Zhi Yang

Synthesis, Reactivity, and Structural Elucidation of Aluminum Compounds with Bulky Ligands

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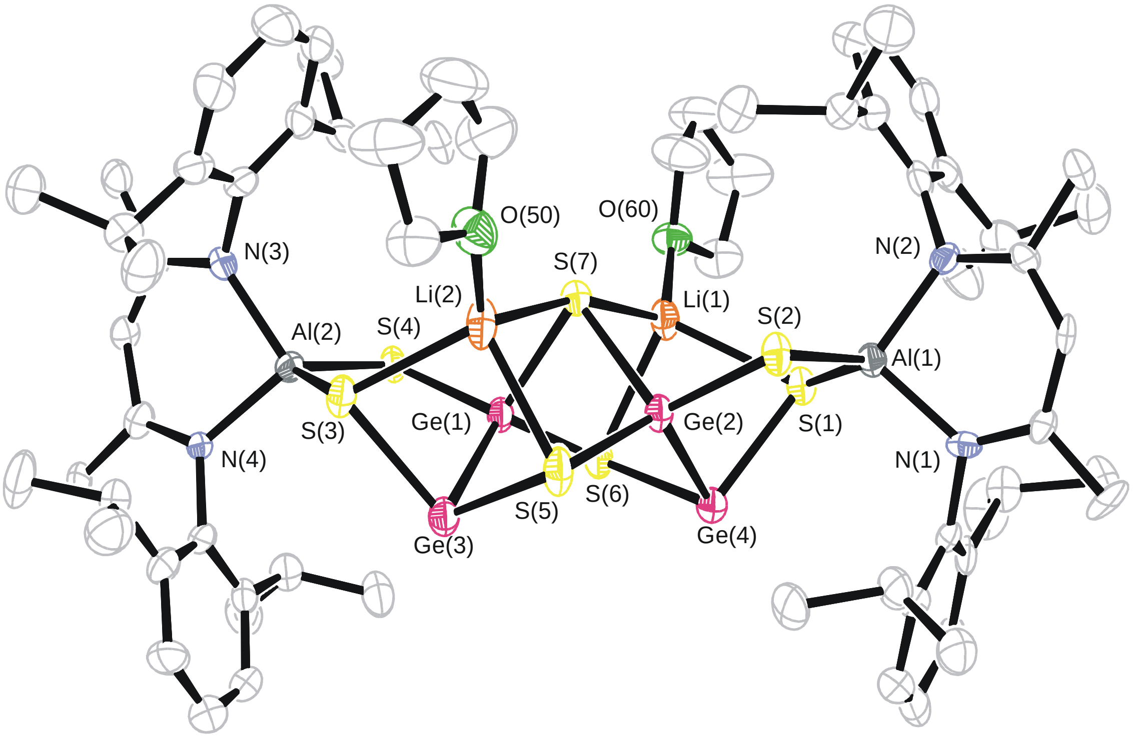

Synthesis, Reactivity, and Structural Elucidation of Aluminum Compounds with Bulky Ligands

Dissertation

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Abbreviations

Δ	chemical shift
Λ	wavelength
M	bridging
N	wave number
Ar	aryl
Av	average
*T*Bu	*tert*-butyl
C	Celsius
calcd.	calculated
Cp	cyclopentadienyl
d	doublet
decomp.	decomposition
DFT	density functional theory
EI	electron impact ionization
Et	ethyl
eqivs.	equivalents
EV	electron volt
G	grams, gaseous
Hz	Hertz
*I*Pr	*i*so-propyl
IR	infrared
J	coupling constant
K	Kelvin
L	ligand
M	metal
M	multiplet
m/z	mass/charge
M.p.	melting point
M^+	molecular ion
Me	methyl
Min.	minutes
MS	mass spectrometry, mass spectra
NMR	nuclear magnetic resonance

Ppm	parts per million
Q	quartet
S	singlet
Sept	septet
Sh	shoulder
St	strong
T	triplet
THF	tetrahydrofuran
TMS	tetramethylsilane
V	volume
Vst	very strong
W	weak
Z	number of molecules in the unit cell

1. Introduction

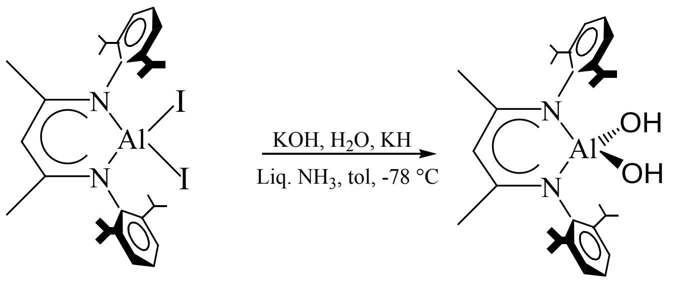
Aluminum is the most abundant metal in the earth's crust. In 1855, this metal was shown next to the crown jewels at the Paris World Exhibition while Napoleon III used aluminum cutlery at state dinners. As an extremely reactive metal, it is only found in its oxidized form in nature because it is easily oxidized. [1]

For the reason of implications and potential, the organoaluminum chemistry has been significant enough to excite widespread industrial interest. In 1859, Hallwachs and Schafarik firstly synthesized ethylaluminum sesquiiodide (a 1:1mixture of $EtAlI_2$ and Et_2AlI) from ethyl iodide and aluminum.[2] However, it took nearly one century before K. Ziegler discovered the synthetic and catalytic potential of organoaluminum compounds and the low pressure polymerization of olefins with organoaluminum/transition metal catalysts.[3,4] These studies open a wide insight into the organoaluminum chemistry and make the potential of organoaluminum reagents for organic synthesis and polymerization come to light. Over the last three decades systematic studies of both the coordination and organometallic chemistry of aluminum have expanded rapidly. Many new properties of organoaluminum compounds are found. For instance, in 1980 methylaluminoxane (MAO) was proved to be the most efficient activator for homogeneous metallocene catalyzed olefin polymerization reaction by Kaminsky and Sinn.[5-13]

The stereoselective catalytic behavior of many aluminum compounds has proved to be of considerable commercial value for stereospecific industrial syntheses of organic compounds. Such properties are also related to the stereochemical specificity of biological systems.[14] In the following part, some of the work which is related to the contents of the present dissertation will be discussed in detail.

1.1. Hydrolysis of organoaluminum compounds

MAO has been proved of remarkable industial importance, while a very important method to prepare alumoxanes is the controlled hydrolysis of organoaluminum compounds. Furthermore, MAO can be used to generate organoaluminum hydroxides, oxides, or oxide hydroxides.[9,15-22] Recent studies demonstrated two effective methods for the hydrolysis of aluminum compounds. In a liquid ammonia/toluene two-phase system the first terminal aluminum dihydroxide $LAl(OH)_2$ ($L = HC(CMeNAr)_2$, Ar = 2,6-$i$$Pr_2C_6H_3$) was obtained by the reaction of $LAlI_2$ with KOH containing water and KH.[23] In the same system a dinuclear aluminoxane[12b] containing a terminal hydroxide and a six-membered aluminoxane was obtained.[24] The other method is using the strong nucleophilic *N*-heterocyclic carbene as a HCl acceptor for the reaction of LAlRCl ($L = HC[(CMe)(NAr)]_2$, Ar = 2,6-$i$$Pr_2C_6H_3$, R = OH,[25] R = I[25], R = Cl[26]) with stiochiometric amounts of water to afford LAlR(OH). However, these two methods have been only used for L ($L = HC[(CMe)(NAr)]_2$, Ar = 2,6-$i$$Pr_2C_6H_3$) systems. The hydrolysis reaction of aluminum compounds supported by other ligand has seldom been reported.



Scheme *1*

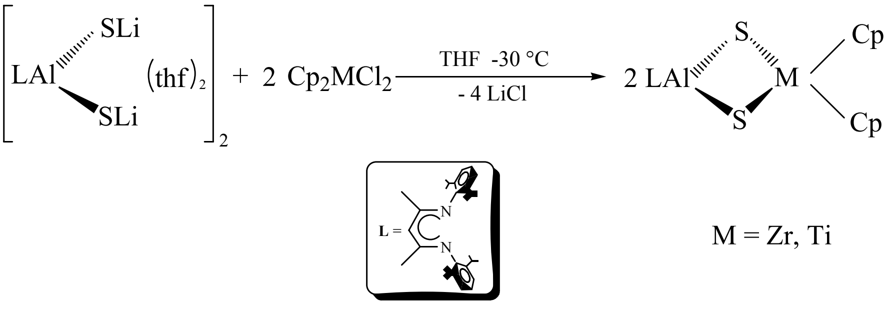
1.2. Aluminum chalcogenides

Aluminum compounds containing Group 16 elements are very important due to their application as catalysts in industry. Although the heavier congeners of oxygen are less studied than those containing Al-O bonds. One route for the preparation of this type of compounds is the reaction of $(Cp^*Al)_4$ ($Cp^* = C_5Me_5$) with elemental chalcogens (E = Se, Te).[27] Recently much attention has been payed to heterobimetallic chalcogen compounds.

$$(Cp^*Al)_4 + 4/xE_x \longrightarrow (Cp^*AlE)_4$$

Scheme ***2***

Organometallic sulfides are less stable than the corresponding oxides and synthetic methods for their preparation are limited. Moreover aluminum-containing heterobimetallic sulfides have been reported very seldom. More recently $\{LAl[(SLi)_2(THF)_2]\}_2$ was prepared and this is a valuable precursor for the preparation of heterobimetallic sulfides. Two aluminum containing transition metal heterobimetalic sulfides $LAl(\mu\text{–}S)_2MCp_2$ (M = Zr, Ti) were prepared. But there is so far no aluminum containing main-group heterobimetallic sulfide or aluminum containing hetertrimetallic sufide known.[28]

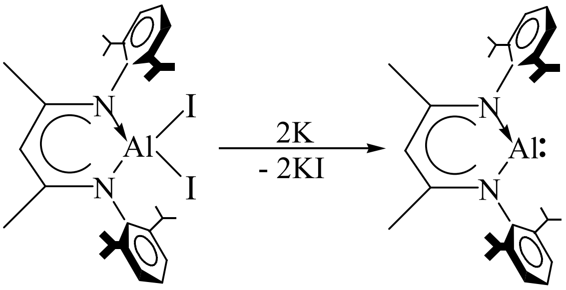


Scheme ***3***

1.3. Aluminum(I) compounds.

The chemistry of aluminum is mainly known of its trivalent state.[29] In comparison to the trivalent organoaluminum chemistry, the aluminum(I) chemistry has been investigated to a lower extend. Schnöckel et al. reported the first stable organoaluminum(I) compound

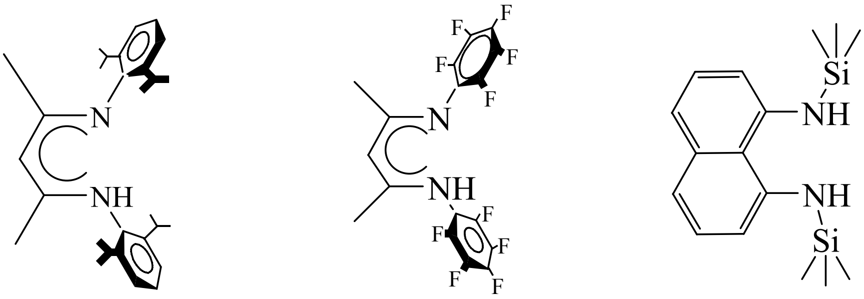
($Cp^*Al)_4$ in 1991.[30] The first example of a room temperature stable monomeric aluminum(I) compound of composition [$HC(CMeNAr)_2$]Al (Ar = 2,6-*i*$Pr_2C_6H_3$) was synthesized by the reduction of [$I_2Al\{HC(CMeNAr)_2\}$] with potassium in 2000.[31] On the basis of ab initio calculation, it was shown that the lone pair electrons of LAl(I) is stereochemically active and possibly has a quasi-trigonal-planar orientation. Charge depletion of the aluminum atom into the semiplane of the ring is also noticed. These features provide scope for observing both Lewis acid and Lewis base behavior of LAl(I). But there is no experimental evidence reported until now.



Scheme ***4***

1.4.Bulky organic ligands

Bulky orgaic ligands are usually used to stabilize the metal center due to their electronic and steric properties. The bulky ligands can reduce the condensation of molecules to form monomic compounds. Using these kinds of ligands, we can selectively shift the functionalities at the Al center, and intendedly design and control the reaction process. The following bulky ligands are employed in this dissertation. Ligand L and L' belong to the *β*-diketiminato ligands. Ligand L* is a bivalent ligand. A seris of important aluminum compounds were synthesised supported by these three ligands. In chapter 2 it will be pointed out in detail the importance, the recent research background, the experimental results, the discussion, the conclusion, and an outline of the chemistry of the bulky ligands stabilized aluminum



L L' L*

Scheme *5*

compounds and their reactions. The objectives of the present work are based on the following topics:

(1) the study of the hydrolysis of aluminum(III) compounds bearing the C_6F_5-substituted *β*-diketiminate $HC[(CMe)(NC_6F_5)]_2$ (L') ligand.

(2) synthesis and characterization of aluminum-containing tin, germanium heterobimetallic sulfides and selenides.

(3) the exploration of the reaction chemistry of the aluminum(I) monomer LAl.

(4) synthesis and characterization of aluminum halides, aluminum hydrides and aluminum alkyls bearing the 1,8-bis-(trimethylsilyamino)naphthalene ligand.

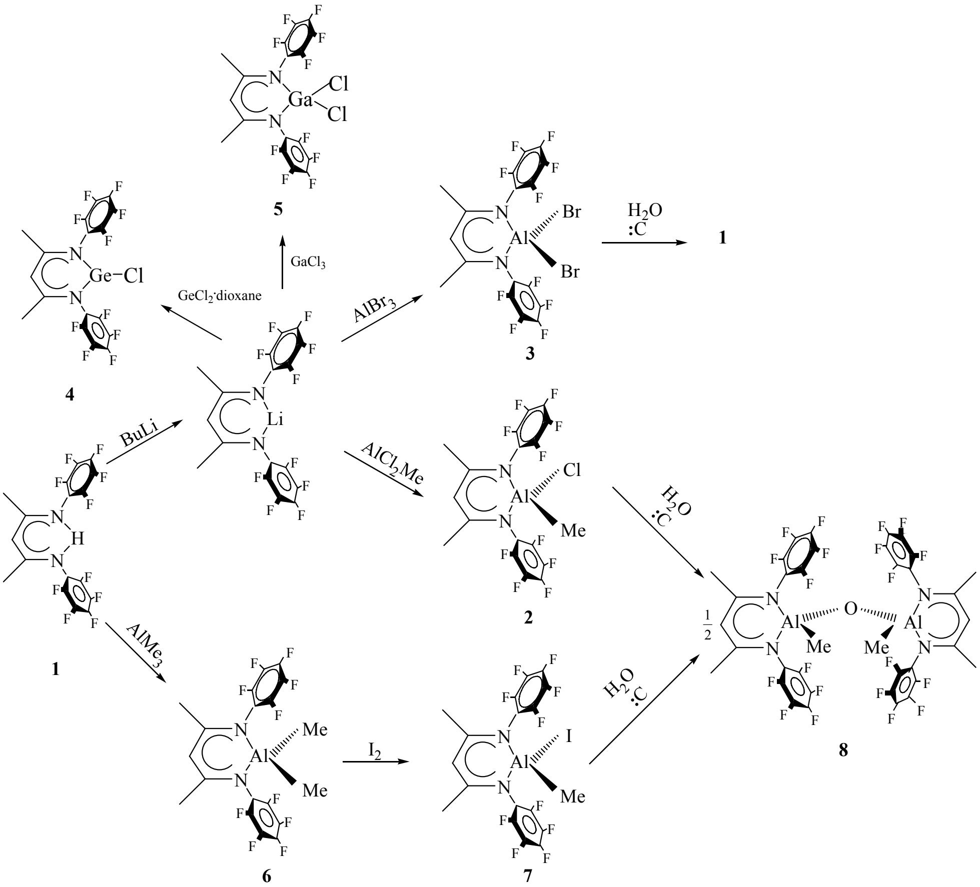
2. Results and Disussion

2.1. Synthesis and Chacterization of Aluminum, Gallium and Germanium Compounds Bearing the C_6F_5-Substituted β-Diketiminate $HC[(CMe)(NC_6F_5)]_2$ (L') Ligand

Organoaluminum compounds containing Al-O bonds have attracted much interest since the discovery of methylalumoxane as an extremely potent cocatalyst in the polymerization of ethylene and propylene by Group 4 metallocenes.[12] The method for the formation of alumoxane is the controlled hydrolysis of organoaluminum compounds with water[3,17,18] or reactive oxygen-containing species.[32] Traditionally, the reaction of AlR_3 compounds (R = Me, *t*Bu, Mes, or Ph)[33, 34] with water or hydrated inert salts afforded some aggregated alumoxanes $[RAlO]_n$, aluminum hydroxides, and oxide hydroxides. In most of the cases the bulky ligand at the aluminum center hinders the aggregation of the hydrolysis product that can result in the formation of unusual mononuclear hydroxide, such as LAlMe(OH) (L = $HC[(CMe)(NAr)]_2$, Ar = 2,6-$i\mathrm{Pr}_2C_6H_3$). This compound was recently prepared by hydrolysis of LAlMeCl with the bulky β-dikeminate ligand $HC[(CMe)(NAr)]_2$ (Ar = 2,6-$i\mathrm{Pr}_2C_6H_3$) (L).[35] In 2002, Power et al. reported on a new C_6F_5 substituted β-diketiminate ligand $HC[(CMe)(NC_6F_5)]_2$ (L') (**1**).[36] Moreover Cowley et al. prepared a Lewis acid stabilized compound with a boron–oxygen double bond using this ligand,[37] and more recently they reported on the X-ray crystal structure of the ligand (L') and also on L'Li·(Et_2O), L'$AlMe_2$, and L'$GaMe_2$ respectively.[38] In these papers, it was demonstrated that this ligand exhibits very interesting reaction properties. In order to investigate the unusual hydrolysis of the aluminum compound with the bulky β-diketiminate ligand in more detail, we selected the C_6F_5 substituted β-diketiminate $HC[(CMe)(NC_6F_5)]_2$ (L') (**1**) as the supporting ligand. Finally a new method has attracted great interest, using the strong nucleophilic *N*-heterocyclic carbene as a HCl acceptor for the reaction of LAlRCl (L = $HC[(CMe)(NAr)]_2$, Ar = 2,6-

i$Pr_2C_6H_3$, R = Cl,[26] R = OH,[25] R = I[25]) with stiochiometric amounts of water to afford LAlR(OH). We used this new technique as well to obtain a high yield methylalumoxane derivative.

Compounds L'AlMeCl (**2**), L'AlBr$_2$ (**3**), L'GeCl (**4**), and L'GaCl$_2$ (**5)** (L' = HC[(CMe)(NC$_6$F$_5$)]$_2$) were prepared according to the silimar procedure given in Scheme 6. The toluene solution of L'Li prepared from L'H and *n*-BuLi was directly used for the reaction with AlCl$_2$Me, AlBr$_3$, GeCl$_2$·dioxane, and GaCl$_3$ respectively. By reaction of L'AlMe$_2$ (**6**) with iodine L'AlMeI (**7**) can be obtained (Scheme 6). While **6** was prepared from L'H and AlMe$_3$ as a crystalline solid. All compounds were characterized by EI-MS and ^{1}H, ^{19}F, and ^{13}C NMR measurements as well as by elemental analysis. The reaction of **6** with 1 equiv of I$_2$ within 3 days at room temperature results in the formation of **7** as light yellow crystals. To our



Scheme 6. Preparation of compounds **2**-**8**

surprise the reaction of **6** with 2 eqiv of I_2 yields only **7** and no formation of L'AlI_2 was observed. In contrast the reaction of $LAlMe_2$ with I_2 resulted in the formation of $LAlI_2$.[39] The most important reason for this behaviour is an increase in the Al–C bond strength which does not allow the cleavage of this bond under the reported condition with iodine. When either **2** or **7** were hydrolysised in the presence of a *N*-heterocycliccarbene, $(L'AlMe)_2(\mu\text{-}O)$ (**8**) was obtained as a methylalumoxane derivative instead of the L'AlMe(OH). This is obviously due to the stronger Brönsted acidity of the proton and the smaller size of the C_6F_5 group in this compound compared to that of the corresponding 2,6-$i$$Pr_2C_6H_3$ derivative. In the ^1H NMR spectrum compounds **2**, **6**, **7**, and **8** respectively show one resonance between δ 0 to –1 ppm, this can be assigned to the Al-*Me.* All compounds exhibit one resonance between δ 4 and 5 ppm, and one signal between δ 1 and 2 ppm with the intensity of 1:6, showing the characteristic β-diketiminate resonances. In the ^{19}F NMR spectra **1**, **3**, **4**, and **6** exhibit three resonances in the ration of 2:1:2, while compounds **2**, **5**, **7**, and **8** respectively show five resonances in the ratio of 1:1:1:1:1. These differences can be attributed to the symmetric arrangement of **1**, **3**, **4**, and **6**, and the asymmetric structures of **2**, **5**, **7**, and **8**. In the EI-MS spectra, the most intense peak of compounds **2**, **6**, **7**, and **8** is attributed to [M^+-Me]. Compounds **3, 4**, and **5** exhibit its most intense peak for the molecular ion [M^+]. In summary the MS data indicate that under these conditions the methyl group at the aluminum is easily eliminated.

The X-ray crystal structures of **3** (Figure 1), **4** (Figure 2), **5** (Figure 3), and **6** (Figure 4) respectively showed mononuclear compounds with aluminum, gallium, and germanium at the center that coordinates to the chelating β-diketiminate ligand with the C_6F_5 groups attachted to the ring. Compounds **3**, **4**, and **6** exhibit a distorted tetrahedral geometry. The molecular structure of **6** is shown in Figure 4. The terminal Al-Me bond length (av 1.956(2)Å) is a little shorter than that (av 1.964(3) Å) in $LAlMe_2$.[40] This is also found for the Al-N bond length (av 1.9213(15) Å, av 1.929(2) Å in $LAlMe_2$). For compound **3**, the Al-N bond length (1.865(2)

Å) is a little shorter than those in **6**, which is in good agreement with the electron donating of the Me group and the electron withdrawing properties of bromine. The X-ray structural analysis of **8** (Figure 5) unambiguously confirms the formation of the Al(1)-O-Al(2) unit, which is almost linear with an angle of 174.42(11)°. The Al-O bond length (1.689(2),

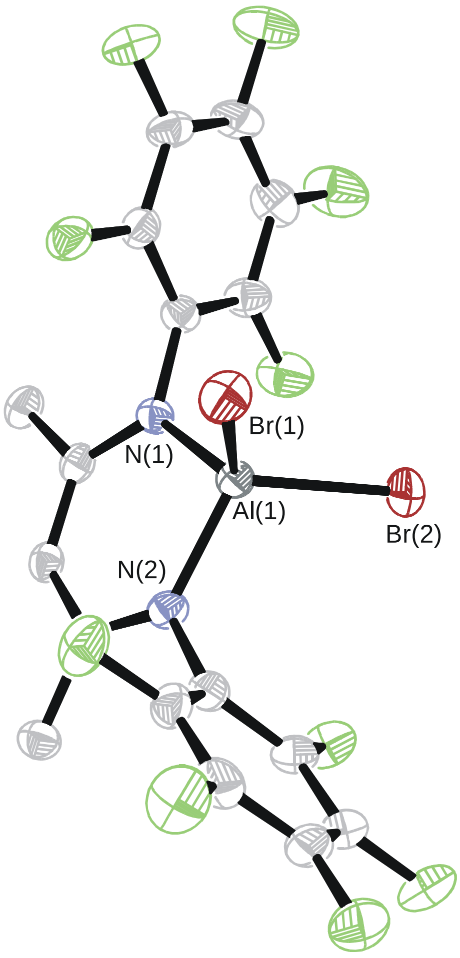


Figure 1. Molecular structure of **3**. Thermal ellipsoids are drawn at 50% level, and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)-N(1) 1.865(2), Al(1)-N(2) 1.865(2), Al(1)-Br(1) 2.267(1), Al(1)-Br(2) 2.271(1), N(1)-Al(1)-N(2) 98.53(9), N(1)-Al(1)-Br(1) 114.08(8), N(1)-Al(1)-Br(2) 112.09(9), Br(1)-Al(1)-Br(2) 109.12(3), N(2)-Al(1)-Br(1) 110.75(9), N(2)-Al(1)-Br(2) 111.99(8)

1.685(2) Å) is shorter compared to those in $[LAl(OH)]_2O$ (1.698(3), 1.694(3) Å),[24] and the two *β*-diketiminate planes are arranged vertical to each other. The two Al-C bonds are in trans position toward the Al(1)-O-Al(2) planes, with bond lengths (av 1.951(3) Å) slightly shorter than those in **6** (av 1.956(2) Å).

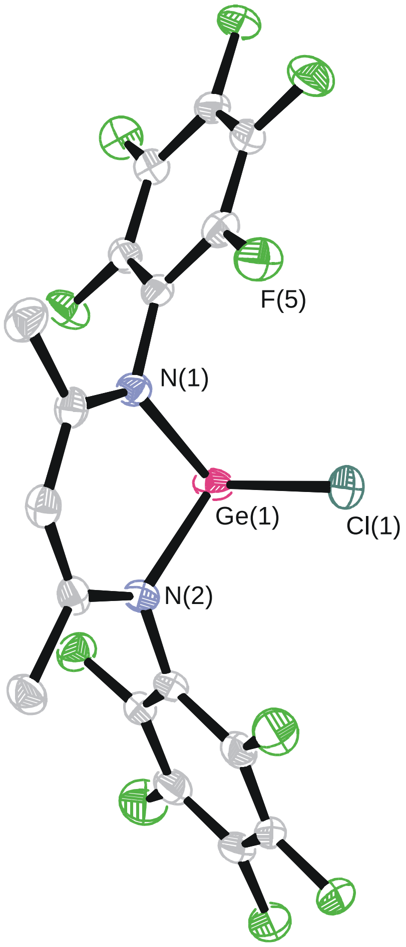


Figure 2. Molecular structure of **4**. Thermal ellipsoids are drawn at 50% level, and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ge(1)-N(1) 1.998(2), Ge(1)-N(2) 2.000(2), Ge(1)-Cl(1) 2.299(1), N(1)-Ge(1)-N(2) 89.01(8), N(1)-Ge(1)-Cl(1) 93.78(6), N(2)-Ge(1)-N(1) 89.01(8), N(2)-Ge(1)-Cl(1) 94.50(6)

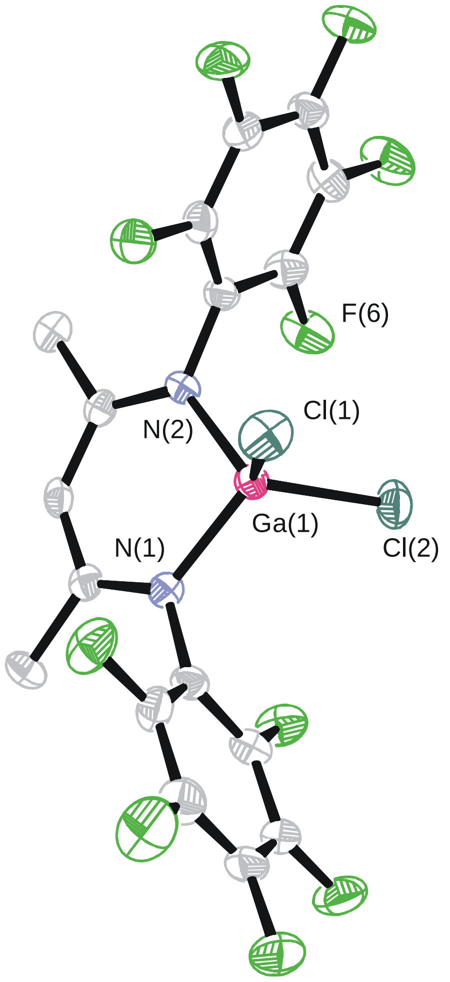


Figure 3**.** Molecular structure of **5**. Thermal ellipsoids are drawn at 50% level, and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ga(1)-N(1) 1.908(3), Ga(1)-N(2) 1.912(3), Ga(1)-Cl(1) 2.154(1), Ga(1)-Cl(2) 2.152(1), N(1)-Ga(1)-N(2) 99.02(15), N(1)-Ga(1)-Cl(1) 112.70(10), N(1)-Ga(1)-Cl(2) 113.53(10), Cl(1)-Ga(1)-Cl(2) 109.54(5), N(2)-Ga(1)-Cl(1) 111.08(11), N(2)-Ga(1)-Cl(2) 110.61(11)

In contrast to $LAl(OH)_2$, which was prepared from $LAlCl_2$ by hydrolysis the corresponding reaction of **3** with water does not yield $L'Al(OH)_2$.[28] The only isolated product was **1**. The difference in the reactivity should be attributed to the strong electron withdrawing properties of the C_6F_5 groups. We have also tried the reaction of H_2S with **2** and **7**

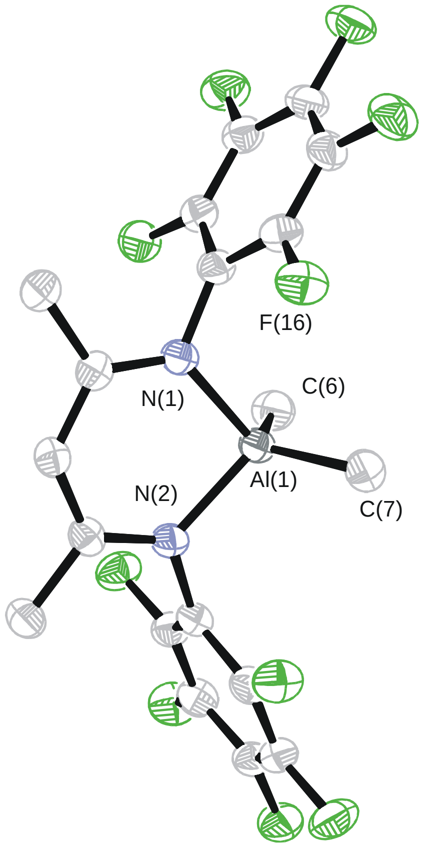


Figure 4. Molecular structure of **6**. Thermal ellipsoids are drawn at 50% level, and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)-N(1) 1.9212(15), Al(1)-N(2) 1.9214(15), Al(1)-C(6) 1.961(2), Al(1)-C(7) 1.951(2), N(1)-Al(1)-N(2) 93.95(6), N(1)-Al(1)-C(6) 108.57(8), N(1)-Al(1)-C(7) 110.55(7), C(6)-Al(1)-C(7) 118.90(9), N(2)-Al(1)-C(6) 110.46(8), N(2)-Al(1)-C(7) 111.55(8)

respectively to get compound $(L'AlMe)_2S$ similar to that of **8**. A mixture of $(L'AlMe)_2(\mu\text{-}S)$ and **8** was formed due to small amounts of H_2O, which we were not able to remove from the starting material H_2S. Moreover we were also not successful in separating the products.

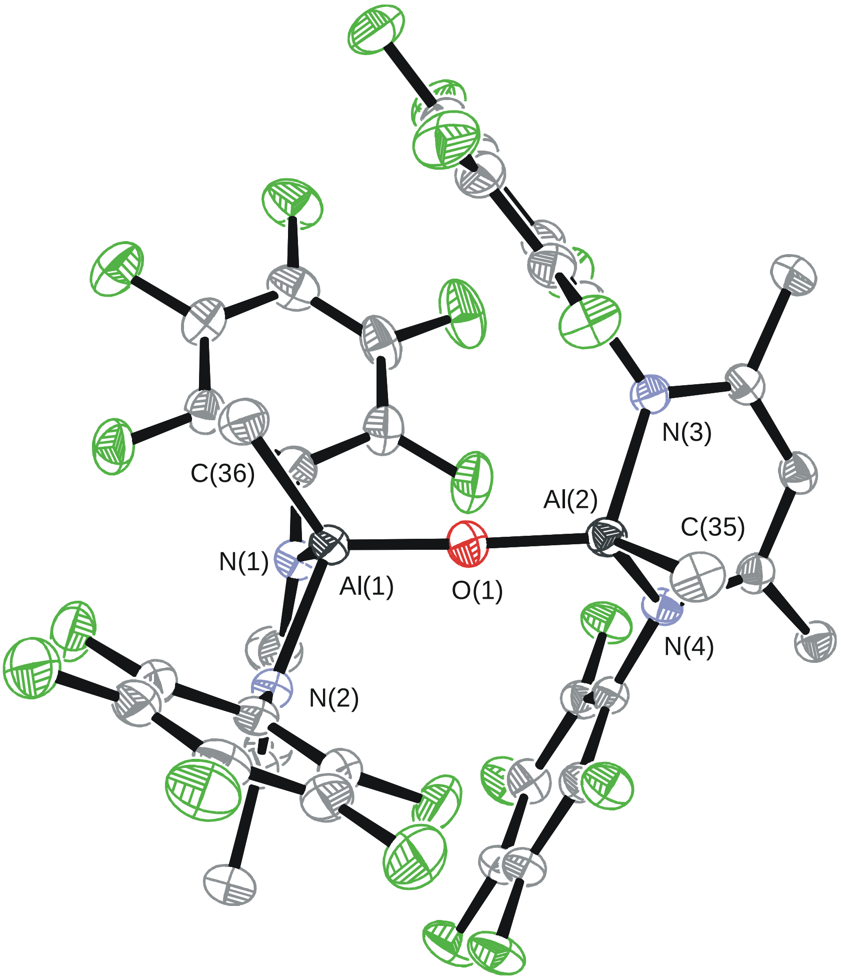


Figure 5. Molecular structure of **8**. Thermal ellipsoids are drawn at 50% level, and the hydrogen atoms and 0.5 molecular toluene are omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)-N(1) 1.926(2), Al(1)-N(2) 1.930(2), Al(1)-C(36) 1.953(2), Al(1)-O(1) 1.689(2), N(1)-Al(1)-N(2) 94.00(9), N(1)-Al(1)-O(1) 111.16(9), N(1)-Al(1)-C(36) 109.95(10), N(2)-Al(1)-O(1) 109.04(8), N(2)-Al(1)-C(36) 113.15(9), O(1)-Al(1)-C(36) 117.16(10), Al(1)-O(1)-Al(2) 174.42(11)

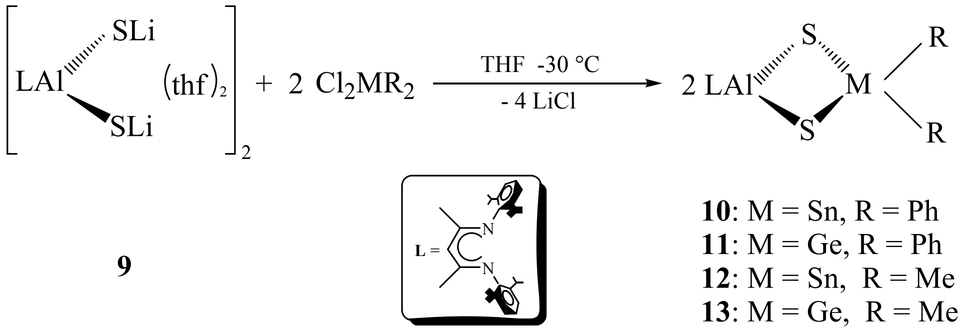
In summary we report on the synthesis of a series of Al, Ga and Ge compounds containing the C_6F_5 substituted *β*-diketiminate as the supporting ligand (**2**, **3**, **4**, **5**, **6**, **7**), and studied the hydrolysis of **2** and **7** in the presence of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (:C). The deprotonation of the coordinated H_2O by :C with formation of the insoluble

$[H{:}C]^+Cl^-$ salts leads to $(L'AlMe)_2(\mu\text{-}O)$ (**8**), a derivative of MAO, which is the first hydrolysis product with the general formula $(RAlMe)_nO$. This reaction demonstrates the powerful acceptor properties of the *N*-heterocyclic carbene. By comparing the product of hydrolysis **8** with that of LAlMeCl we have shown that the Brönsted acidic nature of the proton in the intermediate L'AlMe(OH) and the less steric demand of the C_6F_5 groups are responsible for the further reaction.

2.2. Synthesis and Characterization of Aluminum-Containing Tin and Germanium Heterobimetallic Sulfides and Selenides

Organometallic chalcogen compounds have attracted much interest due to their application as catalysts in industry. More recently attention has been payed to heterobimetallic chalcogen compounds not only from the viewpoint of fundamental chemistry but also due to their catalytic properties.[41] Aluminum is the most abundant metal in the earth's crust, therefore many aluminum-containing heterobimetallic oxides have been synthesised and characterized.[37, 42] Organometallic sulfides are less stable than the corresponding oxides and synthetic methods for their preparation are limited. Moreover aluminum-containing heterobimetallic sulfides have not been reported very often. There are only a few examples known containing the Al–(μ–S)–Fe[43] and Al–(μ–S)–M (M = Zr, Ti) moieties.[28, 44] Recently $\{LAl[(SLi)_2(THF)_2]\}_2$ (L = $HC[(CMe)(NAr)]_2$, Ar = 2,6-$i$$Pr_2C_6H_3$) (**9**) was prepared and this is a valuable precursor for the preparation of heterobimetallic sulfides.[28] The first aluminum-containing heterotrimetallic sulfide of composition $L_2Al_2Ge_4Li_2S_7$ has been prepared by reacting **9** with $GeCl_2$·dioxane.[45] Herein, we report on the reaction of **9** with organotin and organogermanium dichlorides and also on tin and germanium tetrachlorides to yield $LAl(\mu\text{-}S)_2MPh_2$ (**10**: M = Sn; **11**: M = Ge), $LAl(\mu\text{-}S)_2MMe_2$ (**12**: M = Sn; **13**: M = Ge), and the spirocyclic heterotrimetallic sulfide $LAl(\mu\text{-}S)_2M(\mu\text{-}S)_2AlL$ (**14**: M = Sn; **15**: M = Ge).

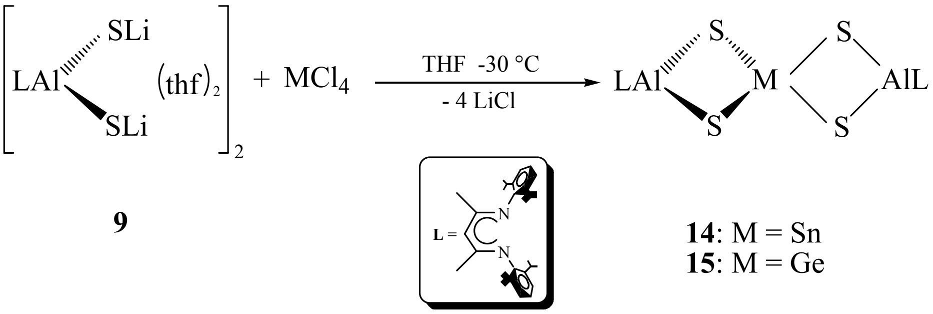
Compounds **10-13** were prepared by adding dropwise in Ph_2SnCl_2, Ph_2GeCl_2, Me_2SnCl_2, and Me_2GeCl_2 dissolved in THF respectively to **9** in THF at low temperature (Scheme 7, 8). Since $SnCl_4$ and $GeCl_4$ are liquid, they are added directly to the THF solution of **9**. Compound **9** is sparingly soluble in THF and therefore it formed a suspension in THF at low temperature. However, after adding Ph_2MCl_2, Me_2MCl_2 or MCl_4 (M = Sn, Ge), the suspension became clear and the light yellow color turned very quickly to colorless. This is an indication for the progress of the reaction. Alternatively, compound **14** can be prepared by direct reaction of **9**



9

10: M = Sn, R = Ph
11: M = Ge, R = Ph
12: M = Sn, R = Me
13: M = Ge, R = Me

***Scheme** 7*. Preparation of compounds **10**, **11**, **12**, and **13**



9

14: M = Sn
15: M = Ge

Scheme 8. Preparation of compounds **14** and **15**

with $SnCl_4{\cdot}2THF$ in toluene to avoid decomposition of **9** by traces of free HCl present in $SnCl_4$.Compounds **10-13** are all colorless solids and well soluble in toluene, benzene etc. They were characterized by EI-MS spectra, elemental analysis, ^{1}H, ^{13}C, ^{27}Al, and ^{119}Sn NMR investigations, and single-crystal X-ray diffraction studies. The ^{1}H NMR spectra of **10-15** exhibit one set of resonances for the ligand (L). **10** and **11** show the M–*Ph* (M = Sn, Ge) resonances in the range from 7.10 to 7.02 ppm, which are distinct from those of the Ar-H resonances (δ 7.23–7.16 ppm). **12** and **13** exhibit M–*Me* (M = Sn, Ge) around δ 0.4 ppm in a 6:1 ratio to that of the γ-H proton. Compounds **14** and **15** display only one set of resonances for the ligand (L) indicating that the two ligands are in the same chemical environment. The ^{27}Al NMR spectra of **10**, **12**, and **14** show the resonances in a narrow range (113 to 114 ppm) which are comparable to those compounds with four coordinate aluminum.[46, 40] The electron impact (EI) mass spectra of **10**-**15** (m/z = 782, 736, 658, 612, 1136, and 1090) show the parent ion [M^+] with their isotopic pattern. Particularly interesting is the ion of composition [LAl(μ-S)$_2$Sn] (m/z = 627), which appears in the fragmentation of both **10** and **12**.

The composition of **10** (Figure 6), **12** (Figure 7), **13** (Figure 8), and **14** (Figure 9) were assigned by X-ray structural analysis. Colorless crystals of **10**·toluene, **12**·toluene, **13**, and **14**·1.5 toluene·THF were obtained from toluene at –28 °C. The structure of **14**·1.5 toluene·1 THF contains disordered solvent molecules, which could be refined using restraints and rigid body constraints. Compound **12**·toluene crystallizes in the triclinic space group $P\bar{1}$, while **10**·toluene, and **14**·1.5 toluene·THF crystallize in the monoclinic space group $P2_1/c$. The characteristics of **10**, **12**, and **13** are the (μ-S)$_2$ bridges between the aluminum and tin or germanium atoms generating novel heterobimetallic sulfides. **14** displays a spirocyclic arrangement with the tin atom at the center of the Al–(μ-S)$_2$–Sn–(μ-S)$_2$–Al moiety and represents the first example of a lipophilic complex of *ortho*- thiostannous acid. In the structures of compounds **10**, **12**, and **13** the AlS_2M (**10**, **12**: M = Sn; **13**: M = Ge) four-membered rings are both perpendicular to the AlN_2C_3 plane of the ligand (L) as well as to the C–M–C planes. Consequently the ligand plane and the C–M–C plane are parallel in **10**, **12**, and **13**. In the structure of compound **14**, there are four conjoint planes: consisting of two six-membered ligand (L) planes, and two four-membered AlS_2Sn planes, where every interfacing plane is perpendicular to its neighbors. The Sn–S bonds in **10** (2.402(1) Å, 2.403(1) Å) are slightly longer than those in **14** (2.378–2.397 Å), similar to those in **12** (2.395(1) Å, 2.413(1) Å). They are in the range of those reported previously (2.329–2.574 Å).[47] The Al–S–Sn angles of **10**, **12**, and **14** are very similar: **10** (81.4°, 81.5°), **12** (81.7°, 82.4°), **14** (81.8°, 82.2°,82.1°, 81.6°).

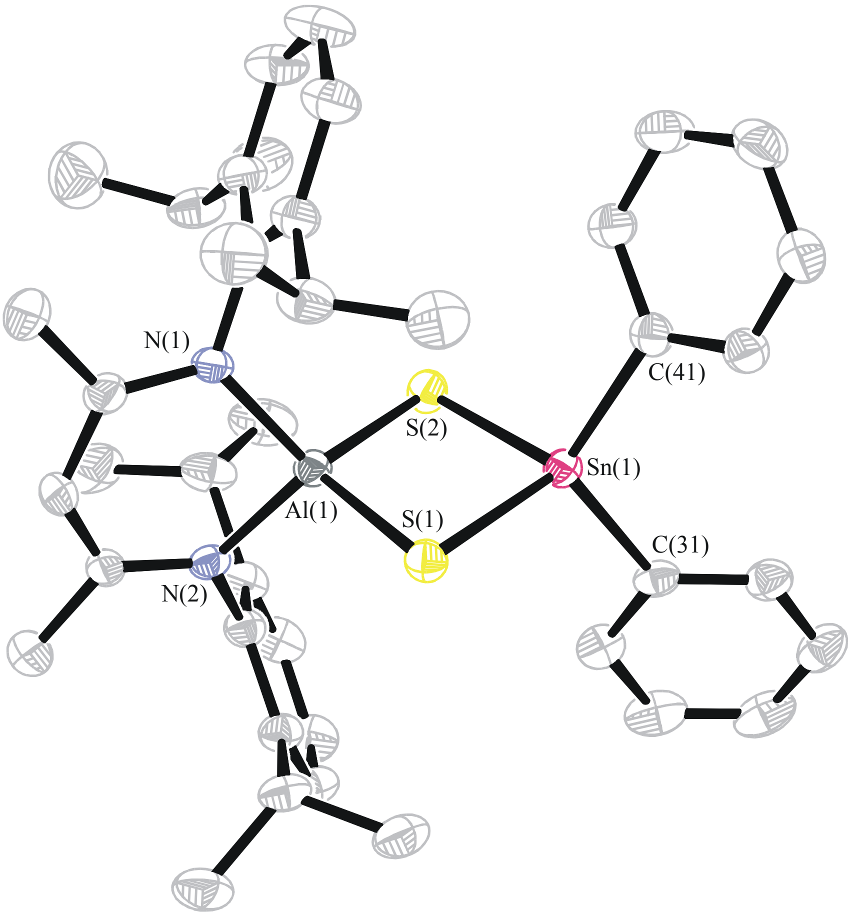


Figure 6. Molecular structure of **10**. Thermal ellipsoids are drawn at 50% level. The solvent molecule and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)–N(1) 1.882(2), Al(1)–N(2) 1.889(2), Al(1)–S(1) 2.233(1), Al(1)–S(2) 2.229(1), Sn(1)–S(1) 2.403(1), Sn(1)–S(2) 2.402(1), Al(1)–Sn(1) 3.026(1), S(1)–Al(1)–S(2) 103.3(1), Al(1)–S(1)–Sn(1) 81.4(1), Al(1)–S(2)–Sn(1) 81.5(1), S(2)–Sn(1)–S(1) 93.5(1), C(31)–Sn(1)–C(41) 117.0(1)

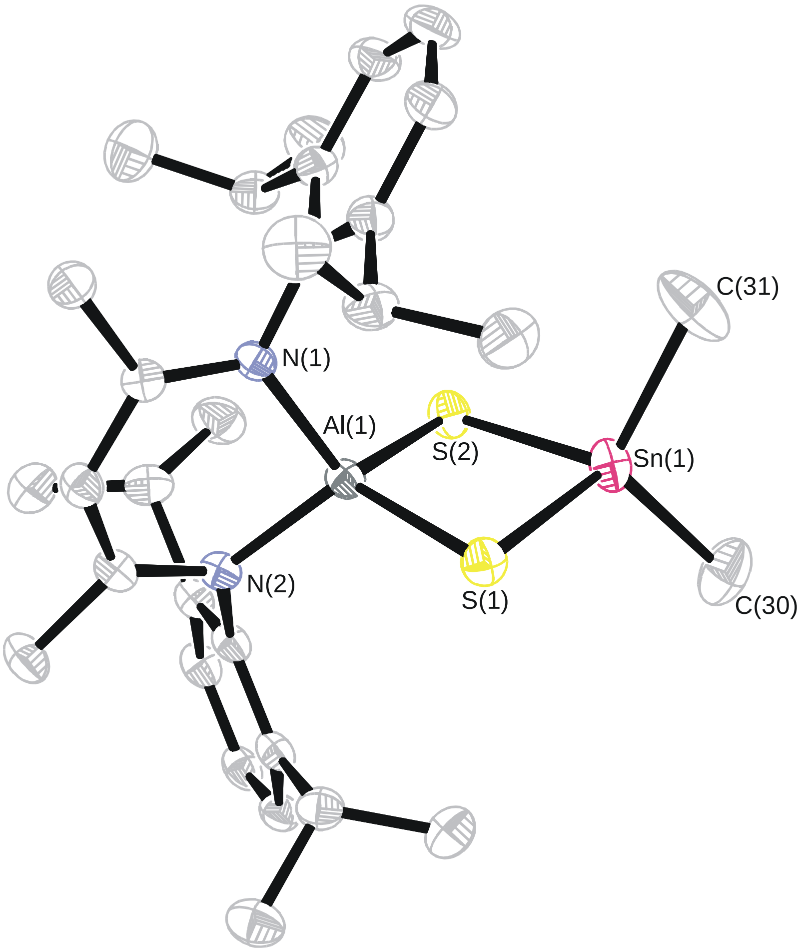


Figure 7. Molecular structure of **12**. Thermal ellipsoids are drawn at 50% level. The solvent molecule and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)–N(1) 1.902(3), Al(1)–N(2) 1.893(3), Al(1)–S(1) 2.227(1), Al(1)–S(2) 2.213(1), Sn(1)–S(1) 2.413(1), Sn(1)–S(2) 2.395(1), Al(1)–Sn(1) 3.037(1), S(2)–Al(1)–S(1) 102.9(1), Al(1)–S(1)–Sn(1) 81.7(1), Al(1)–S(2)–Sn(1) 82.4(1), S(2)–Sn(1)–S(1) 92.5(3), C(30)–Sn(1)–C(31) 111.8(2)

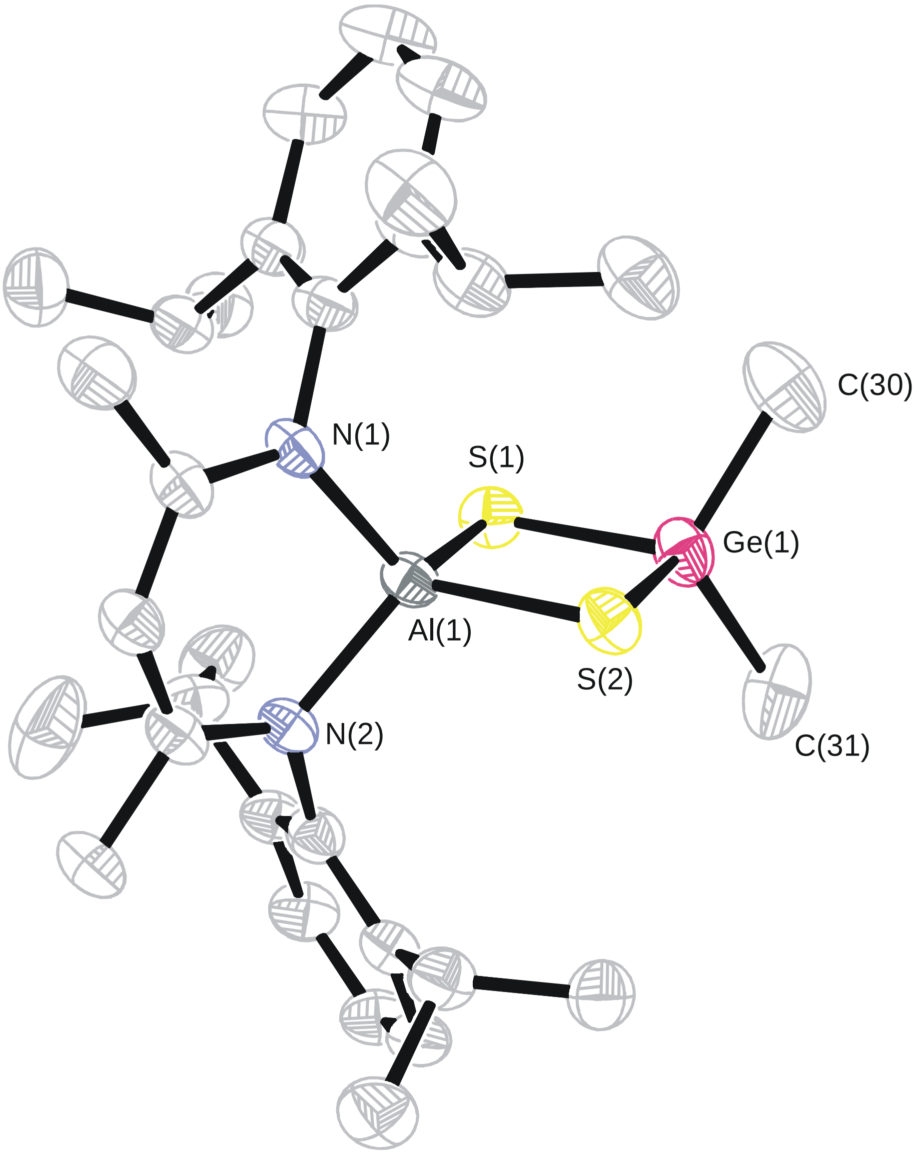


Figure 8. Molecular structure of **13**. Thermal ellipsoids are drawn at 50% level. Selected bond distances (Å) and angles (deg): Al(1)–N(1) 1.886(3), Al(1)–N(2) 1.877(3), Al(1)–S(1) 2.226(1), Al(1)–S(2) 2.229(2), Ge(1)–S(1) 2.225(1), Ge(1)–S(2) 2.227(1), Al(1)–Ge(1) 2.891(1), S(2)–Al(1)–S(1) 114.72(1), Al(1)–S(1)–Ge(1) 81.01(5), Al(1)–S(2)–Ge(1) 80.88(5), S(2)–Ge(1)–S(1) 99.08(4), C(30)–Ge(1)–C(31) 114.0(2)

After the success in the synthesis of aluminum-containing heterobimetallic sulfides, we became interested in preparing aluminum-containing heterobimetallic selenides. First step of our process was the synthesis of LAl(-SeLi)$_2$(THF)$_2$ (**16**) (It has probably an oligomer

$[LAl(SeLi)_2(THF)_2]_n$ composition) by the reaction of $LAl(SeH)_2$ with $LiN(SiMe_3)_2$ at -20 °C, The dilithium salt $LAl(SeLi)_2(THF)_2$ (**16**) was obtained in good yield. The extremely sensitive

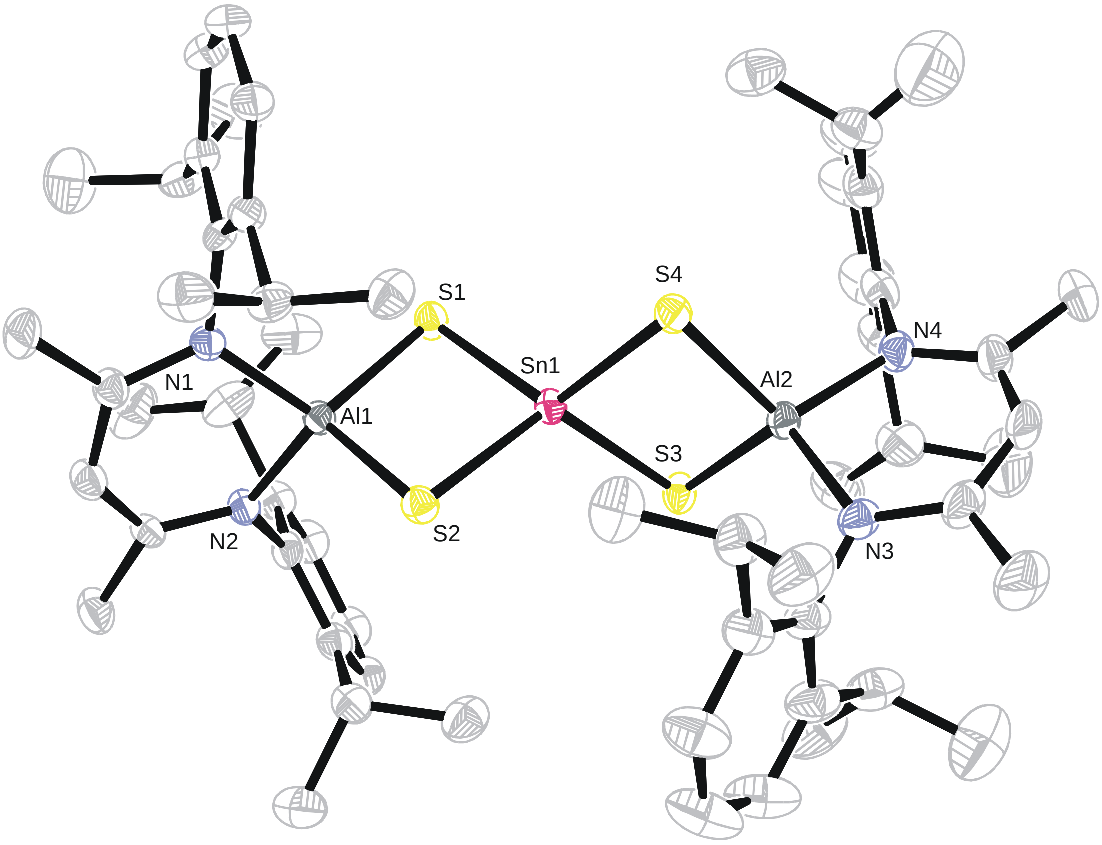
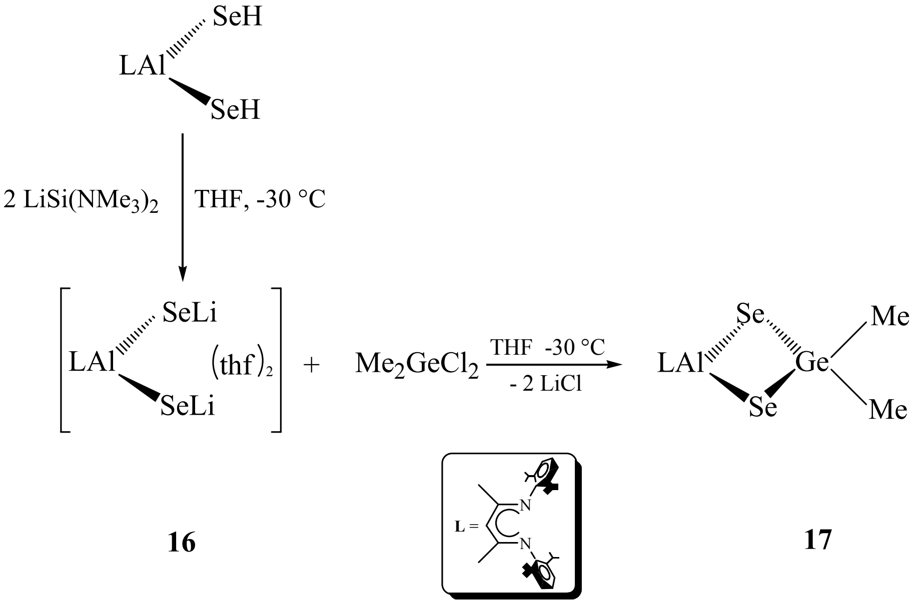


Figure 9. Molecular structure of **14**. Thermal ellipsoids are drawn at 50% level. The solvent molecule and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)–N(1) 1.875(6), Al(1)–N(2) 1.884(6), Al(2)–N(3) 1.882(6), Al(2)–N(4) 1.882(6), Al(1)–S(1) 2.239(3), Al(1)–S(2) 2.239(3), Al(2)–S(3) 2.230(3), Al(2)–S(4) 2.253(3), Sn(1)–S(1) 2.397(2), Sn(1)–S(2) 2.378(2), Sn(1)–S(3) 2.388(2), Sn(1)–S(4) 2.392(2), Sn(1)–Al(1) 3.037(2), Sn(1)–Al(2) 3.035(2), S(1)–Al(1)–S(2) 102.2(1), S(3)–Al(2)–S(4) 102.0(1), Al(1)–S(1)–Sn(1) 81.8(1), Al(1)–S(2)–Sn(1) 82.2(1), Al(2)–S(3)–Sn(1) 82.1(1), Al(2)–S(4)–Sn(1) 81.6(1), S(1)–Sn(1)–S(2) 93.7(1), S(3)–Sn(1)–S(4) 93.6(1), S(1)–Sn(1)–S(4) 122.0(1), S(2)–Sn(1)–S(3) 119.4(1), S(1)–Sn(1)–S(3) 115.6(1), S(2)–Sn(1)–S(4) 114.8(1), Al(1)–Sn(1)–Al(2) 173.3(1)

pale yellow product **16** is coordinated by two molecules of THF as determined by ^{1}H NMR spectroscopy. Then we focused on the reactivity studies of **16** towards the main group metal halide, namely (Me_2GeCl_2). When a solution of (Me_2GeCl_2) in THF was added dropwise to the suspension of **16** in THF at -30 °C, the suspension became clear and the light yellow color turned very quickly to colorless. This is an indication for the progress of the reaction from our experience of the preparation of heterobimetallic sulfides. After removal of the THF and the extraction of the crude product with hexane, compound LAl(μ-Se)$_2$GeMe$_2$ (**17**) was isolated in 85% yield.



Scheme 9. Preparation of compound **16** and **17**

Compound **17** (Figure 10) crystallizes in the monoclinic space group $P2_1/c$. The characteristic of **17** is the (μ-Se)$_2$ bridges between the aluminum and germanium atom generating a novel heterobimetallic selenide. In the structure of compound **17** the AlSe$_2$Ge four-membered ring is both perpendicular to the AlN$_2$C$_3$ plane of the ligand (L) as well as to the C–Ge–C plane. Consequently the ligand plane and the C–Ge–C plane are parallel to each other in **17**.

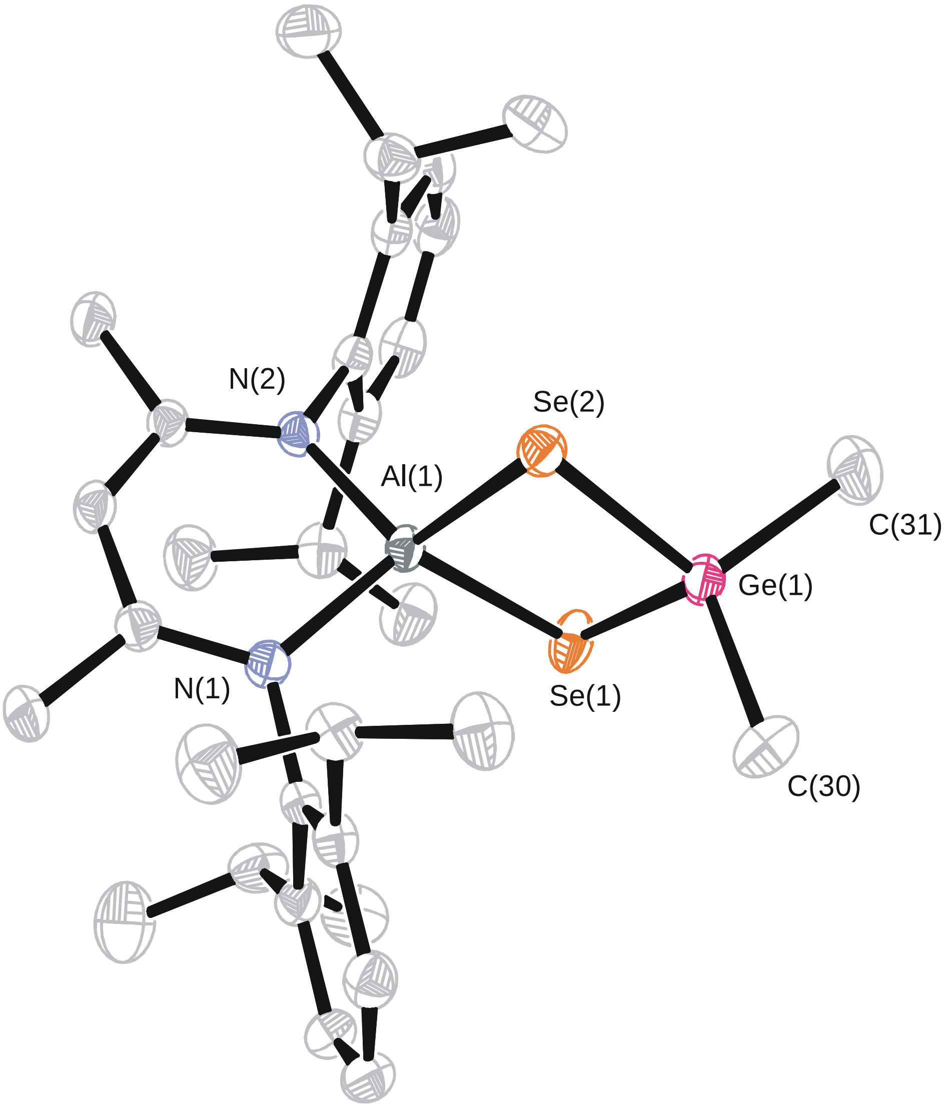


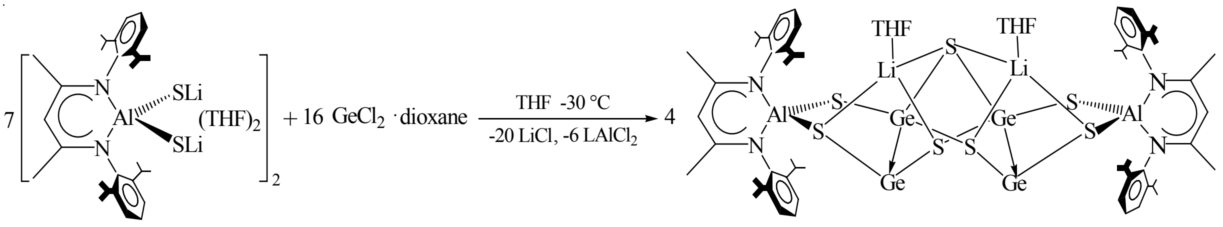
Figure 10. Molecular structure of **17**. Thermal ellipsoids are drawn at 50% level. Selected bond distances (Å) and angles (deg): Al(1)–N(1) 1.897(3), Al(1)–N(2) 1.880(3), Al(1)–Se(1) 2.356(1), Al(1)–Se(2) 2.367(1), Ge(1)–Se(1) 2.350(1), Ge(1)–Se(2) 2.350(1), Se(2)–Al(1)–Se(1) 99.16(3), Al(1)–Se(1)–Ge(1) 79.99(2), Al(1)–Se(2)–Ge(1) 79.75(5), Se(2)–Ge(1)–Se(1) 99.844(16), C(30)–Ge(1)–C(31) 111.10(17)

In summary we synthesised and characterized six novel aluminum-containing tin and germanium heterobimetallic sulfides and two heterobimetallic selenides.

2.3. An Unprecedented Example of A Heterotrimetallic Main Group $L_2Al_2Ge_4Li_2S_7$ Cluster Containing A Ge(II)–Ge(II) Donor-Acceptor Bond

Metal polysulfido complexes, especially of the heteromultimetallic species, have attracted much interest because of inherent fundamental chemistry in addition to their potential applications.[41a] In this field of research much has been focused on transition metals, while main group metal polysulfido complexes, especially those bearing two or more different main group metals, are very rare.[41] Although aluminum is the most abundant metal in the earth's crust, there are only a few aluminum containing heterobimetallic sulfides known (Al–(μ-S)–Fe,[43] Al–(μ-S)–M (M = Zr, Ti),[28, 44]) due to the limited synthetic methods that are available. Furthermore, no aluminum containing main group heterotrimetallic sulfide has been reported. Recently, $\{LAl[(SLi)_2(THF)_2]\}_2$ (L = $HC[(CMe)(NAr)]_2$, Ar = 2,6-$i$$Pr_2C_6H_3$) (**9**) was prepared by our group, that gives access to the preparation of heterobimetallic sulfides containing aluminum.[28] Herein, we report an unique class of a heterotrimetallic main group polysulfido $L_2Al_2Ge_4Li_2S_7$ cluster in which the germanium(II) metal acts both as a donor and an acceptor atom in a single heterotrimetallic species. To the best of our knowledge, such an example has never been demonstrated.

$[LAl(\mu\text{-}S)_2Ge_2]_2(\mu\text{-}S)_3Li_2\cdot(THF)_2]$ (**18**) was synthesized by the reaction of **9** with $GeCl_2$·dioxane in a molar ratio of 1:2 (Scheme 10). $GeCl_2$·dioxane in THF was added to the solution of **9** in THF at –30 °C. Compound **9** is sparingly soluble in THF and therefore it formed a suspension in THF at low temperature. However, after adding $GeCl_2$·dioxane, the suspension became clear very quickly. This is an indication for the progress of the reaction. Subsequently the solution was slowly warmed to room temperature. The solvent was removed in *vacuo* and the residue extracted with toluene. The resulting solution was kept at room temperature to isolate **18** as light-yellow crystals. Corresponding reactions of **9** with $SnCl_2$ and



9 **18**

Scheme 10. Preparation of compound **18**.

$PbCl_2$ respectively have been tried. After adding $SnCl_2$ or $PbCl_2$ to **9** in THF, a dark brown or black suspension appeared immediately, the dark colored solids isolated both are not soluble in organic solvents. They contain SnS and PbS respectively.

Compound **18** was characterized by ^{1}H, ^{13}C, ^{7}Li NMR spectra using [D$_6$]benzene as the solvent, and by elemental analysis. In the ^{1}H and ^{13}C NMR spectra of **18**, only one set of resonances for the ligand L is detected indicating that the two ligands are in the same chemical environment and are symmetrically arranged. Compound **18** is good soluble both in benzene and toluene but sparingly soluble in hexane.

X-ray quality crystals were obtained from the toluene solution of **18** that was kept at room temperature for two days and crystallized in the monoclinic space group $P2_1$. Its molecular structure is shown in Figure 11. It is interesting to note that the whole molecule has a crab-like geometry in which the core cluster is the crab's body, the two ligands are its side claws, and the two Li·THF units are its front pincers. The structure can also be viewed as a derivative of norbornane, if one omits the Li centers. The significant difference in the structure of **18** with that of $[LAl(\mu\text{-}S)_2MCp_2]$ (M = Zr, Ti)[28] was a surprise. The latter was prepared by the reaction of **9** with Cp_2MCl_2. The $[LAl(\mu\text{-}S)_2MCp_2]$ (M = Zr, Ti) contains an AlS_2M four-membered ring, while **18** consists of two AlS_2Ge_2 five-membered rings connected by three sulfur bridges, forming the $L_2Al_2Ge_4Li_2S_7$ cluster. The AlS_2Ge_2 five-

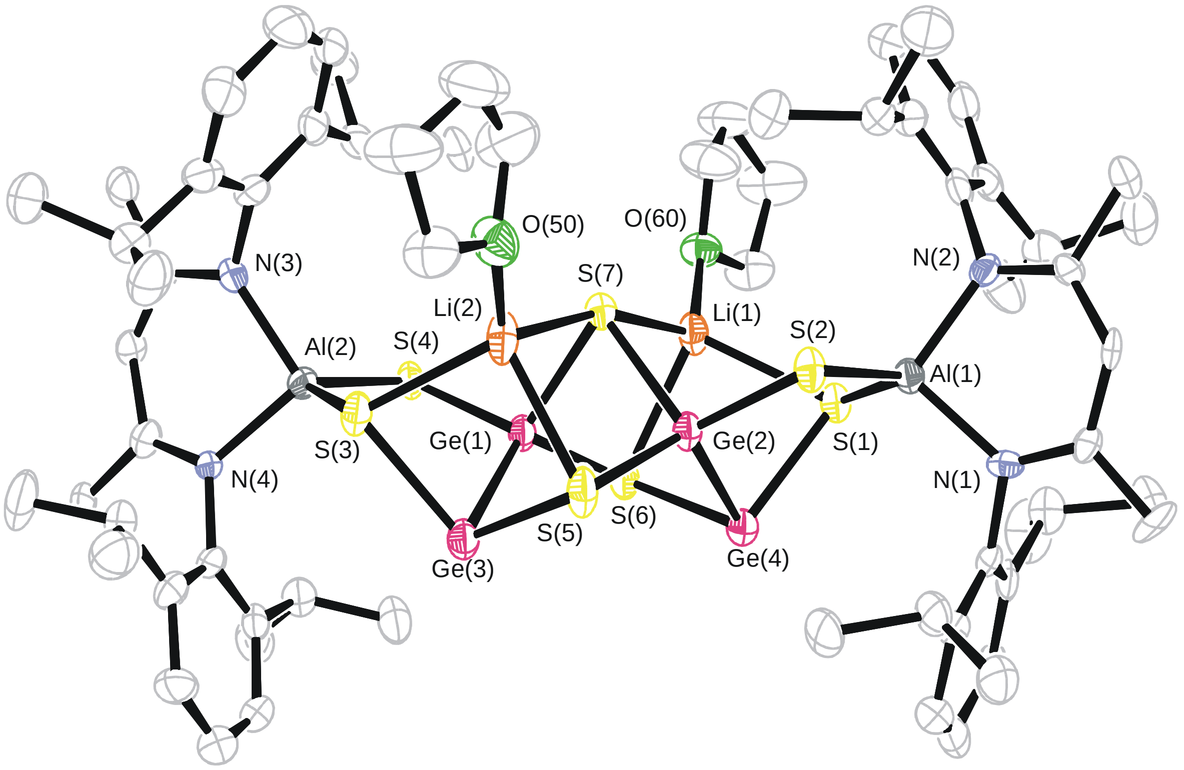
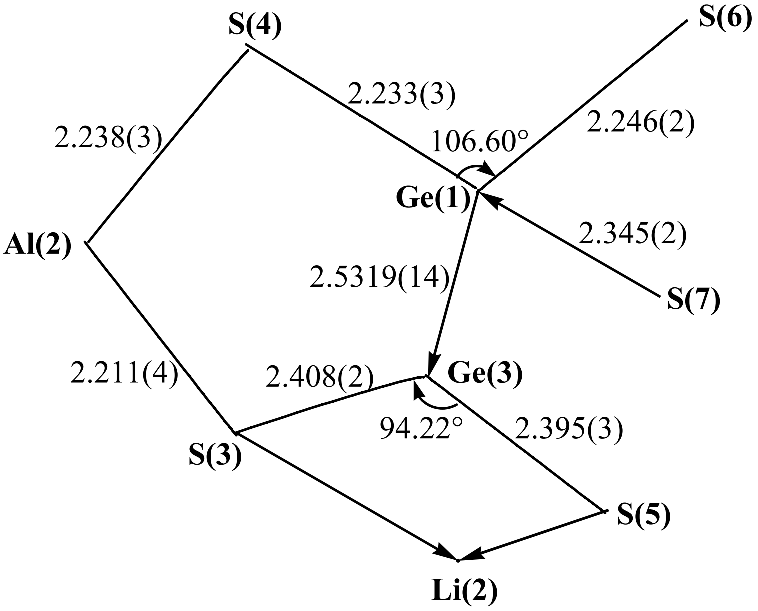


Figure 11. Molecular structure of **18**; Thermal ellipsoids set at 50 % probability. All hydrogen atoms and the toluene molecule are omitted for clarity. Selected bond lengths [Å] and angles [°] : Al(2)–S(4) 2.238(3), Al(2)–S(3) 2.221(4), Ge(1)–S(4) 2.233(3), Ge(3)–S(3) 2.408(2), Ge(1)–Ge(3) 2.532(1), Ge(1)–S(6) 2.246(2), Ge(1)–S(7) 2.345(2), Ge(3)–S(5) 2.395(3), Ge(4)–S(6) 2.386(3), Ge(2)–S(7) 2.332(3), Ge(2)–S(5) 2.256(2), Ge(2)–Ge(4) 2.537(1), Ge(4)–S(1) 2.387(2), Ge(2)–S(2) 2.239(3), Li(2)–S(3) 2.419(15), Li(2)–S(5) 2.455(15), Li(2)–S(7) 2.502(15); S(3)–Al(2)–S(4) 112.73(14), Al(2)–S(3)–Ge(3) 101.48(11), Al(2)–S(4)–Ge(1) 96.40(12), S(4)–Ge(1)–Ge(3) 111.03(7), S(3)–Ge(3)–Ge(1) 85.76(6), S(3)–Ge(3)–S(5) 94.22(9), S(4)–Ge(1)–S(6) 106.60(10), Ge(1)–S(6)–Ge(4) 99.97(10), Ge(1)–S(7)–Ge(2) 82.30(6), Ge(3)–S(5)–Ge(2) 99.94(10).

membered ring is in a gauche conformation. Two germanium atoms are connected by a Ge→Ge bond and are arranged opposite to the AlS_2 plane. The Ge→Ge bond length is 2.537 Å, which is longer than those reported for compounds containing a Ge=Ge double bond (2.213 to 2.347 Å).[48] Therefore, the Ge→Ge interaction in **18** should be considered as a donor-acceptor bond. This kind of bonding has so far only be reported for $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(Ph_2P{=}NSiMe_3)_2]$[49] without giving any support in experiment or theory, in which one germanium atom is four and the other is two coordinated. The four-coordinated germanium atom behaves as the donor and the two-coordinated germanium atom behaves as an acceptor. Each germanium atom is coordinated both by carbon and nitrogen atoms. However, in compound **18**, two germanium atoms are four and the other two germanium atoms are three coordinated. All the germanium atoms are surrounded by sulfur atoms. Obviously, each of the three- coordinated germanium has a lone pair, which is not included in the Ge→Ge bond. The two AlS_2Ge_2 five-membered rings are connected by three sulfur and two lithium atoms. Every sulfur atom is coordinated to two germanium atoms which are part of different five-membered rings. The germanium atoms with coordination number 3 have longer Ge–S bond length (av. 2.394 Å) compared to those with coordination number 4 (av. 2.244 Å). In the AlS_2Ge_2 five-membered ring, the $Ge–S_{(Al–S–Ge)}$ bond lengths for the three coordinated germanium (Ge(3)–S(3), 2.408(2) Å) is longer than that for the four coordinated germanium (Ge(1)–S(4), 2.233(3) Å). However, the remaining Ge–S bond with three coordinated germanium Ge(3) (Ge(3)–S(5), 2.395(3) Å) is also longer than the corresponding four coordinated one (Ge(1)–S(6), 2.246(2) Å). The two $Ge_{(three\ coordinate)}–S$ bond lengths are almost the same and the two $Ge_{(four\ coordinate)}–S$ bond lengths are nearly equal. This could be explained by the fact that $Ge_{(three\ coordinate)}–S$ bonds (Ge(3)–S(3), Ge(3)–S(5)) are part of the Ge(3)–S(5)–Li(2)–S(3) four-membered ring. The strain of the ring makes the two $Ge_{(three\ coordinate)}–S$ bonds longer than those in the non-cyclic units. These Ge–S bond lengths are consistent with those of compounds previously reported (2.129-2.386 Å).[47d, 50] The S(3)–Ge(3)–S(5) angle (94.22°) is more acute than the S(4)–Ge(1)–S(6) (106.60°) angle. This is due to the strain of the GeS_2Li four-membered ring. The two lithium atoms are both coordinated to three sulfur atoms with the Ge–S bond lengths



Scheme 11. The comparison of the different coordination sites of the four coordinate and the three coordinate germanium atoms.

(2.418 to 2.502 Å), which are comparable to those in the structure of the starting material **9** (2.478Å to 2.424Å).

According to the crystallographic data there is a strong indication for the existence of a chemical bond between the germanium atoms. To understand the situation of the Ge–Ge bond the molecule was investigated by means of quantum chemical calculations. In a two step approach the molecule was first fully optimised with the DFT-variant B3LYP[51, 52] as implemented in the Gaussian G03[53] program-suite employing a basis-set termed 6-31G[54-56] and then the resulting electronic structure was analyzed to get insight into the molecular orbitals.

As shown in Table 1 the resulting structure compares well with the data obtained by X-ray analysis and gives a convincing support for the bond analysis. The NBO[57-59] results show that Ge(1) and Ge(2) form one bond to their neighboring germanium atom and three bonds to the sulfur atoms. The bond lengths and bond angles are due to the fact that Ge-Ge and Ge-S bonds are quite different when looking at the orbitals they are built upon. The valence orbitals

Distance	Å	Angle	°
Ge(1)-Ge(3)	2.563	S(4)-Ge(1)-S(6)	110.91
Ge(1)-S(4)	2.308	Ge(1)-S(7)-Ge(2)	83.92
Ge(1)-S(6)	2.321	Al(2)-S(3)-Ge(3)	100.73
Ge(1)-S(7)	2.420	S(4)-Ge(1)-Ge(3)	112.65
Al(2)-S(4)	2.326	Al(2)-S(4)-Ge(1)	95.34
Li(2)-S(7)	2.544	Ge(1)-S(6)-Ge(4)	102.23
Ge(3)-S(3)	2.471	S(3)-Ge(3)-S(5)	92.70
Ge(3)-S(5)	2.513	S(3)-Ge(3)-Ge(1)	86.52
Al(2)-S(3)	2.281	Ge(3)-S(5)-Ge(2)	102.30

Table 1. Calculated bond lengths and angles.

(4s and 4p) of germanium atoms turn into p-rich hybrids of type sp$^{1.6}$, sp$^{3.37}$, sp$^{3.44}$ and sp$^{4.9}$ in the molecule in the case of Ge(1) and Ge(2), while the molecular orbitals of the Ge(3) and Ge(4) can be described as pure p-orbitals.

Bond	occ.	MO 1	contr.	Type	MO 2	Contr.	Type
Ge(1)-Ge(3)	1.878	Ge(1)	67.4%	s(38.1%) p1.62(61.9%)	Ge(3)	32.6%	s(5.1%) p18.55(94.9%)
Ge(1)-S(4)	1.950	Ge(1)	32.0%	s(22.9%) p3.37(77.1%)	S(4)	68.0%	s(17.9%) p4.60(82.1%)
Ge(1)-S(6)	1.960	Ge(1)	32.6%	s(22.5%) p3.44(77.5%)	S(6)	67.4%	s(16.4%) p5.10(83.6%)
Ge(1)-S(7)	1.950	Ge(1)	28.3%	s(16.8%) p4.95(83.2%)	S(7)	71.7%	s(12.6%) p6.94(87.4%)
Ge(3)-S(3)	1.942	Ge(3)	21.2%	s(3.7%) p25.95(96.3%)	S(3)	78.8%	s(17.6%) p4.70(82.4%)
Ge(3)-S(5)	1.941	Ge(3)	21.7%	s(3.6%) p26.58(96.4%)	S(5)	78.3%	s(13.7%) p6.33(86.3%)

Table 2. Selected data of compound **18**.

The orbitals and their contributions are summarized in Table 2 (for clarity reasons only the values for Ge(1) and Ge(3) are given). Looking at the contributions of the germanium atoms in the Ge-Ge bond it is clearly visible that the overlap of the hybrid orbital with the pure p-orbitals is large enough to form a bond with a length of 2.53 Å. An additional stabilization of this bond arises from the donor acceptor interaction with the unoccupied antibinding Ge-S orbitals. The total amount of this two-electron stabilizing interaction is nearly 20 kcal/mol.

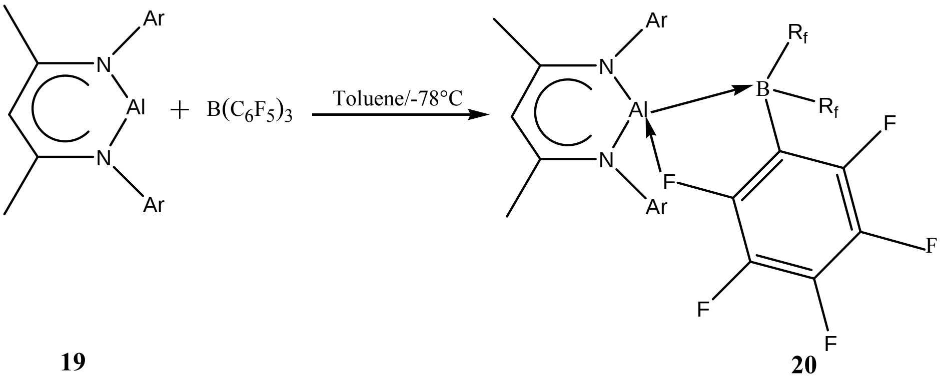
In summary, we have characterized and synthesized a heterotrimetallic $L_2Al_2Ge_4Li_2S_7$ cluster, which is the first polyeder that contains a Ge(II)→Ge(II) donor-acceptor bond with four coordinated germanium atoms behaving as donor and three coordinated germanium atoms showing acceptor properties. Moreover the Ge(II)→Ge(II) donor-acceptor bond is supported by theoretical calculations. In the molecular structure, the AlS_2Ge_2 five-membered rings are unique as such rings have not been reported before.

2.4. Janus[60] –faced Aluminum: A Demonstration of an Unique Lewis-Acid and Lewis-Base Behavior of the Aluminum Atom in $LAlB(C_6F_5)_3$

Compounds of aluminum with the formal +3 oxidation state at aluminum are showing the classical behavior of Lewis acids, such as aluminum trihalides, trialkyls and triaryls.[14] In recent years, another class of compounds containing aluminum with the +1 oxidation state has attracted great interest.[1] The latter, having a nonbonding lone pair of electrons at aluminum, are indicating a singlet carbene-like character and the potential of Lewis base behavior. In 2000 Cowley et al. reported on the first example with an aluminum(I)-boron donor-acceptor bond: $Cp^*Al \rightarrow B(C_6F_5)_3$ ($Cp^* = C_5Me_5$),[61] and one year later on a corresponding Al-Al bond in $Cp^*Al \rightarrow Al(C_6F_5)_3$.[29b] None of these systems show both Lewis acid and Lewis base behavior at the same aluminum atom.

The reduction of $[I_2Al\{HC(CMeNAr)_2\}]$ (Ar = 2,6-$i$$Pr_2C_6H_3$) with potassium resulted in the formation of monomeric [LAl] (L = $HC[(CMe)(NAr)]_2$, Ar = 2,6-$i$$Pr_2C_6H_3$) (**19**).[31] This was the first stable dicoordinate aluminum(I) compound to be prepared and structurally characterized in the solid state. The fascinating aspect of **19** is the dual Lewis acid and Lewis base character. On the basis of *ab initio* calculations,[62] the stereo chemically active lone pair of electrons on the aluminum atom and the probability of quasi trigonal-planar orientation are noticed by analyzing Laplacian of electron density[63] within the plane, which clearly describes the Lewis basicity of compound **19**. Moreover, charge depletion close to the aluminum atom into the semiplane of the six-membered ring is indicating the Lewis acidity of **19**. Herein, we report the reaction of [LAl] (**19**) with $B(C_6F_5)_3$ to yield the first compound of composition $LAlB(C_6F_5)_3$ (**20**) showing both Lewis base and Lewis acid character at the metal center.

The reaction of [LAl] (**19**) with $B(C_6F_5)_3$ in a 1:1 molar ratio in toluene in the temperature range from –78 °C to room temperature resulted in the formation of compound



19 **20**

Scheme 12. Preparation of compound **20,** Ar = 2,6-iPr$_2$C$_6$H$_3$, R$_f$ = C$_6$F$_5$

20 (Scheme 12). **20** was characterized by ^{1}H, ^{13}C, ^{11}B, ^{19}F, and ^{27}Al NMR spectroscopy as well as EI mass spectrometry and elemental analysis. ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectroscopy was carried out at room temperature using [D$_6$]benzene or [C$_7$D$_8$]toluene as a solvent. No resonance signals were observed in C$_6$D$_6$ or C$_7$D$_8$ solution for the ^{27}Al NMR spectrum of **20**, therefore the measurement was carried out in the solid state. The ^{19}F NMR spectrum of **20** exhibits nine partly overlapping resonances, therefore an unambiguously assignment is not possible. Although this pattern indicates a distorted B(C$_6$F$_5$)$_3$ group due to the Al-F bond interaction. The EI mass spectrum shows the molecular ion of **20** (m/z = 956). Single crystals of **20** suitable for X-ray structural analysis were obtained by keeping the hexane solution for two weeks at room temperature. Compound **20** crystallizes in the triclinic space group P-1. The solid state structure consists of individual molecules of the Lewis acid-base adduct. The very close intramolecular contact of one F atom with an Al atom is caused by the interaction of one ortho fluorine atom of one fluorinated phenyl group forming an AlBC$_2$F five-membered ring (Scheme 13). The aluminum atom has a distorted tetrahedral geometry with an average Al-N bond length of 1.892(6) Å. This distance is considerably shorter than the Al-N bond distances in 1 (av. 1.957(6) Å). This is consistent with the partial transfer of the lone pair of electrons at aluminum under formation of the donor-acceptor bond. The Al-B distance of **20** (2.183(3) Å) is slightly longer compared to that in the Cp*Al-B(C$_6$F$_5$)$_3$ (2.169(2) Å).

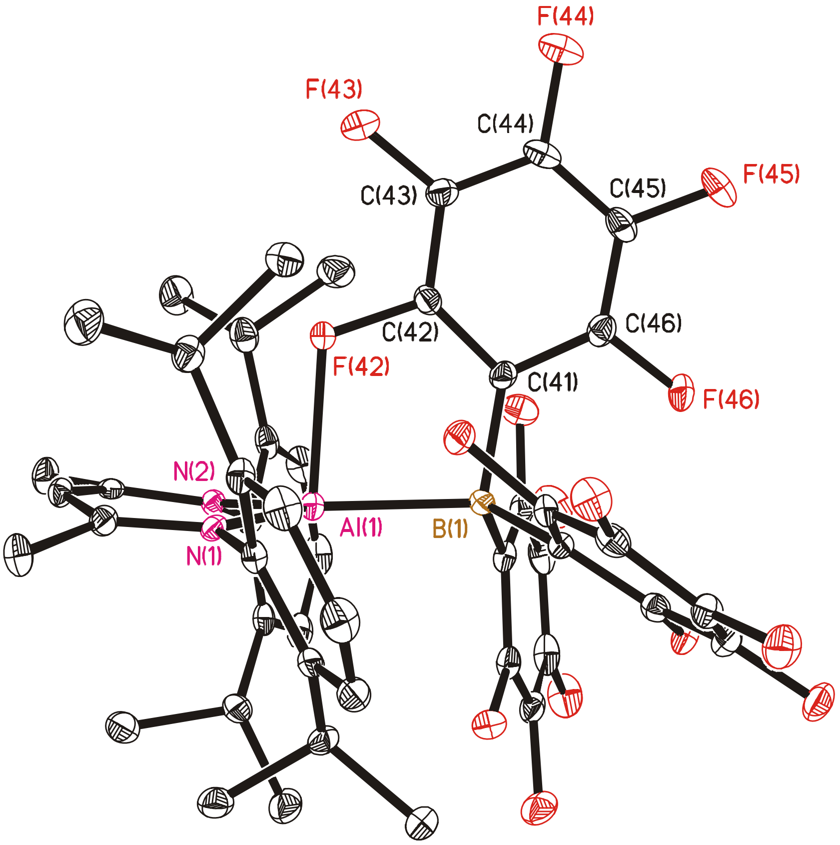
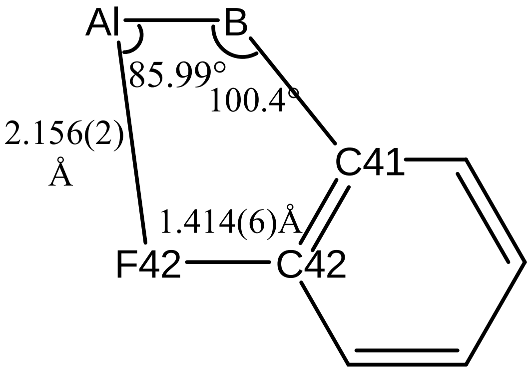


Figure 13. The crystal structure of **20**. Selected bond lengths [Å] and angles [°]: Al(1)-B(1) 2.183(5), Al(1)-F(42) 2.156(3), C(42)-F(42) 1.414(4), Al(1)-N(2) 1.885 (4), Al(1)-N(1) 1.900(3), C(33)-F(33) 1.371(5); C(41)-B(1)-Al(1) 100.4(3), C(51)-B(1)-Al(1) 115.1(3), C(31)-B(1)-Al(1) 110.1(3), F(42)-Al(1)-B(1) 85.99(15), Σ°CBC 330.3(2).



Scheme 13. Al-B-C(41)-C(42)-F(42) five-membered ring

The geometry of the $B(C_6F_5)_3$ changes from trigonal planar to distorted tetrahedral in **20**. The extent of the geometrical change has been taken as an indication for the strength of the donor-acceptor interaction.[64] The sum of C-B-C bond angles at boron in **20** (330.3(2)°) is the smallest compared to those (in the range from 333.5(2)° to 342.2(2)°) reported previously. [61] [65, 66] That suggests that $HC(CMeNAr)_2Al$ (**19**) appears to be a stronger base than Cp^*Al. However it has to be taken into consideration that the relatively close Al-F contact in **20** (2.156(2) Å) changes the electron density on the aluminum. The noticeable Al-F interaction is indicated by the lengthening of the C-F bond (1.414(6) Å) compared to the remaining 14 C-F bond lengths (av. 1.355 Å) in **20**. In addition, the C(41)-B(1)-Al(1) angle in **20** is obviously smaller (100.4(3)°) than the other two $C_{(ipso)}$-B-Al angles (115.1(3)° and 110.1(3)°) of the remaining perfluorophenyl rings. These data indicate that the lengthening of the C-F bond and the narrowing of the Al-B-C angle are due to the F→Al interaction and are consistent with a F→Al donor-acceptor behavior.

Taking a closer look at the crystallographic data it is obvious, that there is a weak interaction between aluminum and fluorine (F42). To have a better understanding of the bonding situation, compound **20** was examined by means of *ab initio* calculations. The following steps are necessary to clarify the binding situation. The first and crucial one is to reproduce the crystallographic data by a reliable quantum-chemical method. Starting from this structure the analysis of the molecular orbitals and the bond-order gives the most accurate picture of the electronic structure.

The structural parameters of Al-F(42) (2.1626 Å), F(42)-C(42) (1.4384 Å) and F(42)-Al-B (85.236°) are in good agreement with the crystallographic data given in the caption of Figure 13. The bond order analysis reveals that the binding of the fluorine atom is distributed between carbon and aluminum with a ratio (Al-F)/(Al-C) of 0.2930/0.7148 which means that there is a significant interaction between fluorine and aluminum. The consequence of this interaction is the elongation of the C(42)-F(42) bond by 0.075 Å (calcd. 1.4385 Å) compared

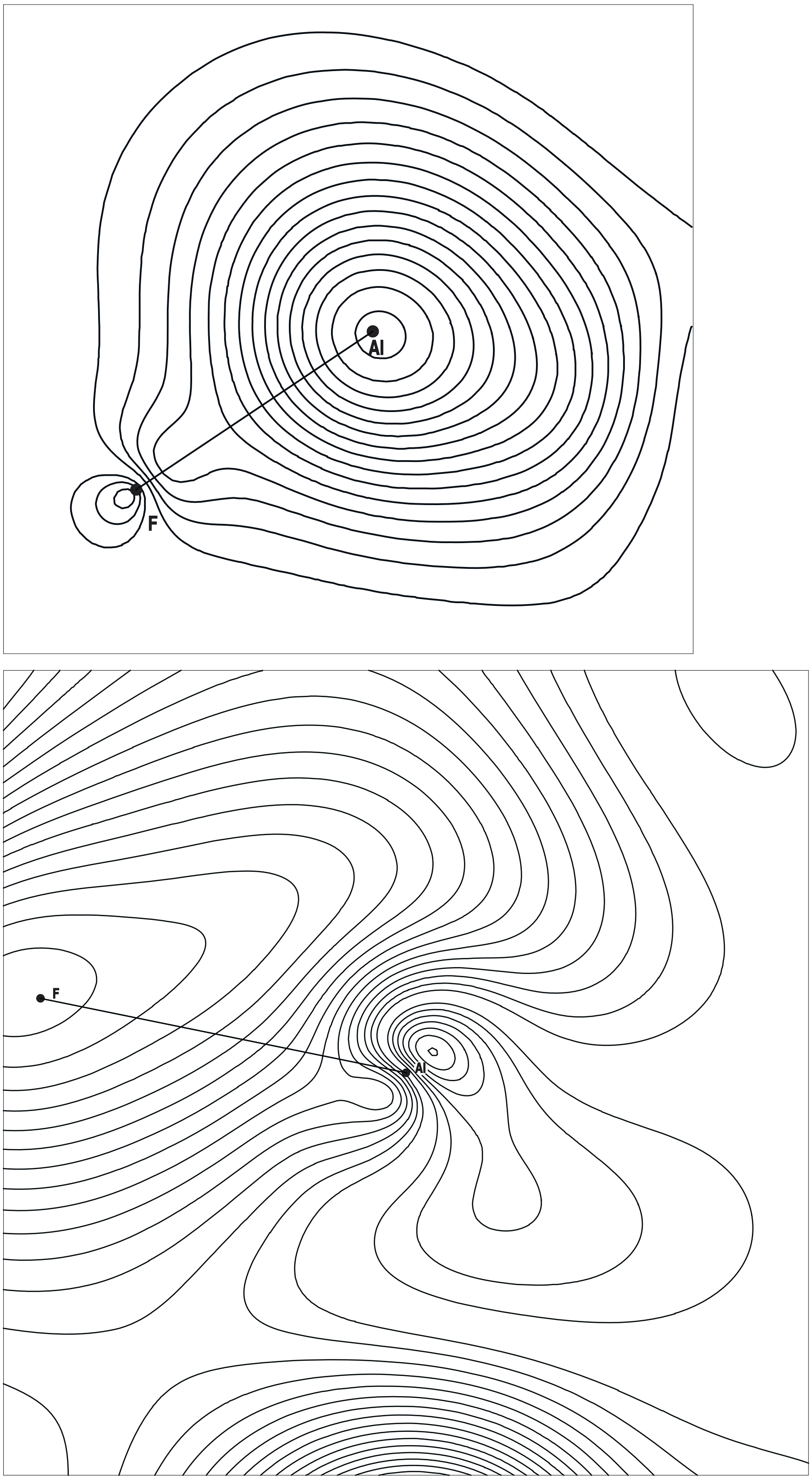


Figure 14. Schematic representation of the Al-F linkage resulting from the overlap of wave functions centered on aluminum and fluorine. Shown here are the two relevant orbitals pictured as contour plots. The clearly visible deformation in the second plot is due to the fact that there is a strong interaction with orbitals forming the Al-F bonds.

with the other C-F bond lengths in the same ring (calcd. range from 1.3633 Å to 1.3636 Å) by 0.075 Å. Performing a NBO[67] (natural bond analysis) analysis the bond between aluminum and fluorine can be described as the overlap of two hybrid orbitals of sp^n type with one located at Al (16.24% s and 83.76% p) and the other at F(42) (11.56% s and 88.44 % p). The binding orbital located on carbon C(42) has $sp^{2.72}$ character while this value is $sp^{2.22}$ for the remaining carbon atoms in this ring. This situation is also clearly visible in the corresponding orbital picture. Figure 14 shows the Al-F linkage illustrated by contour plots of two orbitals contributing to the formation of the Al-F bond.

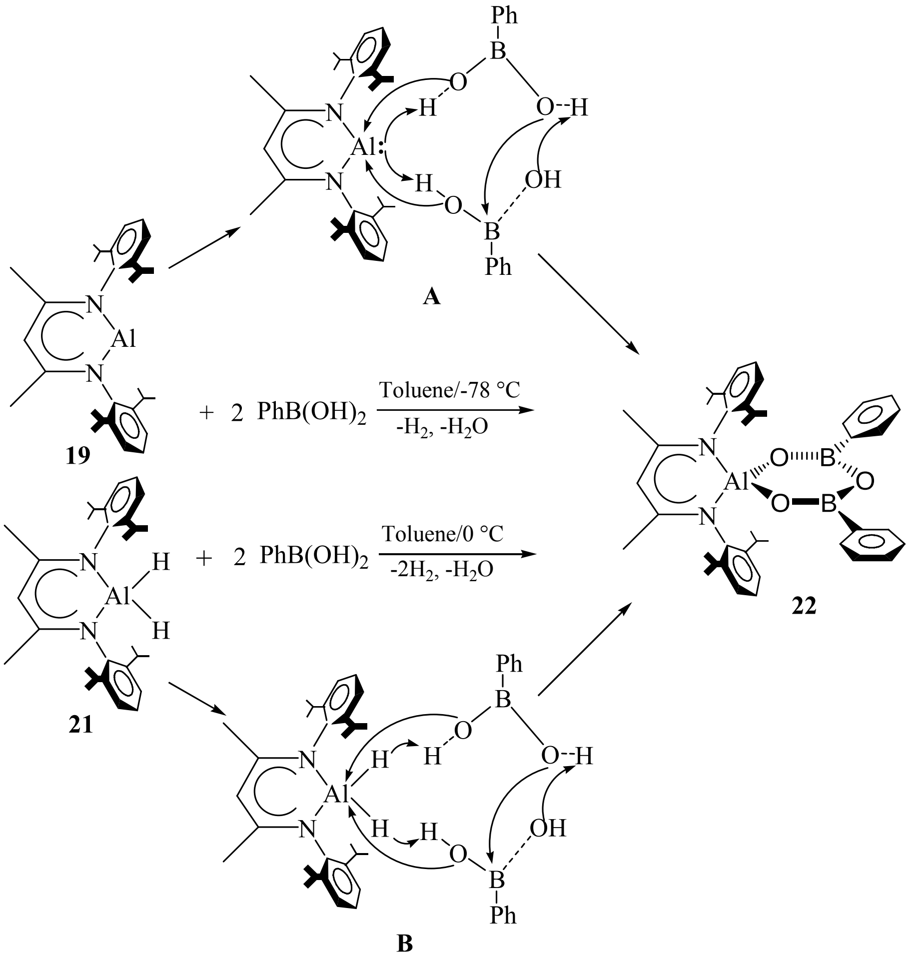
Details of calculations

Due to the size of the system the well established B3LYP [51, 52] method was employed for all the calculations. Two different basis sets were used for the computations, a small one as the 3-21G basis-set and an extended one in which the aluminum atom is described with functions taken from the 631-G basis set including double diffuse functions.[68, 69] Making use of the Gaussian G03 [53] program-suite the structure was optimized with the 3-21G basis first and then starting from this geometry again with the larger basis set thus giving an appropriate description of the aluminum atom and its binding situation. The resulting structure was used for visualization of the orbitals. According to the nature of the quantum-chemical method the resulting wavefunction produces molecular orbitals which involve nearly all the atoms and therefore leading to a picture which is, despite being mathematically correct, difficult to interpret. A more descriptive picture is obtained by localizing the orbitals at those atoms that are originating according to Boys Method.[70] To obtain also quantitative data about the bond between Al and F(42) the bond order was analyzed following a proposal of I. Mayer.[71] In conclusion, we have prepared $LAl\text{-}B(C_6F_5)_3$, an unique compound of aluminum showing Lewis base and Lewis acid character at the aluminum center. There are no precedents known of this type of bonding in literature.

2.5. Synthesis of An Aluminum Spirocyclic Hybrid with An Inorganic B_2O_3 and An Organic C_3N_2 Core

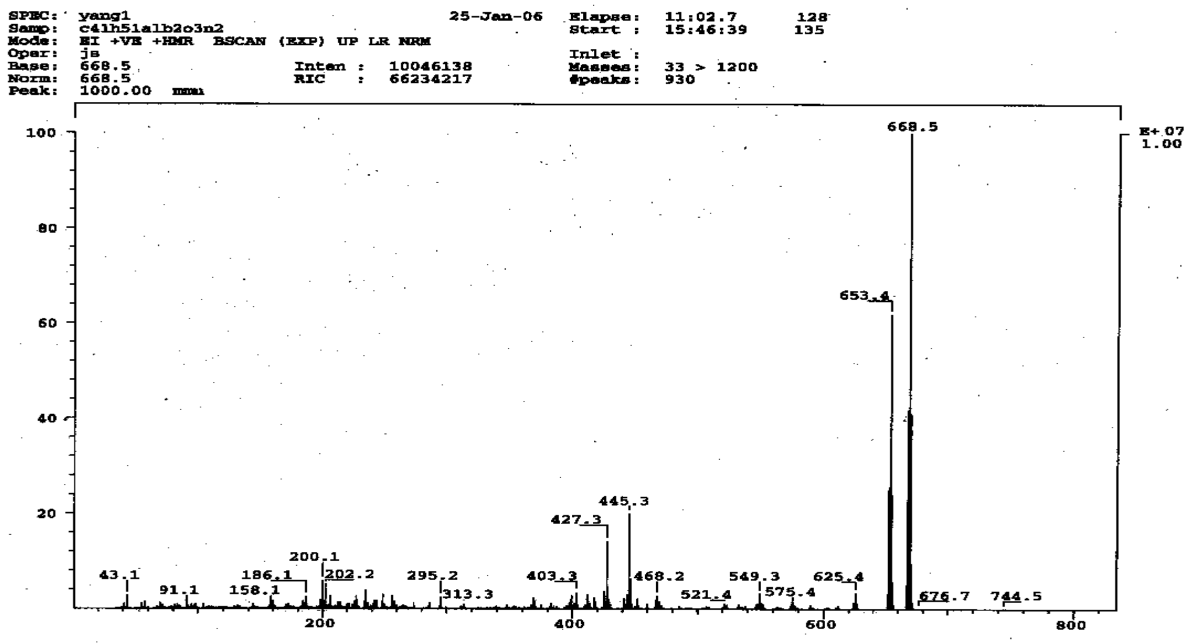
In recent years the synthesis of organic-inorganic hybrid materials has become an important target. This was impressively shown by I. Manners who discovered the ROP of silaferrocenophanes which provide access to poly(ferrocenylsilanes).[72] Today ferrocenophanes with different main group elements in the bridging position are known, including a ferrocenophane with aluminum.[73] Since then, aluminum containing organic-inorganic hybrid materials are a fascinating subject. Current ongoing research in our group showed that the germanium(II) compound $Ge[N(SiMe_3)_2]_2$ can be used to convert a proton to a hydride to generate the germanium(IV) cluster $[(RSiO_3GeH)_4]$.[74] As an alternative powerful reducing agent we introduced the aluminum(I) compound LAl (**19**) (L = $HC(CMeNAr)_2$, Ar = 2,6-$i$$Pr_2C_6H_3$)[31] to transfer two electrons to generate aluminum(III) species such as $(LAl)_2(\mu\text{-}S_3)_2$[75] and $(LAl)_2O_2$.[76] The easy formation of the latter compounds and the $[(RSiO_3GeH)_4]$ cluster prompted us to investigate the redox reaction of LAl and $PhB(OH)_2$ due to the easy electron transfer and the favourable formation of an Al-O-B bond. We investigated the reaction of $LAlH_2$ (**21**)[39] with $PhB(OH)_2$ to take advantage of the different polarity of the hydrogen atoms in both compounds, which should lead to an easy hydrogen elimination.

The reaction of **19** with $PhB(OH)_2$ in a 1:2 molar ratio (Scheme 14) resulted in an unprecedented formation of $LAl[(OBPh)_2O]$ (**22**). The color of the solution changes from red to colorless when the temperature of the solution is slowly raised to 20 °C. During the course of the reaction hydrogen gas evolution was observed. Compound **22** separated after cooling as colorless crystals from the concentrated toluene solution. Compound **22** is soluble in toluene, benzene, and trichloromethane.



Scheme 14. Preparation of compound **22**.

Compound **22** was characterized by ^{1}H and ^{13}C NMR investigation in $CDCl_3$ solution, as well as by EI-MS, IR, and elemental analysis. The ^{1}H and ^{13}C NMR spectra both exhibit one set of resonances for the aryl groups both on boron and on the ligand indicating a symmetric molecule. The EI mass spectrum shows the molecular ion of **22** (*m*/*z* 668) with 100% intensity. In the IR spectrum of **22**, there are no absorption bands above 3000 cm^{-1} which originate from the OH groups of the starting material (br, 3100-3400 cm^{-1}). Compound **22** is thermally stable, as indicated by its melting point (338 °C). To support and understand the easy formation of **22** we also reacted $LAlH_2$ (**21**) with $PhB(OH)_2$. The reaction proceeds under elimination of hydrogen and water. Here too compound **22** is formed in a comparable yield.



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SPEC:  yang1                                25-Jan-06  Elapse:  11:02.7    128
Samp:  c41h51al1b2o3n2                                 Start :  15:46:39    135
Mode:  EI +VE +HMR  BSCAN (EXP) UP LR NRM
Oper:  js                                              Inlet :
Base:  668.5             Inten :  10046138             Masses:  33 > 1200
Norm:  668.5             RIC   :  66234217             #peaks:  930
Peak:  1000.00  mmu
```

Figure 19. EI-MS spectrometry of compound **22**.

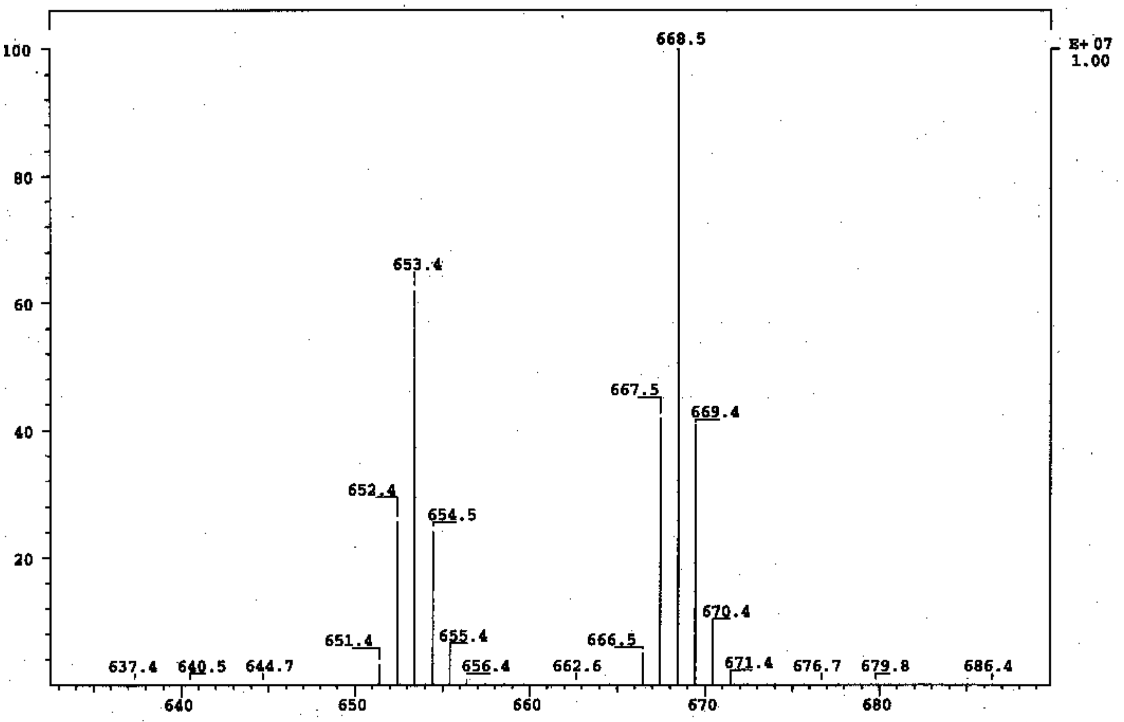

Figure 20. Partly magnified spectrum of the EI-MS spectrometry of Compound **22**.

For the progress of the two reactions we assume two similar concerted mechanisms through the intermediate **A** (from **19**) or **B** (from **21**) shown in Scheme 14. Proceeding from **19** to **22**, the aluminum(I) of **19** is oxidized to aluminum(III) (**22**) under formation of one equivalent of hydrogen resulting from two protons of the two molecules of $PhB(OH)_2$. The exothermic formation of the Al–O bonds is the driving force in this reaction. The increase of the proton acidity of the intermediate $LAl[OB(Ph)OH]_2$ leads to the elimination of water under AlO_3B_2 ring formation. The formation of **22** through the intermediate **B** is driven by the exothermic Al-O bond enthalpy. The H_2 elimination is favoured through the hydridic (**21**) and protonic hydrogen ($PhB(OH)_2$) atoms. Compound **22** is an unique example of a spiro centered aluminum atom showing the inorganic AlO_3B_2 ring fused to the organic C_3N_2 part. There is only one inorganic spiro cyclic aluminum compound known of composition $[(PhBO)_2Al(OBPh)_2Al_2Cl_4]$ which was prepared from $(PhBO)_3$ and $AlCl_3$, where both rings have the same composition.[77]

Single crystals of X-ray quality were obtained from a toluene solution of **22** at low temperature crystallizing in the triclinic space group $P\bar{1}$. The structural analysis unambiguously ascertains the composition of **22**. Its molecular structure is shown in Figure 15. One aluminum atom, two boron atoms and three oxygen atoms form a six-membered planar AlO_3B_2 ring. The central Al atom is located in the spirocyclic center of the two fused six-membered rings (C_3N_2Al and AlO_3B_2). The Al–O bond length (av. 1.750Å) is longer than the terminal Al–OH bond distance (av. 1.705Å) in compound $LAl(OH)_2$.[23] The O–Al–O angle (104.7(3)°) is sharper than that in $LAl(OH)_2$ (115.38(8)°). The difference of bond length and bond angle of **22** with those in $LAl(OH)_2$ might be due to a certain strain within the six-membered rings of **22**. The B(2)–O(2) bond length (1.326(10)Å) adjacent to the aluminum atom is distinctly shorter than that of the B(2)–O(1) (1.415(11) Å) with the consequence that the Al–O bond lengths in **22** increase when compared to those in $LAl(OH)_2$ and $(LAl)_2O_3AlMe$ (1.708-1.726Å).[24] The wider O–B–O bond angles (122.4(7)°, 122.5(8)°) in comparison to the O–Al–O (104.7(3)°) are a consequence of the lower coordination number at boron compared to aluminum.

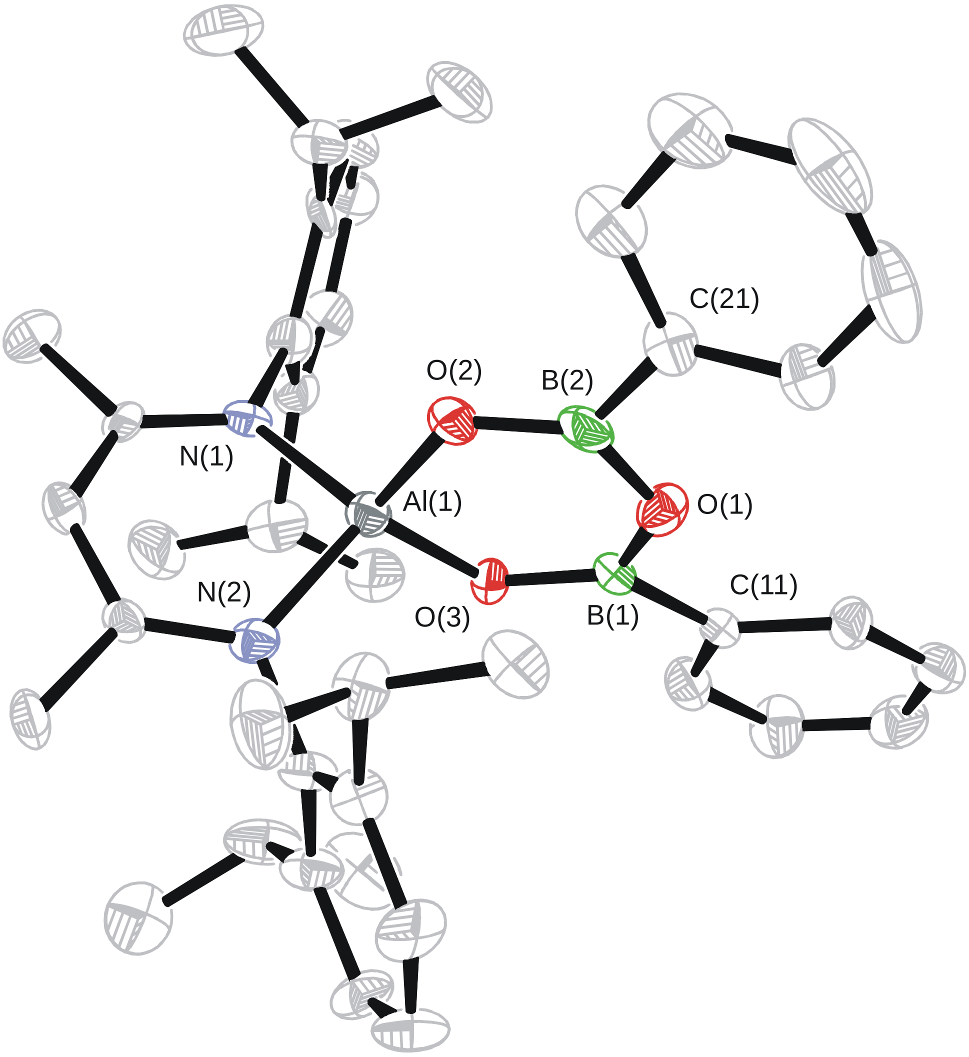

Figure 15. Molecular structure of **22**; thermal ellipsoids set at 50 % probability. All hydrogen atoms and the toluene molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: N(1)–Al(1) 1.877(6), N(2)–Al(1) 1.872(6), Al(1)–O(2) 1.754(5), Al(1)–O(3) 1.745(5), O(2)–B(2) 1.326(10), O(3)–B(1) 1.339(10), B(2)–O(1) 1.415(11), O(1)–B(1) 1.401(10), B(2)–C(21) 1.574(11), B(1)–C(11) 1.559(11); N(2)–Al(1)–N(1) 98.8(3), O(2)–Al(1)–O(3) 104.7(3), O(3)–Al(1)–N(2) 113.2(3), O(2)–Al(1)–N(2) 111.9(3), O(3)–Al(1)–N(1) 115.0(3), O(2)–Al(1)–N(1) 113.6(3), O(3)–B(1)–O(1) 122.4(7), B(2)–O(2)–Al(1) 121.7(5), O(2)–B(2)–O(1) 122.5(8), B(1)–O(3)–Al(1) 121.7(5).

The ab initio calculations were performed with the aim of clarifying the bonding situation in the target molecule and giving further insight into the reaction mechanism. The calculations were performed at the well established DFT level of theory making use of the B3LYP-functional[51, 52] as implemented in the Gaussian program package[57] making use of a basis-set termed 6-31G.[54-56, 78] The analysis of the binding situation was performed at the calculated equilibrium geometry of the compound by means of a NBO-analysis.[57-59] The determination of the reaction mechanism cannot be easily performed due to the fact there are three molecules involved and would surely go far beyond the scope of this work. The approach chosen here was to rule out further possible reaction pathways. As the two reactions result in the same product, herein we only investigate the reaction between compound **19** and $PhB(OH)_2$.

Table 3. Calculated bond lengths and angles.

Distance	[Å]	Angle	[°]
Al(1)-O(2)	1.7901	O(2)-Al(1)-O(3)	100.81
Al(1)-O(3)	1.7896	O(3)-B(1)-O(1)	119.65
B(2)-O(1)	1.4137	O(2)-B(2)-O(1)	119.37
B(2)-O(2)	1.3749	N(1)-Al(1)-N(2)	98.89

As clearly visible from Table 3 the resulting equilibrium structure agrees very well with the experimental X-ray data thus giving the bond-analysis a quite solid foundation. Both Al-N bonds are formed by overlapping a $sp^{3.04}$ hybrid orbital of aluminum with a $sp^{2.50}$ hybrid orbital of nitrogen with the main electronic contribution coming from nitrogen. These bonds are strengthened by a donor-acceptor interaction with the lone pair of nitrogen. The situation is quite similar for the Al-O bonds but in this case the orbitals involved can be described as a $sp^{2.67}$ orbital on Al and a $sp^{2.70}$ orbital on O with most of the electronic density coming from oxygen. The formation of the Al-O bonds also has an effect on the Al-N bonds due to the stabilizing donor-acceptor interaction between antibonding Al-O orbitals and the Al-N bonds.

The investigation of the mechanism was performed by locating a transition state structure on the potential hypersurface and also by taking a closer look at the possible alternative mechanism. The possible routes involving a two-step mechanism start with either hydrogen or water formation. Assuming that H_2 elimination is the first step of the reaction does not lead to the desired compound due to the rearrangement taking place in the Ph-B-OH unit (Figure 16). However the condensation as the first step looks quite promising as the transition state diagram indicates (Figure 17). But trying to reach the target molecule from this transition state is impossible due the fact that the bond formation between aluminum and oxygen does not take place. Having ruled out this possible mechanistic explanation it is quite reasonable that the calculated transition state (shown in Figure 18) is the crucial step in this reaction. The calculations indicate that the reason for the formation of the transition structures **A** and **B** proposed here are valid.

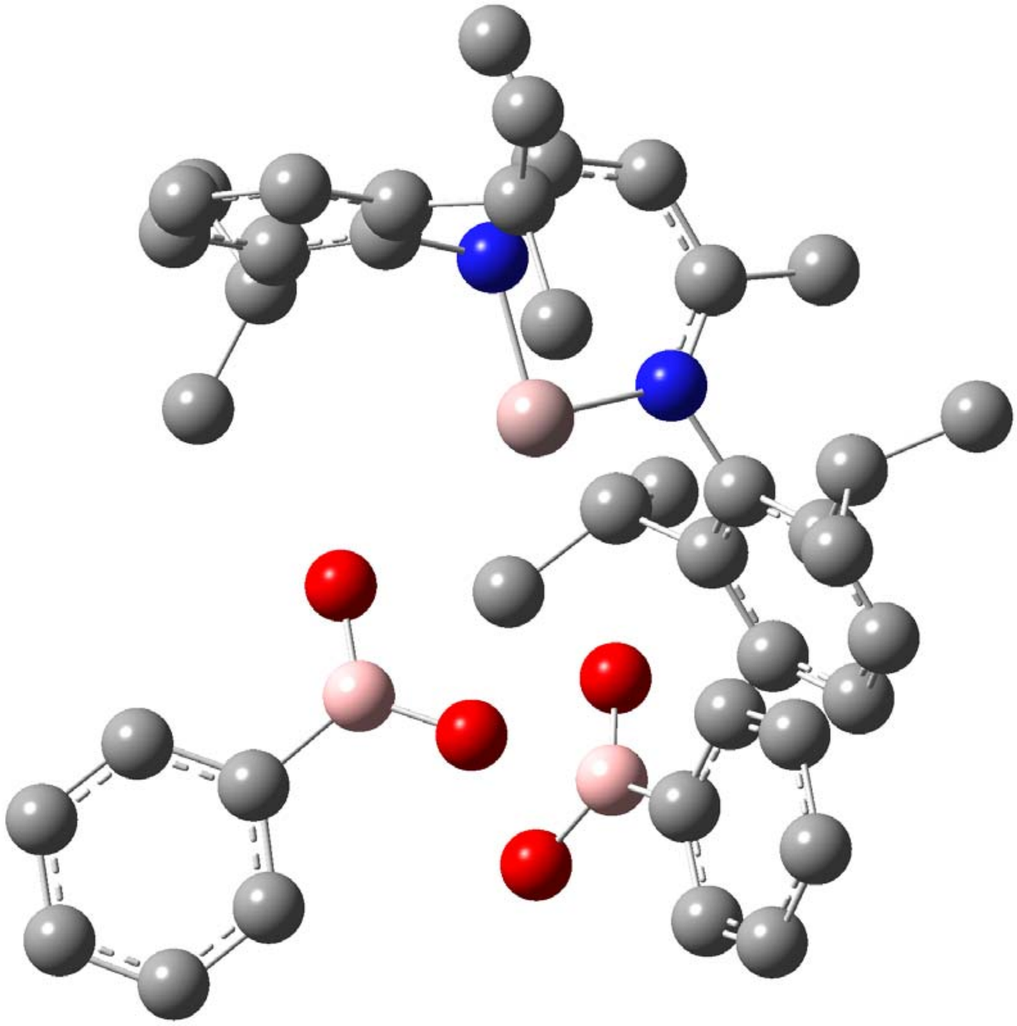

Figure 16. The transition state picture of H_2 condensation as the first step, most of the hydrogen atoms have been omitted for clarity.

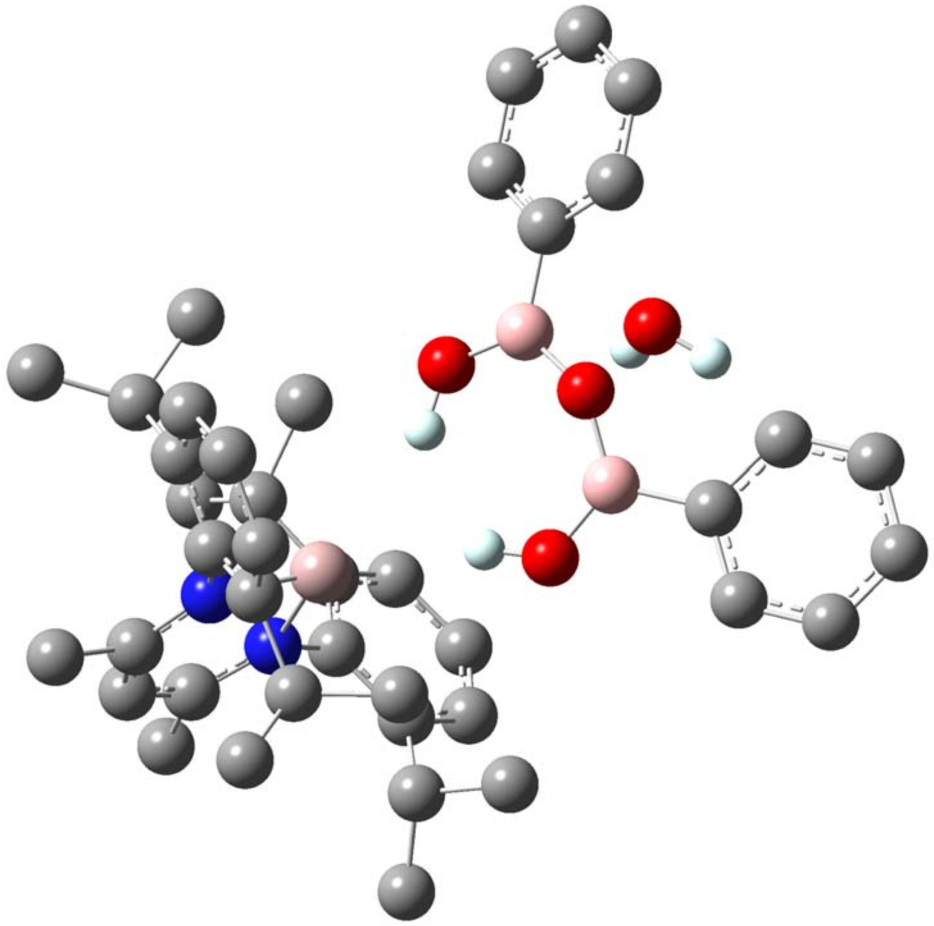

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Figure 17. The transition state picture of H_2O condensation as the first step, most of the hydrogen atoms have been omitted for clarity.

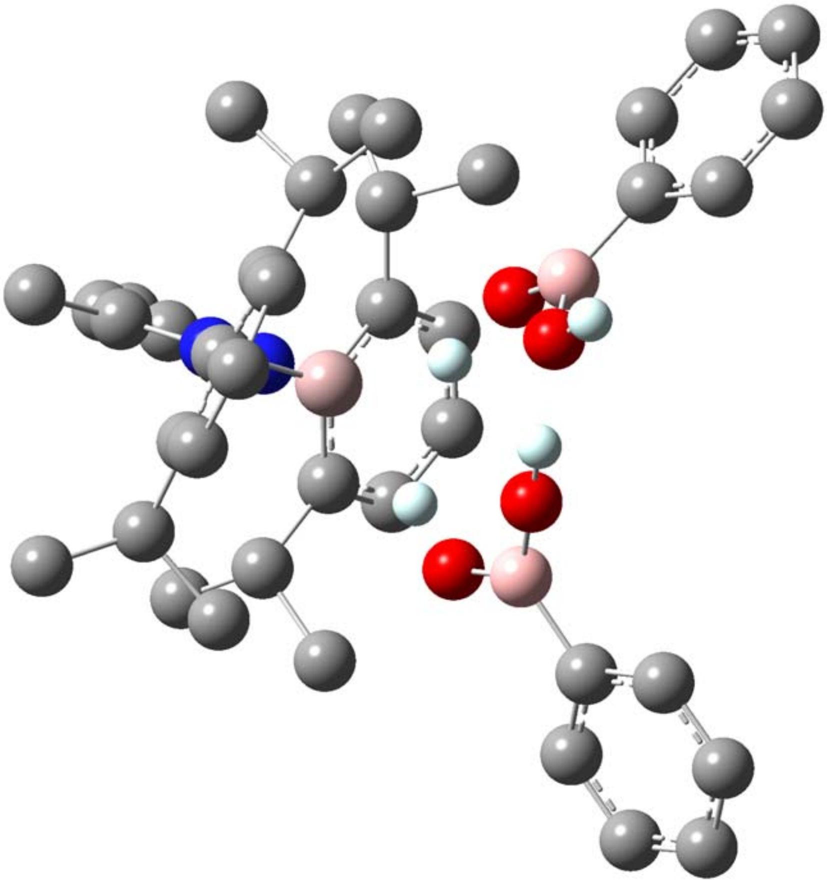


Figure 18. The calculated transition state picture of the concerted mechanism, most of the hydrogen atoms have been removed for clarity.

Table 4.The calculated result of isotope pattern of compound **3** by ChemDraw, m/z:

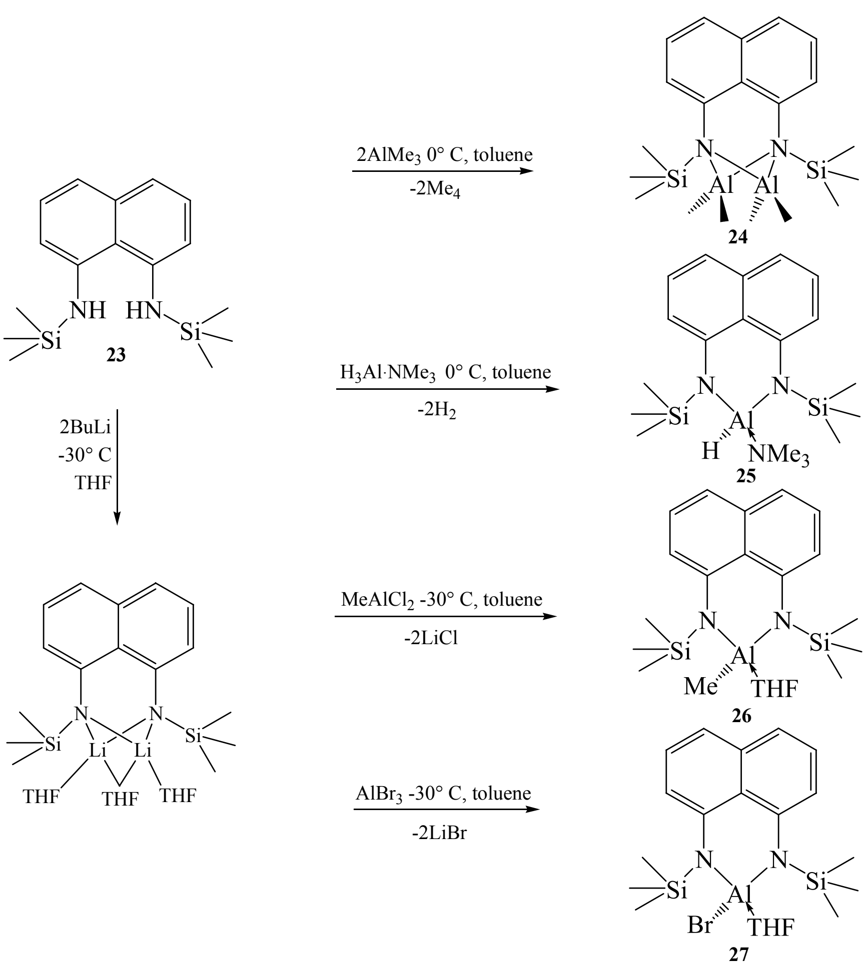
668.4	667.4	669.4	670.4	666.4	671.4
100.0%	42.4%	42.7%	10.0%	5.0%	1.6%

In summary the different reactions between $PhB(OH)_2$ with LAl(I) or $LAlH_2$(III) result in the same compound **22** in high yields.

2.6. Syntheses, Characterization, and X-ray Single Crystal Structures of 1,8-bis-(trimethylsilyamino)naphthalene Aluminum Hydrides, Alkylates and Halides

Aluminum hydrides, alkylates, and halides are involved in most of aluminum containing reactions. They are extraordinary important for aluminum chemistry. Aluminum hydrides are very effective precursors for preparing aluminum chalcogenides[45, 79-81], and also can be used for preparing aluminum containing heteroatom rings[82] by H_2 elimination reactions. Aluminum alkyls can be converted to aluminum halides or aluminum oxides. Recently a seris of aluminum oxides and aluminum hydroxides were synthesized by the hydrolysis reaction of aluminum alkyls.[83] A very important product of these compounds is methylaluminumoxide (MAO). MAO was found to be a highly active cocatalyst for Group 4 metallocenes catalyzing ethylene and propylene polymerization.[12, 13] Reduction reaction of aluminum halides can result in Al(I) or Al-Al bond containing compounds.[31]

A bulky organic ligand is usually employed to stabilize the aluminum center electronically and\or sterically. The introduction of a bulky organic ligand whether as a simple Lewis base donor, or in elimination reactions by gas (H_2, RH) or MX_n salts at the Al center, in fact, can efficetly reduce the condensation of products, and meanwhile, result in the formation of unusual compounds. In recent years, there are big amount of aluminum compounds with monovalent bulky chelating ligands have been reported, but there are not many aluminum compounds known which are supported by divalent bulky ligands. In 1998, a seris of new divalent bulky 1,8-diaminonaphthalene ligands were reported,[84-88] which are currently exhibiting growing interest due to their specific steric and electronic properties to control effectively the geometry at the metal center. The known complexes containing these ligands include main group (Al, Ge, In, Li, Mg, Si, Sn, Tl) and transition metal (Ni, Ti, Zr) derivatives.[85, 96, 89-96] There are still no aluminum monomic complexes reported yet. Herein, we report on the synthesis and characterization of the bulky 1,8-bistrimethylsilyamino)naphthalene (L^*) (**23**) aluminum monohydride, aluminum monobromide, aluminum monomethyl, and aluminum dimethyl derivative.



Scheme 15. Preparation of compounds **24**-**27**.

Ther is so far only one aluminium compound containg 1,8-diaminonaphthalene ligands $L^*(AlMe_2)_2$ (**24**) reported.[94] It's a dinucler compound, and it's synthesis method similar to that of the compound: $L^*AlH(NMe_3)$ (**25**). Synthesis of **24** and **25** have been accomplished by the reaction of L^*H_2 with $AlMe_3$ and ($H_3Al \bullet NMe_3$) respectively. Whether in a ratio of 1:1 or 1:2, L^*H_2 reacts with $AlMe_3$ always to $L^*(AlMe_2)_2$ (**24**). There is no mononuclear $L^*(AlMe)$ found. This can be explained as that after formation of the intermediate $L^*H(AlMe_2)$ by the elimination of one molecule of methane, the second Me group at the same Al center is not reactive enough to interact with the other proton of the ligand to form another molecule of methane elimination. In contrast only the mononuclear L*AlH(NMe$_3$) was obtained from the reaction of L*H$_2$ with (H$_3$Al • NMe$_3$) whether in the ratio of 1:1 or 1:2. This is due to the sufficient reactivity of the second hydride at the same Al center to interact with the other proton of the ligand to eliminate H$_2$. L*Al(Me)THF (**26**) and L*Al(Br)THF (**27**) were prepared by the reaction of L*Li$_2$(THF)$_3$ with AlMeCl$_2$ and AlBr$_3$ respectively. These two reactions involve the elimination of two molecules of LiCl and LiBr respectively. Both lithium salts were prepared at –30 °C, and the other two reactions performed at 0 °C.

Compounds **25**-**27** were charactered by NMR, MS (EI), IR (for **25**), and elemental analyses. The presence of hydride in **25** is evident from the IR spectrum. The broad IR bond at 1869 cm^{-1} is assigned to the Al-H stretching frequency. In ^{1}H NMR, compounds **25**-**27** exhibit resonances in the range of δ 6.6-7.2 and δ 0.1-0.3 in the ration of 6:18, which are assigned to the C$_6$*H*$_{10}$ and Si*Me*$_3$ respectively. They confirm the existence of the backbone of the 1,8-bis-(trimethylsilyamino)naphthalene. **26** and **27** exhibit the resonaces around δ 4.0 and δ 1.6, which are assigned to the THF molecule. In the ^{1}H NMR spectrum of **25** there is a resonance at δ 2.3, which shows the existence of the NMe$_3$ group. There is an resonance at δ –0.55 in **26** which indicates the existence of the Al-Me in the molecule. While two unfield resonances (δ –0.37 and –1.48) can be obsearved in the ^{1}H NMR spectrum of **24**, which can be assigned to the two Me groups at the same Al center having different chemical environments. The ^{13}C NMR spectrum shown the same characters of the ligand for all the compounds.

Compounds **25** (Figure 21) and **26** (Figure 22) crystallize in the orthorhombic system *Ama*2 and the monoclinic system *P*2$_1$/*n*. In all two structures, the aluminum center has a tetrahedral environment. **25** and **26** have almost the same Al-N bond lengths (av. 1.828 Å and 1.83 Å). While the Al-N bonds in compound **24** are much longer (av. 1.98 Å). The Al centers in the dinuclear molecule **24** are much more crowded than those in the mononuclear molecules **25** and **26**. Thus the Al atoms in **24** share the space with each other, which results in the longer bond lengths of the Al-N bonds in **24** compared to those in **25** and **26**. In the dinuclear structure of **24**, it is very clear that the two Me groups at the same aluminum atom have different chemical enviroments. One is near the naphthalene ligand and the other is closer to the other aluminum atom. So the Me groups closer to the other aluminum atom lead to an different upfield chemical shift with the other. While there are only one Me group at the aluminium atom in the mononuclear structure **26**. So there is only one upfield chemical shift. The Al(1)→N(2) bond length (2.021 Å) in **25** and the Al→O bond length (1.920 Å) in **26** are longer than the normal σ bonds of compounds containing Al-N and Al-O moieties.

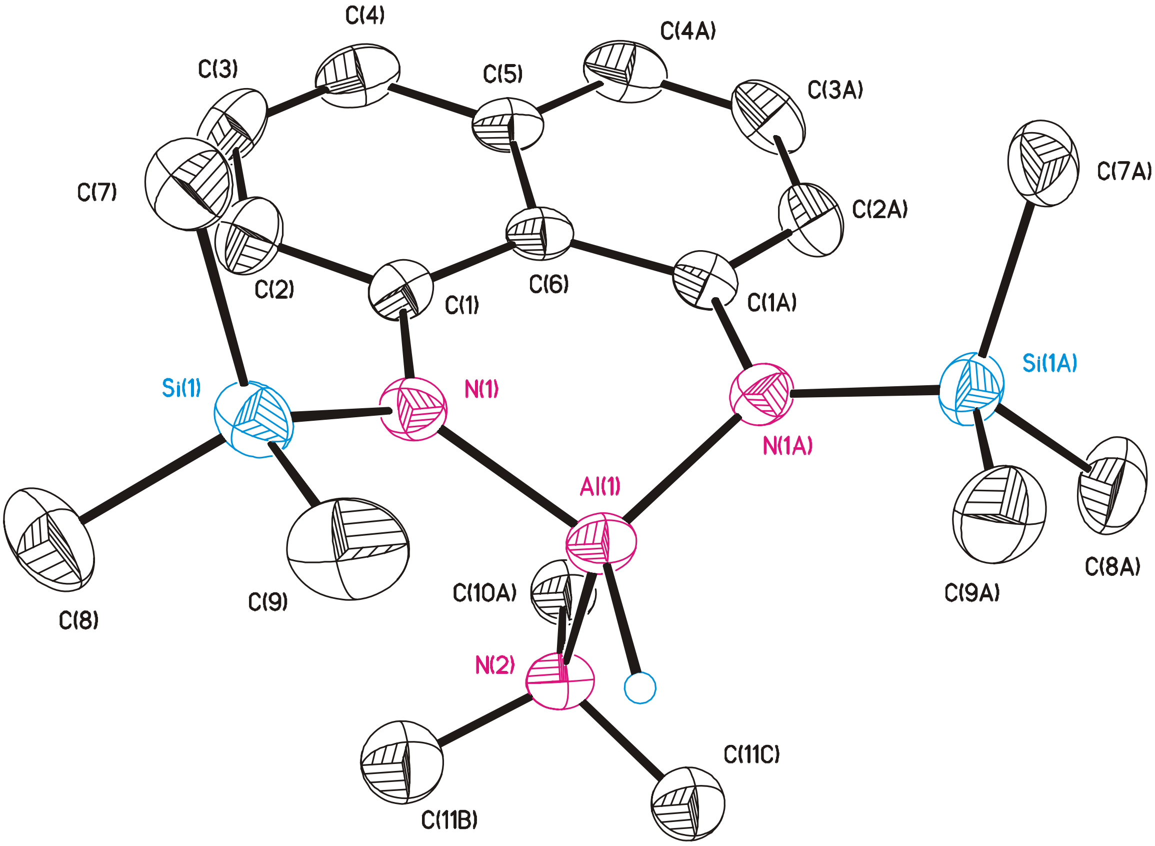


Figure 21. Molecular structure of **25**. Thermal ellipsoids are drawn at the 50% level, and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)-N(1) 1.828(2), Al(1)-N(1A) 1.828(2), Al(1)-N(2) 2.021(3), N(1)-Si(1) 1.744(2), N(1)-Al(1)-N(1A) 102.95(13), N(1)-Al(1)-N(2) 106.85(8), N(1A)-Al(1)-N(2) 106.86(8).

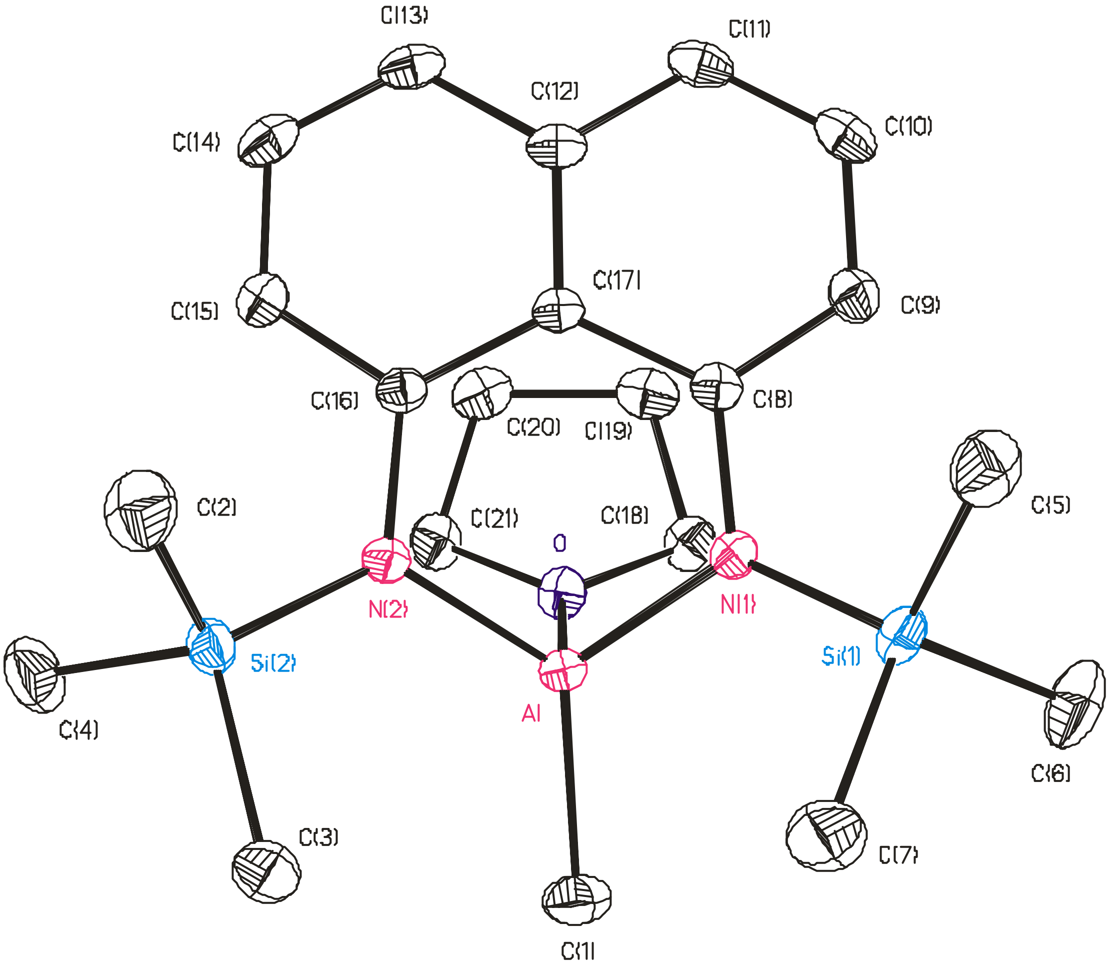


Figure 22. Molecular structure of **26**. Thermal ellipsoids are drawn at the 50% level, and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al-N(1) 1.8298(13), Al-N(2) 1.8311(12), Al-O 1.9202(11), Al-C(1) 1.9482(16), N(1)-Al-N(2) 100.82(6), N(1)-Al-O 101.88(5), N(2)-Al-O 100.33(5), N(1)-Al-C(1) 121.37(7) N(2)-Al-C(1) 125.87(7) O-Al-C(1) 102.09(7)

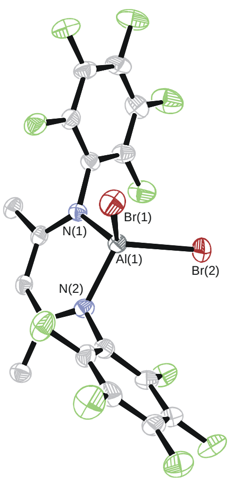
Herein, we have described the syntheses and X-ray structures of aluminum methyl, hydride, and bromide compounds supported by the 1,8-bis-(trimethylsilyamino)naphthalene ligand. The resulting compounds are excellent starting materials and can be used to prepare interesting compounds.

3. Summary and Outlook

1. Summary

This dissertation has laid emphasis mainly on the reaction chemistry of aluminum(I, III) compounds stabilized by sterically bulky ligands. It is comprised of four parts.

The first part of this work is focused on the synthesis and the characterization of aluminum, gallium, and germanium compounds bearing the C_6F_5-substituted β-diketiminate $HC[(CMe)(NC_6F_5)]_2$ (L') (**1**) ligand. The method for the formation of alumoxane is the controlled hydrolysis of organoaluminum compounds. In order to investigate the unusual hydrolysis of the aluminum compound with the bulky β-diketiminate ligand in more detail, we selected the C_6F_5 substituted β-diketiminate $HC[(CMe)(NC_6F_5)]_2$ (L') (**1**) as the supporting ligand. A series of compounds containing the C_6F_5-substituted β-diketiminate ligand L'AlMeCl (**2**), L'AlBr$_2$ (**3**), L'GeCl (**4**), and L'GaCl$_2$ (**5**) L'AlMe$_2$ (**6**), L'AlMeI (**7**), (L' = $HC[(CMe)(NC_6F_5)]_2$) were synthesised.



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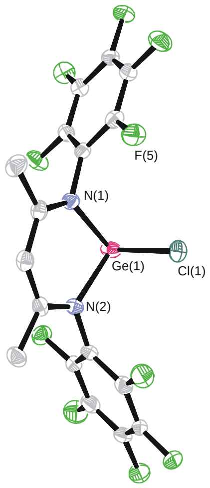

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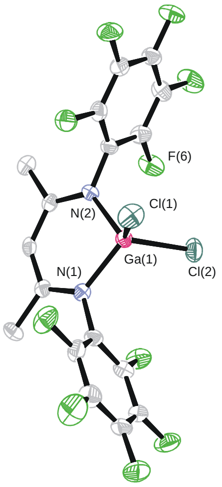

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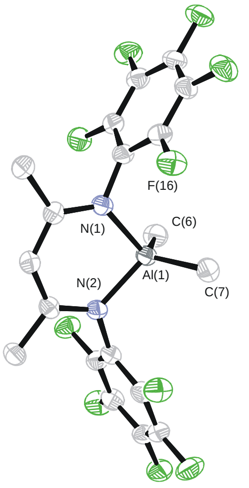
The hydrolysis of **2** and **7** in the presence of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene as hydrogen halide acceptor both leads to (L'AlMe)$_2$(μ-O) (**8**), a methylalumoxane derivative, which is the first hydrolysis product with the general formula of (RAlMe)$_n$O.



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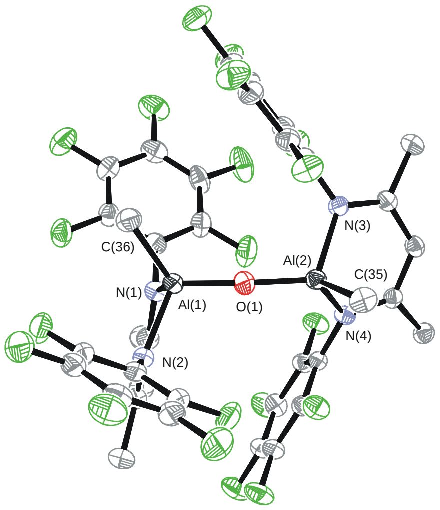

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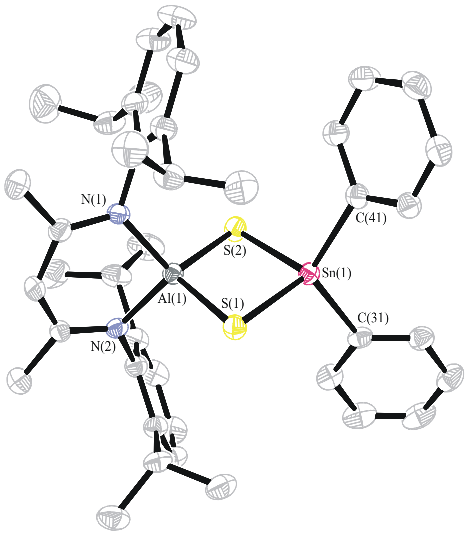
We conclude that the stronger Brönsted acidity of the proton and the smaller size of the C_6F_5 group in this compound compared with that of the corresponding 2,6-iPr$_2$C$_6$H$_3$ derivative is the reason of the different product formation.

In the second part aluminum-containing tin and germanium heterobimetallic sulfides were synthesised and characterized. Heterobimetallic chalcogen compounds have attracted much interest due to their application as catalysts in industry. However there are no aluminum-containing main group heterobimetallic sulfides reported. The reaction of {LAl[(SLi)$_2$(THF)$_2$]}$_2$ (**9**) (L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) with Ph$_2$MCl$_2$ and Me$_2$MCl$_2$ respectively in THF afforded LAl(μ-S)$_2$MPh$_2$ (**10**: M = Sn; **11**: M = Ge) and LAl(μ-S)$_2$Me$_2$ (**12**: M = Sn; **13**: M = Ge) in high yields.



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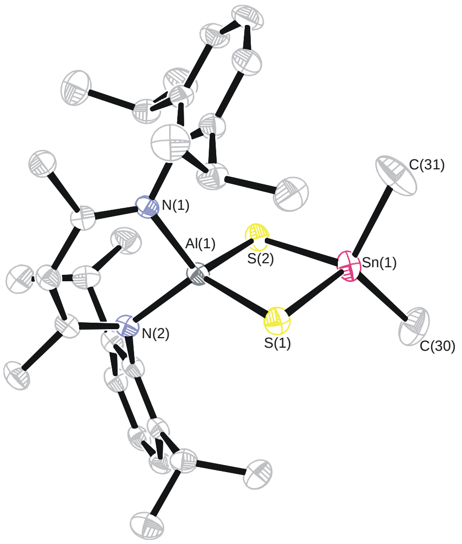

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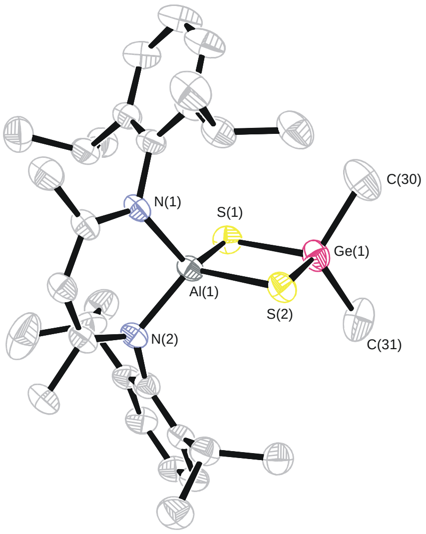
The reaction of **9** with MCl_4 (M = Ge, Sn) in THF results in LAl(μ-S)$_2$M(μ-S)$_2$AlL (**14**: M = Sn; **15**: M = Ge).



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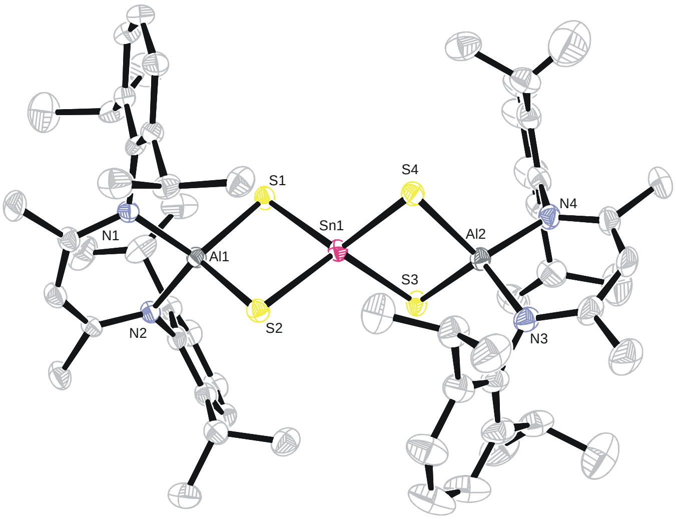
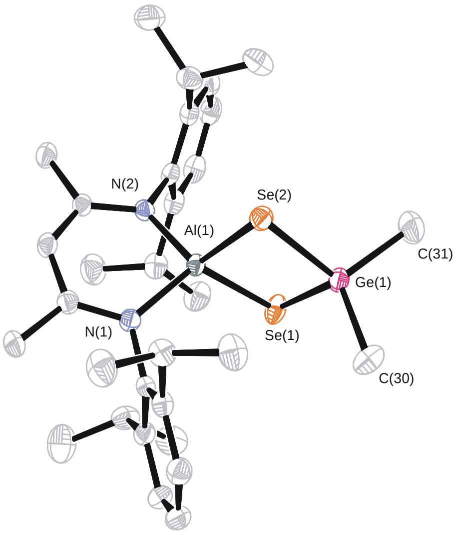


14

Morover we prepared the compound LAl(SeLi)$_2$(THF)$_2$ (**16**) (L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$). **16** reacts with Me_2GeCl_2 in THF to afford LAl(μ-Se)$_2$GeMe$_2$, (**17**) which is an unique aluminum-containing heterbimetallic selenide. Furthermore the reaction of **9** with $GeCl_2$·dioxane yields the novel germanium(II)→germanium(II) containing heterotrimetallic [LAl(μ-S)$_2$Ge$_2$]$_2$(μ-S)$_3$Li$_2$·(THF)$_2$] (**18**) cluster. It is the first aluminum containing heterotrimetallic sulfide.



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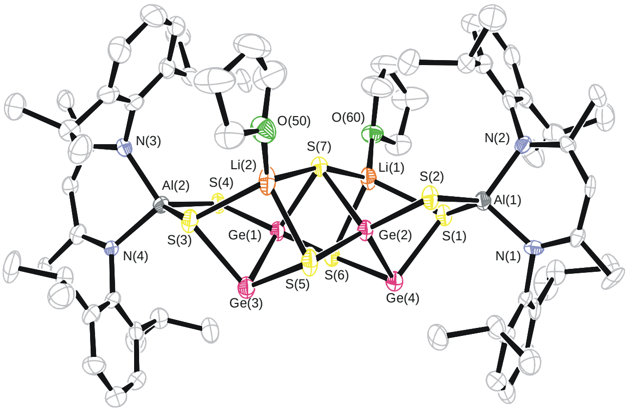

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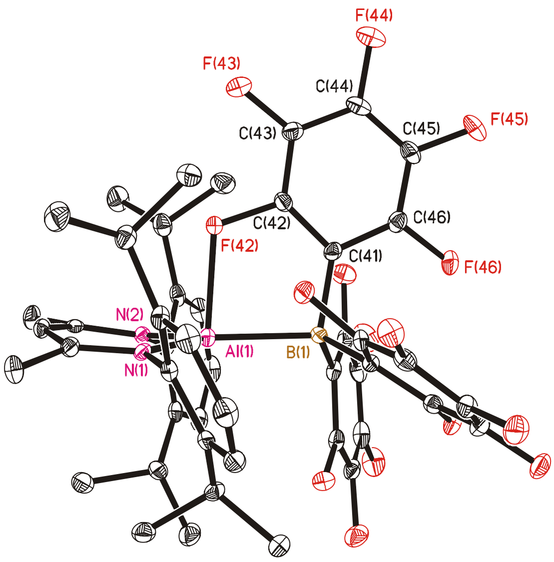
The third part of this thesis is focused on the study of Lewis base, Lewis acid and reduction properties of monomeric [LAl] (L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) (**19**). **19** is the first stable dicoordinate aluminum(I) compound that has been prepared and structurally characterized in the solid state. The fascinating property of **19** is the dual Lewis acid and Lewis base character. However it is only shown by theoretical calculations, there is no experimental evidence. The redox reaction of LAl with B(C$_6$F$_5$)$_3$ yields the first compound of composition LAlB(C$_6$F$_5$)$_3$ (**20**) showing both Lewis base and Lewis acid character at the metal center. The synthesis of organic-inorganic hybrid materials is an important target. Moreover aluminum containing organic-inorganic hybrid materials is another fascinating subject. The reaction of **19** or LAlH$_2$ (**21**) with PhB(OH)$_2$ resulted in an unprecedented formation of LAl[(OBPh)$_2$O] (**22**). It is an unique example of a spiro centered aluminum atom showing the inorganic AlO$_3$B$_2$ ring fused to the organic C$_3$N$_2$ part.



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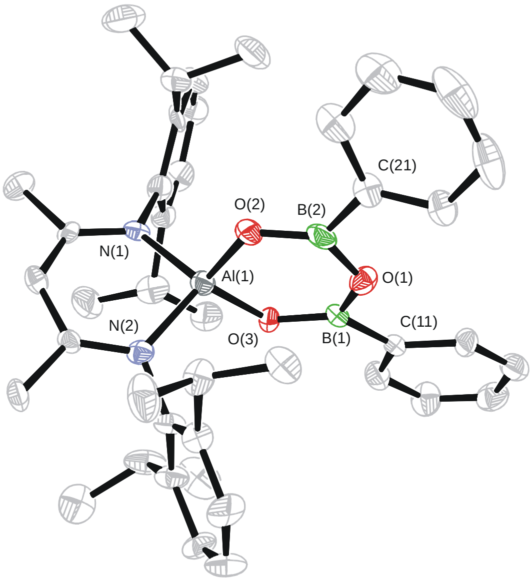

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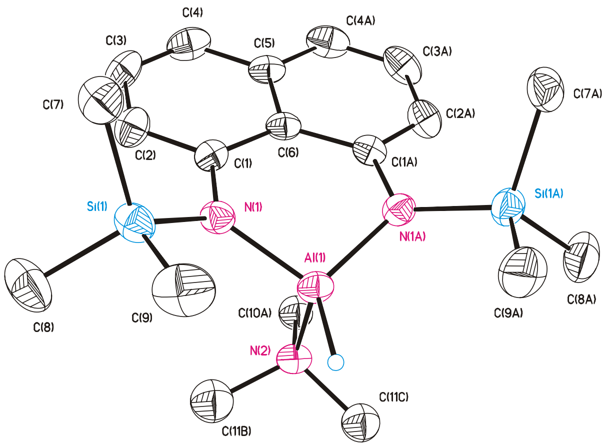
The last part deals with the synthesis of aluminum alkyl, halogen, and hydride supported by the bulky [1,8-(Me$_3$SiNH)$_2$C$_{10}$H$_6$] (L*) (**23**) ligand. Aluminum hydrides, alkylates, and halides are involved in most of aluminum containing reactions and they are extraordinary important for aluminum chemistry. However with 1,8-diaminonaphthalene ligands only one aluminium compound: $[L^{*}(AlMe_2)_2]$ (**24**) has been reported. In this dissertation the novel aluminum hydride compound: $[L^{*}AlH(NMe_3)]$ (**25**) was synthesised by the reaction of $[1,8\text{-}(Me_3SiNH)_2C_{10}H_6]$ (L^{*}) with $H_3Al{\cdot}NMe_3$. One mononuclear aluminum alkyl compound: $[L^{*}Al(Me)THF]$ (**26**) and the other aluminium halogen compound: $[L^{*}Al(Br)THF]$ (**27**) were synthesised by the reaction of $[1,8\text{-}(Me_3SiNLi)_2C_{10}H_6]Li_2(THF)_3$ with $MeAlCl_2$ and $AlBr_3$ respectively. They are the first mononuclear aluminum containing compounds supported by the 1,8-amine-naphthalene ligand.



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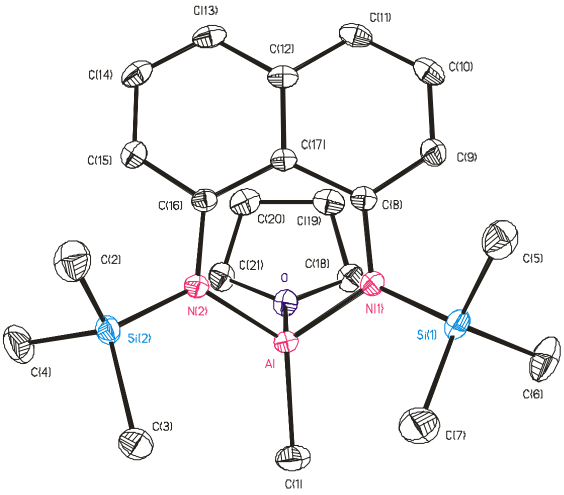

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2. Outlook

The dissertation presented here has emphasized on the strong reduction characteristic of aluminum (I), generating functionalities on aluminum centers such as OH, SH, SeH and studying their reactivity. This resulted in the development of new reaction types for such species. An extention of this work may be the application of the new reaction type on LAl(I), reacting this compound with other main group and transition elements containing acidic OH groups. It is also promising for aluminum (I) compounds to react those with late transition metal peroxide to prepare heterobimetallic oxides. Moreover, rare earth metals are potential candidates for the generation of heterobimetallic sulfides or selenides containing aluminum. The starting matrials are the lithium salts obtained from $LAl(SH)_2$ and $LAl(SeH)_2$ described herein .

4. Experimental Section

4.1. General Procedures

All reactions and handling of reagents were performed under an atmosphere of dry nitrogen or argon using Schlenk techniques[97] or a glovebox where the O_2 and H_2O levels were usually kept below 1 ppm. All glassware was oven-dried at 140 °C for at least 24 h, assembled hot and cooled under high vacuum prior to use. Toluene (Na/benzophenone ketyl and diphenylether), benzene (K/benzophenone ketyl and diphenylether), hexane (Na/K/benzophenone ketyl and diphenylether), pentane (Na/K/benzophenone ketyl and diphenylether), tetrahydrofuran (K/benzophenone ketyl), diethylether (Na/benzophenone ketyl), dichloromethane (CaH_2) were dried and distilled prior to use.[98]

4.2. Physical Measurements

Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus. NMR spectra were recorded on Bruker Avance 200, Bruker Avance 300, and Bruker Avance 500 NMR spectrometers. Chemical shifts are reported in ppm with reference to $SiMe_4$ (external) for ^{1}H, ^{7}Li, ^{11}B, ^{13}C, ^{19}F, ^{27}Al, ^{29}Si, ^{77}Se, and ^{119}Sn nuclei. Downfield shifts from the reference are quoted positive, upfield shifts are assigned negative values. The NMR grade deuterated solvents were dried in following manners: C_6D_6 and toluene − overnight stirring with Na/K alloy followed by vacuum distillation, $CDCl_3$ − 3 min. stirring with P_4O_{10} followed by filtration, THF − storing over freshly activated molecular sieves for one week. Heteroatom NMR spectra were recorded ^{1}H decoupled.

IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer. The samples were prepared normally as Nujol mulls between KBr plates.

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

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

Crystal structure determination: Intensity data for compounds **3**, **4**, **5**, **6**, **8**, **10**, **11**, **12**, **14**, **17**, **20**, **25**, and **26** were collected on a STOE-IPDS II image-plate diffractometer. The diffraction data for the compounds **18** and **22** were measured on a Bruker AXS instrument. The data for all the compounds were collected at low temperature (the temperatures for individual compounds are mentioned in the tables in Section 6 using graphite monochromated MoK_{α} radiation (λ = 0.71073 Å). The data reduction and space group determination were carried out using Siemens SHELXTL program.[99] The structures were solved using either SHELXS-96/97[100, 101] programs. The refinement of the structures was carried out by full-matrix least-squares method against F^2 using SHELXL-97. The various advanced features (*e.g.* restraints and constraints) of SHELXL programs were used to treat the disordered groups, lattice solvents such as THF, and the hydrogen atoms. The non-hydrogen atoms were refined anisotropically A riding model was used for the hydrogen atoms. The crystal data for all compounds along with the final residuals and other pertaining details are listed in Section 6 in tabular form.

4.3 Starting Materials

Commerically available chemicals were purchased from Fluka or Aldrich and used as received. The $HC[(CMe)(NAr)]_2$ (Ar = 2,6-*i*$Pr_2C_6H_3$),[40] $HC[(CMe)(NC_6F_5)]_2$,[36] $\{LAl[(SLi)_2(THF)_2]_2\}_2$,[28] $\{HC(CMeNAr)_2\}Al$,[31] $HC(CMeNAr)_2AlH_2$,[39] [1,8-$(Me_3SiNH)_2C_{10}H_6$],[84] [1,8-$(Me_3SiNH)_2C_{10}H_6](Li)_2(THF)_3$[88]were synthesized using reported procedures. $LiN(SiMe_3)_2$ was prepared prior to use from freshly distilled $HN(SiMe_3)_2$ and MeLi in pentane. Redistilled H_2O was degassed prior to use.

4.4 Syntheses

4.4.1. *Synthesis of* $HC[(CMe)(NC_6F_5)]_2AlMeCl$ **(2)**

To a toluene solution (40 mL) of L'H (4.31 g, 10 mmol) at 0 °C was added dropwised *n*-BuLi (2.5 M, 4 mL, 10 mmol). The mixture was stirred and allowed to warm to room temperature. After additional stirring for 12 h, the solution was cooled to 0 °C and $AlCl_2Me$ (1 M, 10 mL, 10 mmol) was added. The resulting solution was allowed to warm to room temperature and stirred for 12 h. After workup, the insoluble LiCl was removed by filtration and the filtrate was dried in vacuum and washed with *n*-hexane to yield solid **2** (4.60 g, 91%). Mp 180-181 °C. ^1H NMR (500.13 MHz, C_6D_6, 298 K, ppm): δ –0.33 (s, 3 H, Al-*Me*), 1.21 (s, 6 H, β-*Me*), 4.69 (s, 1 H, γ-C*H*). ^{13}C NMR (125.77 MHz, C_6D_6, 298 K, ppm): δ –11.22 (Al-*Me*), 22.65 (β-*Me*), 100.93 (γ-*C*H), 118.09, 137.06, 139.21, 141.65, 142.34, 143.71, 144.33 (C_6F_5), 173.21 (*C*N). ^{19}F NMR (188.28 MHz, C_6D_6, 298 K, ppm): δ –143.25 (m, 2 F, *o*-F), -146.31 (m, 2 F, *o*-F), -153.04 (t, 2 F, *p*-F), -159.54 (m, 2 F, *m*-F), -160.33 (m, 2 F, *m*-F). EI-MS: *m*/*z* (%) 506 (4, [M^+]), 491 (100, [M^+ - Me]). Anal. Calcd for $C_{18}H_{10}AlClF_{10}N_2$ (*M*r = 506.71): C, 42.67; H, 1.99. Found C, 42.09; H, 2.33.

4.4.2. *Synthesis of* $HC[(CMe)(NC_6F_5)]_2AlBr_2$ **(3)**

To a toluene solution (40 mL) of L'H (4.31g, 10 mmol) at 0 °C was added dropwise *n*-BuLi (2.5 M, 4 mL, 10 mmol). The mixture was stirred and allowed to warm to room temperature. After additional stirring for 12 h, the solution was cooled to –0 °C and $AlBr_3$ (2.67 g, 10 mmol) in toluene (10 mL) was added. The resulting solution was allowed to warm to room temperature and stirred for 12 h. After workup, the insoluble LiBr was removed by filtration and the filtrate was dried in vacuum and washed with *n*-hexane to yield crystalline **3**. (6.02 g, 91%). Mp 190-191 °C. ^1H NMR (300.13 MHz, C_6D_6, 298 K, ppm): δ 1.18 (s, 6 H, β-*Me*), 4.67 (s, 1 H, γ-C*H*). ^{13}C NMR (125.77 MHz, C_6D_6, 298 K, ppm): δ 23.00 (β-*Me*), 101.80

(γ-C), 116.75, 137.34, 139.34, 140.06, 142.10, 144.09 (C_6F_5), 174.55 (*C*N). ^{19}F NMR (188.28 MHz, C_6D_6, 298 K, ppm): δ –142.54 (m, 4 F, *o*-F), -151.43 (t, 2 F, *p*-F), -159.46 (m, 4 F, *m*-F). EI-MS: *m*/*z* (%) 615.9 (100, [M^+]). Anal. Calcd for $C_{17}H_7AlBr_2F_{10}N_2$ (*M*r = 616.05): C, 33.15; H, 1.15; N, 4.55. Found C, 32.50; H, 1.40; N, 4.33.

4.4.3. *Synthesis of HC[(CMe)(NC*$_6$*F*$_5$*)]*$_2$*GeCl* **(4)**

To a toluene solution (20 mL) of L'H (0.43g, 1 mmol) at 0 °C was added dropwise *n*-BuLi (2.5 M, 0.4 mL, 1 mmol). The mixture was stirred and allowed to warm to room temperature. After additional stirring for 12 h, the solution was cooled to –0 °C and $GeCl_2$·dioxane (0.23 g, 1 mmol) in toluene (10 mL) was added. The resulting solution was allowed to warm to room temperature and stirred for 12 h. After workup, the insoluble LiCl was removed by filtration and the filtrate was dried in vacuum and washed with *n*-hexane twice to yield crystalline **4**. (0.45 g, 84%). Mp 183 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$, 298 K, ppm): δ 2.08 (s, 6 H, *β-Me*), 5.67 (s, 1 H, *γ*-C*H*). ^{13}C NMR (75.48 MHz, $CDCl_3$, 298 K, ppm): δ 23.43 (*β-Me*), 103.22 (γ-C), 119.22, 137.54, 138.55, 139.15, 139.88, 142.19 (C_6F_5), 167.27 (*C*N). ^{19}F NMR (188.28 MHz, $CDCl_3$, 298 K, ppm): –141.83 (m, 2 F, *o*-F), -146.63 (m, 2 F, *o*-F), -154.23 (t, 2 F, *p*-F), -159.94 (m, 2 F, *m*-F), -160.52 (m, 2 F, *m*-F). EI-MS: *m*/*z* (%) 538 (59, [M^+]), 503 (100, [M^+ - Cl]. Anal. Calcd for $C_{17}H_7ClF_{10}GeN_2$ (*M*r = 537.29): C, 38.00; H, 1.31; N, 5.21. Found C, 39.05; H, 1.67; N, 4.97.

4.4.4. *Synthesis of HC[(CMe)(NC*$_6$*F*$_5$*)]*$_2$*GaCl*$_2$ **(5)**

To a toluene solution (40 mL) of L'H (4.31g, 10 mmol) at 0 °C was added dropwise *n*-BuLi (2.5 M, 4 mL, 10 mmol). The mixture was stirred and allowed to warm to room temperature. After additional stirring for 12 h, the solution was cooled to –0 °C and $GaCl_3$ (1.73 g, 10 mmol) in toluene (20 mL) was added. The resulting solution was allowed to warm to room temperature and stirred for 12 h. After workup, the insoluble LiCl was removed by filtration and the filtrate was dried in vacuum and washed with *n*-hexane twice to yield crystalline **5**. (4.67 g, 82%). Mp 242 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$, 298 K, ppm): δ 2.05 (s, 6 H, *β-Me*), 5.47 (s, 1 H, *γ*-C*H*). ^{13}C NMR (125.77 MHz, C_6D_6, 298 K, ppm): δ 23.82 (*β-Me*), 100.14 (*γ*-C), 117.06, 137.08, 139.13, 139.91, 141.78, 143.75 (*C*$_6$F$_5$), 173.93 (*C*N). ^{19}F NMR (188.28 MHz, C_6D_6, 298 K, ppm): δ –144.24 (m, 4 F, *o*-F), -153.35 (t, 2 F, *p*-F), -160.02 (m, 4 F, *m*-F). EI-MS: *m*/*z* (%) 570 (100, [M^+]). Anal. Calcd for $C_{17}H_7Cl_2F_{10}GaN_2$ (*M*r = 569.87): C, 35.83; H, 1.24; N, 4.92. Found C, 35.60; H, 1.74; N, 4.61.

4.4.5 *Synthesis of* $HC[(CMe)(NC_6F_5)]_2AlMe_2$ **(6)**

To a toluene solution (40 mL) of L'H (4.31g, 10 mmol) at 0 °C was added dropwise $AlMe_3$ (2 M, 5 mL, 10 mmol). The solution was stirred and allowed to warm to room temperature. After additional stirring for 12 h, the solution was dried in vacuum and washed with *n*-hexane to yield crystalline solid **6** (4.52 g, 93%). Mp 141-142 °C. ^{1}H NMR (500.13 MHz, C_6D_6, 298 K, ppm): δ –0.53 (s, 6 H, Al-*Me*), 1.28 (s, 6 H, *β-Me*), 4.75 (s, 1H, *γ*-C*H*). ^{13}C NMR (125.77 MHz, C_6D_6, 298 K, ppm): δ –11.26 (Al-*Me*), 22.59 (*β-Me*), 100.41 (*γ*-C), 119.85, 137.19, 138.88, 139.19, 140.83, 141.99, 143.95 (*C*$_6$F$_5$), 172.07 (*C*N). ^{19}F NMR (188.28 MHz, C_6D_6, 298 K, ppm): δ –146.17 (m, 4 F, *o*-F), -154.91 (t, 2 F, *p*-F), -160.54 (m, 4 F, *m*-F). EI-MS: *m*/*z* (%) 471 (100, [M^+ - Me]). Anal. Calcd for $C_{19}H_{13}AlF_{10}N_2$ (*M*r = 486.29): C, 46.93; H, 2.69; N, 5.76. Found C, 47.00; H, 2.73; N, 5.66.

4.4.6. *Synthesis of* $HC[(CMe)(NC_6F_5)]_2AlMeI$ **(7)**

30 mL of toluene was added to a solid mixture of L'$AlMe_2$ (2.43 g, 5 mmol) and I_2 (1.27 g, 5 mmol) at room temperature. After 3 d of stirring, a light yellow solution was formed. The solvent and volatiles were removed from the solution in vacuum and the residue was washed with *n*-hexane to yield solid **7** (2.66 g, 89%). Mp 164-165 °C. ^{1}H NMR (300.13 MHz, C_6D_6, 298 K, ppm): δ –0.15 (tr, 3 H, Al-*Me*), 1.21 (s, 6 H, *β-Me*), 4.72 (s, 1 H, *γ*-C*H*). ^{13}C NMR

(75.48 MHz, C_6D_6, 298 K, ppm): δ –5.51 (Al-*Me*), 22.94 (β-*Me*), 101.47 (γ-C), 117.97, 136.61, 138.92, 140.01, 141.23, 142.27, 144.60 (C_6F_5), 173.15 (*C*N). ^{19}F NMR (188.28 MHz, C_6D_6, 298K, ppm): δ –139.84 (m, 2 F, *o*-F), -145.80 (m, 2 F, *o*-F), -152.63 (t, 2 F, *p*-F), -159.36 (m, 2 F, *m*-F), -159.57 (m, 2 F, *m*-F). EI-MS: *m*/*z* (%) 598 (1, [M^+]), 583 (30, [M^+ - Me]), 471 (100, [M^+ - I]). Anal. Calcd for $C_{18}H_{10}AlF_{10}IN_2$ (*M*r = 598.16): C, 36.14; H, 1.69; N, 4.68. Found C, 35.49; H, 2.11; N, 4.46.

4.4.7. *Synthesis of {HC[(CMe)(NC₆F₅)]₂AlMe}₂(μ-O)* **(8)**

To a mixture of **2** (0.51 g, 1 mmol) or **7** (0.60 g, 1 mmol) and [CN(*i*Pr_2)C_2Me_2N(*i*Pr)] (**:**C, 0.18g, 1 mmol) in toluene (20 mL) at 0 °C was added distilled H_2O (18 µL, 1 mmol). The suspension was allowed to warm to room temperature and stirred for 12 h. The insoluble solid was removed by filtration, and the filtrate was dried in vacuum and extracted with *n*-hexane (10 mL). The extract was kept at -28 °C to afford colorless crystals of **8**. (0.33 g, 69%). Mp: 184-185 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$, 298 K, ppm): δ –1.38 (t, 6 H, Al-*Me*), 1.85 (s, 12 H, β-*Me*), 5.22 (s, 2 H, γ-C*H*). ^{13}C NMR (75.48 MHz, $CDCl_3$, 298K, ppm): δ –14.57 (Al-*Me*), 22.98 (β-*Me*), 99.22 (γ-C), 119.88, 136.11, 137.77, 139.71, 141.12, 142.89, 144.57 (C_6F_5), 171.04 (*C*N). ^{19}F NMR (188.28 MHz, $CDCl_3$, 298 K, ppm): δ –146.27 (m, 2 F, *o*-F), -149.12 (m, 2 F, *o*-F), -157.99 (t, 2 F, *p*-F), -163.03 (m, 2 F, *m*-F), -163.19 (m, 2 F, *m*-F). EI-MS: *m*/*z* (%) 943 (100, [M^+ - Me]). Anal. Calcd for $C_{36}H_{20}Al_2F_{20}N_4O$ (*M*r = 958.51): C, 45.11; H, 2.10; N, 5.85. Found C, 44.79; H, 2.37; N, 5.67.

4.4.8. *Synthesis of LAl(μ-S)₂SnPh₂* **(10)**

A solution of Ph_2SnCl_2 (0.69 g, 2 mmol) in THF (10 mL) was added dropwise to a solution of **9** (1.33 g, 1 mmol) in THF (20 mL) at – 30 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature. The solvent was removed *in vacuo*. The solid was extracted with toluene (10 mL), and the extract was kept at room temperature for 2 d to afford **10** as colorless crystals. An additional crop of LAl(μ-S)$_2$SnPh$_2$ was obtained from the mother liquor. Total yield: 1.42 g (91 %), mp 251 °C. EI-MS: *m*/*z* (%) 782 (40) [*M*$^+$], 705 (100) [*M*$^+$−Ph], 627 (30) [*M*$^+$−2Ph]. ^{1}H NMR (300.13 MHz, C$_6$D$_6$, 25 °C, TMS): δ 7.23−7.16 (m, 6 H, Ar−*H*), 7.10−7.02 (m, 10 H, *Ph*−Sn), 4.90 (s, 1 H, γ-*H*), 3.55 (sept, $^3J_{\text{H-H}}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 1.60 (s, 6 H, *Me*), 1.49 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.12 ppm (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 12 H, CH*Me*$_2$). ^{13}C NMR (75.48 MHz, C$_6$D$_6$, 25 °C, TMS): δ 170.9 (*C*N), 145.1, 141.3, 139.5, 136.0, 129.3, 125.6, 124.9 (*Ar* and Sn−*Ph*), 98.1 (γ-*C*), 29.2 (*C*HMe$_2$), 25.4 (CH*Me*$_2$), 23.9 (CH*Me*$_2$), 21.4 ppm (*Me*). ^{27}Al NMR (78.21 MHz, C$_6$D$_6$, 25 °C, AlCl$_3$·6H$_2$O) δ 114.5 ppm. ^{119}Sn NMR (186.49 MHz, C$_6$H$_6$, 25 °C, SnMe$_4$) δ −38 ppm. C$_{41}$H$_{51}$AlN$_2$S$_2$Sn·¼C$_7$H$_8$ (804.66) Calcd. C, 63.88; H, 6.59; N, 3.48. Found C, 63.92; H, 6.70; N, 3.35 %.

4.4.9. *Synthesis of LAl(μ-S)$_2$GePh$_2$* **(11)**

Preparation like that of **10** from Ph$_2$GeCl$_2$ (0.30 g, 1 mmol) and **9** (0.67 g, 0.5 mmol). Product **11** was isolated as colorless crystals. Total yield: 0.65 g (88 %), mp 251 °C. EI-MS: *m*/*z* (%) 736 (72) [*M*$^+$], 721 (19) [*M*$^+$-Me], 659 (100) [*M*$^+$−Ph]. ^{1}H NMR (200.13 MHz, C$_6$D$_6$, 25 °C, TMS): δ 7.25−7.20 (m, 6 H, Ar$_{\text{Ge}}$−*H*), 7.11−6.96 (m, 10 H, *Ph*−Me), 4.89 (s, 1 H, γ-*H*), 3.44 (sept, $^3J_{\text{H-H}}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 1.58 (s, 6 H, *Me*), 1.43 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.08 ppm (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 12 H, CH*Me*$_2$). ^{13}C NMR (75.48 MHz, C$_6$D$_6$, 25 °C, TMS): δ 170.82 (*C*N), 144.58, 140.50, 138.79, 133.41, 128.70, 126.53, 124.51 (*Ar* and Ge−*Ph*), 97.73 (γ-*C*), 28.81 (*C*HMe$_2$), 24.96 (CH*Me*$_2$), 24.67 (CH*Me*$_2$), 23.47 ppm (*Me*).

4.4.10. *Synthesis of LAl(μ-S)$_2$SnMe$_2$* **(12)**

Preparation like that of **10** from Me$_2$SnCl$_2$ (0.44 g, 2 mmol) and **9** (1.33 g, 1 mmol). Product **12** was isolated as colorless crystals. Total yield: 1.18 g (90%), mp 214−215 °C. EI-MS: *m*/*z* (%) 658 (20) [*M*$^+$], 643 (100) [*M*$^+$−Me], 627 (5) [*M*$^+$−2Me]. ^{1}H NMR (300.13 MHz,

$CDCl_3$, 25 °C, TMS): δ 7.25−7.17 (m, 6 H, Ar−*H*), 5.25 (s, 1 H, γ-*H*), 3.32 (sept, $^3J_{H-H}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 1.84 (s, 6 H, *Me*), 1.36 (d, $^3J_{H-H}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.12 (d, $^3J_{H-H}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 0.40 ppm (s, 6 H, $^2J_{(117)Sn-H}$ = 1.4 Hz, $^2J_{(119)Sn-H}$ = 1.4 Hz, *Me*−Sn). ^{13}C NMR (75.48 MHz, $CDCl_3$, 25 °C, TMS): δ 170.7 (*C*N), 144.7, 138.9, 127.0, 124.1 (*p*-, *m*-, *o*-, *i*-*C* of Ar), 98.0 (γ-*C*), 28.9 (*C*HMe$_2$), 26.0 (CH*Me*$_2$), 23.6 (CH*Me*$_2$), 21.5 (*Me*). 2.6 ppm (Sn−*Me*). ^{27}Al NMR (78.21 MHz, $CDCl_3$, 25 °C, $AlCl_3{\cdot}6H_2O$) δ 114 ppm. ^{119}Sn NMR (186.49 MHz, $CDCl_3$, 25 °C, $SnMe_4$) δ 133 ppm. $C_{31}H_{47}AlSnN_2S_2$ (658.20) Calcd. C, 56.52; H, 7.20; N, 4.25. Found C, 56.24; H, 7.56; N 3.96 %.

4.4.11. *Synthesis of LAl(μ-S)₂GeMe₂* **(13)**

Preparation like that of **10** from Me_2GeCl_2 (0.17 g, 1 mmol) and **9** (0.67 g, 0.5 mmol). Product **13** was isolated as colorless crystals. Total yield: 0.52 g (85%), mp >180 °C (dec). EI-MS: *m*/*z* (%) 612 (14) [M^+], 597 (100) [M^+−Me]. ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C, TMS): δ 7.15−7.11 (m, 6 H, Ar−*H*), 4.85 (s, 1 H, γ-*H*), 3.42 (sept, $^3J_{H-H}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 1.58 (d, $^3J_{H-H}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.55 (s, 6 H, *Me*), 1.08 (d, $^3J_{H-H}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 0.38 ppm (s, 6 H, *Me*−Ge). $C_{31}H_{47}AlGeN_2S_2$ (612.2) Calcd. C, 60.89; H, 7.75; N, 4.58. Found C, 61.52; H, 7.98; N 4.58 %.

4.4.12. *Synthesis of LAl(μ-S)₂Sn(μ-S)₂AlL* **(14)**

$SnCl_4$ (0.260 g, 0.12 mL, 1 mmol) was added dropwise to a solution of **9** (1.333 g, 1 mmol) in THF (20 mL) at –30 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature. The solvent was removed *in vacuo*. The solid was extracted with toluene (10 mL), kept at room temperature for 2 d to afford colorless crystals. An additional crop of LAl(μ-S)$_2$Sn(μ-S)$_2$AlL was obtained from the mother liquor. Total yield: 0.97 g (85%).

Alternative synthesis of LAl(μ-S)₂Sn(μ-S)₂AlL **(14)**

Compound **9** (1.33 g, 1 mmol) and $SnCl_4 \cdot 2THF$ (0.41 g, 1 mmol) were mixed as solids in a flask. The flask was placed in liquid nitrogen and toluene (50 ml) was added slowly. The reaction mixture was allowed to warm to ambient temperature and stirred overnight. The resulting suspension was filtered and all volatiles from the filtrate were removed in vacuum to leave a residue that was washed with *n*hexane (5 mL) to give 1.1 g of microcrystalline **14**. Yield 97 %. Mp 321 °C. EI-MS: *m*/*z* (%) 1136.4 (12) [M^+], 403 (100) [L–Me]. ^{1}H NMR (300.13 MHz, C_6D_6, 25 °C, TMS): δ 7.17–7.05 (m, 12 H, Ar-*H*), 4.73 (s, 2 H, γ-*H*), 3.35 (sept, $^3J_{H–H}$ = 6.8 Hz, 8 H, C*H*Me$_2$), 1.46 (s, 12 H, *Me*), 1.44 (d, $^3J_{H–H}$ = 6.8 Hz, 24 H, CH*Me*$_2$), 1.05 ppm (d, $^3J_{H–H}$ = 6.8 Hz, 24 H, CH*Me*$_2$). ^{13}C NMR (75.48 MHz, C_6D_6, 25 °C, TMS): δ 171.0 (*C*N), 144.5, 138.9, 129.3, 124.7 (*p*-, *m*-, *o*-, *i*-*C* of Ar), 98.4 (γ-*C*), 29.0 (*C*HMe$_2$), 25.9 (CH*Me*$_2$), 23.8 (CH*Me*$_2$), 21.4 ppm (*Me*). ^{27}Al NMR (78.21 MHz, C_6D_6, 25 °C, $AlCl_3 \cdot 6H_2O$) δ 114 ppm. ^{119}Sn NMR (186.49 MHz, C_6H_6, 25 °C, $SnMe_4$) δ 5 ppm. $C_{58}H_{82}Al_2N_4S_4Sn$ (1136.40) Calcd. C, 61.31; H, 7.27; N, 4.93. Found C, 60.96; H, 6.98; N, 4.50

4.4.13. *Synthesis of LAl(μ-S)$_2$Ge(μ-S)$_2$AlL* **(15)**

Preparation like that of **14** from $GeCl_4$ (0.21 g, 1 mmol) and **9** (1.333 g, 1 mmol). Product **15** was isolated as colorless crystals. Total yield: 0.91 g (83%). 251 °C (dec). EI-MS: *m*/*z* (%) 1090 (53) [M^+], 1075 (58) [M^+–Me], 477 (100) [LAlS]. $C_{58}H_{82}Al_2GeN_4S_4$ (1090.11) Calcd. C, 63.83; H, 7.58; N, 5.14. Found C, 64.32; H, 8.00; N, 5.25

4.4.14. *Synthesis of LAl(SeLi)$_2$(THF)$_2$* **(16)**

Compound LAl(SeH)$_2$ (3.64 g, 6 mmol) and LiN(SiMe$_3$)$_2$ (2.99 g, 12 mmol) were mixed as solids in a flask and subsequently cold THF (60 mL, 0 °C) was added. The reaction mixture was cooled to –20 °C and maintained at this temperature for 15 min under vigorous stirring. After filtration the solid was dried in vacuo **16** was obtained as a pale yellow powder. Yield 3.53 g (77.4%), mp >400 °C (dec). ^{1}H NMR (200.13 MHz, $CDCl_3$, 25 °C, TMS): δ

7.10−7.00 (m, 6 H, Ar−*H*), 5.10 (s, 1 H, γ-*H*), 3.86 (sept, $^{3}J_{H-H}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 3.37 (m, 8 H, O(C*H*$_2$CH$_2$)), 1.68 (m, 8 H, O(CH$_2$C*H*$_2$)), 1.59 (s, 6 H, *Me*), 1.22 (d, $^{3}J_{H-H}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.01 (d, $^{3}J_{H-H}$ = 6.8 Hz, 12 H, CH*Me*$_2$). ^{13}C NMR (50.32 MHz, CDCl$_3$, 25 °C, TMS) δ 24.46 (*C*H$_3$), 24.56 (CH(*C*H$_3$)$_2$), 25.28 (CH(*C*H$_3$)$_2$), 26.84 (O(CH$_2$*C*H$_2$)$_2$)), 28.12 (*C*H(CH$_3$)$_2$), 68.04 (O(*C*H$_2$CH$_2$)$_2$), 98.54 (γ-*C*H), 123.64, 125.48, 142.72, 145.48 (*Ar*), 168.07 ppm (*C*N); $C_{37}H_{57}AlLi_2N_2O_2Se_2$ (760.66) Calcd. C, 58.42; H, 7.55; N, 3.68. Found C, 58.51; H, 7.58; N 3.73 %.

4.4.15. *Synthesis of LAl(μ-Se)$_2$GeMe$_2$* **(17)**

A solution of Me$_2$GeCl$_2$ (0.17 g, 1 mmol) in THF (10 mL) was added dropwise to a suspension of **16** (0.76 g, 1 mmol) in THF (20 mL) at – 30 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature. The solvent was removed *in vacuo*. The solid was extracted with toluene (30 mL), and the toluene was removed *in vacuo*. The residue was washed with cold *n*-hexane to yield solid **17** was isolated as a white powder. Yield: 0.60 g (85%), mp 251 °C. EI-MS: *m*/*z* (%) 706 (23) [M^+], 691 (100) [M^+−Me]. ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 25 °C, TMS): δ 7.18−7.12 (m, 6 H, Ar−*H*), 4.84 (s, 1 H, γ-*H*), 3.50 (sept, $^{3}J_{H-H}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 1.55 (s, 6 H, *Me*), 1.60 (d, $^{3}J_{H-H}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.12 (d, $^{3}J_{H-H}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 0.67 ppm (s, 6 H, *Me*−Ge). ^{13}C NMR (75.48 MHz, CDCl$_3$, 25 °C, TMS): δ 170.5 (*C*N), 144.9, 139.5, 127.8, 124.3 (*p*-, *m*-, *o*-, *i-C* of Ar), 98.4 (γ-*C*), 28.2 (*C*HMe$_2$), 25.3 (CH*Me*$_2$), 24.9 (CH*Me*$_2$), 24.1 (*Me*). 11.49 ppm (Ge−*Me*). $C_{31}H_{47}AlGeN_2Se_2$ (705.20) Calcd. C, 52.53; H, 6.69; N, 3.96. Found C, 53.86; H, 7.03; N 4.06 %.

4.4.16. *Synthesis of [LAl(μ-S)$_2$Ge$_2$]$_2$(μ-S)$_3$Li$_2$·(THF)$_2$* (**18**).

A solution of GeCl$_2$·dioxane (0.23 g, 1 mmol) in THF (10 mL) was added dropwise to a solution of **9** (0.67 g, 0.5 mmol) in THF (20 mL) at –30 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirring was continued for 12 h. Finally the solvent was removed in *vacuo* and the crude product was extracted with toluene (10 mL). After keeping the solution at room temperature for 2 d, **18** was isolated as light yellow crystals. Yield 0.54 g (69 %). Decomposition without melting at 300 °C. ^{1}H NMR (500 MHz,C_6D_6, 25 °C, TMS): δ 1.15 (d, ^3J(H, H) 6.8 Hz, 24 H, CH(C*H*$_3$)$_2$), 1.20 (d, ^3J(H, H) 6.8 Hz, 24 H, CH(C*H*$_3$)$_2$), 1.49 (m, 8 H, O(CH$_2$C*H*$_2$)$_2$), 2.10 (s, 12 H,C*H*$_3$), 3.30 (sept, ^3J(H, H) 6.8 Hz, 8 H, C*H*(CH$_3$)$_2$), 3.63 (m, 8 H, O(C*H*$_2$CH$_2$)$_2$), 4.88 (s, 2 H, C*H*), 7.30-7.40 ppm (m, 12 H, *m*-, *p*-, Ar(*H*)); ^{13}C NMR (125.77 MHz, C_6D_6, 25 °C, TMS) δ 21.39 (*C*H$_3$), 23.41 (CH(*C*H$_3$)$_2$), 24,47 (CH(*C*H$_3$)$_2$), 25.16 (O(CH$_2$*C*H$_2$)$_2$)), 28.63 (*C*H(CH$_3$)$_2$), 67.99 (O(*C*H$_2$CH$_2$)$_2$), 94.28 (γ-*C*H), 123.57, 128.02, 137.86, 142.78 (*Ar*), 161.51 ppm (*C*N); ^{7}Li NMR (116.64 MHz, C_6D_6, 25 °C, $LiNO_3$) δ 0.43 ppm. Elemental analysis calcd (%) for $C_{66}H_{98}Al_2Ge_4Li_2N_4O_2S_7$ (1564.24): C 50.75, H 6.32, N 3.59; found : C 50.21, H 6.14, N 3.14.

4.4.17. *Synthesis of LAlB(C$_6$F$_5$)$_3$* (**20**).

Toluene (20 mL) was added to a mixture of LAl (**19**) (0.223 g, 0.5 mmol) and $B(C_6F_5)_3$ (0.256 g, 0.5 mmol) at –78 °C. The mixture was stirred and slowly warmed to room temperature. After an additional stiring for 15 h, the solvent was removed under reduced pressure, and the solution was treated with *n*hexane (30 mL). Filtering and keeping the solution for two weeks at room temperature afforded colorless crystals of **20**. Yield: 0.09 g (19 %), mp 208-209 °C. EI-MS: *m*/*z* (%) 956 (10) [M^+], 403 (100) [L-Me]. ^{1}H NMR (300.13 MHz, C_6D_6): δ 6.8*0*-6.75 (m, 6H, Ar-*H*), 4.91 (s, 1H, γ-*H*), 2.80 (sept, $^3J_{H-H}$ = 6.8Hz, 4H, C*H*Me$_2$), 1.61 (s, 6H, *Me*), 1.15 (d, $^3J_{H-H}$ = 6.8Hz, 12H, CH*Me*$_2$), 0.87 ppm (d, $^3J_{H-H}$ = 6.8Hz, 12H, CH*Me*$_2$). ^{13}C NMR (75.48 MHz, C_6D_6): δ 173.33 (*C*N), 142.75, 139.49, 129.27, 124.76 (*Ar*), 150.25, 147.13, 140.75, 138.63, 137.38, 134.95 (br, C_6F_5), 102.07 (γ-*C*), 24.53, 25.09(CH*Me*$_2$), 22.68 (CH*Me*$_2$), 20.74 ppm (*Me*). ^{11}B NMR (95.29 MHz, C_6D_6): δ -26.52 ppm. ^{19}F NMR (188.28 MHz, C_7D_8) δ –124.28 (m, br), –128.26 (m, br), –129.97 (d), -154.41 (tr), -

156.49 (m, br), -157.27 (tr), -158.86(m, br), -160.24(tr), -160.99 ppm (tr). ^{27}Al NMR (400 MHz, 16 KHz, MAS, $AlCl_3$) δ 0–50 ppm. $C_{47}H_{41}AlBF_{15}N_2$ (956.61) Calcd. C 59.01, H 4.32, N 2.93. Found C 58.66, H 4.67, N 2.70 %.

4.4.18. *Synthesis of LAl(OBPh)$_2$(μ-O)* (**22**).

Toluene (30 mL) was added to a mixture of **19** (0.22 g, 0.5 mmol) and $PhB(OH)_2$ (0.12 g, 1 mmol) at –78 °C. The resulting suspension was slowly warmed to room temperature and stirred for additional 15 h. The concentrated solution was kept at –28 °C for 3 days to afford colorless crystals of **22**. (0.29 g, 87 %). M. p. 338 °C. EI-Ms: *m*/*z* (%) 668.5 (100) [M^+], 653.4 (65) [M^+-Me]. ^{1}H NMR (300.13 MHz,$CDCl_3$, 25 °C, TMS): δ 1.10 (d, ^3J(H, H) 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.36 (d, ^3J(H, H) 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.53 (s, 6 H,C*H*$_3$), 3.49 (sept, ^3J(H, H) 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$), 4.98 (s, 1 H, C*H*), 7.29-6.92 (m, 12 H, Ar(*H*)), 8.29-8.25 ppm (m, 10 H, B-Ar(*H*)); ^{13}C NMR (125.77 MHz, C_6D_6, 25 °C, TMS) δ 23.3 (*C*H$_3$), 24.7 (CH(*C*H$_3$)$_2$), 25,7 (CH(*C*H$_3$)$_2$), 28.5 (*C*H(CH$_3$)$_2$), 98.1 (γ-*C*H), 124.6, 130.5, 135.9, 138.1, 144.4 (*Ar*), 172.4 ppm (*C*N); ^{27}Al NMR: resonance is silent. Elemental analysis calcd (%) for $C_{41}H_{51}AlB_2N_2O_3$ (668.44): C 73.67, H 7.69, N 4.19; found: C 72.70, H 7.84, N 4.32 %. IR (Nujol): $\tilde{\nu}$ = 2966, 1600, 1533, 1389, 1331, 1231, 1177, 1109, 1025, 897, 807, 701, 676, 564, 428 cm^{-1}.

Alternative preparation of LAl[(OBPh)$_2$O] (**22)** Toluene (20 mL) was added to a mixture of $LAlH_2$ **21** (0.44 g, 1 mmol) and $PhB(OH)_2$ (0.24 g, 2 mmol) at 0 °C. The solution was slowly warmed to room temperature, a small amount of a white deposit appeared. The stirring was continued for 12 h, the solution was filtered, kept at –28 °C for 1 day to afford colorless crystals of **22**. (0.55 g, 82 %).

4.4.19. *Synthesis of [1,8-(Me$_3$SiNH)$_2$C$_{10}$H$_6$]AlH(NMe$_3$)* (**25**).

To a toluene solution (40 mL) of [1,8-$(Me_3SiNH)_2C_{10}H_6$]H_2 (3.02 g, 10 mmol) at 0 °C was added dropwise $H_3Al{\cdot}NMe_3$ in toluene (1 M, 10 mL, 10 mmol). The resulting solution was stirred and allowed to warm to room temperature. After additional stirring for 12 h, the solution was dried in vacuum and the residue washed with cold *n*-hexane (5 mL) twice to yield crystalline **25** (3.29 g, 85%). Mp 213 °C. EI-MS: *m/z* (%) 387 (16) [M^+], 328 (100) [M^+-NMe$_3$]. ^{1}H NMR (500.13 MHz, CDCl$_3$, 298 K, ppm): δ 0.30 (s, 18 H, Si-*Me*), 2.66(s, 9 H, N*Me*$_3$), 6.70 (dd, $^3J_{\mathrm{Ha/c,Hb}}$ = 6.8 Hz, $^4J_{\mathrm{Ha,Hc}}$ = 1.8 Hz, 2 H; H^a, C$_{10}$*H*$_6$), 7.25-7.45 (m, 4 H; H^b + H^c, C$_{10}$*H*$_6$). ^{13}C NMR (125.77 MHz, CDCl$_3$, 298 K, ppm): δ 2.91 (Si-*Me*), 47.60 (N*Me*$_3$), 116.19 (*C*H; *C*$_{10}$H$_6$), 118.54 (*C*H; *C*$_{10}$H$_6$), 125.32 (*C*; *C*$_{10}$H$_6$), 137.98 (*C*H; *C*$_{10}$H$_6$), 144.75 (*C*; *C*$_{10}$H$_6$), 150.64 (*C*N; C$_{10}$H$_6$). ^{29}Si NMR (99.36 MHz, CDCl$_3$, 298 K, ppm): δ –0.55. Anal. Calcd for $C_{19}H_{34}AlN_3Si_2$ (*M*r = 387.2): C, 58.87; H, 8.84; N, 10.84. Found C, 57.76; H, 8.62; N, 10.44. IR (KBr, plate): $\tilde{\nu}$ = 1869 cm^{-1} (m, AlH)

4.4.20. *Synthesis of [1,8-(Me$_3$SiNH)$_2$C$_{10}$H$_6$] Al(Me)THF* (**26**).

To a solution (40 mL) of [1,8-(Me$_3$SiNH)$_2$C$_{10}$H$_6$]H$_2$ (3.02 g, 10 mmol) in THF at -30 °C was added dropwised *n*-BuLi (2.5 M, 8 mL, 20 mmol). The mixture was stirred and allowed to warm to room temperature. After additional stirring for 1 h, all volatites were removed and 40 mL of toluene were added to the solid residue. The solution was cooled to -30 °C and MeAlCl$_2$ (1 M, 10 mL, 10 mmol) was added. The resulting solution was allowed to warm to room temperature and stirred for 2 h. After workup, the insoluble LiCl was removed by filtration and the residue was dried in vacuum and washed with cold *n*-hexane (5 mL) twice to yield solid **26** (2.94 g, 71%). %). Mp 154-155 °C. EI-MS: *m/z* (%) 342 (100) [M^+-THF]. ^{1}H NMR (500.13 MHz, CDCl$_3$, 298 K, ppm): δ -0.55(s, 3 H, Al-*Me*), 0.23 (s, 18 H, Si-*Me*), 1.57 (m, 4 H, O(CH$_2$C*H*$_2$)$_2$), 3.79 (m, 4 H, O(C*H*$_2$CH$_2$)$_2$), 6.63 (dd, $^3J_{\mathrm{Ha/c,Hb}}$ = 6.8 Hz, $^4J_{\mathrm{Ha,Hc}}$ = 2.1 Hz, 2 H; H^a, C$_{10}$*H*$_6$), 7.01-7.05 (m, 4 H; H^b + H^c, C$_{10}$*H*$_6$). ^{13}C NMR (125.77 MHz, CDCl$_3$, 298 K, ppm): δ 2.70 (Si-*Me*), 24.93 (O(CH$_2$*C*H$_2$)$_2$)), 69.78 (O(*C*H$_2$CH$_2$)$_2$), 116.68 (*C*H; *C*$_{10}$H$_6$), 118.21 (*C*H; *C*$_{10}$H$_6$), 125.17 (*C*; *C*$_{10}$H$_6$), 137.66 (*C*H; *C*$_{10}$H$_6$), 144.15 (*C*; *C*$_{10}$H$_6$), 151.01 (*C*N;

$C_{10}H_6$). ^{29}Si NMR (99.36 MHz, $CDCl_3$, 298 K, ppm): δ –1.12. Anal. Calcd for $C_{21}H_{35}AlN_2OSi_2$ (*M*r = 414.2): C, 60.83; H, 8.51; N, 6.76. Found C, 58.94; H, 7.99; N, 6.93.

4.4.21. *Synthesis of* $[1,8\text{-}(Me_3SiNH)_2C_{10}H_6]Al(Br)THF$ (**27**).

To a solution (40 mL) of $[1,8\text{-}(Me_3SiNH)_2C_{10}H_6]H_2$ (3.02 g, 10 mmol) in THF at -30 °C was added dropwise *n*-BuLi (2.5 M, 8 mL, 20 mmol). The mixture was stirred and allowed to warm to room temperature. After additional stirring for 1 h, all volatites were removed and 40 mL of toluene were added to the solid residue. The solution was cooled to -30 °C and $AlBr_3$ (2.67 g, 10 mmol) dissolved in toluene (10 mL) was added. The resulting solution was allowed to warm to room temperature and stirred for 2 h. After workup, the insoluble LiBr was removed by filtration and the filtrate was dried in vacuum and washed with cold *n*-hexane (5 mL) twice to yield solid **27** (3.69 g, 77%). Mp 154-155 °C. EI-MS: *m*/*z* (%) 408 (100) [M^+-THF]. ^{1}H NMR (500.13 MHz, $CDCl_3$, 298 K, ppm): δ 0.48 (s, 18 H, Si-*Me*), 0.55 (m, 4 H, $O(CH_2CH_2)_2$), 3.38 (m, 4 H, $O(CH_2CH_2)_2$), 6.89 (dd, $^3J_{Ha/c,Hb}$ = 7.5 Hz, $^4J_{Ha,Hc}$ = 1.2 Hz, 2 H; H^a, $C_{10}H_6$), 7.24-7.26 (m, 4 H; H^b + H^c, $C_{10}H_6$). ^{13}C NMR (125.77 MHz, $CDCl_3$, 298 K, ppm): δ 3.14 (Si-*Me*), 24.03 ($O(CH_2CH_2)_2$)), 70.79 ($O(CH_2CH_2)_2$), 118.14 (*C*H; $C_{10}H_6$), 120.02 (*C*H; $C_{10}H_6$), 125.33 (*C*; $C_{10}H_6$), 125.94 (*C*H; $C_{10}H_6$), 138.00 (*C*; $C_{10}H_6$), 149.99 (*C*N; $C_{10}H_6$). ^{29}Si NMR (99.36 MHz, $CDCl_3$, 298 K, ppm): δ 1.26.

5. Handling and Disposal of Solvents and Residual Waste

1. The recovered solvents were distilled or condensed into cold-traps under vacuum, collected in halogen-free or halogen-containing solvent containers, and stored for disposal.
2. Used NMR solvents were classified into halogen-free or halogen-containing solvents and were disposed as heavy metal-containing wastes and halogen-containing wastes, respectively.
3. The heavy metal residues were dissolved in nitric acid and after neutralization stored in the container for heavy metal wastes.
4. Drying agents such as KOH, $CaCl_2$, $MgCl_2$, $MgSO_4$, and P_4O_{10} were hydrolyzed and disposed as acid or base wastes.
5. Wherever possible, sodium metal used for drying solvents was collected for recycling. The non-reusable sodium metal was carefully treated with cold ethanol and potassium in cold isopropanol and collected into the base-bath cleaning glassware.
6. Ethanol and acetone used for cooling baths were subsequently used for cleaning glassware.
7. The acid bath for cleaning glassware was neutralized with Na_2CO_3 and the resulting NaCl solution was washed off in the water drainage system.
8. The residual of the base both for cleaning glassware was poured into the container for base wastes.

Amount of various types of disposable wastes generated during the work.

Metal containing wastes	8 L
Halogen-containing wastes	7 L
Halogen-free solvent wastes	50 L
Acid wastes	20 L
Base wastes	18 L

6. Crystal Data and Refinement Details

Table CD1. Crystal Data and Structure Refinement Details for 3.

Identification code	albr2
Empirical formula	$C_{17}H_7AlBr_2F_{10}N_2$
Formula weight	616.05
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.2157(8) Å, $\alpha = \gamma = 90^\circ$.
	b = 14.7816(14) Å, β =103.956(5)°.
	c = 12.8121(9) Å.
Volume	2061.4(3) Å^3
Z	4
Calculated density	1.985 Mg/m^3
Absorption coefficient	4.072 mm^{-1}
$F(000)$	1184
θ range of collection	1.87 to 24.74 deg
Index range	$-12 \leq h \leq 11$, $-17 \leq k \leq 17$, $-15 \leq l \leq 14$
Reflections collected	12231
R (int)	0.0403
Refinement method	Full-matrix least-squares on F^2
Data/ restraints/ parameters	3339/0/291
Goodness-of-fit on F^2	1.030
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0248$, $wR2 = 0.0401$
R indices (all data)	$R1 = 0.0469$, $wR2 = 0.0444$
Largest difference peak and hole	0.240 and –0.307 e·Å^{-3}

Table CD2. Crystal data and structure refinement for 4.

Identification code	test-fgecl
Empirical formula	$C_{17}H_7ClF_{10}GeN_2$
Formula weight	537.29
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 11.0621(6) Å, α = 112.778(4)°.
	b = 12.0853(7) Å, β = 93.632(4)°.
	c = 15.4740(8) Å, γ = 96.160(5)°.
Volume	1883.90(18) $Å^3$
Z	4
Calculated density	1.894 Mg/m^3
Absorption coefficient	1.871 mm^{-1}
$F(000)$	1048
θ range for data collection	1.84 to 24.77 deg.
Index ranges	$-13 <= h <= 13$, $-14 <= k <= 14$, $-18 <= l <= 17$
Reflections collected	28409
R(int)	0.0479
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6408 / 0 / 553
Goodness-of-fit on F^2	1.025
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0260$, $wR2 = 0.0627$
R indices (all data)	$R1 = 0.0308$, $wR2 = 0.0646$
Largest difference peak and hole	0.893 and -0.906 $e \cdot A^{-3}$

Table CD3. Crystal data and structure refinement for 5.

Identification code	fgacl2
Empirical formula	$C_{17}H_7C_{l2}F_{10}GaN_2$
Formula weight	569.87
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.195(2) Å, $\alpha = \gamma$ = 90°. b = 14.386(3) Å, β = 102.75(3)° c = 12.663(3) Å,
Volume	1989.1(7) $Å^3$
Z	4
Calculated density	1.903 Mg/m^3
Absorption coefficient	1.752 mm^{-1}
F(000)	1112
θ range for data collection	1.87 to 24.87°
Index ranges	$-13 \leq h \leq 13, -16 \leq k \leq 17, -14 \leq l \leq 14$
Reflections collected	31949
R (int)	0.0826
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3435 / 0 / 286
Goodness-of-fit on F^2	0.968
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0596, $wR2$ = 0.1515
R indices (all data)	$R1$ = 0.0696, $wR2$ = 0.1599
Largest diffifference peak and hole	3.193 and -0.800 $e \cdot Å^{-3}$

Table CD4. Crystal data and structure refinement for 6.

Identification code	r1189x
Empirical formula	$C_{19}H_{13}AlF_{10}N_2$
Formula weight	486.29
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 9.4204(5) Å, $\alpha = \gamma = 90^{o}$.
	b = 24.4924(10) Å, $\beta = 95.304(4)°$.
	c = 8.5734(5) Å.
Volume	1969.66(17) Å^3
Z	4
Calculated density	1.640 Mg/m^3
Absorption coefficient	0.205 mm^{-1}
$F(000)$	976
θ range for data collection	1.66 to 24.84 deg.
Index ranges	$-11 \leq h \leq 11$, $-28 \leq k \leq 28$, $-10 \leq l \leq 10$
Reflections collected	37437
R (int)	0.0597
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3387 / 0 / 293
Goodness-of-fit on F^2	1.021
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0353$, $wR2 = 0.0914$
R indices (all data)	$R1 = 0.0442$, $wR2 = 0.0945$
Largest difference peak and hole	0.158 and –0.267 e·Å^3

Table CD5. Crystal data and structure refinement for 8· $0.5C_7H_8$.

Identification code	Y0804
Empirical formula	$C_{39.50}H_{24}Al_2F_{20}N_4O$
Formula weight	1004.59
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 13.1892(6) Å, $\alpha = \gamma$ =90°.
	b = 17.0111(9) Å, β = 102.906(4) °.
	c = 18.4350(9) Å,
Volume	4031.6(3) Å^3
Z	4
Calculated density	1.655 Mg/m^3
Absorption coefficient	0.205 mm^{-1}
F(000)	2012
θ for data collection	1.65 to 24.86 deg.
Index ranges	$-15 \le h \le 15$, $-20 \le k \le 20$, $-21 \le l \le 21$
Reflections collected	26861
R(int)	0.0506
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6804 / 0 / 602
Goodness-of-fit on F^2	1.017
Final R indices [$I > 2\sigma$(I)]	$R1$ = 0.0371, $wR2$ = 0.0785
R indices (all data)	$R1$ = 0.0590, $wR2$ = 0.0850
Largest difference peak and hole	0.205 and –0.292 e·A^{-3}

Table CD6. Crystal data and structure refinement for 10· C_7H_8.

Identification code	r1190
Empirical formula	$C_{48}H_{59}AlN_2S_2Sn$
Formula weight	873.76
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 9.5426(3)$ Å, $\alpha = \gamma = 90^\circ$.
	$b = 23.3976(10)$ Å, $\beta = 95.740(2)^\circ$.
	$c = 20.4094(6)$ Å
Volume	4534.0(3) $Å^3$
Z	4
Calculated density	1.280 Mg/m^3
Absorption coefficient	0.709 mm^{-1}
$F(000)$	1824
θ range for data collection	1.74 to 24.84 deg.
Index ranges	$-11 \le h \le 9, -27 \le k \le 27, -24 \le l \le 24$
Reflections collected	64304
R (int)	0.0546
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7812 / 0 / 486
Goodness-of-fit on F^2	0.988
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0312$, $wR2 = 0.0760$
R indices (all data)	$R1 = 0.0443$, $wR2 = 0.0795$
Largest difference peak and hole	0.881 and -0.993 $e{\cdot}A^{-3}$

Table CD7. Crystal data and structure refinement for 11· $0.5C_6H_{14}$.

Identification code	algeme
Empirical formula	$C_{34}H_{54}AlGeN_2S_2$
Formula weight	654.48
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic,
Space group	*C*2/*c*
Unit cell dimensions	a = 24.4937(19) Å, $\alpha = \gamma = 90^\circ$
	b = 19.6182(17) Å, β = 122.057(5) $^\circ$
	c = 17.7381(13) Å,
Volume	7223.9(10) Å^3
Z	8
Calculated density	1.204 Mg/m^3
Absorption coefficient	1.012 mm^{-1}
F(000)	2792
θ range for data collection	1.43 to 24.84 deg.
Index ranges	$-28 \leq h \leq 28$, $-20 \leq k \leq 23$, $-19 \leq l \leq 19$.
Reflections collected	13719
R (int)	0.0572
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5880 / 1 / 372
Goodness-of-fit on F^2	0.887
Final *R* indices [$I > 2\sigma(I)$]	$R1$ = 0.0458, $wR2$ = 0.1064
R indices (all data)	$R1$ = 0.0809, $wR2$ = 0.1201
Largest difference peak and hole	1.075 and –0.608 e·A^{-3}

Table CD8. Crystal data and structure refinement for 12· C_7H_8.

Identification code	yang1
Empirical formula	$C_{19}H_{27.50}Al_{0.50}NSSn_{0.50}$
Formula weight	374.82
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 8.8077(18) Å, α = 79.57(3)°. b = 13.280(3) Å, β = 75.42(3)°. c = 17.283(4) Å, γ = 87.69(3)°.
Volume	1924.1(7) Å^3
Z	4
Calculated density	1.294 Mg/m^3
Absorption coefficient	0.823 mm^{-1}
F(000)	784
θ range for data collection	1.56 to 24.84°.
Index ranges	$-10 \le h \le 10, -15 \le k \le 15, -20 \le l \le 20$
Reflections collected	34091
R (int)	0.0576
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6640 / 0 / 410
Goodness-of-fit on F^2	1.017
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0274$, $wR2 = 0.0677$
R indices (all data)	$R1 = 0.0352$, $wR2 = 0.0700$
Largest difference peak and hole	0.350 and –0.447 e·Å^{-3}

Table CD9. Crystal data and structure refinement for 14·1.5C_7H_8·C_4H_8O

Identification code	r1193
Empirical formula	$C_{72.50}H_{102}Al_2N_4OS_4Sn$
Formula weight	1346.47
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 12.3419(3) Å, $\alpha = \gamma$ = 90°.
	b = 18.6037(7) Å, β = 92.437(2)°.
	c = 30.7624(9) Å,
Volume	7056.8(4) Å^3
Z	4
Calculated density	1.267 Mg/m^3
Absorption coefficient	0.550 mm^{-1}
F(000)	2852
θ range for data collection	1.65 to 24.83°.
Index ranges	$-14 \leq h \leq 14$, $-21 \leq k \leq 21$, $-36 \leq l \leq 36$
Reflections collected	12130
R (int)	0.0838
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12130 / 1279 / 767
Goodness-of-fit on F^2	1.014
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0780$, $wR2 = 0.2297$
R indices (all data)	$R1 = 0.1115$, $wR2 = 0.2509$
Largest difference peak and hole	3.670 and –1.756 e·Å^{-3}

Table CD10. Crystal data and structure refinement for 17

Identification code	segeme2
Empirical formula	$C_{31}H_{47}AlGeN_2Se_2$
Formula weight	705.20
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic,
Space group	$P2_1/c$
Unit cell dimensions	a = 11.9939(10) Å, $\alpha = \gamma = 90^\circ$
	b = 17.4552(9) Å, $\beta = 90.686(6)^\circ$
	c = 16.0281(13) Å,
Volume	3355.3(4) $Å^3$
Z	4
Calculated density	1.396 Mg/m^3
Absorption coefficient	3.130 mm^{-1}
$F(000)$	1440
θ range for data collection	1.72 to 24.83 deg.
Index ranges	$-14 \le h \le 14, -20 \le k \le 18, -18 \le l \le 18.$
Reflections collected	17451
R (int)	0.0553
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5748 / 0 / 334
Goodness-of-fit on F^2	0.963
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0301$, $wR2 = 0.0630$
R indices (all data)	$R1 = 0.0463$, $wR2 = 0.0677$
Largest difference peak and hole	0.459 and –0.437 $e \cdot A^{-3}$

Table CD11. Crystal data and structure refinement for 18· C_7H_8

Identification code	r1197
Empirical formula	$C_{73}H_{106}Al_2Ge_4Li_2N_4O_2S_7$
Formula weight	1654.24
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 17.5307(14) Å, $\alpha = \gamma$ = 90°.
	b = 21.8268(11) Å, β = 100.785(6)°.
	c = 21.3419(14) Å,
Volume	8022.0(9) Å^3
Z	4
Calculated density	1.370 Mg/m^3
Absorption coefficient	1.733 mm^{-1}
F(000)	3440
θ range for data collection	1.67 to 24.66°.
Index ranges	$-18 \le h \le 20$, $-25 \le k \le 25$, $-24 \le l \le 25$
Reflections collected	65056
R (int)	0.2212
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13470 / 1377 / 868
Goodness-of-fit on F^2	0.774
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0599, $wR2$ = 0.0654
R indices (all data)	$R1$ = 0.1970, $wR2$ = 0.0894
Largest difference peak and hole	1.122 and –0.387 e·Å^{-3}

Table CD12. Crystal data and structure refinement for 20

Identification code	r1194
Empirical formula	$C_{47}H_{41}AlBF_{15}N_2$
Formula weight	956.61
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 11.6897(12) Å, α = 74.641(8)°.
	b = 12.6534(13) Å, β = 73.606(8)°.
	c = 16.0785(17) Å, γ = 76.347(8)°.
Volume	2166.4(4) Å^3
Z	2
Calculated density	1.466 Mg/m^3
Absorption coefficient	0.149 mm^{-1}
F(000)	980
θ range for data collection	1.69 to 24.66°.
Index ranges	$–13 \leq h \leq 13$, $-13 \leq k \leq 14$, $-18 \leq l \leq 18$
Reflections collected	21853
R (int)	0.1432
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7306 / 0 / 605
Goodness-of-fit on F^2	0.789
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0557$, $wR2 = 0.0750$
R indices (all data)	$R1 = 0.1524$, $wR2 = 0.0962$
Largest difference peak and hole	0.297 and –0.305 e·Å^{-3}

Table CD13. Crystal data and structure refinement for 22

Identification code	r1198
Empirical formula	$C_{41}H_{51}AlB_2N_2O_3$
Formula weight	668.44
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 11.436(2) Å, α = 74.936(13)°. b = 12.091(2) Å, β = 76.052(13)°. c = 15.359(3) Å, γ = 74.564(13)°.
Volume	1942.8(6) $Å^3$
Z	2
Calculated density	1.143 Mg/m^3
Absorption coefficient	0.091 mm^{-1}
$F(000)$	716
θ range for data collection	1.79 to 24.81°.
Index ranges	$-13 \le h \le 13$, $-14 \le k \le 14$, $-18 \le l \le 18$
Reflections collected	20290
R (int)	0.3176
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6644 / 0 / 452
Goodness-of-fit on F^2	0.815
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0912, $wR2$ = 0.1113
R indices (all data)	$R1$ = 0.2753, $wR2$ = 0.1646
Largest difference peak and hole	0.234 and –0.252 $e\cdot Å^{-3}$

Table CD14. Crystal data and structure refinement for 25

Identification code	tt
Empirical formula	$C_{19}H_{33}AlN_3Si_2$
Formula weight	386.64
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Ama*2
Unit cell dimensions	a = 18.5497(19) Å, α = 90°.
	b = 12.2030(7) Å, β = 90°.
	c = 10.1856(7) Å, γ = 90°.
Volume	2305.6(3) $Å^3$
Z	4
Calculated density	1.114 Mg/m^3
Absorption coefficient	0.199 mm^{-1}
F(000)	836
θ range for data collection	2.20 to 24.80°.
Index ranges	$-21 \le h \le 21$, $-14 \le k \le 14$, $-12 \le l \le 12$
Reflections collected	16394
R (int)	0.0837
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2015 / 1 / 127
Goodness-of-fit on F^2	0.890
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0327$, $wR2 = 0.0623$
R indices (all data)	$R1 = 0.0471$, $wR2 = 0.0654$
Largest difference peak and hole	0.182 and –0.204 $e \cdot Å^{-3}$

Table CD15. Crystal data and structure refinement for 26

Identification code	roetu
Empirical formula	$C_{21}H_{35}AlN_2OSi_2$
Formula weight	414.67
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 7.2999(8) Å, $\alpha = \gamma$ =90°.
	b = 16.7801(18) Å, β = 94.074(4)°.
	c = 19.187(2) Å,
Volume	2344.3(4) $Å^3$
Z	4
Calculated density	1.175 Mg/m^3
Absorption coefficient	0.202 mm^{-1}
$F(000)$	896
θ range for data collection	1.61 to 30.50°.
Index ranges	$-10 \leq h \leq 10$, $-23 \leq k \leq 23$, $-27 \leq l \leq 27$
Reflections collected	49652
R (int)	0.0424
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7143 / 0 / 251
Goodness-of-fit on F^2	1.037
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0392$, $wR2 = 0.0939$
R indices (all data)	$R1 = 0.0646$, $wR2 = 0.1087$
Largest difference peak and hole	0.456 and –0.299 $e \cdot Å^{-3}$

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List of Publications

1. Janus–faced Aluminum: A Demonstration of an Unique Lewis-Acid and Lewis-Base Behavior of the Aluminum Atom in $\mathrm{LAlB(C_6F_5)_3}$
   Zhi Yang, *Xiaoli Ma, Rainer B. Oswald, Herbert W. Roesky, Hongping Zhu, Carola Schulzke, Kerstin Starke, Marc Baldus, Hans-Georg Schmidt, and Mathias Noltemeyer*
   Angew. Chem. Int. Ed. **2005**, *44*, 7072-7074

2. An Unprecedented Example of A Heterotrimetallic Main Group $\mathrm{L_2Al_2Ge_4Li_2S_7}$ Cluster Containing A Ge(II)–Ge(II) Donor-Acceptor Bond
   Zhi Yang, *Xiaoli Ma, Rainer B. Oswald, Herbert W. Roesky, Chunming Cui, Hans-Georg Schmidt, and Mathias Noltemeyer*
   Angew. Chem. Int. Ed. **2006**, *45*, 2277-2280

3. Synthesis of An Aluminum Spirocyclic Hybrid with An Inorganic $\mathrm{B_2O_3}$ and An Organic $\mathrm{C_3N_2}$ Core
   Zhi Yang, *XiaoliMa, Rainer B. Oswald, Herbert W. Roesky, and Mathias Noltemeyer*
   J. Am. Chem. Soc. **2006**, *128*, 12406-12407

4. Synthesis, Characterization, and Hydrolysis of Aluminum(III) Compounds Bearing the $\mathrm{C_6F_5}$-Substituted β-Diketiminate $\mathrm{HC[(CMe)(NC_6F_5)]_2}$ (L) Ligand
   Zhi Yang, *Hongping Zhu, Xiaoli Ma, Jianfang Chai, Herbert W. Roesky, Cheng He, Hans-Georg Schmidt, and Mathias Noltemeyer*
   Inorg. Chem. **2006**, *45*, 1823-1827

5. Synthesis and Characterization of Aluminum-Containing Tin(IV) Heterobimetallic Sulfides
   Zhi Yang*, Xiaoli Ma, Vojtech Jancik, Zhensheng Zhang, Herbert W. Roesky, Jörg Magull, Mathias Noltemeyer, Hans-Georg Schmidt, Raymundo Cea-Olivares, and Rubén. A. Toscano*
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6. Syntheses and Structural Characterization of a $\mathrm{LAl(N_3)N[\mu\text{-}Si(N_3)(\mathit{t}Bu)]_2NAl(N_3)L}$ and a Monomeric Aluminum Hydride Amide LAlH(NHAr) ($\mathrm{L = HC[(CMe)(NAr)]_2}$, Ar = 2,6-$\mathrm{\mathit{i}Pr_2C_6H_3}$)

Hongping Zhu, ***Zhi Yang****, Jörg Magull, Herbert W. Roesky, Hans-Georg Schmidt, and Mathias Noltemeyer*
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7. An unprecedented example of polyoxotungstates: Synthesis and characterization of an octatungstate complex $[W_8O_{19}L_3(acac)_4]$ $(L={}^{-}O(CH_2)_3S(CH_2)_3O^{-})$
   Xiaoli Ma, ***Zhi Yang****, Carola Schulzke, Hans-Georg Schmidt, Mathias Noltemeyer*
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8. Aluminacyclopropene: Syntheses, Characterization, and Reactivity toward Terminal Alkynes
   Hongping Zhu, Rainer B. Oswald, Hongjun Fan, Herbert W. Roesky, Qingjun Ma, ***Zhi Yang****, Hans-Georg Schmidt, Mathias Noltemeyer, Kerstin Starke, and Narayan S. Hosmane*
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9. Synthesis and Structure of Allyl and Alkynyl Complexes of Manganese(II) Supported by a Bulky *β*-Diketiminate Ligand
   Jianfang Chai, Hongping Zhu, Herbert W. Roesky, ***Zhi Yang****, Vojtech Jancik,*
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