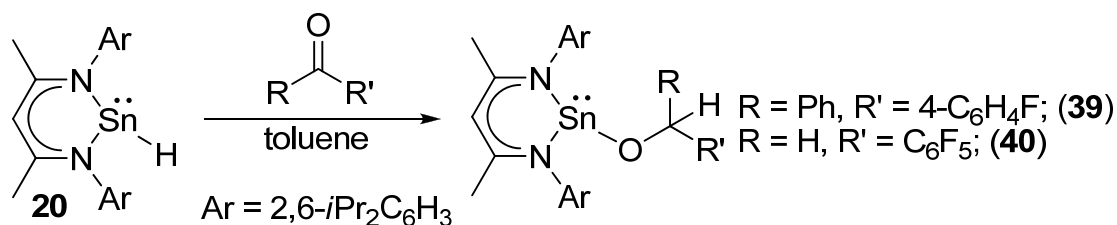
Scheme 4.10. Preparation of compounds **39** and **40**

40 is a yellow solid, soluble in benzene, THF, *n*-hexane, and *n*-pentane and shows no decomposition on exposure to air. The ^{1}H NMR spectrum of **40** exhibits a singlet (δ 4.81 ppm), which can be assigned to the C*H*$_2$ protons and is flanked by Sn satellite lines ($^3J(^{119}$Sn,^{1}H) = 13.5 Hz). The ^{119}Sn NMR resonance of **40** arises at δ-262 ppm. **40** crystallizes in the triclinic space group *P*-1 with one monomer in the asymmetric unit (Figure 4.9). The Sn-O bond lengths (2.0300(14) Å) are comparable with those of compound LSnOCH$_2$Fc, (**22**) (2.0253(13) Å). The O-C bond distances of **40** and LSnOCH$_2$Fc (**22**) are in a narrow range of each other (1.404(2) Å and 1.411(2) Å).
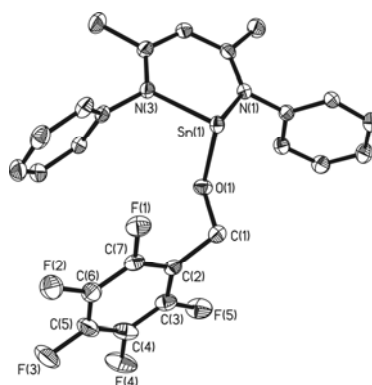
Figure 4.9. Molecular structure of **40**. Thermal elipsoids are shown at 50% probability. Isopropyl groups and H atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Sn1–O1 2.0300(14), O1–C1 1.404(2), Sn1–N1 2.1911(15), Sn1–N3 2.1920(15); Sn1–O1–C1 120.19(11), N1–Sn1–O1 91.85(6), N1–Sn1–N3 83.61(6).

Table 4.1. ^{119}Sn NMR data of Sn(II) compounds

Compound[*]	^{119}Sn NMR (δ, ppm)
LSnCl	-224
LSnF (**1**)	-371.50
LSnH (**20**)	-4.45
LSnOC(O)H (**21**)	-360
LSnOCH$_2$Fc (**22**)	-262
LSnOCHPh$_2$ (**23**)	-218
LSnOCHPh(2-Py) (**24**)	-286
LSnOCH(2-Py)$_2$ (**25**)	-324
LSnOCH(C$_3$H$_5$)$_2$ (**26**)	-190.50
LSnC(CH$_2$)CO$_2$Me (**27**)	-93.28
LSnC(CH$_2$)CO$_2$Et (**28**)	-89.02
LSnC(CHMe)CO$_2$Et (**29**)	-90
LSnC(CHCO$_2$Me)CO$_2$Me (**30**)	-132, -211
LSnC(CHCO$_2$Et)CO$_2$Et (**31**)	-130.36, -211.20
LSnC(CHCO$_2$Me)CO$_2$Et (**32**)	-123.27, -205.75
LSn(*i*PrNCHN*i*Pr) (**33**)	-177.69
LSn(CyNCHNCy) (**34**)	-175
LSnOCH(CF$_3$)Ph (**35**)	-252
LSnOCH(2-C$_4$H$_3$S)CF$_3$ (**36**)	-262
LSnOCHPh(C$_6$F$_5$) (**37**)	-217
LSnOCH(C$_6$F$_5$)$_2$ (**38**)	-252
LSnOCHPh(4-C$_6$H$_4$F) (**39**)	-212
LSnOCH$_2$C$_6$F$_5$ (**40**)	-262

*L = HC(CMeNAr)$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Chapter 5

Synthesis and Reactivity of Six-Membered N-Heterocyclic Germylene

Since the pioneering work on the synthesis of isolable germylenes (R_2Ge) reported by *Lappert et al.*[105] remarkable progress has been made in tuning the reactivity of the low coordinate Ge atom in germylenes through the presence of bulky and/or p-donor substituents R.[106-109] Sterically demanding amido or alkoxo substituents at the two-coordinate Ge atom lead to derivatives which can serve as ligands with different donor–acceptor abilities in coordination compounds.[110-114] Among the amido-substituted germylenes, the N-heterocyclic germylenes deserve particular attention, because they are versatile building blocks for the synthesis of germanium compounds with remarkable electronic features. Recent highlights include the synthesis of compounds with resonance-stabilized X-Ge=Y moieties (X=F, Cl, OH; Y= S,[172, 206] Se,[207] NR[28]) and the formation of the N-heterocyclic germanium(II) cation LGe^+,[208] starting from the sterically encumbered β-diketiminato-substituted chlorogermylene, LGeCl.[146]

5.1. Synthesis of Six-Membered N-Heterocyclic Germylene

In chapter 3 we have already discussed the synthesis of L'Ge (**19**), (L' = CH{(C=CH$_2$)(CMe)(NAr)$_2$}; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) form LGeH (**5**) by a frustrated Lewis carbene borane pair under elimination of dihydrogen. The carbene and borane act as a proton and hydride scavenger respectively, and the formation of imidazolium cation with borate as a counter anion. The naked hydride cannot be a counter anion, therefore there is no reaction between the LGeH and NHC. We changed LGeH (**5**) to LGeCl, where the chloride anion is a counter anion of the imidazolium cation. Herein we describe the synthesis of **19** from LGeCl and also from the LGeOTf as starting materials.

A toluene solution of one equivalent of LGeCl and one equivalent of 1,3-di-*tert*-butylimidazol-2-ylidene[191] under stirring immediately changed the color from yellow to brown-red after a few minutes and a white precipitate is formed (Scheme 5.1). This is in contrast to the observation when a solution of one equivalent of LGeCl and one equivalent of 1,3-di-(2,4,6-Me$_3$C$_6$H$_2$)-2-ylidene was used.[209] The reason are the different nucleophilic properties of NHCs.
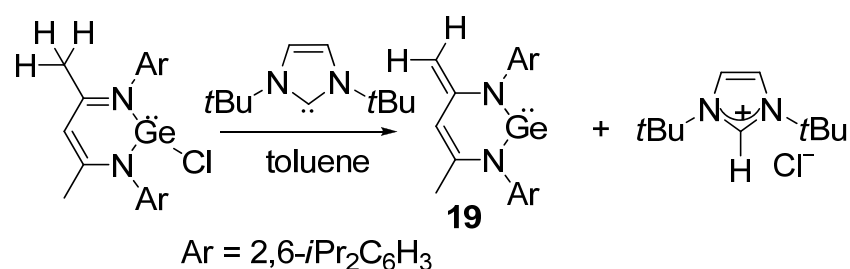
Scheme 5.1. Preparation of compound **19**

The insoluble white precipitate was identified as the 1,3-di-*tert*-butylimidazolium chloride, and the soluble part as the germylene L′Ge (**19**). We postulate that the reaction proceeds via the cleavage of a C–H methyl bond and the formation of the C–H carbonium ion (Scheme 5.1). This type of C–H cleavage reaction was reported for nucleophilic carbenes.[210] The proof for the C–H bond activation at the backbone methyl group of LGeCl by 1,3-di-*tert*-butylimidazol-2-ylidene is given herein by the isolation of 1,3-di-*tert*-butylimidazolium chloride. The previously reported germylene **19** was formed by the reaction of LGeCl with LiN(SiMe₃)₂.[37] Similar deprotonation reactions at the backbone have been observed for the borane stabilized germylene hydride,[28] the tautomerization of an iminogermane bearing the β-diketiminato ligand,[29] a cyclodiazaborane analogue,[32] and related calcium complexes.[33] This is so far a unique example where the deprotonation reaction at the backbone has been demonstrated using 1,3-di-*tert*-butylimidazol-2-ylidene.

In the above discussed reaction the yield is not so high (65 %), it can be improved when instead of LGeCl, LGeOTf and NHC are used. The triflate anion ([OSO₂CF₃]⁻ = OTf⁻) has served here as an excellent leaving group and the conversion is almost quantitative (Scheme 5.2).
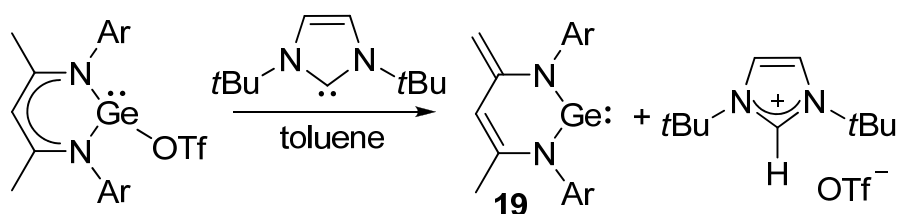
Scheme 5.2. Preparation of compound **19**

5.2. Reaction of L′Ge with Ammonia Borane

The synthesis of L′Ge was achieved either by the dehydrogenation, dehydrohalogenation, or dehydrotriflation of the corresponding germanium(II) compounds LGeH, LGeCl, and LGeOTf respectively. Accordingly it may be possible that L′Ge (**19**) can react with dihydrogen to form LGeH (**5**). Furthermore it should be emphasized that di(amino)carbenes are inert towards dihydrogen,[211] whereas the acyclic and cyclic alkyl(amino)carbenes undergo oxidative addition of dihydrogen at the carbene carbon atom.[212] In addition dihydrogen reacts with digermynes[213] and stannylene[214] respectively. Consequently we selected germylene L′Ge (**19**) for the reaction with dihydrogen. Unfortunately this compound showed no reaction with dihydrogen under mild conditions. Then we used as an alternative source of dihydrogen ammonia borane the preferred precursor for the preparation of boron nitride. Ammonia borane (AB, H_3NBH_3), which has a 19.6 % hydrogen content, has recently attracted great interest due to its potential application for chemical hydrogen storage.[215] The AB molecule contains both hydridic B–H and protic N–H polarized bonds and a strong B–N bond so that hydrogen release from solid AB is more favorable than dissociation into ammonia and diborane under non catalytic conditions.

The 1:1 reaction of L′Ge (**19**) with ammonia borane resulted in the formation of LGeH (**5**) (Scheme 5.3). Even an excess of ammonia borane leads only to **5**. In the latter case we also observe the addition of one molecule of dihydrogen, without oxidation of germanium(II).
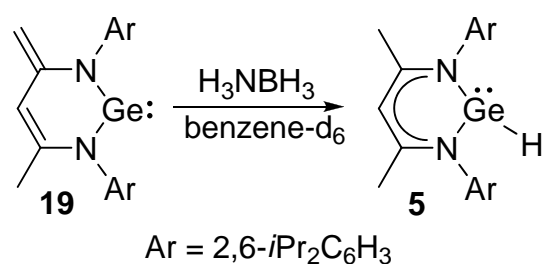
Scheme 5.3. Reaction of L′Ge with H_3NBH_3

Here it is mentioned that the reaction of L′Ge with $Me_3N·HCl$ or1,3-di-(2,6-iPr$_2$C$_6$H$_3$)-2-ylidene hydrochloride salt leads to the LGeCl.[146]

5.3. Reaction of NHC with Ammonia Borane

In this context we did the reaction of ammonia borane with N-heterocyclic carbenes, 1,3-di-*tert*-butylimidazol-2-ylidene.[191] N-heterocyclic carbenes (NHCs) are well studied in terms of ligands (organometallic chemistry), organocatalysis including a number of reports of unique and unexpected reactivity.[86] The hydrogenation energy for the conversion of 1,3-di-*tert*-butylimidazol-2-ylidene is exothermic. In the absence of a catalyst 1,3-di-*tert*-butylimidazol-2-ylidene is inert towards hydrogen but in the presence of catalytic amounts of palladium or platinum a slow uptake of dihydrogen and formation of the 1,1-addition product is observed.[216] The 1:1 reaction of ammonia borane with 1,3-di-*tert*-butylimidazol-2-ylidene at room temperature in the absence of any catalyst in toluene leads to compound **41**.[216] The CC-double bond present in 1,3-di-*tert*-butylimidazol-2-ylidene is unaffected even when we used an excess of ammonia borane. In the ^{1}H NMR there are only three resonances at 5.4, 4.2, and 1.0 ppm in the ratio of 1:1:9 and they are in accordance with an original sample.[216] The conversion of 1,3-di-*tert*-butylimidazol-2-ylidene to **41** at room temperature is quantitative.
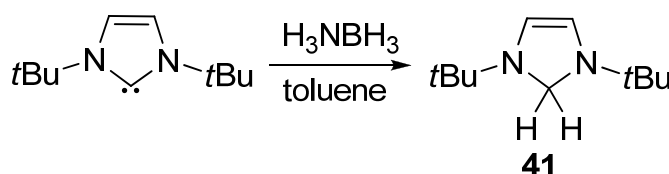
Scheme 5.4. Preparation of compound **41**

5.4. Reaction of L′Ge with Ammonia

In recent years we have been interested in the synthesis of low valent germanium compounds and reported on the preparation and structural characterization of LGeCl,[146] LGeF,[28] LGeOH,[127] and LGeH.[79] These small reactive molecules are ideal precursor for the preparation of heterobimetallic germylenes, which are active catalysts in olefin polymerization reactions.[217, 218] One important missing species in this series is the LGeNH$_2$. To date, there is only one example known of a stable germanium(II) amide featuring the parent NH$_2$ group.[137] A conventional route for the preparation of Ge–NH$_2$ containing compounds is the ammonolysis of the corresponding halide.[139, 143, 144] Therefore it was expected that the reaction of LGeCl with an excess of ammonia leads to the product LGeNH$_2$.

However, in a broad temperature range (–40 to 25 $^{\circ}$C) the starting material does not react with ammonia. From our previous experience for the preparation of LGeOH,[127] and LAl(NH$_2$)$_2$[145] using LGeCl, and LAlCl$_2$ respectively we employed N-heterocyclic carbenes (NHC) as a HCl acceptor. Here we can follow the route for the preparation of LGeNH$_2$ from LGeCl, NH$_3$, and 1,3-di-(2,6-*i*Pr$_2$C$_6$H$_3$)-2-ylidene. May be during the reaction there the intermediate L′Ge (**19**) is formed, and after that it reacts with ammonia. Here we react directly ammonia with L′Ge, and the formation of LGeNH$_2$ under cleavage of one of the N-H bond occured.

The activation of the ammonia molecule has attracted considerable interest over the years. Although ammonia usually forms simple Lewis acid-base adducts with transition metal complexes, there are also some N–H activations of ammonia via transition metal complexes known.[67, 219] In contrast to these studies the corresponding chemistry of stable main group molecular compounds for the activation of ammonia is virtually nonexistent. In 2007, the first example of ammonia splitting was reported by *Bertrand et al.* using stable carbenes.[212] Very recently *Power et al.* reported the activation of ammonia by a carbene analogue SnAr$_2$ (Ar = 2,6(2,6-*i*Pr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$).[214]

Herein we show the N-H bond cleavage of ammonia on employing L′Ge (L′ = CH{(C=CH$_2$)(CMe)(NAr)$_2$}; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$); (**19**), which generates under mild conditions a terminal Ge–NH$_2$ group (Scheme 5.5). The addition of an excess of dry ammonia gas to a red solution of **19** in toluene leads to a rapid change of the color to orange. The solution was evaporated and extracted with *n*-hexane. Concentration of the solution yielded yellow crystals of LGeNH$_2$ (**42**). X-ray crystal structure analysis afforded a monomeric structure as illustrated in Figure 5.1. Surprisingly, **42** is monomeric in the solid state and what is even more striking, the NH$_2$ group is not involved in any kind of hydrogen bonding as shown by X-ray structural analysis and IR spectroscopy.
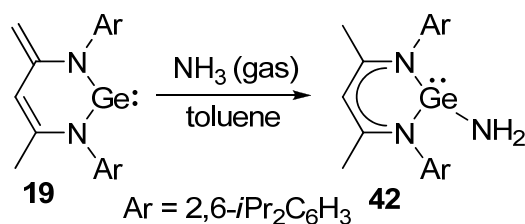
Scheme 5.5. Preparation of compound **42**

The IR spectrum displays two weak sharp bands at 3431 and 3333 cm^{-1} that are attributed to the two N–H stretching modes of the NH$_2$ group. These wave numbers are close to those at 3380 and 3308 cm^{-1} observed for (Ar*GeNH$_2$)$_2$ (Ar* = 2,6-(2,6-iPr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$).[137]
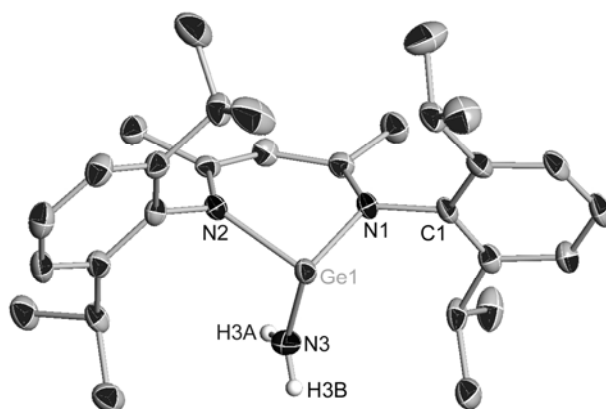
Figure 5.1. Anisotropic displacement parameters, depicted at the 50 % probability level of **42**. Hydrogen atoms, except those vital at the nitrogen atom N3, are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–N3 1.845(2), Ge1–N1 2.030(2), Ge1–N2 2.030(2); N1–Ge1–N2 88.60(8), N3–Ge1–N1 95.52(10), N3–Ge1–N2 95.55(10).

5.5. Synthesis of LGeNHNH$_2$

L´Ge cleaves one of the N-H bonds of NH$_3$ under formation of LGeNH$_2$. Consequently we reacted L´Ge with hydrazine NH$_2$NH$_2$ and it leads to the germanium(II) substituted hydrazine derivative LGeNHNH$_2$ (Scheme 5.6).
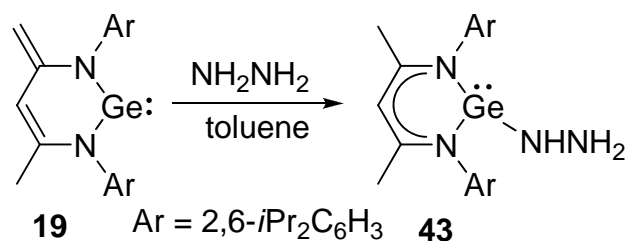
Scheme 5.6. Preparation of compound **43**

Its composition was proven by ^{1}H NMR spectroscopy, EI mass spectroscopy, elemental analysis, and furthermore it was characterized by solid state X-ray structural analysis. The ^{1}H NMR spectrum shows a doublet and triplet resonance (δ 3.16 and 0.87 ppm), which corresponds to the two different amine protons of **43**. Compound **43** crystalizes from saturated n-hexane solution. **43** crystallizes in the triclinic space group *P*-1 with one monomer in the asymmetric unit (Figure 5.2).
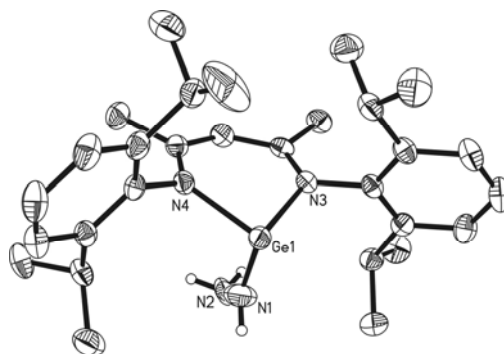
Figure 5.2. Molecular structure of **43**. Anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] are Ge1–N1 1.909(5), N1–N2 1.053(5), Ge1–N3 2.0141(19); N1–Ge1–N3 96.49(13), N2–N1–Ge1 134.6(3).

5.6. Reactions of L′Ge with O-H Bonded Compounds

We have already discussed syntheses of LGeNH$_2$ and LGeNHNH$_2$ compounds by the cleavage of one N-H bond of ammonia and hydrazine respectively by L′Ge (**19**) (L′ = CH{(C=CH$_2$)(CMe)(2,6-iPr$_2$C$_6$H$_3$N)$_2$}). Herein, we report on the synthesis of different heteroleptic germanium(II) compounds by the reaction of L′Ge (**19**) with ROH (R = H, Ph, C$_6$F$_5$, PhCO) under cleavage of the O-H bond (Scheme 5.7).
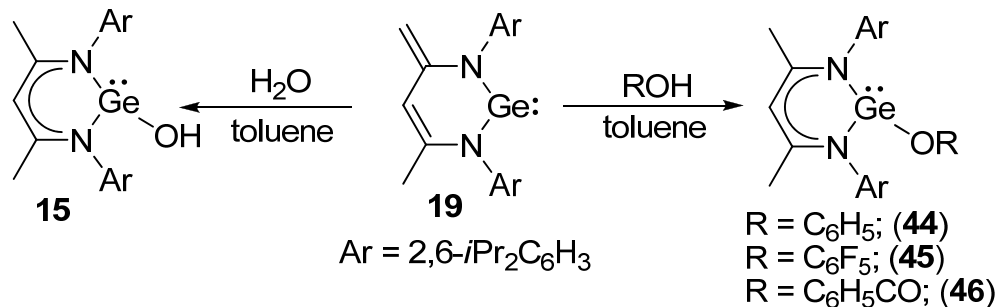
Scheme 5.7. Preparation of compounds **15, 44, 45,** and **46**

The reaction of L′Ge with H$_2$O in a 1:1 ratio at room temperature resulted in the formation of LGeOH (**15**) in almost quantitative yield (Scheme 5.7), and it is an alternative route for the preparation of LGeOH. For a broader feasibility we extended the reaction of L′Ge with PhOH and C$_6$F$_5$OH and obtained products **44** and **45** respectively (Scheme 5.7). **44** and **45** are colorless solids, which are soluble in *n*-hexane, *n*-pentane, THF, dichloromethane, benzene, and diethyl ether. **44** and **45** were characterized by ^{1}H NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray single-crystal structural analysis. The ^{1}H NMR spectra of **44** and **45** show the expected pattern for the *β*-diketiminato ligand. The ^{19}F NMR

spectrum of **45** displays three resonances (–158.8, –166.9, –175.2 ppm) for the *ortho*, *meta*, and *para* fluorine atoms respectively. The most intense peak in the EI mass spectra appeared at $m/z = 491$ [M-OPh]$^+$ and 673 [M]$^+$ for compounds **44** and **45** respectively.

Compounds **44** and **45** crystallize in the orthorhombic *Pnma* and monoclinic $P2_{1/n}$ space group with one monomer in the asymmetric unit respectively. Single crystals of both **44** and **45** were obtained from saturated *n*-hexane solutions at –32 °C after two days. These compounds are stable in the solid state as well as in solution for a long time without any decomposition under inert atmosphere. The coordination polyhedron around the germanium atom features a distorted trigonal pyramidal geometry (Figures 5.3 and 5.4). The germanium is attached to two nitrogen atoms from the backbone of the chelating ligand, and the oxygen atom from the OPh and OC_6F_5 group respectively.

The Ge-N bond lengths and N-Ge-N angles are comparable with those of related compounds. The Ge-O bond length of **44** (1.860 Å) can be compared with that of LGeOH (**15**) (1.828 Å)[127] but in **45** it is a slightly longer Ge-O bond (1.9515 Å), when compared with the latter one.
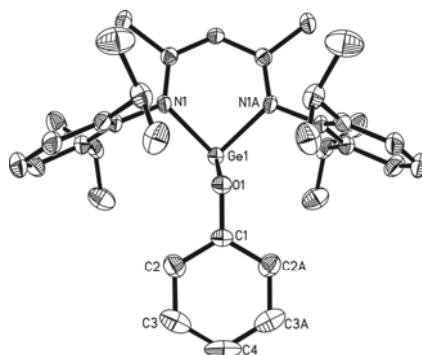
Figure 5.3. Molecular structure of **44**. Selected bond lengths [Å] and angles [°]; anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity: Ge1–O1 1.860(4), Ge1–N1 2.008(3), N1–C17 1.314(5), O1–C1 1.360(7); N1–Ge1–N1A 88.67(16), N1–Ge1–O1 93.88(12), Ge1–O1–C1 117.5(4).
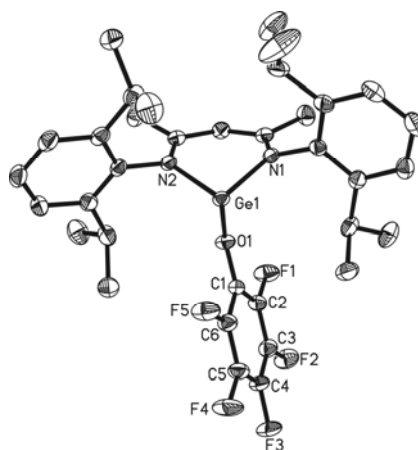
Figure 5.4. Molecular structure of **45**. Selected bond lengths [Å] and angles [°]; anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity: Ge1–O1 1.9515(14), Ge1–N1 1.9785(16), N1–C19 1.338(2), O1–C1 1.319(2); N1–Ge1–N2 90.85(6), N1–Ge1–O1 91.11(6), Ge1–O1–C1 129.25(12).

Subsequently after the successful reaction of L′Ge with H_2O, PhOH, and C_6F_5OH, respectively we used a carboxylic acid as precursor. Treatment of **19** with $PhCO_2H$ in toluene at room temperature after 1 h afforded the corresponding benzoic acid derivative, germylene benzoate LGeOC(O)Ph (**46**) in high yield (85 %) (Scheme 5.7). Compound **46** is thermally stable. No decomposition was observed at temperatures below the melting point (167 °C) under an inert atmosphere. Compound **46** is a white solid that is soluble in benzene, toluene, *n*-hexane, and THF. **46** was characterized by ^{1}H NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The ^{1}H NMR spectrum of compound **46** shows a singlet (δ 5.16 ppm) for the γ-CH protons and two septets (δ 3.61, 3.17 ppm) corresponding to the two different types of C*H* protons of the *i*Pr moieties. EI-MS of **46** gave the corresponding monomeric molecular ion peak M^+ at *m/z* 612.

The molecular structure of **46** has been determined by single crystal X-ray diffraction analysis (Figure 5.5), which demonstrates that the complex exists as a monomer. Colorless crystals of **46** were obtained from a *n*-hexane solution at -30 °C after one day in a freezer. Compound **47** crystallizes in the monoclinic space group $P2_1/c$, with one monomer in the asymmetric unit. The coordination polyhedron around the germanium atom exhibits a distorted trigonal pyramidal geometry. The sum of angles around the germanium atom is 268.59°. The Ge–O bond distance (1.9462 Å) in **46** is quite large when compared with that of **44** (1.860 Å) and it is almost similar to that of **45** (1.9515 Å).
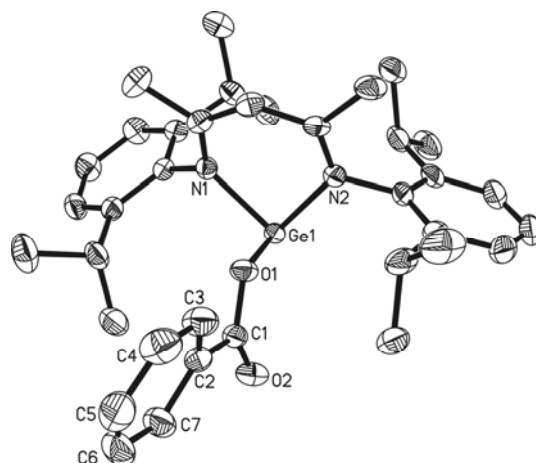
Figure 5.5. Molecular structure of **46**. Selected bond lengths [Å] and angles [°]; anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity: Ge1–O1 1.9462(19), Ge1–N1 1.978(2), O1–C1 1.311(3), C1–O2 1.216(3); N1–Ge1–N2 90.48(9), N1–Ge1–O1 89.43(8), O1–C1–O2 125.0(3).

5.7. Reaction of L'Ge with Ph₂PCl

Consequently we thought that the germylene **19** can be utilized for effecting substitution at the α carbon of the ligand back-bone. In order to introduce the Ph₂P group at this position we have employed Ph₂PCl. A quantitative reaction has occurred when a solution of **19** in *n*-hexane is treated with Ph₂PCl (Scheme 5.8). Product **47** was characterized by NMR and single crystal X-ray studies (Figure 5.6).
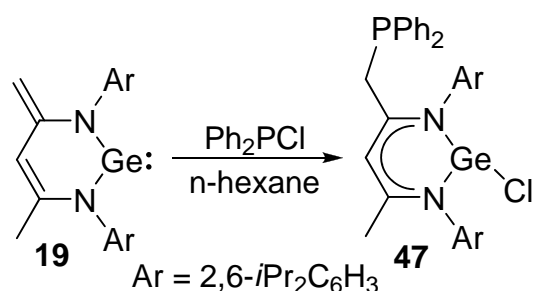
Scheme 5.8. Preparation of compound **47**

As shown in Figure 5.6, the *N, N'*-chelation mode of the ligand is retained and the Ph₂P group does not interact with Ge(II). As with the previously reported β-diketiminate Ge(II) complexes, Ge deviates away from the plane of the ring and, Ge-N and Ge-Cl bonds are also typical of such complexes. As given in Figure 5.6, all the C-C and CN bond lengths of the β-diketiminate skeleton in **47** are almost equal. The ^{31}P NMR chemical shift of **47** (-13.47 ppm) is diagnostic of the coordination mode in this complex. Complex **47** is chiral and the chirality

is due to the presence of out of the plane Ge-Cl bond as well as the unsymmetrical nature of the ligand in **47**. Interestingly, in **47** both enantiomers are present in the same unit cell (Figure 5.6).
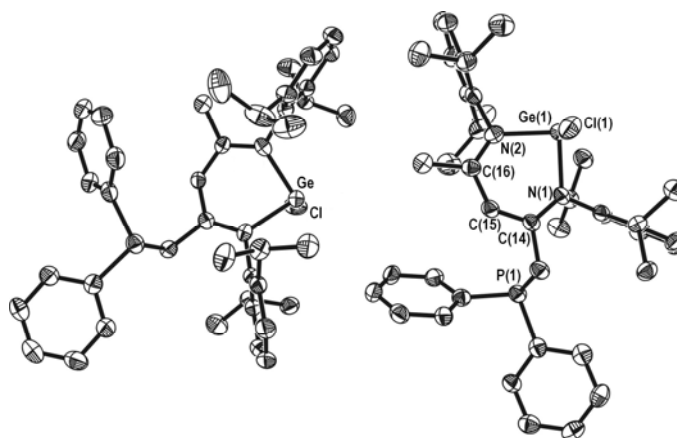
Figure 5.6. Molecular structure of **47** showing both the enantiomers. Relative orientations of enantiomers have been modified to obtain mirror images. Anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.984(3), Ge1–N2 1.967(3), Ge1–Cl1 2.3250(11), N1–C141.348(4), C14–C15 1.400(5), C15–C16 1.387(5), N(2)–C(16) 1.351(5); N2–Ge1–N1 91.35(12), N2–Ge1–Cl1 93.70(9), N1–Ge1–Cl1 94.61(8).

5.8. Reaction of L'Ge with $B(C_6F_5)_3$

We have shown in the previous sections that the heterocyclic germylene **19** cleaves the N–H, and O-H bonds of a variety of species at room temperature upon formation of stable heteroleptic germanium(II) compounds. Moreover *Driess et al.* had independently demonstrated that **19** has a dipolar character.[220] Consequently we reacted **19** with $B(C_6F_5)_3$ at room temperature to afford the zwitterionic compound $[B(C_6F_5)_3L''Ge]$ (**48**), (L″ = $CH\{(CCH_2)(CMe)(NAr)_2\}$; Ar = 2,6-$iPr_2C_6H_3$) containing a germylene moiety (Scheme 5.9).
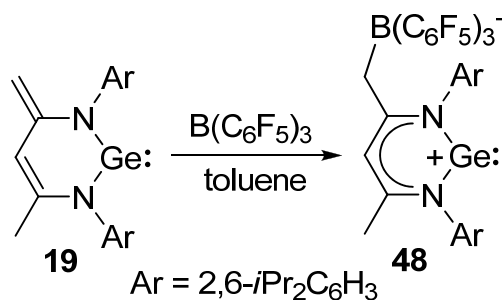
Scheme 5.9. Preparation of compound **48**

Only two reports on the synthesis of germanium(II) cations are in the current literature, one was reported by *Power et al.* where they also used a *β*-diketiminate ligand.[208, 221] Compound **48** was isolated as air and moisture sensitive pale yellow crystals in 78 % yield, which are insoluble in common hydrocarbon solvents but highly soluble in THF. In this solvent there is no equilibrium between **19** and **48** observed in contrast to the isoelectronic silicon analogue of **19**.[222] **48** crystallizes in the triclinic space group *P*-1 and consists of a planar six-membered C_3N_2Ge ring with an exocyclic $B(C_6F_5)_3$ group attached to C13 (Figure 5.7). The *β*-diketiminate N–C and C–C ring bond lengths have average values (1.36 and 1.39 Å) and are shorter than those of **19**, indicative for the delocalization of the *π*-electrons. The Ge–N bond lengths (1.873(2) and 1.881(2) Å) are comparable with those of the cation [LGe]+.[208] The ^1H NMR spectrum exhibits a signal for the *γ*-CH proton at 6.50 ppm, which differs from that of germylene **19** (5.43 ppm). The ^{11}B NMR spectrum shows a singlet resonance at − 14.82 ppm and the ^{19}F NMR spectrum displays three resonances (−131.6, −167.2 , and− 163.40 ppm) for the *ortho*, *para*, and *meta* fluorine atoms respectively.
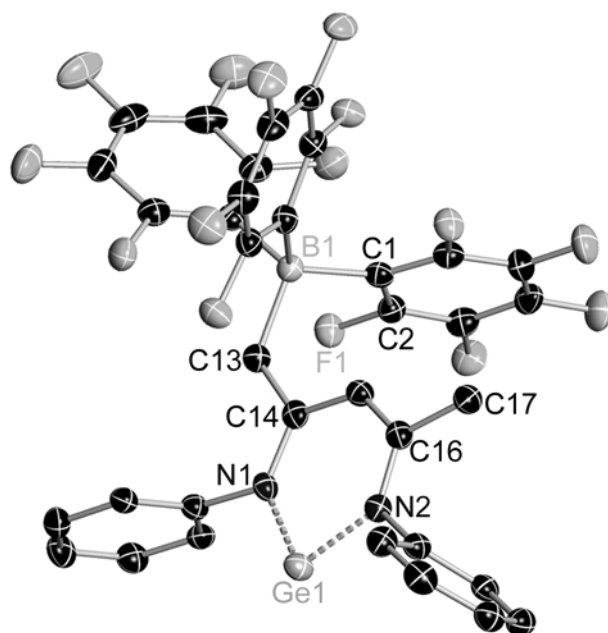
Figure 5.7. Molecular structure of **48**. Anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.845(2), Ge1–N2 2.030(2), C14–C13 1.845(2), C13–B1 1.845(2), C16–C17 2.030(2), B1–C1 2.030(2); N1–Ge1–N2 88.60(8), C14–C13–B1 95.52(10), C13–B1–C1 95.55(10).

Compound **19** might be compared with the monomeric aluminum(I), LAl,[13] although the difference of the two species is one proton. This is demonstrated in the reactivity of **3** and LAl, respectively, with $B(C_6F_5)_3$ (Scheme 5.10). **19** assembled as a zwitterionic germanium(II) species **48** and the LAl forms a compound with a boron–aluminum bond.[223]

Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, Ar^F = C$_6$F$_5$
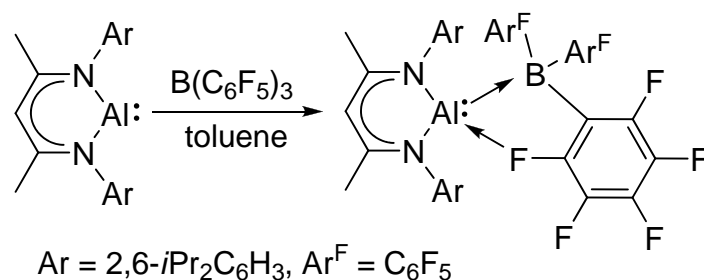
Scheme 5.10. Reaction of LAl with $B(C_6F_5)_3$

Preliminary studies of **48** with 1,3-di-*tert*-butylimidazol-2-ylidene (NHC) show the deprotonation of the second methyl group from the backbone with formation of compound $B(C_6F_5)_3L'''Ge$ (**49**), (L''' = CH{(CCH$_2$)(C=CH$_2$)(NAr)$_2$}; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) under complete conversion (Scheme 5.11). The 1,3-di-*tert*-butylimidazol-2-ylidene reacts (Schemes 3.10, 5.1, 5.2, and 5.11) under formation of the imidazolium cation. However, the counter anion is different. The neutral compound **19** is formed to give the anion [HB(C$_6$F$_5$)$_3$]$^-$, Cl$^-$, or OTf$^-$ repectively, whereas in **49** we assume that the borate anion forms a stable ion pair with the imidazolium cation.
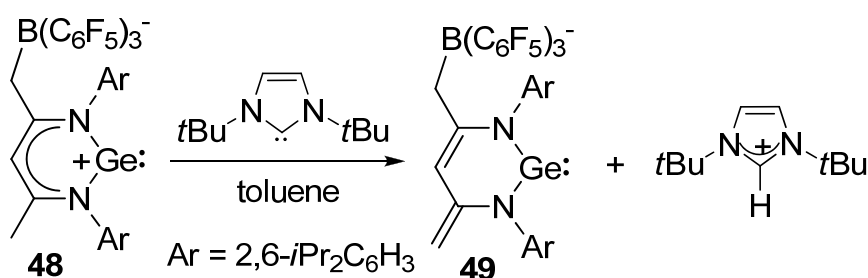
Scheme 5.11. Preparation of compound **49**

The anion of **49** gives rise to the expected resonance with the γ-CH proton at 5.87 ppm, which is comparable with that of **19**. The deprotonation of the second methyl group leads to the exocyclic carbon-carbon double bond. The two vinylic protons exhibit two non-equivalent singlets (δ 3.63, 2.96 ppm), indicating that the germanium(II) atom is neutral in

49. This is the first time we have shown that the double C–H bond activation of the two methyl groups at the ligand backbone has occurred by NHC. So far there is only one C–H bond activation of the methyl group at the ligand backbone reported.[28-33] Unfortunately we were not able to prove this result by an X-ray crystal structural analysis of **49**, due to the lack of single crystals.

Chapter 6

Reactivity of Six-Membered N-Heterocyclic Silylene

In 2006 *Driess et al.* reported the synthesis of compound L′Si (**50**) (L′ = CH{(C=CH$_2$)(CMe)(NAr)$_2$}; Ar = 2,6-iPr$_2$C$_6$H$_3$).[36] In the past 20 years, the chemistry of stable N-heterocyclic silylenes (NHSs) has attracted much attention.[10, 92, 93, 99, 224, 225] Recently, we reported the synthesis and structures of the first monomeric heteroleptic silylene [{PhC(NtBu)$_2$}SiCl],[41] and the derivatives [{PhC(NtBu)$_2$}SiNMe$_2$], [{PhC(NtBu)$_2$}SiR] (R = OtBu, OiPr, and PiPr$_2$),[103] [{PhC(NtBu)$_2$}Si(S)StBu],[226] and [{PhC(NtBu)$_2$}SiOtBu]Fe(CO)$_4$.[227] In this year our group reported the synthesis of SiCl$_2$ coordinated by N-heterocyclic carbene and reactivity towards diphenyl acetylene.[42] The preparation of NHC·SiCl$_2$ might have a similar impact in molecular silicon(II) chemistry as GeCl$_2$·dioxane in the chemistry of divalent germanium.[228] Moreover we have also prepared molecular Si(I)-Si(I) compound, [{PhC(NtBu)$_2$}Si]$_2$ from the reduction of heteroleptic trichlorosilane [{PhC(NtBu)$_2$}SiCl$_3$].[229] *Driess et al.* showed the variety of reactivity[163, 222, 230] of L′Si (**50**). Some of the reactivity of **50** mimic the previously reported *β*-diketiminate substituted aluminum(I) LAl.[30, 231] Herein we describe the reaction of silylene L′Si (**50**) (L′ = CH{(C=CH$_2$)(CMe)(NAr)$_2$}; Ar = 2,6-iPr$_2$C$_6$H$_3$) with ammonia, hydrazine, N-methyl hydrazine, and diphenyl hydrazone respectively, and found a striking difference with the reactions using L′Ge (**19**).

6.1. Activation of Ammonia

The activation of N–H bonds of ammonia is rare. The first example of ammonia splitting by transition metals under the formation of an amido hydride complex was only recently reported by Hartwig and coworkers.[67] Studies on the corresponding chemistry with main group compounds are explored to a lesser extent. In 2007 *Bertrand et al.* showed that the facile splitting of ammonia by nucleophilic activation at a single carbon center is possible.[212] Last year *Power et al.*[214] and *Stephan et al.*[184(c)] independently showed, that the activation of ammonia occurred, when a diarylstannylene or a frustrated Lewis pair are involved. In general oxidative addition of the N–H bond of ammonia to unsaturated species could be very important to generate new products. For example, the catalytic addition of ammonia to olefins and the coupling of ammonia with arenes are considered to be two of the ten greatest current challenges for catalytic chemistry.

Herein we report the oxidative addition of ammonia at the silicon(II) center of L′Si (**50**) which occurs under mild conditions with the formation of L′Si(H)NH$_2$. The addition of an excess of dry ammonia gas to a yellow solution of **50** in toluene leads to a rapid change of the yellow color to colorless (Scheme 6.1). The solution was evaporated and extracted with *n*-hexane. Concentration of the solution yielded colorless crystals of L′Si(H)NH$_2$ (**51**) in 90 % yield. Compound **51** is stable in the solid state as well as in solution for a long time without any decomposition under inert atmosphere.

Its composition was proven by multinuclear NMR and IR spectroscopy, mass spectrometry, and elemental (C, H, N) analysis. The ^{1}H and ^{29}Si NMR spectra revealed that **51** has a Si(H)NH$_2$ moiety. The Si–H proton shows a triplet (δ 4.97 ppm) with a coupling constant of $^3J_{\text{H-H}}$ = 4.5 Hz. Thus the ^{29}Si{^{1}H} proton decoupled spectrum exhibits a singlet resonance (δ –45.00 ppm) while the proton coupled spectrum shows a doublet resonance (δ –43.74 and –46.27 ppm) with a coupling constant of $J_{\text{Si-H}}$ = 251.72 Hz. In addition the ^{1}H NMR spectrum exhibits the expected pattern for the ligand with a singlet of the γ-C*H* proton at 5.31 ppm. The IR spectrum displays two weak sharp bands ($\tilde{\nu}$ = 3477 and 3382 cm^{-1}) that are attributed to the NH$_2$ group and a band at 2633 cm^{-1} for the Si–H bond. The most intense peak in the EI mass spectrum appeared at m/z = 446 [M–CH$_3$]$^+$, and the signal at m/z = 461 (15 %) was assigned to the molecular ion [M]$^+$.
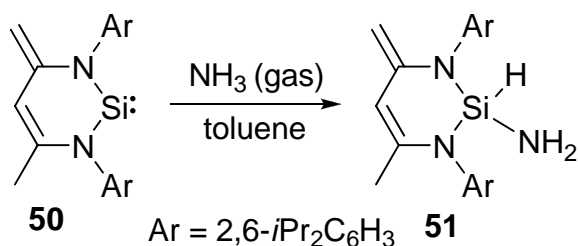
Scheme 6.1. Preparation of compound **51**

Suitable crystals for X-ray structural analysis were obtained from a saturated *n*-hexane solution at –32 °C after two days. Compound **51** crystallizes in the orthorhombic space group *Pbca* with one monomer in the asymmetric unit. X-ray crystal structure analysis afforded monomer in the solid state shown in Figure 6.1. Surprisingly, in **51** the NH$_2$ group is not involved in any kind of hydrogen bonding as shown by X-ray structural analysis and IR spectroscopy. The coordination polyhedron around the silicon atom features a distorted

tetrahedral geometry. The silicon is attached to two nitrogen atoms from the backbone of the chelating ligand, the NH_2 group, and a hydrogen atom.
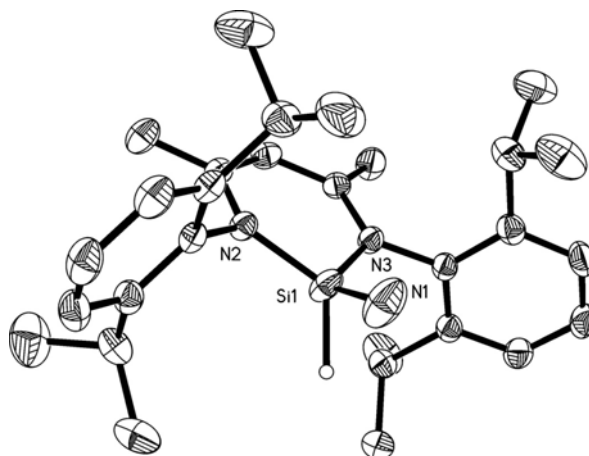
Figure 6.1. Thermal ellipsoid (50%) drawing of **51**. Hydrogen atoms, except those at silicon, are not shown for clarity. Selected bond lengths [Å] and angles [°]: Si1–N1 1.679(2), Si1–N2 1.679(2), Si1–N3 1.730(2); N1–Si1−N2 120.20(19), N1-Si1–N3 114.58(11), N2-Si1–N3 114.58(11).

A noteworthy feature of compound **51** is the Si(H)NH_2 moiety (Si-N 1.653(3) Å); the Si–N1 bond length can be compared with the slightly longer Si–N bond lengths in $RSi(NH_2)_3$[140, 142] (R = 2,4,6-$Ph_3C_6H_2$ av 1.709(7) Å, R = 2,6-iPr$_2$C$_6$H$_3$NSiMe$_3$ av 1.709(2) Å, and R = 2,4,6-tBuC$_6$H$_2$O av 1.692(6) Å). Recently it was reported by *Driess et al*. that L′Si adds water under formation of the intermediate L′Si(H)OH or LSiOH [L = HC{(CMe)(2,6-iPr$_2$C$_6$H$_3$N)}$_2$]. However this intermediate cannot be isolated and reacts further with L′Si in contrast to compound **51**.[230(a)]

6.2. Insertion of Silylene into N-H bond of Hydrazines

Hydrazine and its derivatives are important molecules in the field of organic and inorganic chemistry since the discovery of a new indole synthesis in 1883 by Emil Fischer.[232] Hydrazine is also very well known as an intermediate of nitrogenase in the field of biochemistry.[233] The conversion of N_2 to ammonia by enzymatic or chemical methods (via the intermediates of diimine and hydrazine) results in the cleavage of the N-N bond.[234, 235] In literature the cleavage of the N-N bond of hydrazine is well documented by a variety of model systems, while the N-H bond cleavage of hydrazine is rare.[236] On the metal surface the N-H bond cleavage of hydrazine is reported[237] and substitution reactions of the hydrogen atoms of hydrazine are well known.[238] To the best of our knowledge no insertion reaction at

the N-H bond of hydrazine has been reported. Herein we describe the reaction of silylene L′Si (**50**) with hydrazine, N-methyl hydrazine, and diphenyl hydrazone respectively.

The addition of hydrazine to a yellow solution of **50** in toluene leads to a rapid vanishing of the yellow color (Scheme 6.2). The colorless solution was evaporated and extracted with *n*-hexane. Concentration of the solution yielded colorless crystals of $LSi(H)NHNH_2$ (**52**) in 85 % yield. The composition of **52** was proven by multinuclear NMR spectroscopy, mass spectrometry, and elemental (C, H, N) analysis. The ^{1}H and ^{29}Si NMR spectra revealed that **52** has a $Si(H)NHNH_2$ moiety. The Si–H proton shows a doublet (δ 5.05 ppm) with a coupling constant of ^{3}J(H-H) = 4.34 Hz. The ^{29}Si NMR spectrum exhibits a doublet resonance (δ –42.33 and –44.95 ppm) with a coupling constant of ^{2}J(Si-H) = 260.5 Hz. Each doublet further splits into a doublet with the coupling constant of ^{3}J(Si-H) = 12.73 Hz due to the NH proton. In addition the ^{1}H NMR spectrum exhibits the expected pattern for the ligand (L) with a singlet and doublet of the γ-CH and NH_2 protons at 5.30 and 1.86 ppm, respectively. The most intense peak in the EI mass spectrum appeared at m/z = 461 [M–CH_3]$^{+}$, and the signal at m/z = 476 (10 %) was assigned to the molecular ion [M]$^{+}$.
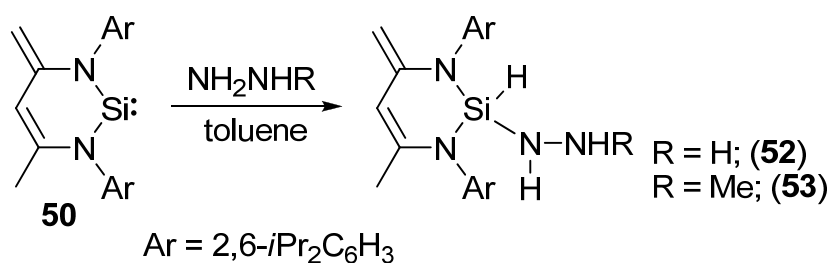
Scheme 6.2. Preparation of compounds **52** and **53**

Furthermore we were interested in the selective N-H bond cleavage of the non-symmetric hydrazine derivative. Therefore we selected N-methyl hydrazine, ($MeNHNH_2$). Compound **50** reacts with N-methyl hydrazine in toluene at room temperature to form exclusively $LSi(H)NHNHMe$ (**53**). This was confirmed by ^{1}H NMR in solution. The ^{1}H NMR spectrum shows a doublet and quartet resonance (δ 2.25 and 1.73 ppm), which corresponds to the two different amine protons of **53**. In addition there are no signals corresponding to the NH_2 protons, therefore we excluded the formation of another isomer of **53**. Also the ^{29}Si NMR spectrum shows a doublet resonance (δ –42.31 and –44.97 ppm) with a coupling constant of

^2J(Si-H) = 263.8 Hz. Each doublet again is splitted into a doublet with the coupling constant of ^3J(Si-H) = 13.17 Hz. This coupling constant is similar to that in compound **53**. Furthermore each doublet again splits into a doublet due to its neighboring proton of the NHMe group, with the coupling constant of ^4J(Si-H) = 2.34 Hz. The most intense peak in the EI mass spectrum appeared at m/z = 475 [M–CH$_3$]$^+$, and the signal at m/z = 490 (25 %) was assigned to the molecular ion [M]$^+$.

Suitable crystals for X-ray structural analysis were obtained from a saturated *n*-hexane solution at –32 °C after two days. Compound **52** crystallizes in the monoclinic space group $P2_1/n$ with one monomer in the asymmetric unit. Surprisingly, in **52** the NHNH$_2$ group is not involved in any kind of hydrogen bonding as shown by X-ray structural analysis (Figure 6.2) and IR spectroscopy. The silicon is attached to two nitrogen atoms from the backbone of the chelating ligand, NHNH$_2$ group, and a hydrogen atom.
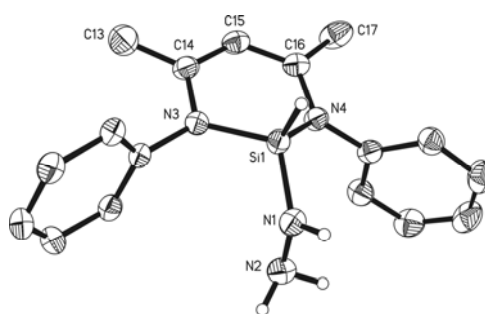
Figure 6.2. Thermal ellipsoid (50%) drawing of **52**. Isopropyl groups of the phenyl rings and hydrogen atoms, except those at silicon and at nitrogen that were found and refined freely, are not shown for clarity. Selected bond lengths [Å] and angles [°]: Si1–N1 1.679(2), N1–N2 1.435(3), Si1–N3 1.730(2); Si1-N1–N2 120.20(19), N1-Si1–N3 114.58(11).

6.3. [1+4] Cycloaddition of Silylene with Diphenyl Hydrazone

The reaction of **50** with an equimolar amount of diphenyl hydrazone in toluene proceeds rapidly even in a broad temperature range (-78 °C to rt) under the formation of the remarkably dearomatized siloxi-indolin-1-amine **54** in almost quantitative yield (Scheme 6.3). To our surprise there was no insertion of the silicon(II) center into the N-H bond of the NH$_2$ group during the reaction. Even after a longer period of time **54** is not converted into an aromatized silyl amine tautomer or any other product.
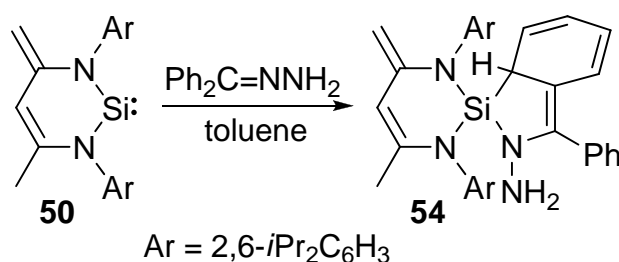
Scheme 6.3. Preparation of compound **54**

Very recently *Driess et al.* reported that **50** reacts with benzophenone under formation of a dearomatized product at low temperatures.[230(e)] However this product converted to the aromatic silyl ether tautomer. This result is in contrast to the formation of compound **54**. **54** is a yellow solid soluble in benzene, THF, *n*-hexane, and *n*-pentane, respectively, and shows no decomposition on exposure to dry air. **54** was characterized by multinuclear spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The ^{1}H NMR spectrum of **54** shows a singlet (δ 2.97 ppm) which can be assigned to the NH$_2$ protons. The ^{29}Si NMR spectrum exhibits a doublet resonance (δ –19.87 and –20.07 ppm) with a coupling constant of ^3J(Si-H) = 20.4 Hz.
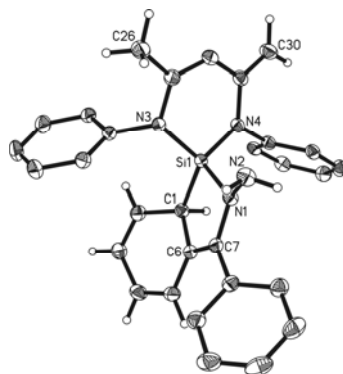
Figure 6.3. Thermal ellipsoid (50%) drawing of **54**. Isopropyl groups of the phenyl rings and hydrogen atoms, except those at N2, C26 and at C30 and non aromatics, that were found and refined freely, are not shown for clarity. Selected bond lengths [Å] and angles [°]: Si1–N1 1.7480(12), N1–N2 1.4322(15), Si1–C1 1.8786(13), C1–C6 1.5260(16), C6–C7 1.3596(17); Si1-N1–N2 117.46(8), Si1-C1–C6 103.70(8), N3-Si1–N4 103.44(9).

Suitable crystals for X-ray structural analysis were obtained from a hot saturated *n*-hexane solution of **54** after keeping this solution overnight at room temperature. **54** crystallizes in the triclinic space group *P*-1, with one molecule of **54** in the asymmetric unit. **54** exists as a monomer in the solid state (Figure 6.3). There are no intermolecular hydrogen bonds

observed in the crystal lattice. The coordination polyhedron around the silicon atom comprises two nitrogen atoms from the supporting ligand, one carbon atom from the dearomatized phenyl group, and one nitrogen atom of the hydrazone moiety, featuring a distorted tetrahedral geometry. Compound **54** represents a spirocyclic compound with the silicon atom at the spiro center within a six-membered SiN_2C_3 ring and a five-membered $SiNC_3$ ring, which are orthogonal arranged to each other.

Compounds **52** and **54** exhibit the Si-N-NH_2 moiety (Si1-N1 1.679(2) Å for **52** and Si1-N1 1.7480(12) Å for **54**); the Si1–N1 bond lengths can be compared with that in **51** (1.653(3) Å) and those in $RSi(NH_2)_3$[140, 142] (R = 2,4,6-$Ph_3C_6H_2$ av 1.709(7) Å, R = 2,6-iPr$_2$C$_6$H$_3$NSiMe$_3$ av 1.709(2) Å, and R = 2,4,6- tBu$_3$C$_6$H$_2$O av 1.692(6) Å). The N-N bond lengths in **52** and **54** (N1-N2; 1.435 (3) Å and 1.4322(15) Å) are comparable with that in $LGeN(CO_2Et)NHCO_2Et$, (**14**) (1.418(14) Å).

Chapter 7

Diazo Alkane an Effective Reagent for Unprecedented Reactions with Compounds of Low Valent Group 14 Elements

The reaction of diazoalkane with transition metals has a long history regarding the utility of carbene transfer for cyclopropanation of olefins.[239] Moreover metal carbene complexes play an important role in olefin metathesis,[240] C-H bond activation,[241] and the synthesis of reactive ylides.[242] In all these examples diazoalkane either interacts with the metal center to form the metal diazoalkane complex or subsequently releases dinitrogen from diazoalkane to form the metal carbene complex. Compared to this, the reaction of diazoalkane with main group metals is scarcely known in literature.[243]

7.1. Reactions of Diazo Compounds with LGeH

We have already described the synthesis of LGeH (**5**); (L = HC(CMeNAr)$_2$; Ar = 2,6-iPr$_2$C$_6$H$_3$) and its reactivity towards multiple bonded carbon-carbon, carbon-oxygen, and nitrogen-nitrogen systems, and also with elemental sulfur, nitrous oxide, and frustrated Lewis carbene-borane pair. Subsequently we became interested in studying the reactivity of **5** with diazoalkane. Some reactions between metal hydrides and diazoalkanes have been reported.[244] We expected from the reaction of diazoalkane with **5** one of the following products: LGe(H)NNCHR, LGeNNCH$_2$R, LGe(H)CHR, or LGeCH$_2$R. To our surprise none of these species was formed.

Treatment of **5** with ethyl diazoacetate and trimethylsilyl diazomethane, respectively leads to the first stable germanium(II) substituted hydrazone derivatives, LGeN(H)NCHR, (R = CO$_2$Et (**55**), SiMe$_3$ (**56**)) in high yield (Scheme 7.1). The reaction proceeds through the unprecedented end-on insertion of diazoalkane into the Ge-H bond. The initial dinitrogen elimination followed by insertion or oxidative addition reaction is generally accepted. Accordingly, the end-on N$_2$CHR insertion into the Ge-H bond unambiguously reveals the initial interaction between the Ge center and the terminal nitrogen atom of the diazo group followed by hydrogen transfer from the germanium center to nitrogen. This type of reaction is, to the best of our knowledge, so far unknown.

Compounds **55** and **56** have been well-characterized by spectroscopic, analytic, and X-ray crystallographic measurements. The ^{1}H NMR spectra of **55** and **56** exhibit a singlet (δ 7.25 and 6.37 ppm) which can be assigned to the N-*H* proton. In addition **55** and **56** show singlet resonances (δ 6.62, 4.91 ppm and δ 6.44 and 4.96 ppm) which corresponds to the imine and γ-C*H* protons. The IR spectrum of **55** exhibits bands at 3188, 2700 and 1641 cm^{-1}, which are assigned to the N-H, C–H and C=O stretching frequencies.
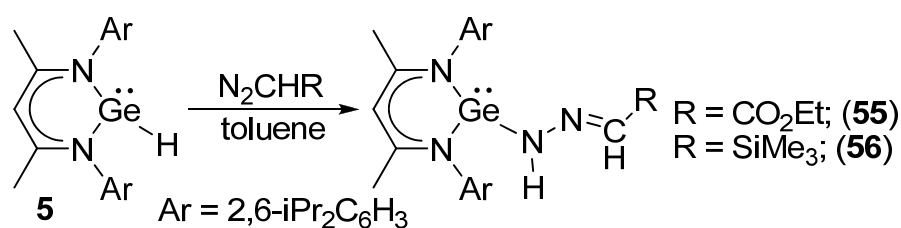
Scheme 7.1. Preparation of compounds **55** and **56**
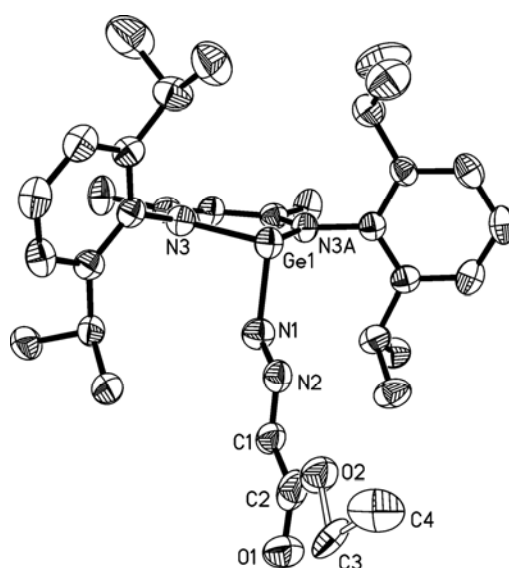
Figure 7.1. Molecular structure of **55**. Thermal elipsoids are shown at 50% probability. H atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.915(7), N1–N2 1.344(10), N2–C1 1.273(10), Ge1–N3 2.015(5), Ge1–N3A 2.015(5); Ge1–N1–N2 117.0(6), N1–N2–C1 118.7(7), N3–Ge1–N3A 94.2(2).

Both **55** and **56** are soluble in benzene, THF, *n*-hexane, and *n*-pentane, respectively and show no decomposition on exposure to air. In the solid state **55** and **56** are yellow colored. **55** crystallizes from saturated toluene solution at room temperature after one day in the tetragonal space group *P*4$_2$/*ncm,* with one monomer in the asymmetric unit (Figure 7.1).

Compound **56** has one SiMe$_3$ group and displays a singlet in the ^{29}Si NMR spectrum (δ 6.28 ppm). **56** crystallizes from saturated *n*-hexane solution at room temperature after two days in the monoclinic space group *C2/m,* with one monomer in the asymmetric unit (Figure 7.2).
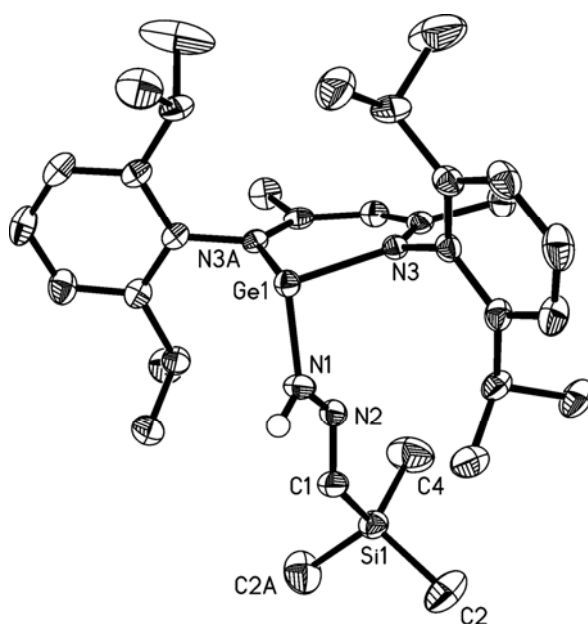
Figure 7.2. Molecular structure of **56**. Thermal elipsoids are shown at 50% probability. H atoms except N1–H are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.878(3), N1–N2 1.351(4), N2–C1 1.303(4), Ge1–N3 1.9913(17), Ge1–N3A 1.9913(17); Ge1–N1–N2 130.6(2), N1–N2–C1 117.4(3), N3–Ge1–N3A 90.41(10).

7.2. Reaction of Trimethylsilyl Diazomethane with LGeMe

In 2002 our group reported the reaction of LGeMe with trimethylsilyl azide under the formation of L′Ge(Me)(NHSiMe$_3$) with a subsequent elimination of dinitrogen gas.[29] Trimethylsilyl azide and trimethylsilyl diazomethane are isoelectronic, therefore we performed the reaction of LGeMe with the latter one, which resulted in the formation of [L′Ge(Me)(NHNCHSiMe$_3$)] (**57**), instead of nitrogen elimination and creation of LGe(Me)CHSiMe$_3$ (Scheme 7.2). The reaction proceeds with migration of a hydrogen atom from a methyl group of the ligand backbone to the end-on nitrogen atom of the diazo group. In the ^{1}H NMR spectrum of **59** the resonances clearly show the existence of N*H* (δ 6.76 ppm) C*H* (δ 5.78 ppm), and the C*H*$_2$ moiety (δ 3.83 and 3.21 ppm).
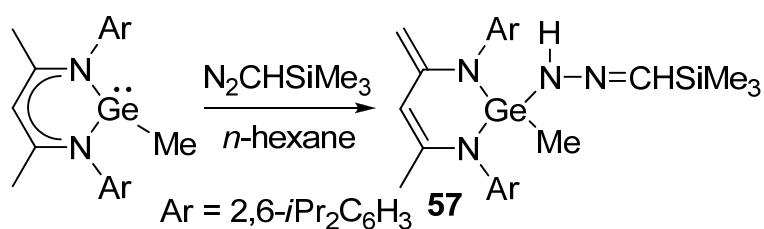
Scheme 7.2. Preparation of compound **57**

This result also unambiguously reveals the initial interaction between the Ge(II) center and the terminal nitrogen atom of the diazo group followed by the hydrogen transfer from the methyl group of ligand backbone to the end-on nitrogen of the diazo group. The formation of **57** may be compared with that of [L′Ge(NHSiMe$_3$)$_2$] (**18**) from the reaction of LGeH (**5**) and trimethylsilyl azide (Chapter 3, Scheme 3.8). In both compounds an oxidation of the Ge(II) to Ge(IV) occurred and a migration of a hydrogen atom from a methyl group of the ligand backbone to the nitrogen atom is observed.

7.3. Reaction of Trimethylsilyl Diazomethane with L′Ge

We have already discussed the cleavage of N-H and O-H bonds using the heterocyclic germylene L'Ge (**19**). Now we reacted **19** with trimethylsilyl diazomethane under formation of the diazogermylene LGeC(N$_2$)SiMe$_3$ (**58**) by a C-H bond cleavage (Scheme 7.3). Here it is also noted that the trimethylsilyl diazomethane reacts with LGeH (**5**) with an unprecedented end-on nitrogen insertion of diazo nitrogen into the Ge-H bond under formation of germanium(II)-substituted hydrazones **55** and **56** (Scheme 7.1). **58** is readily soluble in hydrocarbon and ether solvents and has been fully characterized.
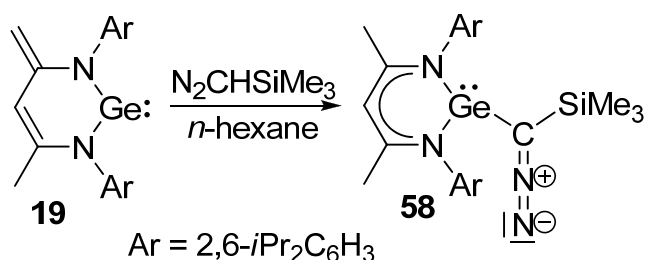
Scheme 7.3. Preparation of compound **58**

The germanium complex **58** crystallizes in the triclinic space group *P*-1 with one molecule in the asymmetric unit (Figure 7.3). The germanium atom is coordinate to two nitrogen atoms of the ligand (N1, N2) and to the carbon atom (C25) of the diazolyl group. The Ge1-C25

(1.9969(14) Å) and Si1-C25 (1.8345(15) Å) bond lengths are close to the normal values for σ bonds of 1.99 and 1.87 Å respectively. Also the C25-N3 bond length with 1.3037(19) Å is in the range of a carbon-nitrogen double bond (1.29 Å) merely the N3-N4 bond length (1.1458(19) Å) lies between a nitrogen-nitrogen double and triple bond (N=N 1.25 Å, N≡N 1.10 Å). The Ge1-C25-Si1 angle of 118.37(7)° is consistent with a sp^2 hybridized carbon atom (C25). These values are closely related to those of a reported diazogermylene compound.[245] Compound **58** has one SiMe₃ group and displays a singlet in the ^{29}Si NMR spectrum (δ -2.43 ppm).
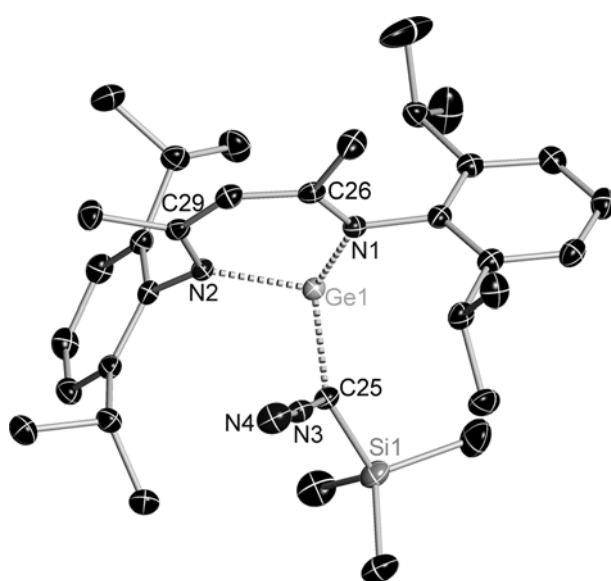
Figure 7.3. Molecular structure of **58**; anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–C25 1.845(2), C25–Si1 1.845(2), C25–N3 1.845(2), N3–N4 1.845(2), Ge1–N1 2.030(2), Ge1–N2 2.030(2); Ge1–C25–N3 88.60(8), C25–N3–N4 88.60(8), N1–Ge1–N2 88.60(8), C25–Ge1–N1 95.52(10), C25–Ge1–N2 95.55(10), N3–C25–Si1 95.55(10).

When a supernatant solution of **58** is stored for a longer period of time (about 3 months) at room temperature, a 1,3-silyl group as well as germanium moiety shift from the diazo carbon atom to the end-on nitrogen atom of the diazogermylene has been observed (Scheme 7.4). Thus the diazo group is converted into an isonitrile species. A comparable migration of a silyl group of azides and the lithium salt of trimethylsilyl diazomethane is known for organolanthanides.[246]
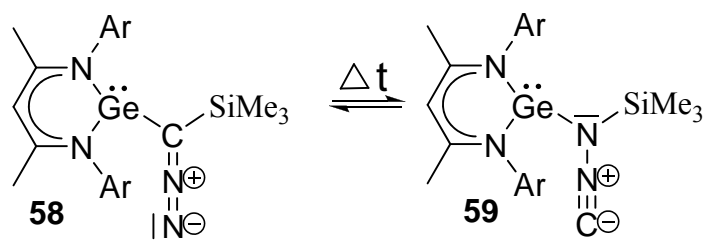
Scheme 7.4. Equilibrium between **58** and **59**

The above described silyl group and germanium substituent migration has been confirmed by X-ray structure analysis of **59** (Figure 7.4). Compounds **58** and **59** are isostructural. The germanium atom in **59** is coordinate to three nitrogen atoms whereas the bond length of Ge1-N3 (1.9491(16) Å) is marginally shorter than the average Ge-N bond lengths of the bidentate ligand (Ge1-N1 (1.9994(16) Å, Ge1-N2 (1.9862(16) Å). The N3-Si2 (1.7699(17) Å) bond length is in the range of a standard N-Si bond (1.74 Å). The N4-C1 bond length (1.154(3) Å) correlates with a normal N-C triple bond (N≡C 1.156 Å) while the N3-N4 bond (1.350(2) Å) lies between a N-N single and double bond (N-N 1.45 Å, N=N 1.25 Å). The ^{29}Si NMR spectrum of **59** exhibits a singlet (δ 12.50 ppm).

Figure 7.4. Molecular structure of **59**; anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–N3 1.845(2), N3–Si2 1.845(2), N3–N4 1.845(2), N4–C1 1.845(2), Ge1–N1 2.030(2), Ge1–N2 2.030(2); Ge1–N3–N4 88.60(8), N3–N4–C1 88.60(8), N1–Ge1–N2 88.60(8), N3–Ge1–N1 95.52(10), N3–Ge1–N2 95.55(10), N4–N3–Si2 95.55(10).

7.4. Reaction of Lithiated Trimethylsilyl Diazomethane with LSnCl

Trialkylsilyl diazomethane derivatives are established for the synthesis of chemical building blocks[247] and they also possess six known or suspected structural isomers including nitrilimine and carbodiimide. In synthetic organic chemistry compounds containing the carbodiimide functionality are used as dehydration agents and to activate carboxylic acids towards amide or ester formation. For this purpose especially dicyclohexylcarbodiimide (DCC) with additives, such as N-hydroxybenzotriazole, is applied for peptide synthesis in biochemistry.[248-251] In literature there are reports on the synthesis of carbodiimides from diazo compounds at very high temperatures or in the presence of a metal catalyst.[252] Herein we report our efforts to exploit diazoalkane main group chemistry with β-diketiminate substituted tin(II) chloride, LSnCl.[146]

The reaction of LSnCl with lithiated trimethylsilyl diazomethane, obtained from nBuLi and Me$_3$SiCHN$_2$ in THF, resulted in the formation of LSnNCNSiMe$_3$ (**60**) (Scheme 7.5). The reaction proceeds at ambient temperature without using any additional catalyst. The formation of the diazo compound LSnC(N$_2$)SiMe$_3$ (**60a**) or nitrilimine compound LSnNNCSiMe$_3$ (**60b**) was not observed, on the basis of analytical and structural data. In this context it is worth mentioning that the synthesis of diazo germylene and stannylene compounds was previously reported using ArGeCl (Ar = 2,6-(CH$_2$NR$_2$)C$_6$H$_3$, R = Et, iPr) and Ar$'$SnCl (Ar$'$ = 2,6-Tip$_2$C$_6$H$_3$, Tip = 2,4,6-iPr$_3$C$_6$H$_2$).[245, 253] Furthermore N-bound silyl products, [(MeC$_5$H$_4$)TiCl(μ-NSiMe$_3$)]$_2$,[254] and [(C$_5$Me$_5$)$_2$Ln{μ-N(SiMe$_3$)NC}]$_2$ (Ln = Sm, La)[246(b)] have been previously observed in the reaction of Li[Me$_3$SiCN$_2$] with (MeC$_5$H$_4$)TiCl$_3$ and [(C$_5$Me$_5$)$_2$Ln][(μ-Ph)$_2$BPh$_2$] (Ln = Sm, La) respectively with migration of the silyl group. However compound **60** represents the first structurally characterized carbodiimide of heavier group 14 elements containing the Sn(II) motif.
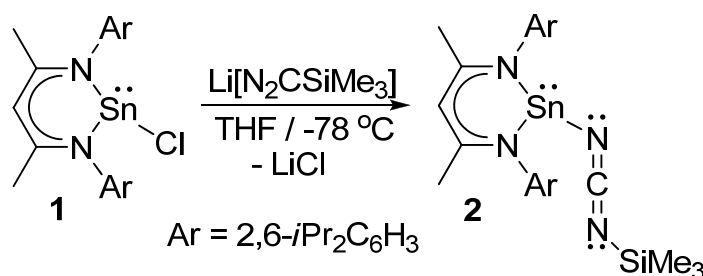
It is well known that the reaction of lithium salts of substituted diazomethane with different electrophiles generates diazo or nitrilimine compounds.[255] Therefore the present observation of a carbodiimide formation requires an unprecedented rearrangement. Wentrup and coworkers reported the evidence for nitrilimine to carbodiimide rearrangement through an isodiazirine and imidoylnitrene intermediate, based on the nature of the products obtained in the pyrolysis of different nitrilimine precursors at 500 to 960 °C.[256] Subsequently Bertrand and coworkers mentioned the direct evidence for the nitrilimine to imidoylnitrene rearrangement by the isolation of a unusual nitrene complex.[257] Considering all the facts we propose the following pathway for the formation of **60** (Scheme 7.6).
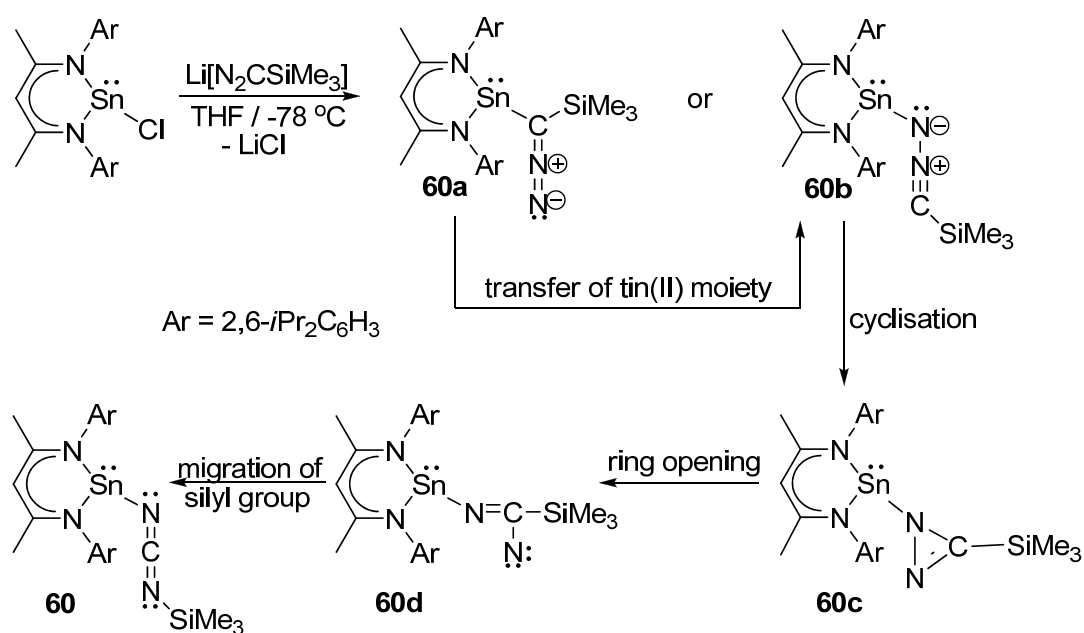
Scheme 7.6. Proposed pathway for the formation of **60**

Compound **60** was characterized by multinuclear NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis (Figure 1). The ^{1}H NMR spectrum of **60** exhibits a singlet (δ 4.96 ppm) corresponding to the γ-C*H* proton. Compound **60** has one SiMe$_3$ group and displays a singlet in the ^{29}Si NMR spectrum (δ -6.0 ppm), and shows only one type of ^{13}C satellite line due to the methyl groups with a coupling constant of 58.3 Hz. This is an indication that the SiMe$_3$ group binds to the N-atom and not anymore to carbon.

Moreover, the ^{29}Si NMR spectrum shows the resonances which are attributed to the ^{15}N satellite with a coupling constant of 16.8 Hz from the nitrogen atom of the carbodiimide backbone. The ratio of the two satellite lines is well matching with their abundances. The ^{119}Sn NMR resonance of **60** arises at δ -321.4 ppm as a triplet ($J(^{119}$Sn-^{14}N$)$ = 250 Hz), which is upfield shifted when compared with that of the starting material LSnCl (δ -224 ppm). In the ^{14}N NMR spectrum the signal at δ -329 ppm corresponds to the N atom bound to the silyl group, which was proven by the ^{15}N-^{1}H correlation experiment. The resonance of the N*C*N carbon is found in the ^{13}C NMR spectrum at δ 129.7 ppm (δ 131.0 ppm; *i*Pr$_3$SiNCNSnMe$_3$).[252] In the EI mass spectrum the molecular ion is observed at *m/z* 649 as the base peak for **60**.

60 crystallizes from a saturated *n*-hexane solution at -30 $^{\circ}$C after two days in the monoclinic space group *C*2/*m*, with one monomer in the asymmetric unit. The coordination around the tin atom features a distorted tetrahedral geometry with one lone pair (Figure 7.5). Crystallographic studies on **60** also indicate that the N-bound silyl group structure LSn−N=C=N−SiMe$_3$ was formed. All the bond lengths and bond angles are as expected. It is worth mentioning that in the solid state of **60** weak Sn−Sn interactions (3.708 Å) are observed which are below the sum of van der Waals radii of 4.40 Å for two tin atoms (Figure 7.6).[258]
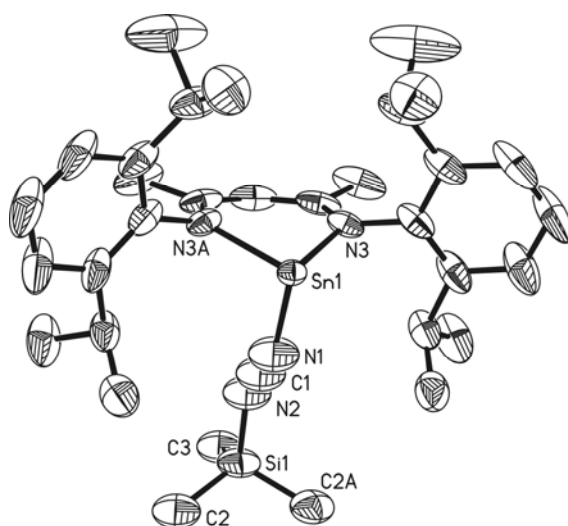
Figure 7.5. Molecular structure of **60**. Thermal ellipsoids are shown at 50% probability. H atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]:Sn1–N1 2.121(7), N1–C1 1.124(10), C1–N2 1.239(11), N2−Si1 1.718(7), Sn1–N3 2.169(3); Sn1–N1–C1 152.5(8), N1–C1–N2 178.6(10), C1−N2−Si1 136.2(7), N1−Sn1−N3 90.35(18), N3−Sn1−N3A 86.5(2).
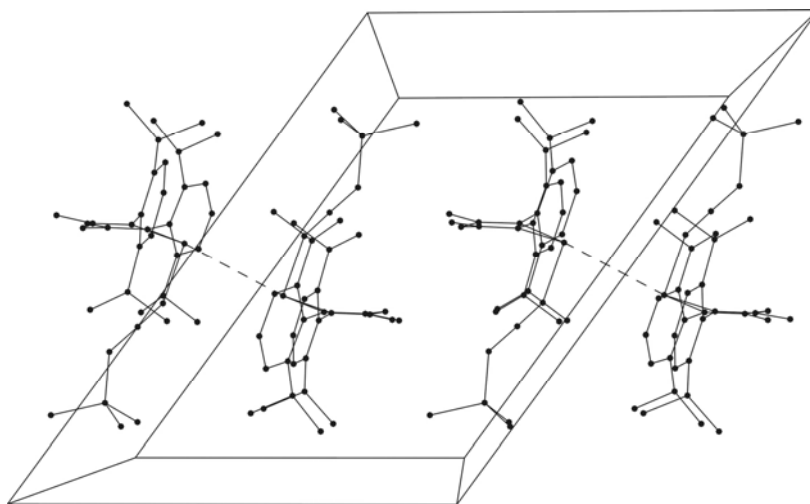
Figure 7.6. Unit cell of **60**, showing the weak Sn−Sn interactions (3.708 Å)

Chapter 8

Synthesis and Reactivity of Germanium(II) and Tin(II) Compounds of the Type LMR

After the successful synthesis of germanium(II) amide $LGeNH_2$, (L = $HC(CMeNAr)_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) (**42**) with the parent NH_2 group, we became interested in the synthesis of another amide derivative of germanium(II). Preparation of $LSnNMe_2$ (**66**) was already reported by *Gibson et al.*[259] Reaction of $LSnNMe_2$ (**66**) with 2-benzoylpyridine, 2,2,2-trifluoro acetophenone generates the tin(II)-alkoxides $LSnOCPh(2-Py)NMe_2$ (**67**) and $LSnOCPh(CF_3)NMe_2$ (**68**) respectively by nucleophilic addition to the carbon oxygen double bond. Furthermore the reaction of **66** with terminal alkine ($HCCCO_2R$, R = Me, Et) forms tin(II)-alkylidene $LSnCCCO_2R$ (R = Me, (**69**); R = Et, (**70**)) compounds under elimination of Me_2NH rather than to undergo nucleophilic addition reaction at the carbon-carbon triple bond.

8.1. Synthesis of LGeNMe₂ and its Reaction with Elemental Sulfur

The synthesis of $LGeNH_2$ (**42**) involves the reaction of L´Ge (**19**) with NH_3 gas, under the cleavage of one N-H bond. The similar reaction of L´Ge with Me_2NH may generate the $LGeNMe_2$. The reaction of LGeCl with $LiNMe_2$ in diethyl ether afforded $LGeNMe_2$ (**61**) in a good yield (Scheme 8.1). It is worth mentioning that the reaction of LGeCl with $LiN(TMS)_2$ in diethyl ether leads exclusively to L´Ge.[37]
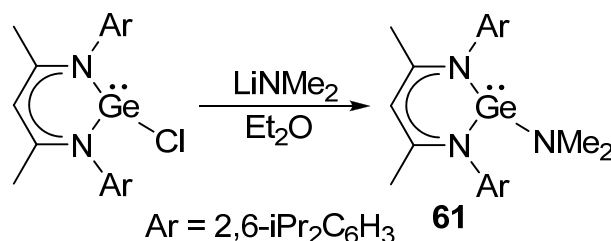
Scheme 8.1. Preparation of compound **61**

61 was characterized by ^{1}H NMR spectroscopy, EI mass spectrometry, and elemental analysis. The ^{1}H NMR spectrum of **61** shows a singlet at 4.82 ppm for the *γ-CH* proton, and two septets (3.43, 3.37 ppm) corresponding to the C*H* protons of the *i*Pr moieties. Moreover the signal arises at δ 2.82 ppm corresponds to the protons of the N*Me*$_2$ group. The most abundant ion peak in the EI mass spectrum appeared at *m/z* 491 for the molecular ion peak

[M-NMe$_2$]$^+$. **61** crystallizes in the triclinic space group *P*-1 with one monomer in the asymmetric unit (Figure 8.1).
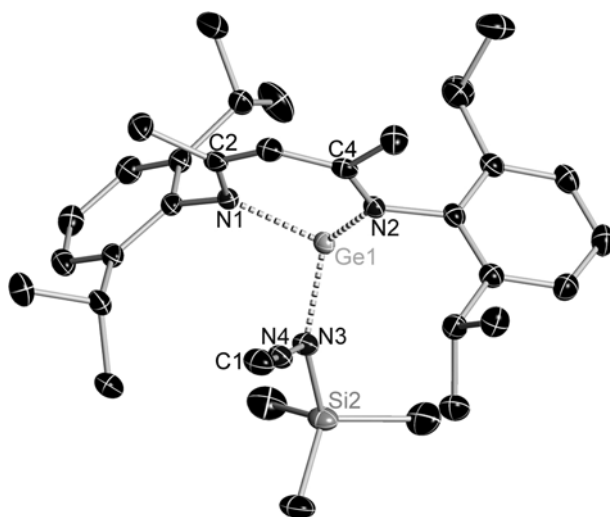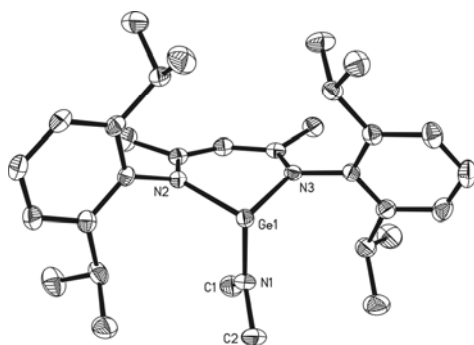

Figure 8.1. Molecular structure of **61**. Anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] are Ge1–N1 1.8712(14), Ge1–N2 2.0309(16); N1–Ge1–N2 99.84(7), N1–Ge1–N3 97.01(6).

We already reported on the synthesis and structure of LGe(S)X[172] (X=Cl, F) with Group 14 and 16 elements bearing a halide as well as the functionalized derivative LGe(S)R] (R=Me).[172] Recently, we succeeded in the isolation and full characterization of a germanium thionoacid LGe(S)OH, which has no isolated precedent in the carbon system.[206] To the best of our knowledge there are no reports on the imide group bearing mixed unsaturated compounds containing elements of Groups 14–16. Herein we describe the formation of the germanium thionamide LGe(S)NMe$_2$ (**62**) (Scheme 8.2). The reaction of LGeNMe$_2$ in the presence of equivalent amounts of elemental sulfur at room temperature in toluene leads after one day to the white compound LGe(S)NMe$_2$ (**62**) in moderate yield.
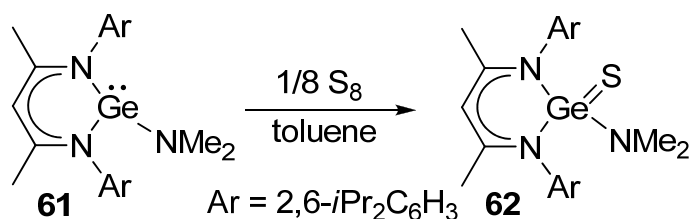
Scheme 8.2. Preparation of compound **62**

Compound **62** is soluble in benzene, THF, and *n*-hexane, and shows no decomposition on exposure to dry air. Compound **62** was characterized by NMR spectroscopy, EI mass spectrometry. The ^{1}H NMR spectrum of **62** exhibits a broad resonance at δ 2.89-2.73 ppm for the amide (N*Me$_2$*) hydrogens, which can be compared with singlet resonance of **61** (δ 2.82 ppm). The most abundant ion peak in the EI mass spectrum appeared at m/z 523 [M-NMe$_2$]$^+$.

8.2. Synthesis of LGeOTf

LGeOTf (**63**) was previously reported by *Driess et al.* by the reaction of LGeP(H)SiMe₃ with Me₃SiOTf in the presence of Et₃N (OTf⁻ = [OSO₂CF₃]⁻).[260] Here we show the easy one pot synthetic method. LGeOTf (**63**) is formed under salt metathesis of LGeCl with AgOTf in toluene and afforded colorless compound **63** in high yield (Scheme 8.3).
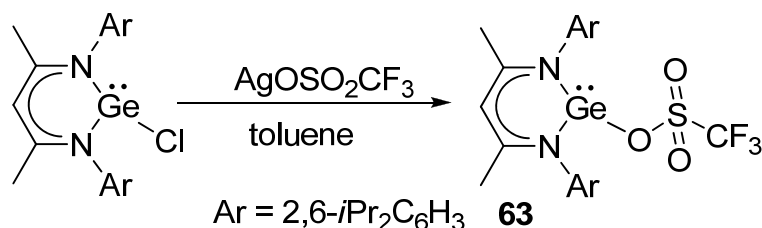
Scheme 8.3. Preparation of compound **63**
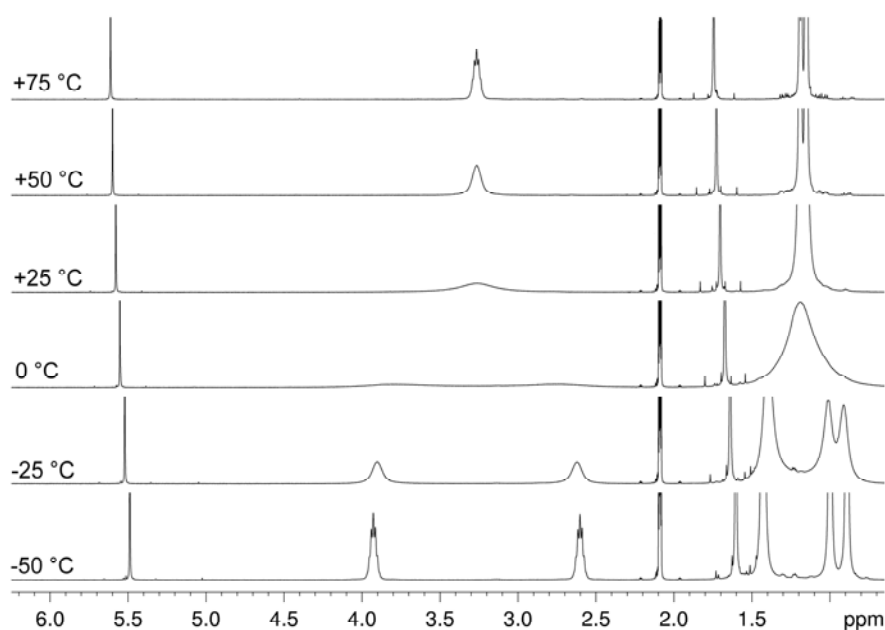
Figure 8.2. ¹H NMR spectrum of **63** at various temperatures

Unlike other *β*-diketiminate germanium compounds, the ¹H NMR spectrum of **63** shows for the *i*Pr substituents at room temperature only one broad resonance (C*H*, δ 3.26 ppm) and one doublet for the methyl groups. This may be due to the rapid exchange of the triflate group at the germanium atom. Therefore we studied the temperature dependence ¹H NMR between +75 and -50 °C. At -50 °C two septets appeared at 3.92 and 2.60 ppm for the C*H* protons (Figure 8.2). However at -50 °C the exchange of the triflate group is slow on the NMR time

scale compared to that at room temperature. The calculated exchange rate at different temperatures is the following: -50 °C, 3.5 sec^{-1}; -25 °C, 28 sec^{-1}; 0 °C, 250 sec^{-1}; +25 °C, 2500 sec^{-1}; +50 °C, 26000 sec^{-1}.

8.3. Synthesis of LSnMe

Treatment of LSnCl with MeLi in diethyl ether at -78 °C then allowing the solution to reach ambient temperature and keeping this for 3 h at this temperature afforded the corresponding methyl derivative LSnMe (**64**) in high yield (88 %) (Scheme 8.4). Yellow crystals of **64** suitable for single crystal X-ray analysis were obtained from a *n*-hexane solution at -30 °C after two days. Compound **64** is thermally stable. No decomposition was observed at temperatures below its melting point (170 °C) under an inert atmosphere. EI-MS of **64** gave the corresponding monomeric molecular ion peak M$^+$. The ^{1}H NMR spectrum of **64** consists of a singlet resonance (0.59 ppm) for Sn-CH_3 and is flanked by Sn satellite lines ($^2J(^{119}$Sn,^{1}H) = 33.07 Hz). Also the ^{119}Sn NMR spectrum exhibits a singlet resonance (δ 192.65 ppm), which is downfield shifted when compared with that of LSnCl (δ -224 ppm)[146]. This change was expected because of the different electronic nature of the substituents on the tin atoms. The other resonances of the ^{1}H NMR spectrum and elemental analyses are in accordance with **64** as formulated.
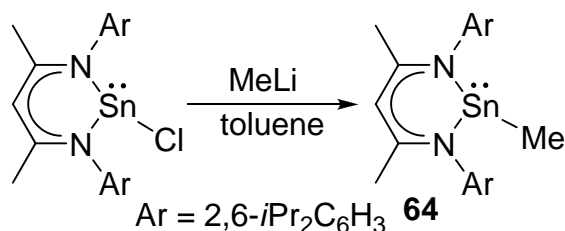
Scheme 8.4. Preparation of compound **64**

The yellow compound **64** was also characterized by single crystal X-ray structural analysis. The molecular structure is depicted in Figure 8.3 and reveals the monomeric feature in the solid state. The Sn–N and Sn–C bond lengths are comparable to those found in literature.
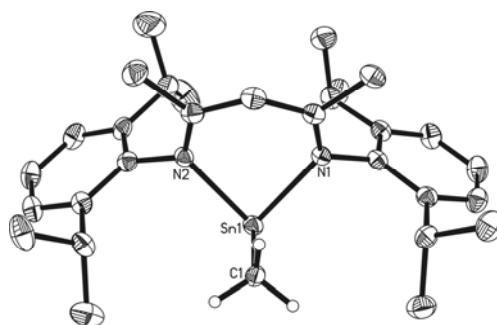
Figure 8.3. Molecular structure of **64**. Selected bond lengths [Å] and angles [°]; anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity except Sn–Me hydrogens: Sn1–C1 2.253(2), Sn1–N1 2.2091(18), N1–C14 1.331(3); N1–Sn1–C1 92.95(8), N2–Sn1–C1 92.69(9), N1–Sn1–N2 84.69(7).

8.4. Synthesis of Tin(II) Amides

The preparation of the parent tin(II) amide $LSnNH_2$ was not successful. *Gibson et al.* reported the synthesis of $LSnNMe_2$.[259] Here we report the synthesis of $LSnN(SiMe_3)_2$. The well-defined compound $LSnN(SiMe_3)_2$ (**65**) was obtained in high yield from the reaction of LH with two equivalents of $KN(SiMe_3)_2$ followed by the reaction with one equivalent of $SnCl_2$ at room temperature in THF (Scheme 8.5).
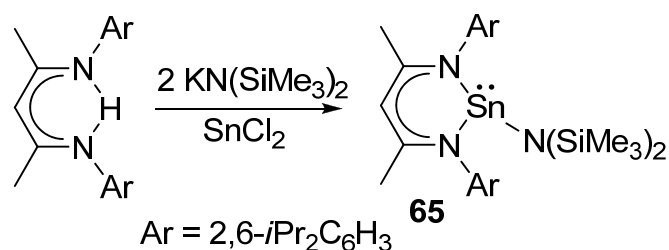
Scheme 8.5. Preparation of compound **65**

Compound **65** is a yellow solid soluble in benzene, THF, *n*-hexane, and pentane and shows no decomposition on exposure to air for a short period of time. **65** was characterized by multinuclear NMR spectroscopy, EI mass spectrometry, elemental, and X-ray structural analysis. The ^{1}H NMR spectrum of compound **65** shows a singlet at 5.01 ppm for the *γ*-C*H* proton, two septets (3.73 and 3.16 ppm) corresponding to the C*H* protons of the *i*Pr moieties and singlets at 0.46 and 0.24 ppm for the two nonequivalent $SiMe_3$ groups. The ^{119}Sn NMR of **65** exhibits a singlet at 134.54 ppm. The most abundant ion peak in the EI mass spectrum appeared at *m/z* 537.
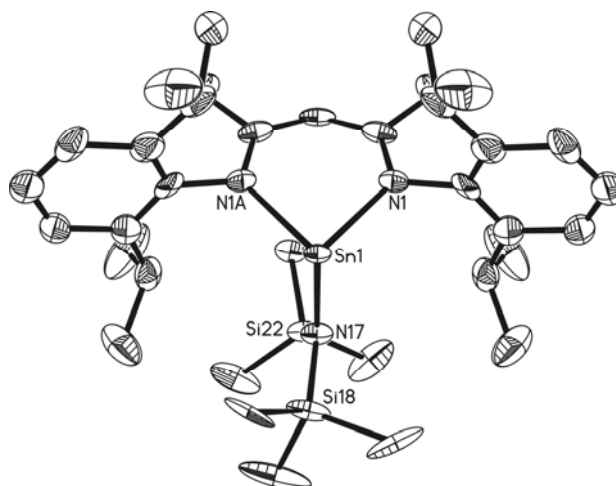
Figure 8.4. Molecular structure of **65**. Anisotropic displacement parameters are depicted at the 30 % probability level and all restrained refined hydrogen atoms are omitted for clarity.

Maintaining a *n*-hexane solution of **65** for one day at 0 °C resulted in the formation of yellow single crystals which are suitable for X-ray structural analysis. Compound **65** crystallizes in the orthorhombic space group P_{nma}, with half a molecule in the asymmetric unit. The coordination environment of the central Sn atom exhibits a distorted tetrahedral geometry.

The di(isopropyl)phenyl moiety of the *β*-diketiminate ligand in **65** was refined with disorder at two discrete positions, applying restraints to the atomic coordinates and thermal displacement parameters (final ratio of the two positions is 50.7: 49.3). Due to disorder of the di(isopropyl)phenyl moiety of the *β*-diketiminate ligand for **65**, a discussion of selected bond lengths or angles is not carried out.

We have already mentioned that LSnNMe$_2$ has already been reported and the ^{119}Sn NMR exhibits a singlet at -172.44 ppm.[259] Here we prepared the LSnNMe$_2$ (**66**) using diethyl ether as a solvent instead of toluene and obtained **66** in an excellent yield (Scheme 8.6). The analytical data matches with previously reported values.
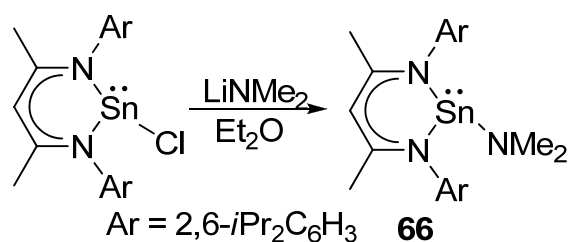
Scheme 8.6. Preparation of compound **66**

8.5. Reaction of LSnNMe$_2$ with Ketones

Lappert et al. described the addition of aminostannanes to a variety of alkines and alkenes and also aminosilylation and aminophosphination reactions with highly electrophilic substrates.[261] Recently *Hartwig et al.* reported transamination of alkenes and vinylarenes by rhodium(I) amides.[262] The insertion of an alkine into a molybdenum–amide bond has also been described.[263] We already discussed the hydrogermylation and hydrostannylation of unsaturated compounds using LGeH (**5**) and LSnH (**20**) respectively. Consequently we became interested in the aminostannylation of unsaturated compounds by using LSnNMe$_2$ (**66**). Although *Gibson et al.* reported already this compound in 2006 and studied the mechanistic properties of single-site β-diketiminate tin(II) initiators for polymerization of *rac*-lactide.[259] Herein we demonstrate for the first time the aminostannylation of a carbonyl group by using tin(II) amide. Examples are the reaction of 2-benzoyl pyridine and 2,2,2-trifluoro acetophenone with **66** (Scheme 8.7).
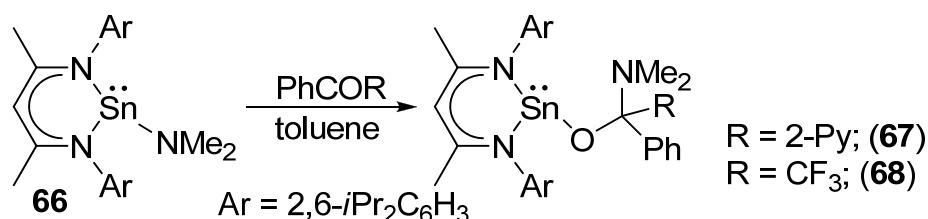
Scheme 8.7. Preparation of compounds **67** and **68**

Treatment of **66** with 2-benzoyl pyridine and 2,2,2-trifluoro acetophenone leads almost quantitatively to the stannylene alkoxides **67** and **68**, respectively (Scheme 8.8) with the Sn–O–CNMe$_2$ core. The ^{1}H NMR spectrum of **67** exhibits a singlet (δ 4.92 ppm) which can be assigned to the γ-C*H* proton and singlet resonance at 1.83 ppm for the NMe$_2$ group. The four isopropyl groups of **67** are showing four different resonances, and even the two methyl groups in the backbone exhibit two different signals in the proton NMR spectrum. The ^{119}Sn NMR resonance of **67** arises at δ -328 ppm. **67** crystallizes in the triclinic space group *P*-1 with one monomer in the asymmetric unit (Figure 8.5).
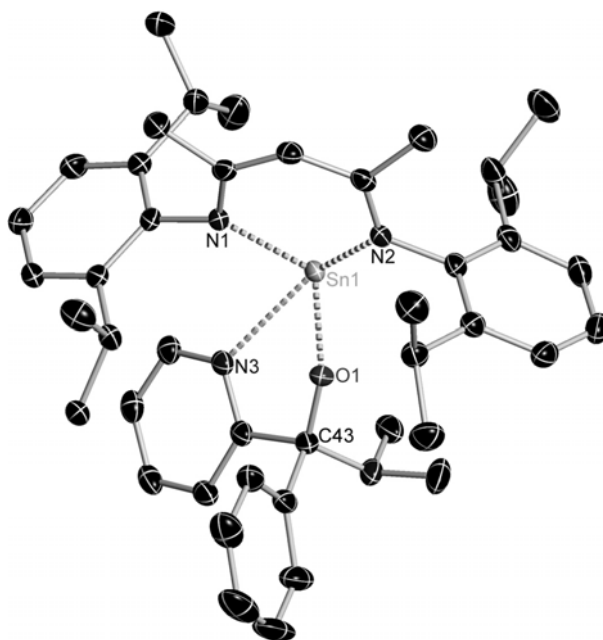
Figure 8.5. Molecular structure of **67**; anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–O1 2.0505(11), Sn1–N1 2.2538(13), Sn1–N3 2.5580(14), O1–C43 1.3907(19); N1–Sn1–N2 83.14(5), N1–Sn1–O1 102.50(5), Sn1–O1–C43 125.03(10).

68 has one CF_3 group and displays interesting NMR spectra. The ^{1}H NMR spectrum of **68** exhibits a quartet (δ 5.15 ppm) which corresponds to the quaternary C*H* proton. The ^{19}F NMR resonance arises as a singlet (δ -69.74 ppm) and is flanked by ^{119}Sn satellite lines ($^4J(^{119}$Sn,^{19}F) = 129 Hz). The ^{119}Sn NMR resonance of **68** arises a quartet at δ -232 ppm with the same coupling constant as $^4J(^{119}$Sn,^{19}F) = 129 Hz. The two ^{119}Sn NMR values of **67** and **68** are different due to the non identical electronic nature of the phenyl rings when compared with those of the CF_3 group.

8.6. Reaction of LSnNMe$_2$ with Terminal Alkines

Compound **66** reacts with HC≡CCO$_2$Me and HC≡CCO$_2$Et at room temperature in quantitative yield to the alkynyl linked stannylenes **69** and **70**, respectively, with a Sn(II)–C≡C framework that is formed by elimination of Me$_2$NH due to the different polarized Sn–NMe$_2$ and C–H bonds (Scheme 8.8). **69** and **70** were monitored by their ^{1}H NMR spectra. Sharp resonances in the ^{1}H NMR of **69** and **70** indicated that the products have been formed in high yield. In the course of reaction there is no sign that some side products are formed by nucleophilic addition of LSnNMe$_2$ to the carbon carbon triple bond, which we observed exclusively in the case of LSnH.
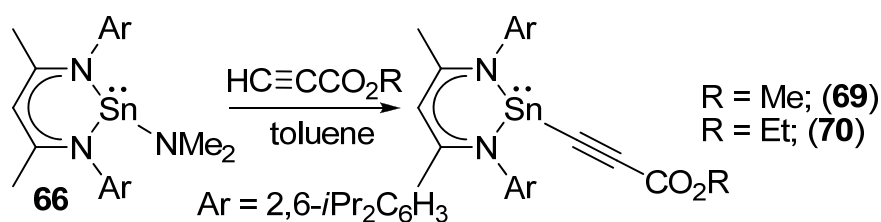
Scheme 8.8. Preparation of compounds **69** and **70**

In the ^{1}H NMR spectra of **69** and **70**, the complete disappearance of the proton resonance of Sn–N*Me*$_2$ was observed. This indicates the complete conversion of the tin amide to the corresponding tin-alkenyl compounds.

69 and **70** are yellow solids soluble in benzene, THF, *n*-hexane, and *n*-pentane, respectively and show no decomposition on exposure to air. **69** and **70** were characterized by multinuclear NMR and IR spectroscopy, EI mass spectrometry, and elemental analysis. Furthermore **70** was characterized by X-ray structural analysis (Figure 8.6).
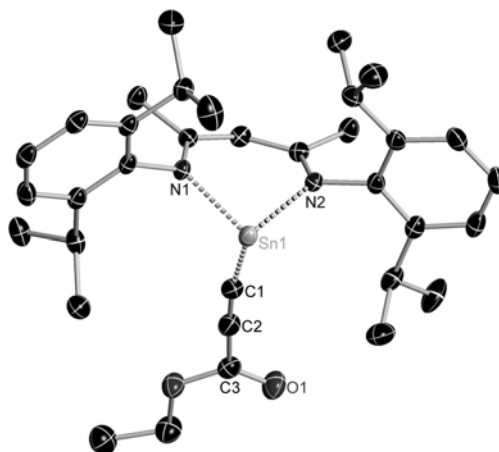
Figure 8.6. Molecular structure of **70**; anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–N1 2.1802(16), Sn1–C1 2.214(2), C1–C2 1.213(3); C2-C3 1.447(3), C3-O1 1.208(3), C3-O2 1.343(3); N1–Sn1–N2 86.33(6), N1–Sn1–C1 89.90(7), Sn1–C1–C2 168.83(19), C1-C2-C3 176.9(2).

The ^{1}H NMR spectrum of **70** shows a quartet and a triplet resonance (δ 3.92 and 0.92 ppm) corresponding to the two different types of C*H* protons of the ethyl moieties. The ^{119}Sn NMR resonance of **69** and **70** arises at δ -254.91 and -252.97 ppm, which are very close to each

other. In Table 8.1 we have summarised all the ^{119}Sn NMR data of related compounds including LSnNMe$_2$ (**66**). Compound **70** crystallizes in the monoclinic space group $P2_1/n$, with one monomer in the asymmetric unit, and with four molecules in each unit cell. Single crystals were obtained after two days from a saturated *n*-hexane solution at -32 ^{o}C in a freezer. The coordination polyhedron around the tin atom features a distorted tetrahedral geometry with a stereochemically active lone pair.

Table 8.1. ^{119}Sn NMR data of Sn(II) compounds

Compound*	^{119}Sn{^{1}H} NMR (δ, ppm)
LSnMe (**64**)	192.65
LSnN(SiMe$_3$)$_2$ (**65**)	-134.54
LSnNMe$_2$ (**66**)	-172.44
LSnOCPh(NMe$_2$)(2-Py) (**67**)	-328
LSnOCPh(NMe$_2$)(CF$_3$) (**68**)	-232
LSnCCCO$_2$Me (**69**)	-254.91
LSnCCCO$_2$Et (**70**)	-252.97

* L = HC(CMeNAr)$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Chapter 9

Synthesis of a Monomeric Tin(II) Hydroxide

The synthesis of tin(II) hydroxide has a long standing interest especially using aqueous routes. In the course of this approach no successful preparation of tin(II) hydroxide was reported but a number of tin(II) oxy-hydroxide species with varying ratios of tin, oxygen, and hydrogen have been prepared. In 1968 Howie and Moser were able to present a compound of composition $3SnO \cdot H_2O$ which was structurally characterised as $Sn_6O_4(OH)_4$.[264] The eight oxygen atoms are forming a regular cube joined by hydrogen bonds and superimposed by an octahedron of tin atoms. The structural unit is related to $Sn_3(OH)_4^{2+}$, which was demonstrated to exist in solution by *Tobias et al.*[265] and it can be derived by a condensation-deprotonation reaction. Finally in 1995 the cationic structure was determined by *Donaldson et al.*[266] Therefore, it is not surprising that all attempts to isolate tin(II) hydroxides have been unsuccessful till to date via an aqueous route. Additionally a tin(II) hydroxide has been synthesized by an anhydrous organometallic method involving the exchange of substituents between a triorganotin hydroxide and tin(II) dichloride.[267] The resulting product was only characterised by Mössbauer and IR spectroscopy and elemental analysis. In 2005 Power and coworkers reported on a structurally characterised dimeric tin(II) hydroxide stabilised by a bulky aryl ligand.[132] This hydroxide was prepared from $Ar'SnSnAr'$ ($Ar' = C_6H_3\text{-}2,6(C_6H_3\text{-}iPr_2)_2$) and 2,2,6,6-tetramethylpiperidine-N-oxide (TEMPO) or nitrous oxide (N_2O) by serendipity. Moreover, only a few examples of well-characterized tin(IV) hydroxides are known in literature.[131] To the best of our knowledge there is presently no report available on a well-designed synthesis and structural characterization of any monomeric tin(II) hydroxide.

9.1. Synthesis of LSnClFe(CO)$_4$

The reaction of LSnCl with diiron nonacarbonyl, $Fe_2(CO)_9$ in THF leads to $LSnClFe(CO)_4$ (**71**) (Scheme 9.1). Compound **71** is insoluble in *n*-hexane or *n*-pentane, but soluble in the benzene, toluene, diethyl ether, and THF.
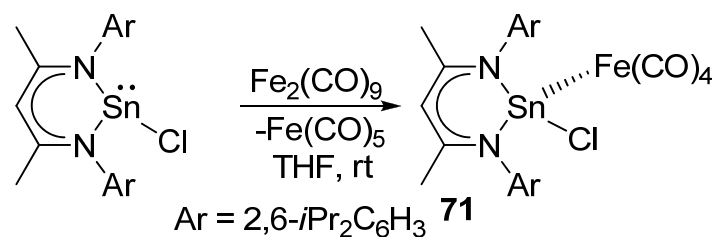
Scheme 9.1. Preparation of compound **71**

The ^{119}Sn NMR spectrum exhibits a singlet resonance (δ 88.98 ppm). This is downfield shifted compared with that of the starting precursor LSnCl (δ -224 ppm),[146] because of the change of coordination number around the tin center. Moreover, carbonyl absorptions for **71** were found at $\tilde{\nu}$ = 2043 s, 1968 s, 1939 s cm^{-1}, these are in the expected range for terminal carbonyl groups.

The molecular structure of **71** has been determined by single crystal X-ray diffraction analysis (Figure 9.1) which demonstrates that the complex exists as a monomer. Colorless compound **71** crystallizes in the monoclinic space group $P2_1/n$, with one monomer in the asymmetric unit from saturated toluene solution at -32 $^{\circ}$C after four days. The coordination polyhedron around the tin atom features a distorted tetrahedral geometry with unique Cl group (Figure 9.1).
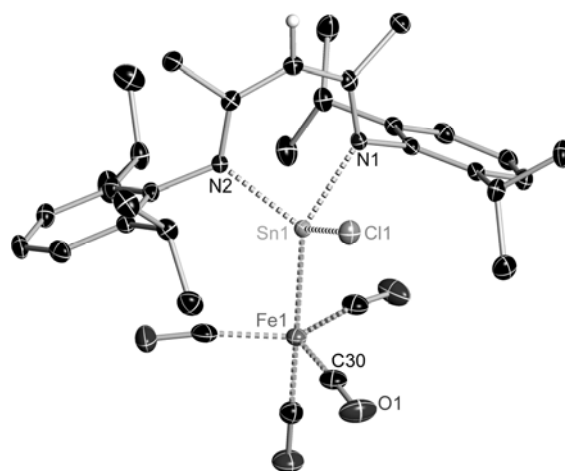

Figure 9.1. Molecular structure of **71**. Anisotropic displacement parameters are depicted at the 50 % probability level and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–Cl1 2.3893(6), Sn1–N1 2.1132(16), Sn1–Fe1 2.4823(4), Fe1–C30 1.793(2), C30-O1 1.148(3); N1–Sn1–Cl1 94.94(5), N1–Sn1–N2 88.90(6), Cl1–Sn1–Fe1 118.200(15), Fe1–C30–O1 175.75(19).\

9.2. Synthesis of LSn(NMe₂)Fe(CO)₄

The reaction of LSnNMe₂ (**66**) in the presence of one equivalent of Fe₂(CO)₉ in THF leads after 24 h to the pale-orange compound LSn(NMe₂)Fe(CO)₄ (**72**) in good yield (85 %) (Scheme 9.2). Compound **72** is soluble in benzene, THF, and diethyl ether and shows no decomposition on exposure to dry air. The ¹H NMR spectrum of **72** shows a broad resonance at (2.8-3.1 ppm) which can be assigned to the NMe₂ protons.
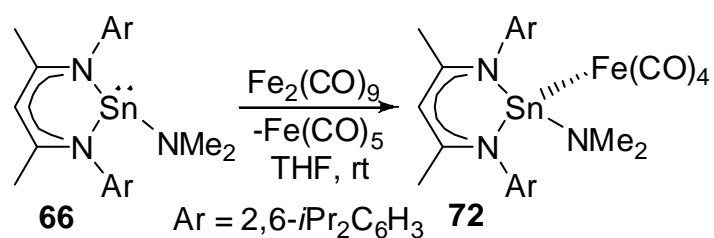
Scheme 9.2. Preparation of compound **72**
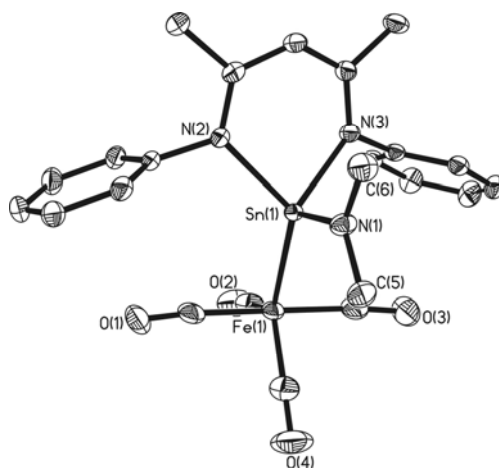
Figure 9.2. Molecular structure of **72·0.5THF**. Thermal elipsoids are shown at 50% probability. One of the two molecules of **72**, solvent THF, isopropyl groups and H atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Sn1–N1 2.014(3), Sn1–Fe1 2.4832(7), Sn1–N2 2.151(2), Fe1–C1 1.794(4), C1–O1 1.142(4); N1–Sn1–N2 100.70(10), N2–Sn1–N3 86.36(9), N2–Sn1–Fe1 125.80(7).

Maintaining a THF solution of **72** for two days at -32 °C resulted in pale-orange single crystals suitable for X-ray structural analysis. Compound **72** crystallizes in the monoclinic

space group $P2_1/c$, with two molecules of **72** and one THF molecule in the asymmetric unit. Complex **72** exists as a monomer in the solid state (Figure 9.2). The coordination polyhedron around the tin atom comprises two nitrogen atoms from the supporting ligand, one nitrogen atom from NMe_2 group, and one iron atom from the coordinated $Fe(CO)_4$ in a distorted tetrahedral geometry.

9.3. Synthesis of a Monomeric Tin(II) Hydroxide

Based on our experience in the synthesis of LGeOH (**15**),[127] we reacted $LSnCl$[146] (L = $HC(CMeNAr)_2$; Ar = 2,6-iPr$_2$C$_6$H$_3$) with water in the presence of a N-heterocyclic carbene in a broad temperature range (-78 ^{o}C to rt) in coordinating as well as in non coordinating solvents. From the reaction mixture we obtained the protonated ligand (LH) and a hydrocarbon insoluble white precipitate. This insoluble part mainly contained the N-heterocyclic carbene HCl adduct and tin hydroxy species. Also the reaction of $LSnNR_2$ (R = Me (**66**) and SiMe$_3$ (**65**)) with equivalent amounts of water leads preferentially to LH elimination. Finally under the protection with a metal fragment we shielded the tin(II) center to avoid protonation at the tin.

The slow addition of an equivalent amount of degassed water to a THF solution of **72** at -60 ^{o}C resulted in the formation of the orange compound $LSn(OH)Fe(CO)_4$ (**73**) in good yield (73 %) under elimination of volatile Me_2NH (Scheme 9.3).
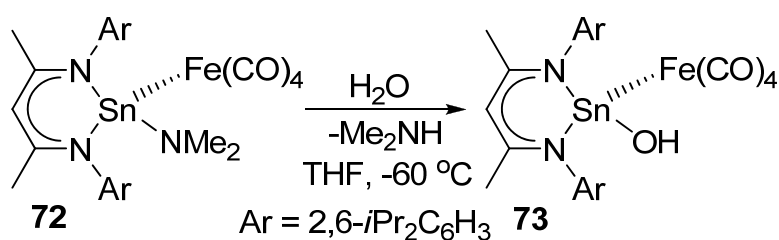
Scheme 9.3. Preparation of compound **73**

Compound **73** is a brown solid soluble in benzene, THF, and diethyl ether and insoluble in *n*-hexane, and *n*-pentane, and it is showing remarkable stability to dry air. **73** was characterized by ^{1}H, ^{119}Sn NMR, and IR spectroscopy, EI mass spectrometry, elemental analysis and X-ray structural analysis. In the ^{1}H NMR spectrum of **73**, the Sn-O*H* proton resonance was detected (δ 1.66 ppm), and the complete disappearance of the proton resonance of Sn(N*Me$_2$*) was

observed. This indicates the conversion of the tin amide to the corresponding tin hydroxide. Moreover the ^{119}Sn NMR for **73** shows a resonance at δ 45 ppm which is shifted upfild when compared with that of **72** (δ 94 ppm). The EI mass spectrum of **73** exhibits the molecular ion peak at *m/z* 722 albeit in low intensity. The base peak for **73** was found at *m/z* 705 corresponding to [M-OH]$^{+}$. The IR spectrum of **73** displays a band at 3615 cm^{-1}, a plausible range in light of the 3390 cm^{-1} band measured for $Sn(OH)_2$[267] and 3480 cm^{-1} for $(Ar'SnOH)_2$ (Ar' = 2,6-(2,6-iPr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$)[132] and 3599 cm^{-1} for LGe(OH)Fe(CO)$_4$.[268] In the IR spectrum of LSn(OD)Fe(CO)$_4$, which we have prepared accordingly from **72** and D$_2$O, no band is observed at 3615 cm^{-1}. The measured O–D wave number of 2690 cm^{-1} is in the range of the calculated one (2631 cm^{-1}).
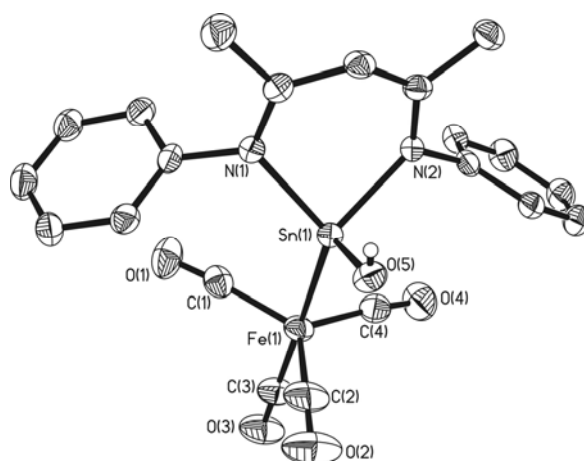
Figure 9.3. Molecular structure of **73**. Thermal elipsoids are shown at 50% probability. Isopropyl groups and H atoms except at O5 are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Sn1–O5 2.001(3), Sn1–Fe1 2.4719(7), Sn1–N1 2.130(3), Fe1–C1 1.796(4), C1–O1 1.146(5); N1–Sn1–N2 88.41(10), N1–Sn1–O5 97.26(12), N1–Sn1–Fe1 125.31(7).

Compound **73** crystallizes in the monoclinic space group *P*2$_1$/*n,* with one monomer in the asymmetric unit from a saturated toluene solution at -32 ^{o}C after four days. The coordination polyhedron around the tin atom features a distorted tetrahedral geometry with unique OH group (Figure 9.3). More interestingly the OH group is not involved in any kind of hydrogen bonding which is reflected in the IR spectrum. Its structure is very similar to that of its germanium analogue LGe(OH)Fe(CO)$_4$.[268] In the structures of **72** and **73** the Sn-N bond lengths are 2.151(2), 2.130(3) Å and N-Sn-N bond angles are 86.36(9), 88.41(10)^{o}, respectively (N are the nitrogen atoms of the ligand backbone) . Comparing this data with the slightly longer Sn-N bond lengths and smaller N-Sn-N angles in LSnF (**1**) and LSnMe (**64**)

(2.178(3), 2.2091(18) Å and 86.22(10), 84.69(7)°) illustrates the influence of the different coordination numbers around the tin atom. A noteworthy feature of compound **73** is the SnOH moiety. The crystallographic O-H distance (0.60 Å) is very short but the hydrogen was found and refined without any restraints. The Sn-O distance (2.001(3) Å) is indicative for a Sn-O single bond and the Sn-O-H angle (109.58(2)°) is as expected. Due to the absence of any involvement in hydrogen bonding the Sn-O bond length is slightly shorter than those in the dimeric structure (Ar′SnOH)$_2$ (av 2.147 Å) (Ar′ = 2,6-(2,6-iPr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$)[132] and the values predicted for Sn$_3$(OH)$_4{}^{2+}$ (av 2.217 Å).[266] Interestingly, and as might be expected, shorter Sn-OH bond lengths are found in tin(IV) compounds due to the smaller radius of Sn(IV) compared to that of Sn(II) (e.g. Sn-O 1.968(4) Å for Sn-OH, in [(Me$_3$Si)$_3$CSnO(OH)]$_3$.[115]

Table 9.1. Comparison of ^{119}Sn NMR data of Sn(II) Compounds with and without Coordination to an Iron-Carbonyl Fragment.

Compound*	^{119}Sn NMR (δ ppm)
LSnCl	-224
LSnNMe$_2$ (**66**)	-172
LSnClFe(CO)$_4$ (**71**)	88.98
LSn(NMe$_2$)Fe(CO)$_4$ (**72**)	94.00
LSn(OH)Fe(CO)$_4$ (**73**)	45.03

* L = HC(CMeNAr)$_2$; Ar = 2,6-iPr$_2$C$_6$H$_3$

Chapter 10

Summary

In this thesis unprecedented synthetic and reactivity studies of the compounds with low valent group 14 elements are reported. We have demonstrated the reactivity of the first isolable three coordinate germanium(II) and tin(II) hydride toward unsaturated molecules. Reactions of LGeH (**5**) and LSnH (**20**) with gaseous carbon dioxide resulted in the formation of the germanium(II) and tin(II) ester of formic acid (**6**) and (**21**) respectively, which represent a new class of compounds of group 14 elements. For example a low valent stable carbon analogue of composition RC–O–C(O)H has so far not been reported. A RC–O–C(O)H species should be extremely unstable and rearrange to the corresponding 1,2-dicarbonyl compound, RC(O)–C(O)H. Compounds **6** and **21** are potential C1 synthons for further synthesis of organic compounds.
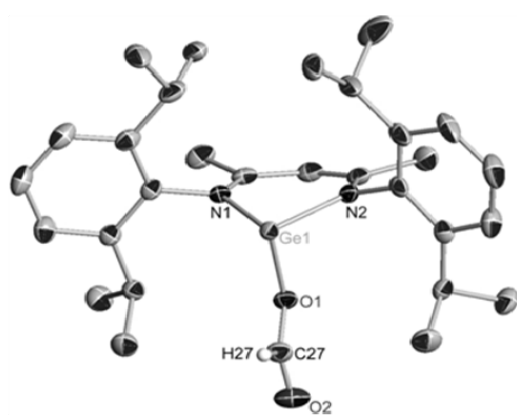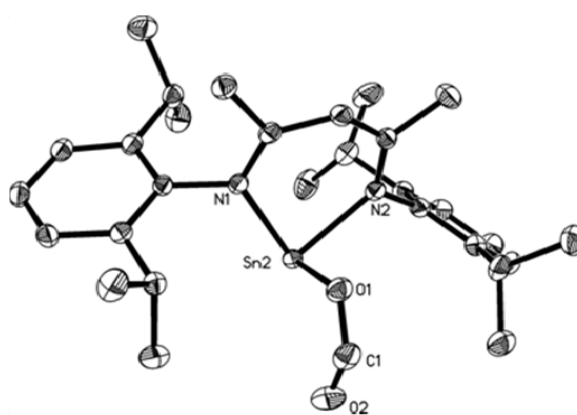
6   **21**

Germanium(II) and tin(II) alkoxides have been prepared by the reaction of **5** and **20** with carbonyl compounds with the outcome of compounds containing the M(II)–O–CH (M = Ge and Sn) core. LGeH (**5**) reacts only with activated carbonyl compounds, namely 2,2,2-trifluoro acetophenone and 2,2,2-trifluoroacetothiophane (**7-8**), which is in contrast to LSnH (**20**). Compound **20** reacts with a variety of carbonyl compounds such as ferrocene carbaldehyde, benzophenone etc. (**22-26, 35-40**).
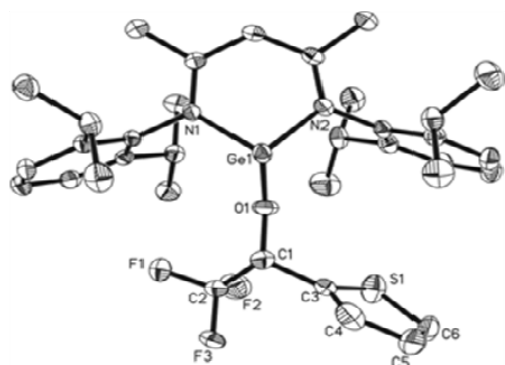
8
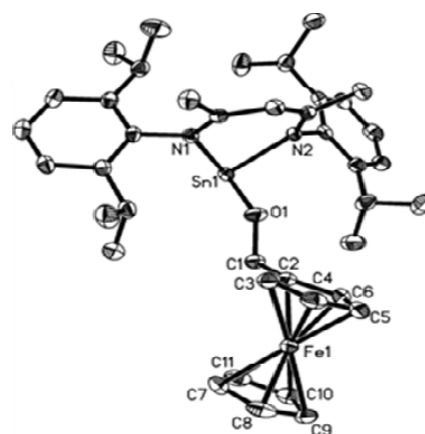
22

The reaction of **5** and **20** with terminal and internal alkines generated the vinyl substituted germylene and stannylene (**9-13**, **27-32**) rather than products under elimination of dihydrogen in the case of terminal alkines. These vinyl substituted alkenes have a lone pair of electrons on the germanium or tin center and a carbon carbon double bond. They are prone for further reactions. The unique pathways of these reactions are the simultaneous transfer of hydrogen and germylene or stannylene from **5** and **20** respectively.
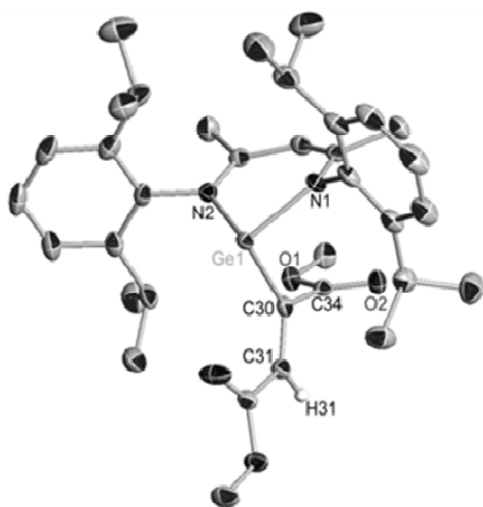
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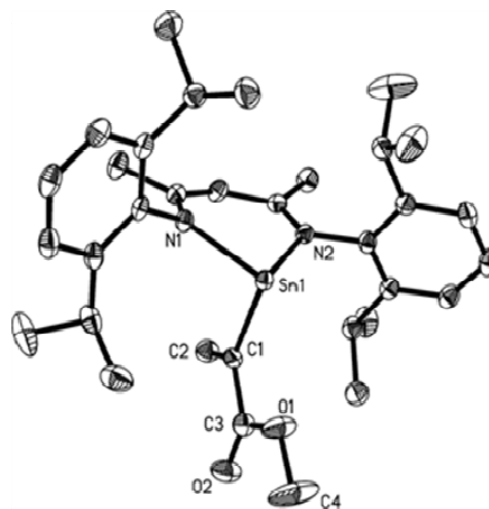
27

5 also reacts with diethyl azodicarboxylate (DEAD) under oxidative addition to give the germylene substituted hydrazine compound **14**. Germanium(II) hydroxide, LGeOH (**15**), has been prepared by the reaction of LGeH with nitrous oxide as a mono oxygen source. The reaction of **5** with elemental sulfur resulted in the formation of a germanium analogue of dithiocarboxylic acid (**16**), which represents a new precursor for many metal complexes.
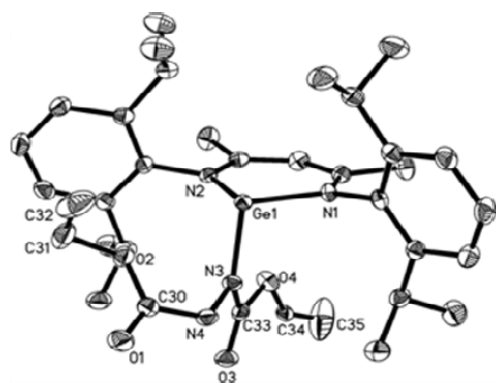
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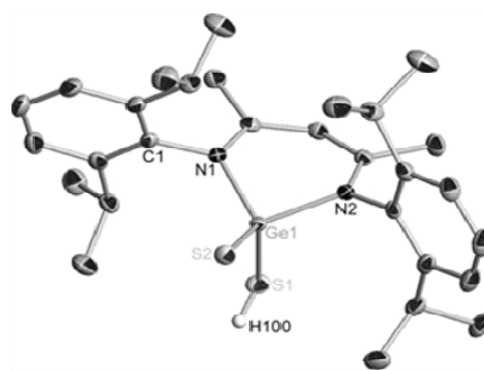
16

The corresponding reaction of LGeH with trimethylsilyl azide resulted in the formation of two compounds, the terminal germanium(II) azide (**17**) and germanium(IV) diamide (**18**), under migration of a hydrogen atom from a methyl group of the ligand backbone to the coordinate N atom in the latter case. The formation of compounds **16** and **18** involves the change of oxidation state of germanium from two to four.
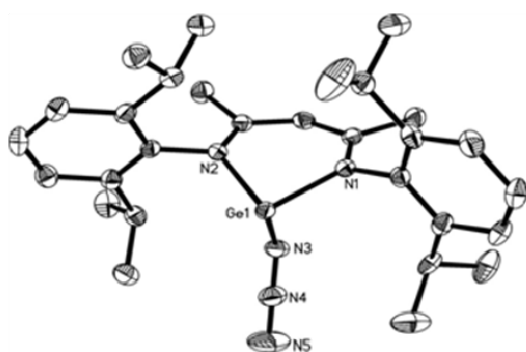
17
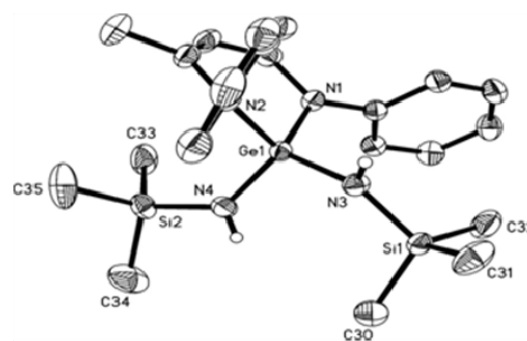
18

There are striking differences between the reactions of LSnH (**20**) with and without fluorinated carbonyl compounds. There is a competition between the addition reaction *vs* exchange reaction. Considering 4-fluoro benzophenone and pentafluoro benzaldehyde as precursors the carbonyl group is more prone to addition reaction (**39**-**40**) than to the exchange reaction of fluorine of a C-F bond with LSnH. In the case of pentafluoro benzophenone and perfluoro benzophenone there is a competition between the addition *vs* exchange reaction. Two products are formed with the selective *para* fluorine exchange under formation of LSnF (**1**). In this context it is interesting to mention that the bond energy of the aliphatic C-F bond is smaller than that of the aromatic C-F bond, although there are exclusively addition reactions to the trifluoro acetyl group (**35**-**36**) rather than the exchange reaction of C–F bond with LSnH (**20**).

1   **36**
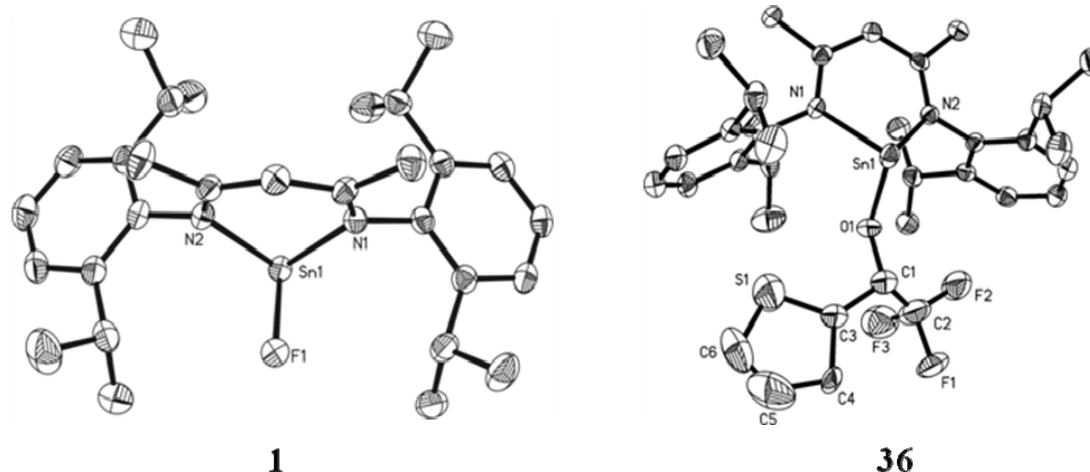
Moreover it was shown that the synthesis of the N-heterocyclic germylene L´Ge (**19**) achieved the dehydrogenation of LGeH (**5**) by using a frustrated carbene borane Lewis pair. The sequential cleavage of C–H and Ge–H bonds without a catalyst is shown herein. Compound **19** is also formed by the reaction of 1,3-di-*tert*-butylimidazol-2-ylidene with LGeCl or LGeOTf (**63**) under the activation of the C–H bond of one of the methyl groups of the ligand backbone.

Herein we have also shown that the germylene, L′Ge (**19**) and silylene, L′Si (**50**) have striking differences in their reactivity. **19** reacts with N–H and O–H bonded compounds including gaseous ammonia and water under formation of stable unique germanium(II) compounds (**15**, **42-46**), demonstrating an example of sustainable chemistry. L′Si (**50**) reacts with ammonia to afford compound **51** under oxidative addition at the silicon(II) atom. The result reported here shows that the silylene can mimic to some extent the behavior of a transition metal. The oxidative addition of NH_3 under very mild conditions offers an alternative paradigm in the ongoing search for catalytic systems capable of transforming ammonia efficiently into useful amino compounds. Moreover diphenyl hydrazone reacts with the silylene **50** to form the non-aromatic siloxi-indolin-1-amine derivative **54** instead of an N-H bond cleavage of the NH_2 group. Here it is noticed that in the case of **19** there is no change of the oxidation state of germanium, whereas in the case of **50** there is always oxidative addition at the silicon center.
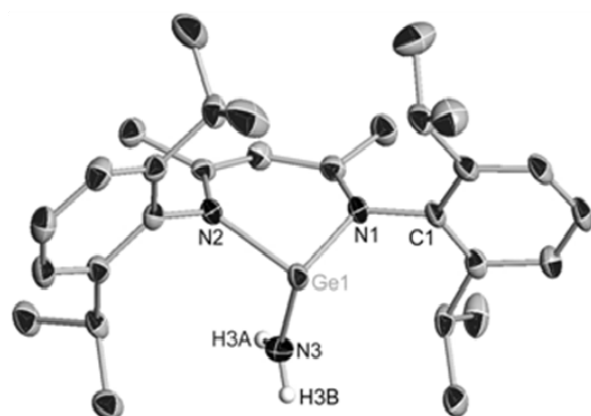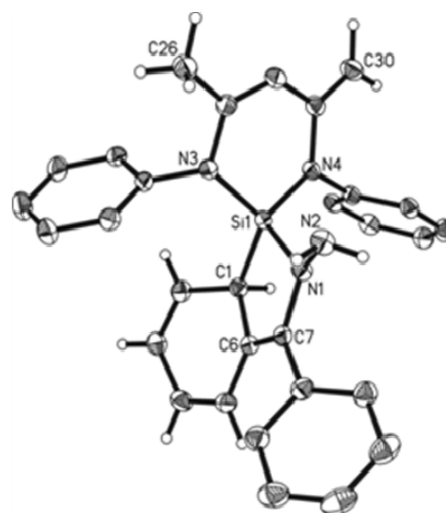
42   **54**

Moreover H_3NBH_3 delivered the dihydrogen to N-heterocyclic carbene, 1,3-di-*tert*-butylimidazol-2-ylidene as well as to germylene **19** at room temperature without any additional catalyst by oxidative addition. The latter examples demonstrate that the solid H_3NBH_3 can be used instead of gaseous hydrogen for hydrogenation reactions without any additional catalyst. In comparison to the carbon(II) in N-heterocyclic carbene, we found that the oxidation of the acyclic carbon carbon double bond in L′Ge (**19**) occured.

Germylene **19** also reacts with $B(C_6F_5)_3$ and trimethylsilyl diazomethane at room temperature to form the zwitterionic germanium(II) compound **48** under C–B bond formation and diazogermylene compound $LGeC(N_2)SiMe_3$ (**58**) by cleavage of a C–H bond. The diazogermylene compound $LGeC(N_2)SiMe_3$ (**58**) rearranges after about 3 months to the isonitriletrimethylsilyl germanium(II) amide $LGeN(SiMe_3)NC$ (**59**).
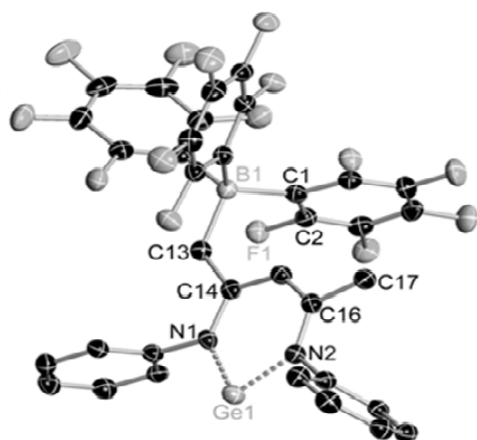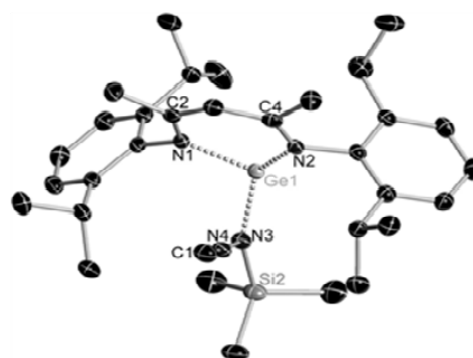
48   **59**

The reaction of ethyl diazoacetate and trimethylsilyl diazomethane with **5** leads to the first stable germanium(II) substituted hydrazone derivatives, LGeN(H)NCHR, (R = CO_2Et (**55**), $SiMe_3$ (**56**)) in high yield. In this reaction we are showing for the first time the unprecedented end-on nitrogen insertion of a diazo compound into a germanium(II) hydrogen bond. The reaction of a methyl analogue, LGeMe, with trimethylsilyl diazomethane forms the germanium(IV) amide, L´Ge(Me)NHNCHSiMe$_3$ (**57**) with migration of hydrogen from the methyl group of the ligand backbone. Finally the reaction of the lithium salt of trimethylsilyl diazomethane with LSnCl yields the LSn−N=C=N−SiMe$_3$ (**60**) under migration of the silyl group. This result shows that for the first time a compound with the unique Sn(II) substituted carbodiimide was isolated.

56   **60**
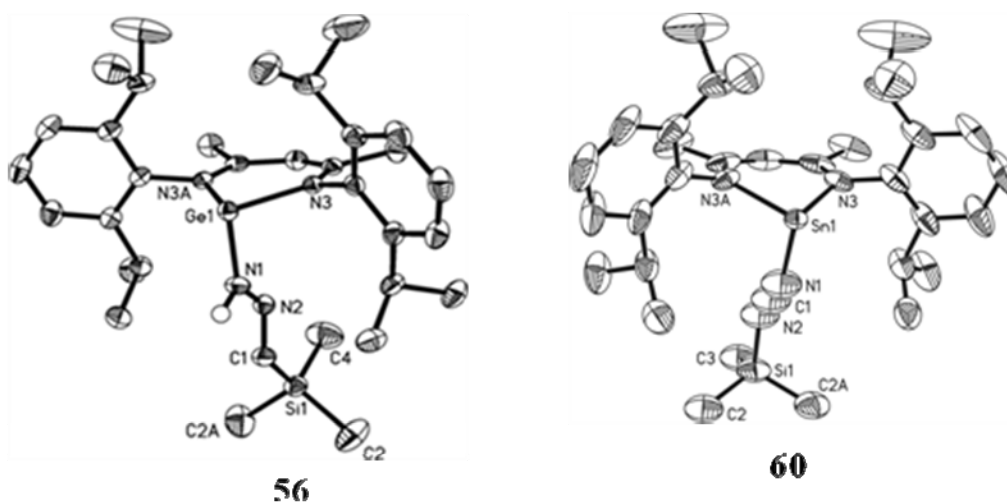
Similar to the transfer of the hydride described, the reaction of **5** and **20** with unsaturated compounds, leads to the transfer of "NMe$_2$" when LSnNMe$_2$ (**66**) is used. Compound **66** reacts with ketones to generate tin(II)-alkoxide compounds (**67-68**) containing the Sn(II)–O–CNMe$_2$ core. Furthermore tin(II)-dimethylamide reacts with terminal alkines generating the alkinyl substituted stannylene (**69-70**) under elimination of dimethyl amine rather than the insertion of Sn-NMe$_2$ into the carbon carbon triple bond, which is observed in the reaction of **5** and **20** with terminal alkines.

67

70
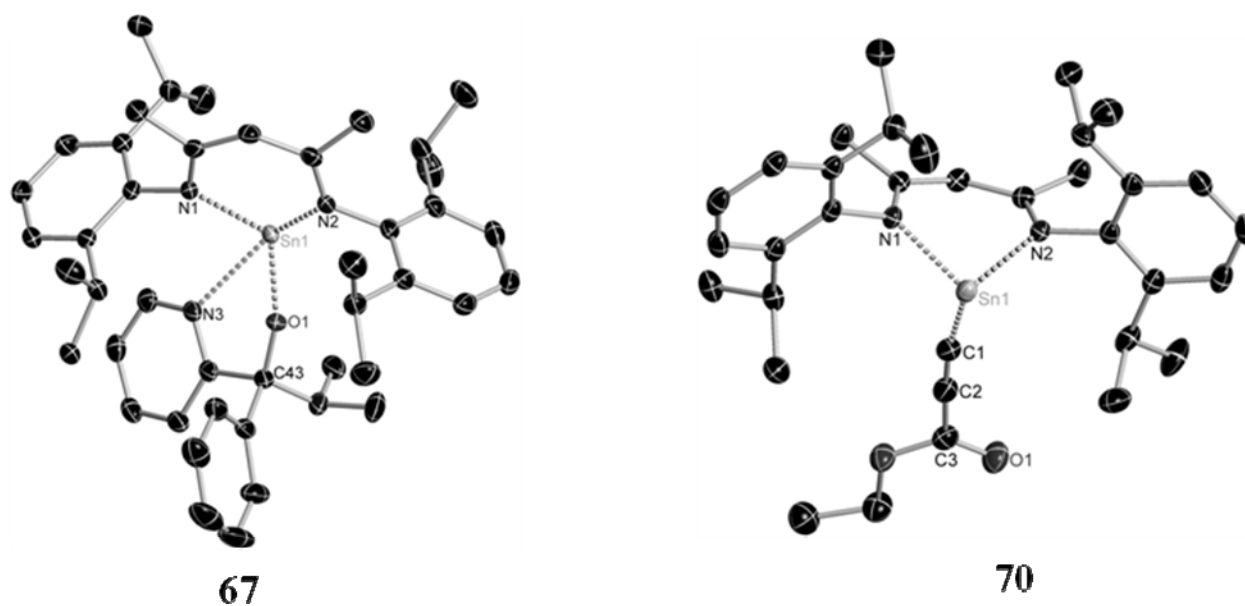
Finally we have prepared the monomeric tin(II) hydroxide, $LSn(OH)Fe(CO)_4$ (**73**) for the first time under the protection of a metal fragment that shielded the tin(II) center to avoid protonation at the tin. The synthesis of **73** might have a similar impact on molecular tin(II) chemistry as this has been shown for its analogue LGeOH.

73
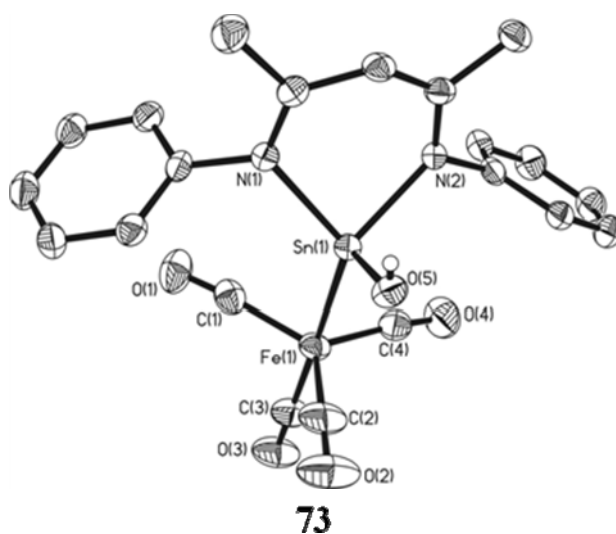
It is interesting to mention that most of the compounds are stable at room temperature and highly soluble in common organic solvents and therefore favor their further functionalization as metal complexes and metal catalysts.

Chapter 11
Experimental Section
11.1. General Procedures
All reactions and handling of reagents were performed under an atmosphere of dry nitrogen or argon using Schlenk techniques or a glovebox where the O_2 and H_2O levels were usually kept bellow 1 ppm. All glassware was oven-dried at 160 °C for at least 24 h, assembled hot and cooled under high vacuum prior to use. Toluene, benzene, *n*-hexane, *n*-pentane, tetrahydrofuran, and diethylether were purified with the M-Braun solvent drying system. Dichloromethane (CaH_2) were dried and distilled prior to use.

11.2. Physical Measurements
Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus.

NMR spectra were recorded on Bruker Avance 200, Bruker Avance 300, and Bruker Avance 500 NMR spectrometers. Downfield shifts from the reference are quoted positive; upfield shifts are assigned negative values for the case of external references. Deuterated NMR solvents C_6D_6, C_7H_8, and THF–D_8 were dried by stirring for 2 days over Na/K alloy followed by distillation *in vacuo* and degassed. CD_2Cl_2 stirring with CaH_2 for 6 hrs followed by filtration. Heteroatom NMR spectra were recorded ^{1}H decoupled with the exception of [19]F. Chemical shifts are reported in ppm with reference to residual deutorited solvent peak (internal) for ^{1}H nuclei, $SnMe_4$ (external) for [119]Sn nuclei, $CFCl_3$ (external) for ^{19}F nuclei, $BF_3·OEt_2$ (external) for [11]B nuclei, 85% H_3PO_4 (external) for ^{31}P nuclei, $SiMe_4$ (external) for [29]Si nuclei.

IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer in the range 4000−350 cm^{-1} as KBr pellets. Only the absorption of significant moieties (N–H, O–H, O–D, CO, C=C) are assigned.

Mass spectra were obtained with a Finnigan MAT 8230 or a Varian MAT CH5 instrument (70 eV) by EI-MS methods.

Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen.

11.3. Starting Materials
MeLi (1.6 M in Et_2O, Aldrich), $LiNMe_2$ (Aldrich), $KN(SiMe_3)_2$ (Aldrich), $GeCl_2·$di-oxane (Aldrich), $SnCl_2$ (Aldrich), $B(C_6F_5)_3$ (TCI Organic Chemicals), N_2CHCO_2Et (Aldrich), $N_2CHSiMe_3$ (Aldrich), N_3SiMe_3 (Aldrich), $Fe_2(CO)_9$ (Aldrich), sulfur (Aldrich), AgOTf (Aldrich), $HCCCO_2Me$ (Aldrich), $HCCCO_2Et$ (Aldrich), $MeCCCO_2Et$ (Aldrich), MeO_2CCCCO_2Me (Aldrich), EtO_2CCCCO_2Et (Aldrich), $tBuO_2CCCCO_2tBu$ (Aldrich), EtO_2CNNCO_2Et (Aldrich), *i*PrNCN*i*Pr (Aldrich), CyNCNCy (Aldrich), FcCHO (Aldrich), Ph_2CO (Aldrich), PhCO(2-py) (Aldrich), $(2-Py)_2CO$ (Aldrich), $(C_3H_5)_2CO$ (Aldrich), $PhCOCF_3$ (Aldrich), $(2-C_4H_3S)COCF_3$ (Aldrich), $PhCOC_6F_5$ (Aldrich), $(C_6F_5)_2CO$ (Aldrich), $PhCO(4-C_6H_4F)$ (Aldrich), and C_6F_5CHO (Aldrich) were used as received. LH,[12] LLi·OEt$_2$,[146] LGeCl,[146] LSnCl,[146] L´Si,[36] N,N´-*bis*-tertbutylimidazolyl-2-ylidene,[191] and $AlH_3·NMe_3$,[155] were prepared by literature procedures. Demineralized, degassed H_2O was used for hydrolysis experiments.

11.4. Syntheses of Compounds

11.4.1. Synthesis of LSnF (**1**)
Method A: A solution of LSnMe (0.550 g, 1 mmol) in toluene (20 mL) was added to a stirred suspension of Me_3SnF (0.200 g, 1.1 mmol) in toluene (10 mL), and the reaction mixture was refluxed for 3 h. After removal of all the volatiles the residue was extracted with *n*-hexane (30 mL) and concentrated to about 10 mL and stored in a -30 °C freezer. Colorless crystals of **1** suitable for X-ray diffraction analysis are formed after one day. Yield: 0.470 g (85 %). Method B: A solution of $LSnN(SiMe_3)_2$ (0.700 g, 1 mmol) in toluene (20 mL) was added to a stirred suspension of Me_3SnF (0.200 g, 1.1 mmol) in toluene (10 mL), and the reaction mixture was refluxed for 3 h. After removal of all the volatiles the residue was extracted with *n*-hexane (30 mL) and the resulting solution was concentrated to about 10 mL and stored in a -30 °C freezer. Colorless crystals of **1** suitable for X-ray diffraction analysis are formed after one day. Yield: 0.390 g (70 %). Mp 130 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.04-7.17 (m, 6H, Ar-*H*), 4.99 (s, 1H, γ-C*H*), 3.84 (sept, 2H, C*H*(CH$_3$)$_2$), 3.09 (sept, 2H, C*H*(CH$_3$)$_2$), 1.63 (s, 6H, C*H*$_3$), 1.41 (d, 6H, CH(C*H*$_3$)$_2$), 1.18 (q, 12H, CH(C*H*$_3$)$_2$), 1.09 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{19}F {^{1}H} NMR

(188.31 MHz, C_6D_6): δ -125.29 ppm. ^{119}Sn $\{^1H\}$ NMR (186.50 MHz, C_6D_6): δ -371.52 ppm. EI-MS: m/z (%) 556 (20) [M]$^+$. Anal. calcd for $C_{29}H_{41}FN_2Sn$ (556.23): C 62.72, H 7.44, N 5.04; Found: C 62.38, H 8.67, N 5.00.

11.4.2. Synthesis of LGeBr (2)

A solution of LLi(OEt$_2$) (0.498 g, 1.0 mmol) in diethyl ether (20 mL) was added dropwise to a stirred suspension of GeBr$_2$ (0.230 g, 1.0 mmol) in diethyl ether (10 mL) at -78 ^{o}C. The reaction mixture was warmed to room temperature and was stirred for another 12 h. The precipitate was filtered, and the solvent was partially reduced (ca. 15 mL). Keeping the solution in a -32 ^{o}C freezer for overnight afforded colorless crystals of **2**, which are suitable for X-ray diffraction analysis. Yield: 0.480 g (85 %). Mp 214 ^{o}C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.03-7.18 (m, 6H, Ar-*H*), 5.22 (s, 1H, γ-C*H*), 4.01 (sept, 2H, C*H*(CH$_3$)$_2$), 3.13 (sept, 2H, C*H*(CH$_3$)$_2$), 1.59 (s, 6H, C*H*$_3$), 1.48 (d, 6H, CH(C*H*$_3$)$_2$), 1.20 (q, 12H, CH(C*H*$_3$)$_2$), 1.00 (d, 6H, CH(C*H*$_3$)$_2$) ppm. EI-MS (70 eV): m/z (%): 570 (100) [M]$^+$. Anal. calcd for $C_{29}H_{41}BrGeN_2$(570.17): C 61.09, H 7.25, N 4.91; Found: C 60.46, H 7.10, N 4.87.

11.4.3. Synthesis of LSnBr (3)

A solution of LLi(OEt$_2$) (0.498 g, 1.0 mmol) in diethyl ether (20 mL) was added dropwise to a stirred suspension of SnBr$_2$ (0.280 g, 1.0 mmol) in diethyl ether (10 mL) at -78 ^{o}C. The reaction mixture was warmed to room temperature and was stirred for another 12 h. The precipitate was filtered, and the solvent was partially reduced (ca. 20 mL). StoraSn of the remaining solution in a -32 ^{o}C freezer for overnight afforded colorless crystals of **3** suitable for X-ray diffraction analyses. Yield: 0.490 g (80 %). Mp 206 ^{o}C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.02-7.17 (m, 6H, Ar-*H*), 5.11 (s, 1H, γ-C*H*), 3.99 (sept, 2H, C*H*(CH$_3$)$_2$), 3.11 (sept, 2H, C*H*(CH$_3$)$_2$), 1.61 (s, 6H, C*H*$_3$), 1.44 (d, 6H, CH(C*H*$_3$)$_2$), 1.19 (q, 12H, CH(C*H*$_3$)$_2$), 1.03 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn $\{^1H\}$ NMR (186.50Hz, C_6D_6): δ -180.47 ppm. EI-MS (70 eV): m/z (%): 616 (100) [M]$^+$. Anal. calcd for $C_{29}H_{41}BrN_2Sn$ (616.15): C 56.52, H 6.71, N 4.55. Found: C 55.58, H 6.55, N 4.42.

11.4.4. Synthesis of LSnI (4)

A solution of LLi(OEt$_2$) (0.498 g, 1 mmol) in diethyl ether (20 mL) was added drop by drop to a stirred suspension of SnI$_2$ (0.375 g, 1 mmol) in diethyl ether (10 mL) at -78 ^{o}C. The reaction mixture was warmed to room temperature and stirring was continued for another 12 h. The precipitate was filtered and the solvent was partially reduced (ca. 20 mL). Keeping the remaining solution in a -32 ^{o}C freezer, afforded colorless crystals of **4** suitable for X-ray diffraction analyses. Yield: 0.510 g (77 %). Mp 197 ^{o}C. ^{1}H NMR (300 MHz, C_6D_6): δ 7.01-7.15 (m, 6H, Ar-*H*), 5.20 (s, 1H, γ-C*H*), 4.05 (sept, 2H, C*H*(CH$_3$)$_2$), 3.09 (sept, 2H, C*H*(CH$_3$)$_2$), 1.59 (s, 6H, C*H*$_3$), 1.42 (d, 6H, CH(C*H*$_3$)$_2$), 1.17 (q, 12H, CH(C*H*$_3$)$_2$), 1.06 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn $\{^1H\}$ NMR (112.00Hz, C_6D_6): δ -107.33 ppm. EI-MS (70 eV): m/z (%): 663 (100) [M]$^+$. Anal. calcd for $C_{29}H_{41}IN_2Sn$(664): C 52.51, H 6.23, N 4.22; Found: C 51.55, H 5.78, N 4.06.

11.4.5. Synthesis of LGeH (5)

Method A: A solution of K[HB(*sec*Bu)$_3$] in THF (2.00 mL, 1 M, in THF) was slowly added drop by drop to a stirred solution of LGeCl (1.050 g, 2 mmol) in toluene (30 mL) at -10 ^{o}C. The reaction mixture was warmed to room temperature and was stirred for additional 3 h. After removal of all the volatiles, the residue was extracted with *n*-hexane (30 mL) and concentrated to about 10 mL and stored in a -30 ^{o}C freezer. Red crystals of **5** are formed after one day. Yield: 0.80 g (88 %). Method B: L'Ge (**19**) (0.490 g, 1 mmol) and NH$_3$BH$_3$ (0.030 g, 1.0 mmol) were dissolved in toluene (20 mL) at room temperature. The color of the reaction mixture changed from brown red to red. The reaction mixture was stirred further for one hour. Then the solvent was removed *in vacuo* and the residue was extracted with *n*-hexane (30 mL). Yield: 0.42 g (85 %). Mp 170 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 7.10-7.15 (m, 6H, Ar-*H*), 4.86 (s, 1H, γ-C*H*), 3.59 (sept, 2H, C*H*(CH$_3$)$_2$), 3.37 (sept, 2H, C*H*(CH$_3$)$_2$), 1.60 (s, 6H, C*H*$_3$), 1.35 (d, 6H, CH(C*H*$_3$)$_2$), 1.22 (d, 6H, CH(C*H*$_3$)$_2$), 1.19 (d, 12H, CH(C*H*$_3$)$_2$), ppm.

11.4.6. Synthesis of LGeOC(O)H (6)

In a 100 mL Schlenk flask a solution of **5** (0.490 g, 1.00 mmol) in 20 mL toluene was treated with dry carbon dioxide gas at room temperature. After the addition of carbon dioxide under stirring the reaction mixture slowly

changed the color from red to yellow and stirring was continued for 15 min. After removal of all the volatiles, the residue was extracted with *n*-hexane (20 mL) and concentrated to about 10 mL and stored in a -30 °C freezer. Yellow crystals of **6** suitable for X-ray diffraction analysis are formed after one day. Yield (0.48 g, 90 %). Mp 183 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 8.64 (s, 1H, C*H*), 7.05-7.19 (m, 6H, Ar-*H*), 5.06 (s, 1H, γ-C*H*), 3.53 (sept, 2H, C*H*(CH$_3$)$_2$), 3.08 (sept, 2H, C*H*(CH$_3$)$_2$), 1.54 (s, 6H, C*H$_3$*), 1.28 (d, 6H, CH(C*H$_3$*)$_2$), 1.20 (d, 6H, CH(C*H$_3$*)$_2$), 1.14 (d, 6H, CH(C*H$_3$*)$_2$), 1.12 (d, 6H, CH(C*H$_3$*)$_2$) ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 2854 (C-H), 1690 cm^{-1} (C=O). EI-MS (70 eV): *m/z* (%): 536 (20) [M]$^+$, 491 (100) [M-HCO$_2$]$^+$. Anal. calcd for C$_{30}$H$_{42}$GeN$_2$O$_2$ (535.25): C 67.31, H 7.91, N 5.23; Found: C 66.87, H 8.85, N 5.21.

11.4.7. Synthesis of LGeOCHPh(CF$_3$) (7)

A solution of 2,2,2-trifluoro acetophenone (0.175 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **5** (0.49 g, 1.00 mmol in toluene 20 mL) at room temperature. After 12 h all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL). The solution was concentrated and kept in a freezer to obtain **7** as yellow crystals, which are suitable for X-ray diffraction analysis. Yield: 0.545 g (82 %). Mp 182 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 6.74-7.28 (m, 11H, Ar-*H*), 4.73 (q, 1H, C*H*), 4.65 (s, 1H, γ-C*H*), 3.73 (sept, 2H, C*H*(CH$_3$)$_2$), 3.29 (sept, 1H, C*H*(CH$_3$)$_2$), 3.07 (sept, 1H, C*H*(CH$_3$)$_2$), 1.60 (d, 3H, CH(C*H$_3$*)$_2$), 1.50 (d, 3H, CH(C*H$_3$*)$_2$), 1.48 (s, 3H, C*H$_3$*), 1.41 (s, 3H, C*H$_3$*), 1.35 (d, 3H, CH(C*H$_3$*)$_2$), 1.21 (d, 3H, CH(C*H$_3$*)$_2$), 1.15 (d, 3H, CH(C*H$_3$*)$_2$), 1.11 (d, 3H, CH(C*H$_3$*)$_2$), 1.02 (d, 3H, CH(C*H$_3$*)$_2$), 0.72 (d, 3H, CH(C*H$_3$*)$_2$) ppm. ^{19}F{^{1}H} NMR (188.29 MHz): δ -75.76 (d, 3F, C*F$_3$*, ^3J (^{19}F-^{1}H) = 8 Hz) ppm. EI-MS (70 eV): *m/z* (%): 666 (100) [M]$^+$. Anal. calcd for C$_{37}$H$_{47}$F$_3$GeN$_2$O (665.36): C 66.78, H 7.12, N 4.21; Found: C 66.65, H 7.24, N 4.12.

11.4.8. Synthesis of LGeOCH(2-C$_4$H$_3$S)(CF$_3$) (8)

A solution of 2,2,2-trifluoro thiophenone (0.175 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **5** (0.49 g, 1.00 mmol in toluene 20 mL) at room temperature. After 12 h all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL). The extract was concentrated to about 15 mL and stored in a -30 °C freezer. Yellow crystals of **8** suitable for X-ray diffraction analysis had formed after two days. Yield: 0.570 g (85 %). Mp 171 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 6.93-7.12 (m, 6H, Ar-*H*), 6.67 (d, 1H, C$_4$*H$_3$*S), 6.45 (dd, 1H, C$_4$*H$_3$*S), 6.26 (d, 1H, C$_4$*H$_3$*S), 5.04 (q, 1H, C*H*), 4.66 (s, 1H, γ-C*H*), 3.69 (sept, 1H, C*H*(CH$_3$)$_2$), 3.63 (sept, 1H, C*H*(CH$_3$)$_2$), 3.28 (sept, 1H, C*H*(CH$_3$)$_2$), 3.15 (sept, 1H, C*H*(CH$_3$)$_2$), 1.58 (d, 3H, CH(C*H$_3$*)$_2$), 1.48 (s, 3H, C*H$_3$*), 1.42 (s, 3H, C*H$_3$*), 1.41 (d, 3H, CH(C*H$_3$*)$_2$), 1.32 (d, 3H, CH(C*H$_3$*)$_2$), 1.20-1.14 (m, 6H, CH(C*H$_3$*)$_2$), 1.12 (d, 3H, CH(C*H$_3$*)$_2$), 1.07 (d, 3H, CH(C*H$_3$*)$_2$), 0.98 (d, 3H, CH(C*H$_3$*)$_2$) ppm. ^{19}F{^{1}H} NMR (188.29 MHz): δ -76.29 (d, 3F, C*F$_3$*, ^3J (^{19}F-^{1}H) = 7 Hz) ppm. EI-MS (70 eV): *m/z* (%): 672 (100) [M]$^+$. Anal. calcd for C$_{35}$H$_{45}$F$_3$GeN$_2$OS (671.38): C 62.61, H 6.76, N 4.17, S 4.78; Found: Found: C 62.58, H 6.68, N 4.17, S 5.33.

11.4.9. Synthesis of LGeC(CO$_2$Me)CH$_2$ (9)

A solution of HC≡CCO$_2$Me (0.085 g, 1.00 mmol in 5 mL toluene) was added drop by drop by cannula to a solution of **5** (0.490 g, 1.00 mmol in toluene 15 mL) at room temperature. After overnight constant stirring at ambient temperature all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (15 mL) and after removal of all the volatiles compound **9** was obtained as a yellow powder. Yield: 0.49 g (85 %). Mp 161 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.09-7.16 (m, 6H, Ar-*H*), 6.20 (br, 1H, C*H*$_2$), 5.82 (br, 1H, C*H$_2$*), 4.88 (s, 1H, γ-C*H*), 3.70 (sept, 2H, C*H*(CH$_3$)$_2$), 3.47 (s, 3H, CO$_2$C*H$_3$*), 3.46 (sept, 2H, C*H*(CH$_3$)$_2$), 1.58 (s, 6H, C*H$_3$*), 1.31 (d, 6H, CH(C*H$_3$*)$_2$), 1.27 (d, 6H, CH(C*H$_3$*)$_2$), 1.18 (d, 6H, CH(C*H$_3$*)$_2$), 1.15 (d, 6H, CH(C*H$_3$*)$_2$) ppm. EI-MS: *m/z* (%) 576 (100) [M]$^+$. Anal. calcd for C$_{33}$H$_{46}$GeN$_2$O$_2$ (576): C 68.89, H, 8.06, N 4.87; Found: C, 68.89; H, 8.16; N, 4.20.

11.4.10. Synthesis of LGeC(CO$_2$Et)CH$_2$ (10)

A solution of HC≡CCO$_2$Et (0.100 g, 1.00 mmol in 5 mL toluene) was added drop by drop by cannula to a solution of **5** (0.490 g, 1.00 mmol in toluene 15 mL) at room temperature. After 0.5 h under constant stirring at ambient temperature the red solution turned deep-red. All volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a -30 °C freezer. Red crystals of **10** suitable for X-ray diffraction analysis are formed after two days. Yield: 0.50 g (85 %). Mp

170 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.09-7.16 (m, 6H, Ar-*H*), 6.20 (d, 1H,), 5.82 (d, 1H,), 4.89 (s, 1H, γ-C*H*), 4.07 (q, 2H, C*H$_2$*), 3.65 (sept, 2H, C*H*(CH$_3$)$_2$), 3.48 (sept, 2H, C*H*(CH$_3$)$_2$), 1.59 (s, 6H, C*H$_3$*), 1.31 (d, 6H, CH(C*H$_3$*)$_2$), 1.27 (d, 6H, CH(C*H$_3$*)$_2$), 1.18 (d, 6H, CH(C*H$_3$*)$_2$), 1.15 (d, 6H, CH(C*H$_3$*)$_2$), 0.87 (t, 3H, CH$_2$C*H$_3$*) ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 2854 (C-H), 1690 cm^{-1} (C=O). EI-MS: *m/z* (%) 590 (100) [M]$^+$. Anal. calcd for C$_{34}$H$_{48}$GeN$_2$O$_2$ (589.40): C 69.29, H 8.21, N 4.75; Found: C 68.25, H 9.83, N 4.53.

11.4.11. Synthesis of LGeC(CO$_2$Me)CHCO$_2$Me (11)

A solution of dimethyl acetylenedicarboxylate (0.145 g, 1.00 mmol in 5 mL) toluene was added drop by drop by cannula to a solution of **5** (0.490 g, 1.00 mmol in toluene 15 mL) at room temperature. After 15 min under constant stirring at ambient temperature the red solution turned deep-red. All volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a -30 °C freezer. Red crystals of **11** suitable for X-ray diffraction analysis are formed after one day. Yield: 0.510 g (80 %); Mp 162 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.05-7.15 (m, 6H, Ar-*H*), 6.64 (s, 1H, C*H*), 4.89 (s, 1H, γ-C*H*), 3.90 (sept, 2H, C*H*(CH$_3$)$_2$), 3.43 (s, 3H, C*H$_3$*), 3.33 (sept, 2H, C*H*(CH$_3$)$_2$), 3.16 (s, 3H, C*H$_3$*), 1.59 (s, 6H, C*H$_3$*), 1.32 (d, 6H, CH(C*H$_3$*)$_2$), 1.24 (q, 12H, CH(CH$_3$)$_2$), 1.12 (d, 6H, CH(C*H$_3$*)$_2$) ppm. EI-MS: *m/z* (%) 634 (100) [M]$^+$. Anal. calcd for C$_{37}$H$_{52}$GeN$_2$O$_4$ (633.41): C 66.37, H 7.64, N 4.42; Found: C 66.21, H 7.64, N 4.38.

11.4.12. Synthesis of LGeC(CO$_2$Et)CHCO$_2$Et (12)

A solution of diethyl acetylenedicarboxylate (0.170 g, 1.00 mmol in 5 mL toluene) was added drop by drop by cannula to a solution of **5** (0.490 g, 1.00 mmol in toluene 15 mL) at room temperature. After 24 h under constant stirring at ambient temperature the red solution turned yellow. All volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL) and concentrated to about 15 mL and stored in a -30 °C freezer. Yellow crystals of **12** suitable for X-ray diffraction analysis are formed after two days. Yield: 0.53 g (80 %). Mp 117 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.07-7.15 (m, 6H, Ar-*H*), 6.68 (s, 1H, C*H*), 4.91 (s, 1H, γ-C*H*), 3.99 (q, 2H, C*H$_2$*), 3.91 (sept, 2H, C*H*(CH$_3$)$_2$), 3.82 (q, 2H, C*H$_2$*), 3.34 (sept, 2H, C*H*(CH$_3$)$_2$), 1.63 (s, 6H, C*H$_3$*), 1.34 (d, 6H, CH(C*H$_3$*)$_2$), 1.29 (d, 6H, CH(C*H$_3$*)$_2$), 1.21 (d, 6H, CH(C*H$_3$*)$_2$), 1.14 (d, 6H, CH(C*H$_3$*)$_2$), 1.05 (t, 3H, CH$_2$C*H$_3$*), 0.74 (t, 3H, CH$_2$C*H$_3$*) ppm. EI-MS: *m/z* (%) 633 (100) [M-Et]$^+$. Anal. calcd for C$_{37}$H$_{52}$GeN$_2$O$_4$(661.40): C 69.29, H 8.21, N 4.75; Found: C 68.25, H 9.83, N 4.53.

11.4.13. Synthesis of LGeC(CO$_2$*t*Bu)CHCO$_2$*t*Bu (13)

A solution of ditertbutyl acetylenedicarboxylate (0.230 g, 1.00 mmol in 5 mL toluene) was added drop by drop by cannula to a solution of **5** (0.490 g, 1.00 mmol in toluene 15 mL) at room temperature. After 45 min under constant stirring at ambient temperature the red solution turned yellow. All volatiles were removed *in vacuo* and the remaining residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a -30 °C freezer. Red crystals of **13** suitable for X-ray diffraction analysis are formed after two days. Yield: 0.630 g (88 %). Mp 168 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.04-7.15 (m, 6H, Ar-*H*), 6.65 (s, 1H, C*H*), 4.96 (s, 1H, γ-C*H*), 3.77 (sept, 2H, C*H*(CH$_3$)$_2$), 3.38 (sept, 2H, C*H*(CH$_3$)$_2$), 1.67 (s, 6H, C*H$_3$*), 1.41 (s, 9H, C(C*H$_3$*)$_3$), 1.34 (d, 6H, CH(C*H$_3$*)$_2$), 1.32 (d, 6H, CH(C*H$_3$*)$_2$), 1.28 (d, 6H, CH(C*H$_3$*)$_2$) 1.18 (s, 9H, C(C*H$_3$*)$_3$), 1.15 (d, 6H, CH(C*H$_3$*)$_2$) ppm. EI-MS: *m/z* (%) 718 (100) [M]$^+$. Anal. calcd for C$_{37}$H$_{52}$GeN$_2$O$_4$ (717.57): C 68.63, H 8.43, N 3.90; Found: C 68.83, H 8.26, N 3.88.

11.4.14. Synthesis of LGe(NHCO$_2$Et)NCO$_2$Et (14)

A solution of diethyl diazadicarboxylate (0.145 g, 1.00 mmol in 5 mL) toluene was added drop by drop by cannula to a solution of **5** (0.490 g, 1.00 mmol in toluene 15 mL) at room temperature. After 15 min under constant stirring at ambient temperature the red solution turned yellow. All volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a -30 °C freezer. Yellow crystals of **14** suitable for X-ray diffraction analysis are formed after three days. Yield: 1.10 g (95 %). Mp 162 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.03-7.16 (m, 6H, Ar-*H*), 6.43 (br, 1H, N*H*), 5.14 (s, 1H, γ-C*H*), 4.00 (q, 2H, C*H$_2$*CH$_3$), 3.91 (sept, 2H, C*H*(CH$_3$)$_2$), 3.13 (sept, 2H, C*H*(CH$_3$)$_2$), 1.65 (s, 6H, C*H$_3$*), 1.36 (d, 6H, CH(C*H$_3$*)$_2$), 1.25 (d, 6H, CH(C*H$_3$*)$_2$), 1.15 (d, 6H, CH(C*H$_3$*)$_2$), 1.14 (d, 6H, CH(C*H$_3$*)$_2$), 0.88 (t, 3H, CH$_2$C*H$_3$*) ppm. EI-MS (70 eV): *m/z* (%): 491 (100) [M-N$_2$C$_6$H$_{11}$O$_4$]$^+$. Anal. calcd for C$_{35}$H$_{52}$GeN$_4$O$_4$ (665.45): C 63.17, H 7.88, N 8.42; found: C 61.63, H 7.93, N 8.46.

11.4.15. Synthesis of LGeOH (**15**)

Method A: Dry N_2O was bubbled into a solution of **5** (0.49 g, 1.00 mmol) in toluene (20 mL) at room temperature. After 30 min the gas flow of N_2O was disconnected, and all the volatiles were removed *in vacuo*. The residue was treated with *n*-hexane (40 mL) and after filtration and drying *in vacuo*, **15** was obtained as a yellow microcrystalline powder. Yield: 0.480 g (95%). Method B: Water (18 μl, 1 mmol) was added to a red solution of **19** (0.490 g, 1 mmol) in toluene (20 mL) under stirring at room temperature. The reaction mixture became yellow. Stirring of the reaction mixture was continued for about 15 min. After that the solvent was removed *in vacuo* and the residue was extracted with *n*-hexane (15 mL). The solution was reduced to half of the volume. Storage of the solution at –30 °C for one day yielded yellow crystals of **15**. Yield: 0.480 g (95%). ^{1}H NMR (500 MHz, C_6D_6): δ 7.09-7.17 (m, 6H, Ar-*H*), 4.91 (s, 1H, γ-C*H*), 3.71 (sept, 2H, C*H*(CH$_3$)$_2$), 3.31 (sept, 2H, C*H*(CH$_3$)$_2$), 1.65 (s, 1H, O*H*), 1.60 (s, 6H, C*H$_3$*), 1.30 (d, 6H, CH(C*H$_3$*)$_2$), 1.28 (d, 6H, CH(C*H$_3$*)$_2$), 1.20 (d, 6H, CH(C*H$_3$*)$_2$), 1.11 (d, 6H, CH(C*H$_3$*)$_2$) ppm.

11.4.16. Synthesis of LGe(S)SH (**16**)

A solution of **5** (1.47 g, 3.00 mmol) in toluene (30 mL) was slowly added to a suspension of elemental sulfur (0.192 g, 6.00 mmol) in toluene (15 mL) by cannula at room temperature. After 0.5 h under constant stirring at ambient temperature the red solution turned slightly yellow. All volatiles were removed *in vacuo*, and the remaining residue was extracted with toluene (15 mL). The solvent was removed *in vacuo* to yield **16** as a slight yellow powder. Yield: 0.980 g (60 %). Mp 220 °C (decomp). ^{1}H NMR (500 MHz, C_6D_6): δ 6.99-7.14 (m, 6H, Ar-*H*), 4.83 (s, 1H, γ-C*H*), 3.56 (sept, 2H, C*H*(CH$_3$)$_2$), 3.33 (sept, 2H, C*H*(CH$_3$)$_2$), 1.72 (s, 6H, C*H$_3$*), 1.65 (d, 6H, CH(C*H$_3$*)$_2$), 1.49 (d, 12H, CH(C*H$_3$*)$_2$), 1.13 (d, 6H, CH(C*H$_3$*)$_2$), -0.094 (s, 1H, S*H*) ppm. IR (Nujol, KBr): $\widetilde{\nu}$ = 2590 cm^{-1} (S-H). EI-MS (70 eV): *m/z* (%): 522 (40) [M-SH]$^+$, 506 (100) [M-SH, -Me]$^+$. Anal. calcd for $C_{29}H_{42}GeN_2S_2$ (552.25): C 62.71, H 7.62 N 5.04; Found: C 61.26, H 7.70, N 4.89.

11.4.17. Synthesis of LGeN$_3$ (**17**) and L´Ge(NHSiMe$_3$)$_2$ (**18**)

An excess of trimethylsilyl azide was slowly added drop by drop to a 20 mL toluene solution of **5** (0.98 g, 2 mmol). Then the reaction mixture was stored overnight. After that the solvent and excess trimethylsilyl azide were removed *in vacuo*. The residue was extracted with *n*-hexane (35 mL) and the extract concentrated to about 20 mL. After one day at room temperature colorless crystals of **17** are formed. Then the residual extract is stored in a freezer at -30 ^{0}C. After two days colorless crystals of **18** had formed. **17**: Yield: 0.34 g (32 %). Mp 190 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.04-7.13 (m, 6H, Ar-*H*), 4.98 (s, 1H, γ-C*H*), 3.73 (sept, 2H, C*H*(CH$_3$)$_2$), 3.10 (sept, 2H, C*H*(CH$_3$)$_2$), 1.53 (s, 6H, C*H$_3$*), 1.32 (d, 6H, CH(C*H$_3$*)$_2$), 1.18 (d, 12H, CH(C*H$_3$*)$_2$), 1.15 (d, 6H, CH(C*H$_3$*)$_2$), 1.05 (d, 6H, CH(C*H$_3$*)$_2$) ppm. IR (Nujol, KBr, cm^{-1}): $\widetilde{\nu}$ = 2068 (N$_3$); EI-MS (70 eV): *m/z* (%): 491 (100) [M-N$_3$]$^+$. Anal. calcd for $C_{29}H_{41}GeN_5$ (532.26): C 65.43, H 7.76; Found: C 64.06, H, 8.11. **18**: Yield: 0.37 g (28 %). Mp 200 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.21 (s, 2H, N*H*), 7.04-7.13 (m, 6H, Ar-*H*), 5.29 (s, 1H, γ-C*H*), 3.87 (s, 1H, C*H*), 3.86 (sept, 2H, C*H*(CH$_3$)$_2$), 3.74 (sept, 2H, C*H*(CH$_3$)$_2$), 3.28 (s, 1H, C*H*), 1.58 (s, 6H, C*H$_3$*), 1.32 (d, 6H, CH(C*H$_3$*)$_2$), 1.18 (d, 12H, CH(C*H$_3$*)$_2$), 1.15 (d, 6H, CH(C*H$_3$*)$_2$), 1.05 (d, 6H, CH(C*H$_3$*)$_2$), 0.01 (s, 18H, Si(C*H$_3$*)$_3$) ppm. ^{29}Si{^{1}H} NMR (125.77 Hz, C_6D_6): δ 5.53 (*Si*(CH$_3$)$_3$) ppm. EI-MS (70 eV): *m/z* (%): 651 (100) [M-Me]$^+$. Anal. calcd for $C_{35}H_{60}GeN_4Si_2$ (665.64): C 63.15, H 9.08; Found: C 64.83, H 8.36.

11.4.18. Synthesis of L´Ge (**19**)

Method A: A solution of B(C$_6$F$_5$)$_3$ (0.51 g, 1.0 mmol) in toluene (10 mL) was added drop by drop to a stirred solution of **5** (0.49 g, 1.0 mmol) in toluene (10 mL) at room temperature. Immediately the red color of the reaction mixture changed to colorless. The reaction mixture was stirred for additional 10 min. After that a solution of 1,3-di-*tert*-butylimidazol-2-ylidene (0.18 g, 1.0 mmol) in toluene (10 mL) was added drop by drop to the reaction mixture. During this time the reaction mixture turns to brown-red with the formation of a white precipitate. After another 10 min the solvent was removed *in vacuo* and the residue was extracted with *n*-hexane (15 mL). The extracted brown-red solution was identified as **19**. The insoluble part was collected and identified as imidazolium borate salt. Both are formed almost quantitatively and the NMR data matches with the previously reported samples. Method B: 1,3-di-*tert*-butylimidazol-2-ylidene (0.360 g, 2.0 mmol) and LGeCl (1.050 g, 2.0 mmol) were dissolved in toluene (30 mL) at room temperature. The reaction mixture was stirred

and the color of the solution changed from yellow to brown-red. A white precipitate was formed. The reaction mixture was stirred for another hour, then the white precipitate was separated by filtration and the remaining red solution was evaporated. The residue was dissolved in *n*-hexane. Storage of the solution at –30 °C for one day yielded brown-red crystals suitable for a single crystal X-ray diffraction experiment. Yield: 0.630 g (65%). Method C: 1,3-Di-*tert*-butylimidazol-2-ylidene (0.360 g, 2.0 mmol) and LGeOTf (1.280 g, 2.0 mmol) were dissolved in toluene (30 mL) at room temperature. The reaction mixture was stirred and the color of the solution changed from colorless to brown-red. A white precipitate was formed. The reaction mixture was stirred for another hour, then the white precipitate was separated by filtration and the remaining red solution was evaporated. The residue was dissolved in *n*-hexane (20 mL). Storage of this solution at –30 °C for one day in a freezer yielded brown-red crystals. Yield: 0.880 g (90%). ^{1}H NMR (500 MHz, C_6D_6): δ 7.04-7.21 (m, 6H, Ar-*H*), 5.43 (s, 1H, γ-C*H*), 3.91 (s, 1H, C*H*$_2$), 3.69 (sept, 2H, C*H*(CH$_3$)$_2$), 3.44 (sept, 2H, C*H*(CH$_3$)$_2$), 3.26 (s, 1H, C*H*$_2$), 1.41 (s, 3H, C*H*$_3$), 1.35 (d, 6H, CH(C*H*$_3$)$_2$), 1.29 (d, 6H, CH(C*H*$_3$)$_2$), 1.20 (d, 6H, CH(C*H*$_3$)$_2$), 1.15 (d, 6H, CH(C*H*$_3$)$_2$) ppm.

11.4.19. Synthesis of LSnH (**20**)

A solution of K[HB(*sec*Bu)$_3$] in THF (2.00 mL, 1 M, in THF) was slowly added drop by drop to a stirred solution of LSnCl (1.140 g, 2 mmol) in toluene (30 mL) at -10 °C. The reaction mixture was warmed to room temperature and was stirred for additional 30 min. After removal of all the volatiles, the residue was extracted with *n*-hexane (30 mL) and concentrated to about 10 mL and stored in a -30 °C freezer. Yellow crystals of **20** are formed after one day. Yield: 0.94 g (88 %). Mp 125 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 13.83 (s, 1H, Sn-*H*), 7.15-7.06 (m, 6H, Ar-*H*), 4.89 (s, 1H, γ-C*H*), 3.52 (sept, 2H, C*H*(CH$_3$)$_2$), 3.46 (sept, 2H, C*H*(CH$_3$)$_2$), 1.62 (s, 6H, C*H*$_3$), 1.34 (d, 6H, CH(C*H*$_3$)$_2$), 1.27 (d, 6H, CH(C*H*$_3$)$_2$), 1.19 (d, 12H, CH(C*H*$_3$)$_2$), ppm. ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -4.45 ppm (^2J(^{119}Sn,^{1}H)=64 Hz).

11.4.20. Synthesis of LSnOC(O)H (**21**)

Dry CO_2 was bubbled into a solution of **20** (1.08 g, 2.00 mmol) in toluene (40 mL) at room temperature. Immediately after the addition of CO_2, the color of the solution changed to colorless. After 10 min the gas flow of CO_2 was disconnected, and the solution was stirred for additional 30 min. All the volatiles were removed *in vacuo*. The residue was treated with *n*-hexane (40 mL) and after filtration and drying *in vacuo*, **21** was obtained as a yellow microcrystalline powder. Yield (1.10 g, 95 %). Mp 183 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 8.97 (s, 1H, C*H*), 7.02-7.15 (m, 6H, Ar-*H*), 4.96 (s, 1H, γ-C*H*), 3.61 (sept, 2H, C*H*(CH$_3$)$_2$), 3.06 (sept, 2H, C*H*(CH$_3$)$_2$), 1.58 (s, 6H, C*H*$_3$), 1.32 (d, 6H, CH(C*H*$_3$)$_2$), 1.18 (d, 12H, CH(C*H*$_3$)$_2$), 1.15 (d, 6H, CH(C*H*$_3$)$_2$), 1.05 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -360 ppm. IR (Nujol, KBr, cm^{-1}): $\widetilde{\nu}$ = 2700 (C-H), 1641 (C=O). EI-MS (70 eV): *m/z* (%): 582 (100) [M]$^+$. Anal. calcd for $C_{30}H_{42}N_2O_2Sn$ (582.23): C 61.98, H 7.28, N 4.82; Found: C 61.69, H 7.39, N 4.82.

11.4.21. Synthesis of LSnOCH$_2$Fc (**22**)

A solution of ferrocene carbaldehyde (0.210 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **20** (0.54 g, 1.00 mmol in toluene 15 mL) at room temperature under stirring. After 12 h all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a -30 °C freezer. Red-yellow crystals of **22** suitable for X-ray diffraction analysis are formed after one day. Yield: 0.635 g (85 %). Mp 143 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.06-7.17 (m, 6H, Ar-*H*), 4.87 (s, 1H, γ-C*H*), 4.81 (s, 2H, C*H*$_2$), 4.09 (t, 2H, α-C$_5$H$_4$), 4.01 (s, 5H, C$_5$H$_5$), 3.92 (t, 2H, β-C$_5$H$_4$), 3.83 (sept, 2H, C*H*(CH$_3$)$_2$), 3.19 (sept, 2H, C*H*(CH$_3$)$_2$), 1.62 (s, 6H, C*H*$_3$), 1.44 (s, 6H, C*H*$_3$), 1.30 (d, 6H, CH(C*H*$_3$)$_2$), 1.20 (d, 6H, CH(C*H*$_3$)$_2$), 1.12 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -262 ppm. EI-MS (70 eV): *m/z* (%): 752 (100) [M]$^+$. Anal. calcd for $C_{40}H_{52}FeN_2OSn$ (752.25): C 63.94, H 6.98, N 3.73; Found: C 63.76, H 7.01, N 3.65.

11.4.22. Synthesis of LSnOCHPh$_2$ (**23**)

A solution of Ph$_2$CO (0.180 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **20** (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After 12 h all volatiles were removed *in vacuo*, and the

remaining residue was extracted with *n*-hexane (25 mL) and concentrated to about 15 mL and stored in a -30 $^\circ$C freezer. After four days yellow crystals of **23** are formed. Yield: 0.590 g (82 %). Mp 76 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 6.86-7.70 (m, 16H, Ar-*H*), 5.97 (s, 1H, C*H*), 4.80 (s, 1H, γ-C*H*), 3.67 (sept, 2H, C*H*(CH$_3$)$_2$), 3.15 (sept, 2H, C*H*(CH$_3$)$_2$), 1.57 (s, 6H, C*H*$_3$), 1.19 (d, 6H, CH(C*H*$_3$)$_2$), 1.14 (d, 6H, CH(C*H*$_3$)$_2$), 1.12 (d, 6H, CH(C*H*$_3$)$_2$), 1.07 (d, 6H, CH(C*H*$_3$)$_2$). ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -218 ppm. EI-MS (70 eV): *m/z* (%): 719 (100) [M]$^+$. Anal. calcd for C$_{42}$H$_{52}$N$_2$OSn (719.59): C 70.10, H 7.28, N 3.89; Found: C 72.71, H 7.53, N 3.32.

11.4.23. Synthesis of LSnOCHPh(2-Py) (**24**)

A solution of 2-benzol pyridine (0.180 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **20** (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After 12 h all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL) and concentrated to about 15 mL and stored in a -30 $^\circ$C freezer. Yellow crystals of **24** suitable for X-ray diffraction analysis are formed after four days. Yield: 0.660 g (92 %). Mp 180 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 6.34-7.15 (m, 15H, Ar-*H*), 6.28 (s, 1H, C*H*), 4.78 (s, 1H, γ-C*H*), 4.02 (sept, 1H, C*H*(CH$_3$)$_2$), 3.88 (sept, 1H, C*H*(CH$_3$)$_2$), 3.41 (sept, 1H, C*H*(CH$_3$)$_2$), 3.34 (sept, 1H, C*H*(CH$_3$)$_2$), 1.69 (s, 3H, C*H*$_3$), 1.59 (s, 3H, C*H*$_3$), 1.44 (d, 3H, CH(C*H*$_3$)$_2$), 1.39 (d, 3H, CH(C*H*$_3$)$_2$), 1.27 (d, 3H, CH(C*H*$_3$)$_2$), 1.22 (d, 3H, CH(C*H*$_3$)$_2$), 1.16 (d, 3H, CH(C*H*$_3$)$_2$), 1.11 (d, 3H, CH(C*H*$_3$)$_2$), 1.05 (d, 3H, CH(C*H*$_3$)$_2$), 0.88 (d, 3H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -286 ppm. EI-MS (70 eV): *m/z* (%): 721 (100) [M]$^+$. Anal. calcd. for C$_{41}$H$_{51}$N$_3$OSn (721.31): C 68.34, H 7.13, N 5.83; Found: C 68.13, H 7.25, N 5.80.

11.4.24. Synthesis of LSnOCH(2-Py)$_2$ (**25**)

A solution of (2-Py)$_2$CO (0.185 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **20** (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After overnight stirring all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL). The solvent from the solution was completely removed and compound **25** was obtained as a powder. Yield: 0.560 g (78 %). Mp 160 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 6.38-7.60 (m, 14H, Ar-*H*), 6.59 (s, 1H, C*H*), 4.85 (s, 1H, γ-C*H*), 3.93 (sept, 2H, C*H*(CH$_3$)$_2$), 3.55 (sept, 2H, C*H*(CH$_3$)$_2$), 1.72 (s, 3H, C*H*$_3$), 1.44 (d, 6H, CH(C*H*$_3$)$_2$), 1.23 (d, 6H, CH(C*H*$_3$)$_2$), 1.17 (d, 6H, CH(C*H*$_3$)$_2$), 0.90 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -324 ppm. EI-MS (70 eV): *m/z* (%): 722 (100) [M]$^+$. Anal. calcd for C$_{40}$H$_{50}$N$_4$OSn (722.30): C 66.58, H 6.98, N 7.76; Found: C 66.74, H 6.94, N 7.67.

11.4.25. Synthesis of LSnOCH(C$_3$H$_5$)$_2$ (**26**)

A solution of dicyclopropylketone (0.110 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **20** (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After that the solution was heated under reflux for 12 h. Then all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL). The solution was concentrated and stored in a freezer, after four days yellow crystals of **26** are formed which are suitable for X-ray structural analysis. Yield: 0.480 g (74 %). Mp 169 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.06-7.20 (m, 6 H, Ar-*H*), 4.71 (s, 1H, γ-C*H*), 3.81 (sept, 2H, C*H*(CH$_3$)$_2$), 3.24 (sept, 2H, C*H*(CH$_3$)$_2$), 2.47 (q, 1H, C*H*), 1.58 (s, 6H, C*H*$_3$), 1.52 (s, 6H, C*H*$_3$), 1.28 (d, 6H, CH(C*H*$_3$)$_2$), 1.24 (d, 6H, CH(C*H*$_3$)$_2$), 1.14 (d, 6H, CH(C*H*$_3$)$_2$), 0.75 (m, 2H, C*H*), 0.21 (m, 2H, C*H*$_2$), 0.02 (m, 2H, C*H*$_2$), -0.07 (m, 2H, C*H*$_2$), -0.25 (m, 2H, C*H*$_2$) ppm. ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -190.50 ppm. EI-MS (70 eV): *m/z* (%): 648 (100) [M]$^+$. Anal. calcd for C$_{36}$H$_{52}$N$_2$OSn (648.31): C 66.78, H 8.09, N 4.33; Found: C 65.19, H 8.00, N 4.13.

11.4.26. Synthesis of LSnC(CO$_2$Me)CH$_2$ (**27**)

A solution of HC≡CCO$_2$Me (0.085 g, 1.00 mmol in 5 mL toluene) was added drop by drop by cannula to a solution of **20** (0.540 g, 1.00 mmol in toluene 15 mL) at room temperature. After 0.5 h under constant stirring at ambient temperature all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a -30 $^\circ$C freezer. Yellow crystals of **27** suitable for X-ray diffraction analysis are formed after two days. Yield: 0.435 g (70 %). Mp 170 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.08-7.14 (m, 6H, Ar-*H*), 6.45 (br, 1H, C=C*H*$_2$), 6.15 (br, 1H, C=C*H*$_2$), 4.81 (s, 1H, γ-C*H*), 3.67 (sept, 2H, C*H*(CH$_3$)$_2$), 3.42 (s, 3H, C*H*$_3$), 3.40 (sept, 2H, C*H*(CH$_3$)$_2$), 1.60 (s, 6H, C*H*$_3$), 1.27 (m, 12H, CH(C*H*$_3$)$_2$), 1.16 (m, 12H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -93.28 ppm. EI-MS: *m/z* (%) 622 (100) [M]$^+$. Anal. calcd for C$_{33}$H$_{46}$N$_2$O$_2$Sn (622.26): C 63.78, H 7.46, N 4.51; Found: C 63.80, H 7.84, N 4.47.

11.4.27. Synthesis of LSnC(CO$_2$Et)CH$_2$ (**28**)

A solution of HC≡CCO$_2$Et (0.100 g, 1.00 mmol in 5 mL toluene) was added drop by drop by cannula to a solution of **20** (0.490 g, 1.00 mmol in toluene 15 mL) at room temperature. After 0.5 h under constant stirring at ambient temperature the yellow solution remains unchanged. All volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a -30 °C freezer. Yellow crystals of **28** are formed after one week. Yield: 0.460 g (72 %). Mp 168 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.10-7.20 (m, 6H, Ar-*H*), 6.70 (br, 1H, C=C*H*$_2$), 6.10 (br, 1H, C=C*H*$_2$), 4.82 (s, 1H, γ-C*H*), 4.08 (q, 2H, C*H*$_2$), 3.67 (sept, 2H, C*H*(CH$_3$)$_2$), 3.42 (sept, 2H, C*H*(CH$_3$)$_2$), 1.62 (s, 6H, C*H*$_3$), 1.28 (m, 12H, CH(C*H*$_3$)$_2$), 1.18 (m, 12H, CH(C*H*$_3$)$_2$), 1.03 (t, 3H, CH$_2$C*H*$_3$) ppm. ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -89.02 ppm. EI-MS: *m/z* (%) 636 (100) [M]$^+$. Anal. calcd for C$_{34}$H$_{48}$N$_2$O$_2$Sn (636.27): C 64.26, H 7.61, N 4.41; Found: C 63.98, H 7.92, N 4.38.

11.4.28. Synthesis of LSnC(CO$_2$Et)CHMe (**29**)

A solution of ethyl but-2-ynoate (0.110 g, 1.00 mmol in 5 mL toluene) was added drop by drop by cannula to a solution of **20** (0.54 g, 1.00 mmol in toluene 15 mL) at room temperature. After 12 h all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a -30 °C freezer. Yellow crystals of **29** suitable for X-ray diffraction analysis are formed after four days. Yield: 0.570 g (88 %). Mp 129 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.07-7.20 (m, 6H, Ar-*H*), 5.84 (br, 1H, C*H*), 4.82 (s, 1H, γ-C*H*), 4.09 (q, 2H, C*H*$_2$), 3.93 (sept, 2H, C*H*(CH$_3$)$_2$), 3.41 (sept, 2H, C*H*(CH$_3$)$_2$), 1.77 (d, 3H, C*H*$_3$),1.64 (s, 6H, C*H*$_3$), 1.37 (d, 6H, CH(C*H*$_3$)$_2$), 1.29 (d, 6H, CH(C*H*$_3$)$_2$), 1.22 (d, 6H, CH(C*H*$_3$)$_2$), 1.17 (d, 6H, CH(C*H*$_3$)$_2$), 1.11 (t, 3H, C*H*$_3$) ppm. ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -90 ppm. IR (Nujol, KBr): $\widetilde{\nu}$ = 1686 cm^{-1} (C=O). EI-MS (70 eV): *m/z* (%): 650 (100) [M]$^+$. Anal. calcd for C$_{35}$H$_{50}$N$_2$O$_2$Sn (650.29): C 67.83, H 8.67, N 7.53; found: C 67.78, H 8.97, N 7.69.

11.4.29. Synthesis of LSnC(CO$_2$Me)CHCO$_2$Me (**30**)

A solution of dimethyl acetylenedicarboxylate (0.140 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **20** (0.490 g, 1.00 mmol in toluene 15 mL) at room temperature. After 3 h all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (15 mL). The solvent was removed *in vacuo* and compound **30** obtained as a red yellow solid. Yield: 0.610 g (90 %). Mp 179 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 6.34-7.15 (m, 15H, Ar-*H*), 6.92 (s, 1H, C*H*), 6.26 (s, 1H, C*H*), 4.85 (s, 1H, γ-C*H*), 4.83 (s, 1H, γ-C*H*), 3.88 (sept, 2H, C*H*(CH$_3$)$_2$), 3.66 (s, 3H, C*H*$_3$), 3.35 (s, 3H, C*H*$_3$), 3.29 (sept, 2H, C*H*(CH$_3$)$_2$), 1.65 (s, 6H, C*H*$_3$), 1.61 (s, 6H, C*H*$_3$), 1.36 (d, 6H, CH(C*H*$_3$)$_2$), 1.34 (d, 6H, CH(C*H*$_3$)$_2$), 1.23 (d, 6H, CH(C*H*$_3$)$_2$), 1.21 (d, 6H, CH(C*H*$_3$)$_2$), 1.20 (d, 6H, CH(C*H*$_3$)$_2$), 1.19 (d, 6H, CH(C*H*$_3$)$_2$), 1.17 (d, 6H, CH(C*H*$_3$)$_2$), 1.15 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -132, -211 ppm.

11.4.30. Synthesis of LSnC(CO$_2$Et)CHCO$_2$Et (**31**)

A solution of diethyl acetylenedicarboxylate (0.170 g, 1.00 mmol in 5 mL) toluene was added drop by drop by cannula to a solution of **20** (0.540 g, 1.00 mmol in toluene 15 mL) at room temperature. After 6 h under constant stirring at ambient temperature the yellow solution turned red. All volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a -30 °C freezer. Red crystals of **31** suitable for X-ray diffraction analysis are formed after one day. Yield: 0.480 g (68 %). Mp 138 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.05-7.16 (m, 6H, Ar-*H*), 6.93 (s, C*H*), 6.26 (s, C*H*), 4.87 (s, γ-C*H*), 4.85 (s, γ-C*H*), 4.22 (q, C*H*$_2$), 4.03 (q, C*H*$_2$), 3.98 (q, C*H*$_2$), 3.88 (m, C*H*(CH$_3$)$_2$), 3.84 (q, C*H*$_2$), 3.28 (m, C*H*(CH$_3$)$_2$), 1.65 (s, C*H*$_3$), 1.64 (s, C*H*$_3$), 1.35 (t, C*H*$_3$), 1.32-1.12 (m, CH(C*H*$_3$)$_2$), 1.06 (t, C*H*$_3$), 0.95 (t, C*H*$_3$), 0.87 (t, C*H*$_3$), 0.82 (t, C*H*$_3$) ppm. ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -130.36, -211.20 ppm. EI-MS: *m/z* (%) 708 (100) [M]$^+$. Anal. calcd for C$_{37}$H$_{52}$N$_2$O$_4$Sn (708.29): C 62.87, H 7.41, N 3.96; Found: C 60.63, H 7.41, N 3.64.

11.4.31. Synthesis of LSnC(CO$_2$*t*Bu)CHCO$_2$*t*Bu (**32**)

A solution of ditertiary butylacetylenedicarboxylate (0.225 g, 1.00 mmol in 5 mL toluene) was added drop by drop by cannula to a solution of **20** (0.540 g, 1.00 mmol in toluene 15 mL) at room temperature. After overnight constant stirring at ambient temperature, all the volatiles were removed *in vacuo* and the remaining residue was

extracted with *n*-hexane (25 mL). Complete evaporation of the filtrate resulted in a red power of the title compound **32**. Yield: 0.490 g (64 %). Mp 179 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.06-7.15 (m, 6H, Ar-*H*), 6.93 (s, C*H*), 6.18 (s, C*H*), 4.92 (s, γ-C*H*), 4.90 (s, γ-C*H*), 3.82 (m, 2H, C*H*(CH$_3$)$_2$), 3.36 (sept, 2H, C*H*(CH$_3$)$_2$), 1.72 (s, 6H, C*H$_3$*), 1.65 (s, 9H, C(C*H$_3$*)$_3$), 1.37-1.15 (m, 24H, CH(C*H$_3$*)$_2$), 1.25 (s, 9H, C(C*H$_3$*)$_3$) ppm. ^{119}Sn$\{^1$H$\}$ NMR (186.46 MHz): δ -123.27, -205.75 ppm. EI-MS: *m/z* (%) 707 (100) [M-*t*Bu]$^+$. Anal. calcd for $C_{41}H_{60}N_2O_4Sn$ (764.36): C 64.49, H 7.92, N 3.67; Found: C 64.38, H 8.08, N 3.59.

11.4.32. Synthesis of **33**

A solution of *i*PrNCN*i*Pr (0.210 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **20** (0.540 g, 1.00 mmol in toluene 15 mL) at room temperature. After 12 h all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL). The solvent was removed and compound **33** obtained as a yellow powder. Yield: 0.610 g (82 %). Mp 190 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 8.26 (s, 1H, C*H*), 7.07-7.16 (m, 6H, Ar-*H*), 4.80 (s, 1H, γ-C*H*), 3.42 (sept, 2H, C*H*(CH$_3$)$_2$), 3.28 (sept, 2H, C*H*(CH$_3$)$_2$), the two other septet of the carbodiimde rings are overlapped with the base line, 1.57 (s, 6H, C*H$_3$*), 1.38-1.10 (m, 36H, CH(C*H$_3$*)$_2$) ppm. ^{119}Sn$\{^1$H$\}$ NMR (186.46 MHz): δ -177.69 ppm. EI-MS (70 eV): *m/z* (%): 664 (100) [M]$^+$. Anal. calcd for $C_{36}H_{56}N_4Sn$ (664.35): C 65.16, H 8.51, N 8.44; found: C 65.21, H 8.57, N 8.24.

11.4.33. Synthesis of **34**

A solution of DCC (0.210 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **20** (0.540 g, 1.00 mmol in toluene 15 mL) at room temperature. After 12 h all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL). The solvent was removed and compound **34** obtained as a yellow powder. Yield: 0.610 g (82 %). Mp 129 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 8.30 (s, 1H, C*H*), 7.08-7.19 (m, 6H, Ar-*H*), 4.80 (s, 1H, γ-C*H*), 3.49 (m, 2H, Cy), 3.31 (sept, 4H, C*H*(CH$_3$)$_2$), 1.10-1-90 (m, 20H, Cy), 1.58 (s, 6H, C*H$_3$*), 1.45 (d, 6H, CH(C*H$_3$*)$_2$), 1.33 (d, 6H, CH(C*H$_3$*)$_2$), 1.27 (d, 6H, CH(C*H$_3$*)$_2$), 1.13 (d, 6H, CH(C*H$_3$*)$_2$), 1.16 (d, 3H, CH(C*H$_3$*)$_2$), 1.11 (d, 3H, CH(C*H$_3$*)$_2$), 1.05 (d, 3H, CH(C*H$_3$*)$_2$), 0.88 (d, 3H, CH(C*H$_3$*)$_2$) ppm. ^{119}Sn$\{^1$H$\}$ NMR (186.46 MHz): δ -175 ppm. EI-MS (70 eV): *m/z* (%): 744 (100) [M]$^+$. Anal. calcd for $C_{42}H_{64}N_4Sn$ (744.42): C 67.83, H 8.67, N 7.53; found: C 67.78, H 8.97, N 7.69.

11.4.34. Synthesis of LSnOCHPhCF$_3$ (**35**)

A solution of 2,2,2-trifluoro acetophenone (0.175 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **20** (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After 12 h all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL). The solvent was removed and compound **35** obtained as a powder. Yield: 0.640 g (90 %). Mp 172 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.00-7.27 (m, 11H, Ar-*H*), 5.15 (q, 1H, C*H*), 4.84 (s, 1H, γ-C*H*), 3.76 (sept, 1H, C*H*(CH$_3$)$_2$), 3.63 (sept, 1H, C*H*(CH$_3$)$_2$), 3.10 (sept, 1H, C*H*(CH$_3$)$_2$), 3.04 (sept, 1H, C*H*(CH$_3$)$_2$), 1.56 (s, 3H, C*H$_3$*), 1.50 (s, 3H, C*H$_3$*), 1.43 (d, 3H, CH(C*H$_3$*)$_2$), 1.36 (d, 3H, CH(C*H$_3$*)$_2$), 1.20 (d, 3H, CH(C*H$_3$*)$_2$), 1.18 (d, 3H, CH(C*H$_3$*)$_2$), 1.12 (d, 3H, CH(C*H$_3$*)$_2$), 1.09 (d, 3H, CH(C*H$_3$*)$_2$), 1.07 (d, 3H, CH(C*H$_3$*)$_2$), 1.00 (d, 3H, CH(C*H$_3$*)$_2$) ppm. ^{19}F$\{^1$H$\}$ NMR (188.29 MHz): δ -76.29 (d, 3F, C*F$_3$*) ppm. ^{119}Sn$\{^1$H$\}$ NMR (186.46 MHz): δ -252 ppm. EI-MS (70 eV): *m/z* (%): 712 (100) [M]$^+$. Anal. calcd for $C_{37}H_{47}F_3N_2OSn$ (712.27): C 62.46, H 6.66, N 3.94; Found: C 62.50, H 6.77, N 3.98.

11.4.35. Synthesis of LSnOCH(2-C$_4$H$_3$S)CF$_3$ (**36**)

A solution of 2,2,2-trifluoro2-thiophene (0.180 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **20** (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After 12 h all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL). The resulting solution was concentrated and stored in a freezer, after three days yellow crystals of **36** are formed which are suitable for X-ray structural analysis. Yield: 0.610 g (85 %). Mp 158 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.03-7.20 (m, 6H, Ar-*H*), 6.81 (m, 2H, C$_4$*H$_3$*S), 6.64 (m, 1H, C$_4$*H$_3$*S), 5.45 (q, 1H, C*H*), 4.87 (s, 1H, γ-C*H*), 3.78 (sept, 1H, C*H*(CH$_3$)$_2$), 3.61 (sept, 1H, C*H*(CH$_3$)$_2$), 3.30 (sept, 1H, C*H*(CH$_3$)$_2$), 3.09 (sept, 1H, C*H*(CH$_3$)$_2$), 1.57 (s, 3H, C*H$_3$*), 1.53 (s, 3H, C*H$_3$*), 1.42 (d, 3H, CH(C*H$_3$*)$_2$), 1.37 (d, 3H, CH(C*H$_3$*)$_2$), 1.24 (d, 3H, CH(C*H$_3$*)$_2$), 1.21 (d, 3H, CH(C*H$_3$*)$_2$), 1.19-1.12 (m, 12H, CH(C*H$_3$*)$_2$) ppm. ^{19}F$\{^1$H$\}$ NMR (188.29 MHz): δ -77.39 (br, 3F, C*F$_3$*) ppm. ^{119}Sn$\{^1$H$\}$ NMR (186.46 MHz): δ -262 ppm. EI-MS (70 eV): *m/z* (%): 718 (100) [M]$^+$. Anal. calcd for $C_{35}H_{45}F_3N_2OSSn$ (718.22): C 58.59, H 6.32, N 3.90, S 4.47; Found: C 58.57, H 6.52, N 3.84, S 4.81.

11.4.36. Synthesis of LSnOCHPh(C_6F_5) (**37**)

In a NMR tube PhCOC_6F_5 (0.136 g, 0.50 mmol) and **20** (0.270 g, 0.50 mmol) were talken and 1 mL C_6D_6 was added at room temperature. After 24 h measuring the NMR showing the formation of title compound **37** along with the LSnF and PhCO(4-C_6F_4H). ^{1}H NMR (200 MHz, C_6D_6): δ 6.85-7.65 (m, 6H, Ar-*H*), 6.41 (s, 1H, C*H*), 4.78 (s, 1H, γ-C*H*), 3.56 (sept, 2H, C*H*(CH$_3$)$_2$), 3.13 (sept, 2H, C*H*(CH$_3$)$_2$), 1.53 (s, 6H, C*H$_3$*), 1.44 (d, 6H, CH(C*H$_3$*)$_2$), 1.23 (d, 6H, CH(C*H$_3$*)$_2$), 1.11 (d, 6H, CH(C*H$_3$*)$_2$), 0.90 (d, 6H, CH(C*H$_3$*)$_2$). ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -217 ppm.

11.4.37. Synthesis of LSnOCH(C_6F_5)$_2$ (**38**)

A solution of C_6F_5COC_6F_5) (0.360 g, 1.00 mmol in 10 mL toluene) was added by cannula to a solution of **20** (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After 24 h all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL). After evaporation of solvent the title compounds **38** are obtained along with the LSnF and C_6F_5CO(4-C_6F_4H). ^{1}H NMR (500 MHz, C_6D_6): δ 6.99-7.13 (m, 15H, Ar-*H*), 6.72 (s, ^{1}H, C*H*), 4.77 (s, 1H, γ-C*H*), 3.46 (sept, 2H, C*H*(CH$_3$)$_2$), 3.02 (sept, 2H, C*H*(CH$_3$)$_2$), 1.48 (s, 6H, C*H$_3$*), 1.17 (d, 6H, CH(C*H$_3$*)$_2$), 1.14 (d, 6H, CH(C*H$_3$*)$_2$), 1.08 (d, 6H, CH(C*H$_3$*)$_2$), 1.06 (d, 6H, CH(C*H$_3$*)$_2$). ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -252 ppm. EI-MS (70 eV): *m/z* (%): 900 (100) [M]$^+$.

11.4.38. Synthesis of LSnOCHPh(4-C_6H_4F) (**39**)

A solution of PhCO(4-C_6H_4F) (0.200 g, 1.00 mmol in 10 mL toluene) was added by cannula to a solution of **20** (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After 24 h all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL). After evaporation of solvent the title compounds **39** are obtained. Yield: 0.605 g (82 %). Mp 130 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 6.65-7.63 (m, 15H, Ar-*H*), 5.88 (s, 1H, C*H*), 4.75 (s, 1H, γ-C*H*), 3.63 (sept, 2H, C*H*(CH$_3$)$_2$), 3.11 (sept, 2H, C*H*(CH$_3$)$_2$), 1.55 (s, 6H, C*H$_3$*), 1.20 (d, 3H, CH(C*H$_3$*)$_2$), 1.18 (d, 3H, CH(C*H$_3$*)$_2$), 1.13 (d, 3H, CH(C*H$_3$*)$_2$), 1.12 (d, 3H, CH(C*H$_3$*)$_2$), 1.11 (d, 3H, CH(C*H$_3$*)$_2$), 1.10 (d, 3H, CH(C*H$_3$*)$_2$), 1.08 (d, 3H, CH(C*H$_3$*)$_2$), 1.07 (d, 3H, CH(C*H$_3$*)$_2$). ^{19}F NMR (188.29 MHz, C_6D_6): δ −112.3 (m, 1F, *p*-F). ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -212 ppm. EI-MS (70 eV): *m/z* (%): 737 (90) [M]$^+$, 652 (100) [M-C_6H_4F]$^+$. Anal. calcd for $C_{42}H_{51}FN_2$OSn (738.30): C 68.39, H 6.97, N 3.80; Found: C 68.75, H 7.16, N 3.62.

11.4.39. Synthesis of LSnOCH$_2C_6F_5$ (**40**)

A solution of C_6F_5CHO (0.196 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **20** (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After 24 h all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL) and concentrated to about 15 mL and stored in a -30 °C freezer. After four days yellow crystals of **40** are formed. Yield: 0.600 g (82 %). Mp 138 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 6.95-7.13 (m, 6H, Ar-*H*), 4.80 (s, 1H, γ-C*H*), 4. 67 (t, ^4J(F-H) = 4.18 Hz, 2H, C*H$_2$*), 3.57 (sept, 2H, C*H*(CH$_3$)$_2$), 3.13 (sept, 2H, C*H*(CH$_3$)$_2$), 1.58 (s, 6H, C*H$_3$*), 1.31 (d, 6H, CH(C*H$_3$*)$_2$), 1.24 (d, 6H, CH(C*H$_3$*)$_2$), 1.20 (d, 6H, CH(C*H$_3$*)$_2$), 1.09 (d, 6H, CH(C*H$_3$*)$_2$). ^{19}F NMR (188.29 MHz, C_6D_6): δ −143.9 (dd, 2F, *o*-F), −158.95 (t, 2F, *p*-F), −163.95 (td, 2F, *m*-F). ^{119}Sn{^{1}H} NMR (186.46 MHz): δ -262 ppm. EI-MS (70 eV): *m/z* (%): 537 (100) [M-OCH$_2C_6F_5$]$^+$, 198 (100) [OCH$_2C_6F_5$]$^+$.

11.4.40. Synthesis of (CH*t*BuN)$_2$CH$_2$ (**41**)

1,3-Di-*tert*-butylimidazol-2-ylidene (0.360 g, 2.0 mmol) and NH$_3$BH$_3$ (0.060 g, 2.0 mmol) were dissolved in toluene (30 mL) at room temperature. The reaction mixture was stirred overnight, then the solvent was removed *in vacuo* and the residue was extracted with *n*-hexane (30 mL). Yield: 0.630 g (95%). ^{1}H NMR (200 MHz, C_6D_6): δ 5.48 (s, 2H, C-*H*), 4.24 (s, 2H, C*H$_2$*), 1.01 (s, 18H, C(C*H$_3$*)$_3$) ppm.

11.4.41. Synthesis of LGeNH$_2$ (**42**)

Dry ammonia gas was added to a red solution of **19** (0.490 g, 1 mmol) in toluene (20 mL) at room temperature. The reaction mixture became orange. Futher 5 min the ammonia gas was bubbled through the solution. After that the solvent was removed *in vacuo* and the residue was extracted with *n*-hexane. The solution was reduced to half of the volume. Storage of the solution at −30 °C for one day yielded yellow crystals of **42** suitable for a

single crystal X-ray diffraction experiment.. Yield: 0.455 g (95%). m.p. 162 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.12-7.18 (m, 6H, Ar-*H*), 4.79 (s, 1H, γ-C*H*), 3.54 (sept, 2H, C*H*(CH$_3$)$_2$), 3.47 (sept, 2H, C*H*(CH$_3$)$_2$), 1.60 (s, 6H, C*H*$_3$), 1.35 (d, 6H, CH(C*H*$_3$)$_2$), 1.28 (d, 6H, CH(C*H*$_3$)$_2$), 1.24 (d, 6H, CH(C*H*$_3$)$_2$), 1.14 (d, 6H, CH(C*H*$_3$)$_2$) ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 3431 vw, 3333 vw (N-H) cm $^{-1}$. EI-MS (70 eV): *m/z* (%): 507 (100) [M]$^+$. Anal. calcd for $C_{29}H_{43}GeN_3$ (507.27): C 68.79, H 8.56, N 8.30; Found: C 69.25, H 8.82, N 7.66.

11.4.42. Synthesis of LGeNHNH$_2$ (**43**)

NH$_2$NH$_2$ (1 mL, 1 M in THF) was added to a yellow solution of **19** (0.490 g, 1 mmol) in toluene (20 mL) at 0 °C. Then the reaction mixture was allowed to come to room temperature. After that the reaction mixture was stirred for additional 30 min. All the volatiles were removed *in vacuo* and the residue was extracted with *n*-hexane (30 mL). The solution was reduced to half of the volume. Storage of the solution at −32 °C in a freezer for two days yielded **43** as colorless crystals suitable for single crystal X-ray diffraction studies. Yield: 0.40 g (85%); Mp 134 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 7.10-7.17 (m, 6H, Ar-*H*), 4.71 (s, 1H, γ-C*H*), 3.50-3.43 (m, 4H, C*H*(CH$_3$)$_2$), 3.16 (d, 1H, N*H*$_2$), 1.59 (s, 6H, C*H*$_3$), 1.41 (d, 6H, CH(C*H*$_3$)$_2$), 1.33 (d, 6H, CH(C*H*$_3$)$_2$), 1.25 (d, 6H, CH(C*H*$_3$)$_2$), 1.13 (d, 6H, CH(C*H*$_3$)$_2$), 0.87 (t, 1H, N*H*) ppm. EI-MS (70 eV): *m/z* (%): 475 (100) [M-(NHNH$_2$, Me)]$^+$. Anal. calcd for $C_{29}H_{44}GeN_4$ (522.28): C 66.81, H 8.51, N 10.75; Found: C 66.73, H 8.97, N 9.70.

11.4.43. Synthesis of LGeOPh (**44**)

A 10 mL toluene solution of phenol (0.095 g, 1 mmol) was added to a solution of **19** (0.490 g, 1 mmol) in toluene (20 mL) under stirring at room temperature and the color of the solution changed immediately from red to colorless. After 30 min all the volatiles were removed *in vacuo* and the residue extracted with *n*-hexane (30 mL) and concentrated to give colorless crystals of **44** after two days, which are suitable for X-ray structural analysis. Yield: 0.475 g (82%); Mp 203 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 6.63-7.13 (m, 11H, Ar-*H*), 4.98 (s, 1H, γ-C*H*), 3.77 (sept, 2H, C*H*(CH$_3$)$_2$), 3.27 (sept, 2H, C*H*(CH$_3$)$_2$), 1.60 (s, 6H, C*H*$_3$), 1.28 (d, 6H, CH(C*H*$_3$)$_2$), 1.18 (d, 6H, CH(C*H*$_3$)$_2$), 1.10 (d, 6H, CH(C*H*$_3$)$_2$), 1.06 (d, 6H, CH(C*H*$_3$)$_2$) ppm. EI-MS (70 eV): *m/z* (%): 491 (100) [M-OPh]$^+$. Anal. calcd for $C_{35}H_{46}GeN_2O$ (583.39): C 72.06, H 7.95, N 4.80; Found: C 70.18, H 7.91, N 4.59.

11.4.44. Synthesis of LGeOC$_6$F$_5$ (**45**)

A 10 mL toluene solution of C$_6$F$_5$OH (0.190 g, 1 mmol) was added to a solution of **19** (0.490 g, 1 mmol) in toluene (20 mL) under stirring at room temperature and the color of the solution changed immediately from red to colorless. After 30 min all the volatiles were removed *in vacuo* and the residue extracted with *n*-hexane (30 mL) and concentrated to give colorless crystals of **45** after four days, which are suitable for X-ray structural analysis. Yield: 0.540 g (80%); Mp 155 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 6.99-7.10 (m, 6H, Ar-*H*), 5.10 (s, 1H, γ-C*H*), 3.48 (sept, 2H, C*H*(CH$_3$)$_2$), 3.05 (sept, 2H, C*H*(CH$_3$)$_2$), 1.55 (s, 6H, C*H*$_3$), 1.18 (d, 6H, CH(C*H*$_3$)$_2$), 1.11 (d, 6H, CH(C*H*$_3$)$_2$), 1.03 (d, 6H, CH(C*H*$_3$)$_2$), 0.88 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{19}F{^{1}H} NMR (188.31 MHz, C_6D_6): δ −158.8 (d, 6F, *o-F*), −166.9 (t, 6F, *m-F*), −175.2 (t, 3F, *p-F*). EI-MS (70 eV): *m/z* (%): 673 (100) [M]$^+$. Anal. calcd for $C_{35}H_{41}F_5GeN_2O$ (673.34): C 62.43, H 6.14, N 4.16; Found: C 62.24, H 6.05, N 4.16.

11.4.45. Synthesis of LGeOC(O)Ph (**46**)

A 10 mL toluene solution of PhCO$_2$H (0.122 g, 1 mmol) was added to a solution of **19** (0.490 g, 1 mmol) in toluene (20 mL) under stirring at room temperature and the color of the solution changed immediately from red to colorless. After 30 min all the volatiles were removed *in vacuo* and the residue extracted with *n*-hexane (30 mL) and concentrated to give colorless crystals of **46** after one day, which are suitable for X-ray structural analysis. Yield: 0.520 g(85%); Mp 167 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 6.99-8.44 (m, 11H, Ar-*H*), 5.16 (s, 1H, γ-C*H*), 3.61 (sept, 2H, C*H*(CH$_3$)$_2$), 3.17 (sept, 2H, C*H*(CH$_3$)$_2$), 1.61 (s, 6H, C*H*$_3$), 1.21 (d, 6H, CH(C*H*$_3$)$_2$), 1.13 (d, 6H, CH(C*H*$_3$)$_2$), 1.07 (d, 6H, CH(C*H*$_3$)$_2$), 1.05 (d, 6H, CH(C*H*$_3$)$_2$) ppm. EI-MS (70 eV): *m/z* (%): 612 (100) [M]$^+$. Anal. calcd for $C_{36}H_{46}GeN_2O_2$ (611.40): C 70.72, H 7.58, N 4.55; Found: C 70.11, H 7.52, N 4.55.

11.4.46. Synthesis of L´´GePPh₂ (47)

To a cooled (-60 oC) solution of **19** (1.40g, 2.86 mmol) in *n*-hexane (30 mL) was added a solution of Ph₂PCl (0.64 g, 2.90 mmol) in *n*-hexane (20 mL). The solution turned yellow and a yellow precipitate started forming while the mixture was brought to rt. After stirring the mixture overnight it was filtered and the precipitate was dried under vacuum. Keeping the filtrate at room temperature for one day also afforded orange yellow crystals of **47** along with some powder (1.82 g. Yield 1.82 g (90%). Mp 174 °C. ^{1}H NMR (500 MHz, C₆D₆) δ 1.09 (d, 3H, CH(CH_3)₂), 1.15 (d, 3H, CH(CH_3)₂), 1.26–1.32 (3d, 9H, CH(CH_3)₂), 1.39 (s, 3H, CH_3), 1.42 (d, 3H, CH(CH_3)₂), 1.47 (d, 3H, CH(CH_3)₂), 1.52 (d, 3H, CH(CH_3)₂), 3.14 (q, 2H, CH_2), 3.23 (m, 1H, CH(CH₃)₂), 3.39 (m, 1H, CH(CH₃)₂), 3.93 (m, 1H, CH(CH₃)₂), 4.03 (m, 1H, CH(CH₃)₂), 4.92 (d, 1H, CH), 6.88 – 8.05 (16H, Ar-H) ppm. ^{31}P{^{1}H} NMR (121.50 MHz, C₆D₆) δ -13.47 ppm. Anal. calcd for C₄₁H₅₀ClGeN₂P(709.84): C 69.37, H 7.10, N 3.95; Found: C 69.45, H 7.08, N, 3.34.

11.4.47. Synthesis of L´´GeB(C₆F₅)₃ (48)

A solution of B(C₆F₅)₃ (0.51 g, 1.0 mmol) in toluene (10 mL) was added to a solution of **19** (0.49 g, 1.0 mmol) in toluene (10 mL) at room temperature. The brown-red color of the solution of **19** vanished slowly and pale yellow crystals of **48** were formed after two days at room temperature. Yield: 0.78 g (78%). Mp 265 °C. ^{1}H NMR (500 MHz, THF-D₈): δ 7.37-7.44 (m, 6H, Ar-H), 6.50 (s, 1H, γ-CH), 2.73 (sept, 2H, CH(CH_3)₂), 2.61 (sept, 2H, CH(CH_3)₂), 2.47 (s, 2H, CH_2), 1.84 (s, 3H, CH_3), 1.39 (d, 6H, CH(CH₃)₂), 1.25 (d, 6H, CH(CH₃)₂), 1.19 (d, 6H, CH(CH₃)₂), 1.15 (d, 6H, CH(CH₃)₂) ppm. ^{11}B{^{1}H} NMR (96.29 MHz, THF-D₈): δ −14.82. ^{19}F{^{1}H} NMR (188.31 MHz, THF-D₈): δ −131.60 (d, 6F, *o*-F), −163.40 (t, 6F, *m*-F), −167.28 (t, 3F, *p*-F). EI-MS (70 eV): *m/z* (%): 475 (100) [M-(B(C₆F₅)₃, Me)] $^+$. Anal. calcd for C₄₇H₄₀BF₁₅GeN₂ (1001.26): C 56.38, H 4.03, N 2.80; Found: C 56.27, H 3.82, N 2.68.

11.4.48. Synthesis of L´´´GeB(C₆F₅)₃ (49)

A solution of 1,3-di-*tert*-butylimidazol-2-ylidene (0.18 g, 1.0 mmol) in toluene (10 mL) was added to a solution of **48** (0.49 g, 1.0 mmol) in toluene (10 mL) at room temperature. Immediately the reaction mixture turns to red in color. After 10 min the solvent was removed *in vacuo* and the title compound **49** was isolated as a red oil. ^{1}H NMR (500 MHz, C₆D₆): δ 7.32 (s, 1H, NCH), 6.99-7.20 (m, 6H, Ar-H), 6.33 (s, 2H, NCH), 5.87 (s, 1H, γ-CH), 3.86 (sept, 2H, CH(CH_3)₂), 3.63(s, 1H, CH), 3.60 (sept, 2H, CH(CH_3)₂), 2.96 (s, 1H, CH), 2.45 (s, 2H, CH_2), 1.70 (d, 6H, CH(CH₃)₂), 1.35 (d, 12H, CH(CH₃)₂), 1.32 (d, 6H, CH(CH₃)₂), 0.75 (s, 18H, C(CH_3)₃) ppm. ^{11}B{^{1}H} NMR (96.29 MHz, C₆D₆): δ −13.66. ^{19}F{^{1}H} NMR (188.31 MHz, C₆D₆): δ −130.65 (br, 6F, *o*-F), −163.77 (t, 6F, *m*-F), −167.32 (br, 3F, *p*-F). From analytical data we do not obtain satisfactory results.

11.4.49. Synthesis of L´Si(H)NH₂ (51)

Dry ammonia gas was added to a yellow solution of **50** (0.45 g, 1 mmol) in toluene (20 mL) at room temperature. The reaction mixture became colorless. Then the ammonia gas was bubbled through the solution for additional 15 min. After that the solvent was removed *in vacuo* and the residue was extracted with *n*-hexane (30 mL). The solution was reduced to half of the volume. Storage of the solution at −32 °C in a freezer for two days yielded colorless crystals of **51**, which are suitable for single crystal X-ray diffraction studies. Yield: 0.41 g (90%); Mp 223 °C. ^{1}H NMR (500 MHz, C₆D₆): δ = 7.02-7.22 (m, 6H, Ar-H), 5.31 (s, 1H, γ-CH), 4.97 (t, 1H, Si-H), 3.93 (s, 1H, CH_2), 3.62 (sept, 2H, CH(CH₃)₂), 3.59 (sept, 2H, CH(CH₃)₂), 3.35 (s, 1H, CH_2), 1.49 (s, 3H, CH_3), 1.40 (d, 6H, CH(CH_3)₂), 1.22-1.18 (m, 18H, CH(CH_3)₂), 0.35 (br, 2H, NH_2) ppm. IR (Nujol, KBr): $\tilde{v}$ = 3477, and 3382 (N-H), and 2633 (Si-H) cm $^{-1}$. EI-MS (70 eV): *m/z* (%): 446 (100) [M-Me]$^+$. Anal. calcd for C₂₉H₄₃N₃Si (461.76): C 75.43, H 9.39, N 9.10; Found: C 75.10, H 9.41, N 9.14.

11.4.50. Synthesis of L´Si(H)NHNH₂ (52)

NH₂NH₂ (1 mL, 1 M in THF) was added to a yellow solution of **50** (0.45 g, 1 mmol) in toluene (20 mL) at 0 °C. Then the reaction mixture was allowed to come to room temperature. After that the reaction mixture was stirred for additional 30 min. All the volatiles were removed *in vacuo* and the residue was extracted with *n*-hexane (30 mL). The solution was reduced to half of the volume. Storage of the solution at −32 °C in a freezer for two days

yielded **52** as colorless crystals suitable for single crystal X-ray diffraction studies. Yield: 0.40 g (85%). Mp 177 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.03-7.19 (m, 6H, Ar-*H*), 5.30 (s, 1H, γ-C*H*), 5.05 (d, 1H, Si-*H*), 3.94 (s, 1H, C*H*$_2$), 3.65 (sept, 2H, C*H*(CH$_3$)$_2$), 3.55 (sept, 2H, C*H*(CH$_3$)$_2$), 3.30 (s, 1H, C*H*$_2$), 2.41 (br, 1H, N*H*), 1.85 (d, 2H, N*H*$_2$), 1.47 (s, 3H, C*H*$_3$), 1.39-1.17 (m, 24H, CH(C*H*$_3$)$_2$) ppm. ^{29}Si NMR (99.35 Hz, C$_6$D$_6$): δ -43.63(dd, ^2J(Si-H) = 260.5 Hz, ^3J(Si-H) = 12.73 Hz) ppm. EI-MS (70 eV): *m/z* (%): 461 (100) [M-Me]$^+$. Anal. calcd for C$_{29}$H$_{44}$N$_4$Si (476.33): C 73.06, H 9.30, N 11.75; Found: C 72.47, H 9.14, N 11.65.

11.4.51. Synthesis of L´Si(H)NHNHMe (**53**)

MeNHNH$_2$ (0.05 g, 1 mmol) was added to a yellow solution of **50** (0.45 g, 1 mmol) in toluene (20 mL) at room temperature. After that the reaction mixture was stirred for additional 30 min. All the volatiles were removed *in vacuo* and the residue was extracted with *n*-hexane (30 mL). Yield: 0.39 g (80%). Mp 73 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.04-7.22 (m, 6H, Ar-*H*), 5.34 (d, 1H, Si-*H*), 5.33 (s, 1H, γ-C*H*), 3.99 (s, 1H, C*H*$_2$), 3.71 (sept, 1H, C*H*(CH$_3$)$_2$), 3.65 (sept, 1H, C*H*(CH$_3$)$_2$), 3.59 (sept, 1H, C*H*(CH$_3$)$_2$), 3.50 (sept, 1H, C*H*(CH$_3$)$_2$), 3.35 (s, 1H, C*H*$_2$), 2.25 (d, 1H, SiN*H*), 1.73 (q, 1H, N*H*CH$_3$), 1.66 (br, 3H, NC*H*$_3$), 1.49 (s, 3H, C*H*$_3$), 1.42 (d, 3H, CH(C*H*$_3$)$_2$), 1.38 (d, 3H, CH(C*H*$_3$)$_2$), 1.37 (d, 3H, CH(C*H*$_3$)$_2$), 1.13-1.31 (m, 15H, CH(C*H*$_3$)$_2$) ppm. ^{29}Si NMR (99.35 Hz, C$_6$D$_6$): δ -43.64(ddd, ^2J(Si-H) = 263.8 Hz, ^3J(Si-H) = 13.17 Hz, ^4J(Si-H) = 2.34 Hz) ppm. EI-MS (70 eV): *m/z* (%): 475 (100) [M-Me]$^+$. Anal. calcd for C$_{30}$H$_{46}$N$_4$Si (490.35): C 73.42, H 9.45, N 11.42; Found: C 73.74, H 9.34, N 10.48.

11.4.52. Synthesis of **54**

A solution of Ph$_2$C=NNH$_2$ (0.20 g, 1 mmol) in toluene (5 mL) was added to a yellow solution of **50** (0.45 g, 1 mmol) in toluene (20 mL) at room temperature. After that the reaction mixture was stirred for additional 1 h. All the volatiles were removed *in vacuo* and the residue was extracted with *n*-hexane (30 mL). Suitable crystals for X-ray structural analysis are obtained from a hot saturated *n*-hexane solution of **54** after keeping the solution overnight at room temperature. Yield: 0.41 g (90%). Mp 192 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.00-7.17 (m, 6H, Ar-*H*), 6.04 (d, 1H, C*H*), 5.67 (m, 1H, C*H*), 5.56 (s, 1H, γ-C*H*), 5.52 (m, 1H, C*H*), 5.41(m, 1H, C*H*), 4.02 (s, 1H, C*H*$_2$), 3.88 (sept, 1H, C*H*(CH$_3$)$_2$), 3.74 (sept, 1H, C*H*(CH$_3$)$_2$), 3.57 (sept, 2H, C*H*(CH$_3$)$_2$), 3.43 (s, 1H, C*H*$_2$), 3.08 (m, 1H, SiC*H*), 2.97 (s, 2H, N*H*$_2$), 1.54 (s, 3H, C*H*$_3$), 1.42 (d, 3H, CH(C*H*$_3$)$_2$), 1.40 (d, 3H, CH(C*H*$_3$)$_2$), 1.38 (d, 3H, CH(C*H*$_3$)$_2$), 1.31 (d, 3H, CH(C*H*$_3$)$_2$), 1.30 (d, 3H, CH(C*H*$_3$)$_2$), 1.28 (d, 3H, CH(C*H*$_3$)$_2$), 1.23 (d, 3H, CH(C*H*$_3$)$_2$), 1.20 (d, 3H, CH(C*H*$_3$)$_2$) ppm. ^{29}Si NMR (99.35 Hz, C$_6$D$_6$): δ -19.97(d, ^3J(Si-H) = 20.4Hz) ppm. EI-MS (70 eV): *m/z* (%): 625 (100) [M-Me]$^+$. Anal. calcd for C$_{42}$H$_{52}$N$_4$Si (640.97): C 78.70, H 8.18, N 8.74; Found: C 77.18, H 8.01, N 8.44.

11.4.53. Synthesis of LGeNHNCHCO$_2$Et (**55**)

A solution of ethyl diazoacetate (0.27 g, 2.4 mmol) in toluene (10 mL) was slowly added drop by drop to a stirred solution of **5** (0.98 g, 2 mmol) in toluene (20 mL) at room temperature. During this time the color of the reaction mixture changed from red to yellowish. The reaction mixture was stirred for additional 30 min. After removal of all the volatiles, the residue was extracted with toluene (20 mL) and concentrated to about 10 mL and stored at room temperature. Yellow crystals of **55** are formed after two days. Yield: 1.15 g (95 %). Mp 160 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.25 (br, 1H, N*H*), 7.05-7.15 (m, 6H, Ar-*H*), 6.62 (s, 1H, C*H*), 4.91 (s, 1H, γ-C*H*), 4.11 (q, 2H, C*H*$_2$CH$_3$), 3.27 (sept, 2H, C*H*(CH$_3$)$_2$), 3.16 (sept, 2H, C*H*(CH$_3$)$_2$), 1.56 (s, 6H, C*H*$_3$), 1.27 (d, 6H, CH(C*H*$_3$)$_2$), 1.13 (d, 12H, CH(C*H*$_3$)$_2$), 1.07 (d, 6H, CH(C*H*$_3$)$_2$), 1.03 (t, 3H, CH$_2$C*H*$_3$) ppm. IR (Nujol, KBr, cm^{-1}): $\widetilde{\nu}$ = 3188 (N-H), 2726 (C-H), 1684 (C=O). EI-MS (70 eV): *m/z* (%): 491(100) [M-NHNCHCO$_2$Et]$^+$. Anal. calcd for C$_{33}$H$_{48}$GeN$_4$O$_2$ (605.40): C 65.47, H 7.99, N 9.25; Found: C 65.34, H 8.53, N 9.37.

11.4.54. Synthesis of LGeNHNCHSiMe$_3$ (**56**)

In a dry box an excess solution of trimethylsilyl diazomethane (1.5 mL, ~2 M, in *n*-hexane) was slowly added drop by drop to a schlenk flask containing **5 (**0.98 g, 2 mmol) in 10 mL *n*-hexane. Then the flask was kept at room temperature for one day and after that the yellow crystals of **56** are formed nearly quantitatively, which are suitable for X-ray structural analysis. Yield: 1.10 g (90 %). Mp 153 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.02-7.15

(m, 6H, Ar-*H*), 6.44 (d, 1H, C*H*), 6.37 (d, 1H, N*H*), 4.96 (s, 1H, γ-C*H*), 3.47 (sept, 2H, C*H*(CH₃)₂), 3.30 (sept, 2H, C*H*(CH₃)₂), 1.63 (s, 6H, C*H₃*), 1.36 (d, 6H, CH(C*H₃*)₂), 1.25 (d, 12H, CH(C*H₃*)₂), 1.15 (d, 6H, CH(C*H₃*)₂), 1.14 (d, 6H, CH(C*H₃*)₂), 0.25 (s, 9H, Si(C*H₃*)₃) ppm. ^{29}Si{^{1}H} NMR (125.77 Hz, C₆D₆): δ 6.28 (*Si*(CH₃)₃) ppm. EI-MS (70 eV): *m/z* (%): 580 (100) [M-Me]⁺. Anal. calcd for C₃₃H₅₂GeN₄Si (605.52): C 65.46, H 8.66, N 9.25; Found: C 65.27, H 9.12, N 8.50.

11.4.55. Synthesis of L´Ge(Me)(NHNCHSiMe₃) (**57**)
A solution of trimethylsilyl diazomethane (0.5 mL, 2 M, in *n*-hexane) was slowly added drop by drop to a Schlenk flask containing LGeMe **(**0.50 g, 1 mmol) in 15 mL *n*-hexane. The solution slowly changed the color from red to yellow. After constant stirring overnight at ambient temperature all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (15 mL) and after removal of all the volatiles from the extract compound **57** was obtained as a yellow solid. Yield: 0.45 g (72 %). Mp 103 °C. ^{1}H NMR (500 MHz, C₆D₆): δ 7.02-7.14 (m, 6H, Ar-*H*), 6.76 (s, 1H, N*H*), 5.78 (s, 1H, γ-C*H*), 5.26 (s, 1H, C*H*), 3.83 (s, 1H, C*H₂*), 3.71 (sept, 1H, C*H*(CH₃)₂), 3.58 (sept, 2H, C*H*(CH₃)₂), 3.51 (sept, 1H, C*H*(CH₃)₂), 3.21 (s, 1H, C*H₂*), 1.54 (s, 3H, C*H₃*), 1.41 (d, 3H, CH(C*H₃*)₂), 1.39 (d, 3H, CH(C*H₃*)₂), 1.22-1-27 (m, 12H, CH(C*H₃*)₂), 1.16 (d, 3H, CH(C*H₃*)₂), 1.05 (d, 3H, CH(C*H₃*)₂), 0.17 (s, 9H, Si(C*H₃*)₃) ppm. ^{29}Si{^{1}H} NMR (125.77 Hz, C₆D₆): δ -8.76 (*Si*(CH₃)₃) ppm. EI-MS (70 eV): *m/z* (%): 605 (25) [M-Me]⁺, 491 (100) [M-Me, NHNCHTMS]⁺. Anal. calcd for C₃₄H₅₄GeN₄Si (620.33): C 65.91, H 8.79; Found: C 65.81, H 9.14.

11.4.56. Synthesis of LGeC(N₂)SiMe₃ (**58**)
A solution of N₂CHSiMe₃ (0.7 mL, 2 M, in *n*-hexane) was added to a solution of **19** (0.49 g, 1.0 mmol) in *n*-hexane (10 mL) at room temperature. Then the flask was kept at room temperature for three days and after that yellow crystals of **58** were obtained, which are suitable for X-ray structural analysis. Yield: 0.53 g (88%). Mp 244 °C. ^{1}H NMR (500 MHz, C₆D₆): δ 7.09-7.17 (m, 6H, Ar-*H*), 4.51 (s, 1H, γ-CH), 3.63 (sept, 2H, CH(C*H₃*)₂), 3.60 (sept, 2H, CH(C*H₃*)₂), 1.62 (s, 6H, C*H₃*), 1.58 (d, 6H, C*H*(CH₃)₂), 1.43 (d, 6H, C*H*(CH₃)₂), 1.25 (d, 6H, C*H*(CH₃)₂), 1.13 (d, 6H, C*H*(CH₃)₂), −0.07 (Si(C*H₃*)₃) ppm. ^{29}Si{^{1}H} NMR (99.35 Hz, C₆D₆): δ -2.43 (*Si*(CH₃)₃) ppm EI-MS (70 eV): *m/z* (%): 561 (100) [M-*i*Pr]⁺. Anal. calcd for C₃₃H₅₀GeN₄Si (603.50): C 65.68, H 8.35, N 9.28; Found: C 64.96, H 8.62, N 8.87.

11.4.57. Synthesis of LGeN(NC)SiMe₃ (**59**)
After keeping the supernatant solution of **58** for about 3 months at room temperature we observed the conversion of **58** to **59**. Mp 210 °C. ^{1}H NMR (500 MHz, C₆D₆): δ 7.06-7.18 (m, 6H, Ar-*H*), 4.75 (s, 1H, γ-CH), 3.89 (sept, 2H, CH(C*H₃*)₂), 3.39 (sept, 2H, CH(C*H₃*)₂), 1.66 (s, 6H, C*H₃*), 1.57 (d, 6H, C*H*(CH₃)₂), 1.37 (d, 6H, C*H*(CH₃)₂), 1.26 (d, 6H, C*H*(CH₃)₂), 1.07 (d, 6H, C*H*(CH₃)₂), −0.04 (Si(C*H₃*)₃) ppm. ^{29}Si{^{1}H} NMR (99.35 Hz, C₆D₆): δ 12.50 (*Si*(CH₃)₃) ppm EI-MS (70 eV): *m/z* (%): 604 (100) [M]⁺.

11.4.58. Synthesis of LSnNCNSiMe₃ (**60**)
A solution of lithiotrimethylsilyldiazomethane (4.0 mmol) prepared from a solution of trimethylsilyldiazomethane (2.0 mL, 2 M in hexane) and *n*-BuLi (2.5 mL, 1.6 M in hexane) in THF (15 mL) was added dropwise to the solution of LSnCl (2.20 g, 4.0 mmol) in THF (35 mL) at -78 °C, and the solution was allowed to warmed up room temperature and stirred for another 30 min. Solvents were removed *in vacuo*, and the residue was dissolved in *n*-hexane. The mixture was filtered, the solvent was partially removed, and **60** were obtained as a crystalline solid after keeping two days at -30 °C, which was also suitable for X-ray structural analysis. Yield: 2.16 g (60 %). Mp 177 °C. ^{1}H NMR (500 MHz, C₆D₆): δ 7.02-7.15 (m, 6H, Ar-*H*), 4.96 (s, 1H, γ-C*H*), 3.82 (sept, 2H, C*H*(CH₃)₂), 3.14 (sept, 2H, C*H*(CH₃)₂), 1.61 (s, 6H, C*H₃*), 1.51 (d, 6H, CH(C*H₃*)₂), 1.32 (d, 12H, CH(C*H₃*)₂), 1.18 (d, 6H, CH(C*H₃*)₂), 1.07 (d, 6H, CH(C*H₃*)₂), 0.27 (s, 9H, Si(C*H₃*)₃) ppm. ^{29}Si{^{1}H} NMR (125.77 Hz, C₆D₆): δ -6.05 (*Si*(CH₃)₃) ppm. ^{119}Sn{^{1}H} NMR (186.46 MHz, C₆D₆): δ -321.26 ppm. EI-MS (70 eV): *m/z* (%): 649 (100) [M]⁺. Anal. calcd for C₃₃H₅₀N₄SiSn (649.57): C 61.02, H 7.76, N 8.63; Found: C 61.42, H 8.04, N 8.42.

11.4.59. Synthesis of LGeNMe$_2$ (**61**)

A solution of LGeCl (0.498 g, 1.0 mmol) in diethyl ether (20 mL) was added dropwise to a stirred suspension of LiNMe$_2$ (0.051 g, 1.0 mmol) in diethyl ether (10 mL) at -78 $^{\circ}$C. The reaction mixture was warmed to room temperature and was stirred for another 12 h. The precipitate was filtered, and the solvent was partially reduced (ca. 20 mL). Storage of the remaining solution in a -32 $^{\circ}$C freezer for overnight afforded colorless crystals of **61** suitable for X-ray diffraction analyses. Yield: 0.448 g (84 %). Mp 225 $^{\circ}$C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.12-7.18 (m, 6H, Ar-*H*), 4.82 (s, 1H, γ-C*H*), 3.43 (sept, 2H, C*H*(CH$_3$)$_2$), 3.37 (sept, 2H, C*H*(CH$_3$)$_2$), 2.82 (s, 6H, N(C*H*$_3$)$_2$), 1.59 (s, 6H, C*H*$_3$), 1.33 (d, 6H, CH(C*H*$_3$)$_2$), 1.29 (d, 6H, CH(C*H*$_3$)$_2$), 1.26 (d, 6H, CH(C*H*$_3$)$_2$), 1.13 (d, 6H, CH(C*H*$_3$)$_2$) ppm. EI-MS (70 eV): *m/z* (%): 491 (100) [M-NMe$_2$]$^+$. Anal. calcd for C$_{31}$H$_{47}$GeN$_3$ (534.36): C 69.68, H 8.87, N 7.86; Found: C 69.82, H 9.54, N 7.80.

11.4.60. Synthesis of LGe(S)NMe$_2$ (**62**)

A solution of **61** (0.530 g, 1.00 mmol) in toluene (30 mL) was slowly added to a suspension of elemental sulfur (0.032 g, 1.00 mmol) in toluene (15 mL) by cannula at room temperature. After 0.5 h under constant stirring at ambient temperature the red solution turned slightly yellow. All volatiles were removed *in vacuo*, and the remaining residue was extracted with toluene (15 mL). The solvent was removed *in vacuo* to yield **62** as a slight yellow powder. Yield: 0.340 g (60 %). Mp 230 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 7.02-7.16 (m, 6H, Ar-*H*), 4.70 (s, 1H, γ-C*H*), 3.47 (sept, 2H, C*H*(CH$_3$)$_2$), 3.15 (sept, 2H, C*H*(CH$_3$)$_2$), 2.89-2.73 (br, 6H, N(C*H*$_3$)$_2$), 1.60 (d, 6H, CH(C*H*$_3$)$_2$), 1.44 (s, 6H, C*H*$_3$), 1.29 (d, 6H, CH(C*H*$_3$)$_2$), 1.18 (d, 6H, CH(C*H*$_3$)$_2$), 1.07 (d, 6H, CH(C*H*$_3$)$_2$) ppm. EI-MS (70 eV): *m/z* (%): 523 (100) [M-NMe$_2$]$^+$.

11.4.61. Synthesis of LGeOTf (**63**)

A solution of LGeCl (0.520 g, 1mmol) in toluene (15 mL) was added drop by drop to a stirred suspension of AgOSO$_2$CF$_3$ (0.26 g, 1 mmol) in toluene (10 mL) at room remperature. The solution was stirred for additional 2 h. After filtration the filtrate was concentrated to about 10 mL and stored in a -30 $^{\circ}$C freezer. Colorless crystals of **63** were formed after two days. Yield: 0.575 g (90 %). Mp 216 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.06-7.15 (m, 6H, Ar-*H*), 5.58 (s, 1H, γ-C*H*), 3.27 (sept, 4H, C*H*(CH$_3$)$_2$), 1.68 (s, 6H, C*H*$_3$), 1.19 (d, 12H, CH(C*H*$_3$)$_2$), 1.15 (d, 12H, CH(C*H*$_3$)$_2$) ppm. ^{19}F {^{1}H} NMR (188.28 MHz, C$_6$D$_6$): δ -76.5 ppm. EI-MS: *m/z* (%) 640 (100) [M]$^+$. Anal. calcd for C$_{30}$H$_{41}$F$_3$GeN$_2$O$_3$S (640.20): C 56.36, H 6.46, N 4.38, S 5.02; Found C 56.55, H 6.93, N 4.35, S 5.02.

11.4.62. Synthesis of LSnMe (**64**)

A solution of MeLi in diethyl ether (0.63 mL, 1.6 M) was added drop by drop to a stirred solution of LSnCl (0.570 g, 1 mmol) in diethyl ether (25 mL) at -78 $^{\circ}$C. The reaction mixture was warmed to room temperature and was stirred for an additional 3 h. After removal of all the volatiles, the residue was extracted with *n*-hexane (20 mL) and concentrated to about 10 mL and stored in a -30 $^{\circ}$C freezer. Yellow crystals of **64** suitable for X-ray diffraction analysis are formed after two days. Yield: 0.485 g (88 %). Mp 170 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.10-7.15 (m, 6H, Ar-*H*), 4.86 (s, 1H, γ-C*H*), 3.59 (sept, 2H, C*H*(CH$_3$)$_2$), 3.37 (sept, 2H, C*H*(CH$_3$)$_2$), 1.60 (s, 6H, C*H*$_3$), 1.35 (d, 6H, CH(C*H*$_3$)$_2$), 1.22 (d, 6H, CH(C*H*$_3$)$_2$), 1.19 (d, 12H, CH(C*H*$_3$)$_2$), 0.59 (t, 3H, Sn-C*H*$_3$) ppm. ^{119}Sn {^{1}H} NMR (186.50 MHz, C$_6$D$_6$): δ 192.65 ppm. EI-MS: *m/z* (%) 537 (100) [M-Me]$^+$. Anal. calcd for C$_{30}$H$_{44}$N$_2$Sn (552.25): C 65.35, H 8.04, N 5.08; Found C 64.96, H 8.64, N 5.09.

11.4.63. Synthesis of LSnN(SiMe$_3$)$_2$ (**65**)

A solution of LH (0.418 g, 1 mmol) in THF (15 mL) was added drop by drop to a stirred suspension of KN(SiMe$_3$)$_2$ (0.400 g, 2 mmol) in THF (10 mL) at room temperature and stirring was continued overnight. The resulting solution was added drop by drop to a stirred suspension of SnCl$_2$ (0.190 g, 1 mmol) in THF (20 mL) at room temperature under stirring for another 24 h. After removal of all the volatiles, the residue was extracted with *n*-hexane (30 mL) and concentrated to about 5 mL and finally stored in a 0 $^{\circ}$C freezer. Yellow crystals of **65** suitable for X-ray diffraction analysis are formed after one day. Yield: 0.570 g (82 %). Mp 202 $^{\circ}$C. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 6.98-7.21 (m, 6H, Ar-*H*), 5.01 (s, 1H, γ-C*H*), 3.73 (sept, 2H, C*H*(CH$_3$)$_2$), 3.16 (sept, 2H, C*H*(CH$_3$)$_2$), 1.52 (s, 6H, C*H*$_3$), 1.45 (d, 6H, CH(C*H*$_3$)$_2$), 1.22 (q, 12H, CH(C*H*$_3$)$_2$), 1.13 (d, 6H, CH(C*H*$_3$)$_2$), 0.46 (s, 9H, Si(C*H*$_3$)$_3$), 0.24 (s, 9H, Si(C*H*$_3$)$_3$) ppm. ^{29}Si {^{1}H} NMR (99.36 Hz, C$_6$D$_6$): δ 0.61 (*Si*Me$_3$), -4.70 (*Si*Me$_3$)

ppm. ^{119}Sn {^{1}H} NMR (112.00Hz, C$_6$D$_6$): δ -134.54 ppm. EI-MS (70 eV): *m/z* (%): 682 (100) [M-Me]$^+$. Anal. Calcd for C$_{35}$H$_{59}$N$_3$SnSi$_2$(697): C 60.33, H 8.54, N 6.03; Found C 60.20, H 8.49, N 5.88.

11.4.64. Synthesis of LSnNMe$_2$ (**66**)
A solution of LSnCl (0.570 g, 1.0 mmol) in diethyl ether (20 mL) was added dropwise to a stirred suspension of LiNMe$_2$ (0.051 g, 1.0 mmol) in diethyl ether (10 mL) at -78 ^{o}C. The reaction mixture was warmed to room temperature and was stirred for another 12 h. The precipitate was filtered, and the solvent was partially reduced (ca. 20 mL). Keepimg the flask in a -32 ^{o}C freezer for overnight afforded title compound **66**. Yield: 0.533 g (92 %). ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 7.02-7.16 (m, 6H, Ar-*H*), 4.82 (s, 1H, γ-C*H*), 3.45 (sept, 2H, C*H*(CH$_3$)$_2$), 3.37 (sept, 2H, C*H*(CH$_3$)$_2$), 3.00 (s, 6H, N(C*H*$_3$)$_2$), 1.65 (s, 6H, C*H*$_3$), 1.27-1.35 (m, 18H, CH(C*H*$_3$)$_2$), 1.17 (d, 6H, CH(C*H*$_3$)$_2$) ppm.

11.4.65. Synthesis of LSnOCPh(2-Py)(NMe$_2$) (**67**)
A solution of 2-benzol pyridine (0.180 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **66** (0.540 g, 1.00 mmol in toluene 20 mL) at room temperature. After 12 h all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL) and concentrated to about 15 mL and stored in a -30 ^{o}C freezer. Yellow crystals of **67** suitable for X-ray diffraction analysis are formed after four days. Yield: 0.670 g (88 %). Mp 176 °C. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 8.24 (d, 2H, *o*-Ph), 7.60 (d, 1H, *o*-Py), 7.33 (t, 2H, *m*-Ph), 7.03-7.16 (m, 6H, Ar-*H*), 6.83-6.79 (m, 2H, *p*-Ph, *p*-Py), 6.3 (m, 2H, *m*-Py), 4.95 (s, 1H, γ-C*H*), 4.21 (sept, 1H, C*H*(CH$_3$)$_2$), 3.79 (sept, 1H, C*H*(CH$_3$)$_2$), 3.66 (sept, 1H, C*H*(CH$_3$)$_2$), 3.32 (sept, 1H, C*H*(CH$_3$)$_2$), 1.86 (s, 6H, N(C*H*$_3$)$_2$), 1.79 (s, 3H, C*H*$_3$), 1.72 (s, 3H, C*H*$_3$), 1.56 (d, 6H, CH(C*H*$_3$)$_2$), 1.31-1.11 (m, 15H, CH(C*H*$_3$)$_2$), -0.12 (d, 3H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn {^{1}H} NMR (186.50 MHz, C$_6$D$_6$): δ -328 ppm. EI-MS: *m/z* (%) 537 (100) [M-OCPh(2-Py)NMe$_2$] $^+$. Anal. calcd for C$_{43}$H$_{56}$N$_4$OSn (764.35): C 67.63, H 7.39, N 7.34; Found C 67.79, H 7.96, N 7.24.

11.4.66. Synthesis of LSnOCPh(CF$_3$)(NMe$_2$) (**68**)
A solution of 2,2,2-trifluoro acetophenone (0.175 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **66** (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After 12 h all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL). The solvent was removed and compound **68** obtained as a powder. Yield: 0.550 g (73 %). Mp 178 °C. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 7.32 (d, 2H, *o*-Ph), 7.08-7.17 (m, 6H, Ar-*H*), 7.00 (m, 3H, *p*-Ph, *m*-Ph), 4.66 (s, 1H, γ-C*H*), 3.99 (sept, 2H, C*H*(CH$_3$)$_2$), 3.14 (sept, 2H, C*H*(CH$_3$)$_2$), 1.99 (s, 6H, N(C*H*$_3$)$_2$), 1.59 (s, 3H, CH(C*H*$_3$)$_2$), 1.55 (s, 3H, C*H*$_3$), 1.53 (s, 3H, C*H*$_3$), 1.51 (d, 3H, CH(C*H*$_3$)$_2$), 1.12-1.27 (m, 15H, CH(C*H*$_3$)$_2$), 1.14 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn {^{1}H} NMR (186.50 MHz, C$_6$D$_6$): δ -232 ppm. EI-MS: *m/z* (%) 537 (100) [M-OCPh(CF$_3$)NMe$_2$]$^+$. Anal. calcd for C$_{39}$H$_{52}$F$_3$N$_3$OSn (755.31): C 62.08, H 6.95, N 5.57; Found C 61.55, H 6.67, N 5.47.

11.4.67. Synthesis of LSnCCCO$_2$Me (**69**)
A solution of HCCCO$_2$Me (0.085 g, 1.00 mmol in 5 mL toluene) was added drop by drop by cannula to a solution of **66** (0.540 g, 1.00 mmol in toluene 15 mL) at room temperature. After 0.5 h under constant stirring at ambient temperature all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a -30 ^{o}C freezer. After two days yellow crystalline compound of **69** are formed. Yield: 0.545 g (88 %). Mp 124 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.03-7.16 (m, 6H, Ar-*H*), 4.98 (s, 1H, γ-C*H*), 3.88 (sept, 2H, C*H*(CH$_3$)$_2$), 3.29 (s, 3H, CO$_2$C*H*$_3$), 3.23 (sept, 2H, C*H*(CH$_3$)$_2$), 1.58 (s, 6H, C*H*$_3$), 1.47 (d, 6H, CH(C*H*$_3$)$_2$), 1.36 (d, 6H, CH(C*H*$_3$)$_2$), 1.21 (d, 6H, CH(C*H*$_3$)$_2$), 1.08 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn {^{1}H} NMR (111.92 MHz, C$_6$D$_6$): δ -254.91 ppm. EI-MS: *m/z* (%) 620 (85) [M]$^+$, 562 (100) [M-(Me, *i*Pr)]$^+$. Anal. calcd for C$_{33}$H$_{44}$N$_2$O$_2$Sn (620.24): C 63.99, H 7.16, N 4.52; Found C 63.28, H 7.51, N 4.73.

11.4.68. Synthesis of LSnCCCO$_2$Et (**70**)
A solution of HCCCO$_2$Et (0.100 g, 1.00 mmol in 5 mL toluene) was added drop by drop by cannula to a solution of **66** (0.540 g, 1.00 mmol in toluene 15 mL) at room temperature. After 0.5 h under constant stirring at ambient temperature the red solution turned deep-red. All volatiles were removed *in vacuo*, and the remaining

residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a -30 °C freezer. Yellow crystals of **70** suitable for X-ray diffraction analysis are formed after two days. Yield: 0.495 g (78 %). Mp 164 °C. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 7.05-7.19 (m, 6H, Ar-*H*), 4.99 (s, 1H, γ-C*H*), 3.84-4.01 (m, 4H, C*H*(CH$_3$)$_2$, C*H*$_2$CH$_3$), 3.26 (sept, 2H, C*H*(CH$_3$)$_2$), 1.60 (s, 6H, C*H*$_3$), 1.51 (d, 6H, CH(C*H*$_3$)$_2$), 1.40 (d, 6H, CH(C*H*$_3$)$_2$), 1.23 (d, 6H, CH(C*H*$_3$)$_2$), 1.11 (d, 6H, CH(C*H*$_3$)$_2$), 0.92 (t, 3H, CH$_2$C*H*$_3$) ppm. ^{119}Sn NMR (186.50 MHz, C$_6$D$_6$): δ -252.97 ppm. EI-MS: *m/z* (%) 562 (100) [M-(Et, *i*Pr)] $^+$. Anal. calcd for C$_{34}$H$_{46}$N$_2$O$_2$Sn (634.26): C 64.47, H 7.32, N 4.42; Found C 63.88, H 6.98, N 4.48.

11.4.69. Synthesis of LSnClFe(CO)$_4$ (**71**)

A flask was charged with LSnCl (0.570 g, 1.00 mmol) and Fe$_2$(CO)$_9$ (0.370 g, 1.00 mmol) in THF (30 mL). The solution was stirred 24 h at ambient temperature. The byproduct was removed by filtration over celite, resulting in a clear pale brown filtrate. From the resulting solution the volatiles were removed, giving a pale brown solid of **71**. The crystals suitable for X-ray structural analysis were obtained from the saturated toluene solution of **71**.Yield: 0.630 g (85%). Mp 230 °C. IR (KBr pellet): $\widetilde{\nu}$ = 2043 s, 1968 s, 1939 s (CO) cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$, 25 °C): δ 7.03-7.16 (m, 6H, Ar*H*), 5.09 (s, 1H, γ-C*H*), 3.79 (sept, 2H, C*H*(CH$_3$)$_2$), 3.06 (sept, 2H, C*H*(CH$_3$)$_2$), 1.52 (s, 6H, C*H*$_3$), 1.49 (d, 6H, CH (C*H*$_3$)$_2$), 1.35 (d, 6H, CH(C*H*$_3$)$_2$), 1.17 (d, 6H, CH(C*H*$_3$)$_2$), 1.01 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn NMR (111.92 MHz, C$_6$D$_6$, 25 °C): δ 88.98 ppm. EI-MS (70 eV; *m/z* (%)):628 (100) [M-4CO]$^+$. Anal. Calcd for C$_{33}$H$_{41}$ClFeN$_2$O$_4$Sn (740.11): C 53.58, H 5.59, N 3.79; Found: C 53.29, H 5.95, N 3.66.

11.4.70. Synthesis of LSn(NMe$_2$)Fe(CO)$_4$ (**72**)

A flask was charged with **66** (5.80 g, 10.00 mmol) and Fe$_2$(CO)$_9$ (3.70 g, 10.20 mmol) in THF (140 mL). The solution was stirred 24 h at ambient temperature. The byproduct was removed by filtration over celite, resulting in a clear pale brown filtrate. From the resulting solution the volatiles were removed, giving a pale brown solid. Crystallization of the crude product was attained by saturated THF solution of **72** and keeping it at -30 °C temperature. **72** deposited as pale orange crystals as a formula **72$_2$·THF**. Yield: 6.35 g (85%). Mp 218 °C. IR (KBr pellet): $\widetilde{\nu}$ = 2034 s, 1957 s, 1935 s (CO) cm^{-1}. ^{1}H NMR (300.13 MHz, C$_6$D$_6$, 25 °C): δ 7.07-7.16 (m, 6H, Ar*H*), 4.75 (s, 1H, γ-C*H*), 3.27 (sept, 2H, C*H*(CH$_3$)$_2$), 3.15 (sept, 2H, C*H*(CH$_3$)$_2$), 1.49 (s, 6H, C*H*$_3$), 1.42 (d, 6H, CH (C*H*$_3$)$_2$), 1.32 (d, 6H, CH(C*H*$_3$)$_2$), 1.21 (d, 6H, CH(C*H*$_3$)$_2$), 1.01 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn NMR (111.92 MHz, C$_6$D$_6$, 25 °C): δ 94.00 ppm. EI-MS (70 eV; *m/z* (%)): 749 (45) [M]$^+$, 705 (100) [M-NMe$_2$]$^+$. Anal. Calcd for C$_{35}$H$_{47}$FeN$_3$O$_4$Sn (749.19): C 56.18, H 6.33, N 5.62; Found: C 56.24, H 6.78, N 5.51.

11.4.71. Synthesis of LSn(OH)Fe(CO)$_4$ (**73**)

Degassed water (72 μL, 4.00 mmol) was added to a solution of **72** (3.00 g, 4.00 mmol) in THF (50 mL) at -60 °C. Then, it was taken to room temperature and stirred for 1 h. Followed by removal of the solvent in a vacuum to give compound **73** as a solid. It was washed with a small amount of *n*-hexane and crystallized from toluene at -32 °C to exhibit compound **73** as brown crystals. Yield: 2.10 g (73%). Mp 233 °C. IR (KBr pellet): $\widetilde{\nu}$ = 3615 s (OH), 2038 s, 1959 s, 1944 s (CO) cm^{-1}. ^{1}H NMR (300.13 MHz, C$_6$D$_6$, 25 °C): δ 7.04-7.15 (m, 6H, Ar*H*), 4.86 (s, 1H, γ-C*H*), 3.75 (sept, 2H, C*H*(CH$_3$)$_2$), 3.07 (sept, 2H, C*H*(CH$_3$)$_2$), 1.66 (s, 1H, O*H*), 1.51 (s, 6H, C*H*$_3$), 1.39 (d, 6H, CH (C*H*$_3$)$_2$), 1.34 (d, 6H, CH(C*H*$_3$)$_2$), 1.18 (d, 6H, CH(C*H*$_3$)$_2$), 1.04 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn NMR (111.92 MHz, C$_6$D$_6$, 25 °C): δ 45.03 ppm. EI-MS (70 eV; *m/z* (%)): 722 (10) [M]$^+$, 705 (100) [M-OH]$^+$, 666 (85) [M-2CO]$^+$. Anal. Calcd for C$_{33}$H$_{42}$FeN$_2$O$_5$Sn (722.15): C 54.95, H 5.87, N 3.88; Found: C 55.61, H 6.43, N 4.17.

11.5. Crystallographic Details

Complete crystallographic data are deposited at the Cambridge Crystallographic Data Centre, where it can be downloaded free of charge from www.ccdc.cam.ac.uk/ data_request/cif: at CCDC-697821 (**1**), CCDC-743152 (**2**), CCDC-743153 (**3**), CCDC-706811 (**4**), CCDC-706621 (**6**), CCDC-730408 (**7**), CCDC-738339 (**8**), CCDC-706622 (**10**), CCDC-706623 (**11**), CCDC-730403 (**12**), CCDC-706624 (**13**), CCDC-710236 (**14**), CCDC-667925 (**16**), CCDC-713790 (**17**), CCDC-715866 (**18**), CCDC-709476 (**21**), CCDC-709478 (**22**), CCDC-709477 (**24**), CCDC-730399 (**26**), CCDC-730401 (**27**), CCDC-709479 (**29**), CCDC-730400 (**31**), CCDC-

705305 (**36**), CCDC-745457 (**40**), CCDC-705305 (**42**), CCDC-745454 (**43**), CCDC-715867 (**44**), CCDC-715868 (**45**), CCDC-715869 (**46**), CCDC-741341 (**47**), CCDC-720891 (**48**), CCDC-717497 (**51**), CCDC-740333 (**52**), CCDC-740334 (**54**), CCDC-713788 (**55**), CCDC-713789 (**56**), CCDC-734212 (**58**), CCDC-728257 (**59**), CCDC-745456 (**60**), CCDC-730406 (**61**), CCDC-697820 (**64**), CCDC-706812 (**65**), CCDC-743154 (**67**), CCDC-743155 (**70**), CCDC-740971 (**72**), CCDC-740972 (**73**).

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List of Scientific Contributions

Publications

1. Functionalization of Aminophosphanes: Synthesis and X-Ray Crystal Structure of Novel Dilithium and Trilithium Complexes Containing Silicon-Fused Heteronuclear SiN$_2$PLi Five-Membered Rings
Anukul Jana, Gerald Schwab, Herbert W. Roesky and Dietmar Stalke
***Inorg. Chem.* 2008**, *47*, 8990-8994

2. Facile Access of Stable Divalent Tin Compounds with Terminal Methyl, Amide, Fluoride, and Iodide Substituents
Anukul Jana, Herbert W. Roesky, Carola Schulzke, Alexander Dring, Tobias Beck, Aritra Pal and Regine Herbst-Irmer
***Inorg. Chem.* 2009**, *48*, 193–197

3. Cleavage of a N−H Bond of Ammonia at Room Temperature by a Germylene
Anukul Jana, Ina Objartel, Herbert W. Roesky and Dietmar Stalke
***Inorg. Chem.* 2009**, *48*, 798–800

4. A Germanium(II) Hydride as an Effective Reagent for Hydrogermylation Reactions
Anukul Jana, Debajyoti Ghoshal, Herbert W. Roesky, Ina Objartel, Gerald Schwab and Dietmar Stalke
***J. Am. Chem. Soc.* 2009**, *131*, 1288–1293

5. Reactions of Tin(II) Hydride Species with Unsaturated Molecules
Anukul Jana, Herbert W. Roesky, Carola Schulzke and Alexander Döring
***Angew. Chem. Int. Ed.* 2009**, *48*, 1106-1109.

6. Preparation and Structural Characterization of Molecular Al−O−Sn(II) and Al−O−Sn(IV) Compounds
Sharanappa Nembenna, Sanjay Singh, **Anukul Jana**, Herbert W. Roesky, Ying Yang, Hongqi Ye, Holger Ott and Dietmar Stalke
***Inorg. Chem.* 2009**, *48*, 2273–2276

7. Oxidative Addition of Ammonia at a Silicon(II) Center and an Unprecedented Hydrogenation Reaction of Compounds with Low-Valent Group 14 Elements Using Ammonia Borane
Anukul Jana, Carola Schulzke and Herbert W. Roesky
***J. Am. Chem. Soc.* 2009**, *131*, 4600–4601

8. Unprecedented End-On Nitrogen Insertion of a Diazo Compound into a Germanium(II) Hydrogen Bond and a Comparable Reaction with Diethyl Azodicarboxylate
Anukul Jana, Sakya S. Sen, Herbert W. Roesky, Carola Schulzke, Sudipta Dutta and Swapan K. Pati
***Angew. Chem. Int. Ed.* 2009**, *48*, 4246-4248.

9. Facile Access of Well-Defined Stable Divalent Lead Compounds with Small Organic Substituents
Anukul Jana, Sankaranarayana Pillai Sarish, Herbert W. Roesky, Carola Schulzke, Alexander Dring and Michael John
***Organometallics*, 2009**, *28*, 2563–2567

10. A Silylene with a Tricoordinate Silicon Atom as a Ligand for a Metal Complex
Wei Yang, Hao Fu, Haijun Wang, Mingqing Chen, Yuqiang Ding, Herbert W. Roesky and **Anukul Jana**
***Inorg. Chem.* 2009**, *48*, 5058-5060

11. Stable Compounds of Composition LGe(II)R (R = OH, PhO, C_6F_5O, $PhCO_2$): Prepared by Addition Reactions
Anukul Jana, Bijan Nekoueishahraki, Herbert W. Roesky and Carola Schulzke
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12. Dehydrogenation of LGeH by a Lewis Carbene-Borane Pair Under the Formation of L′Ge and its Reactions with $B(C_6F_5)_3$ and Trimethylsilyl Diazomethane. An Unprecedented Rearrangement of a Diazocompound to an Isonitrile
Anukul Jana, Ina Objartel, Herbert W. Roesky and Dietmar Stalke
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13. Hydrostannylation of Ketones and Alkynes with LSnH [L = HC(CMeNAr)₂; Ar = 2,6-*i*Pr₂C₆H₃]
Anukul Jana, Herbert W. Roesky and Carola Schulzke
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14. Synthesis and Structural Characterization of Heterobimetallic Bismuth Complexes with Main Group and Transition Metals
Bijan Nekoueishahraki, **Anukul Jana**, Herbert W. Roesky, Daniel Stern and Dietmar Stalke
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15. A Remarkable Base Stabilized Bis Silylene with a Si(I)-Si(I) Bond
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16. Insertion Reaction of a Silylene into a N-H bond of Hydrazine and a [1+4] Cycloaddition with Diphenyl Hydrazone
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17. Reactivity of Germanium(II) Hydride with Nitrous Oxide, Trimethylsilyl Azide, Ketones, and Alkynes and the Reaction of a Methyl Analogue with Trimethylsilyl Diazomethane
Anukul Jana, Herbert W. Roesky and Carola Schulzke
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18. Synthesis of Phosphine Substituted *β*-Diketiminate Based Isomeric Ge(II) Complexes
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21. Heavier Alkaline Earth Metal Borohydride Complexes Stabilized by *β*-Diketiminate Ligand
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22. Reaction of *β*-diketiminate tin(II) dimethylamide LSnNMe$_2$ [L = HC(CMeNAr)$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$] with ketones and alkynes
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23. Preparation of iron carbonyl complexes of germanium(II) and tin(II) each with a terminal fluorine atom
Anukul Jana, Prinson P. Samuel, Herbert W. Roesky and Carola Schulzke
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Lebenslauf

Name	Anukul Jana
Geboren	27. January 1984 in Krishnakhayratibar
Staatsangehörigkeit	Indisch

Schulbesuch

1989-1998	Primary School (Class I-IX)
1998-1999	Secondary School Examinations (Class X)
1999-2001	Higher Secondary School Examinations (Class XII)

Studium

2001-2004	B. Sc. (Hons.) in Chemie, Calcutta University, Indien
2004-2006	M. Sc. in Chemie, Indian Institute of Technology Kanpur, Indien

Promotion

Oktober 2006 - September 2009	Anorganische Chemie Göttingen unter der Leitung von Prof. Dr. Dr. h.c. mult. H. W. Roesky
	Ph.D. Thesis "*Unprecedented Synthetic and Reactivity Studies of Compounds with Low Valent Group 14 Elements*"