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Reviews

The Chemistry of Aluminum(I), Silicon(II), and Germanium(II)

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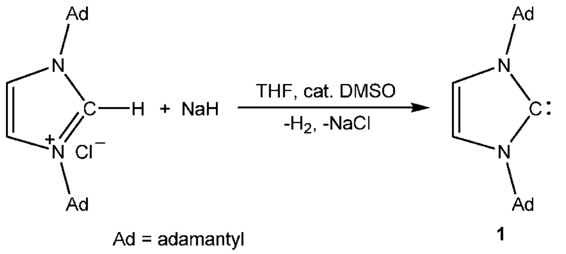
Although tetrameric Al(I) compounds have been known for a long time, the monomeric Al(I) compounds that are analogous to carbenes are very recent entrants in Al(I) chemistry. They possess novel structural features and exhibit distinct reactivity. This has resulted in the isolation and characterization of various unusual aluminum(III) compounds such as the aluminatetrazoles and aluminacyclopropenes. In comparison to the recent emergence of monomeric aluminum(I) compounds, stable silylenes and germylenes (carbene analogues of silicon and germanium) were recognized much earlier. This led to the evolution of the Si(II) and Ge(II) chemistry that at times surpasses the sophistication achieved in divalent carbon chemistry. Thus, while carbon lacks an example of a stable chlorocarbene (LCCl), for silicon there is one example of LSiCl, and for germanium there are a fair number of LGeCl compounds. While reactivity studies on LSiCl are anticipated, the utility of RGeCl as a synthon is well documented. Exotic compounds such as a germanethioacid chloride, a germanium(II) hydride, and a germanium(II) hydroxide are some of the examples that were derived from LGeCl. Recent results from our laboratory at Göttingen have helped in the development of these interesting areas of research, and the present account summarizes our contributions to the chemistry of Al(I), Si(II), and Ge(II).

General Introduction

Carbenes are compounds in which the carbon atom is in a formal divalent state.[1] Arduengo and co-workers isolated the first stable and structurally characterized N-heterocyclic carbene (NHC) (**1**) in 1991.[2] Compound **1** was obtained by reduction of 1,3-di-1-adamantylimidazol-2-ylidene (Scheme 1).

The key stabilizing effect in **1** is the donation of electron density from the nitrogen atoms into the empty p-orbital of carbon, which reduces its electrophilicity and increases its thermodynamic stability. By extending this stabilization principle, a large number of stable N-heterocyclic carbenes (NHCs) have been prepared.[3] The NHCs have emerged as an important class of compounds due to their broad applications in organometallic chemistry, organic synthesis, and homogeneous catalysis.[4] In view of this, there is a great deal of interest in the synthesis of NHC analogues of heavier group 14 (Si,[5] Ge,[6] Sn[7]) and group 13 (B,[8] Al,[9] Ga,[10] In,[11a,b] Tl[11b,c]) elements.[12] This has been achieved through various ligand systems that are either

Scheme 1. Synthesis of the First Stable N-Heterocyclic Carbene



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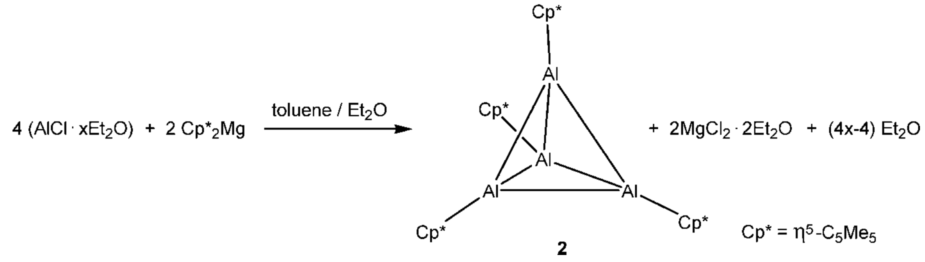
10.1021/om7007869 CCC: $40.75

Scheme 2. Synthesis of Tetrameric Al(I) Compound 2



monoanionic or dianionic.[13] Owing to our continuing interest in the chemistry of aluminum,[14] silicon,[15] and germanium,[16] in recent years we are probing their subvalent chemistry as well. Our findings pertaining to Al(I), Si(II), and Ge(II) chemistry are discussed in this account, and we mention also very closely related results of other research groups. Also, this account has been written in order to catch the eye of both the novice and the expert of the field.

1. Aluminum(I) Chemistry

1.1. Introduction. Aluminum prefers to be in the +3 oxidation state because of the stability associated with this oxidation state. In numerous compounds, aluminum also exhibits an oxidation state of +2.[17] However, the +1 oxidation state of aluminum is not thermodynamically stable, and therefore the synthesis of kinetically stable aluminum(I) compounds is quite challenging.[18] Even though low-valent aluminum compounds such as AlH, AlX (X = F, Cl, Br, I), and Al_2O are known, they are stable only at high temperature and low pressure.[19] For example, gaseous AlCl can be obtained by the reaction of metallic aluminum with gaseous HCl at a temperature of 927 °C and at a pressure less than 0.2 mbar.[20] Nevertheless, by utilizing cryochemical methods and by preparing metastable solutions of AlX at −78 °C Schnöckel and co-workers were able to demonstrate the reactivity of aluminum(I) halides.[18b,21] In 1991 the same group reported the first example of an organometallic Al(I) compound, $(Cp^*Al)_4$ (**2**), that is stable under normal conditions by reacting the metastable solution of AlCl with Cp^*_2Mg ($Cp^* = \eta^5\text{-}C_5Me_5$) (Scheme 2).[22]

Compound **2** was structurally characterized and found to be tetrameric in the solid state. It retains its tetrameric structure also in solution. However, at temperatures above 30 °C there exists an equilibrium between tetrameric $(Cp^*Al)_4$ and monomeric Cp^*Al.[23] As expected, it is monomeric in the gas phase, and its molecular structure was determined by means of gas-phase electron diffraction.[24] As the synthesis of AlCl (a key precursor for the synthesis of **2**) is very complicated, we developed a facile synthesis of **2** in 1993 by reducing Cp^*AlCl_2 with potassium in refluxing toluene (eq 1).[25]

$$4\,Cp^*AlCl_2 + 8\,K \xrightarrow[\text{reflux}]{\text{toluene}} \underset{\mathbf{2}}{(Cp^*Al)_4} + 8\,KCl \qquad (1)$$

In addition, we investigated the first reactivity studies of **2** by carrying out its reactions with elemental selenium and tellurium.[25] Utilizing the Al(I) tetramer **2** various novel aluminum compounds have been synthesized.[26] Due to the propensity of the neutral tetrameric aluminum(I) compound $(RAl)_4$ to disproportionate into elemental aluminum and R_3Al, only few examples of such tetramers are known. These can be stabili-

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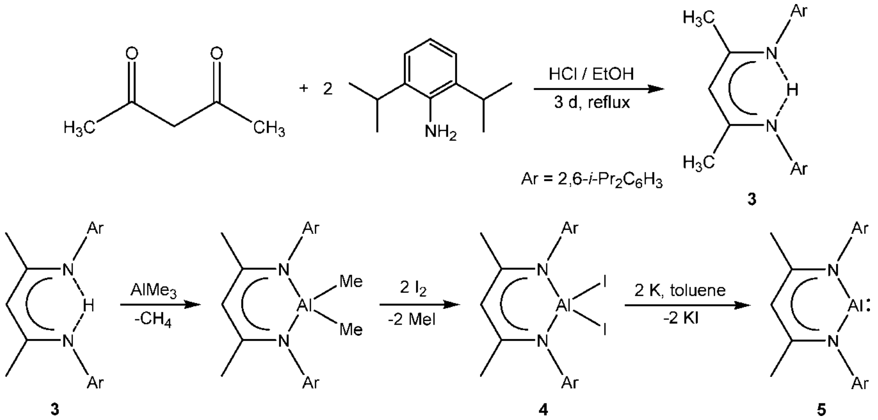
Scheme 3. Synthesis of LAl 5 by Reducing the Aluminum Diiodide 4



zed by bulky substituents on aluminum: [(*t*-Bu)$_3$SiAl]$_4$,[27] Cp*$_3$Al$_3$AlN(SiMe$_3$)$_2$,[28] [(Me$_3$Si)$_3$SiAl]$_4$,[29] [(Me$_3$Si)$_3$CAl]$_4$,[30] and [2,6-*i*-Pr$_2$C$_6$H$_3$N(SiMe$_3$)Al]$_4$.[31] The first three compounds were synthesized by Schnöckel and co-workers, and the last two were obtained by us. Another example of composition [*t*-BuCH$_2$Al]$_4$ with neopentyl groups also was reported.[32] Except for the Al(I) tetramer with Cp* ligands (which form π-bonds), all other such compounds have σ-bonded substituents. Reported in 1998, the compound [(Me$_3$Si)$_3$CAl]$_4$ was the first example of a structurally characterized aluminum(I) tetramer with σ-bonded alkyl groups.[30] At this juncture, we reasoned that the tetramerization is due to the lack of sufficient steric protection of the Al(I) center, and we assumed that a very bulky and bidentate β-diketiminate (**3**) might bestow the desired steric stabilization.[13a,33] Accordingly, we prepared the β-diketiminatoaluminum diiodide LAlI$_2$ (L = CH{(CMe)(2,6-*i*-Pr$_2$C$_6$H$_3$N)}$_2$) (**4**) by following the synthetic route shown in Scheme 3.[34]

Reduction of the aluminum diiodide **4** with 2 equiv of potassium at room temperature gave **5**, the first example of a well-defined monomeric aluminum(I) derivative.[9] Compound **5** is the first aluminum analogue of a carbene, and it exhibits a singlet carbene-like behavior. Theoretical studies on LAl **5** show that it has both Lewis acid as well as Lewis base character. It also can behave as a reducing agent. The unique properties of the monomeric LAl **5** that arise from the special steric and electronic effects offered by the β-diketiminato ligand are suggestive of an entirely different reaction pathway for **5** than that of the tetrameric Al(I) derivative **2**. In reality this is so, and they hardly match each other. Since the report of LAl **5** in 2000, we have developed its amazing chemistry. We reviewed these results in 2004;[35] therefore, the progress made by us since then will be described in more detail here after giving a summary of our earlier work.

Carbenes undergo a [1+2] cycloaddition reaction with alkynes to afford cyclopropene derivatives.[36] Like carbenes, LAl **5** reacts with acetylene at low temperature to afford the first stable aluminacyclopropene (**6**) as an orange, crystalline solid.[37] When an excess of acetylene was present and the temperature was raised, compound **6** reacted further with acetylene to give **7**, which contains terminal C≡CH and CH=CH$_2$ groups linked to the same Al atom (Scheme 4).[37]

In contrast to the reaction of **5** with acetylene, the [1+2] cycloaddition reaction of **5** with bis(trimethylsilyl)acetylene did not occur.[38] Therefore, a different synthetic route was devised to obtain the desired aluminacyclopropene **8**, which involves the reductive coupling of **4** in the presence of bis(trimethylsilyl)acetylene. In this way, two other aluminacyclopropenes, **9** and **10**, were prepared (Scheme 5). A similar reductive coupling reaction of **4** with potassium in the presence of benzophenone gave the aluminum pinacolate **11** (Scheme 5).[38]

The reaction of **5** with 2 equiv of Me$_3$SiN$_3$ resulted in the first aluminatetrazole (**12**) that contains a five-membered AlN$_4$

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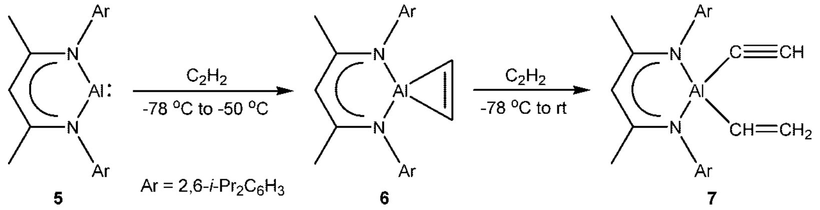
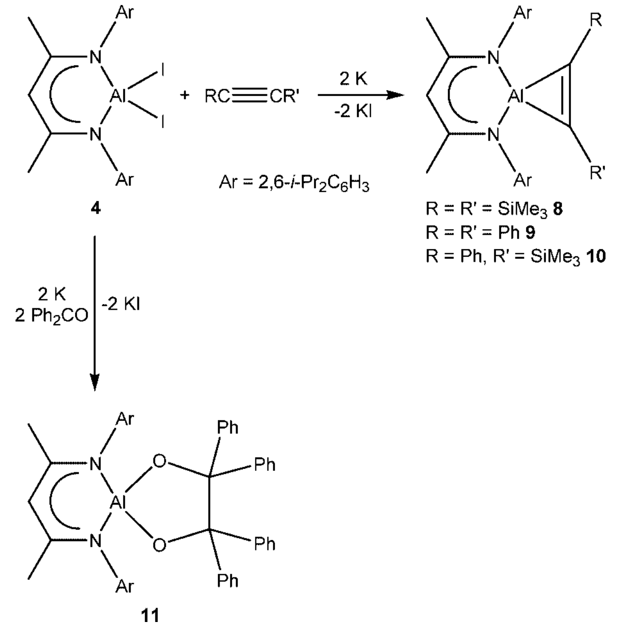
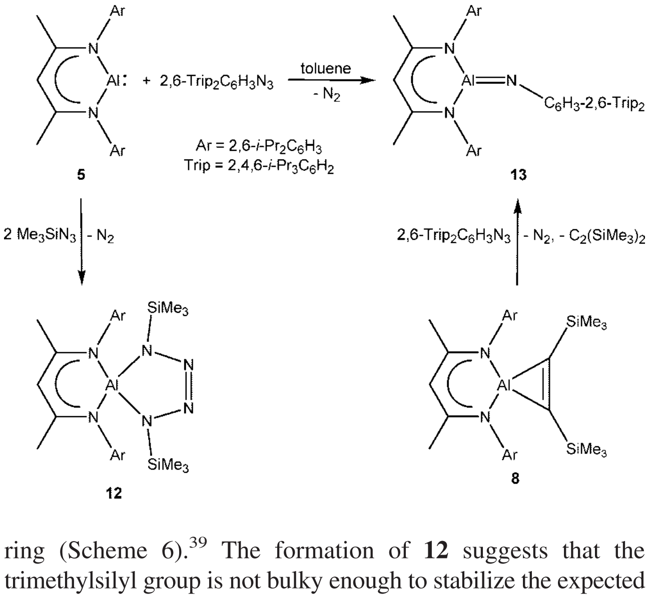
Scheme 4. Reaction of 5 with Acetylene to Form Aluminacyclopropene 6 and 7



Scheme 5. Reductive Coupling of 4 in the Presence of Alkynes and Benzophenone

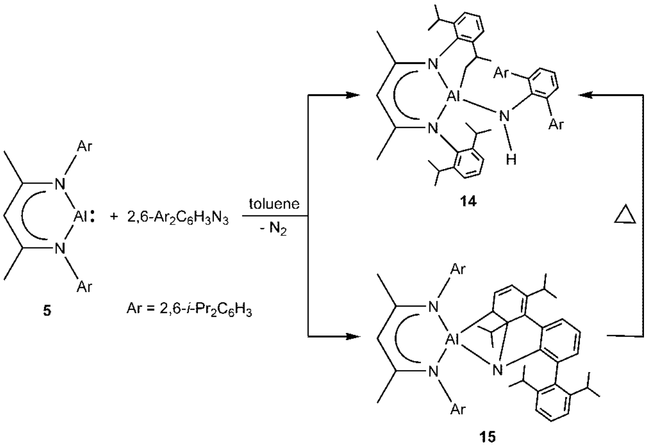


Scheme 6. Reaction of 5 with Azides (Me_3SiN_3 and 2,6-$Trip_2C_6H_3N_3$) and the Reaction of 8 with 2,6-$Trip_2C_6H_3N_3$



ring (Scheme 6).[39] The formation of **12** suggests that the trimethylsilyl group is not bulky enough to stabilize the expected monomeric imine $LAlNSiMe_3$ with an Al═N double bond. However, a 1:1 reaction of **5** with the bulky azide 2,6-$Trip_2C_6H_3N_3$ (Trip = 2,4,6-i-$Pr_3C_6H_2$) resulted in the formation of an unprecedented monomeric imine, **13** (Scheme 6).[38,40]

Scheme 7. Reaction of 5 with the Bulky Azide 2,6-$Ar_2C_6H_3N_3$



The reaction of aluminacyclopropene **8** with the same azide also gave **13** by eliminating a molecule of bis(trimethylsilyl)-acetylene (Scheme 6).[38] Compound **13** has not been structurally characterized, since our efforts to grow single crystals of **13** were unsuccessful. When the azide 2,6-$Ar_2C_6H_3N_3$ (Ar = 2,6-i-$Pr_2C_6H_3$) was reacted with **5**, two different isomers, **14** and **15**, were obtained as crystals one after the other (Scheme 7).[41] These two products are formed as a result of the two different types of intramolecular addition reactions that can occur by way of the formal Al═N double-bonded monomeric intermediate LAlN2,6-$Ar_2C_6H_3$. Interestingly, compound **15** undergoes a thermal isomerization and forms **14** to alleviate the strain present in it (Scheme 7).

The reaction of **5** with 2 equiv of diphenyldiazomethane (a source for the transient carbene, :CPh_2) gave the diiminylaluminum derivative **16** (Scheme 8).[42] A 1:1 reaction of **5** with the electron-rich N-heterocyclic carbenes **17** and **18** in the solid state gave the aluminum monohydride carbene adducts **19** and **20**, respectively, as colorless crystals (Scheme 8).[42] The reaction of **5** with white phosphorus at room temperature resulted in the formation of red crystals of composition $[(LAl)_2P_4]$, **21** (Scheme 8).[43] Compound **21** is one of the two known main group derivatives with a $\{P_4\}^{4-}$ moiety.[44] In the reaction of elemental sulfur with **5**, the homobimetallic compound $[LAl(\mu\text{-}S_3)_2AlL]$ (**22**) was obtained as pale yellow crystals (Scheme 8).[45] The derivative **22** contains two aluminum atoms bridged by two μ-S_3 units, resulting in formation of an eight-membered Al_2S_6 ring.

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(39) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4531–4533.

(40) Hardman, N. J.; Cui, C.; Roesky, H. W.; Fink, W. H.; Power, P. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2172–2174.

(41) Zhu, H.; Chai, J.; Chandrasekhar, V.; Roesky, H. W.; Magull, J.; Vidovic, D.; Schmidt, H.-G.; Noltemeyer, M.; Power, P. P.; Merrill, W. A. *J. Am. Chem. Soc.* **2004**, *126*, 9472–9473.

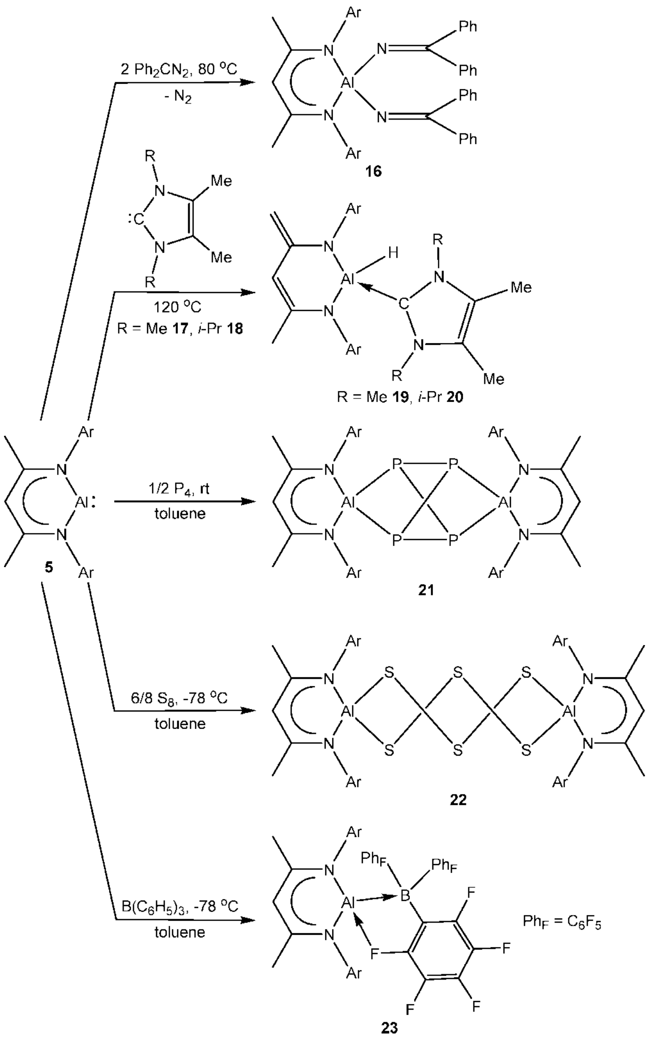
(42) Zhu, H.; Chai, J.; Stasch, A.; Roesky, H. W.; Blunck, T.; Vidovic, D.; Magull, J.; Schmidt, H.-G.; Noltemeyer, M. *Eur. J. Inorg. Chem.* **2004**, 4046–4051.

(43) Peng, Y.; Fan, H.; Zhu, H.; Roesky, H. W.; Magull, J.; Hughes, C. E. *Angew. Chem., Int. Ed.* **2004**, *43*, 3443–3445.

(44) Xiong, Y.; Yao, S.; Brym, M.; Driess, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4511–4513.

(45) Peng, Y.; Fan, H.; Jancik, V.; Roesky, H. W.; Herbst-Irmer, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6190–6192.

Scheme 8. Reaction of 5 with Ph_2CN_2, N-heterocyclic carbene, phosphorus, sulfur, and $B(C_6F_5)_3$

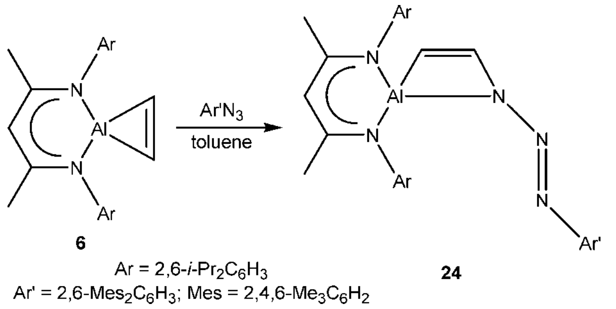


As shown by theoretical calculations, compound **5** has both Lewis acid and Lewis base properties. The experimental evidence for this comes from its reactivity with $B(C_6F_5)_3$.[46] Interestingly, a 1:1 reaction of $B(C_6F_5)_3$ with **5** gave the first example of a Janus-faced aluminum compound, $[LAlB(C_6F_5)_3]$ (**23**), in which the Al atom shows its Lewis acid and base character simultaneously (Scheme 8).

Apart from studying the reactivity of LAl **5**, it also was fascinating to study the high reactivity of aluminacyclopropene derivatives (**6**, **8**, **9**, and **10**, *vide supra*) with their strained three-membered AlC_2 rings. In line with the reactivity of cyclopropenes and the cyclopropene derivatives with MC_2 rings (M = heavier main group element)[47] one may anticipate reactions such as ring opening, insertion, substitution, dimerization, and hydrogen [1,2] sigmatropic shift with the aluminacyclopropenes as well.

The insertion of $Ar'N_3$ (Ar′ = 2,6-$Mes_2C_6H_3$; Mes = 2,4,6-$Me_3C_6H_2$) into the AlC_2 ring of aluminacyclopropene **6** at low temperature gave a novel aluminaazacyclobutene derivative **24** as an orange-yellow solid (Scheme 9).[37] This end-on insertion of an azide group is quite unique and demonstrates the atom economic reaction of azides.

Scheme 9. Reaction of the Aluminacyclopropene 6 with the Azide $Ar'N_3$



The reaction of **8** with CO_2 takes place at room temperature and afforded the insertion product $LAl[OC(O)C_2(SiMe_3)_2]$ (**25**) (Scheme 10).[38,48] Similar is the reaction of **8** with Ph_2CO, in which the aluminadihydrofuran **26** was formed by a C−C coupling reaction (Scheme 10).[38] Compound $LAl[OC(Ph_2)C_2(SiMe_3)_2]$ (**26**) is the first aluminum compound with a metalladihydrofuran ring. In addition, PhCN also inserted into the Al−C bond of the three-membered AlC_2 ring of **8**, producing aluminum compound **27**, with a five-membered AlC_3N unsaturated ring (Scheme 10).[38] In contrast, the reaction of **8** with *t*-BuCN occurred with elimination of $C_2(SiMe_3)_2$.[38] Thus a novel aluminum bis(iminato) derivative, **28**, that contains an aluminaimidazole ring was formed (Scheme 10). This disparity may be due to the bulky and electron-donating *t*-Bu group. The reaction of CS_2 was similar to the reaction of CO_2 with **8**, but the five-membered ring product formed by the CS_2 insertion reacted further with **8**, resulting in the formation of a heterocyclic aluminum compound, **29** (Scheme 10).[48] Compound **29** contains a seven-membered $Al_2C_3S_2$ ring with a C=C=C allenylene, the formation of which is unprecedented in organoaluminum chemistry.

1.2. Reaction of LAl 5 with $PhB(OH)_2$. Recently we have shown that LAl is a powerful reducing agent[43] [for example, in the reaction of **5** with P_4 (Scheme 8)], and in view of this, the redox reaction of **5** with $PhB(OH)_2$ was investigated.[49] Treatment of LAl **5** with 2 equiv of $PhB(OH)_2$ gave the spirocyclic aluminum(III) hybrid $LAl[(OBPh)_2O]$ (**30**) as colorless crystals (87% yield) (Scheme 11). Compound **30** was also obtained in a 1:2 reaction of the aluminum dihydride $LAlH_2$ **31** (obtained by the reaction of **3** with $AlH_3 \cdot NMe_3$)[33] with $PhB(OH)_2$ (82% yield) (Scheme 11).

These reactions are driven by the exothermic formation of the Al−O bonds, and it is postulated that the formation of **30** from **5** and **31** involves the intermediates **A** and **B**, respectively. Thus in a concerted mechanistic sequence the interaction of **5** with $PhB(OH)_2$ leads to the elimination of a H_2 molecule from two molecules of $PhB(OH)_2$ to form $LAl[OB(Ph)OH]_2$, which further eliminates a water molecule to afford **30** with a six-membered AlO_3B_2 ring. In the reaction of **31** with $PhB(OH)_2$ a similar mechanism operates, but two molecules of hydrogen (formed from the two hydride substituents of **31** and two protons of $PhB(OH)_2$) are eliminated instead of one in the earlier case. The molecular structure of **30** clearly shows the presence of two six-membered rings (AlB_2O_3 and AlC_3N_2) centered around

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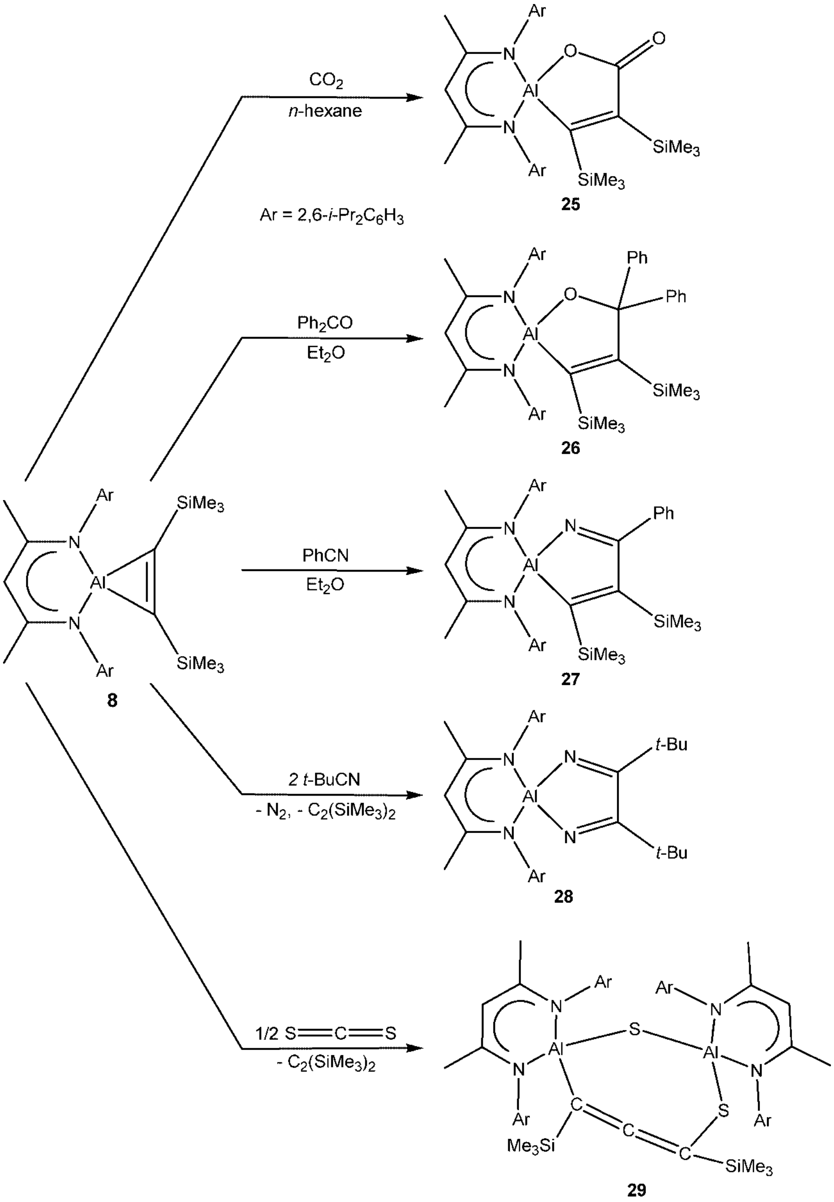
(46) Yang, Z.; Ma, X.; Oswald, R. B.; Roesky, H. W.; Zhu, H.; Schulzke, C.; Starke, K.; Baldus, M.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 7072–7074.

(47) Roskamp, E.; Roskamp, C. In *Comprehensive Heterocyclic Chemistry II, Vol. 2*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, 1996; pp 305–332.

(48) Zhu, H.; Chai, J.; Ma, X.; Jancik, V.; Roesky, H. W.; Fan, H.; Herbst-Irmer, R. *J. Am. Chem. Soc.* **2004**, *126*, 10194–10195.

(49) Yang, Z.; Ma, X.; Oswald, R. B.; Roesky, H. W.; Noltemeyer, M. *J. Am. Chem. Soc.* **2006**, *128*, 12406–12407.

Scheme 10. Reaction of 8 with CO_2, Ph_2CO, PhCN, *t*-BuCN, and CS_2



the Al(III) and reveals its spirocyclic nature (Figure 1). A dihedral angle of 88.63° between these two planes indicates that they are almost perpendicular to each other.

The Al—O bond lengths (1.750_{av} Å) are longer than the Al—O bond lengths (1.705_{av} Å) found for the aluminum(III) dihydroxide [LAl(OH)$_2$], **32**.[50] When compared with the O—Al—O bond angle (115.38°) of **32**, the O—Al—O bond angle (104.7°) in **30** is significantly acute. These discrepancies may arise due to the strain associated with the six-membered rings of **30**. The O—B—O and the B—O—B bond angles in **30** are 122.45_{av}° and 125.81°, respectively.

Theoretical calculations revealed that the lone pair of electrons on the nitrogen atoms in **30** enhances the stability of the Al—N bonds by means of donor–acceptor interaction. Also, a similar type of interaction exists between the antibonding Al—O bonds and the Al—N bonds. Each Al—N bond is formed by the overlap of an aluminum $sp^{3.04}$ and a nitrogen atom $sp^{2.50}$ hybrid orbital. This situation is true with the Al—O bond, but the orbitals involved are a $sp^{2.67}$ hybrid on the aluminum atom and a $sp^{2.70}$ hybrid on the oxygen atom. In addition, calculations support the proposed concerted mechanism for the formation of **30** from **5** by ruling out the possibility of a two-step pathway.

1.3. Reaction of LAl 5 with Azobenzene. Aluminum(I) compound **5** is reminiscent of a singlet carbene.[1b] Thus, it undergoes a [1+2] cycloaddition reaction with substituted (*vide infra*) and unsubstituted[37] (Scheme 4) alkynes to afford aluminacyclopropene derivatives. To extend the reactivity studies to related systems, we explored the reaction of **5** with azobenzene.[51] When LAl **5** was heated with azobenzene, a five-membered ring compound **33** was formed as orange crystals in 81% yield (Scheme 12). The reaction of aluminacyclopropene **8** with azobenzene also gave **33** (Scheme 12).

It is assumed that the reaction of **5** with azobenzene results in the formation of an intermediate **C** by means of a [1+2]

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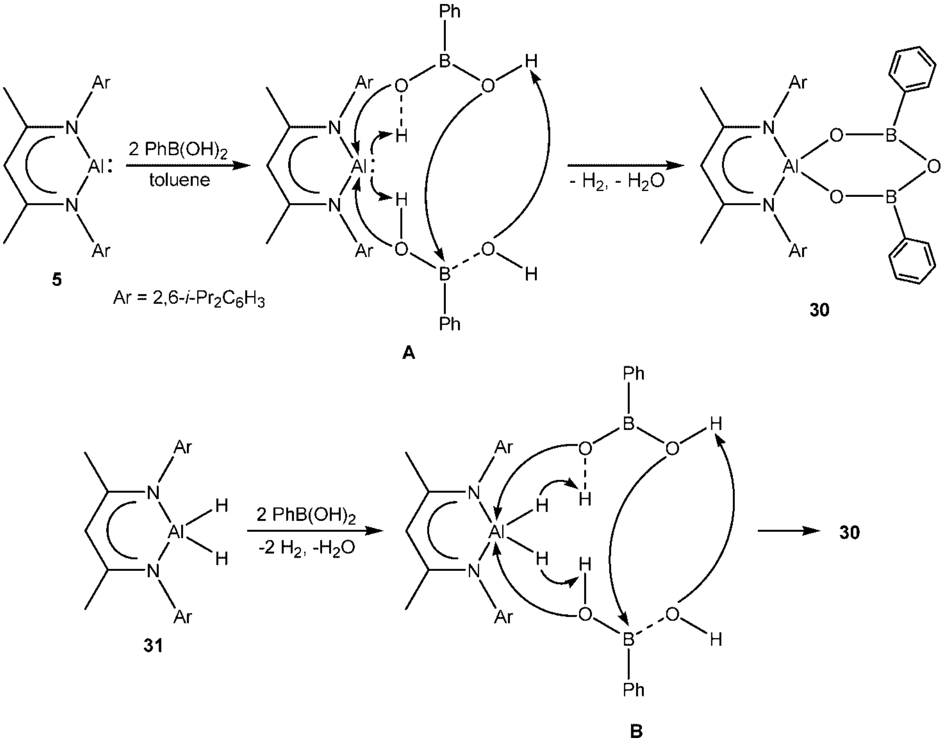
(50) (a) Bai, G.; Peng, Y.; Roesky, H. W.; Li, J.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1132–1135. (b) Jancik, V.; Pineda, L. W.; Pinkas, J.; Roesky, H. W.; Neculai, D.; Neculai, A. M.; Herbst-Irmer, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 2142–2145. (c) Zhu, H.; Chai, J.; He, C.; Bai, G.; Roesky, H. W.; Jancik, V.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **2005**, *24*, 380–384.

(51) Zhu, H.; Chai, J.; Fan, H.; Roesky, H. W.; Nehete, U. N.; Schmidt, H.-G.; Noltemeyer, M. *Eur. J. Inorg. Chem.* **2005**, 2147–2150.

Scheme 11. Reaction of LAl 5 and $LAlH_2$ 31 with $PhB(OH)_2$ to Afford the Spirocyclic Aluminum(III) Hybrid 30



cycloaddition. This intermediate is highly strained due to the presence of a three-membered AlN_2 ring. The strain is relieved by a rearrangement that involves N−N bond cleavage and migration of an *ortho* hydrogen atom from one of the N−Ph rings. This is supported by theoretical calculations on a model system in which the ligand L is replaced by L′ (L′ = $HC[(CMe)(NPh)]_2$). The complexation energy for the formation of the intermediate $[L'Al(\eta^2\text{-}N_2Ph_2)]$ (−39 kcal mol^{-1}) is even lower than the calculated energy for the complexation of LAl with an alkyne (−21 kcal mol^{-1}) and favors the formation of the intermediate **C**. Also, the energy difference of −76 kcal mol^{-1} between the isomeric intermediate and the product (i.e., between the intermediate $[L'Al(\eta^2\text{-}N_2Ph_2)]$ with a three-membered ring and the final complex $[L'AlN(H)\text{-}o\text{-}C_6H_4NPh]$ with a five-membered ring) is evocative of an energetically favorable rearrangement. The presence of a NH proton in **33** was confirmed by means of its ^1H NMR spectrum (singlet at 3.06 ppm) and by an IR (absorption at 3220 cm^{-1}) study. Furthermore, the structure of the complex **33** was confirmed by means of single-crystal X-ray analysis (Figure 2).

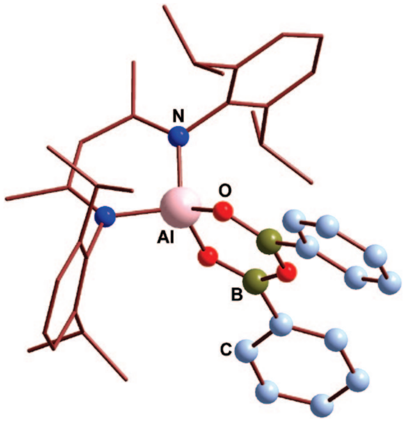


Figure 1. Molecular Structure of the Aluminum(III) Hybrid **30**.

The structure consists of a five-membered AlN_2C_2 and a six-membered AlN_2C_3 ring, and both these rings merge at the Al atom. In addition, the former ring is almost planar (Δ = 0.72 Å) and the latter ring has an envelope conformation (the aluminum atom is above the plane of the almost planar C_3N_2 skeleton by a distance of 0.43 Å). Both these rings are nearly perpendicular with a dihedral angle of 86.31°. The Al−N bond lengths [1.807 Å (Al−NH) and 1.847 Å (Al−N(Ph))] in the five-membered ring are comparable to the Al−N bond lengths [1.815 and 1.851 Å] found for the compound $LAl[(NSiMe_3)_2N_2]$ (**12**) with an AlN_4 tetrazole ring.[39] The Al center is tetracoordinate with four nitrogen atoms and adopts a distorted tetrahedral geometry.

1.4. Reaction of LAl 5 with Azides. As discussed earlier the reaction of **5** with trimethylsilyl azide gave the aluminatet-

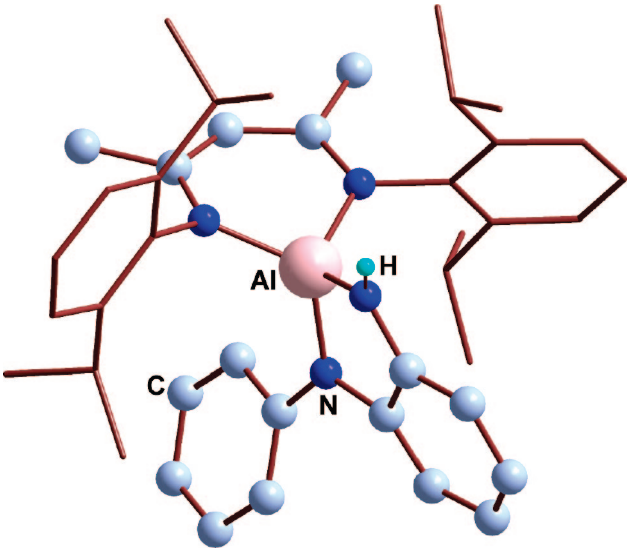
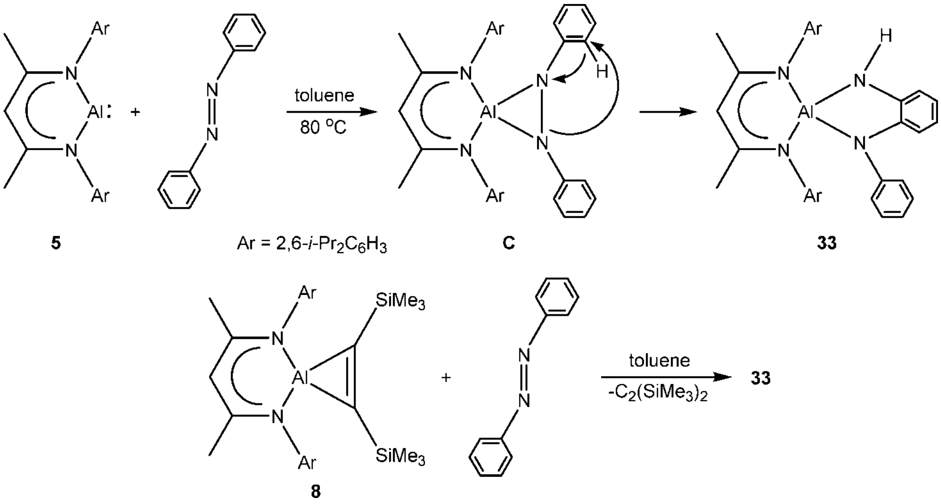
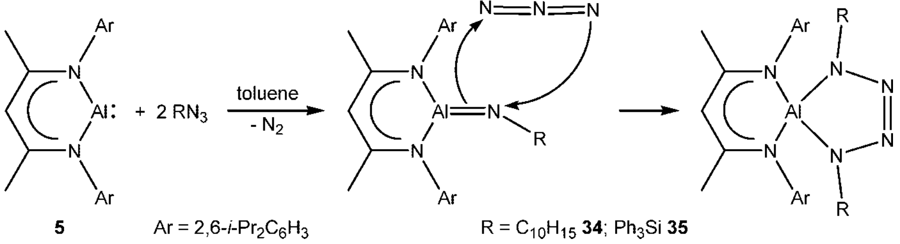


Figure 2. Molecular structure of complex **33**, with a five-membered ring.

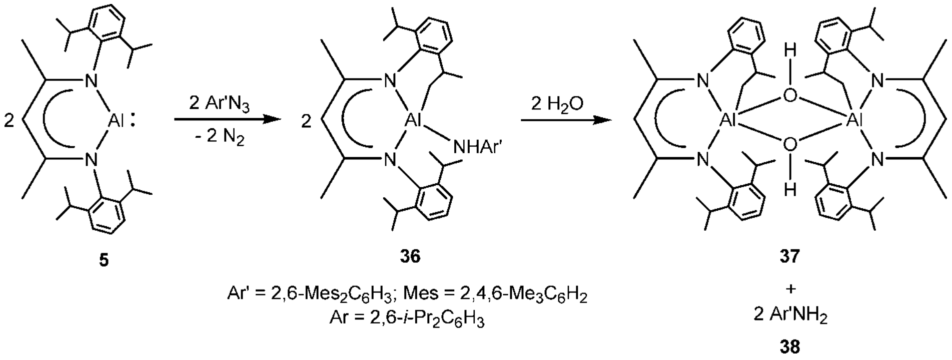
Scheme 12. Reaction of LAl 5 and the Aluminacyclopropene 8 with Azobenzene to Form 33



Scheme 13. Reaction of 5 with the Azides $C_{10}H_{15}N_3$ and Ph_3SiN_3



Scheme 14. Reaction of LAl 5 with 2,6-$Mes_2C_6H_3N_3$ to Form the Compounds 36, 37, and 38



razole **12** (Scheme 6), as the corresponding monomeric imine LAlNSiMe$_3$ could not be stabilized.[39] But by utilizing a bulky azide, 2,6-Trip$_2$C$_6$H$_3$N$_3$ (Trip = 2,4,6-*i*-Pr$_3$C$_6$H$_2$), we were able to obtain the stable monomeric imine **13**, with a formal Al=N double bond (Scheme 6).[38,40] In contrast, the reaction of **5** with the azide 2,6-Ar$_2$C$_6$H$_3$N$_3$ (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) gave two compounds, **14** and **15** (Scheme 7).[41] To throw more light on the reactivity of **5** with azides, we carried out the reaction of **5** with various other azides such as C$_{10}$H$_{15}$N$_3$, Ph$_3$SiN$_3$, 2,6-Mes$_2$C$_6$H$_3$N$_3$, and *t*-BuSi(N$_3$)$_3$. The reactivity of C$_{10}$H$_{15}$N$_3$ and Ph$_3$SiN$_3$ is similar to that of Me$_3$SiN$_3$. However, the reactivities of the latter two azides are unparalleled.

1.4.1. Reaction of 5 with $C_{10}H_{15}N_3$ and Ph_3SiN_3. The reaction of the aluminum(I) compound **5** with adamantyl azide and triphenylsilyl azide in a 1:2 ratio gave the aluminatetrazoles **34** and **35**, respectively, in good yields (~80%) (Scheme 13).[52]

Because of the inability of the R groups (adamantyl and triphenylsilyl) to stabilize the monomeric imides LAlNR, the initially formed imides undergo [2+3] cycloaddition reaction with another molecule of the azide to form the aluminatetrazoles **34** and **35**. As mentioned above, these results are analogous to the reaction of **5** with Me$_3$SiN$_3$.[39]

The molecular structures of the aluminatetrazoles **34** and **35** were confirmed by single-crystal X-ray studies (Figures 3 and 4). Both the structures show the presence of a six-membered AlC$_3$N$_2$ ring in envelope conformation and a planar five-membered AlN$_4$ tetrazole ring. Both the rings are arranged orthogonally to each other. The dihedral angle between these two planes in **34** is 90.6°, and the same angle in **35** is 87.1°. The Al−N bond lengths in the AlN$_4$ tetrazole rings of **35** (1.842, 1.871 Å) are longer than those found for similar compounds, **34** (1.818, 1.854 Å) and LAl[(NSiMe$_3$)$_2$N$_2$] (**12**) (1.815, 1.851 Å).[39] Also, the N−N bond lengths observed in the tetrazole rings (**34**: 1.390, 1.272, 1.391 Å; **35**: 1.412, 1.259, 1.427 Å)

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(52) Zhu, H.; Yang, Z.; Magull, J.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **2005**, *24*, 6420–6425.

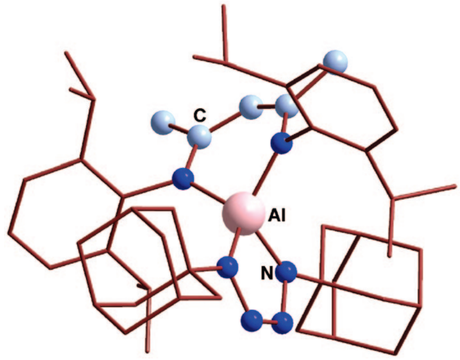

Figure 3. Molecular structure of the aluminatetrazole **34**.

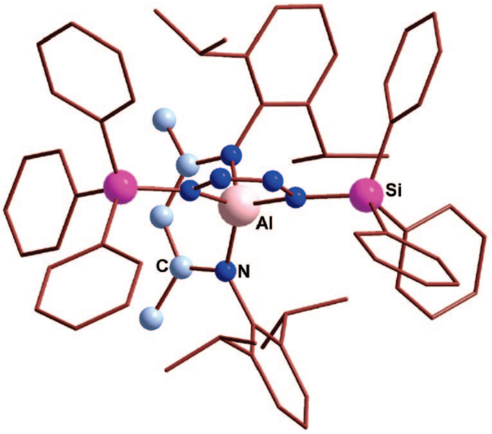

Figure 4. Molecular structure of the aluminatetrazole **35**.

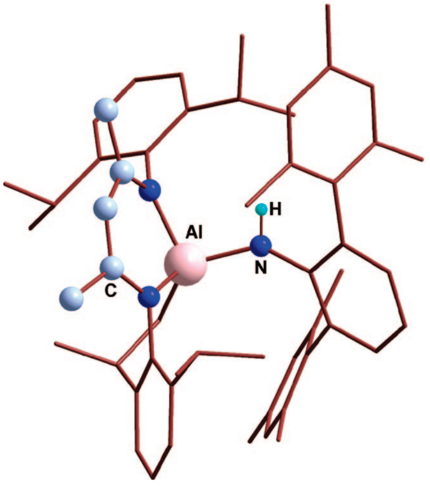

Figure 5. Molecular structure of compound **36** with an Al−NH bond.

are comparable to the N−N bond lengths (1.414, 1.263, 1.414 Å) present in $LAl[(NSiMe_3)_2N_2]$.

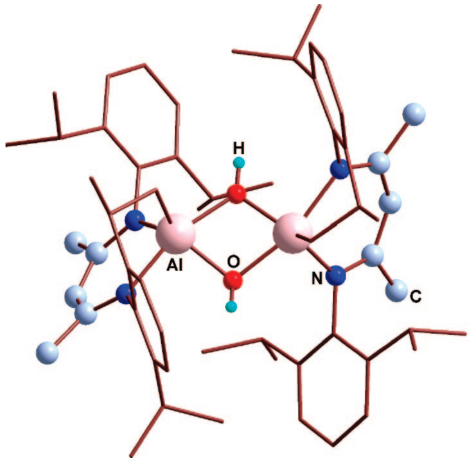

Figure 6. Molecular structure of the C−H activated aluminum hydroxide **37**.

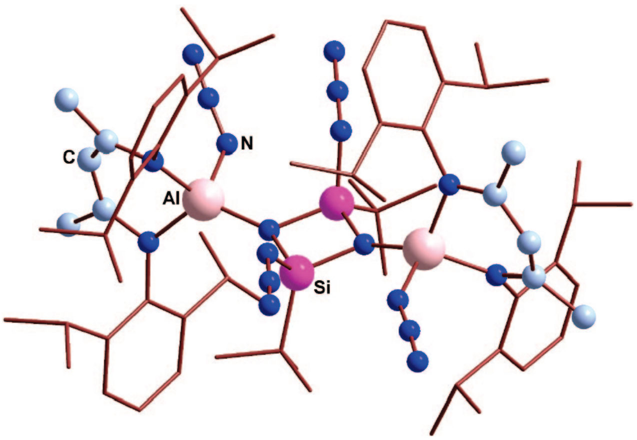

Figure 7. Molecular structure of compound **39** with a four-membered N_2Si_2 ring.

1.4.2. Reaction of 5 with 2,6-$Mes_2C_6H_3N_3$. In a reproducible 2:2 reaction of **5** with 2,6-$Mes_2C_6H_3N_3$ (Mes = 2,4,6-$Me_3C_6H_2$) containing a very small amount of water, the three compounds **36**, **37**, and **38** were obtained as crystalline solids one after the other (Scheme 14).[53] This complex outcome can be explained in the following manner: the reaction of **5** with the azide 2,6-$Mes_2C_6H_3N_3$ (Mes = 2,4,6-$Me_3C_6H_2$) results in formation of an unstable monomeric imide LAlNAr′ (Ar′ = 2,6-$Mes_2C_6H_3$; Mes = 2,4,6-$Me_3C_6H_2$) that further undergoes an intramolecular C−H activated addition reaction to form **36** (an isomer of LAlNAr′). This C−H activation occurs at one of the methyl groups of the 2,6-*i*-$Pr_2C_6H_3$ groups attached to the nitrogen atoms of the β-diketiminato ligand. Due to the presence of water, the Al−NH bond in **36** is hydrolyzed to form the C−H activated aluminum hydroxide **37** with elimination of two molecules of the amine **38**, $Ar'NH_2$ (Ar′ = 2,6-$Mes_2C_6H_3$; Mes = 2,4,6-$Me_3C_6H_2$).

As mentioned earlier, in the reaction of **5** with the azide 2,6-$Ar_2C_6H_3N_3$ (Ar = 2,6-*i*-$Pr_2C_6H_3$) two different compounds, **14** and **15**, were formed.[41] Compound **36** is reminiscent of one of those two isomers, **14**, but in the present instance, an isomeric equivalent of **15** is not formed. The NH proton of **36** appears as a singlet (3.47 ppm) in the ^1H NMR spectrum and can also be seen in the IR spectrum (3265 cm^{-1}). These observations match with that of **14** (3.41 ppm and 3298 cm^{-1}).[41] In compound **36** the Al-CH_2 protons appear as two doublets of doublets (−0.19, −0.94 ppm). Nevertheless, in the ^1H NMR spectrum of the aluminum hydroxide **37** one of the Al-CH_2 protons appears as a triplet (−1.69 ppm) and the other as a doublet of a doublet (−0.35 ppm). It is reminiscent of the situation found for **14** (−1.75 (t), −0.28 (dd)). The bridging hydroxyl protons of **37** resonate at 0.29 ppm and the O−H bond is evidenced by a broadband at 3400 cm^{-1} in the IR spectrum.

The molecular structures of compounds **36** and **37** were established by single-crystal X-ray diffraction studies (Figures

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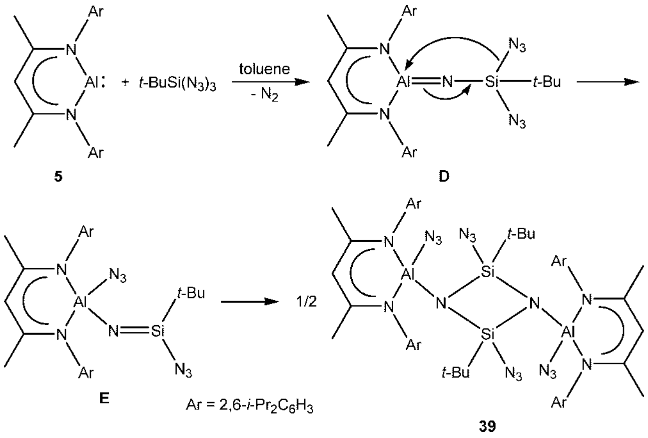
(53) Zhu, H.; Chai, J.; Jancik, V.; Roesky, H. W.; Merrill, W. A.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 10170–10171.

Scheme 15. Reaction of 5 with *t*-BuSi(N_3)$_3$ to Afford 39



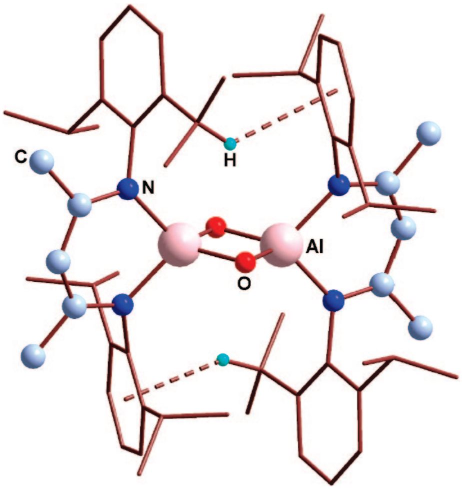
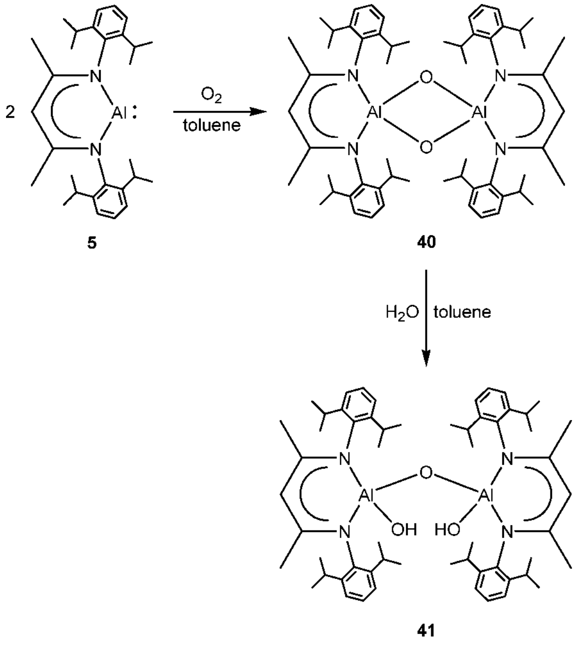


Figure 8. Molecular structure of the aluminum oxide **40**.

Scheme 16. Reaction of 5 with O_2 to Yield the Aluminum Oxide 40 and the Hydrolysis of 40 with Water to Form the Aluminum Oxide Hydroxide 41



5 and 6). In the structure of **36**, an AlN_2C_3 and a six-membered $AlNC_4$ ring are present. These rings merge at the aluminum center, which is tetracoordinate with three nitrogen atoms and a carbon atom. The Al—C bond length (1.967 Å) is almost equal to that of **14** (1.961 Å) and is evocative of an Al—C single bond. In addition, the Al—NH bond length (1.840 Å) is comparable to the Al—NH bond length (1.858 Å) in **14**.

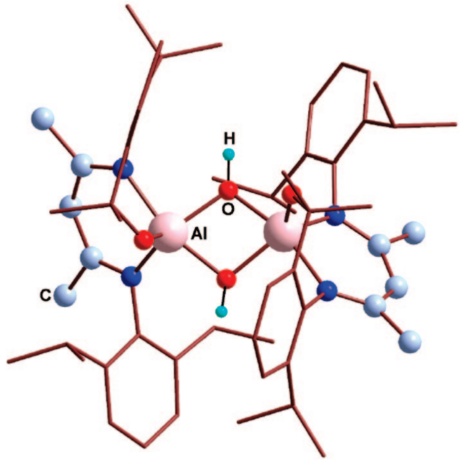
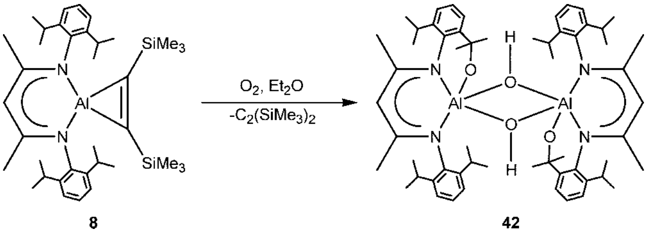


Figure 9. Molecular structure of the aluminum hydroxide **42**.

Scheme 17. Reaction of Aluminacyclopropene 8 with Molecular Oxygen to Form the Aluminum Hydroxide 42

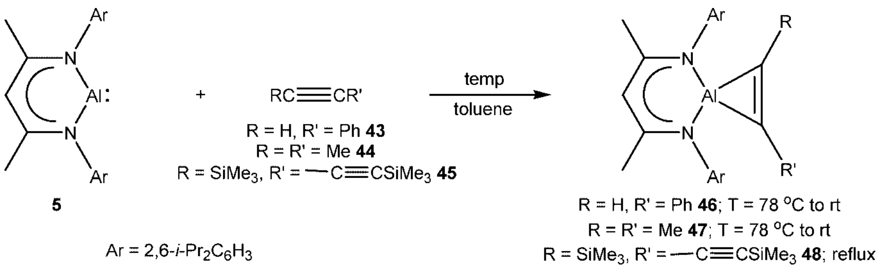


In the case of **37** two six-membered AlN_2C_3 and two six-membered $AlNC_4$ rings are present. In addition, there is a nonplanar four-membered $Al_2(\mu\text{-OH})_2$ ring. The aluminum centers are pentacoordinate, with two nitrogen atoms, two oxygen atoms, and a carbon atom. The Al—C (1.988_{av} Å) and the C_{Al}—C (1.552_{av} Å) bond lengths clearly indicate their single-bond nature. However, the former distances are slightly longer than the Al—C bond of **36**. In the four-membered $Al_2(\mu\text{-OH})_2$ ring the average Al—O bond length is 1.879 Å and the average O—Al—O angle is 73.88°. The Al—O—Al bond angle is 103.40°.

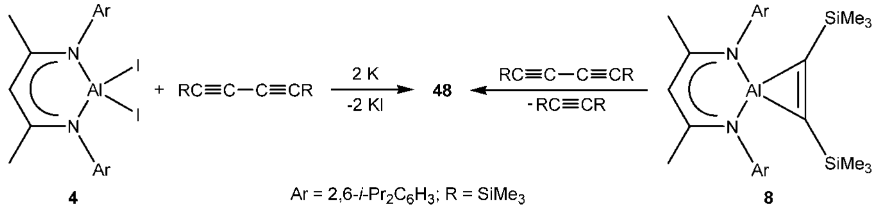
1.4.3. Reaction of 5 with *t*-BuSi(N_3)$_3$. Interestingly, a 1:1 reaction of LAl **5** with *t*-BuSi(N_3)$_3$ gave LAl(N_3)N[μ-Si(N_3)(*t*-Bu)]$_2$NAl(N_3)L (**39**), which contains a four-membered N_2Si_2 ring, as colorless crystals (83% yield) (Scheme 15).[52] The formation of compound **39** can be explained by considering the involvement of the intermediates **D** and **E**. Accordingly, the reaction of **5** with *t*-BuSi(N_3)$_3$ proceeds via an unstable monomeric imide, LAlNSi(*t*-Bu)(N_3)$_2$ (**D**), by eliminating a N_2 molecule. Then the migration of an N_3 group from the Si atom to the aluminum atom takes place to form intermediate **E**, with a formal N═Si bond. Ultimately, two molecules of **E** couple by a [2+2] cycloaddition reaction to give **39**, which contains a four-membered N_2Si_2 ring. The characteristic N_3 stretching frequencies (2113, 2067 cm^{-1}) were found in the IR spectrum of **39**.

The molecular structure of **39** (Figure 7) shows the presence of a planar (Δ = 0.010 Å) four-membered N_2Si_2 ring with both the N-AlL moieties oriented in a *syn* fashion due to the steric effect exerted by the *t*-Bu group on the silicon atoms. However, both the N_3 groups on the respective aluminum atoms are arranged *trans* to each other. The aluminum centers are

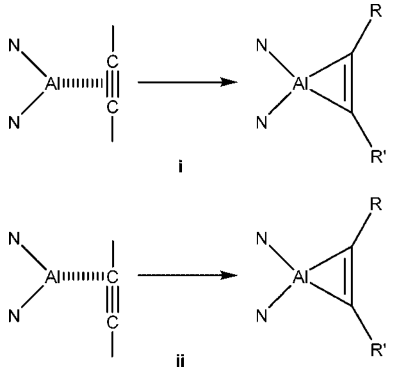
Scheme 18. Reaction of LAl with the Alkynes 43, 44, and 45



Scheme 19. Synthesis of Aluminacyclopropene 48 from 4 and 8



Scheme 20. Plausible Approaching Modes (i and ii) in the Interaction of LAl 5 with Alkynes



tetracoordinate (with two nitrogen atoms of the β-diketiminato ligand, one N_3 group, and one nitrogen atom of the N_2Si_2 ring) and adopt a distorted tetrahedral geometry. The LAl—N bond lengths (1.808, 1.812 Å) agree with those (1.781–1.819 Å) in the compound Cp*{$(Me_3Si)_2N$}AlN(μ-AlCp*)(μ-Al{N-$(SiMe_3)_2$})NAlCp*$_2$.[26c]

1.5. Reaction of 5 and 8 with Molecular Oxygen. It has been established in recent years that the reaction of alkylaluminum(III) compounds with oxygen leads to the formation of aluminum alkoxides[54] or alkylperoxides[55] by an insertion reaction into the Al—alkyl bond. Nevertheless, there is no report of a reaction of a monomeric Al(I) compound with molecular oxygen even though such a reaction has the potential to afford an alumoxane[56] directly. Therefore, the reaction of **5** with O_2 was studied in detail along with that of the aluminacyclopropene **8**, which contains an Al—alkenyl bond.

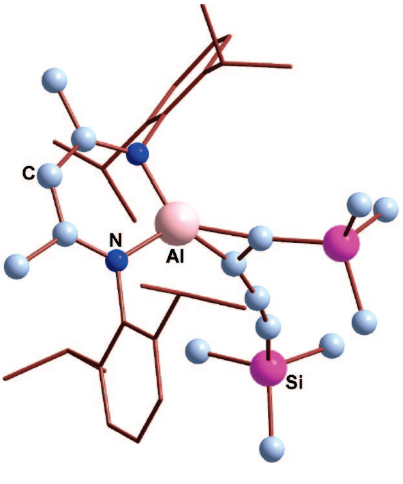
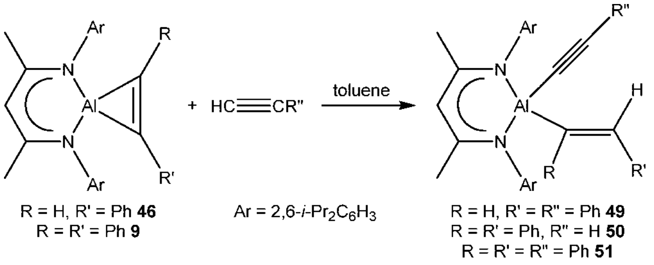


Figure 10. Molecular structure of the aluminacyclopropene derivative **48**.

Scheme 21. Preparation of Alkenylalkynylaluminum Derivatives 49–51



1.5.1. Reaction of 5 with O_2. In an oxygen atmosphere, two molecules of LAl **5** undergo oxidation and produce colorless crystals of aluminum oxide **40** in 80% yield (Scheme 16).[53] It is proposed that the intermediate LAl(η^2-O_2) is initially formed, and due to its kinetic instability, it reacts with another molecule of **5** to give **40**. This reaction is comparable to the matrix

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[54] (a) Ziegler, K. *Angew. Chem.* **1956**, *68*, 721–760. (b) Davies, A. G.; Roberts, B. P. *J. Chem. Soc. B* **1968**, 1074. (c) Lewiński, J.; Zachara, J.; Goś, P.; Grabska, E.; Kopeć, T.; Madura, I.; Marciniak, W.; Prowotorow, I. *Chem.—Eur. J.* **2000**, *6*, 3215–3227.

[55] Lewiński, J.; Zachara, J.; Grabska, E. *J. Am. Chem. Soc.* **1996**, *118*, 6794–6795.

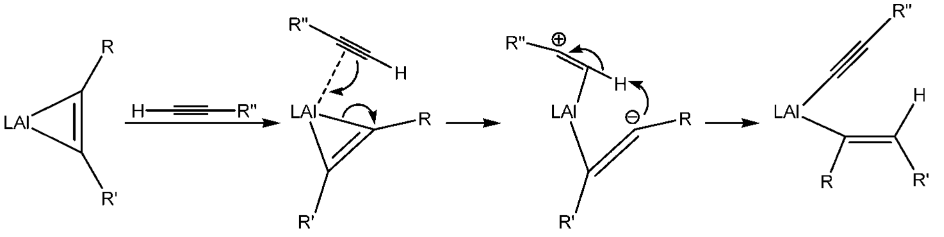
[56] (a) Sinn, H.; Kaminsky, W.; Vollmer, H.-J.; Woldt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 390–392. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99–149. (c) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971–4984. (d) Harlan, C. J.; Mason, M. R.; Barron, A. R. *Organometallics* **1994**, *13*, 2957–2969. (e) Uhl, W.; Koch, M.; Hiller, W.; Heckel, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 989–990. (f) Storre, J.; Schnitter, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Fleischer, R.; Stalke, D. *J. Am. Chem. Soc.* **1997**, *119*, 7505–7513. (g) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 8387–8388. (h) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391–1434. (i) Peng, Y.; Bai, G.; Fan, H.; Vidovic, D.; Roesky, H. W.; Magull, J. *Inorg. Chem.* **2004**, *43*, 1217–1219. (j) van Rensburg, W. J.; van den Berg, J.-A.; Steynberg, P. J. *Organometallics* **2007**, *26*, 1000–1013.

Table 1. Selected Bond Lengths and Bond Angles for 5, 8, 53, and Related Compounds

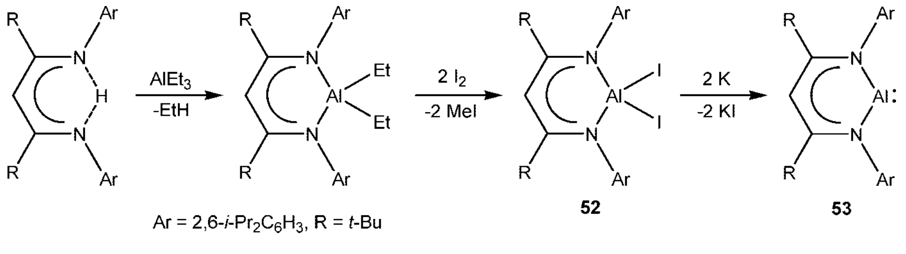
compound	Al−N^a$_{(av)}$ (Å)	X/X′	Al−X/Al−X′ (Å)	N^a−Al−N^a (deg)	X−Al−X′ (deg)	ref
5	1.957			89.86(8)		9
6	1.880	C/C	1.885(2)/1.878(2)	97.98(5)	42.30(7)	37
7	1.903	C/C	1.944(11)/1.962(11)	96.99(6)	110.8(4)	37
8	1.891	C/C	1.908(3)/1.899(3)	97.33(10)	42.57(11)	38
9	1.880	C/C	1.889(4)/1.894(3)	97.03(13)	42.02(14)	38
12	1.898	N/N	1.851(2)/1.815(15)	96.50(6)	87.15(7)	39
14	1.927	C/N	1.961(3)/1.858(2)	95.69	122.34(10)	41
25	1.879	C/O	1.770(22)/1.989(17)	98.61(6)	93.07(7)	38, 48
30	1.875	O/O	1.754(5)/1.745(5)	98.8(3)	104.7(3)	49
32	1.889	O/O	1.711(2)/1.695(2)	96.97(7)	115.38(8)	50
33	1.878	N/N	1.807(2)/1.847(1)	97.68(6)	90.39(6)	51
34	1.901	N/N	1.818(1)/1.854(1)	95.38(5)	85.08(5)	52
35	1.894	N/N	1.871(2)/1.842(2)	96.99(7)	87.38(8)	52
36	1.928	C/N	1.967(26)/1.840(16)	98.12(6)	101.98(6)	53
37	1.946, 2.011	O/O^b	1.852(6)/1.905(6), 1.850(1)/1.910(16)	91.06(6), 92.09(6)	73.92(5), 73.84(5)	53
39	1.912, 1.911	N/N	1.811(4)/1.852(5), 1.808(4)/1.839(5)	97.55(12), 97.06(12)	102.90(12), 101.18(11)	52
40	1.936	O/O	1.760(1)/1.763(1)	94.39(1)	90.86(5)	53
41	1.920, 1.915	O/O	1.738(3)/1.698(3), 1.741(3)/1.694(3)	95.64(13), 95.59(14)	112.34(13), 111.65(14)	58
42	1.954	O/O^c	1.868(2)/1.860(2), 1.862(3)/1.868(2)	94.77(10), 93.92(11)	75.09(10), 75.04(9)	61
48	1.882, 1.860	C/C	1.862(8)/1.909(9), 1.904(8)/1.918(9)	97.50(19), 98.78(19)	42.00(3), 43.40(3)	64
50	1.900	C/C	1.91(2)/1.952(2)	97.47(5)	114.22(7)	64
51	1.895	C/C	1.972(2)/1.941(2)	97.04(7)	111.15(8)	64
53	1.964^d			91.85(9)^d		77
54	1.904^d	C/N	2.003(5)/1.818(4)	100.38(13)^d	75.19(18)	77
55	−^{e}	C/N	2.020(2)/1.856(2)		72.38(7)	77
58^f	1.915^d	C/N	1.974(6)/1.838(4)	96.5(2)^d	92.00(2)	78
60	1.916^d	C/O	1.985(2)/1.704(2)	96.27(7)^d	113.25(8)	78
62	1.922^d	C/C	2.024(2)/1.962(2)	95.74(6)^d	91.92(6)	81
65b	1.908^d	C/C	1.989(2)/1.9842(19)	95.88(7)^d	72.94(8)	80

[a] If not mentioned, the nitrogen atoms are part of the ligand L. [b] The aluminum atoms are pentacoordinate and contain an Al−C bond (the distances are 1.989(5) and 1.986(3) Å. [c] With another Al−O bond the aluminum atoms are pentacoordinate (the Al−O bond lengths are 1740(2) and 1.741(2) Å. [d] The nitrogen atoms belong to the ligand system L′. [e] The ligand is [C(*t*-Bu)CHC(*t*-Bu)N(Ar)] (Ar = 2,6-*i*-$Pr_2C_6H_3$) [Al−N = 1.980(2), Al−C = 1.969(2) Å, N−Al−C = 86.71(8)]°. [f] Data for one of the two independent molecules are given.

Scheme 22. Proposed Mechanism for the Formation of Alkenylalkynylaluminum Derivatives 7, 49, 50, and 51



Scheme 23. Synthesis of L′Al 53



reaction of AlX (X = F, Cl, Br) with O_2.[57] Moreover, the reaction of **40**[53] with 1 equiv of water gave the known aluminum oxide hydroxide[58] **41**, with two terminal Al-OH groups. The aluminum oxide hydroxide **41** was formed even when a screw-capped NMR tube containing a solution of **40** was kept at room temperature for about one month.[53]

In the ^{1}H NMR spectrum of **40** the resonances due to the *i*-Pr methine and methyl protons appear as four septets and eight doublets. For one such methine (2.63 ppm (sept)) and methyl group (0.22 ppm (d)) the observed resonances are significantly upfield shifted (common range for methine: 4.14–3.06 (sept); methyl: 1.58–0.72 (d)). These observations suggest severe steric crowding in the structure of **40**, which is further supported by the appearance of an *i*-Pr methine carbon atom at 71.4 ppm in the ^{13}C NMR spectrum.

The X-ray structural analysis of **40** shows the expected structure with a planar $Al_2(\mu\text{-}O)_2$ core (Figure 8). The Al−O bond lengths (1.760, 1.763 Å) are appreciably shorter than that expected (1.96 Å, obtained by adding the atomic radii of Al

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(57) (a) Bahlo, J.; Himmel, H.-J.; Schnöckel, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 4696–4700. (b) Bahlo, J.; Himmel, H.-J.; Schnöckel, H. *Inorg. Chem.* **2002**, *41*, 2678–2689. (c) Bahlo, J.; Himmel, H.-J.; Schnöckel, H. *Inorg. Chem.* **2002**, *41*, 4488–4495.

(58) Bai, G.; Roesky, H. W.; Li, J.; Noltemeyer, M.; Schmidt, H.-G. *Angew. Chem., Int. Ed.* **2003**, *42*, 5502–5506.

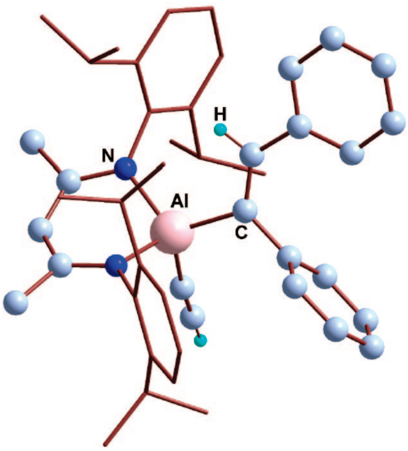

Figure 11. Molecular structure of the alkenylalkynylaluminum derivative **50**.

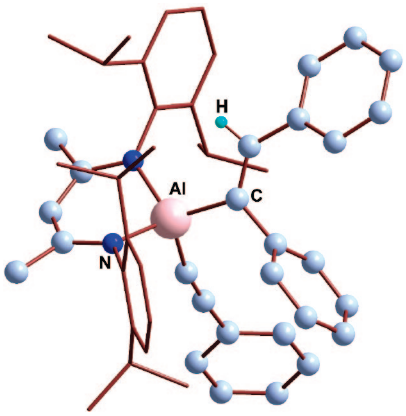

Figure 12. Molecular structure of the alkenylalkynylaluminum derivative **51**.

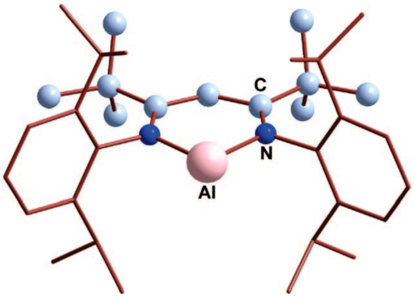

Figure 13. Molecular structure of L′Al **53**.

(1.3 Å) and O (0.66 Å)).[59] This may be due to the ionic character in the Al−O bonds.[60] The Al−O bond shortening makes the nonbonding distance between the two aluminum atoms small and subsequently creates steric crowding between the Ar substituents present in the *β*-diketiminato ligands, which was observed, *vide supra*, in the ^{1}H and ^{13}C NMR spectra of **40**. The O−Al−O and Al−O−Al bond angles found in **40** are 90.89° and 89.11°, respectively.

1.5.2. Reaction of 8 with O$_2$. The reaction of oxygen with the aluminacyclopropene **8** produced the C−H activated aluminum hydroxide **42** as a colorless solid in 45% yield (Scheme 17).[61] A plausible reaction pathway involves the insertion of an oxygen molecule into one of the Al−C bonds, which results in the formation of a peroxide intermediate. The O−O bond cleavage and the subsequent α-hydrogen abstraction from one of the CHMe$_2$ groups with elimination of an alkyne molecule result in the formation of **42**.

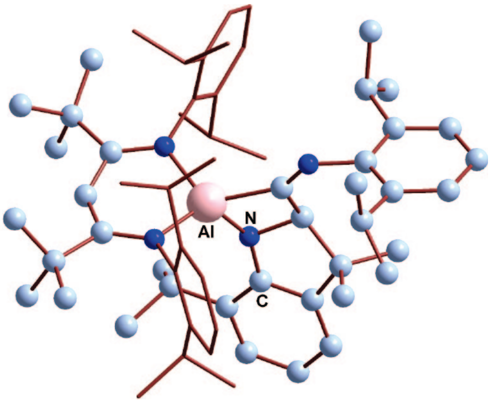

Figure 14. Molecular structure of compound **54**.

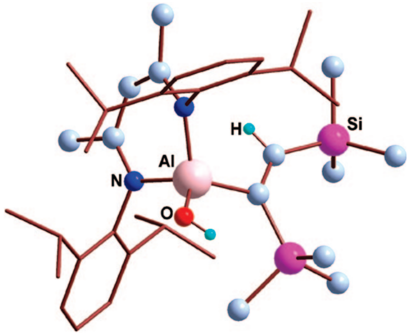

Figure 15. Molecular structure of the aluminum alkenyl hydroxide **60**.

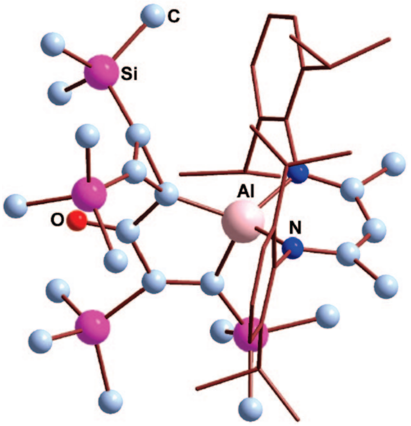

Figure 16. Molecular structure of the cyclopropenylaluminum derivative **62**.

The hydroxyl protons in the ^{1}H NMR spectrum of **42** appear as a singlet (0.85 ppm), and this value is shifted downfield when compared with that of the aluminum hydroxide **37** (0.29 ppm). A broad absorption band corresponds to the bridging hydroxyl groups in the IR spectrum of **42** (3450 cm^{-1}) and is comparable with **37** (3400 cm^{-1}).

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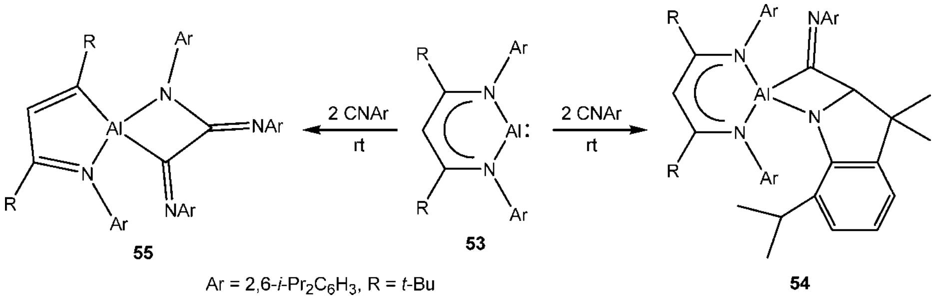
[59] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 221.

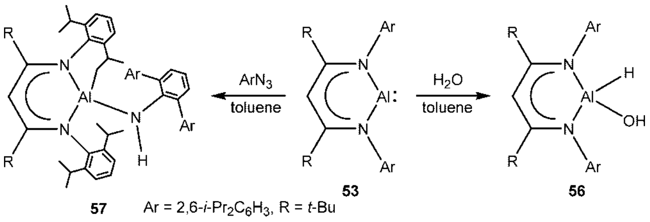
[60] Petrie, M. A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8704–8708.

[61] Li, X.; Song, H.; Duan, L.; Cui, C.; Roesky, H. W. *Inorg. Chem.* **2006**, *45*, 1912–1914.

Scheme 24. Reaction of L′Al 53 with 2,6-Diisopropylphenyl Isocyanide



Scheme 25. Reaction of L′Al 53 with H_2O and $2,6\text{-}Ar_2C_6H_3N_3$ ($Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3$)



Single crystals suitable for X-ray diffraction were obtained from the solution of **42** in diethyl ether at low temperature. The structure (Figure 9) shows a nonplanar four-membered Al_2O_2 ring ($\Delta = 0.137$ Å) and a six-membered $AlNC_3O$[62] ring. Both the aluminum atoms are pentacoordinate and adopt distorted trigonal bipyramidal geometry with two nitrogen and three oxygen atoms. The axial positions are occupied by one of the hydroxyl oxygen atoms and by a nitrogen atom of the β-diketiminato ligand. The Al−O$_{alkyl}$ (1.741, 1.740 Å) and the C−O (1.424, 1.402 Å) bond lengths are consistent with the usual Al−OR[50,63] (R = alkyl group) and C−O single bond lengths. The bridging Al−O distances are in the range 1.860 to 1.868 Å.[53]

1.6. Reaction of LAl with Mono- and Disubstituted Alkynes and Diyne. When LAl **5** reacted with 1 equiv of acetylene, aluminacyclopropene **6** was formed. Use of an excess of acetylene resulted in the formation of alkenylalkynylaluminum compound **7** (Scheme 4).[37] However, the reaction of **5** with $Me_3SiC{\equiv}CSiMe_3$ did not proceed under similar conditions.[38] In order to understand the underlying principles in the reaction of **5** with alkynes, we carried out detailed studies with $PhC{\equiv}CH$ **43**, $MeC{\equiv}CMe$ **44**, and $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ **45**.

1.6.1. Reaction of 5 with the Alkynes 43, 44, and 45. Similar to the reaction of LAl **5** with acetylene (Scheme 4), a 1:1 reaction of **5** with phenylacetylene **43** proceeded even at low temperature (−100 °C) to afford the aluminacyclopropene[64] **46** (Scheme 18) which has the tendency to react further with an excess of alkyne **43** (*vide infra*). The reaction of **5** with the dimethylacetylene **44** also occurred at very low temperature (Scheme 18), but the product **47** did not react with an excess of the alkyne.[64] In contrast, the diyne **45** reacted with **5** only in refluxing toluene and gave only the monoadduct aluminacyclopropene **48** (Scheme 18).[64] Like **47**, compound **48** is also inert toward **45**.

Interestingly, the aluminacyclopropene **48** can also be obtained by two other routes: (a) by the reductive coupling reaction of **4** with potassium in the presence of **45** (Scheme 19) and (b) by the substitution reaction of **8** with **45** (Scheme 19).[64]

Compounds **6**[37] and **46** have two (^{1}H NMR: 8.82 ppm (s)) and one (^{1}H NMR: 8.66 ppm (s)) AlC_2 ring C-H proton(s), respectively. In the ^{13}C NMR spectra, the AlC_2 ring carbon atoms in the compounds **6** and **46−48** resonate at the following frequencies: **6** 177.2; **46** 165.4, 170.2; **47** 169.4; **48** 190.0, 193.3 ppm. These values (proton and carbon resonances of the AlC_2 rings) are downfield shifted in comparison to the values found for the protons and carbon atom signals in the organic cyclopropenyl compounds.[65] However, the ^{13}C resonance (163.9 ppm) observed for a stannacyclopropene derivative[66] falls near the range (165.4 to 193.2 ppm) observed for compounds **6** and **46−48**. This is indicative of the distinct nature of the olefinic bond present in metallacyclopropenes.

The molecular structure of compound **48** was obtained by single-crystal X-ray diffraction studies (Figure 10). It is compared with the structure of the other aluminacyclopropenes **6**, **8**,[38] and **9**[38] in order to analyze systematically the bonding in the three-membered AlC_2 rings. The aluminum(III) center in **48** is tetracoordinate and is part of two ring systems, namely, the six-membered AlN_2C_3 and the three-membered AlC_2 rings. A dihedral angle of 88.55°$_{(av)}$ between these two ring planes indicates that they are orthogonally arranged to each other, and this is reminiscent of the situation found for the other structurally characterized aluminacyclopropenes **6**, **8**, and **9**. The Al−C and the C−C bond lengths (Table 1) in the AlC_2 ring of **48** are comparable to those of **6**, **8**, and **9**. Coupled with the theoretically obtained bonding parameters for $HAl(\eta^2\text{-}C_2H_2)$[67] the ranges for the Al−C and C−C bond lengths in the AlC_2 ring of these compounds are derived to be 1.844 to 1.918 Å and 1.356 to 1.395 Å, respectively.

The Al−C bonds are shorter than the usual covalent Al−C single bonds,[68] and the C−C bonds are longer than the normal C=C double bonds,[69] being in between single- and double-bond distances. To explain these observations and to understand the exact bonding situation in the AlC_2 ring of these aluminacyclopropenes, DFT calculations were carried out. An Al−C bond order (in the range of 1.01 to 1.10 for compounds **6**, **8**, **9**, **46**, and **48**) close to 1 is suggestive of an Al−C σ-bond and less π-electron delocalization over the AlC_2 ring. Such an indication is contradicted by the lowering of the C−C bond order (1.67 to 1.44 in the AlC_2 ring of compounds **6**, **8**, **9**, **46**,

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[62] Kumar, S. S.; Singh, S.; Roesky, H. W.; Magull, J. *Inorg. Chem.* **2005**, *44*, 1199–1201.

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[66] Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 5208–5209.

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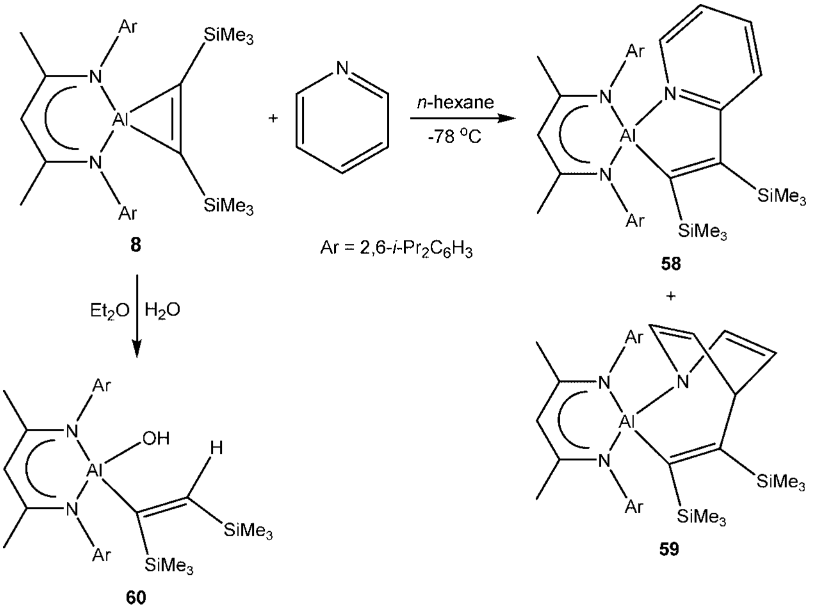
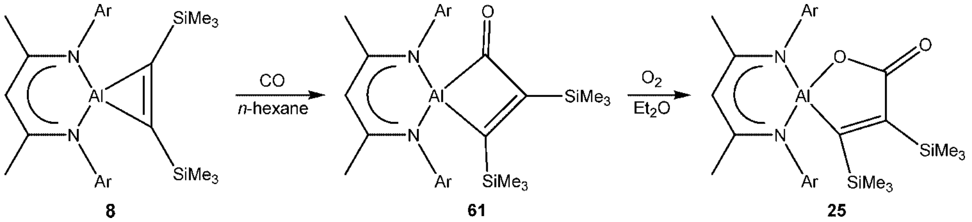
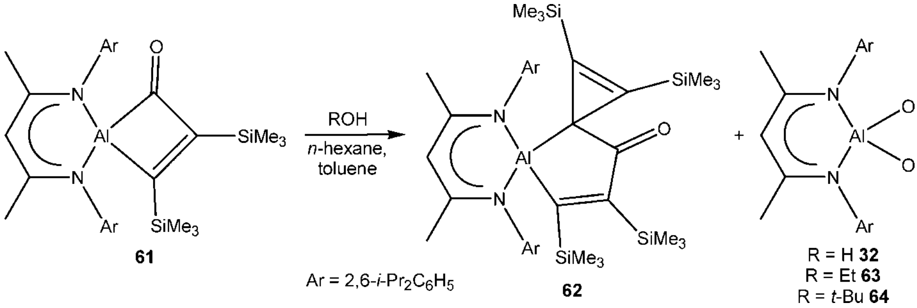
Scheme 26. Reaction of Aluminacyclopropene 8 with Pyridine and Water



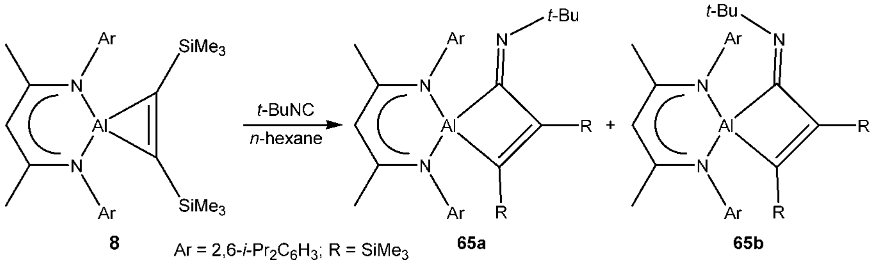
Scheme 27. Reaction of 8 with CO to Obtain the Aluminacyclobutenone 61 and Its Reaction with Molecular Oxygen



Scheme 28. Reaction of Aluminacyclobutenone 61 with Water, EtOH, and *t*-BuOH



Scheme 29. Reaction of 8 with *tert*-Butyl Isocyanide



and **48**) and is evocative of a π-electron delocalization. This situation can be compared with the borirenes, where the π-electron delocalization over the three-membered BC_2 ring is invoked by both experimental[70] and theoretical studies.[71] Thus the calculations on the model compound $HB(CH)_2$ (B−C vs C−C bond order: by INDO: 1.623 vs 1.737 and by SINDO1 1.614 vs 1.899) did not show any discrepancy as encountered with aluminacyclopropenes. Therefore, it can be concluded that the bonding situation is complex in the case of aluminacyclopropenes, and this may be due to the tetracoordinate tetrahedral

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(70) Eisch, J. J.; Shafii, B.; Odom, J. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 1847–1853.

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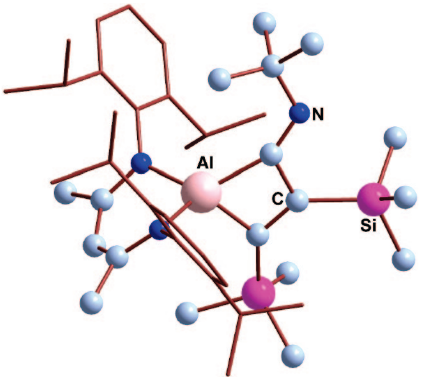
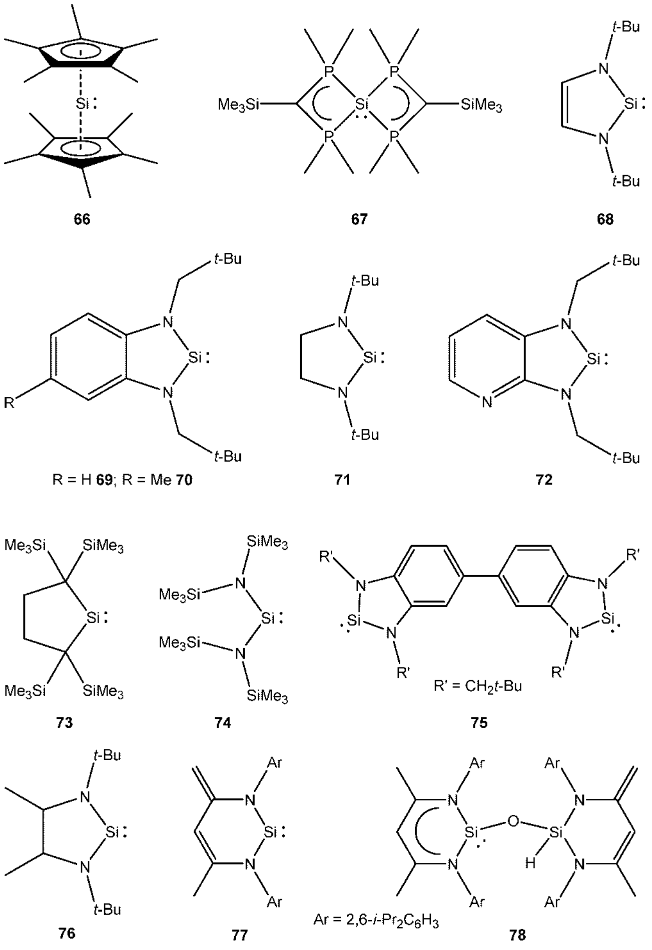


Figure 17. Molecular structure of the isomer **65b** with a C_3Al ring.

Chart 1. Diagram for the Silylenes 66 to 78



Al center with two fused ring systems. Similar studies by preparing an aluminacyclopropene with a planar tricoordinate Al center may untie these knots.[72] On the basis of the aforementioned observations, the reaction of **5** with an alkyne can be considered an oxidative cycloaddition. Calculations have shown that such reactions are driven by the complexation energy.[67] This means that the interaction between the Al(I) center and the carbon atoms of the C≡C bond correlates to the energy changes in the reaction system. Two interaction modes (**i** and **ii**) (Scheme 20) can be considered. In **i** the C≡C center is set close to the Al(I) center, and in **ii** one terminal carbon atom of the C≡C bond is arranged close to the Al(I) center.

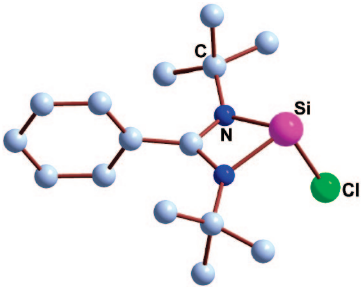


Figure 18a. Molecular structure of the chlorosilylene **81a**.

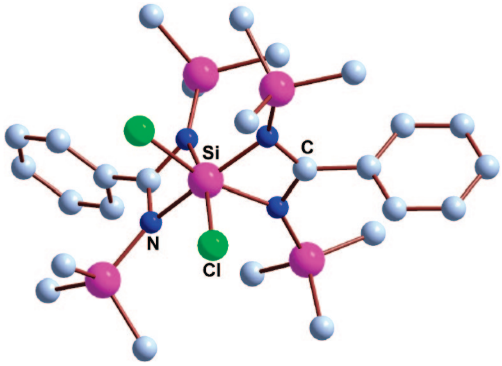


Figure 18b. Molecular structure of compound **81b** with hexacoordinate silicon atom.

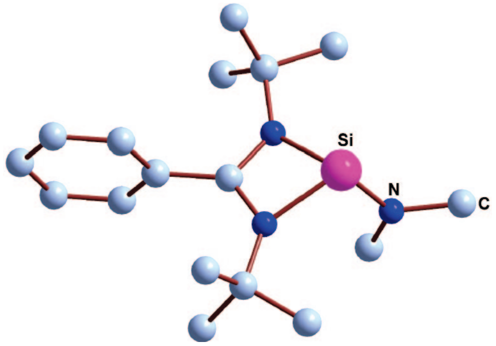


Figure 18c. Molecular structure of the silylene **81c** with an acyclic Si(II)−N bond.

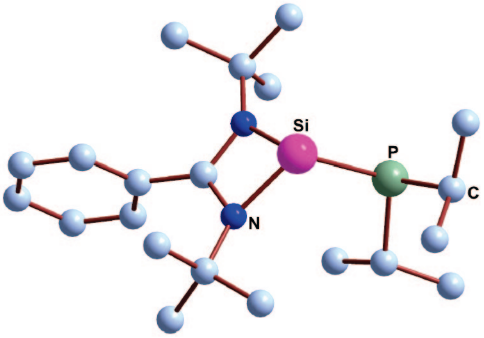


Figure 18d. Molecular structure of the silylene **81d** with an acyclic Si(II)−P bond.

By means of theoretical calculations (on the interaction of LAl with C_2H_2), we have shown that the approaching mode **i** involves an energy barrier of 145 kJ/mol and in mode **ii** there is no such energy barrier. Therefore, the latter mode is energetically favored and portrays that no activation energy is needed for the reaction of LAl with C_2H_2, which matches exactly

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(72) Volpin, M. E.; Koreshkov, Y. D.; Dulova, V. G.; Kursanov, D. N. *Tetrahedron* **1962**, *18*, 107–122.

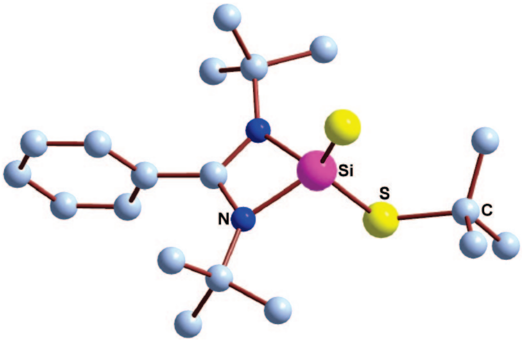
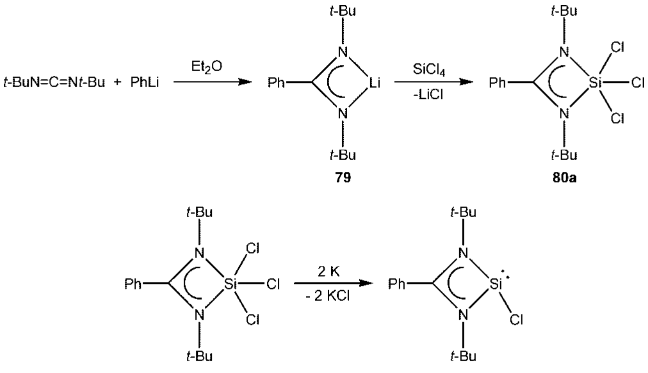


Figure 18e. Molecular structure of the silicon thioester analogue **81g** with the Si(=S)−S skeleton.

Scheme 30a. Synthesis of Chlorosilylene 81a



with our experimental observation (where **5** and acetylene reacted even at a temperature of −100 °C). Also the calculated Al−η^2-C_2 bond dissociation energies ($D_{\mathrm{Al}-\eta2\text{-}\mathrm{C_2}}$) in the compounds **6**, **8**, **9**, **46**, and **48** range from 155 to 82.62 kJ/mol. This reveals that the Al−η^2-C_2 bonding is weak[73] and provides an explanation for its reactive nature. In addition, it is explicit that the $D_{\mathrm{Al}-\eta2\text{-}\mathrm{C_2}}$ values are influenced by the substituents (R and R′) on the AlC_2 carbon atoms. This substituent effect (steric and electronic) therefore affects the complexation of LAl with alkynes. Thus, when **6** (R = R′ = H), **46** (R = H; R′ = Ph), and **47** (R = R′ = Me) were obtained at low temperatures, the compounds **8** (R = R′ = $SiMe_3$) and **9** (R = R′ = Ph) could be prepared only at room temperature. (The formation of **8** and **9** at room temperature was confirmed by NMR tube experiments.) Furthermore, the formation of compound **48** (R = $SiMe_3$; R′ = C≡C$SiMe_3$) requires refluxing conditions.

1.6.2. Reaction of Aluminacyclopropene 9 with Acetylene and 43. As mentioned earlier, the reaction of LAl **5** with an excess of acetylene gave the vinyl(ethynyl)aluminum derivative **7**, and it was proposed that its formation involves the intermediacy of **6**.[37] This is supported by the reaction of **5** with an excess of **43** in which the expected product **49** was formed as a colorless crystalline solid (Scheme 21).[64] To prove the intermediacy of aluminacyclopropene in these reactions, the reaction of aluminacyclopropene **9** was carried out with an excess of acetylene and phenylacetylene. As anticipated, the alkenylalkynylaluminum compounds **50** and **51** were formed exclusively (Scheme 21).[64]

In addition, it is proposed that the reaction of aluminacyclopropene with an alkyne proceeds by the route shown in Scheme 22. Even though the Al(III) center is tetracoordinate, the existing Lewis acidity may induce the initial formation of a π-complex.[73,74] Then an acetylenic proton migration to one of the olefinic carbon atoms occurs with opening of the AlC_2 ring. To support and further understand this process, the reaction of **9** with phenylacetylene in toluene-d_8 was monitored by ^{1}H NMR spectroscopy.[64] Evidence for the hydrogen migration process resulted, so the π-complexation of the aluminum(III) center by the alkyne is only a transition state.

The molecular structure of compounds **7**,[37] **49**, **50** (Figure 11), and **51** (Figure 12) were determined by single-crystal X-ray diffraction. The C=C double bond lengths and the C≡C triple bond lengths compare well with the values found for the organic olefins and acetylenes, respectively.[75] Similarly, the Al−C=C and Al−C≡C bond angles and the Al−$C_{C=C}$ and Al−$C_{C\equiv C}$ bond distances[68] are devoid of surprises. Therefore, one may state that the interaction of the π-electrons in the C−C multiple bonds with the adjacent Lewis acidic Al center is negligible.

1.7. Other Relevant Studies. By following our synthetic work, C. Cui and co-workers have reported the synthesis of aluminum(I) carbenoid L′Al (L′ = CH{(C*t*-Bu)(2,6-*i*-$Pr_2C_6H_3N$)}$_2$) **53** and examined its reactivity with an isocyanide (CNAr; Ar = 2,6-*i*-$Pr_2C_6H_3$), H_2O, and an azide (2,6-$Ar_2C_6H_3N_3$; Ar = 2,6-*i*-$Pr_2C_6H_3$). In addition, they have extended the chemistry of aluminacyclopropene **8** by studying the reaction of **8** with pyridine, H_2O, CO, and *t*-butyl isocyanide.

1.7.1. Synthesis and Reactions of L′Al 53. Reduction of the aluminum diiodide L′AlI_2 **52** with 2 equiv of potassium at room temperature gave L′Al **53** as red crystals (20%) (Scheme 23).[76,77] Compound **53**[77] is the second example of the aluminum(I) carbenoid family, and it has bulky *t*-Bu groups in the ligand skeleton instead of the methyl groups present in **5**.[9]

Compound **53** is thermally stable, and in contrast to **5** it is partially soluble in toluene. Analogous to **5** the molecular structure of **53** (Figure 13) shows the presence of a planar six-membered AlN_2C_3 ring.

The reaction of **53** with 1 equiv of 2,6-diisopropylphenyl isocyanide at low temperature gave a mixture of products from which compound **54** was isolated (30% yield).[77] If the same reaction was carried out at high concentration by adding 2 equiv of neat isocyanide CNAr to a suspension of **53** in toluene at room temperature, compound **54** could be obtained as yellow crystals (72% yield) (Scheme 24).

Interestingly, the reaction of **53** with 2 equiv of CNAr in a dilute solution of toluene at room temperature gave product **55** as purple crystals (61% yield) (Scheme 24).[77] Compounds **54** and **55** are stable and were not interconvertible. This suggests that these compounds are formed by two different mechanistic pathways.

The structure of **54** (Figure 14) consists of three heterocyclic rings. They are the six-membered C_3N_2Al, the four-membered C_2NAl, and the five-membered C_4N ring. The six- and the five-membered rings have the envelope conformation, and the four-membered ring is nearly planar. The six- and the four-membered rings are almost perpendicular to each other (86.4°), and the

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(73) Eisch, J. J. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Elsevier: Oxford, UK, 1982; pp 555–682.

(74) (a) Ziegler, K. In *Organometallic Chemistry*; Zeiss, H. H., Ed.; Reinhold Publishing Corp.: New York, 1960; pp 195–269. (b) Stucky, G. D.; McPherson, A. M.; Rhine, W. E.; Eisch, J. J.; Considine, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1941–1942. (c) Dolzine, T. W.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 1737–1740.

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(76) Budzelaar, P. H. M.; Oort, A. B. v.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485–1494.

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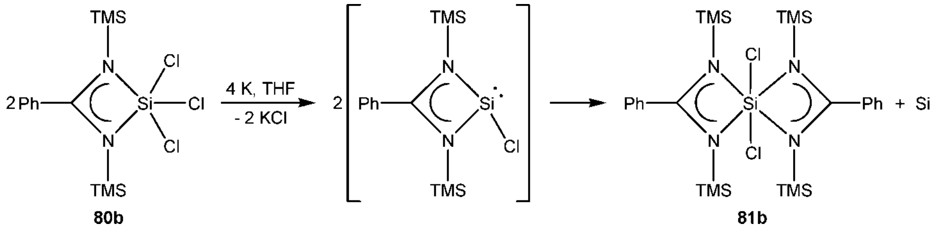
Table 2. ^{29}Si NMR Value for 81 and Related Silylenes

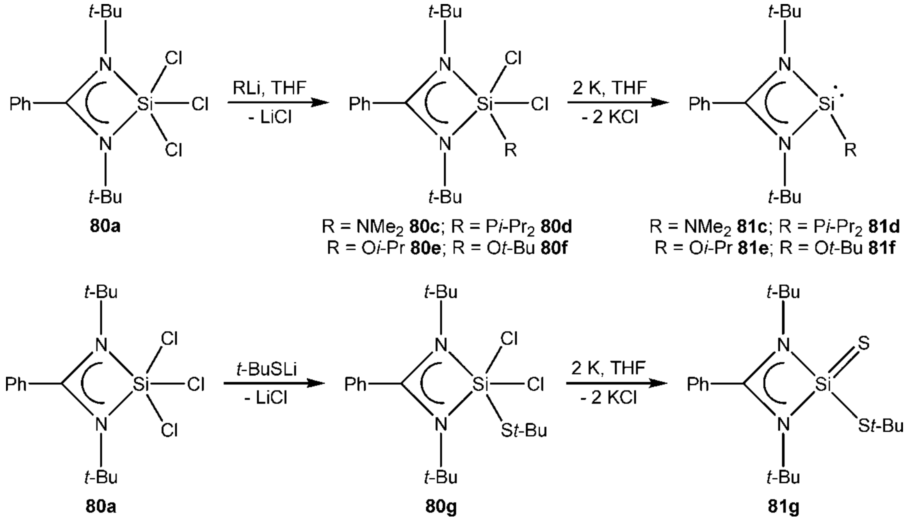
compound	solvent/ temperature (K)	^{29}Si NMR (ppm)	ref
$(\mathrm{Me_5C_5})_2\mathrm{Si}$, **66**	$\mathrm{C_6D_6}$/−	−398.00	87
$\mathrm{Si[(Me_2P)_2C(SiMe_3)]_2}$, **67**			88
$\mathrm{Si}(t\text{-BuNCHCHN}t\text{-Bu})$, **68**	$\mathrm{C_6D_6}$/rt	+78.30	5
$\mathrm{Si[N(CH_2}t\text{-Bu)]}_2\mathrm{C_6H_4}$-1,2, **69**	$\mathrm{C_6D_6}$/293	+96.92	90
$\mathrm{Si[N(CH_2}t\text{-Bu)]}_2\mathrm{C_6H_3}$-1,2-Me-4, **70**	$\mathrm{C_6D_6}$/293	+97.72	90
$\mathrm{Si}(t\text{-BuNCH_2CH_2N}t\text{-Bu})$, **71**		+119.00	91
$\mathrm{Si[N(CH_2}t\text{-Bu)]}_2\mathrm{C_5H_3N}$-1,2, **72**	$\mathrm{C_6D_6}$/−	+95.1	92
$\mathrm{Si[C(SiMe_3)_2CH_2]_2}$, **73**	$\mathrm{C_6D_6}$/−	+567.40	89
$\mathrm{Si[N(SiMe_3)_2]_2}$, **74**	THF−$\mathrm{C_6D_6}$/253	+223.90	85
$[\mathrm{Si\{(NCH_2}t\text{-Bu})_2\mathrm{C_6H_3}\text{-3,4}\}]_2$, **75**	$\mathrm{C_6D_6}$/298	+96.62	93
$\mathrm{Si}(t\text{-BuNCH(Me)CH(Me)N}t\text{-Bu})$,^{g} **76**	$\mathrm{C_6D_6}$/−	+123.4	94
$\mathrm{Si[CH(C(CH_2)2,6\text{-}}i\text{-}\mathrm{Pr_2C_6H_3N)(C(Me)\text{-}2,6\text{-}}i\text{-}\mathrm{Pr_2C_6H_3N)]}$, **77**	$\mathrm{C_6D_6}$/298	+88.4	95
$(\mathrm{Si[CH\{(CMe)(2,6\text{-}}i\text{-}\mathrm{Pr_2C_6H_3N)\}_2]) OSiH[CH(C(CH_2)2,6\text{-}}i\text{-}\mathrm{Pr_2 C_6H_3N)(C(Me)2,6\text{-}}i\text{-}\mathrm{Pr_2C_6H_3N)]}$, **78**	$\mathrm{C_6D_6}$/298	−7.9 and −9.6^{h}	96
$\mathrm{ClSi[(N}t\text{-Bu})_2\mathrm{CPh]}$, **81a**	$\mathrm{C_6D_6}$/298	+14.6	99
$\mathrm{Me_2NSi[(N}t\text{-Bu})_2\mathrm{CPh]}$, **81c**	$\mathrm{C_6D_6}$/298	−2.62	103c
$i\text{-}\mathrm{Pr_2PSi[(N}t\text{-Bu})_2\mathrm{CPh]}$, **81d**	$\mathrm{C_6D_6}$/−	56.2^{i}	103c
$i\text{-}\mathrm{PrOSi[(N}t\text{-Bu})_2\mathrm{CPh]}$, **81e**	$\mathrm{C_6D_6}$/−	−13.4	103c
$t\text{-}\mathrm{BuOSi[(N}t\text{-Bu})_2\mathrm{CPh]}$, **81f**	$\mathrm{C_6D_6}$/−	−5.19	103e

[g] Exists as a racemic mixture. [h] Two singlet resonances are due to the presence of two rotational isomers. [i] Appears as a doublet with $J_{\mathrm{Si\text{-}P}} = 154$ Hz (it shows a singlet resonance (−16.5 ppm) in its ^{31}P NMR spectrum).

Scheme 30b. Formation of Compound 81b with Hexacoordinate Silicon Atom by the Reduction of Amidinatotrichlorosilane 80b



Scheme 30c. Preparation of Silylenes 81c−81f and the Silicon Thioester Analogue 81g



angle between the four- and the five-membered rings is around 29°. In the structure of **55**, a five-membered $\mathrm{C_3NAl}$ ring and a four-membered $\mathrm{C_2NAl}$ ring can be seen. The former ring has an envelope conformation, the latter ring is planar, and the angle between them is 65°.

A 1:1 reaction of **53** with water resulted in the formation of hydroxyaluminum hydride **56** as colorless crystals (78%) (Scheme 25).[77] The 1:1 reaction of **53** with the azide (2,6-$\mathrm{Ar_2C_6H_3N_3}$) (Ar = 2,6-i-$\mathrm{Pr_2C_6H_3}$) afforded the derivative **57**, with an Al−NH bond, as yellow crystals (55%) (Scheme 25).[77]

This is in contrast to the reaction of **5** with (2,6-$\mathrm{Ar_2C_6H_3N_3}$) (Ar = 2,6-i-$\mathrm{Pr_2C_6H_3}$) (Scheme 7) in which two products[41] (**14** and **15**) were formed instead of a single product, **57**. Nevertheless, compound **57** is analogous to **14**, and its formation implies that even the bulkiness of **53** with t-Bu groups is not sufficient to stabilize the monomeric imide L′AlNAr. So far, compounds **56** and **57** have not been structurally characterized by X-ray structural analysis.

1.7.2. Reactions of Aluminacyclopropene 8 (with pyridine, H$_2$O, CO, and t-BuNC).

The regiospecific insertion of pyridine into one of the Al−C bonds of aluminacyclopropene **8** gave the (1,2-dihydropyridyl)aluminum derivative **58** as orange crystals (41%) along with minor amounts (10:1) of **59**

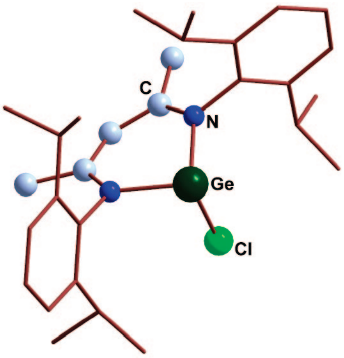


Figure 19. Molecular structure for the germylene monochloride **84**.

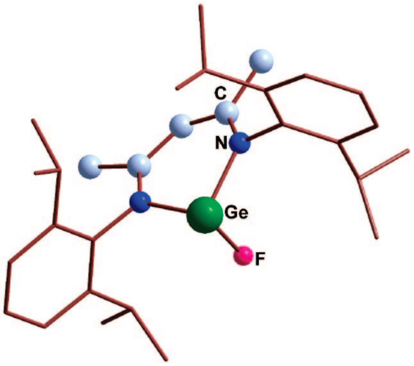


Figure 20. Structure of germylene monofluoride **86**.

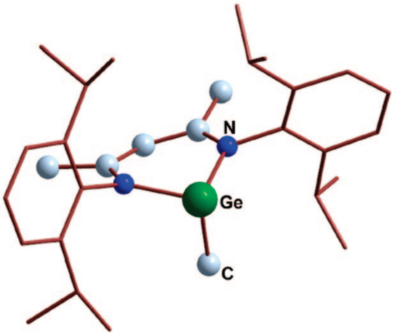
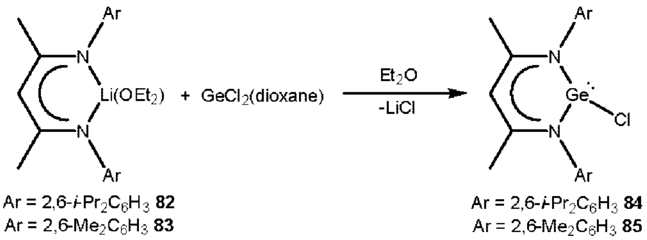
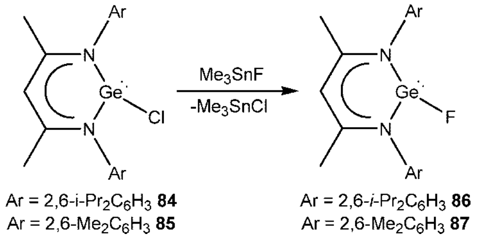


Figure 21. Molecular structure of methyl-substituted germylene **88**.

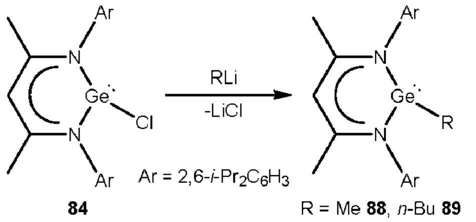
Scheme 31. Syntheses of Germylene Monochlorides 84 and 85



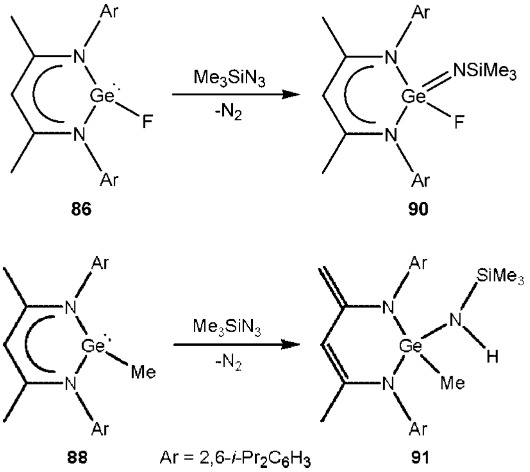
Scheme 32. Preparation of Ge(II) Fluorides 86 and 87



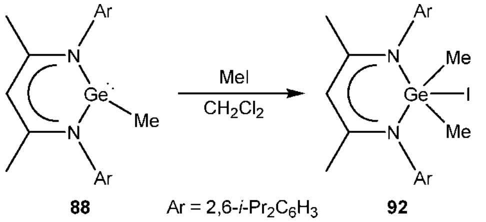
Scheme 33. Preparation of Alkyl-Substituted Germylenes 88 and 89



Scheme 34. Reaction of Trimethylsilyl Azide with Compounds 86 and 88



Scheme 35. Reaction of Germylene 88 with MeI



(Scheme 26).[78] It is assumed that **59** is the 1,4-addition product, and its solubility, similar to that of **58**, precludes its isolation in pure form. Interestingly, compound **58** is stable and did not undergo isomerization to the 1,4-dihydropyridyl derivative.[79] The hydrolysis of **8** with 1 equiv of water resulted in the cleavage of an Al−C bond to give aluminum alkenyl hydroxide **60** as colorless crystals (79% yield) (Scheme 26).[78]

In the structure of **58** the six-membered C_3N_2Al ring (in envelope conformation) is orthogonal (89.7°) to the planar five-membered C_3NAl ring. The structure of **60** (Figure 15) shows the presence of an Al−OH bond whose Al−O bond length (1.704 Å) is comparable to that of $[LAl(OH)_2]$ **32** (1.705_{av} Å).[50]

The insertion of oxygen-free CO into the Al−C bond of **8** afforded the aluminacyclobutenone derivative **61**, with a four-membered AlC_3 ring, as a pale yellow solid (72%) (Scheme 27).[80] The reaction of **61** with oxygen resulted in the selective

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[78] Li, X.; Duan, L.; Song, H.; Ni, C.; Cui, C. *Organometallics* **2006**, *25*, 5665–5667.

[79] Lichtenberger, D. L.; Hogan, R. H.; Healy, M. D.; Barron, A. R. *Organometallics* **1991**, *10*, 609–614.

[80] Li, X.; Ni, C.; Song, H.; Cui, C. *Chem. Commun.* **2006**, 1763–1765.

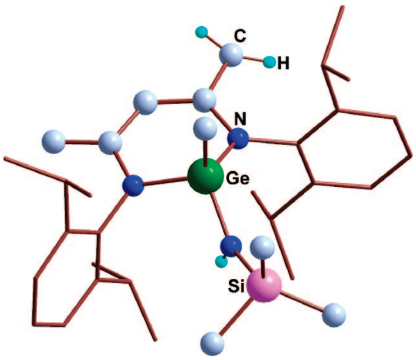


Figure 22. Molecular structure for the germanium compound **91**.

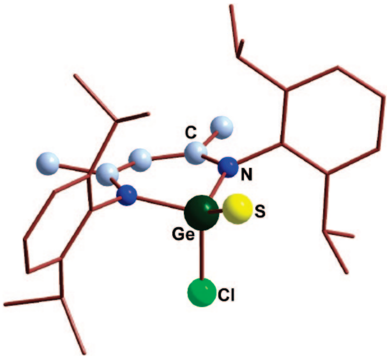


Figure 23. Molecular structure of germanethioacid chloride **93**.

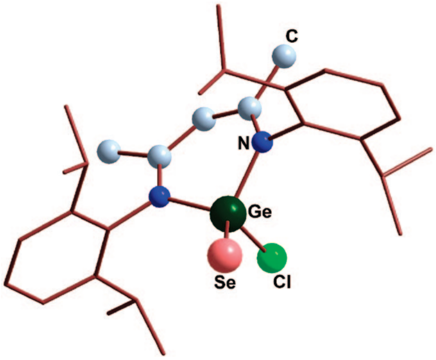


Figure 24. Molecular structure of germaneselenoacid chloride **94**.

insertion of an oxygen atom into the Al−C(O) bond[80] and gave a ring-expanded product, $\mathrm{LAl[OC(O)(CSiMe_3)_2]}$[38,48] (**25**), which had been obtained earlier in the reaction of **8** with CO_2 (Scheme 10).

Furthermore, the hydrolysis of the aluminacyclobutenone derivative **61** at low temperature gave the first example of a cyclopropenylaluminum compound[81] (**62**) as yellow crystals (59%) and the aluminum dihydroxide[50] $\mathrm{LAl(OH)_2}$ **32** as colorless crystals (20%) one after the other (Scheme 28). Similarly, the alcoholysis of **61** with EtOH and *t*-BuOH also gave **62** with the elimination of the corresponding aluminum monohydroxides **63** and **64**, respectively (Scheme 28).[81]

In the structure of **62** (Figure 16), the six-membered C_3N_2Al ring (in envelope conformation) is perpendicular to the five-membered C_4Al ring (89.13°). The latter ring is planar and is nearly perpendicular to the cyclopropene ring (86.76°). The single bond distance between the aluminum center and the spirocyclic carbon atom shows that the cyclopropene ring has an η^1-mode of connectivity to the aluminum center.

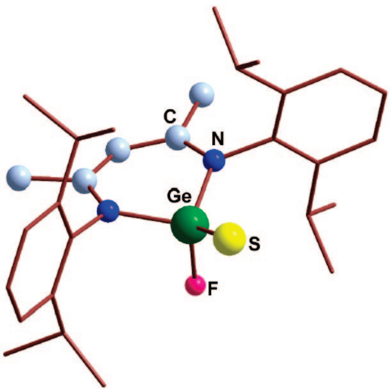
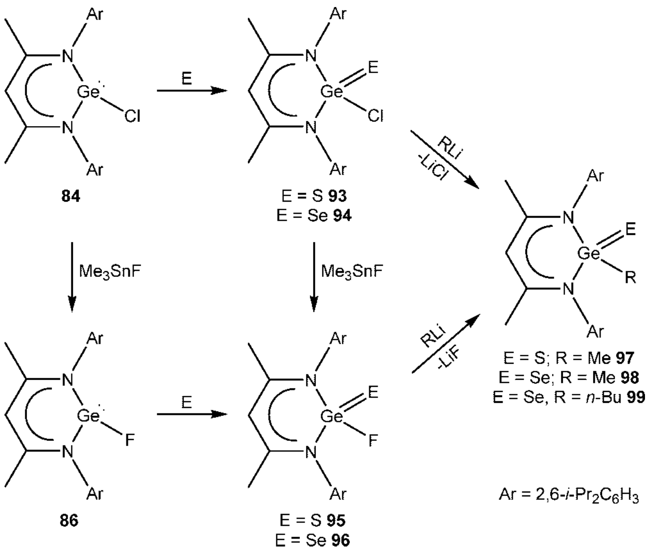
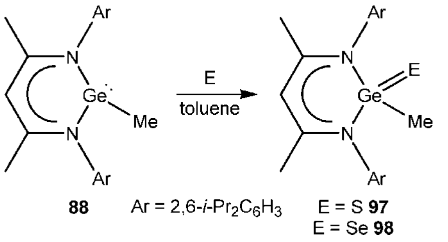


Figure 25. Molecular structure of germanethioacid fluoride **95**.

Scheme 36. Syntheses of Germanium Compounds 93–99 Formally Double Bonded to Chalcogens



Scheme 37. Preparation of Methyl Germanethione 97 and Methyl Germaneselone 98



The insertion of *tert*-butyl isocyanide into **8** at low temperature resulted in two isomeric aluminacyclobutene derivatives, **65a** and **65b**, as orange crystals (Scheme 29).[80] These two isomers arise due to two different orientations of the *t*-Bu group and are stable. They are inseparable and their interconversion was not possible.

The structure of the isomer **65b** (Figure 17) was determined by single-crystal X-ray diffraction studies, and it reveals the presence of a planar four-membered C_3Al ring that is orthogonal (89.20°) to the six-membered C_3N_2Al ring in envelope conformation. The aluminum center has a distorted tetrahedral

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[81] Gao, Y.; Cheng, X.; Song, H.; Zhang, J.; Cui, C. *Organometallics* **2007**, *26*, 1308–1310.

Table 3. NMR Spectral Data for the Germylenes and Their Derivatives[a]

compound	γ-CH (^{1}H NMR)	^{19}F/^{77}Se NMR	ref
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]GeCl$, **84**	5.14 (s)		113
$[CH\{(CMe)(2,6\text{-}Me_2C_6H_3N)\}_2]GeCl$, **85**	5.50^b (s)		118
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]GeF$, **86**	5.05 (s)	50.58/−	118
$[CH\{(CMe)(2,6\text{-}Me_2C_6H_3N)\}_2]GeF$, **87**	5.40^b (s)	54.46^b/−	118
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]GeMe$, **88**	4.80 (s)		122
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]Ge\text{-}n\text{-}Bu$, **89**	4.72 (s)		122
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]Ge(F)NSiMe_3$, **90**	4.98 (s)	71.05/−	118
$[CH(C(CH_2)2,6\text{-}i\text{-}Pr_2C_6H_3N)(C(Me)2,6\text{-}i\text{-}Pr_2C_6H_3N)]\text{-}GeMe(N(H)SiMe_3)$, **91**	5.25 (s)		122
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]GeMe_2I$, **92**	5.85 (s)		122
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]Ge(S)Cl$ **93**	4.96 (s)		129, 130
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]Ge(Se)Cl$, **94**	5.00 (s)	−/−287.90	130
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]Ge(S)F$, **95**	4.82 (s)	49.23/−	129, 130
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]Ge(Se)F$, **96**	4.89 (s)	54.2/−465.1	130
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]Ge(S)Me$, **97**	4.84 (s)		122, 129, 130
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]Ge(Se)Me$, **98**	4.81 (s)	−/−349	122, 130
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]Ge(Se)n\text{-}Bu$, **99**	4.93 (s)	−/−297	130
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]GeH(BH_3)$, **100**	4.88 (s)		118
$[CH\{(CMe)(2,6\text{-}Me_2C_6H_3N)\}_2]GeH(BH_3)$, **101**	5.32^b (s)		118
$[CH(C(CH_2)2,6\text{-}i\text{-}Pr_2C_6H_3N)(C(Me)2,6\text{-}i\text{-}Pr_2C_6H_3N)]GeH(BH_3)(Li(Et_2O)_3)$, **102**	5.38^c (s)		118
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]GeH$, **103**	4.92 (s)		137

[a] All the spectra were recorded in C_6D_6 if not mentioned. [b] In $CDCl_3$. [c] In toluene-d_8.

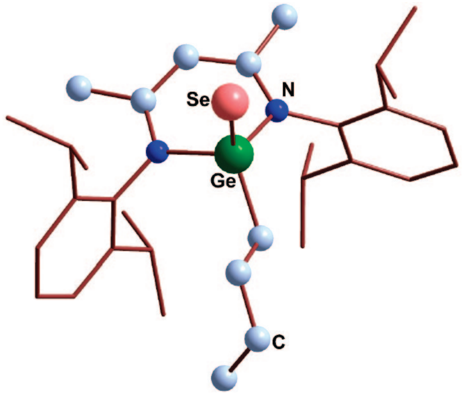
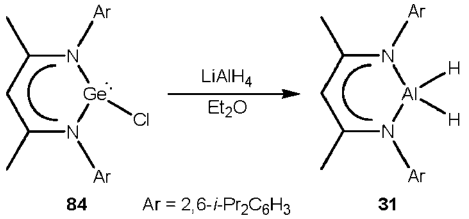
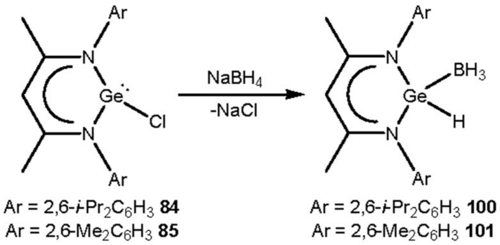


Figure 26. Molecular structure of *n*-butyl germaneselone **99**.

Scheme 38. Reaction of Germylene Chloride 84 with LiAlH$_4$



Scheme 39. Reaction of Germylene Chlorides 84 and 85 with NaBH$_4$



geometry, and the Al−C$_{=N}$ bond length (1.984 Å) agrees with the normal Al−C$_{sp2}$ single bond distance.[38]

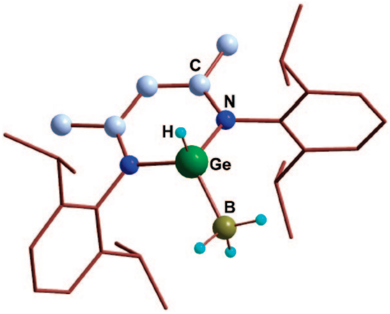
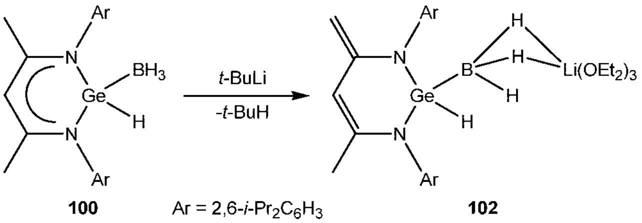


Figure 27. Molecular structure of germylene hydride adduct with BH$_3$ **100**.

Scheme 40. Reaction of Borane Adduct 100 with *tert*-Butyl Lithium



2. Silicon(II) Chemistry

2.1. Introduction. Silylenes (R_2Si:, R = alkyl or aryl) are neutral molecules with a formal divalent silicon atom. They are the heavier analogues of carbenes and normally have a singlet ground state ($^1A_1$), in contrast to the often observed typical triplet ground state of carbenes (N-heterocyclic- and dihalocarbenes are singlets) due to the large energy gap between the 3s and 3p orbitals of the silicon atom.[82] In organosilicon chemistry, they are key intermediates in various thermal and photochemical reactions. They are very reactive, and most of them decompose immediately at temperatures above 77 K.[83] However, by means of tailor-made synthetic strategies that utilize ligands with exact

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(82) Gaspar, P. P.; Xiao, M.; Pae, D. H.; Berger, D. J.; Haile, T.; Chen, T.; Lei, D.; Winchester, W. R.; Jiang, J. P. *J. Organomet. Chem.* **2002**, *646*, 68–79.

(83) Weidenbruch, M. *Coord. Chem. Rev.* **1994**, *130*, 275–300.

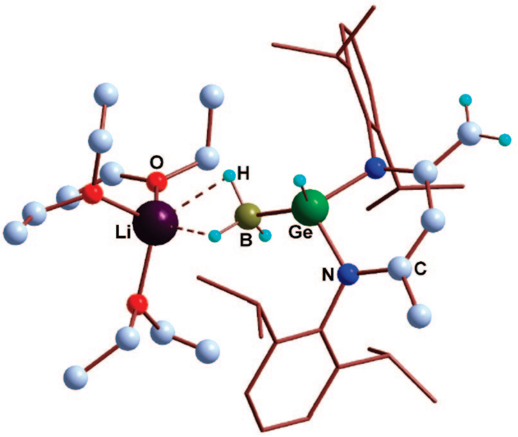


Figure 28. Molecular structure of lithium-coordinated borane adduct **102**.

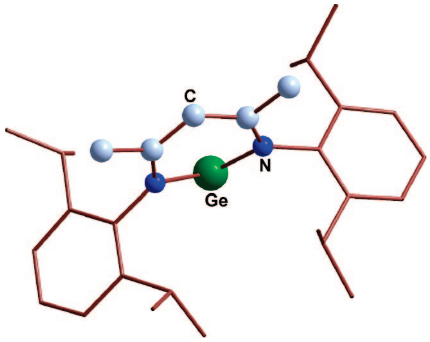
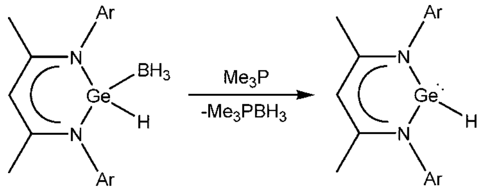


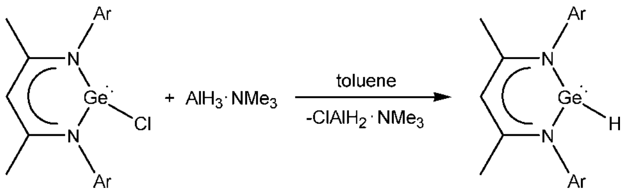
Figure 29. Molecular structure of germylene hydride **103**.

Scheme 41. Synthesis of Germylene Hydride 103



100 Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$ **103**

Scheme 42. Sythesis of Germylene Hydride 103 Starting from Germylene Chloride 84



84 Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$ **103**

steric and electronic balance, a fair number of stable silylenes have been prepared and characterized (Chart 1).[84] In this chart apart from the silylene **74**,[85] all the other silylenes are quite stable. The silylene **74** is an acyclic silylene, which is stable in solution below 0 °C. West and co-workers reported the first stable dicoordinate silylene (**68**) in 1994 by reducing the corresponding dichloride with potassium at elevated temperatures,[5,86] which is analogous to the N-heterocyclic carbene reported by Arduengo et al. in 1991.[2] Even though the silylenes **66**[87] (it crystallizes in two conformations: linear and bent; in Chart 1, the linear conformer is shown) and **67**[88] were known much earlier than the silylene **68**,[5] the former silylenes contain the formal Si(II) center with coordination number higher than two. Except for the kinetically stabilized dialkylsilylene[89] **73** of Kira et al., all the other cyclic diaminosilyenes (**68**−**72**[5,90–92] and **75**−**78**[93–96]) are stabilized electronically by the interaction between the π-type lone pair orbital of the nitrogen atoms and the vacant pπ-orbital of the divalent silicon atom. The N-heterocyclic silylene **75** reported by Lappert and co-workers[93] is the first example of a bis(silylene) and was obtained by reducing the corresponding bis(dichlorosilane) with potassium graphite. In the recent example of the siloxy silylene[96] **78** by Driess et al. there exists a formal Si(II)−O−Si(IV) bond, which is an example of a mixed-valent disiloxane. It was obtained by a 2:1 reaction of silylene **77**[95] with water as brown-red crystals.[96]

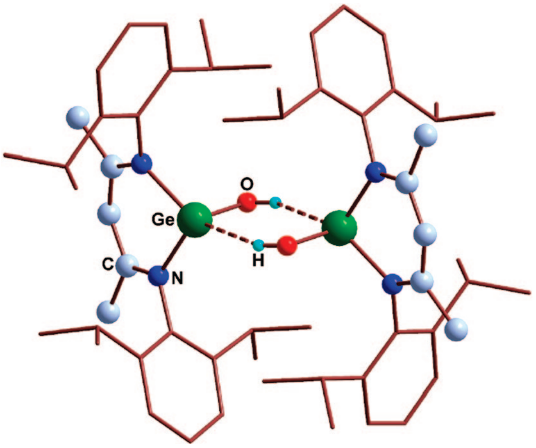


Figure 30. Molecular structure of germylene hydroxide **105**.

Although various stable silylenes are known, there is no example of a stable monochlorosilylene of the type RSiCl (R

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(84) (a) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373–381. (b) Tokitoh, N.; Okazaki, R. *Coord. Chem. Rev.* **2000**, *210*, 251–277. (c) Gehrhus, B.; Lappert, M. F. *J. Organomet. Chem.* **2001**, *617–618*, 209–223. (d) Hill, N. J.; West, R. *J. Organomet. Chem.* **2004**, *689*, 4165–4183. (e) Kira, M. *J. Organomet. Chem.* **2004**, *689*, 4475–4488. (f) Kira, M.; Iwamoto, T.; Ishida, S. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 258–275.

(85) Lee, G.-H.; West, R.; Müller, T. *J. Am. Chem. Soc.* **2003**, *125*, 8114–8115.

(86) (a) Denk, M.; Green, J. C.; Metzler, N.; Wagner, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2405–2410. (b) Haaf, M.; Schmiedl, A.; Schmedake, T. A.; Powell, D. R.; Millevolte, A. J.; Denk, M.; West, R. *J. Am. Chem. Soc.* **1998**, *120*, 12714–12719.

(87) (a) Jutzi, P.; Kanne, D.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 164. (b) Jutzi, P.; Holtmann, U.; Bögge, H.; Müller, A. *J. Chem. Soc., Chem. Commun.* **1998**, 305–306. (c) Jutzi, P.; Möhrke, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 762–763. (d) Jutzi, P.; Holtmann, U.; Kanne, D.; Krüger, C.; Blom, R.; Gleiter, R.; Hyla-Kryspin, I. *Chem. Ber.* **1989**, *122*, 1629–1639.

(88) Karsch, H. H.; Keller, U.; Gamper, S.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 295–296.

(89) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, *121*, 9722–9723.

(90) (a) Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Bläser, D. *J. Chem. Soc., Chem. Commun.* **1995**, *193*, 1–1932. (b) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Bläser, D. *J. Organomet. Chem.* **1996**, *521*, 211–220.

(91) West, R.; Denk, M. *Pure Appl. Chem.* **1996**, *68*, 785–788.

(92) Heinicke, J.; Oprea, A.; Kindermann, M. K.; Karpati, T.; Nyulászi, L.; Veszprémi, T. *Chem.−Eur. J.* **1998**, *4*, 541–545.

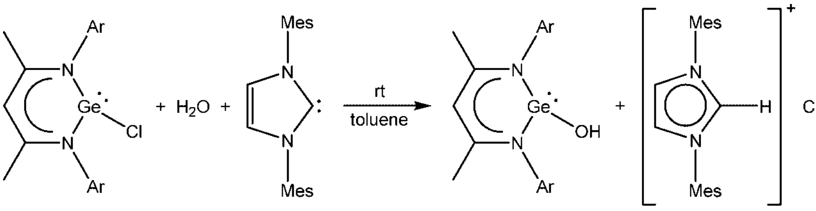
(93) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1383–1386.

(94) Li, W.; Hill, N. J.; Tomasik, A. C.; Bikzhanova, G.; West, R. *Organometallics* **2006**, *25*, 3802–3805.

(95) Driess, M.; Yao, S.; Brym, M.; van Wüllen, C.; Lentz, D. *J. Am. Chem. Soc.* **2006**, *128*, 9628–9629.

(96) Yao, S.; Brym, M.; van Wüllen, C.; Driess, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4159–4162.

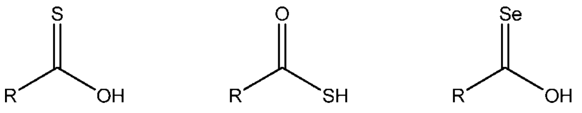
Scheme 43. Synthesis of Germylene Hydroxide 105



84 **104** **105** **106**

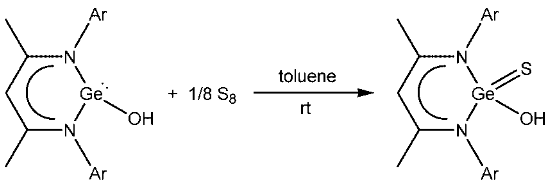
Ar = 2,6-*i*-$Pr_2C_6H_3$; Mes = 2,4,6-$Me_3C_6H_2$

Chart 2. Diagram for the Carboxylic Acids iii, iv, and v with Heavier Chalcogens



iii **iv** **v**

Scheme 44. Synthesis of Geranium Thionoacid 107



105 Ar = 2,6-*i*-$Pr_2C_6H_3$ **107**

= monoanionic ligand) that contains a Si(II)−Cl bond. Also, this would be a model compound for the silicon dichloride ($SiCl_2$) that is unstable at room temperature.[97] We were able to achieve this milestone by exploiting the donor ability of the amidinato ligand[98] with the *tert*-butyl substituents on the nitrogen atoms.

2.2. Synthesis and Structure of Chlorosilylene 81. The 1:1 reaction of *tert*-butylcarbodiimide with phenyllithium in ether gave the amidinatolithium compound **79**, which upon subsequent treatment with silicon tetrachloride afforded the amidinatotrichlorosilane **80a** in 47% yield (Scheme 30a).[99] The reduction of **80a** with 2 equiv of finely divided potassium at room temperature resulted in amidinatochlorosilylene **81a** as colorless crystals (10% yield) (Scheme 30a).[99,100]

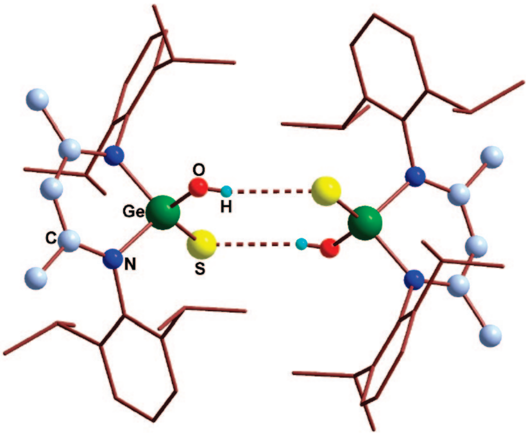
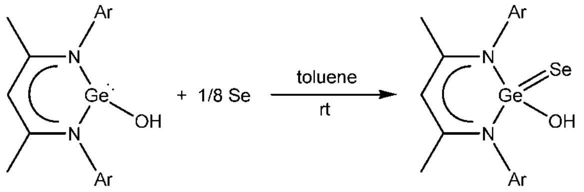


Figure 31. Molecular structure of germanium thionoacid **107**.

Scheme 45. Synthesis of Germanium Selenoacid 108



105 Ar = 2,6-*i*-$Pr_2C_6H_3$ **108**

Scheme 46. Thermodynamic Cycle Used for Calculating the Acid Strength of 107 and 108

$$\begin{tikzcd} BH_{(g)} \arrow[r] \arrow[d, "A"] & B^{-}_{(g)} \arrow[d, "C"] & + & H^{+}_{(g)} \arrow[d] \\ BH_{(aq)} \arrow[r] & B^{-}_{(aq)} & + & H^{+}_{(aq)} \end{tikzcd}$$

The chlorosilylene **81a** shows excellent solubility in organic solvents and is thermally stable. In the ^1H NMR spectrum the resonance due to the *t*-Bu groups appears as a singlet (1.08 ppm) and is slightly upfield shifted when compared with the amidi-

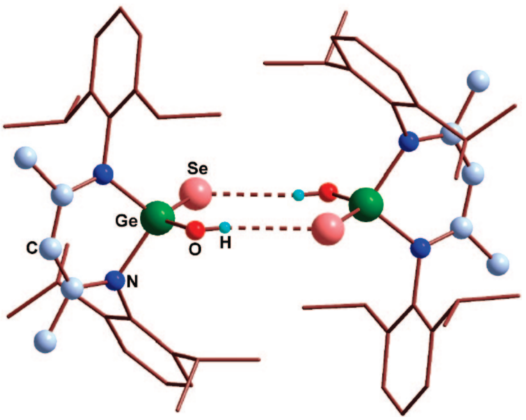


Figure 32. Molecular structure of germanium selenoacid **108**.

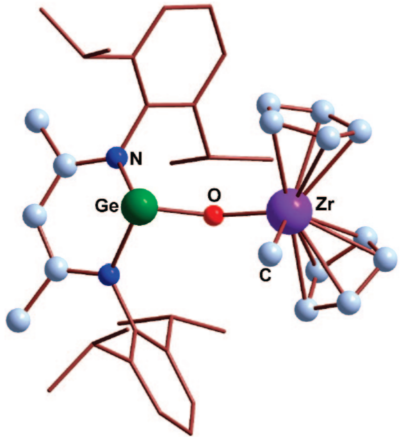
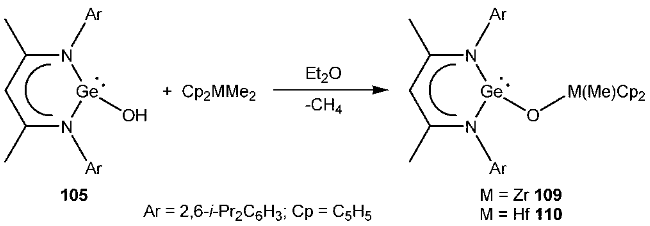
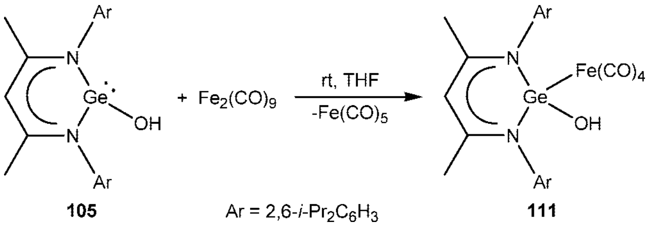


Figure 33. Molecular structure of the heterobimetallic oxide **109** with the Ge(II)−O−Zr motif.

Scheme 47. Syntheses of Heterobimetallic Oxides 109 and 110



Scheme 48. Synthesis of Germanium Hydroxide, with a Ge−Fe Bond, 111 from the Ge(II) Hydroxide 105



natotrichlorosilane **80a** (1.17 ppm). Also, the ^{29}Si NMR spectrum shows a singlet resonance (14.6 ppm) for the tricoordinate silicon atom of **81a** and is significantly downfield shifted relative to the pentacoordinate silicon atom present in trichlorosilane **80a** (−98.6 ppm). The ^{29}Si NMR spectral data of the silylene provide one of the important means to assess the degree of electronic perturbation.[84e,101] A detailed comparison with the ^{29}Si NMR values for the other silylenes **66**−**78** is shown in Table 2. The electronically least perturbed silylene, **73**, appears at +567.40 ppm, and due to the N−Si π-overlap that leads to electronic perturbation in N-heterocyclic (five- and six-membered) silylenes (**68**−**72** and **75**−**77**), the deshielding is greatly reduced and appears between +78.30 and +123.40. A value of +14.6 ppm for the chlorosilylene **81a** indicates that the deshielding is further reduced when compared with the five- and six-membered N-heterocyclic silylenes (**68–72** and **75–77**). The molecular structure of **81a** (Figure 18a) shows a four-membered CN_2Si ring.

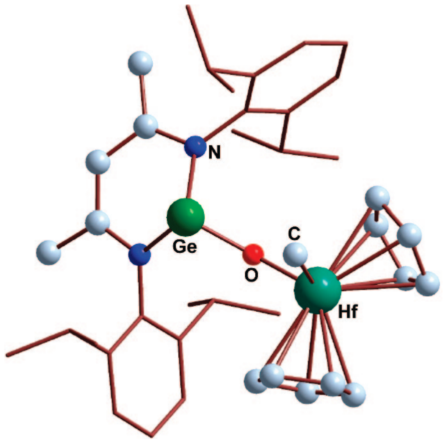


Figure 34. Molecular structure of the heterobimetallic oxide **110** with the Ge(II)−O−Hf motif.

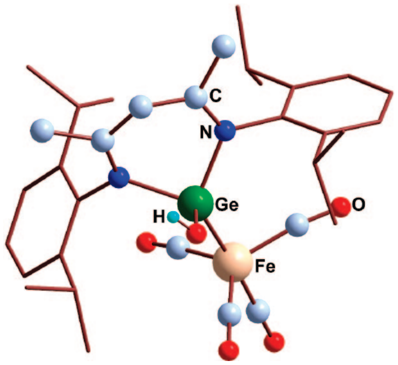


Figure 35. Molecular structure of germanium hydroxide **111** with a Ge−Fe bond.

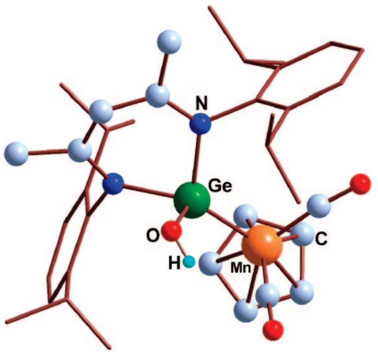
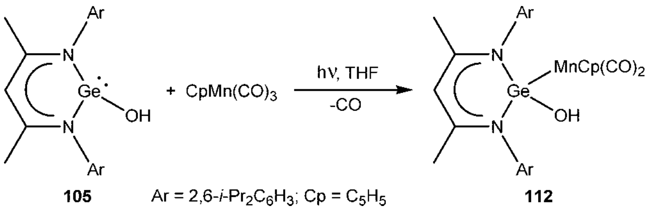
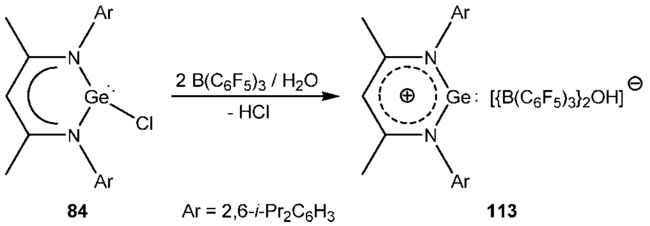


Figure 36. Molecular structure of germanium hydroxide **112** with a Ge−Mn bond.

Scheme 49. Synthesis of Germanium Hydroxide, with a Ge−Mn Bond, 112 Starting from the Ge(II) Hydroxide 105



Scheme 50. Synthesis of Germylenium Cation 113



The Si(II) center is tricoordinate (with two nitrogen atoms of the amidinato ligand and a chlorine atom) and has a trigonal pyramidal geometry with a stereoactive lone pair of electrons. The Si(II)−Cl bond length (2.156 Å) agrees well with the Si−Cl bond lengths (2.120 and 2.088 Å) found in perchloropolysi-

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(97) (a) Schmeisser, M.; Voss, P. *Z. Anorg. Allg. Chem.* **1964**, *334*, 50–56. (b) Timms, P. L. *Inorg. Chem.* **1968**, *7*, 387–389. (c) Timms, P. L. *Acc. Chem. Res.* **1973**, *6*, 118–123.

(98) (a) Bailey, P. J.; Pace, S. *Coord. Chem. Rev.* **2001**, *214*, 91–141. (b) Baker, R. J.; Jones, C. *J. Organomet. Chem.* **2006**, *691*, 65–71. (c) Coles, M. P. *Dalton Trans.* **2006**, 985–1001.

(99) So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 3948–3950.

(100) Weidenbruch, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 4241–4242.

(101) Müller, T. *J. Organomet. Chem.* **2003**, *686*, 251–256.

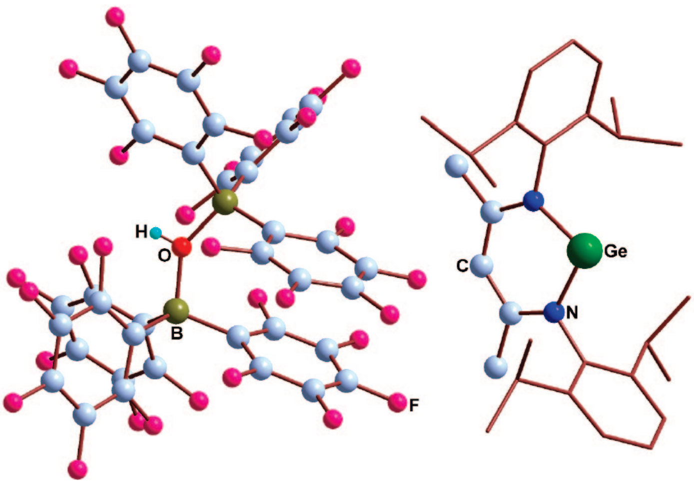


Figure 37. Molecular structure of the germylenium cation **113**.

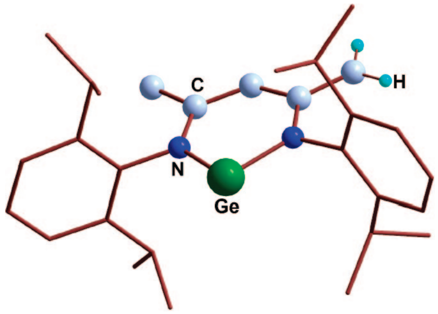
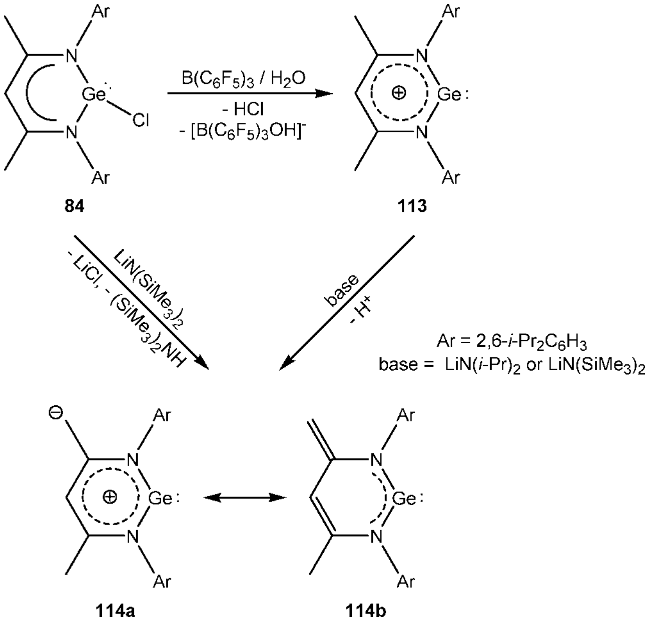


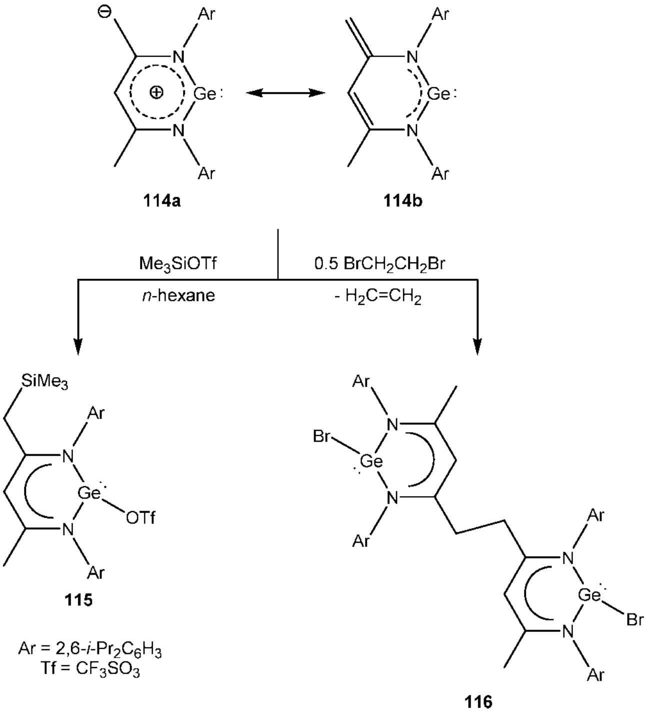
Figure 38. Molecular structure of the heterofulvene-like germylene **114**.

Scheme 51. Synthesis of Heterofulvene-like Germylene 114



lane[102] $[SiCl_2]_n$ and also matches the Si−Cl bond length (2.083 Å) found for the gaseous silicon dichloride by means of electron-diffraction studies. The acute N−Si−N (68.35°) bond angle of **81a** compares well with similar bond angles (68.8° and 69.0°) found for the hexacoordinate silicon in $[MeC(Ni\text{-}Pr)_2]_2SiCl_2$.[103a]

Scheme 52. Reaction of Germylene 114 with Me_3SiOTf and $BrCH_2CH_2Br$



The N−Si−Cl bond angles in the silylene monochloride **81a** are 95.82° and 96.56°.

Theoretical calculations further reveal the bonding situation present in chlorosilylene **81a**. The pure p-orbital of the silicon atom and the p-rich hybrid orbital of the chlorine atom overlap to form the Si−Cl bond. The contribution of the nitrogen atom to the Si−N bond is 85% and is made by the overlap of a nitrogen orbital with s character and a pure p-orbital of the silicon atom. Also, this sort of orbital overlapping accounts for the acute N−Si−N bond angle (*vide supra*) present in the silylene **81a**.

In order to prepare chlorosilylenes with different substituents on the ligand backbone, reduction of amidinatotrichlorosilane **80b**[103b] (containing trimethylsilyl groups on nitrogen atoms) was carried out with 2 equiv of potassium (Scheme 30bb).[103c] Instead of the expected chlorosilylene $[PhC(NTMS)_2]SiCl$, compound **81b** with hexacoordinate silicon atom was formed.[103c]

This is due to the less bulky trimethylsilyl groups that make $[PhC(NTMS)_2]SiCl$ unstable and favor a disproportionation

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(102) Koe, J. R.; Powell, D. R.; Buffy, J. J.; Hayase, S.; West, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1441–1442.

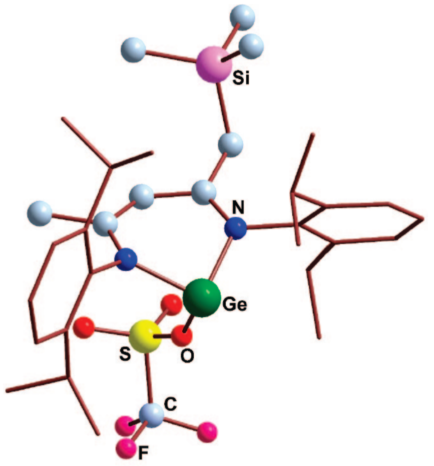

Figure 39. Molecular structure of (trifluoromethylsulfonato)germylene **115**.

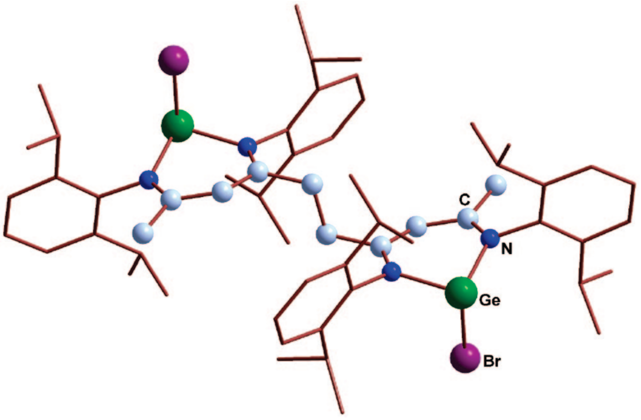

Figure 40. Molecular structure of bis(bromogermylene) **116**.

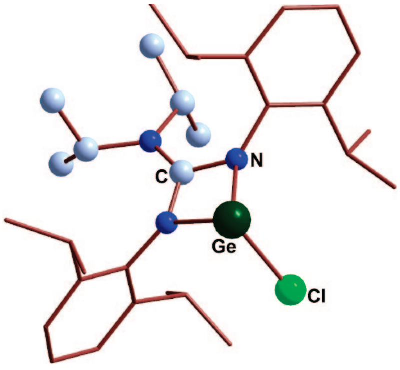

Figure 41. Molecular structure of guanidinato germylene chloride **120**.

reaction to give **81b** and silicon (Scheme 30b), which is supported by DFT calculations ($\Delta H = -65$ kcal/mol). The resonance for the hexacoordinate silicon (−175.98 ppm) in the ^{29}Si NMR spectrum of **81b** is comparable to that of [MeC(N*i*-Pr)$_2$]$_2$SiCl$_2$ (−169.33 ppm).[103a] The structure of **81b** was confirmed by single-crystal X-ray diffraction (Figure 18b), and the bonding parameters agree with that of [MeC(N*i*-Pr)$_2$]$_2$SiCl$_2$.[103a]

To confirm the effect of substituents on the nitrogen atoms, amidinatotrichlorosilanes [PhC(N*i*-Pr)$_2$]SiCl$_3$, [PhC(NCy)$_2$]SiCl$_3$, and [PhC(NAr)$_2$]SiCl$_3$[103d] (Cy = *c*-C$_6$H$_{11}$; Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) were prepared and reduced with 2 equiv of potassium at room temperature.[103c] None of these precursors produced chorosilylene, and this study underlines the importance of the substituents on the nitrogen atoms to obtain a stable chlorosilylene. To understand the substituent effect at the carbon atom of the amidinato ring, compounds [*t*-BuC(N*t*-Bu)$_2$]SiCl$_3$ and [*i*-PrC(N*t*-Bu)$_2$]SiCl$_3$ were prepared (by replacing the Ph group of **80a** by *t*-Bu and *i*-Pr groups, respectively) and reduced.[103c] Reduction with potassium did not result in chlorosilylene but revealed that an aromatic substituent is required to stabilize the electron density present in the delocalized amidinato ring.

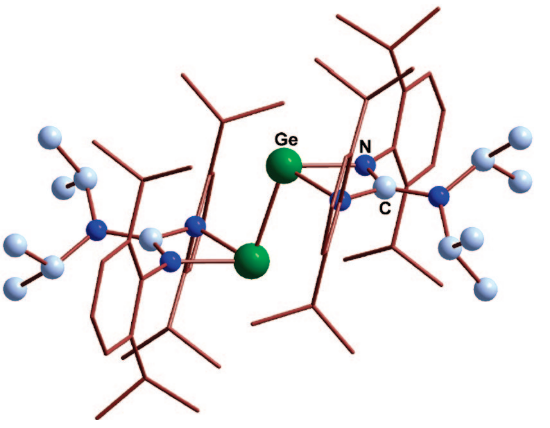

Figure 42. Molecular structure of the germanium(I) dimer **122**.

By adopting the protocol used for the synthesis of chlorosilylene **81a**, we aimed at the synthesis of unusual heteroleptic silylene L″SiR (L″ = (N*t*-Bu)$_2$CPh) (R = NMe$_2$, P*i*-Pr$_2$, O*i*-Pr, O*t*-Bu, S*t*-Bu). Accordingly, substituted amidinatodichlorides **80c**−**80g** ([PhC(N*t*-Bu)$_2$]SiCl$_2$R; R = NMe$_2$ **80c**, P*i*-Pr$_2$ **80d**, O*i*-Pr **80e**, O*t*-Bu **80f**, S*t*-Bu **80g**) were prepared by a 1:1 reaction of **80a** with RLi (R = NMe$_2$, P*i*-Pr$_2$, O*i*-Pr, O*t*-Bu, S*t*-Bu) and reduced with 2 equiv of potassium at ambient temperature (Scheme 30c).[103c,e]

While compounds **80c**−**80f** gave the expected silylenes **81c**−**81f** ([PhC(N*t*-Bu)$_2$]SiR; R = NMe$_2$ **81c**, P*i*-Pr$_2$ **81d**, O*i*-Pr **81e**, O*t*-Bu **81f**), compound **80g** resulted in the first silicon thioester analogue [PhC(N*t*-Bu)$_2$]Si(S)S*t*-Bu, **81g**. It is interesting to note that compounds **81c** and **81d** are the first stable silylenes with acyclic Si(II)−N and Si(II)−P bonds, respectively.

Silylenes **81c**−**81f**[103c] and the silicon thioester analogue **81g**[103e] showed good solubility in common organic solvents. In the ^{29}Si NMR spectra (**81c**, **81e**, and **81f**), the resonances for Si(II) centers appear as singlets (−2.64, −13.4, and −5.19 ppm) and are upfield shifted in comparison with that of chlorosilylene **81a** (14.6 ppm) due to the shielding caused by electron-donating substituents (NMe$_2$, O*i*-Pr, and O*t*-Bu), respectively. In contrast, the Si(II) center of **81d** appears as a doublet (56.2 ppm, $J_{\text{Si-P}} = 154$ Hz) in its ^{29}Si NMR spectrum and is downfield shifted with respect to that of chlorosilylene **81a** (14.6 ppm). Theoretical calculations explain this observa-

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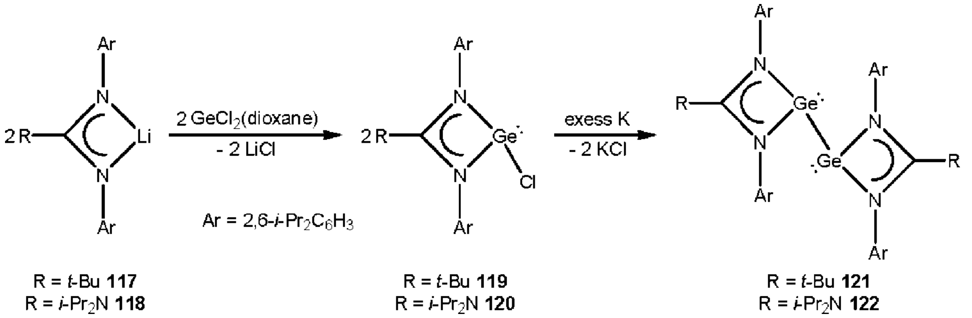
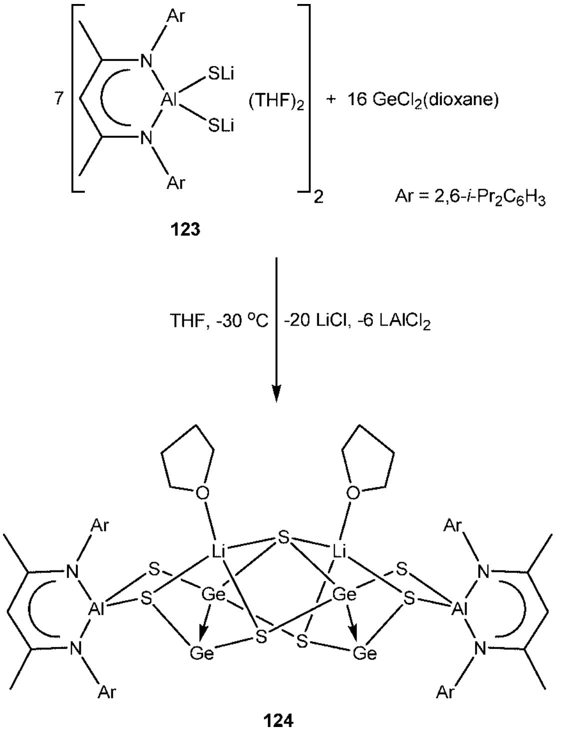
(103) (a) Karsch, H. H.; Schlüter, P. A.; Reisky, M. *Eur. J. Inorg. Chem.* **1998**, 433–436. (b) Roesky, H. W.; Meller, B.; Noltemeyer, M.; Schmidt, H.-G.; Scholz, U.; Sheldrick, G. M. *Chem. Ber.* **1988**, *121*, 1403–1406. (c) So, C-W.; Roesky, H. W.; Gurubasavaraj, P. M.; Oswald, R. B.; Garmer, M. T.; Jones, P. G.; Blaurock, S. *J. Am. Chem. Soc.* **2007**, *129*, 12049–12054. (d) Recent results show that reduction of [PhC(N*i*-Pr)$_2$]SiCl$_3$ with potassium gives [PhC(N*i*-Pr)$_2$]$_2$SiCl$_2$ as the major product. Nagendran, S.; Roesky, H. W.; Pal, A.; Herbst-Irmer, R. Unpublished results. (e) So, C-W.; Roesky, H. W.; Oswald, R. B.; Pal, A.; Jones, P. G. *Dalton Trans.* **2007**, 5241–5244. (f) Iwamoto, T.; Sato, K.; Ishida, S.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2006**, *128*, 16914–16920. (g) Arya, P.; Boyer, J.; Carré, F.; Corriu, R.; Lanneau, G.; Lapasset, J.; Perrot, M.; Priou, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1016–1019.

Scheme 53. Syntheses of Germanium(I) Dimers 121 and 122



Scheme 54. Synthesis of Heterotrimetallic Main Group Cluster 124



tion. The Si(II)−P bond is polarized with larger electron density on P than on Si, resulting in donor–acceptor-type interactions between the localized orbitals. These interactions may lead to the formation of ionic species in solution. In the ^{29}NMR spectrum, the silicon thioester analogue **81g** exhibits a singlet resonance at 1.57 ppm.

The structure of compounds **81c**, **81d**, and **81g** (Figures 18c, 18d, and 18e) were confirmed by single-crystal X-ray diffraction, and due to nonmerohedral twinning, structural elucidation was not possible for compounds **81e** and **81f**.

In all these structures, the phenyl ring is almost perpendicular to the planar CN_2Si four-membered ring. In **81c** and **81d**, the Si(II) centers adopt distorted trigonal pyramidal geometry. In **81c**, the Si(II)−NMe_2 (1.723$_{av}$ Å) bond is a little shorter than the Si(II)−N bonds present in silylenes **70** (1.75$_{av}$ Å)[90a] and **77** (1.735$_{av}$ Å).[95] Also, it is shorter than the value theoretically calculated for **74** (1.779 Å).[85] The Si(II)−P bond length (2.307 Å) in compound **81d** agrees with that of the tetracoordinate silylene **67** (2.271 Å).[88] The silicon center in **81g** is tetracoordinate and has a distorted tetrahedral geometry. The Si−S (1.984 Å) bond is 0.15 Å shorter than that of the Si−S*t*-Bu bond (2.131 Å). This unequivocally confirms the double-bonded nature of the Si−S bond, and it is longer than that of the dialkylsilanethione (1.958 Å) reported by Kira and co-workers.[103f] However, it is shorter than that of the silanethione (2.013 Å) prepared by Corriu and co-workers.[103g] Theoretical calculations further reveal that the Si−S bond is not a pure double bond, but it has a bond order of 1.5.

3. Germanium(II) Chemistry

3.1. Introduction. Germylenes are analogues of carbenes, and the germanium atom in these compounds exists in a formal divalent oxidation state.[104] In contrast to carbenes[1–4] and silylenes,[84] the germylenes are less reactive due to the larger energy gap between the s- and p-orbitals of germanium.[104–107] Consequently, the germanium dichloride adducts $GeCl_2$(1,4-dioxane)[105] and $GeCl_2$(benzthioazole)[106] were prepared and structurally characterized in the early 1970s, and the germylene monoiodide complex (acac)GeI (Hacac = acetylacetone) was reported together with its structure in the late 1970s by Stobart.[107] The acyclic germylene diamide $[(Me_3Si)_2N]_2Ge$[108] was prepared by Lappert et al. in 1974, and a cyclic version, namely, the N-heterocyclic germylene $[Me_2Si(Nt\text{-}Bu)_2]Ge$,[109] was isolated by Veith and co-workers in 1982. Interestingly, the germanium analogue of Arduengo's carbene (*t*-BuNCHCHN*t*-Bu)Ge[6] was obtained by Herrmann et al. in 1992.[110] In view of this, the present Ge(II) chemistry is very rich and much diversified with different types of germylene derivatives,[111]

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(104) Barrau, J.; Rima, G. *Coord. Chem. Rev.* **1998**, *178–180*, 593–622.

(105) Kolesnikov, S. P.; Shiryaev, V. J.; Nefedov, O. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, 584.

(106) Jutzi, P.; Hoffmann, H. J.; Brauer, D. J.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 1002–1003.

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(109) Veith, M.; Grosser, M. *Z. Naturforsch.* **1982**, *37b*, 1375.

(110) (a) Meller, A.; Gräbe, C.-P. *Chem. Ber.* **1985**, *118*, 2020–2029. (b) Pfeiffer, J.; Noltemeyer, M.; Meller, A. *Z. Anorg. Allg. Chem.* **1989**, *572*, 145–150. (c) Pfeiffer, J.; Maringgele, W.; Noltemeyer, M.; Meller, A. *Chem. Ber.* **1989**, *122*, 245–252.

(111) (a) Dias, H. V. R.; Wang, Z. *J. Am. Chem. Soc.* **1997**, *119*, 4650–4655. (b) Barrau, J.; Rima, G.; Amraoui, T. E. *Organometallics* **1998**, *17*, 607–614. (c) Ayers, A. E.; Marynick, D. S.; Dias, H. V. R. *Inorg. Chem.* **2000**, *39*, 4147–4151. (d) Zemlyansky, N. N.; Borisova, I. V.; Kuznetsova, M. G.; Khrustalev, V. N.; Ustynyuk, Y. A.; Nechaev, M. S.; Lunin, V. V.; Barrau, J.; Rima, G. *Organometallics* **2003**, *22*, 1675–1681. (e) Driess, M.; Dona, N.; Merz, K. *Dalton Trans.* **2004**, 3176–3177. (f) Khrustalev, V. N.; Portnyagin, I. A.; Zemlyansky, N. N.; Borisova, I. V.; Ustynyuk, Y. A.; Yu. Antipin, M. *J. Organomet. Chem.* **2005**, *690*, 1056–1062. (g) Khrustalev, V. N.; Portnyagin, I. A.; Zemlyansky, N. N.; Borisova, I. V.; Nechaev, M. S.; Ustynyuk, Y. A.; Yu. Antipin, M.; Lunin, V. *J. Organomet. Chem.* **2005**, *690*, 1172–1177.

which have been reviewed periodically.[84a,b,112] The success achieved by us in stabilizing the monomeric Al(I) complex LAl **5** by means of a β-diketiminato ligand[9] (L) encouraged us to evaluate the efficacy of the ligand L as a support for the Ge(II) center. Accordingly, we prepared a β-diketiminato germylene monochloride (LGeCl, **84**) in 2001.[113] Nevertheless, two other germylene monochlorides based on the similar β-diketiminato platform appeared almost at the same time. They are the germylene monochloride complexes $[CH\{(CMe)(2,4,6\text{-}Me_3C_6H_2N)\}_2]GeCl$[114] and $[CH\{(CMe)(2,6\text{-}Ph_2C_6H_3N)\}_2]GeCl$.[115,112f] Dias et al. reported the former complex, and the latter one was isolated by Barrau and co-workers. The discussion concerning these complexes and their derivatives[116,112f] is beyond the scope of this account.

3.2. Syntheses of Germylene Monochlorides and Their Conversion to Germylene Monofluorides and Germylenes with an Alkyl Substituent. Addition of an equimolar amount of *n*-BuLi to LH **3** at low temperature afforded the lithium derivative $LLi\cdot OEt_2$ **82** as colorless crystals.[117] Subsequent reaction of $LLi\cdot OEt_2$ **82** with $GeCl_2$(dioxane) gave germylene monochloride **84** (Scheme 31).[113] By following a similar strategy, we also prepared germylene monochloride **85**, which contained the $2,6\text{-}Me_2C_6H_3-$ groups on the nitrogen atoms (Scheme 31).[118]

Both **84** and **85** have a six-membered C_3N_2Ge ring with delocalized electron density. In addition, the molecular structure of **84** reveals that the C_3N_2 ring system is almost planar and the germanium atom lies 0.56 Å above this plane, leading to an envelope conformation for the six-membered C_3N_2Ge ring (Figure 19). This is reminiscent of the situation found for a closely related germylene monochloride, $[CH\{(CMe)(2,4,6\text{-}Me_3C_6H_2N)\}_2]GeCl$, reported by Dias et al.[114]

Although Ge(IV) fluorides are common, the Ge(II) fluorides are quite rare and have been studied only as reactive intermediates. In order to prepare stable Ge(II) monofluorides, we utilized germylene monochlorides **84**[113] and **85**[118] as starting materials. Thus, the action of trimethyltin fluoride on **84** and **85** gave the desired Ge(II) monofluorides **86** and **87**, respectively (Scheme 32) as colorless crystals in excellent yields.[118]

As expected, both compounds **86** and **87** showed a singlet resonance (50.58 and 54.46 ppm) in the ^{19}F NMR spectrum. In addition, the IR spectra of these two compounds exhibited the Ge(II)−F bond stretching frequencies at 534 and 539 cm^{-1}, respectively, and these values agree well with the Ge−F frequencies found for compounds $[(CF_3)GeF_2]^-$ and $[GeF_6]^{2-}$ (545 and 563 cm^{-1}).[119,120] The molecular structure of **86** clearly shows the presence of a six-membered C_3N_2Ge ring (Figure 20). This ring also takes up the envelope conformation by having the Ge atom above the plane of the planar C_3N_2 ring system (0.37 Å). The Ge(II) center is also tricoordinate and pyramidal, with the sum of the angles around it equal to 277.87°.

The successful syntheses of Ge(II) monochlorides and monofluorides incited us to explore their reactivity. We attempted to prepare germylenes with small alkyl substituents such as Me, Et, and Bu. Except for the structurally ill-characterized examples of Jutzi et al.,[121] these compounds are known only as intermediates due to their feeble steric shielding. As expected, the reaction of **84** with MeLi and *n*-BuLi afforded the alkyl-substituted germylene(II) compounds **88** (orange-red crystals) and **89** (deep-red crystals), respectively (Scheme 33).[122]

Both compounds were structurally characterized. The molecular structure of **88** is shown here as a representative example (Figure 21). These structures are monomeric and reveal the strongly distorted tetrahedral geometry around the tricoordinate Ge(II) center. Although the Ge(II)−C[121] and Ge(II)−N[123] bond lengths are within the expected range (Table 4), the latter are slightly longer than those of the corresponding precursor **84**. This is not unusual when one considers the electronegativity difference between the Cl and C atoms.

It is very well established that the synthetic route to compounds with a formal Ge=N double bond involves the reaction between germylenes and trimethylsilyl azide.[110c,123b,d,124] In order to probe this generality with our ligand system, the reactions of compounds **86** and **88** with trimethylsilyl azide were examined. The reaction of **86** proceeds in accord with the generalization to afford the iminogermane **90** (Scheme 34).[118] The reaction of **88**, however, proceeds via the migration of a proton from the methyl group of the ligand to afford the isomer of the iminogermane **91** with a Ge−N single bond (Scheme 34).[122]

Confirmation of the atom connectivities of compound **91** by means of single-crystal X-ray studies was possible (Figure 22), but the disorder associated with it leads us to refrain from discussing its structural parameters.

The insertion of methyl-substituted germylene **88** into the C−I bond of methyl iodide proceeded as expected to give the dimethylgermanium iodide **92** (Scheme 35).[122]

3.3. Syntheses of Heavier Acid Halides and Ketones of Germanium. In view of the importance of heavier analogues of ketones, the synthesis and characterization of multiple-bonded species (>M=E) formed between the heavier group 14 elements (M = Si, Ge, and Sn) and heavier group 16 elements (E = S,

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(112) (a) Veith, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1–14. (b) Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311–334. (c) Dias, H. V. R.; Wang, Z.; Jin, W. *Coord. Chem. Rev.* **1998**, *176*, 67–86. (d) Klinkhammer, K. W. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*, Vol. 2; Rappoport, Z., Ed.; Wiley: New York, 2002; pp 284–332. (e) Kühl, O. *Coord. Chem. Rev.* **2004**, *248*, 411–427. (f) Saur, I.; Alonso, S. G.; Barrau, J. *Appl. Organomet. Chem.* **2005**, *19*, 414–428. (g) Leung, W.-P.; Kan, K.-W.; Chong, K.-H. *Coord. Chem. Rev.* **2007**, *251*, 2253–2265.

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Se, and Te) is of great significance.[66,125] The literature shows various interesting examples for this type of compounds,[126–128] but what is rarely seen are examples of the heavier analogues of acid halides, i.e., the species of type −M(X)=E where M is formally double bonded to E and singly bonded to a halogen atom X. With our continuing effort to understand the potential of the halogermylenes **84** and **86**, we carried out their oxidation reactions with elemental sulfur and selenium and found the first structurally characterized heavier acid halides. The oxidation of germylene chloride **84** with sulfur and selenium gave the germanethioacid chloride **93** and germaneselenoacid chloride **94** as yellow crystals, respectively (Scheme 36).[129,130] The corresponding fluorides **95** and **96** were obtained in two different ways. One route involved the direct oxidation of germylene fluoride **86** with either elemental S or Se, and the other was based on the fluorination of compounds **93** and **94** with trimethyltin fluoride (Scheme 36).[129,130] Furthermore, the reaction of **93**−**96** with MeLi gave the methylgermanethione **97** and methylgermaneselone **98** as yellow crystals.[122,129,130] The *n*-butylgermaneselone **99** was obtained by the action of *n*-BuLi on either **94** or on **96** (Scheme 36).[130] We also demonstrated that the methylgermanethione **97** and the methylgermaneselone **98** could be obtained by reacting the methyl-substituted germylene **88** with elemental sulfur and selenium, respectively (Scheme 37).[122]

All these chalcogen derivatives were obtained in excellent yield, and what is intriguing is their stability, especially of the ones that have sterically less crowded substituents such as Me and *n*-Bu. The formal >Ge=E double bond in these compounds may be viewed as a resonance hybrid of two canonical forms >Ge=E and $>\mathrm{Ge}^+{-}\ddot{\mathrm{E}}^-$. This assumption stems from the polarity of the germanium chalcogen double bond. Even though Veith and co-workers[123a] have proposed such resonance structures, there was no direct evidence for it. Recently, Tokitoh et al. have demonstrated the >Ge=S bond polarization in germanethione Tbt(Tip)Ge=S (Tbt = 2,4,6-tris(bis(trimethylsilyl)-methyl)phenyl, Tip = 2,4,6-triisopropylphenyl) by means of its chemical reactivity.[127c] To probe the nature of the >Ge=E in the compounds reported by us, we utilized ^{77}Se NMR as a probe.[122,130] The resonance due to the >Ge−Se single bond in compound $(H_3Ge)_2Se$ appears at −612 ppm,[131] and the resonance due to the >Ge=Se bond in reported germanium selenones appears around 800 to 1100 ppm.[127c,132] The ^{77}Se NMR resonance for the compounds **94**, **99**, **98**, and **96** appears at −287.9, −297, −349, and −465.1 ppm, respectively (Table 3).[122,130] These values lie in between the single- and double-bond resonances and may be suggestive of a bonding situation stabilized by resonance ($>\mathrm{Ge}{=}\mathrm{E} \leftrightarrow >\mathrm{Ge}^+{-}\ddot{\mathrm{E}}^-$). To understand the bonding situation further, all the chalcogen derivatives **93**−**99** were structurally characterized by means of single-crystal X-ray diffraction. Representative examples are shown here (Figures 23−26).

It is explicit that all structures are monomeric and the germanium centers are tetracoordinate with distorted tetrahedral environment. The Ge−S bond length of 2.053(6) Å in **93** is shorter than the Ge−S single bond length of 2.239(1) Å found for the Ge(IV) compound reported by Meller et al.[132a] It agrees very well with the 2.049(3) Å bond length observed for the germanethione Tbt(Tip)Ge=S.[127c] Also, in the case of **94** the observed Ge−Se contact of 2.197(6) Å is well within the range observed for the >Ge=Se species (2.180(2)–2.247(3) Å)[127c,132a] and shorter than the Ge−Se distance of 2.433(1) Å observed for $[\mathrm{Tbt(Mes)GeSe}]_2$.[127c] This situation is also true for compounds **95**−**99** (Table 4), and therefore it can be unequivocally stated that the germanium chalcogen bond found in compounds **93**−**99** is either a formal double bond or a >Ge−E σ-bond with significant ionic character.

3.4. Preparation of Terminal Germylene Hydride 103.

Even though the existence of hypothetical MH_2 species (M = Si−Pb) is predicted by theoretical calculations, none exist at room temperature because of their extremely high reactivity.[133] The Sn(II) hydride $[\{2,6\text{-Trip}_2C_6H_3Sn(\mu\text{-H})\}_2]$ reported by Power et al. is the only known stable low-valent terminal hydride, but it is dimeric with bridging hydrogen atoms.[134] In order to obtain a stable, monomeric, terminal low-valent metal hydride of a group 14 element, the reaction of germylene chloride **84** with $LiAlH_4$ was performed.[118] Instead of the expected germylene hydride, this reaction gave the known aluminum dihydride[33] **31** (Scheme 38).[118]

Therefore, the reaction of **84** with $NaBH_4$ was carried out.[118] Here compound **100**, an adduct of germylene hydride with BH_3, was formed instead of the free germylene hydride. When the germylene chloride **85** was used in place of **84**, the reaction proceeds in a similar manner to afford compound **101** as colorless crystals (Scheme 39).[118]

The resonance due to the Ge−H proton in compounds **100** and **101** was not found in their ^{1}H NMR spectra. This may be due to the rapid exchange of hydrogen with respect to the NMR time scale or due to an overlap with the signals of aryl protons. Nevertheless, the IR spectral absorptions (1928 cm^{-1} **100** and 1949 cm^{-1} **101**) confirmed the presence of a Ge−H bond. The molecular structure of **100** (Figure 27) shows a tetracoordinate Ge center with tetrahedral geometry.

Adduct formation with Lewis acids was reported for carbenes, silylenes, and stannylenes,[135] and such adduct formation with base-stabilized germylenes was reported by Lappert et al. (with

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(125) (a) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283–319. (b) Tokitoh, N.; Okazaki, R. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, Chapter 17, pp 1063–1103. (c) Okazaki, R.; Tokitoh, N. *Acc. Chem. Res.* **2000**, *33*, 625630. (d) Tokitoh, N.; Okazaki, R. *Adv. Organomet. Chem.* **2001**, *47*, 121–166.

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(127) (a) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2316–2317. (b) Foley, S. R.; Bensimon, C.; Richeson, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 10359–10363. (c) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1999**, *121*, 8811–8824.

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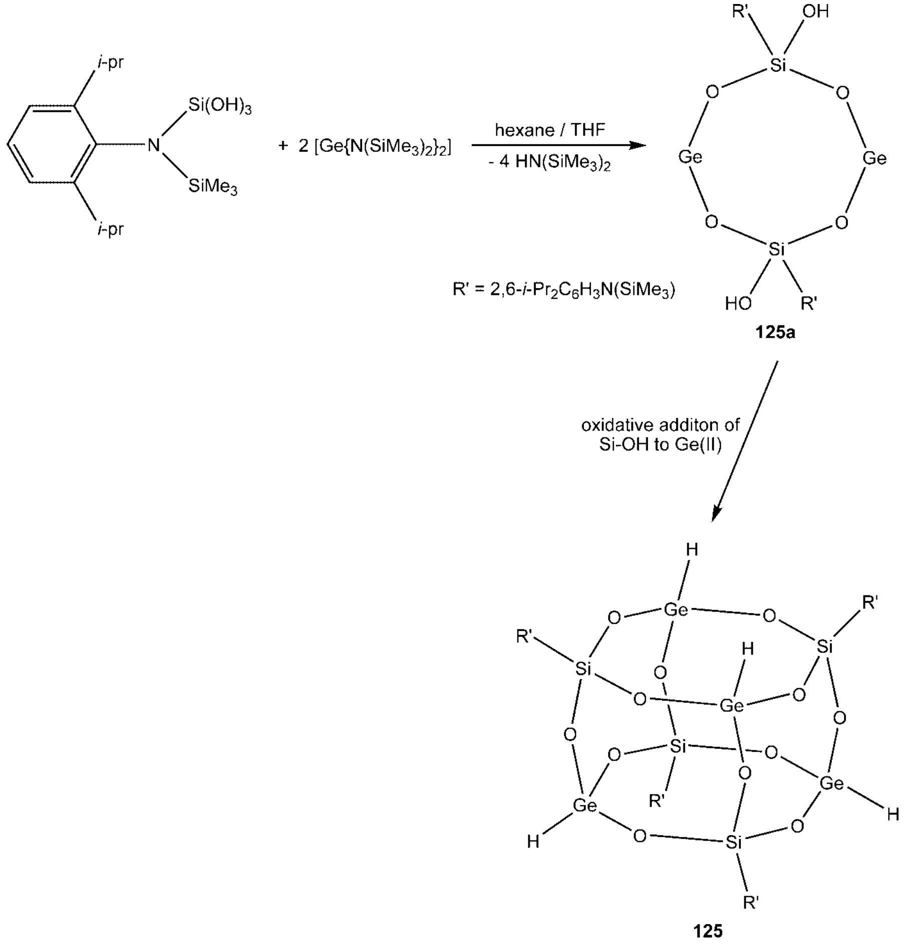
(134) Eichler, B. E.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 8785–8786.

Scheme 55. Synthesis of Polyhedral Germanium Siloxane 125



BH3)[136] and Dias et al. (with BPh3).[111a] However, the borane adducts **100** and **101** obtained by us are unique, as they have an additional Ge−H bond. So, we became interested in studying its reactivity. Thus, the reaction of the borane adduct **100** with *t*-BuLi was found to occur by cleavage of a hydrogen atom from the methyl group (of the ligand backbone) to give compound **102** with a lithium ion coordinated to two B−H hydrido substituents (Scheme 40).[118]

Because of this hydrogen elimination, a methylene group is formed on the ligand and the β-diketiminato ligand becomes dianionic instead of monoanionic. The preferential elimination of the hydrogen atom from the methyl group may be due either to the relative inertness of the Ge−H or to its severe steric protection. In the lithium-coordinated borane adduct **102**, the Ge−H resonance appears as a broad singlet (6.70 ppm) and the methylene proton signals appear as two singlets (3.20 and 3.92 ppm). The molecular structure of **102** obtained by X-ray diffraction analysis clearly shows the dianionic nature of the ligand system and the noncovalent nature of the B−Li bond (2.03Å) (Figure 28).

As mentioned, *vide supra*, the Ge−H bond in borane adduct **100** is inert, and this could be of great significance to remove the Lewis acid (BH3) preferentially from **100** to obtain the desired germylene hydride. Accordingly, the reaction of **100** with PMe3 to scavenge the BH3 moiety as Me3PBH3 went smoothly at room temperature and afforded the first stable terminal germylene hydride **103** (Scheme 41).[118]

Amazed by the stability of the germylene hydride **103**, we screened various reagents that can generate **103** by means of a direct reaction with germylene chloride **84**. Finally, we found that $AlH_3 \cdot NMe_3$ is the suitable candidate.[137] The addition of 1 molar equiv of $AlH_3 \cdot NMe_3$ to a solution of germylene chloride **84** in toluene gave exclusively the expected germylene hydride **103** as an orange-red solid (Scheme 42).[137]

The hydride **103** is thermally stable and can be kept under an inert atmosphere for a long time without decomposition. The resonance of the Ge(II)−H proton appears at 8.08 ppm in the ^1H NMR spectrum and is in a range close to Ge(IV) hydrides. This is in contrast to the similar resonance (3.48 ppm) observed for the related Ge(II) hydride Ar′(H)GeGe(H)Ar′ (Ar′ = 2,6-Dipp$_2$C$_6$H$_3$; Dipp = 2,6-*i*-Pr$_2$C$_6$H$_3$).[138] In the IR spectrum of **103** a strong absorption at 1733 cm^{-1} that corresponds to the Ge(II)−H stretching mode was observed. This value agrees well with the Ge−H stretching frequency observed (1785 cm^{-1}) for the aforementioned Ge(II) hydride Ar′(H)GeGe(H)Ar′.[138] By means of theoretical studies (NBO and NLMO analysis), it was found that the contribution of the lone pair on germanium to

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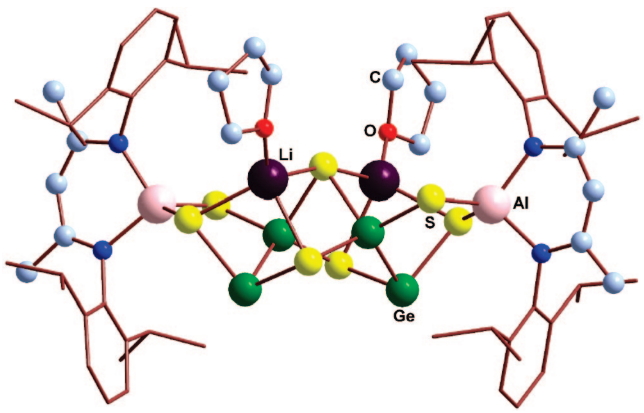

Figure 43. Molecular structure of the crab-like heterotrimetallic cluster **124**.

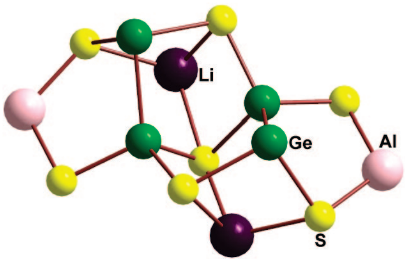

Figure 44. The $Al_2Ge_4Li_2S_7$ core of the main group cluster **124**.

the Ge(II)−H bond can be described as an $sp^{0.32}$ hybrid. In addition, the contribution of the hydrogen atom to the Ge−H bond in **103** is calculated to be around 65%. It is also interesting to note that the donor–acceptor interaction with the nitrogen atoms[139] of the ring system releases electron density into the Ge(II)−H bond. Structural analysis was carried out on an orange-red crystal obtained from the hexane solution of **103** (Figure 29). But the hydrogen atom attached to the Ge(II) center could not be traced from its difference electron density map.

3.5. Synthesis and Reactivity of Germylene Hydroxide 105. Alcohols contain the carbon−OH bond. They are basic and versatile reagents in organic chemistry. Because of this, the study of heavier group 14 hydroxides gains importance.[14a,140] Though various silanols are known, compounds of the type $RSi(OH)_3$ suffer from various disadvantages such as low chemical stability and poor solubility.[15a,b,141] We have prepared a stable and soluble aminosilanetriol, 2,6-*i*-$Pr_2C_6H_3N(SiMe_3)$-$Si(OH)_3$,[142a,] and used it as a synthon to assemble a plethora of metallosiloxanes with high metal to silicon ratio.[15,143] Hydroxides of germanium are known but are few in number. Some examples are Ph_3GeOH,[144] $(C_{10}H_7)_3GeOH$,[144] $(C_6H_{11})_3GeOH$,[144] *t*-$Bu_2Ge(OH)_2$,[145] 2*t*-$Bu_2Ge(OH)_2 \cdot (t\text{-}Bu_2GeOH)_2O \cdot H_2O$,[146] $[CpFe(\eta^5\text{-}C_5H_4)(t\text{-}Bu)(OH)Ge]_2O$,[147] and $(FcN)_3GeOH$[148] ($FcN = CpFe[\eta^5\text{-}C_5H_3(CH_2NMe_2)\text{-}2]$). In all of these compounds, the oxidation state of the group 14 element is +4. There is no example of a hydroxide compound R−M−OH (R = monoanionic ligand; M = C−Ge) where M is in the formal +2 oxidation state. The successful isolation of germylene monochloride **84** gave us an opportunity to attempt the isolation of such an unusual species. Accordingly, germylene monochloride **84** was hydrolyzed with water in the presence of an amine or liquid ammonia.[149] However, both reactions failed. When **84** was reacted with water in the presence of a N-heterocyclic carbene (1,3-dimesitylimidazole-2-ylidene),[3,150] **104**, the expected germylene hydroxide **105** was obtained as a yellow solid.[149] The key to the success was the use of carbene **104**, which neatly trapped the HCl formed and deposited from the solution as salt **106** (Scheme 43).

A singlet resonance (1.54 ppm) corresponding to the Ge(II)−OH proton was observed in the ^1H NMR spectrum of **105**. This agreed with the chemical shift (1.49 ppm) found for the Ge−OH group in *t*-$Bu_2Ge(OH)_2$.[145] In the IR spectrum of **105**, the O−H stretching frequency appears at 3571 cm^{-1} as a sharp band. The molecular structure of germylene hydroxide **105** (Figure 30) shows the presence of a tetracoordinate Ge(II) center in a distorted tetrahedral geometry. The four coordination sites are occupied by two nitrogen atoms of the ligand, the oxygen atom of the hydroxyl group, and a lone pair of electrons. The hydroxyl proton was located from the difference electron density map, and the germanium hydroxide **105** exists as a hydrogen-bonded dimer in the solid state. This hydrogen bonding is due to the interaction of the hydrogen atom of the hydroxyl group with the lone pair of electrons on germanium (H–Ge 3.064 Å). In addition, the Ge−O (1.828 Å) and O−H (0.795 Å) distances are in the normal range.

Like the halogermylenes **84** and **86**, the germylene hydroxide **105** is yet another potential and unique starting material for the preparation of compounds with novel functional groups. As performed earlier with compounds **84** and **86**, the oxidation of **105** with elemental sulfur and selenium was pursued with an anticipation to realize heavier analogues of carboxylic acids. In the carbon chemistry, the

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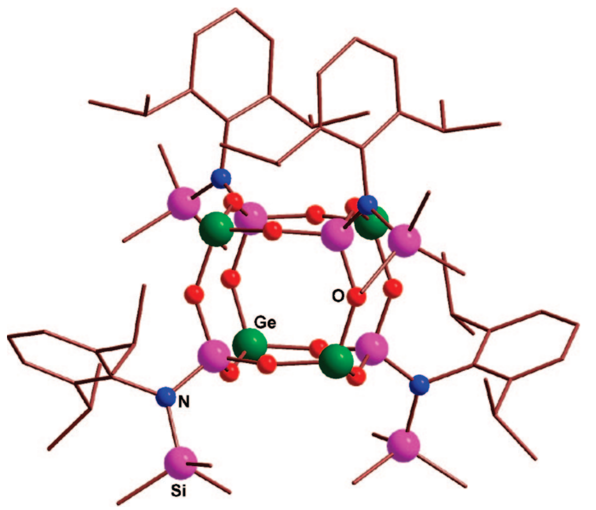

Figure 45. Molecular structure of the Ge(IV) hydride cluster **125**.

thionocarboxylic acid (**iii**) [RC(S)OH] does not exist in the free state and it tautomerizes to the thiolocarboxylic acid (**iv**) [RC(O)SH].[151] There exists a tautomeric equilibrium between the two species **iii** and **iv** (Chart 2).

Similarly, the selenocarboxylic acid (**v**) [RC(Se)OH] (R = alkyl or aryl) is not stable at ambient temperature, and therefore well-defined examples are not known so far.[152] By utilizing the germylene hydroxide **105** stabilized by the β-diketiminato ligand we were able to isolate the germanium analogues of **iii** and **v** as stable compounds. These findings are summarized below.

The oxidation of **105** with elemental sulfur at room temperature gave the first germanium thionoacid **107** as a colorless solid (Scheme 44).[153]

The germanium thionoacid **107** is freely soluble even in hexane and astonishingly stable in air. In its ^{1}H NMR spectrum the O−H resonance (2.30 ppm) is shifted downfield in comparison with germylene hydroxide (1.54 ppm) **105** and indicates the acidic nature of **107**. This may be due to intermolecular hydrogen bonding (*vide infra*) and change in the oxidation state of germanium. In the IR spectrum of **107**, the O−H stretching frequency appears at a lower wavenumber (3238 cm^{-1}) in comparison to **105** (3571 cm^{-1}), and this may be due to the hydrogen-bonding interaction (*vide infra*). The molecular structure of **107** shows (Figure 31) the distorted tetrahedral environment of germanium with two nitrogen atoms, one oxygen atom of the hydroxyl group, and one sulfur atom.

Due to the smaller atomic radius of Ge(IV) than that of Ge(II), the Ge−O bond length in **107** (1.751 Å) is considerably shorter than the Ge−O distance found for **105** (1.828 Å). Also, the Ge═S bond length (2.077 Å) agrees well with the same distance found for **93** (2.053 Å), **95** (2.050 Å), and [{η^3-[(μ-*t*-BuN)$_2$(SiMeN*t*-Bu)$_2$]}GeS] (2.063 Å).[123a,154] The hydrogen atom of the hydroxyl group can be located from the difference electron density map, and this hydrogen atom interacts with the S atom of the other molecule to form a O-H---S intermolecular hydrogen bonding.[155] Because of this interaction (O−H 0.716; H---S 2.537, and O---S 3.234 Å), a dimer is formed in the solid state.

Reaction of **105** with selenium at room temperature results in the germanium selenoacid **108** as a pale green solid in 77% yield (Scheme 45).[156]

In its ^{1}H NMR spectrum the chemical shift for the −OH proton is (2.19 ppm) downfield shifted when compared with that of **105** (1.54 ppm) and upfield shifted to that of **107** (2.30 ppm). The latter observation shows that the germanium thionoacid **107** is more acidic than **108**. The resonance due to the Se atom appears at −439 ppm in the ^{77}Se NMR spectrum. This value falls within the range (−287.90 to −465.1 ppm) observed for compounds **94** (−287.9 ppm),[130] **96** (−465.1 ppm),[130] **98** (−349 ppm),[122] and **99** (−297 ppm)[130] and is indicative of a Ge−Se bond stabilized by resonance ($>\mathrm{Ge}{=}\mathrm{E} \leftrightarrow >\mathrm{Ge}^+{-}\ddot{\mathrm{E}}^-$). Structural studies on a light green single crystal of **108** show the tetracoordinate Ge(IV) center with distorted tetrahedral geometry (Figure 32).

The Ge−O bond length (1.756 Å) is almost the same as that of **107** (1.751 Å). The Ge−Se bond length (2.206 Å) agrees with those found in **94**, **96**, **98**, and **99** (Table 4). In line with **107**, the germanium selenoacid **108** also exists as a hydrogen-bonded dimer in the solid state due to the O−H---Se interaction (O−H 0.76 Å; H---Se 2.61 Å, O---Se 3.336 Å and the O−H---Se angle is 163°).

The strengths of the acids **107** and **108** were calculated using the thermodynamic cycle (Scheme 46) and DFT calculations.

The pK_a values were calculated by employing the following equations:

$$\triangle G^0_{\mathrm{aq}} = G^0(\mathrm{B}_{\mathrm{gas}^-}) + \triangle G_{\mathrm{solv}}(B^-) + G^0(\mathrm{H}^+_{\mathrm{gas}}) + G^0_{\mathrm{solv}}(H^+) - G^0(\mathrm{BH}_{\mathrm{gas}}) - \triangle G^0_{\mathrm{solv}}(\mathrm{BH})$$

and

$$\mathrm{p}K_a = \triangle G^0_{\mathrm{aq}}/2.303RT$$

In analogy with the ^{1}H NMR spectroscopic predictions the pK_a values (37.2 for **107** and 38.3 for **108**) further confirm the higher acidity of **107** over **108**. This also shows that both **107** and **108** are weak acids and that their acidity is in the range for aromatic (pK_a ~33) and aliphatic (pK_a ~48) compounds. Both are weaker acids compared to oxygen-containing organic Brønsted acids (pK_a ~15).[157]

By means of natural bond analysis[158] (NBO) on **107** and **108**, it was predicted that the germanium−chalcogen bond is formed by the overlap between a p-rich sp hybrid of the chalcogen atom and a sp^2 hybrid of the germanium atom. Nevertheless, the contribution of the germanium atom to the molecular orbital is higher in the case **108**. Because of this electron drain, the hydroxide group of **108** shows a positive interaction with the Ge−O bond. This type of interaction is not seen in the case of the germanium thionoacid **107**.

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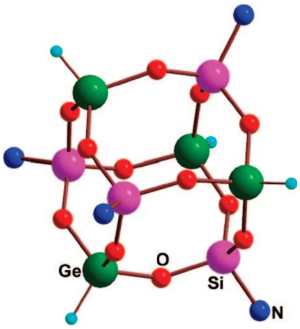

Figure 46. Polyhedral cubic core of the Ge(IV) hydride cluster **125**.

As the carbon analogue of **105** is not known, it is very interesting to study its reactivity toward transition metals.[159] The germylene hydroxide **105** has a lone pair of electrons and an −OH group. Therefore, two modes of reactivity can be anticipated. Its reactivity through the −OH group was observed with group 4 derivatives (Cp_2ZrMe_2 and Cp_2HfMe_2).[160] This mode of reactivity led to the formation of μ-oxo heterobimetallic oxides with metal centers in high and low oxidation states. In recent years, the heterobimetallic oxides have been studied for their improved catalytic activity and also for their use as precursors in the synthesis of polymetallic heterogeneous catalysts.[161] In the other mode of reactivity through the lone pair of electrons, germylene hydroxide **105** acts as an electron donor.[162] This mode of reactivity was observed with group 7 and 8 metal–carbonyls ($CpMn(CO)_3$ and $Fe_2(CO)_9$).[163]

Accordingly, the reaction of germylene hydroxide **105** with Cp_2ZrMe_2 and Cp_2HfMe_2 gave the μ-oxo heterobimetallic oxides **109** and **110** as yellow-orange solids (Scheme 47).[160]

In their ^1H NMR spectra, both the compounds contain a singlet resonance due to the Cp (5.39 ppm for **109** and 5.33 ppm for **110**) and M(Me) protons (0.14 ppm for **109** and 0.02 ppm for **110**). Single crystals suitable for X-ray analysis were obtained from a solvent mixture of toluene and hexane at low temperature. The molecular structures (Figures 33 and 34) show the presence of the Ge(II)−O−M motif in these compounds.

The Ge(II) centers in both compounds are tetrahedral, with two nitrogen atoms of the β-diketiminato ligand, an oxygen atom, and the lone pair of electrons occupying the four coordination sites. Similarly, the metal centers are also tetrahedral, with the coordination sphere consisting of two Cp ligands, one methyl group, and an oxygen atom. The C_3N_2Ge rings in both compounds are boat shaped due to the deviation of the Ge and γ-C atoms from the plane defined by the C_2N_2 ring atoms. The magnitude of deviation (**109**: Ge (1.020 Å), γ-C (0.152 Å); **110**: Ge (1.038 Å), γ-C (0.154 Å)) is nearly equal in both cases. The Cp rings deviate from the eclipsed conformation by an angle of 21° in the case of **109**, and the same deviation for **110** is 23°. The torsion angles for the Ge(II)−O−M−C(Me) skeleton in **109** and **110** are −41.7° and −12.3°, respectively.

The Ge(II)−O−M motifs in both compounds are bent (143.8° for **109** and 141.9° for **110**) with the O−M distance being 1.951 and 1.940 Å for **109** and **110**, respectively. The Ge(II)−O distances (**109** 1.797 Å; **110** 1.799 Å) are shorter than the Ge(II)−O distance (1.828 Å) found for the germylene hydroxide **105** and reveal the enhanced interaction between these two atoms. This is due to the tendency of both the transition metals (Zr and Hf) to form strong bonds with hard donors such as oxygen, which shifts the electron density from the oxygen atom to the transition metal.

The reaction of diiron nonacarbonyl with Ge(II) hydroxide **105** at room temperature gave the germanium hydroxide **111**, with a Ge−Fe bond, as pale brown crystals (Scheme 48).[163] The germanium hydroxide **112** with a Ge−Mn bond was obtained as orange-yellow crystals by UV irradiation of **105** with cyclopentadienylmanganese tricarbonyl (Scheme 49).[163]

Compound **111** is soluble in THF, but compound **112**, with the Ge−Mn bond, is not soluble in any of the common organic solvents, which precludes its characterization by NMR spectroscopy. The ^1H NMR spectrum of **111** shows a singlet resonance for the −OH proton in the downfield region (4.24 ppm) and also a single resonance for the −CO ligands at 214.8 ppm in the ^{13}C NMR spectrum. In the IR spectrum both the −OH and −CO absorptions were found. Thus, the sharp band at 3599 cm^{-1} and three bands around 2000 cm^{-1} (2039, 1956, and 1942 cm^{-1}) correspond to the hydroxyl and carbonyl absorptions of compound **111**, respectively. Similar absorptions for compound **112** were found at 3642 cm^{-1} and at 1864 and 1846 cm^{-1}.

The molecular structures (Figures 35 and 36) show the tetracoordinate Ge centers in a distorted tetrahedral geometry. Two nitrogen atoms of the ligand, an oxygen atom of the hydroxyl group, and a metal (M) center (M = Fe **111**; M = Mn **112**) occupy the four coordination sites. In compound **111**, the Fe atom is pentacoordinate and has trigonal bipyramidal geometry with the Ge atom at one of the axial positions. The carbonyl ligands occupy the remaining four positions. In contrast, the Mn center in **112** is tetracoordinate and has a distorted tetrahedral geometry with two carbonyl ligands, one cyclopentadienyl group, and a germanium atom.

The Ge−M bond lengths in these compounds (**111** 2.330 Å; **112** 2.345 Å) are in accordance with the earlier reports on compounds with similar motifs.[116a,123b,164] In the case of **111** the Ge−O bond length (1.840 Å) is slightly longer (1.828 Å) than that of the Ge(II) hydroxide **105**, but in the case of **112** it is slightly shorter (1.816 Å) than that of **105**. Both the hydroxyl protons were located from the difference electron density map, and the O−H bond lengths are almost the same (**111** 0.840 Å; **112** 0.841 Å). Also, the orientation of the −OH group in **111** is toward the β-diketiminato ligand. By contrast, it is oriented toward the transition metal center in **112** (Figures 35 and 36).

3.6. Other Relevant Studies. Power and co-workers have reported the preparation of germylenium cation **113** by reacting

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Table 4. Selected Bond Lengths and Bond Angles for the Germylenes and Their Derivatives

compound	Ge−N$_{av}$ (Å)	X	Ge−X (Å)	E/Ge═E (Å)	N−Ge−X (deg)	ref
84	1.993	Cl	2.295(12)		95.00(8); 95.60(8)	113
86	1.977	F	1.805(17)		93.67(8); 93.16(8)	118
88	2.023	Me	2.002(4)		97.13(13); 92.81(12)	112
89	2.024	*n*-Bu	2.014(3)		97.52(10); 100.06(10)	112
93	1.896	Cl	2.195(7)	S/2.053(6)	98.18(6); 99.51(4)	129, 130
94	1.901	Cl	2.164(8)	Se/2.197(6)	100.04(7); 100.09(6)	130
95	1.888	F	1.848(2)	S/2.050(9)	99.07(9); 99.61(9)	129, 130
96	1.892	F	1.758(3)	Se/2.176(7)	98.72(14); 97.17(14)	130
97	1.941	Me	2.009(2)	S/2.104(7)	107.69(8); 109.66(8)	129, 130
98	1.939	Me	1.973(2)	Se/2.1992(5)	103.64(11); 102.70(11)	122
99	1.936	*n*-Bu	1.961(5)	Se/2.219(6)	106.52(17); 108.29(17)	130
100	1.925	B	2.015(7)		118.3(3); 117.9(3)	118
102	1.877	B	2.016(8)		115.8(3); 116.7(3)	118
103	1.99	H				137

Table 5. NMR Spectral Data for the Germylene Hydroxide and Its Derivatives[a]

compound	γ-CH (^{1}H NMR)	OH (^{1}H NMR)	ref
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]GeOH$, **105**	4.91 (s)	1.54	149
$[CH\{(CMe)(2,6\text{-}Me_2C_6H_3N)\}_2]Ge(S)OH$, **107**	4.83 (s)	2.30	153
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]Ge(Se)OH$, **108**	4.85 (s)	2.19[b]	156
$[CH\{(CMe)(2,6\text{-}Me_2C_6H_3N)\}_2]Ge(\mu\text{-}O)Zr(Me)Cp_2$, **109**	4.65 (s)		160
$[CH\{(CMe)(2,6\text{-}Me_2C_6H_3N)\}_2]Ge(\mu\text{-}O)Hf(Me)Cp_2$, **110**	4.65 (s)		160
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]Ge(OH)Fe(CO)_4$, **111**	5.69 (s)[c]	4.24	163
$[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]Ge(OH)Mn(CO)_2Cp$, **112**			163

[a] All the spectra were recorded in C_6D_6 if not mentioned. [b] ^{77}Se NMR (C_6D_6): $\delta \pm 439.8$ ppm. [c] In THF-d_8.

the chlorogermylene **84** with tris(pentafluorophenyl)borane in the presence of water (Scheme 50).[165]

The cation **113** is colorless and isoelectronic with $[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]Ga$.[10b] The molecular structure (Figure 37) of **113** shows a planar C_3N_2Ge ring with delocalized π-electrons. This is in contrast to the envelope conformation (*vide supra*) found for the C_3N_2Ge ring in chlorogermylene **84**.

The Ge−N bond distance of **113** (1.894 Å) is slightly shorter than the Ge−N distances (1.988 and 1.997 Å) in germylene **84**. However, the N−Ge−N bond angle (93.0°) is a little wider than that of **84** (90.89°). In the resonance-stabilized germylenium cation, the germanium atom is dicoordinate by means of the β-diketiminato nitrogen atoms.

By utilizing the chlorogermylene **84** and germylenium cation **113** Driess et al. have synthesized the heterofulvene-like germylene **114**, which exists as a dipolar resonance hybrid of **114a** and **114b**, with the higher contribution from the less polar resonance form **114b** (Scheme 51).[166] Accordingly, the dehydrochlorination of **84** in the presence of lithium bis(trimethylsilyl)amide gave brown-red crystals of **114** in good yield (~80%) (Scheme 51). The deprotonation of germylenium cation **113** by a strong base such as $LiN(i\text{-}Pr)_2$ or $LiN(SiMe_3)_2$ also led to the formation of germylene **114** but in only low yield (~10%) (Scheme 51).[166]

When compared with the germylenium cation **113** (1.894 Å), the Ge−N bond lengths (1.865 and 1.866 Å) of **114** are nearly the same. The N−Ge−N bond angle (95.84°) of **114** is wider than the same angle observed in the cation **113** (93.0°). In addition, the exocyclic methylene group has the C−C bond length of 1.413 Å, which is indicative of a conjugated double bond. Due to the involvement of two resonance forms, **114a** and **114b**, the germylene **114** shows a betain-like reactivity.

Thus, the reaction of Me_3SiOTf with **114** gave the (trifluoromethylsulfonato)germylene **115** with an exocyclic $-CH_2SiMe_3$ group in about 85% yield (Scheme 52).[166] Also, when $BrCH_2CH_2Br$ was treated with **114**, a C−C homocoupling reaction occurred between two germylene units with simultaneous addition of a bromine atom to each germylene center, resulting in the formation of bis(bromogermylene) **116** (~70% yield) (Scheme 52).[166]

The molecular structures of the germylenes **115** and **116** (Figures 39 and 40) show the presence of a nonplanar C_3N_2Ge ring with the associated bond lengths and bond angles comparable to that of the chlorogermylene **84**.

In germylene **115**, with the OTf substituent, the Ge−O bond length is 2.082 Å, and the Ge−Br bond length in the bis(bromogermylene) **116** is 2.472 Å. Also, the C−C bond that couples the two bromogermylene units in **116** is purely a single bond (1.525 Å).

Recently, Jones and co-workers have reported the syntheses of germanium(I) dimers **121** and **122** by reducing the amidinato- and guanidinatogermylene chlorides **119** and **120**, respectively, with potassium in toluene at room temperature (Scheme 53).[167] The germylene chlorides **119**−**120** were obtained in the reaction of lithium amidinate and guanidinate salts **117** and **118** with $GeCl_2\cdot$dioxane (Scheme 53).[10e,168]

The molecular structure of amidinato- and guanidinatogermylene chlorides **119**−**120** (Figure 41) is comparable to the structure of germylene monochloride **84** and reveals the delocalization in the CN_2Ge ring. The Ge−Cl bond lengths in **119** and **120** are 2.174 and 2.263 Å, respectively.

The molecular structures of the Ge(I) dimers **121** and **122** (Figure 42) confirm the existence of a Ge−Ge single bond (**121** 2.6380 Å; **122** 2.6721Å) and preclude the possibility of digermene- and digermyne-like character in the Ge−Ge bond. This is further supported by DFT calculations on a model system $[\{Ge[2,6\text{-}Me_2C_6H_3N)_2CMe]\}_2]$ that also reveals the π-bonding nature of the LUMO similar to that in distannynes.

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Table 6. Selected Bond Lengths and Bond Angles for the Germylene Hydroxide and Its Derivatives

compound	Ge−N_{av} (Å)	X	Ge−O/O−X (Å)	E/Ge−$E^{a/b}$ (Å)	N−Ge−O/E−Ge−O (deg)	ref
105	2.008	H	1.828(1)/0.795(7)		93.90(6); 94.80(6)/–	149
107	1.914	H	1.751(2)/0.716(29)	S/2.077^{a}	99.6(1); 102.2(1)/121.4(1)	153
108	1.914	H	1.756(1)/0.760(2)	Se/2.206(1)^{a}	99.3(1); 102.0(1)/121.4(1)	156
109	2.046	Zr	1.797(2)/1.951(2)		99.0(1); 99.3(1)/−	160
110	2.045	Hf	1.799(3)/1.940(3)		97.5(2); 100.7(2)/−	160
111	1.947	H	1.840(2)/0.840(2)	Fe/2.330(1)^{b}	98.3(1); 98.8(1)/113.5(1)	163
112	1.967	H	1.816(2)/0.841(4)	Mn/2.345(1)^{b}	93.7(1); 93.4(1)/119.0(1)	163

^{a} Ge−E formal double bond. ^{b} Ge−E single bond.

3.7. Ge(II) Chemistry Based on Main Group Clusters.

Apart from the extensive Ge(II) chemistry developed by us using the β-diketiminato ligand system, we were also successful in preparing main group clusters that either contain Ge(II) centers or involve the Ge(II) centers during synthesis. A donor–acceptor type Ge→Ge bond in the compound $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(Ph_2P{=}NSiMe_3)_2]$[169] has been reported, but it is not supported by experimental and/or theoretical data. By utilizing the lithium salt $[\{LAl[(SLi)_2(THF)_2]\}_2]$[170] **123** we were able to assemble the well-defined heterotrimetallic polysulfido cluster $[L_2Al_2Ge_4Li_2S_7]$[171] (L = CH{(CMe)(2,6-*i*-$Pr_2C_6H_3N$)}$_2$]) **124** with two donor–acceptor-type Ge→Ge bonds. We also have reported the synthesis and characterization of a Ge(IV) hydride cluster $[(R'SiO_3GeH)_4]$[172] (R′ = 2,6-*i*-$Pr_2C_6H_3N(SiMe_3)$), **125**, obtained by the reaction of an aminosilanetriol with a Ge(II) amide. The synthesis of **125** involves the oxidative addition of the Si−OH bond to the Ge(II) center, which further leads to the formal conversion of the −OH proton to hydride. While the oxidative addition reaction is common in organometallic chemistry and even the oxidative addition of alcohol to the Ge(II) center is known,[173] the oxidative addition reaction that involves the Si−OH group is unprecedented.

When the lithium salt **123**[170] was reacted with $GeCl_2 \cdot$dioxane in a 7:16 molar ratio, the heterotrimetallic polysulfido cluster $[\{LAl(\mu\text{-}S)_2Ge_2\}_2(\mu\text{-}S)_3Li_2(THF)_2]$ **124** was obtained as pale yellow crystals (∼70% yield) (Scheme 54).[171] Compound **124** is soluble in aromatic solvents (such as benzene, toluene). Both β-diketiminato ligands are symmetric, as evident from its ^{1}H and ^{13}C NMR spectra.

The molecular structure of **124** is analogous to the crab scaffold (Figure 43). Thus, the core of the cluster forms the body of the crab, the two β-diketiminato ligands act as its side claws, and its front pincers are the two Li(THF) moieties.

Compound **124** consists of two unprecedented five-membered AlS_2Ge_2 rings in *gauche* conformation. Each of the five-membered rings has two germanium atoms; one is tetracoordinate (Ge_{4C}) and the other is tricoordinate (Ge_{3C}). Both of these germanium atoms are connected to each other by means of a donor–acceptor $Ge_{4C}{\rightarrow}Ge_{3C}$ bond (2.537 Å). This bond is considerably longer than the Ge═Ge double bond distances found in digermenes (2.213 to 2.347 Å).[174] It is apparent that the tetracoordinate germanium acts as the donor and the tricoordinate germanium acts as the acceptor with a lone pair of electrons that are not involved in the Ge→Ge bond formation. Both the five-membered AlS_2Ge_2 rings are connected by means of three sulfur and two lithium atoms (Figure 44). Each of these three sulfur atoms is bonded to two germanium atoms. Finally, both the lithium atoms are coordinated to three sulfur atoms and to an oxygen atom of the THF. This intricate connectivity also generates two highly strained four-membered $Ge_{3C}S_2Li$ rings.

Because of this ring strain, the Ge_{3C}−S bond lengths (2.394$_{av}$ Å) are longer than the Ge_{4C}−S bonds (2.244$_{av}$ Å) and the S−Ge_{3C}−S bond angle is more acute than the S−Ge_{4C}−S bond angles. The Li−S bond lengths (2.418 to 2.502 Å) are similar to the Li−S bond lengths (2.478 to 2.424 Å) found in the lithium salt **123**. The donor–acceptor-type Ge→Ge bonding in the compound **124** is further supported by theoretical calculations, which showed that the valence orbitals of the tetracoordinate germanium atoms form p-rich hybrids (of the type $sp^{1.62}$, $sp^{3.37}$, $sp^{3.44}$, and $sp^{4.95}$) and overlap with the pure p-orbitals of the tricoordinate germanium atoms.

The germanium siloxane $[(R'SiO_3GeH)_4]$[172] **125** was obtained in a 1:1 reaction (Scheme 55) of aminosilanetriol 2,6-*i*-$Pr_2C_6H_3N(SiMe_3)Si(OH)_3$[142] with germanium(II) amide $[Ge\{N(SiMe_3)_2\}_2]$.[108] As shown, the condensation of the Ge(II) amide with the silanetriol results in the formation of the intermediate $[\{RSi(OH)O_2Ge\}_2]$ **125a** with Ge(II) centers. Two molecules of **125a** then couple together by means of intermolecular oxidative addition of Si−OH bonds into the germanium(II) centers, resulting in the formation of **125** with Si−O−Ge and Ge−H bonds.

Instead of the aforementioned two-step process that leads to the formation of **125**, its formation may also be envisaged simply as the oxidation addition of the aminosilanetriol to the Ge(II) amide. The germanium siloxane **125** is a colorless solid with excellent solubility in a wide range of organic solvents. The resonance for the germanium hydride signal appears as a singlet (5.83 ppm) in the ^{1}H NMR spectrum, and two absorption bands (2211 and 2184 cm^{-1}) due to the Ge−H bond stretching vibration can be seen in its IR spectrum. The molecular structure of **125** (Figures 45 and 46) shows its cubic nature, with the germanium and silicon atoms occupying alternate corners.

There are six puckered eight-membered $Ge_2O_4Si_2$ rings in the structure of **125**, and these form the six faces of the cube. The oxygen atoms that connect the germanium and silicon atoms occupy the edges of the cube. The Ge−O (1.7405$_{av}$ Å) and the Ge−H (1.39$_{av}$ Å) bond lengths agree well with the distances found in related compounds.[175,176]

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Summary and Outlook

We have demonstrated the synthesis of a monomeric Al(I) derivative LAl by utilizing a β-diketiminato ligand (L) and report extensive studies of its chemical reactivity with alkynes, azides, oxygen, phosphorus, sulfur, etc. This has opened up a new realm in aluminum chemistry that should lead to many new Al(I) compounds. This has been made possible by the synthesis of L′Al, a bulky version of LAl. Nevertheless, more examples with entirely different substituent and ligand systems are required to understand the effects of such substitutents and/or ligands on the structure and reactivity of the resulting Al(I) monomers.

The first example of a chlorosilylene L″SiCl (L″ = (N*t*-Bu)$_2$CPh) represents a major breakthrough in silylene chemistry and offers a new dimension to it. The synthesis of additional examples of chlorosilylene will be an interesting target. The chlorosilylenes possibly will display a new reactivity pattern in comparison to the known silylenes. The chlorosilylene should serve as a starting material for the synthesis of other functionalized silicon(II) derivatives such as silylene hydroxide (L″SiOH), silylene hydride (L″SiH), and fluorosilylene (L″SiF).

By preparing the novel germylene monochloride LGeCl with its β-diketiminato (L) backbone, we have been able to develop the synthesis of hitherto unknown germanium compounds. Thus, germylene monofluoride, germylenes with alkyl substituents, and heavier acid halides of germanium were derived from LGeCl. Terminal germylene hydride and germylene hydroxide complexes were also obtained for the first time as stable species. We are engaged in reactivity studies of germylene hydroxide, which have provided examples of a germanium thionoacid and germanium selenoacid. Both acid derivatives are well-defined and await further exploration. As expected, the germylene hydroxide showed two modes of reactivity through the lone pair of electrons and the hydroxyl group.

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Note Added in Proof. Recently, we have extended the studies on germylene hydroxide (LGeOH) **105** by reacting it with lanthanide derivatives. In these reactions the reactivity through the hydroxyl group of **105** was observed. Thus, the reaction of **105** with Cp$_3$Yb and Cp$_3$Y led to the formation of heterobimetallic oxides LGe(μ-O)Yb(THF)Cp$_2$ and LGe(μ-O)Y(THF)Cp$_2$. Yang, Y.; Roesky, H. W.; Jones, P. G.; So, C.-W.; Zhang, Z.; Herbst-Irmer, R.; Ye, H. *Inorg. Chem.* **2007**, *46*, 10860–10863.

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