Aluminum (I, II, III) Compounds with Multidentate Ligands: Syntheses, Reactivity, and Structures

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Chunming Cui

aus Shaanxi (CHINA)

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

Korreferent: Prof. Dr. U. Klingebiel

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Abbreviations

Ar	aryl, aromatic group
av	average
Bp	boiling point
bipy	2,2′–bipyridine
i-Bu	*iso*-butyl
t-Bu	*tert*-butyl (tertiary butyl)
Calcd	calculated
Cp^*	pentamethylcyclopentadienyl
d	day(s)
d	density
D	donor
dec	decompose
deg	degree
Dipp	2,6-i-$Pr_2C_6H_3$
DME	dimethoxyethane
η	hapto
EI	electron impact ionization
Et	ethyl
IR	infrared
J	coupling constant
K	Kelvin
L, L′	β-diketiminato groups (ligands)
NMR	nuclear magnetic resonance
m/e	mass/charge

Me	methyl
Mes	2,4,6-trimethylphenyl (mesityl)
Mes*	2,4,6-tri(*tert*-butyl)phenyl
min	minute(s)
Mp	melting point
MS	mass spectrum
Ph	phenyl
ppm	parts per million
i-Pr	*iso*-propyl
R, R', R^1, R^2	organic groups
tbp	trigonal bipyramidal
THF	tetrahydrofuran
TMEDA	N, N, N`, N`–tetramethylethylenediamine
TMS	tetramethylsilane
Trip	2,4,6-tris-*iso*-propylphenyl
μ	bridging
V	volume
$\tilde{\nu}$	wave number
$\nu_{1/2}$	width of half peak
Z	number of molecules in the unit cell

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1 Introduction

Aluminum is the most abundant metal in the lithosphere. As an extremely reactive metal it is easily oxidized so that it is only found in its oxidized form in nature. The most important minerals are the aluminosilicates which form the matrix upon which plant life grows and terrestrial animals roam. By contrast, the soluble aluminum cation is now recognized to be the cause of severe damage to plants and animals.[1a]

Already in 1859 ethylaluminum sesquiiodide (a 1:1 mixture of $EtAlI_2$ and Et_2AlI) was obtained from ethyl iodide and aluminum.[2] Not until the studies of Ziegler et al. in the early 1950′s was the potential of the organoaluminum reagents for organic synthesis and polymerization recognized.[1b] Systematic studies of both the coordination and organometallic chemistry of aluminum have expanded rapidly over the last three decades.[1c] The stereoselective catalytic behavior of many aluminum compounds has proved to be of considerable commercial value for stereospecific industrial syntheses of organic compounds. In some ways, such properties are also related to the stereochemical specificity of biological systems.[1a]

Main features of interest in aluminum chemistry include the dependence of Lewis acidities on both R and X ligands of compounds R_3Al, R_2AlX and $RAlX_2$, affecting the behavior of these species towards potential ligands, and selectivity of donor sites in cases of multidentate ligands. One of the most unusual properties of simple aluminum alkyls and halides is their tendency to associate through alkyl or halide moieties due to the electron deficiency of the aluminum atom. The bonding situations in these simple systems have been well documented as models for nonclassical three-center or even four-center electron pair bonds.[1b]

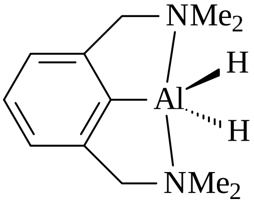
Neutral aluminum complexes, such as alklys or halides, are widely used as reagents or catalysts for Lewis acid-mediated reactions (Friedel-Crafts, Diels-Alder, etc.), alkylating agents, initiators for cationic polymerizations, and cocatalysts/activators in transition metal catalyzed olefin polymerizations.[1b] Additionally, aluminum alkyls catalyze the oligomerization of ethylene to α-olefins at elevated temperatures and ethylene pressures.[3] In recent years, modifications of aluminum systems for these applications have attained much attention. Especially the studies of cationic aluminum species have led to an extensive research on their applications in organic and catalytic transformations since they possess enhanced Lewis acidity due to the positive charge on the aluminum center.[4] They may also be rendered coordinatively unsaturated by the use of labile ligands. One of the important results is the fact that low-coordinated cationic aluminum alkyls could act as the catalysts for olefin polymerization to generate high molecular weight polyolefins although the activity of the known systems is relatively low.[5] Methylaluminoxane (MAO) has proved to be the most efficient activator for homogeneous metallocene catalyzed olefin polymerization reactions.[6] Another important approach is the modification of the steric factors of coordinatively unsaturated aluminum compounds to improve the stereo- and regioselectivity of aluminum complexes to promote organic reactions, for example reduction of cycloketones or prochiral carbonyls.[7] In all these cases, design and choice of the ligands are important for these purposes. In the following part, some of the work which is related to the contents of the present thesis will be discussed in detail.

1.1 Aluminum hydrides

Simple aluminum hydrides usually have oligomeric structures in condensed phases. However, it has been shown recently that low-aggregated aluminum hydrides are accessible by using either multidentate or bulky organic groups. Examples of monomeric aluminum dihydrides stabilized by intramolecular coordination include 2,6-$(Me_2NCH_2)_2C_6H_3AlH_2$[8]and $[(i\mathrm{Pr})_2\mathrm{ATI}]\mathrm{AlH}_2$ (ATI = 2-aminotroponiminate).[9] Only one example of an aluminum hydride with a three-coordinated aluminum atom $(\mathrm{Mes}^*)_2\mathrm{AlH}$ (Mes^* = 2,4,6-t-$Bu_3C_6H_2$) is known.[10]

The other known hydrides which are stabilized by bulky, donor-free ligands are dimers or higher aggregates in the solid state.

Scheme 1



The synthetic routes for neutral aluminum hydrides are various depending on the starting materials or ligands employed. However, they can be rationalised as follows.

(1) Reduction of aluminum halides with $LiAlH_4$

$$RAlX_2 + 2\,LiAlH_4 \rightarrow RAlH_2 + 2\,LiAlH_3X$$

(2) $AlH_3{\cdot}NMe_3$ as aluminum hydride source.

$$[R]EH + AlH_3{\cdot}NMe_3 \rightarrow [R]EAlH_2 + H_2 + NMe_3$$

E = O, N; [R] = organic group or groups directly bonded to E

(3) Lithium hydridoaluminates as aluminum hydride sources

$$RAlH_3Li(D)_x + SiMe_3Cl \rightarrow RAlH_2 + SiMe_3H + LiCl + x\,D$$

The first route is generally applicable for the synthesis of aluminum hydrides where the appropriate aluminum halides are easily available. The second can be used when the substrates contain acidic hydrogen atoms. The last one may be employed when the aluminum halides are not easily accessible. Other routes involve alkene elimination from triorganoaluminum compounds, redistribution of triorganoaluminum compounds and aluminum hydrides, and hydrogenolysis of triorganoaluminum compounds.[8]

Aluminum hydride moieties have been detected on surfaces during thin film growth from organoaluminum sources.[8] They are also well-known reducing agents for unsaturated molecules such as ketones, nitriles, alkenes, and alkynes.[1b] In addition, some the aluminum hydrides can be used as starting materials for the preparation of new classes of aluminum compounds by condensation of small molecules. For example, the reaction of the sterically crowded dimeric arylalane $(Mes^*AlH_2)_2$ with some aryl amines, phosphanes, or arsanes afforded interesting Al-N (P, As) ring systems by elimination of H_2.[11] $(Mes^*AlH_2)_2$ also reacts with $[O(SiMe_2)]_3$ and $S(SiMe_3)_2$ to generate Al-O or Al-S ring compounds by elimination of $SiMe_2H_2$ or $SiMe_3H$ respectively.[12]

$$3(Mes^*AlH_2)_2 + 2(Me_2SiO)_3 \longrightarrow 2(Mes^*AlO)_3 + 3Me_2SiH_2$$

1.2 Aluminum chalcogenides

Group 13 - 16 binary systems are of interest for the preparation of Group 13 - 16 materials and catalysis.[13] Synthetic and structural studies of these compounds are of fundamental interest as they exhibit a variety of structural types depending on the metal, the chalcogen, and the substituents on both. Chalcogens (S, Se, Te) can insert into Al-C bonds of aluminum trialkyls or triaryls very easily; however, the products are of polymeric nature with small alkyl groups. In case of bulky trialkyl or triaryl aluminum compounds, low aggregated products have been isolated. With very bulky alkyl groups (*t*-Bu, $EtMe_2C$, $(SiMe_3)_3C$) the insertion of chalcogens (Se, Te) occurs only into one Al-C bond to afford compounds R^1R^2AlER which have been isolated. Under thermal conditions these compounds eliminate small molecules to give $(RAlE)_4$ compounds with a cubic core structure.[14c] An alternative 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).[15] However, the two routes mentioned above have limitations for the application for the synthesis of group 13 - 16 compounds with the formula of $(RAlE)_n$.

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

1.3 Low valent aluminum compounds

The aluminum chemistry is dominated by the prevailing oxidation state Al(III), low valent Al (I, II) compounds are less documented. Only in 1988, the first well characterized divalent organoaluminum compound $\{[(SiMe_3)_2CH]Al\}_2$ was reported.[16]

$$2\,[(SiMe_3)_2CH]_2AlCl \quad + \quad 2\,K \;\rightarrow\; \{[(SiMe_3)_2CH]_2Al\}_2 \quad + \quad 2\,KCl$$

The first stable organometallic Al(I) compound $(Cp^*Al)_4$ was reported by Schnöckel in 1991, which was prepared by the reaction of the meta-stable high temperature species AlCl with Cp^*MgCl.[17] The more convenient route developed by our group involved the reduction of Cp^*AlCl_2 by potassium in refluxing toluene.[15]

$$4\,Cp^*AlCl_2 \quad + \quad 8\,K \;\rightarrow\; (Cp^*Al)_4 \quad + \quad 8\,KCl$$

The synthesis of this unique species has stimulated much interest in exploring Al(I) chemistry in the following years. It has been shown that Al(I) species can be used as Lewis bases and reducing reagents. In recent years, other stable tetrahedral Al(I) compounds were reported, prepared either by reduction of the corresponding dihalides or by reaction of AlX species with appropriate ligand transfer reagents.[18] Obviously, reduction of aluminum dihalides is the more facile way to prepare low valent aluminum compounds. Since Al(I) species are kinetically unstable, very bulky ligands are necessary to stabilize these unusual compounds.

For several known homogeneous Al(II) compounds Al-Al bond lengths range from 2.6 - 2.7 Å.[19] A radical anion $[TripAl\text{-}AlTrip]^{\cdot-}$ (Trip = 2,4,6-i-$Pr_3C_6H_2$) which has the shortest Al-Al bond distance (2.46 Å) reported to date was suggested to have an Al-Al bond order of 1.5.[20] The structurally characterized neutral Al(I) compounds all are tetramers in the solid state, the Al-Al bond lengths in these compounds differ largely depending on the ligands, for example in $(Cp^*Al)_4$ the average Al-Al bond length is 2.78 Å,[17] and in $(t\text{-}Bu_3SiAl)_4$, 2.58

Å.[18a] In the gas phase or in solution at higher temperatures, $(Cp^*Al)_4$ dissociates to monomeric Cp^*Al[21] which can act as a donor ligand possessing a lone pair of electrons.[22]

$$(Cp^*Al)_4 + 4\ B(C_6F_5)_3 \rightarrow 4\ Cp^*AlB(C_6F_5)_3$$

$$Cp^*AlCl_2 + K_2[Fe(CO)_4] \xrightarrow{-2\ KCl} Cp^*AlFe(CO)_4$$

In addition, $(Cp^*Al)_4$ has been used as an insertion reagent to prepare interesting aluminum compounds.[23]

$$(Cp^*Al)_4 + 4\ N_3Si(t\text{-}Bu)_3 \rightarrow 2\ [Cp^*AlNSi(t\text{-}Bu)_3]_2 + 4\ N_2$$

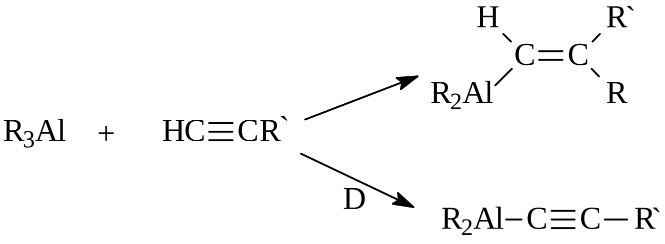
Despite of the interesting perspectives of monovalent aluminum compounds, well-characterized monomeric and dimeric Al(I) species stable at room temperature have not yet been described in the literature. In this connection, one can realize that the ligand design combined with the corresponding synthetic methodology for these unique species is an exciting challenge.

1.4 Hydroalumination and carbalumination of unsaturated compounds

The reactions of aluminum alkyls or hydrides with alkenes and alkynes can generate different products depending on the nature of the aluminum precursors and the unsaturated molecules. Using donor-free aluminum alkyls or hydrides in hydrocarbon solvents normally addition to alkenes or alkynes takes place. This is due to possible complexation of the aluminum species to the unsaturated units. However the addition reaction is retarded by donors such as ethers and amines, in addition, in the case of unsubstituted acetylene metallation is dominant.[24]

Vinylaluminum compounds resulting from the hydroalumination of alkynes are capable of undergoing further insertion into alkynes, in which the vinyl-aluminum bond undergoes preferential reaction. Usually the reaction ceases after the cyclotrimerization of the alkyne to yield a benzene derivative.[25]

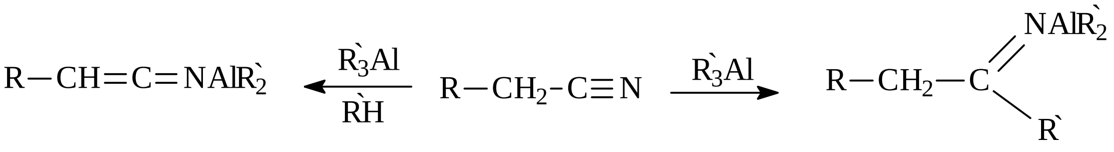
Scheme 2



R, R′ = alkyl or aryl group

Aluminum alkyls or hydrides can react with carbonyl derivatives to give aluminum alkoxides.[26] Often alkylation and reduction of the carbonyl group occur. The carbalumination is generally achieved cleanly only when the aluminum reagent cannot eliminate R_2AlH, as with Me_3Al, Ph_3Al, $(PhCH_2)_3Al$, and when the carbonyl substrate has no α-hydrogen atoms. Usually only one Al-C bond of R_3Al will insert into the C=O bond. The use of β-branched aluminum alkyls like *i*-Bu_3Al, with ketones or hindered carbonyls especially at high temperature with nickel promotors generally favors hydroalumination. The solubility of R_3Al or R_2AlH in hydrocarbons makes such reducing agents valuable alternatives to $LiAlH_4$ for converting ketones to secondary alcohols.[27]

Scheme 3



A **B**

R, R′ = alkyl or aryl group

Aluminum alkyls or hydrides also react with nitriles to lead either to carbalumination products or substitution of their α-hydrogen atoms as a side reaction.[28] With some nitriles carbalumination leads to satisfactory yields of ketones by the hydrolysis of intermediates (**B**). This addition is significantly promoted by the presence of nickel salts. Hydroalumination predominates with *i*-Bu_2AlH, where stepwise reduction followed by hydrolysis can lead to aldehydes or amines through intermediate **A**.

1.5 Aims and objectives of this dissertation

Based on the above introduction, it can be summarized that by carefully selecting or designing ligands it is possible to synthesize low aggregated, low-valent aluminum species or aluminum group 16 (or 15) multiple bonded species and low-coordinated cationic aluminum alkyls. In addition, low-aggregated aluminum fluorides or hydrides can also be obtained by the same strategy. The aims of this thesis are the following by designing the appropriate ligand systems:

(1) Examination of the reactivities of intramolecular stabilized aluminum hydrides, especially towards chalcogens, and investigation of the reaction mechanism.

(2) Synthesis of low-valent aluminum (I, II) compounds by alkali metal reduction.

(3) Reactions of low valent aluminum compounds.

(4) Reductive coupling reactions of aluminum halides in the presence of unsaturated molecules for the synthesis of strained aluminum containing cyclic systems.

(5) Applications of aluminum compounds in C-C bond formation.

2 Results and Discussion

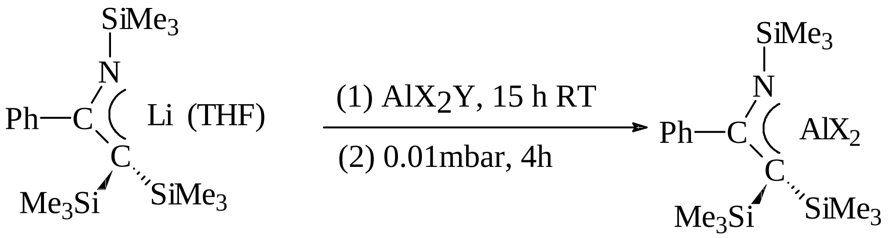
2.1 1-Aza-allyl complexes of aluminum, gallium and bismuth

The important series of first-row triatom-centered, monoanionic ligands $(XYZ)^-$ include allyl, triazenide and amidinate, with the carboxylates as the archetype, which have been widely used in coordination and organometallic chemistry. The 1-aza-allyl ligands are of recent date,[29] only a few main group (K, Li, Na, Pb, Sn) and transition metal (Cu, Hg, Zr, Sm, Yb, Th) complexes have been reported so far.[30-35] One of the most interesting features of these ligands is their various bonding modes, including chelating, η^2-bridging, and η^1-enamido, depending strongly on the metal centers, substituents on the ligand backbone, and the supporting ligands on the central atom. However, to the best of our knowledge, aluminum, gallium and bismuth complexes with 1-aza-allyl ligands have not been described previously. We hoped by using very bulky 1-aza-allyl ligands on aluminum compounds to prepare some unique compounds (low-coordinated aluminum cations and low-valent aluminum species).

2.1.1 Synthesis of mono(1-aza-allyl)-complexes of auminum

The reaction of RLi·THF (R = $[N(SiMe_3)C(Ph)C(SiMe_3)_2]$)[30] with $AlMe_2Cl$, $AlMeCl_2$, $AlCl_3$, and $AlBr_3$ in ether or *n*-hexane afforded $RAlMe_2$ (**1**), RAlMeCl (**2**), $RAlCl_2$ (**3**), and $RAlBr_2$ (**4**), respectively, in high yield (Scheme 4). Initially, these products are in equilibrium with their corresponding THF adducts as confirmed by ^1H NMR analysis. The solvent-free compounds were accessible by sublimation or pumping for a prolonged time in high vacuum at ambient temperature, and crystallization from *n*-hexane yielded solvent-free products. Pure THF adducts have been obtained by dissolving the compounds **1** - **4** in an excess of THF. According to this procedure, we prepared the adducts RAlMeCl·THF (**5**) and $RAlCl_2$·THF (**6**) (Scheme 5). Both compounds are not stable, they are easily oxidized and hydrolyzed on exposure to air as indicated by an immediate color change from colorless to red. The different stabilities of compounds **1** - **4** and their corresponding THF adducts can be explained by the different bonding modes of the ligand as demonstrated by the X-ray structure analyses of compound **3** and **6**.

Scheme 4

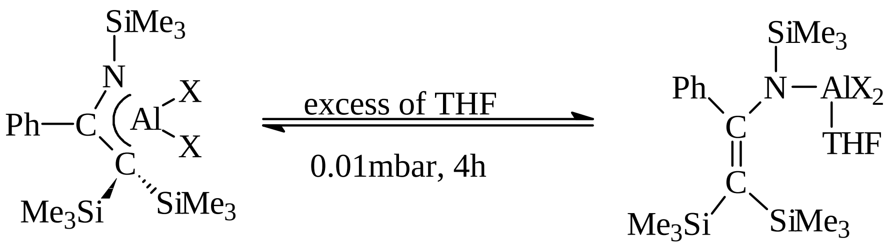


Y = Cl; X = Me (**1**), Me, Cl (**2**), Cl (**3**)

Y = Br; X = Br (**4**)

The solvents seem to be important for the synthesis of compounds **1** - **4**. Complex **1** has been obtained in ether in high yield (85 - 98 %). For **2** - **4**, the synthesis in ether resulted in low yields (around 20 %), but in *n*-hexane gave satisfactory yields (61 - 84 %) for all compounds.

Scheme 5



X = Cl, Me (**2**) (**5**)

X = Cl (**3**) (**6**)

The reaction of $RAlMe_2$ (**1**) with 2 equivalents of Me_3SnF in toluene yielded the dimeric difluoride $[RAlF(\mu\text{-}F)]_2$ (**7**), while the reaction of **1** with 2 equivalents of I_2 in toluene at room temperature generated the diiodide $RAlI_2$ (**8**).

$$2\ RAlMe_2 + 4\ Me_3SnF \rightarrow [RAlF(\mu\text{-}F)]_2 + 4\ SnMe_4$$

7

$$RAlMe_2 + 2\ I_2 \rightarrow RAlI_2 + 2\ MeI$$

8

Unlike the trimeric aminoalane difluorides $[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)AlF_2]_3$[36] and $[(Me_3Si)_3CAlF_2]_3$,[37] compound **7** is a dimer in the solid state as demonstrated by X-ray crystallography, representing the first example of a dimeric aluminum difluoride.

2.1.2 Dynamic behavior of 7

The ^{19}F NMR spectra of **7** at room temperature in C_6D_6 and d_8-toluene both show only one broad singlet, indicating rapid exchange of the bridging and terminal fluorine atoms. This intramolecular exchange was also observed for the previously reported compounds $[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)AlF_2]_3$ and $[(Me_3Si)_3CAlF_2]_3$. When a solution of **7** in d_8-toluene was cooled below 213 K (to 193 K), five separated signals in the ^{19}F NMR spectrum (δ -159.69 (t, J = 15.0 Hz), -158.36 (t, J = 13.4 Hz), -141.13 (d, J = 82.4 Hz), -133.29 (s), -120.61 ppm (d, J = 81.9 Hz)) in an intensity ratio of 2 : 3 : 1 : 3 : 1 were observed. The ambient temperature ^1H NMR spectrum of **7** exhibits only one broad singlet for the $CSiMe_3$ protons and one singlet for the $NSiMe_3$ protons in d_8-toluene. When the solution was cooled to 273 K, the former became broad, and separated into two singlets at 253 K. The singlet for the $NSiMe_3$ protons at ambient temperature clearly splitted at 238 K. At 213 K, two separated singlets for the $CSiMe_3$ protons and two for the $NSiMe_3$ protons were observed while the singlet for the $CSiMe_3$ protons at 0.30 ppm became broad at 193 K. Based on ^1H NMR shifts for the

$CSiMe_3$ at 193 K at δ 0.62 and 0.31 ppm, respectively, we conclude that partial change in the ligand backbone takes place since the chemical shifts differ largely. Thus a rapid dissociation/association of the Al-C bonds can be considered responsible for the fluxional process of **7** in solution. This dynamic process achieves equilibrium at 213 K between five- and four-coordinated species while the $[Al\text{-}(\mu\text{-}F)]_2$ core is maintained at this temperature, forming a mixture of several possible isomers. The broadening of the singlet at 0.31 ppm for the $CSiMe_3$ protons is probably caused by the formation of a C = C bond in a four-coordinated species. The dissociation/association process is rapid at ambient temperature, therefore only one singlet can be observed for the $CSiMe_3$ protons on the NMR time scale. This conclusion is supported further by the splitting of the Ph proton signals in the ^1H NMR spectra at low temperatures. An analogous M-C bond cleavage mechanism was also suggested for the compounds $(RMCl)_2$ (M = Sn, Pb; R = $[N(SiMe_3)C(Ph)C(SiMe_3)_2]$).[30] Herein, assignment of the two signals (δ –159.69 and –158.36 ppm) to the bridging F atoms and the others to the terminal F atoms seems reasonable due to the large coupling constant difference of the two groups of signals as well as their correct integration (2 : 2).

Compounds **1** - **8** have been fully characterized by ^1H NMR, ^{13}C NMR spectra as well as elemental analyses (see Experimental Section). It is interesting to note that the ^{13}C chemical shifts of C(1) atom in the compounds **2** and **3** are significantly high field of those found for compounds **5** and **6**, representing the most typical characteristics of a chelating mode of the ligand in these compounds due to the delocalization of the electrons in the backbone of the ligand. ^{27}Al NMR and MS spectra demonstrate that compounds **1** - **4** and **8** have the coordination number four at the aluminum centers in solution and are monomeric in the gas phase, respectively.

2.1.3 Molecular structure of [RAlF(μ-F)]$_2$·0.5 C_6H_{14} (7·0.5 C_6H_{14})

The molecular structure of **7**·0.5 C_6H_{14} was determined by X-ray diffraction. Single crystals were obtained from *n*-hexane/toluene at -20 °C. The structure of **7** with the atom-labeling scheme is shown in Figure 1 (solvent molecules in the unit cell have been omitted for clarity) with selected bond distances and angles. Compound **7** adopts a dimeric structure in which the two bridging F atoms link two RAlF units in a planar four-membered ring (Al(1)-F(2)-Al(2)-F(3)) with the mean deviation of the ring (Δ = 0.0002 Å), and has approximately C_2 symmetry with the bridging F(2) and F(3) residing on a two-fold axis. Thus, each Al atom is bonded to a chelating R ligand, one terminal F atom and two bridging F atoms, resulting in three fused four-membered rings (Al(1)-C(2)-C(1)-N(1), Δ = 0.0052; Al(2)-C(4)-C(3)-C(2), Δ = 0.0431 Å).

An important structural feature is the observation that every Al atom is penta-coordinated and the geometry of each aluminum coordination sphere can be described best as a distorted trigonal-bipyramid (tbp). A terminal fluorine, a bridging fluorine atom, and a carbon atom occupy the equatorial plane with bond distances to Al of average 1.668 Å, 1.835 Å, and 2.053 Å, respectively. The Al atom lies almost exactly in this plane with a negligible displacement. The sum of bond angles involving Al in this plane is 359.33° for Al(1) and 359.66° for Al(2), the angles F(1)-Al(1)-F(3) (102.23(15)°) and F(3)-Al(2)-F(4) (102.56(15)°) are significantly smaller than the angles F(3)-Al(1)-C(2) (142.2(3)°) and F(3)-Al(2)-C(4) (137.1(2)°), resulting from crowded environments around C(2) and C(4). The apical positions of this array are occupied by the bridging fluorine atom for both tbp geometries and the N(1) for Al(1) and N(2) for Al(2) with bond angles of N(1)-Al(1)-F(2) 152.4(2)° and N(2)-Al(2)-F(2) 153.6(2)°. The deviation of the apical axis N(1)-F(2) is 13.8^o arising from the constraints caused by the specific angles in the chelating bidentate monoanionic ligand (average 71.4°) as well as in the acute F(2)-Al-F(3) angles of average 75.8° in the (μ-F)$_2$Al$_2$ ring.

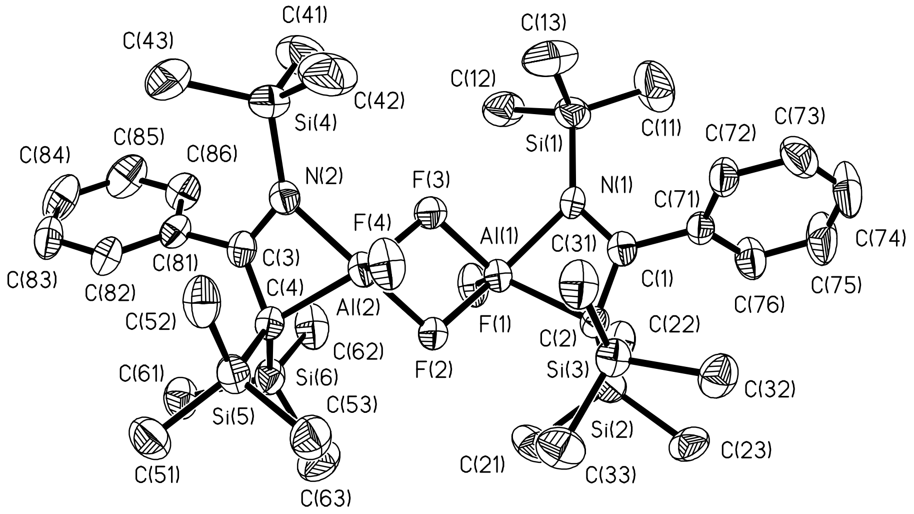


Figure 1. ORTEP drawing of **7** (50 % probability). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)-F(1) 1.665(3), Al(1)-F(2) 1.837(3), Al(1)-F(3) 1.841(3), Al(1)-N(1) 1.977(4), Al(1)-C(2) 2.051(5), Al(2)-F(4) 1.670(3), Al(2)-F(2) 1.850(3), Al(2)-F(3) 1.829(3), Al(2)-N(2) 1.964 (4), Al(2)-C(4) 2.055(5), Al(1)-Al(2) 2.902(2); F(1)-Al(1)-F(2) 101.40(14), F(1)-Al(1)-F(3) 102.23(15), F(2)-Al(1)-F(3) 75.86(13), F(1)-Al(1)-N(1) 105.6(2), F(2)-Al(1)-N(1) 152.4(2), F(3)-Al(1)-N(1) 92.7(2), F(1)-Al(1)-C(2) 114.9(2), F(2)-Al(1)-C(2) 102.5(3), Al(1)-F(2)-Al(2) 103.81(14), Al(1)-F(3)-Al(2) 104.52(15), N(1)-Al(1)-C(2) 71.3(2), F(3)-Al(2)-F(4) 102.56(15), F(2)-Al(2)-F(4) 99.10(15), F(2)-Al(2)-F(3) 75.81(12), F(3)-Al(2)-N(2) 92.6(2), F(4)-Al(2)-N(2) 106.6(2), F(2)-Al(2)-N(2) 153.6(2), F(4)-Al(2)-C(4) 120.0(2), F(3)-Al(2)-C(4) 137.1(2), F(2)-Al(2)-C(4) 100.9(2), N(1)-C(1)-C(2) 114.2(4), Al(1)-N(1)-C(1) 91.1(3), Al(1)-C(2)-C(1) 83.4(3), N(2)-C(3)-C(4) 114.2(4), Al(2)-N(2)-C(3) 90.8(3), Al(2)-C(4)-C(3) 82.8(3), N(2)-Al(2)-C(4) 71.4.

The most unique and interesting feature in this structure is that the bridging F(2) and F(3) atoms connect the two units in such a way that F(2) occupies the same apical position and F(3) lies in the same equatorial position in the two tbp coordination spheres, resulting in a slightly longer Al-F(2) distance (average 1.844 Å) than Al-F(3) (average 1.836 Å). The distance of Al(1)-F(2) (1.837(3) Å) is shorter than that of Al(2)-F(2) (1.850(3) Å), leading to a longer Al(1)-N(1) distance (1.977(4) Å) than Al(2)-N(2) (1.964(4) Å), and to the slightly unequal environments around Al(1) and Al(2). The N(1)-Al(1)-C(2) and N(2)-Al(2)-C(4) angles are very acute (average 71.3°), slightly smaller than that found in compound **3** (73.68(10)°) because of the different coordination number of the Al atoms of the two compounds. The acute angles of F(2)-Al(1)-F(3) (75.86(13)°) and F(2)-Al(2)-F(3) (75.81(12)°) lead to a rather long Al-Al distance (2.902(2) Å). Compared to compound **3**, the Al-N (average 1.971 Å) and Al-C (average 2.053 Å) bond lengths in the chelating plane are longer than those observed in **3** (Al-N, 1.918(2) Å; Al-C, 2.015(3) Å). The average Al-F distance (bridging, 1.839 Å) is consistent with those found in compound $[(Cp^*AlF_2)_2SiPh_2]_2$ (average 1.846 Å)[38] and slightly longer than those found by electron diffraction for $(Me_2AlF)_4$ (1.808 Å)[39] or by X-ray diffraction for $[(Me_3Si)_3CAlF_2]_3$ (1.785 to 1.815 Å)[37] and for $[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)AlF_2]_3$ (1.770 to 1.815 Å).[36] The terminal Al-F distances are 1.665 Å (Al(1) -F(1)) and 1.670 Å (Al(2)-F(4)), and are somewhat longer than those observed in $[(2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)N(SiMe_3)AlF_2]_3$ (1.634 to 1.642 Å), and AlF_3 (1.63 Å)[40] determined by electron diffraction due to the higher coordination number of aluminum in compound **7**. No examples of five-coordinated aluminum compounds containing both bridging and terminal F atoms can be found in the literature for comparison.

2.1.4 X-ray crystallographic analyses of compounds 3 and 6

The molecular structures of compounds **3** and **6** are shown in Figures 2 and 3, respectively, with selected bond distances and angles. Single crystals of compounds **3** and **6** suitable for X-ray diffraction analyses were obtained by recrystallization from *n*-hexane at –8 °C. Compound **3** adopts a distorted tetrahedral structure. The core angle (N(1)-Al(1)-C(2)) is acute (73.68(10)°), which is compensated by opening of the N-Al-Cl and C-Al-Cl angles. The structure of **3** is similar to that of a reported amidinato aluminum dichloride Ph-C$(NSiMe_3)_2AlCl_2$.[41] Because the chelating backbones in the two compounds are different, some differences in the structures are obvious: (1) The core angle N(1)-Al(1)-C(2) (73.68(10) °) is slightly larger than N-Al-N (72.9(7)°) in compound Ph-C$(NSiMe_3)_2AlCl_2$; (2) the Al(1)-C(2)-Si(2, 3) (118.75(13) and 108.84(12)°) angles in **3** are significantly smaller than the Al-N-Si angles in Ph-C$(NSiMe_3)_2AlCl_2$ (average 139°), indicating that the ligand R is more shielding than the amidinate.

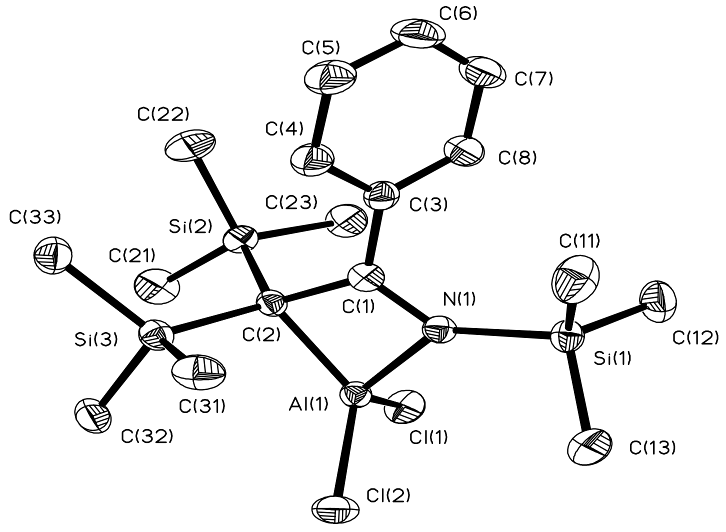


Figure 2. ORTEP drawing of **3** (50 % probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)-N(1) 1.918(2), Al(1)-C(2) 2.015(3), Al(1)-Cl(1) 2.1321(10), Al(1)-Cl(2) 2.1276, C(1)-C(3) 1.484(4); N(1)-Al(1)- C(2) 73.68(10), N(1)-Al(1)-Cl(2) 113.05(7), C(2)-Al(1)-Cl(2) 124.28(8), N(1)-Al(1)-Cl(1) 114.57(7), C(2)-Al(1)-Cl(1) 120.70(8), Cl(2)-Al(1)-Cl(1) 106.53(4).

The structure of compound **6** was also determined by X-ray crystallography for comparison (Figure 3). Interestingly, in the monomeric molecule of **6** the geometry of the aluminum coordination sphere is distorted tetrahedral, while the aluminum atom is surrounded by two chlorine atoms, one oxygen atom and one nitrogen atom. The ligand R in this compound, in contrast to **3**, is η^1-coordinated. The Al(1)-N(1) distance (1.806(3) Å) in **6** is much shorter than that in compound **3** (1.918(2) Å).

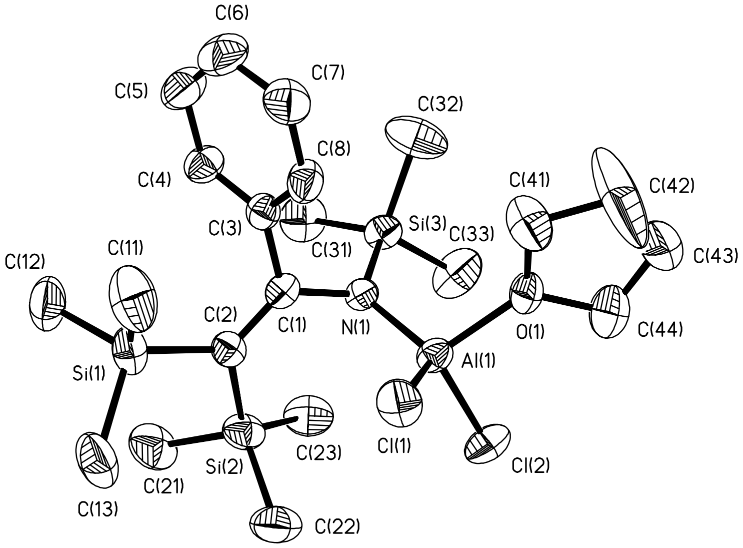


Figure 3. ORTEP drawing of **6** (50 % probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)-N(1) 1.806(3), Al(1)-O(1) 1.872(3), Al(1)-Cl(1) 2.135(2), Al(1)-Cl(2) 2.134 (2), C(1)-C(2) 1.356(6); N(1)-O(1)-Al(1) 109.0(2), N(1)-Al(1)-Cl(2) 118.98(13), O(1)-Al(1)-Cl(2) 99.61(11), N(1)-Al(1)-Cl(1) 114.00(12), O(1)-Al(1)-Cl(1) 102.64(11), Cl(1)-Al(1)-Cl(2) 110.34(8), Al(1)-N(1)-C(1) 117.7(2), N(1)-C(1)-C(2) 124.9(4).

The different bonding modes in **3** and **6** are also reflected in the different bond distances in the backbone of the ligand (long C(1)-N(1) and short C(1)=C(2) distances for **6** versus short C(1)-N(1) and long C(1)-C(2) contacts for **3**). The long C(1)-C(2) and short C(1)-N(1) distances in compound **3** are indicative of the delocalization of the electrons in the N(1)-C(1)-C(2) unit. The Al-Cl distances are comparable to those of compound **3**, while the Cl-Al-Cl angle (110.34(8)°) is slightly larger than that of compound **3** (106.53(4)°), reflecting the greater steric demand for the chelating mode even though a THF molecule is coordinated to Al in compound **6**. The Al-O distance (1.872(3) Å) is in agreement with that observed for $(Me_3Si)_3CAlCl_2(THF)$ (1.887 Å).[37] Although in the solid state, the THF in compound **6** seems as tightly coordinated to the aluminum atom as in $(Me_3Si)_3CAlCl_2(THF)$ by comparison of the Al-O bond lengths of the two compounds, its instability is obviously due to the easy removal of the THF molecule *in vacuo*. Thus, the bonding fashions of the ligand change from η^1 to chelating so as to stabilize the $AlCl_2$ unit. The distances between Al(1) and C(1) as well as Al(1) and C(2) are ca. 2.79 and 3.50 Å, respectively, which are in the range of the sum of van der Waals interactions, indicating that the C(1)=C(2) bond is not free in the solid state. This observation is in accordance with the fact that only one signal for the protons of the two $CSiMe_3$ groups on C(2) is present in the ^1H NMR spectrum of **6** in C_6D_6 at ambient temperature and the ^{13}C NMR signal for C(2) is significantly shifted downfield compared to those of normal C=C bonds. The ^{27}Al NMR spectrum shows a broad signal at δ 62.66 ppm, which is low field from those in other four-coordinated compounds described herein, indicating enhanced electron density on Al atom and partial interactions between Al and the C=C bond in solution, which may result from the acidic aluminum center attached by four electron-withdrawing groups, leading to flexibility of the C=C bond, indicating fluxional behavior of the two $SiMe_3$ groups.

2.1.5 Syntheses of the bis(1-aza-allyl) aluminum complexes 9, 10, 11

Reaction of the 1-aza-allyl lithium salt $(R'Li)_2$ ($R' = N(SiMe_3)C(t\text{-}Bu)CH(SiMe_3)$)[29] with $AlCl_3$ and $AlMeCl_2$ in diethyl ether afforded the bis(1-aza-allyl) aluminum complexes R'_2AlCl (**9**) and R'_2AlMe (**10**) in good yield, respectively. Compounds **9** and **10** were fully characterized by ^1H, ^{13}C and ^{29}Si NMR, mass spectroscopy, and elemental analyses. Spectroscopic data for **9** indicate that two ligands are coordinated to the aluminum center in different bonding modes: one is chelating and the other is η^1-amido. The NMR spectra of **10** are rather complicated due to rapid exchange of the ligands in solution compared to **9** with a more polarized Al-Cl bond. EI-MS spectra show both **9** and **10** to be monomers in the gas phase. Initial efforts to examine the reactivities of the two compounds showed that **10** did not react with the fluorinating reagent Me_3SnF in CH_2Cl_2 or toluene to give the corresponding fluoride; **9** was not reduced by alkali metals (Na or K) in hydrocarbon solvents even at elevated temperatures as indicated by recovery of 70 - 80 % of **9** after refluxing for 24 h in *n*-hexane. Treatment of **9** with the Lewis acid $AlCl_3$ in toluene afforded a yellow oil that separated from the solvent. Obviously a liquid clathrate (an oil containing **11** and solvent) was formed. Many ionic aluminum compounds exhibit a similar behavior in aromatic solvents yielding a two phase system.[42] A white solid **11** has been obtained after treating the crude product with pentane, extremely air-sensitive and unstable in THF and CH_2Cl_2. Attempts to crystallize the solid from THF or CH_2Cl_2 led to the formation of $AlCl_3(THF)_2$[43] and **9** or decomposition of **11** into $AlCl_3$ and **9** respectively. The formation of $AlCl_3(THF)_2$ from **11** in THF is particularly noteworthy since the direct interaction of aluminum trichloride, Al_2Cl_6, and THF has been shown to give the ionic compound $[AlCl_2(THF)_4](AlCl_4)$.[44] The mechanism may involve the initial interaction of the cation $R'_2Al^+$with THF, which is in contrast to the related cation-anion pair $[(2\text{-}C(SiMe_3)\text{-}C_5NH_4)_2Al][AlCl_4]$ which could be crystallized from THF.[45] The different stabilities may be due to the flexibility of the 1-aza-allyl ligand. Compound **11** can be dissolved in CD_2Cl_2, the solution is stable for a few days allowing characterization of the product by NMR spectroscopy. The ^1H NMR spectrum of **11** contains four singlets (δ 0.30, 0.42, 1.39, and 3.03 ppm) which are assigned to the $NSi\mathit{Me}_3$, $CSi\mathit{Me}_3$, *t*-Bu, and C*H* protons, respectively. The chemical shift for the CH proton indicates that the ligand is coordinated to the aluminum atom in a chelating fashion indicated by the high field signal compared to those found for the protons of ‘normal’ C=C double bonds.

Further evidence for the formation of a cationic species was provided by the ^{27}Al NMR spectrum, in which two signals are observed: one at δ 103 ppm is indicative for the $AlCl_4^-$ anion;[46] the second (δ 111 ppm) is assigned to R_2Al^+, in the typical range for a four-coordinated aluminum center.

Attempts to synthesize bis(1-aza-allyl) aluminum compounds containing the more bulky ligand R (R = $N(SiMe_3)C(Ph)C(SiMe_3)_2$) in solvents such as diethyl ether, *n*-hexane, THF and toluene even under reflux conditions were unsuccessful.

2.1.6 Synthesis and characterization of complexes 12 and 13

The reaction of RLi·THF (R = $[N(SiMe_3)C(Ph)C(SiMe_3)_2]$) with $GaCl_3$ and $BiBr_3$ in toluene/*n*-hexane afforded the corresponding mono(1-aza-allyl) gallium dichloride $RGaCl_2$ (**12**) and bismuth dibromide $RBiBr_2$ (**13**), respectively.

$$RLi\cdot THF \;+\; MX_3 \;\rightarrow\; RMX_2 \;+\; LiX \;+\; THF$$

M = Ga, X = Cl (**12**); M = Bi, X = Br (**13**)

The two compounds have been characterized by MS, multinuclear NMR spectra, and elemental analysis. The MS spectra of **12** and **13** indicate that the two compounds are monomers in the gas phase. The ^{1}H and ^{29}Si NMR spectra of **12** and **13** contain only one singlet for the $CSiMe_3$ protons (see Experimental) indicating that R is coordinated to the central atom in a chelating mode as proved for the corresponding compound $RAlCl_2$ (**3**) by X-ray structural analysis. Compound **12** is soluble in hydrocarbon solvents while **13** has only very limited solubility in *n*-hexane but is soluble in aromatic solvents. **13** is not stable in solution and slowly decomposes even under an inert atmosphere. Reduction of **13** with potassium in toluene afforded a yellowish oil, which we were not able to characterize completely. Compounds **12** and **13** represent the first known 1-aza-allyl compounds of gallium and bismuth. Further investigation of the chemistry of 1-aza-allylgallium and -bismuth compounds is in progress.

2.1.7 X-ray structure of [{N($SiMe_3$)C(*t*-Bu)CH($SiMe_3$)}$_2$AlCl] (9)

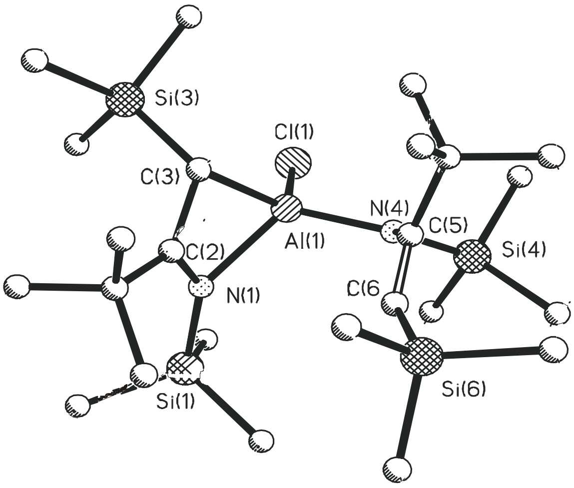


Figure 4. Molecular structure of **9** in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)-N(1) 1.9701(15), Al(1)-N(4) 1.8194(15), Al(1)-C(3) 2.003(2), Al(1)-Cl(1) 2.1504(8), C(2)-C(3) 1.478(2), C(5)-C(6) 1.349(2), N(1)-C(2) 1.321(2), N(4)-C(5) 1.450(2); N(1)-Al(1)-Cl(1) 116.66(5), N(1)-Al(1)-C(3) 71.44(6), N(1)-Al(1)-N(4) 115.59(7), N(1)-C(2)-C(3) 111.82(14), N(4)-Al(1)-Cl(1) 108.81(5), N(4)-Al(1)-C(2) 116.87(6), N(4)-Al(1)-C(3) 119.93(7), C(6)-C(5)-N(4) 119.2(2).

Single crystals of **9** were obtained from *n*-hexane solution at -30 °C. The structure of **9** with the atom labeling scheme is shown in Figure 4 followed by selected bond lengths and angles. Compound **9** adopts a distorted tetrahedral structure with aluminum bonded to C(3), Cl(1), N(1) and N(4), thus one ligand R is coordinated to the aluminum atom in a chelating fashion with an acute core angle N(1)-Al(1)-C(3) (71.44(6)°), the other ligand acts as an amido ligand only with N(4) being coordinated to the aluminum atom. The different bonding modes of the ligands can be further rationalized by comparing selected bond parameters. The

Al(1)-N(1) (1.9701(15) Å) distance is longer than Al(1)-N(4) (1.8194(15) Å)), moreover, the C(2)-C(3) (1.478(2)Å) bond length is longer than C(5)-C(6) (1.349(2) Å) while N(1)-C(2) (1.321(2) Å) is shorter than N(4)-C(5) (1.450(2) Å) due to electron delocalization in the chelating ligand backbone. The bond angle C(3)-C(2)-N(1) (111.82(14)°) reflects an sp^3 electron distribution at C(2) while the angle N(4)-C(5)-(C(6) (119.2(2)°) indicates an sp^2 electron distribution at C(5). These data are in agreement with the different bonding modes of the ligands.

The ^{1}H NMR spectrum of **9** clearly shows two sets of signals for the R′ groups, indicating that the solid state structure is maintained in C_6D_6 solution at room temperature. The singlets (δ 2.33 and 4.94 ppm) for the CH protons in the ^{1}H NMR spectrum are also indicative for the different bonding interactions in the compounds incorporating this ligand.

2.1.8 Synthesis and molecular structure of [RAlH(μ-H)]$_2$ (14)

The reaction of $RAlBr_2$ (**4**) with an excess of $LiAlH_4$ in diethyl ether afforded [RAlH(μ-H)]$_2$ (**14**) in nearly quantitative yield. **14** was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectra, elemental analysis, and X-ray structural analysis. Single crystals of **14** have been grown from *n*-hexane at 0 ºC. The molecular structure of **14** is shown in Figure 5 with selected bond distances and angles. It adopts a dimeric structure in the solid state, as a consequence, the whole structure features three fused four-membered rings with asymmetric 1-aza-allyl ligands in *trans* configuration. Each aluminum atom is five-coordinated, and the geometry of the Al atoms can be described as trigonal bipyramidal with the axis going through H(1A)-Al(1)-N(1) (165.6º). The two bridging Al-H bonds at the same aluminum atom differ in length by 0.363 Å due to the asymmetry of the bulky ligand, which is in sharp contrast to the compound $(Mes^*AlH_2)_2$, where the two bridging Al-H bonds are nearly equal.[47] The terminal Al-H bonds (1.509 Å) are comparable to those (1.52(2) Å) in the compound $[HAl(NMe_2)_3]^-$,[48] while the two bridging Al-H bonds (1.603 Å) are shorter than those observed in the compounds [(*t*-Bu)$_2$Al(μ-H)]$_2$ (1.68(2) Å)[49] and [*o*-(Me$_2$NCH$_2$)C$_6$H$_4$]AlH(μ-H)]$_2$ (1.688 Å).[50] The two other bridging Al-H separations (1.966 Å) of **14** are much longer than the sum of the covalent radii of Al and H (1.67 Å) and the longest observed in organoaluminum dihydrides, indicating weak bonding interactions between two loosely associated monomers.

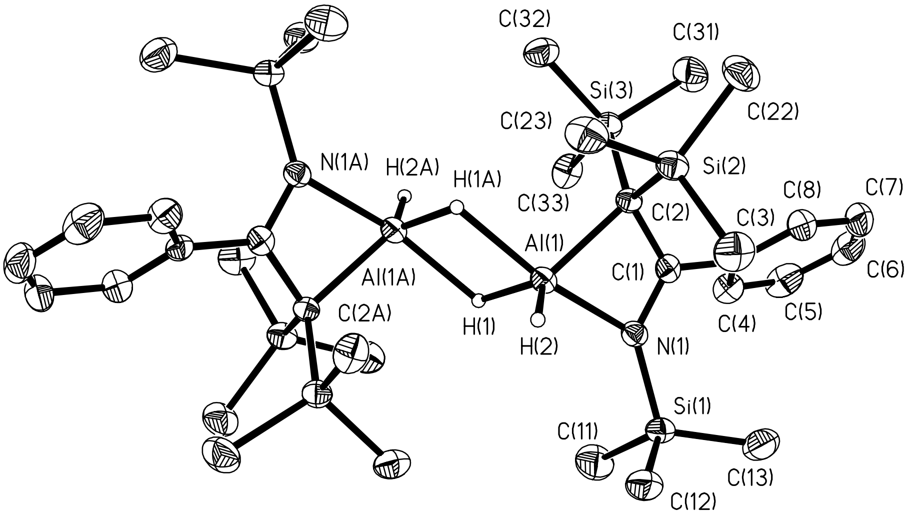


Figure 5. ORTEP drawing of **14** (50 % probability): Hydrogen atoms except those in central core have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)-H(1) 1.603, Al(1)-N(1) 2.026(2), Al(1)-H(2) 1.509, Al(1)-H(1A) 1.966, Al(1)-C(1) 2.418(2), C(1)-C(2) 1.495(2), C(1)-N(1) 1.301(2), Al(1)-Al(1A) 2.8154(11), Al(1)-C(2) 2.058(2); H(1)-Al(1)-H(2) 117.2, H(1)-Al(1)-H(1A) 76.3, H(1A)-Al(1)-N(1) 165.6, H(1)-Al(1)-N(1) 100.1, N(1)-Al(1)-C(2) 70.39.

The ^{1}H NMR spectra (C$_6$D$_6$ and d$_8$-toluene) at room temperature show only one sharp signal for AlH protons, and the ^{27}Al NMR resonance (δ 131.6 ppm) indicates a four-coordinated aluminum center present in solution. Therefore a monomeric structure of **14** in solution can be assumed. At lower temperatures (233 K, 193 K) the signal for AlH only broadens as well as the other singlets in the spectra, indicating that the monomeric structure is maintained in solution at these temperatures.

2.1.9 Synthesis and structures of $[RAl(\mu\text{-}E)]_2$ (E = S, (15), Se (16), Te (17))

The reactions of **14** with sulfur (S_8), selenium or metallic tellurium proceeded smoothly in toluene at elevated temperature to afford dimeric aluminum sulfide (**15**), selenide (**16**) and telluride (**17**) in good yields, respectively.

$$[RAlH(\mu\text{-}H)]_2 + 2/x\, E_x \longrightarrow [RAl(\mu\text{-}E)]_2 + 2\, H_2$$

E = S (**15**), Se (**16**), Te (**17**)

This reaction type obviously represents a new and facile route to organoaluminum chalcogenides. The detailed reaction pathway is not yet understood. The reactions may be comparable to those of group 13 alkyls with elemental S, Se and Te, where products $[R'_2M(\mu\text{-}ER')]_2$ (R′ = alkyl; E = S, Se, Te; M = Al, Ga) have been isolated.[51] In a similar way, this reaction presumably involves a hydrochalcogenide (SH, SeH, TeH) intermediate,[52] followed by elimination of hydrogen. The related cleavage reactions of element-element bonds of group 16 using aluminum hydrides include the reactions of diorganodiselenides or –ditellurides with $i\text{-}Bu_2AlH$[53] or $Me_3N{\cdot}AlH_3$.[54]

Compounds **15** - **17** are very air and moisture sensitive, but thermally quite stable as indicated by their high melting points and EI mass spectra, where the molecular ions were observed for the three compounds as the base peaks. In addition they have been characterized by ^1H and ^{29}Si NMR spectroscopy and elemental analysis.

The structures of the three compounds have been determined by X-ray diffraction analyses. The structure of **15** is shown in Figure 6 with important bond lengths and angles. It consists of a dimeric structure with an Al_2S_2 core. Its structure is related to the dimeric $(Mes^*AlS)_2$ ($Mes^* = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$)[12a] synthesized by the reaction of $(Mes^*AlH_2)_2$ with $S(SiMe_3)_2$

except that in the latter compound the aluminum atoms are three-coordinated. The insertion of S into Al-H bonds has not been observed previously. The Al-S bond length (av 2.22 Å) is in agreement with the reported aluminum sulfides $Al_4S_5H_2(NMe_3)_4$ and $Al_4S_6(NMe_3)_4$ (av 2.22 Å)[55], and only slightly longer than those of $(Mes^*AlS)_2$ (2.21 Å). The tetrameric Al-S species $((Me_2Et)CAlS)_4$ has an Al_4S_4 cubane structure with Al-S distances in the range from 2.295(8) to 2.319(9) Å.[14c] The longer Al-S distances in that compound are due to the higher coordination number of S. The Al(1)-S-Al(1A) angle (79.84(6)°) is much more acute compared to those of $(Mes^*AlS)_2$ (101.91°) due to the higher coordination number of Al in **15**.

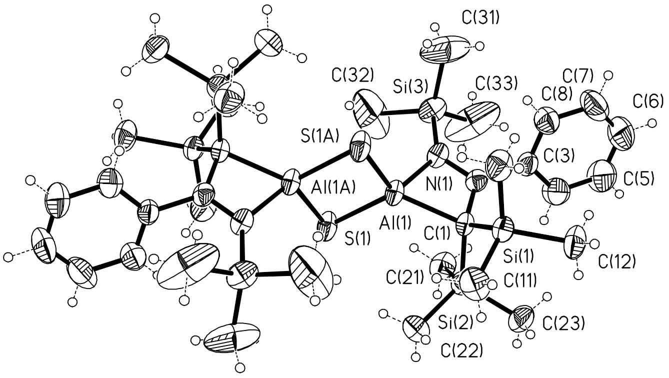


Figure 6. ORTEP drawing of **15** (50 % probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1A)-S(1) 2.2169(15), Al(1)-S(1) 2.2198(17), Al(1)-N(1) 1.950(3), Al(1)-C(1) 2.052(4), Al(1)-S(1A) 2.2170(15), Al(1)-C(2) 2.359(4); Al(1)-S(1)-Al(1A) 79.84(6), N(1)-Al(1)-C(1) 71.82(14), S(1A)-Al(1)-S(1) 100.16(6).

The molecular structure of **16** is shown in Figure 7 (**16** and **17** are isostructural) with the atom-labeling scheme and selected bond lengths and angles. X-ray quality crystals of **16** (colorless) and **17** (greenish) were obtained from a toluene/*n*-hexane solution at –20 °C and a benzene/*n*-hexane at 6 °C, respectively. Both compounds crystallize in the triclinic space group *P*-1. The two molecules in the unit cell, only marginally different in bond lengths and angles, are crystallographically centrosymmetric (Figure 7 shows only one of two independent molecules of **16**). The structure of **16** consists of three fused four-membered rings with a central Al(1)-Se(1)-Al(1A)-Se(1A) core (the sum of the internal angles = 360.0º, the central core of the other molecule in the unit cell is represented by Al(2)-Se(2)-Al(2A)-Se(2A) nearly perpendicular to the two other rings (the angles between two adjacent planes in the two different molecules are 92.7° and 91.8°, respectively). The internal angles at Al (102.42(3)°, 102.39(3)º) are wider than at Se (77.58(3)°, 77.61(3)°) due to the acute angles N-Al-C (72.01(10)°, 71.74(10)°), which are only slightly larger than those in the five coordinated aluminum atoms of **14**. The Al-Se distances (2.3424 to 2.3563 Å) are shorter than those in the compounds $(Cp^*AlSe)_4$ (2.462- 2.497 Å)[15] and $(Me_2EtCAlSe)_4$ (2.444 to 2.481 Å)[14a] with a cubic core due to the lower coordination number of Se (two) atoms in **16**. The Al-Al separations (2.9412(16) Å, 2.9473(15) Å) are slightly longer than that in the starting material **14** (2.8154(11) Å) due to longer Al-Se bonds compared to the bridging Al-H bonds even though the aluminum atoms in the latter are five-coordinated. Only one isomer is present in the crystal investigated with the backbone of the ligands in *trans* configuration.

Compound **17** is the second example of a monoorganoaluminum telluride to be fully structurally characterized. The other example is the tetrameric $(Cp^*AlTe)_4$ reported by our group, which has an Al_4Te_4 cubane core with Al-Te distances in the range from 2.688 to 2.750 Å.[15] The longer Al-Te bond lengths in the latter are due to the higher coordination number of Te (three). The short Al-Te distances (2.5619(12) to 2.5768(14) Å) in **17** are similar to those found for the compound $\{[(SiMe_3)_2HC]_2Al\}_2Te$ (2.549 Å).[56] It is noteworthy that the internal angles at Al and at Te in **17** are quite similar to those at Al and at Se in **16**, respectively, despite the longer Al-Te bond lengths compared to the Al-Se bonds (the central cores of the two different molecules in the unit cell of **17** are represented by Al(1)-Te(1)-Al(1A)-Te(1A) and Al(2)-Te(2)-Al(2A)-Te(2A), respectively).

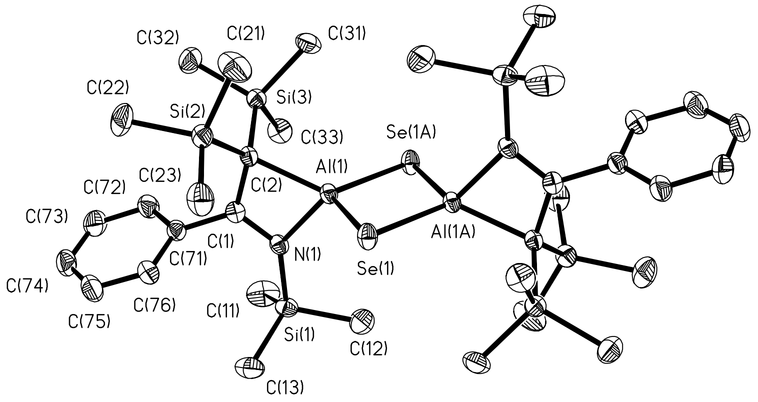
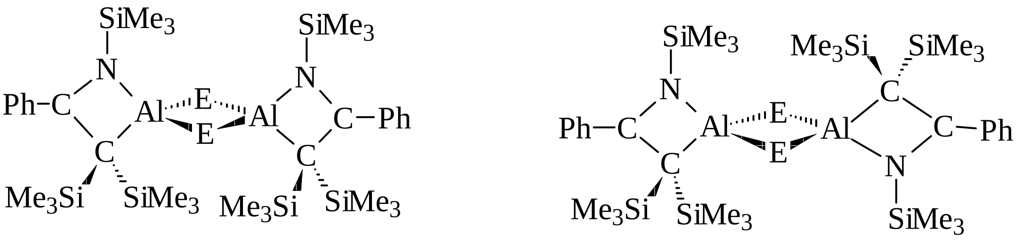


Figure 7. ORTEP drawing of **16** (50 % probability). Hydrogen atoms have been omitted for clarity. Compound **17** is isostructural with **16**. Selected bond lengths (Å) and angles (deg) for one of two independent molecules of **16**: Al(1)-Se(1) 2.3424(8), Al(1)-Se(1A) 2.3527(9), Al(1)-N(1) 1.948(2), Al(1)-C(2) 2.051(3), Al(1)-Al(1A) 2.9412(16), N(1)-C(1) 1.308(3), C(1)-C(2) 1.491(4), Al(2)-Se(2) 2.3469(8), Al(2)-Se(2A) 2.3563(2), Al(2)-N(2) 1.953(2), Al(2)-C(4) 2.052(3), Al(2)-Al(2A) 2.9473(15); Se(1)-Al(1)-Se(1A) 102.42(3), Al(1)-Se(1)-Al(1A) 77.58(3), N(1)-Al(1)-C(2) 72.01(10), Se(2)-Al(2)-Se(2A) 102.39(3), Al(2)-Se(2)-Al(2A) 77.61(3), C(2)-Al(1)-Se(1) 123.17(8). One of two indipendent molecules of **17**: Al(1)-Te(1) 2.5619(12), Al(1)-Te(1A) 2.5768(14), Al(2)-Te(2) 2.5753(12), Al(2)-Te(2A) 2.5765(14), Al(1)-N(1) 1.946(3), Al(1)-C(2) 2.064(4), N(1)-C(1) 1.319(5), C(1)-C(2) 1.484(6); N(1)-Al(1)-C(2) 71.80(15), N(1)-Al(1)-Te(1) 110.03(11), Te(1)-Al(1)-Te(1A) 103.12(4), C(2)-Al(1)-Te(1) 123.06(12), Te(2)-Al(2)-Te(2A) 102.79(4), Al(2)-Te(2)-Al(2A) 77.21(4), Al(1)-Te(1)-Al(1A) 76.88(4).

Both ^{1}H and ^{29}Si NMR spectra indicate the existence of an equilibrium of two isomers of **15 - 17** in C_6D_6 solution, which is probably caused by the relative orientation of the chelating ligands. The variable temperature (295 to 193 K) ^{1}H NMR spectra of **16** indicate that the conversion of the two isomers in d_8-toluene becomes slow at 193 K as indicated by only one singlet for the $NSiMe_3$ and $CSiMe_3$ protons each present at this temperature. Due to the ligand backbone, which is arranged nearly perpendicularly to the central core, two isomers (*trans* and *cis*) are possible shown in Scheme 6. The ratio of the two isomers (approximately 1 : 2) for both **16** and **17** at room temperature was estimated from the ^1H NMR intensities. Due to the flexibility of the ligand R, an M-C bond cleavage mechanism has been proposed to explain the dynamic processes in compounds $(RMCl)_2$ (M = Sn, Pb)[30] and $[RAlF(\mu\text{-}F)]_2$. In analogy, the Al-C bond dissociation/association process might also be responsible for the interconversion of the two isomers in solution.

Scheme 6



cis isomer *trans* isomer

2.1.10 Reduction of aluminum dihalides

The 1-aza-allyl-aluminum dihalides $RAlX_2$ (X = Cl, Br, I) have been reduced with potassium. The diiodide derivative was found to be reduced more easily than the dichloride and dibromide. No products could be isolated or identified in the case of using pure halides. However, when a mixture of $RAlI_2$ and RAlClI was used for the reduction, the first example of a divalent aluminum species RClAl-AlIR (**18**), which contains both organic and halide ligands, was obtained. The EI-MS spectrum clearly shows $(RAlCl)^+$ and $(RAlI)^+$ fragments. The ^1H and ^{29}Si NMR spectra are complicated due to the different halogens on the two aluminum atoms, which may give rise to several species in solution (RClAl-AlClR, RIAl-

AlIR, RClAl-AlIR). The formation of **18** may be explained by the simultaneous reduction of $RAlI_2$ and RAlClI. RAlClI might have formed by the reaction of I_2 with RAlClMe generated by the reaction of RLi(THF) with $MeAlCl_2$ (commercially available Me_2AlCl solutions normally contain some $MeAlCl_2$). However, attempts to isolate pure RAlClI from the reaction of RAlClMe and I_2 were unsuccessful.

$$\mathrm{RAlI_2} \;+\; \mathrm{RAlClI} \;+\; 2\,\mathrm{K} \;\rightarrow\; \mathrm{(R)IAl\text{-}AlCl(R)} \;+\; 2\,\mathrm{KI}$$

18

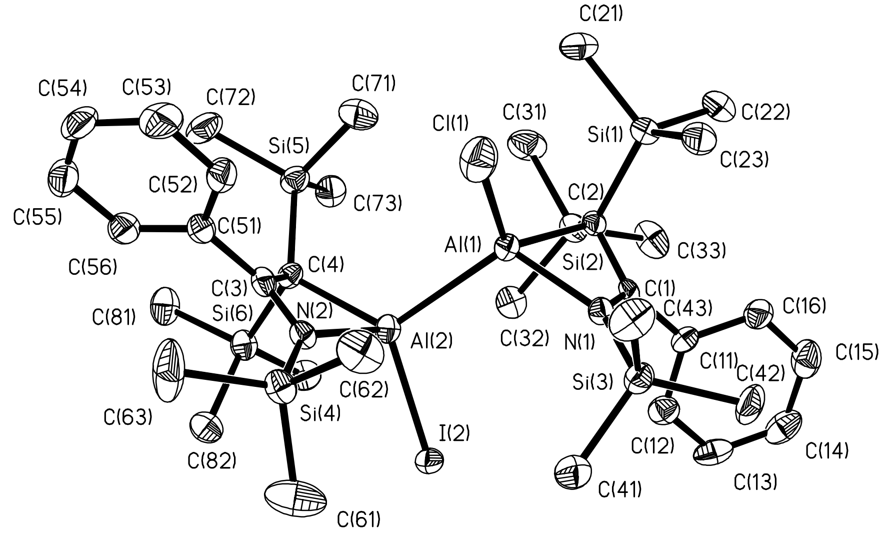


Figure 8. ORTEP drawing of **18** (50 % probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): I(1)-Al(1) 2.553(3), I(2)-Al(2) 2.546(2), Cl(1)-Al(1) 2.286(11), Cl(2)-Al(2) 2.347(11), Al(1)-Al(2) 2.593(2), Al(1)-N(1) 1.960, Al(1)-C(2) 2.095(4); N(1)-Al(1)-C(2) 71.14(13), N(1)-Al(1)-Cl(1) 108.6(3), C(2)-Al(1)-Cl(1) 120.7(4), N(1)-Al(1)-I(1) 113.08(12), N(1)-Al(1)-Al(2) 113.45(10), Cl(1)-Al(1)-Al(2) 111.9(3), I(1)-Al(1)-Al(2) 110.40.

The structure of this unique divalent species was determined by single crystal X-ray structural analysis shown in Figure 8 with selected bond lengths and angles. The two ligands are bonded to the aluminum atom in a chelating fashion in *trans* conformation, leading to four coordinated Al centers with distorted tetrahedral geometry. The Al(1)-Al(2) bond distance (2.593(2) Å) is the shortest one reported so far for neutral Al compounds.[57] The Al-Cl bond length (2.347(11) Å) is longer by ca. 0.2 Å than those in the Al(III) compound $RAlCl_2$ (average 2.13 (10) Å).

2.2 Aluminum compounds with chelating aryl ligands

Aryl ligands of the type $2,6\text{-}(R_2NCH_2)_2C_6H_3$ and $2\text{-}(R_2NCH_2)C_6H_4$ (R = Me, Et, *i*-Pr or other organic groups) with one or two donor side arms have been widely used in late transition metal chemistry,[58] some group 13 and 14 element compounds with this type of ligands have also been reported.[59] These ligands can effectively control the geometry of the metal centers and prevent association. This has been demonstrated by the synthesis of monomeric aluminum and gallium hydrides using the tridentate $2,6\text{-}(Me_2NCH_2)_2C_6H_3$ ligand.[8,60] However, aluminum chalcogenides with this type of ligands have not been reported so far. The only related compound is the dimeric $(Mes^*AlS)_2$ ($Mes^* = 2,4,6\text{-}(t\text{-}Bu)_3C_6H_2$).[12a] In this part we describe the first examples of aryl aluminum selenides and a telluride of formula $(ArAlE)_n$.

2.2.1 Synthesis of aryl aluminum dihydrides

Aluminum dihydrides can be easily prepared by the reduction of the corresponding dihalides.[8] The reactions of $2\text{-}(Et_2NCH_2)\text{-}6\text{-}MeC_6H_3Li$ and $2,6\text{-}(Et_2NCH_2)_2C_6H_3Li$ with equimolar of $AlCl_3$ yielded the aluminum dichlorides and the reduction with an excess of $LiAlH_4$ in diethyl ether afforded the intramolecular stabilized aryl aluminum dihydrides $2\text{-}(Et_2NCH_2)\text{-}6\text{-}MeC_6H_3AlH_2$ (**19**) and $2,6\text{-}(Et_2NCH_2)_2C_6H_3AlH_2$ (**20**), respectively, in moderate yields. The dichlorides were not isolated and characterized but directly reduced *in situ* to yield **19** and **20**. The similar aluminum dichlorides $2,6\text{-}(Me_2NCH_2)_2C_6H_3AlCl_2$ and 2-

$(Me_2NCH_2)C_6H_4AlCl_2$ have been prepared in an analogous way.[8, 59a] The dihydrides **19** and **20** have been characterized by ^1H and ^{13}C NMR, EI–MS spectroscopy as well as elemental analysis. The EI-MS spectra of **19** and **20** show the peak of the highest mass corresponding to the (M^+ - H) fragments, indicating both compounds are monomeric in the gas phase. The ^1H NMR spectra of **19** and **20** both show broad hydride resonances, characteristic for aluminum hydrides. Compound **20** might also be monomeric in the solid state like the structurally characterized compound 2,6-$(Me_2NCH_2)_2C_6H_3AlH_2$.[8]

2.2.2 Synthesis of aryl aluminum chalcogenides

Reactions of **19** and **20** with selenium at 80 °C afforded the first examples of arylaluminum selenides $\{[2-(Et_2NCH_2)-6-MeC_6H_3]AlSe\}_2$ (**21**) and $\{[2,6-(Et_2NCH_2)_2C_6H_3]AlSe\}_2$ (**22**) in good yields, respectively. We have briefly mentioned the mechanism of this type of reaction in section 2.1.9. The isolation of an aluminum SeH compound $LAl(SeH)_2$ (L = $HC[C(Me)N(Ar)]_2$, Ar = 2,6-*i*-$Pr_2C_6H_3$) (section 2.3) suggests that this reaction proceeds through an aryl Al–SeH intermediate. It was supposed that the coordination of a Se_2 unit to the aluminum atom forms an hypervalent aluminum center[61] and the activated Se_2 unit is concertedly reduced by the two hydride ligands to yield $ArAl(SeH)_2$, which reacts immediately with another molecule of $ArAlH_2$ to eliminate hydrogen (Scheme 7). When two equivalents of selenium were used for the reaction, only half of the selenium was consumed. This observation indicates that in this case the reaction of $ArAl(SeH)_2$ with $ArAlH_2$ is much faster. In contrast, when a very bulky chelating group L is used, the reaction of $LAl(SeH)_2$ with $LAlH_2$ is markedly slowed down due to the steric effect of the ligand. Unfortunately, we were unable to monitor this reaction by NMR spectroscopy due to its heterogeneous nature. Reaction of **2** with tellurium in refluxing toluene gave an aryl aluminum telluride $\{[2,6-(Et_2NCH_2)_2C_6H_3]AlTe\}_2$ (**23**) in good yield. The mechanism might be similar to the reaction of the hydrides with selenium. Compounds **21** and **22** are inert to donor reagents such as phosphanes, pyridine and tmeda [$(Me_2NCH_2)_2$] and are only poorly soluble in toluene, THF and DME, and have a limited solubility in $CHCl_3$.

Scheme 7

$$ArAlH_2 \xrightarrow{2\ Se} ArAl(SeH)_2 \xrightarrow[-\ 2H_2]{ArAlH_2} (ArAlSe)_2$$

Ar = 2-(Et_2NCH_2)-6-MeC_6H_3 (**21**), 2,6-$(Et_2NCH_2)_2C_6H_3$ (**22**)

2.2.3 Characterization of 21 - 23 and X-ray structures of 21·C_7H_8 and 23

The three compounds were fully characterized by multinuclear NMR spectroscopy, EI mass spectra and elemental analysis. The MS spectra of the compounds **21 - 23** show the molecular ion peaks of the dimers. The NMR spectra give the expected resonances. In order to elucidate the role of the NEt_2 donors, single crystal X-ray structural determinations of compounds **21** and **23** were carried out. Single crystals suitable for X-ray crystal studies of **21** and **23** were obtained from toluene at -20 °C and room temperature, respectively. Compound **21** crystallizes as a dimer with a crystallographically imposed inversion center in the solid state (Figure 9). The NEt_2 arms are coordinated to the aluminum atoms with a Al-N distance of 2.052(3) Å, which is in accordance with that of compound $(Me_2NCH_2)C_6H_4AlCl_2$.[59b] The Se(1)-Al(1) and Se(1)-Al(1A) distances differ in length (ca 0.014 Å) probably due to different steric effects at the two sides of the aryl ligands. They are slightly longer that those of the previously described dimeric compound $\{[N(SiMe_3)C(Ph)C(SiMe_3)_2]AlSe\}_2$ (**16**, average 2.35 Å). The internal angle Al(1)-Se-Al(1A) is acute (77.52(4)°) is close to that of $\{[N(SiMe_3)C(Ph)C(SiMe_3)_2]AlSe\}_2$ (**16**).

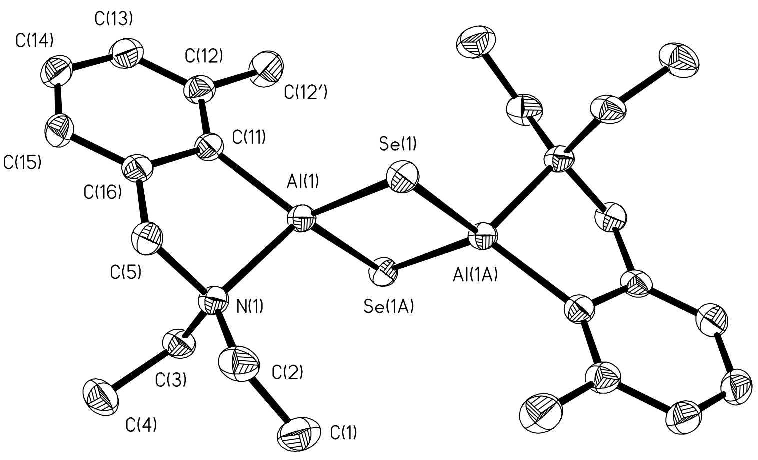


Figure 9. ORTEP drawing of **21** (50 % probability). Solvent C_7H_8 and hydrogen atoms have been omitted for clarity. Selected bond length (Å) and angles (deg) for two independent molecules in the unit cell: Se(1)-Al(1A) 2.352(7), Se(1)-Al(1) 2.366(4), Al(1)-C(11) 1.960(3), Al(1)-N(1) 2.052 (3); Al(1)-Se(1)-Al(1A) 77.52(4), C(11)-Al(1)-N(1) 86.79(12), C(11)-Al(1)-Se(1) 119.58 (12), C(11)-Al(1)-Se(1A) 122.99(11), N(1)-Al(1)-Se(1) 108.70, N(1)-Al(1)-Se(1A) 115.58(8), Se(1)-Al(1)-Se(1A) 102.48(4), C(11)-Al(1)-Al(1A) 146.00(11).

Compound **23** crystallizes in the monoclinic space group $P2_1/c$, as a centrosymmetric dimer (Figure 10). The most interesting structural feature is that only one arm of the two NEt_2 sites of both aryl ligands is coordinated to one aluminum atom and the other arm is dangling freely. In contrast, the ^1H and ^{13}C NMR spectra show only one set of signals for the Et_2NCH_2 groups, it can be assumed that in solution a rapid exchange of coordination and dissociation of the two NEt_2 groups takes place. Due to the poor solubility of these compounds we were not able to perform low temperature NMR studies. A similar behavior has already been observed with the dimeric gallium compound $(2,6\text{-}(NMe_2CH_2)_2C_6H_3GaPSiPh_3)_2$.[62]

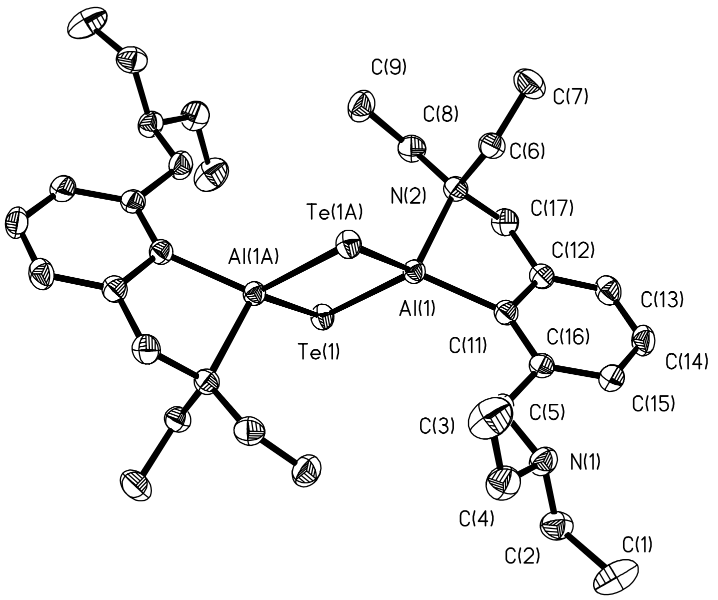


Figure 10. ORTEP drawing of **23** (50 % probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for two independent molecules in the unit cell: Te(1)-Al(1) 2.588(7), Te(1)-Al(1A) 2.581(8), Al(1)-C(11) 1.976(3), Al(1)-N(2) 2.054(2), Al(1)-Te(1)-Al(1A) 76.30(3), C(11)-Al(1)-N(2) 86.74(9), C(11)-Al(1)-Te(1A) 122.62(8), N(2)-Al(1)-Te(1A) 113.80(6), C(11)-Al(1)-Te(1) 119.59(7), N(2)-Al(1)-Te(1) 109.22(6), Te(1)-Al(1)-Te(1A) 103.70(3).

Compound **23** is the third structurally characterized organoaluminum telluride with formula $(RAlTe)_n$, the others are $(Cp^*AlTe)_4$ ($Cp^* = C_5Me_5$)[15] and $\{[N(SiMe_3)C(Ph)C(SiMe_3)_2]AlTe\}_2$ (**17**). The Te(1)-Al(1) (2.588(7) Å) and Te(1)-Al(1A) (2.581(8) Å) distances are only marginally different from each other. They are shorter than those of the $(Cp^*AlTe)_4$ (2.688 to 2.750 Å) due to the lower coordination number of the Te atom in compound **23**, and only slightly longer than those in compound **17** (2.562 to 2.577 Å). The Al(1)-C(11) distance (1.976(3) Å) is only slightly longer than that of compound **21** (1.960 Å), and both are in the range of those reported for $[(Me_2NCH_2)C_6H_4]AlCl_2{\cdot}THF$ (1.987 Å) and dimeric $\{[(Me_2NCH_2)C_6H_4]AlCl_2\}_2$ (1.941 Å).[59b] The Te-Al-Te (103.70(3)°) and Al-

Te-Al (76.30(3)°) angles are quite similar to those of dimeric **17** (103.12(4)°, 76.88(4)°) even though the Al_2Te_2 core binds to quite different ligands in the two compounds. In addition, the angles of the Al_2Te_2 unit are also nearly equal to those of Al_2Se_2 in compound **21** (102.48(4)°, 77.52(4)°) and $\{[N(SiMe_3)C(Ph)C(SiMe_3)_2]AlSe\}_2$ (**16**) (average 102.4°, 77.6°) despite the longer Al-Te distances.

The result of the synthesis of compounds **22** and **23** indicates that the dimeric form with one dangling NEt_2 group is energetically favored in comparison to the corresponding monomeric species with two chelating arrangements at the aluminum atom. With the bulkier aryl ligand 2,6-[(*t*-Bu)(Me)$NCH_2]_2C_6H_3$, a dimer was also obtained (according to the mass spectrum of the compound {2,6-[(*t*-Bu)(Me)$NCH_2]_2C_6H_3AlSe\}_2$ (**c**)). The ^{1}H NMR spectrum shows broad singlets for the *t*-Bu and Me protons, indicating that the bulky substituents at the nitrogen atoms are responsible for the slower exchange (coordination and dissociation) on the NMR time scale. The dimeric compounds **21** - **23** as well as compounds $\{[N(SiMe_3)C(Ph)C(SiMe_3)_2]AlE\}_2$ (E = Se (**16**), Te (**17**)) are thermally quite stable systems. They do not dissociate in polar solvents (THF, DME), even under reflux conditions. In addition, strong donors such as pyridine, TMEDA or phosphanes have no effect on the dissociation of the dimer. The utilization of the bulky bidentate ligand $HC[(CMe)(NAr)]_2$ (Ar = 2,6-*i*-$Pr_2C_6H_3$) unexpectedly led to the isolation of the first example of an aluminum SeH compound. This compound will be discussed in detail in the following section.

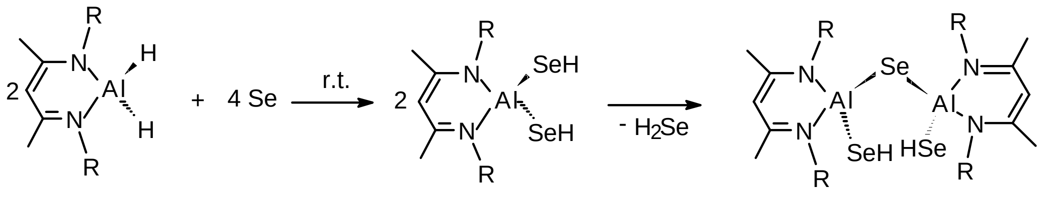
2.3 The Chemistry of *β*-diketiminato ligands

The β-diketonate ligands have long held an important place in coordination chemistry, the acetylacetonate (acac) and the conjugate base of dibenzoylmethane (dbzm), among many others, being the most widely used.[63] The isoelectronic *β*-diketiminato ligands (NCCCN backbone) have received scant attention, although their potential should be considerable, not only because the groups on the nitrogen atom on the ligand backbone may be varied. In the following sections, aluminum compounds with bulky *β*-diketiminato ligands are described.

2.3.1 Synthesis of aluminum hydride LAlH$_2$ (24) and chalcogenides (25, 26)

Reaction of the *β*-diketimine LH (L = N(Ar)C(Me)CHC(Me)N(Ar), Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$)[64] with AlH$_3$·NMe$_3$ at room temperature in *n*-hexane led in high yield to the corresponding dihydride LAlH$_2$ (**24**). The IR spectrum shows typical asymmetric and symmetric Al-H absorptions[8] at 1832 and 1795 cm^{-1}, and the mass spectrum gives the peak of highest mass for [M^+–H], indicating the formation of monomeric dihydride (**24**). Compound **24** is related to the [(*i*-Pr)$_2$ATI]AlH$_2$ (ATI = 2-aminotroponiminate) with a monomeric structure in the solid state.[9] Compound **24** reacted smoothly with two equivalents of elemental selenium at room temperature to afford the bis(hydroselenide) LAl(SeH)$_2$ (**25**) in medium yield. It is noteworthy that **25** was also formed when only one equivalent of Se was used for the reaction. **25** has been found unstable in solution over a longer period of time (*n*-hexane, THF) at room temperature and slowly eliminates H$_2$Se to give orange L(HSe)AlSeAl(SeH)L (**26**) (Scheme 8). Compound **26** has also been obtained by the reaction of **24** with two equivalents of Se at 60 °C.

Scheme 8



24 **25** **26**

Compounds **25** and **26** have been characterized by multinuclear NMR spectroscopy, mass spectra as well as elemental analyses. The ^{1}H NMR spectra of **25** and **26** both show high field singlets at δ -2.82 and -2.83 ppm, respectively, which can be assigned to SeH.[65] The IR spectra also give weak SeH stretching frequencies at 2318 cm^{-1} for **25** and at 2276 and 2292 cm^{-1} for **26**, respectively.[66] The ^{1}H NMR spectrum of **26** shows two sets of singlets for the C*H*Me$_2$ protons, indicating C_s symmetry of the molecule. The ^{77}Se NMR spectrum of **26** gives two broad signals (δ –341 and –535 ppm) in an approximate intensity ratio of 2 : 1, the former can be assigned to SeH (A ^{77}Se NMR spectrum of **25** could not be obtained because of the decomposition of the compound in solution).

In contrast, the reaction of **24** with metallic tellurium needed more vigorous condition. No reaction was observed at room temperature. However, when the mixture was refluxed in toluene for several hours, a green solution was obtained. After work-up green needles could be isolated which were characterized by EI-MS spectrum to be dimeric (LAlTe)$_2$ (**d**)

$$\underset{\mathbf{24}}{\mathrm{LAlH_2}} \quad + \quad \mathrm{Te} \;\rightarrow\; \underset{\mathbf{d}}{\mathrm{(LAlTe)_2}} \quad + \quad \mathrm{H_2}$$

2.3.2 Molecular structures of 25 and 26

The molecular structures of **25** and **26** were determined by single crystal X-ray structural analysis. Pale yellow crystals of **25** suitable for single crystal X-ray structural analysis were grown from *n*-hexane at -30 °C. Unfortunately, the quality of the crystal structure did not allow to locate the hydrogen atoms on the selenium atoms. Nevertheless, the presence of terminal SeH groups was established unequivocally by IR and ^{1}H NMR spectra. The molecular structure of **25** is shown in Figure 11 with important bond lengths and angles. The Al-Se bond lengths (2.340(3) and 2.331(3) Å) are in accordance with those of the dimeric $\{[N(SiMe_3)C(Ph)C(SiMe_3)_2]AlSe\}_2$ (**16**) (average 2.35 Å). The Al-N bond distances of **25** are equal and the Al atom resides slightly out of the ligand NCCCN plane.

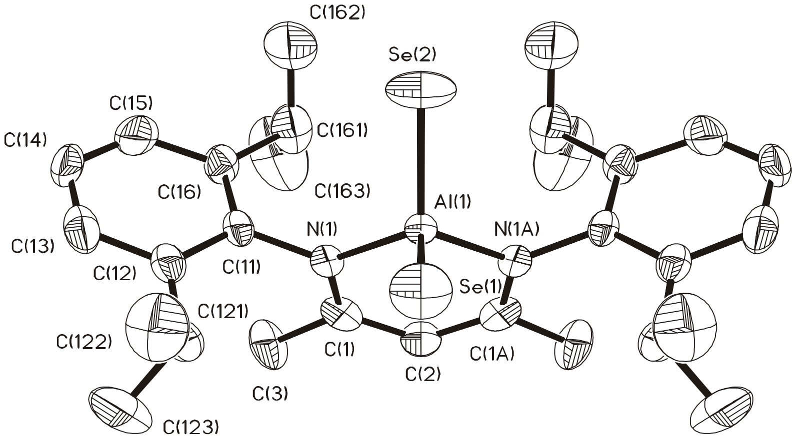


Figure 11. ORTEP drawing of **25** (50 % probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å)and angles (deg): Al(1)–N(1) 1.899(6), Al(1)–N(1A) 1.899(6), Al(1)–Se(2) 2.331(3), Al(1)–Se(1) 2.340(3); N(1)–Al(1)–N(1A) 97.1(4), N(1)–Al(1)–Se(2) 113.5(2), N(1A)–Al(1)–Se(2) 113.5(2), N(1)–Al(1)–Se(1) 114.8(2), N(1A)–Al(1)–Se(1) 114.8(2), Se(2)–Al(1)–Se(1) 103.73(12).

Compound **26** crystallizes in the monoclinic space group $P2_1/n$. The structure is shown in Figure 12 with selected bond lengths and angles. The bridging Al-Se bond distances (2.326(2) and 2.333(2) Å) of the Al-Se-Al unit are among the shortest reported so far. They are slightly shorter than the Al-SeH bonds (2.375(2) and 2.371(2) Å) due to the more highly polarized Al-Se-Al bonds. The internal angle at Se(2) (116.77(7)°) is much more open compared to those of the dimeric Al_2Se_2 core compounds (average 78°) and is only slightly larger than that of $\{[(SiMe_3)_2CH]_2Al\}_2Se$ (114.71°)[67] probably due to the bulky nature of the ligand L. The hydrogen atoms could be located at the selenium atoms (the Se-H distances are ca. 1.50 Å), free refinement, however, shortens these distances (as expected for the hydrogen atoms on heavy atoms). There is very little information in the literature concerning Se-H bond. The computed Se-H bond lengths (with the MINI-1, 3-21-G/LWD and STO-3G basis sets) for organic RSeH compounds range from 1.42 to 1.57 Å.[68] Compounds **25** and **26** are well separated monomers in the solid state, which excludes any intermolecular hydrogen bonds, and represent the first structurally characterized organometallic compounds which contain covalent metal-SeH units.

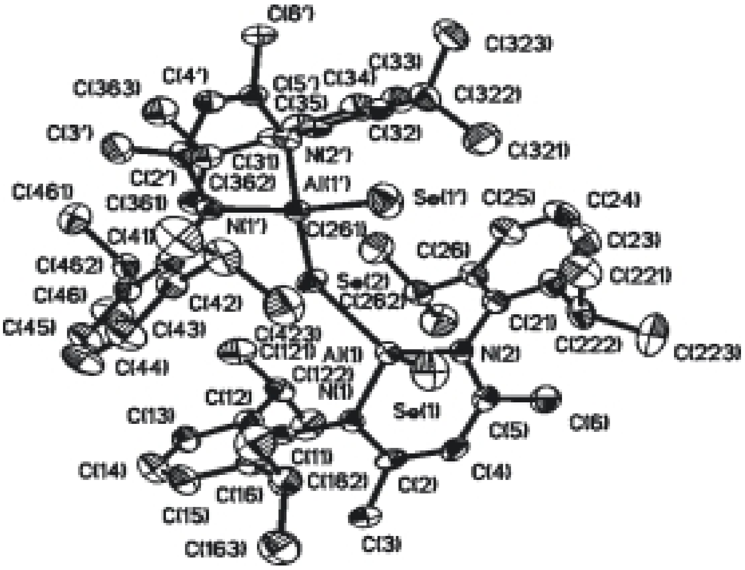


Figure 12. ORTEP drawing of **26** (50% probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1′)–N(2′) 1.912, Al(1′)–N(1′) 1.918(5), Al(1′)–Se(2) 2.326(2), Al(1′)–Se(1′) 2.375(2), Al(1)–N(2) 1.906(5), Al(1)–N(1) 1.906(5), Al(1)–Se(2) 2.333(2), Al(1)–Se(1) 2.371(2); N(1′)–Al(1′)–N(2′) 96.7(2), N(2′)–Al(1′)–Se(2) 108.2(2), N(1′)–Al(1′)–Se(1′) 109.5(2), N(1′)–Al(1′)–Se(1′) 106.0(2), Se(2)–Al(1′)–Se(1′) 117.29(9), N(2)–Al(1)–N(1) 97.3(2), N(2)–Al(1)–Se(2) 115.4(2), N(1)–Al(1)–Se(2) 108.5(2), N(2)–Al(1)–Se(1) 107.0(2), N(1)–Al(1)–Se(1) 107.5(2), Se(2)–Al(1)–Se(1) 118.69(8), Al(1)–Se(2)–Al(1′) 116.77(7).

The X-ray structural analyses of **25** and **26** disclose the lability of the Se-H bonds[69] and provide the direct evidence that the tendency of forming hydrogen bonds is much lower than in the case of the lighter congeners (S, O). The stabilization of **25** and **26** might be attributed to the bulky chelating ligand. Due to the acidic nature of the SeH protons, compounds **25** and **26** may be useful synthons for preparing Se bridged heterometallic compounds. Moreover, the synthesis of **25** and **26** also suggests that the selenium atom can insert very easily into the Al-H bond.

Why the reaction of $LAlH_2$ with one equivalent of selenium only yields **25** instead of LAl(H)SeH is presently not clear. It is difficult to monitor the reaction by NMR spectroscopy due to its heterogeneous nature. However, it was supposed that a Se_2 unit is involved in this reaction. It has been argued[70c] that the reactions of diorgano-diselenides with $AlH_3 \cdot NMe_3$ proceed via initial complexation of a selenium species creating a hypervalent aluminum center.[70a, 70b] Following this argument the reaction proceeds via coordination of a Se_2 unit to the aluminum center, followed by a concerted reduction of the activated Se_2 by the two hydride ligands to cleave the Se_2 unit. This assumption can well explain our experimental results that the product is always **25** at room temperature independently of the amount of selenium used for this reaction. The conversion of **25** to **26** clearly indicates that intermolecular elimination of H_2Se is more favored than the intramolecular one.

2.3.3 Aluminum diiodide $LAlI_2$ (27) (L = HC[(CMe)(NAr)]$_2$, Ar = 2, 6-*i*-$Pr_2C_6H_3$)

The dimethyl compound $LAlMe_2$ has been easily prepared by the condensation reaction of LH with equivalent amount of $AlMe_3$ at room temperature.[64] Reaction of the dimethyl compound with 2 equivalents of I_2 proceeded under mild conditions to afford the diiodide $LAlI_2$ (**27**) in high yield.

$$[HC(CMeNAr)_2]AlMe_2 + 2\ I_2 \rightarrow \underset{\textbf{27}}{[HC(CMeNAr)_2]AlI_2} + 2\ MeI$$

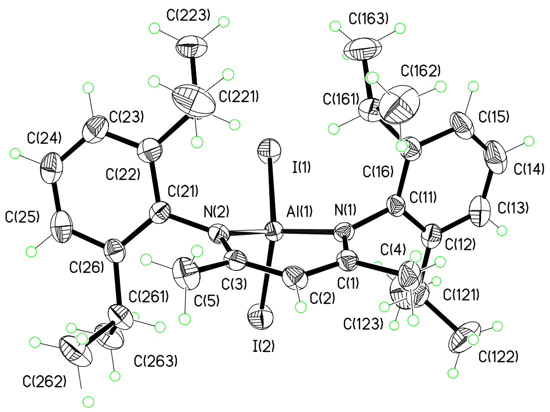


Figure 13. ORTEP drawing of **27** (50 % probability). Selected bond lengths (Å) and angles (deg): Al(1)-N(1) 1.872(2), Al(1)-N(2) 1.892(3), Al(1)-I(1) 2.5010(12), Al(1)-I(2) 2.541(2); N(1)-Al(1)-N(2) 99.93(10), N(1)-Al(1)-I(1) 111.31(7), N(2)-Al(1)-I(1) 116.89(8), N(1)-Al(1)-I(2) 112.66(7), N(2)-Al(1)-I(2) 107.53(8), I(1)-Al(1)-I(2) 108.40(5).

Compound **27** has been characterized by multinuclear NMR spectroscopy, EI-MS and elemental analysis. The EI mass spectrum shows the peak of the highest mass at (M^+ - I). The formation of **27** was finally confirmed by single crystal X-ray structural analysis, its structure is shown in Figure 13, followed by selected bond distances and angles. The aluminum atom is four coordinated and has a distorted tetrahedral environment. The Al-I distances (2.5010(12), 2.541(2)Å) lie in the range of the few known structurally characterized organoaluminum iodide compounds.[37] The Al-N bond lengths (1.872(2), 1.892(3)Å) are shorter than those of the corresponding dimethyl compound $LAlMe_2$.[64]

2.3.4 Reduction of $LAlI_2$ – synthesis of a monomeric Al(I) compound LAl (28)

Reduction of **27** with potassium for 3 days afforded the first example of a monomeric Al(I) species LAl (**28**) stable at room temperature in ca. 21 % yield.

$$\underset{\textbf{27}}{\{[HC(CMeNAr)_2]AlI_2\}} + 2\,K \rightarrow \underset{\textbf{28}}{\{[HC(CMeNAr)_2]Al\}} + 2\,KI$$

Compound **28** crystallized as orange-red crystals from toluene and is soluble in aromatic solvents but only little soluble in aliphatic solvents. It is stable at room temperature under an inert atmosphere, however significant decomposition has been observed above 150 °C. **28** has been characterized by ^{1}H and ^{13}C NMR spectroscopy, EI-mass spectroscopy, elemental analysis, and a single crystal X-ray structural analysis. The NMR spectra of **28** show the expected pattern, which are different from those of the colorless dihydride {$[HC(CMeNAr)_2]AlH_2$} (**24**). Single crystals suitable for X-ray structural analysis were obtained from toluene at -30 °C. It crystallizes in the monoclinic space group $P2_1/n$. The structure is shown in Figure 14 with selected bond lengths and angles. It consists of well separated {$[HC(CMeNAr)_2]Al$} monomers. No close contacts between Al and other atoms are present as indicated by the closest Al–H distance (*i*-Pr, 3.142 Å). As expected, the Al–N bond lengths (1.957(2) Å) are longer than those of the Al(III) compounds $[HC(CMeNAr)_2]AlMe_2$ (av 1.922 Å)[64] and $[HC(CMeNAr)_2]Al(SeH)_2$ (**25**) (av 1.899 Å). A similar lengthening has been noted for InC_6H_3-2,6-Trip$_2$ (Trip = 2,4,6-*i*-$Pr_3C_6H_2$) where the In-C distance is ca. 0.10 Å longer than that of the corresponding In(III) derivative.[71] Similarly, the In-N distance in monomeric In(I) tri(pyrazolyl)borates are up to ca. 0.20 Å longer than those in related In(III) derivatives.[72] Furthermore, the N-Al-N angle (89.86(8)°) in **28** is more acute than those of $[HC(CMeNAr)_2]AlMe_2$ (96.18(9)°)[64] and $[HC(CMeNAr)_2]Al(SeH)_2$ (**25**) (97.1(4)°). The lengthening of the N-Al bonds and the nearly perpendicular N-Al-N angle indicate that two 3p orbitals on the aluminum are essentially involved in the bonding to the two nitrogen atoms. It has been argued that Al-N bonds in aluminum(III) amide derivatives are largely ionic, which usually leads to relatively short Al-N distances due to the Lewis acidic Al(III) centers.[73] The lengthening of the Al-N bonds in **28** also indicates that these bonds are more covalent than those of the Al(III) derivatives and the Al(I) center is much less acidic. It is noteworthy that in **28** the Al atom and the ligand backbone (NCCCN) form an essentially planar six-membered ring, which is in contrast to the Al(III) compounds $[HC(CMeNAr)_2]AlMe_2$ and $[HC(CMeNAr)_2]Al(SeH)_2$ (**25**), in which the Al atoms are located outside the planar ligand backbone.

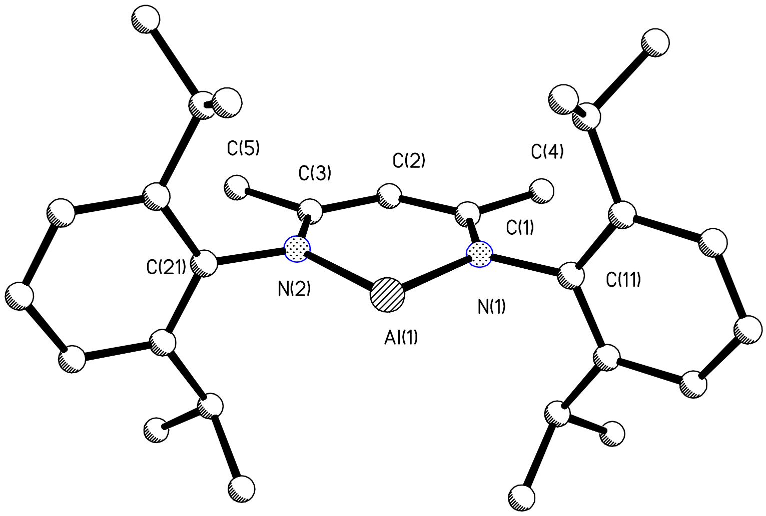


Figure 14. Molecular structure of **28** in the crystal. The hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)-N(1) 1.957(2), Al(1)–N(2) 1.957(2), N(1)–C(1) 1.340(3), N(2)–C(3) 1.342(3), C(1)–C(2) 1.391(3), C(2)–C(3) 1.391(3); N(1)–Al(1)–N(2) 89.86(8), C(1)–N(1)–Al(1) 128.87(15), C(1)–C(2)–C(3) 126.8(2), N(1)–C(1)–C(2) 122.8 (2).

A further noticeable aspect of the structure of **28** is the coordination number two at the Al center. Compounds with three- and four-coordinated aluminum centers are well established,[74] however no compounds having aluminum atoms with a two coordinated environment at ambient conditions are reported so far. The unique two-coordinated nature of the Al atom in **28** is undoubtedly due to the protection rendered by the aryl groups and the presence of a non-bonding lone pair of electrons at the Al atom.

A preliminary insight into the peculiarities of the aluminum heterocycle has been gained from *ab initio* calculations,[75] analyzing the Laplacian of electronic density[76] within the plane.

First of all, it is noteworthy that a lone pair located at the metal atom is present[77] forming a quasi-trigonal-planar arrangement around the Al atom with the two Al-N bonds, which allows to argue that the electrons originating from s^2 configuration of the Al(I) atom are stereochemically active, leading to a *sp*-like hybrid. In this connection, one may assimilate the off-cycle side of the aluminum(I) atom to a Lewis base. At the same time, the charge deficiency close to the Al atom in the semi-plane of the cycle can be described as a Lewis acid type of behavior.

In summary, we have prepared and structurally characterized the first example of a monomeric Al(I) compound stable at room temperature. The existence of a non-bonding lone pair of electrons at aluminum indicates a singlet carbene-like character of the aluminum atom. The other reported group 13 carbene is the anionic $[CHN(t\text{-}Bu)]_2Ga^-$.[78] Compound **28** could be used in carbene type reactions and as a Lewis base as well as a reducing reagent, which may result in a broad and interesting chemistry.

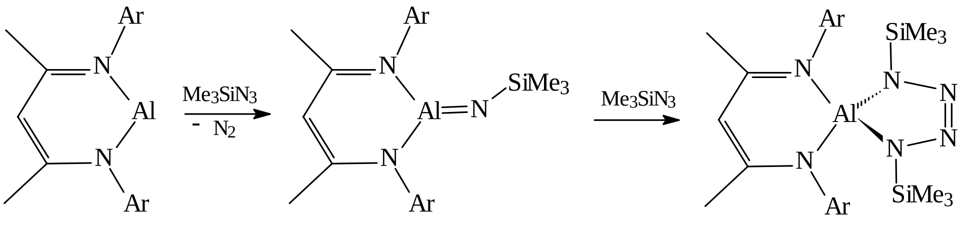
2.3.5 Reaction of LAl (28) with bulky organic azides

The reactions of $[Cp^*Al]_4$ ($Cp^* = C_5Me_5$) with various organic azides at elevated temperatures have been reported to yield four-membered Al_2N_2 ring systems.[23] Being interested in binary Al-N systems, we began to explore the reactivity of compound **28** with selected organic azides. Reaction of **28** with 2 equivalents of trimethylsilyl azide $SiMe_3N_3$ at low temperatures (-78 °C to room temperature) afforded the first Group 13 metalloid MN_4 ring system $\{HC[(CMe)(NAr)]_2\}Al[(NSiMe_3)_2N_2]$ (**29**) (Scheme 9).

The higher reactivity of **28** compared to $[Cp^*Al]_4$ toward the azide at low temperature may be attributed to the monomeric nature of **28**. The formation of an aluminum containing tetrazole **29** is particularly interesting since the heavier Group 14 elements containing tetrazoles were prepared by [2+3] cycloaddition reactions of $R_2M{=}NR'$ (M = Si, Sn; R, R′ =

organic group) unit with organic azides.[79] Similarly, we therefore assume that the reaction of **28** with Me_3SiN_3 proceeds through transient '{HC[(CMe)(NAr)]$_2$]Al=NSiMe$_3$}', although stable compounds containing an Al=N unit have not yet been reported (Scheme 9). When only one equivalent of Me_3SiN_3 was employed, the sole isolated products were **29** and unreacted **28**, indicating that the transient '{HC[(CMe)(NAr)]$_2$]Al=NSiMe$_3$}' is highly reactive. No dimerization of the intermediate has been observed due to the bulky chelating *β*-diketoiminato ligand which obviously prevents association.

Scheme 9



28 **29**

Compound **29** has been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, EI mass spectrum, and elemental analysis. The EI mass spectrum shows a peak of highest mass which is consistent with the formulation as **29**. The NMR spectra all give two distinct singlets for the $SiMe_3$ groups, indicating the two groups in different environments. This is also reflected from the ^{1}H NMR pattern of the *β*-diketiminato ligand, in which two sets of signals for the *γ*-C*H* and four doublets for C*H*Me$_2$ protons are observed. In order to confirm the bonding in the AlN_4 ring system, it was important to perform single crystal X-ray structural analysis. Yellow crystals of **29** suitable for X-ray analysis were obtained from toluene at -30 °C. **29** crystallizes in the monoclinic space group $P2_1/n$. Its structure is shown in Figure 15 with selected bond distances and angles. The aluminum atom is coordinated by four nitrogen atoms and connects the two rings in a distorted tetrahedral arrangement. The Al(1)-N(5) (1.896(2) Å) and Al(1)-N(6) (1.8997(14) Å) distances fall within the range of those in other *β*-diketoiminato aluminum derivatives. The Al(1)-N(4) distance (1.8152(15) Å) is shorter (ca. 0.036 Å) than that of Al(1)-N(1) (1.851(2) Å), which is in accordance with the NMR signals for the $SiMe_3$ nuclei, indicating the solid state structure of **29** is maintained in solution. Similar short Al-N bond lengths have only been found in three coordinated aluminum amide complexes[80] and a few four coordinated aluminum amide dihalides.[81] However, they are unusual for the very crowded molecule **29**. The shortening of the Al-N bond length and the N(1)-Al(1)-N(4) angle (87.15(7)°) are indications of increased ionic interactions between Al and the N_4 unit. The N(2)-N(3) bond length (1.263(2) Å) is consistent with a N=N double bond. The N(1)-N(2) and N(3)-N(4) (1.414(2) Å) bond lengths are slightly shorter than a N-N single bond (ca 1.50 Å).

It is interesting to note that the five-membered AlN_4 ring is essentially planar and that the geometries at N(1) and N(4) are both trigonal planar (sums of angles 360.0° and 359.7°, respectively). This planar arrangement of the AlN_4 ring may be comparable to Group 13 element diazabutadiene complexes which feature planar C_2N_2M (M = B, Ga) five-membered rings. In the latter case, a 6π-electron system for the C_2N_2M ring is suggested to explain the bonding situation of the diazabutadiene derivatives.[82]

Compound **29** represents the first structurally characterized Group 13 element MN_4 system although various binary M-N (M = Group 13 element) rings have been reported, which show unique structural features.[83] Boron tetrazoles have been reported previously, but not structurally characterized.[84] The synthesis of **29** under mild conditions indicates that **28** is very reactive toward organic azides.

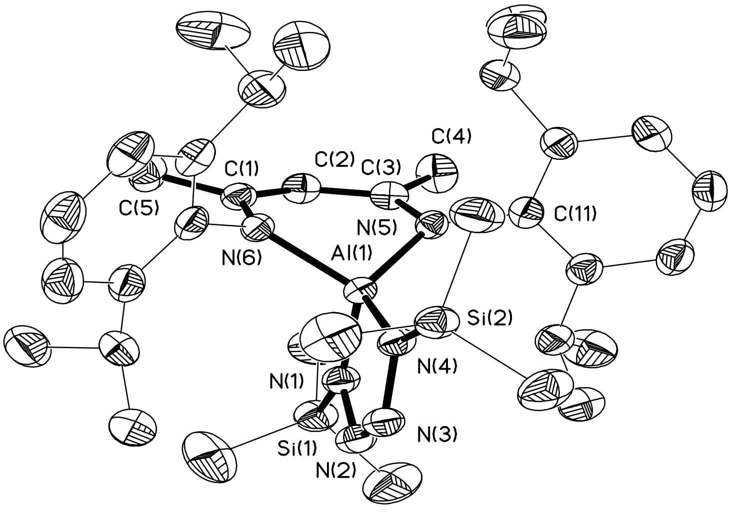
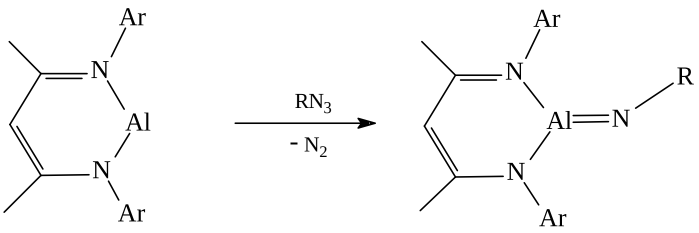


Figure 15. ORTEP drawing of **29** (50 % probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)-N(1) 1.851(2), Al(1)-N(4) 1.8152(15), Al(1)-N(5) 1.896(2), Al(1)-N(6) 1.8997(14), N(1)-N(2) 1.414(2), N(2)-N(3) 1.263(2), N(3)-N(4) 1.414(2), Si(1)-N(1) 1.749(2); N(1)-Al(1)-N(4) 87.15(7), N(1)-Al(1)-N(5) 117.01(7), N(2)-N(1)-Al(1) 109.10(11), N(2)-N(1)-Si(1) 108.20(11), N(2)-N(3)-N(4) 116.44(14), N(3)-N(2)-N(1) 116.68(15), N(4)-Al(1)-N(6) 117.70(7), N(5)-Al(1)-N(6) 96.50(6), Si(1)-N(1)-Al(1) 142.66(9).

Indeed, reactions of **28** with the extremely bulky aryl azide 2,6-$Trip_2C_6H_3N_3$ (Trip = 2, 4, 6-*i*-$Pr_3C_6H_2$)[85] and the silyl azide Ph_3SiN_3 [23b] afforded $LAlNC_6H_3$-2,6-$Trip_2$ (**30**) and $LAlNSiPh_3$ (**31**) in good yields, respectively. Both compounds are soluble in aromatic solvents CH_2Cl_2, and THF, but sparingly soluble in hydrocarbon solvents. The compounds have been characterized by EI-MS, IR and multinuclear NMR spectra. The EI-MS spectra for both compounds show the molecular ions which is consistent with the formulations of **30** and **31** as monomers. The NMR spectra of **30** suggest a highly asymmetric molecule which may arise from steric factors. Unfortunately attempts to grow single crystals of the two interesting compounds in various solvents (toluene, benzene, CH_2Cl_2, $CHCl_3$, THF) at different temperatures were unsuccessful to date.

Scheme 10



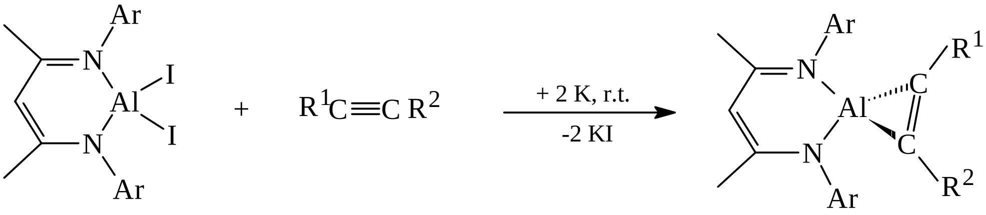
R = 2,6-$Trip_2C_6H_3$ (Trip = 2,4,6-*i*-$Pr_3C_6H_2$) **30**

R = $SiPh_3$ **31**

2.3.6 Reductive coupling reaction of $LAlI_2$ (27) in the presence of alkynes

The compound $LAlI_2$ (**27**) is the first aluminum dihalide that can be reduced to a monomeric Al(I) compound at room temperature. We benefitted from this precursor to prepare some unique species by facile alkali metal reduction which otherwise are not easily available. Reduction of **27** with potassium in the presence of bis(trimethylsilyl)alkyne, diphenylalkyne and 1-phenyl-2-trimethylsilylalkyne at room temperature afforded the aluminum η^2-alkine complexes LAl[η^2-$C_2(SiMe_3)_2$] (**32**), LAl[η^2-C_2Ph_2] (**33**) and LAl[η^2-C(Ph)C($SiMe_3$)] (**34**) in modest yields, respectively (Scheme 11). Compound **32** was isolated as red-black crystals. It is soluble in hydrocarbon solvents and extremely air- and moisture-sensitive as indicated by the immediate color change from red black to yellow when crystalline **32** was exposed to air. Yellow crystals of **33** and orange crystals of **34** were obtained from toluene, they are only little soluble in *n*-hexane. Reductive coupling reactions in the presence of alkynes have been widely used for the preparation of various Group 4 metallocene alkine complexes[86] and have also been employed for trapping reactive silylene intermediates.[87] In order to gain insight into the possible reductive coupling mechanism, the straightforward reaction of the monomeric aluminum(I) compound **28** with bis(trimethylsilyl)alkyne was attempted. The reaction was carried out under the same conditions as the reductive coupling reaction, and after work-up only the starting materials were recovered. This result indicates that reductive coupling does not occur through a [1+2] cycloaddition of **28** with the alkyne. A different route involving in a stepwise reduction of **27** to generate an intermediate aluminum(II) species, which subsequently couples with alkynes, might be a plausible mechanism.

Scheme 11



27

$R^1 = R^2 = SiMe_3$ **32**

$R^1 = R^2 = Ph$ **33**

$R^1 = SiMe_3$, $R^2 = Ph$ **34**

Compounds **32** -**34** have been characterized by EI-mass, ^1H, ^{13}C NMR, and IR spectra. The EI-MS spectrum of **32** shows the (M^+ - $SiMe_3$) ion as the fragment with the highest mass, while those of **33**, **34** give the parent ions. The ^{13}C NMR spectrum of **32** shows a weak resonance at δ 228.5 ppm, corresponding to the coordinated C=C group. In the ^{13}C NMR spectrum of **33** the corresponding resonance appears at δ 177.2 ppm, and in that of **34** two resonances (δ 211.9, 187.2 ppm) for the carbon atoms of the coordinated C=C group were observed. The IR spectra for the three compounds all show a characteristic absorption band centering 1590 cm^{-1}, which could be assigned to the stretching frequencies of the coordinated C=C groups.

The variable temperature ^1H NMR investigations of **32** (193 - 373 K) show that **32** does not dissociate up to 373 K, indicating that the C=C moiety is strongly bonded to the aluminum atom of **32** and the Al-C-C ring is intact in toluene solution even at high temperature. This result suggests that the compound can be described as rather a metallocyclopreopene (Al(III)) than an aluminum alkyne complex (π complexation). The assumption is also supported by ESR studies of compounds **32** and **33,** in those spectra no signals were observed for both compounds. Furthermore the ^{27}Al NMR spectrum of **32** shows a resonance (90 ppm) in the range of those for four coordinated aluminum compounds. In contrast, the Al(I) compound **28** gives the most highly shieded singlet (590 ±40 ppm, $\nu_{1/2} \approx 30{,}000$ Hz) experimentally observed so far. The detailed explanation for this data is currently unavailable although the ^{27}Al NMR resonaces for monovalent aluminum compounds have been computed ranging from -170 to 850 ppm.

The UV spectra of the colored solution of compounds **32** and **33** in *n*-hexane show several maxima in the range of 240 to 400 nm. A maximum at 320 nm ($\varepsilon \approx 4000$ $M^{-1}cm^{-1}$) for **32** as well as a maximum at 340 ($\varepsilon \approx 3000$ $M^{-1}cm^{-1}$) for **33** disappears when the solutions are exposed to air. The absorptions might be due to electronic transitions within the Al-C-C three-membered ring system.

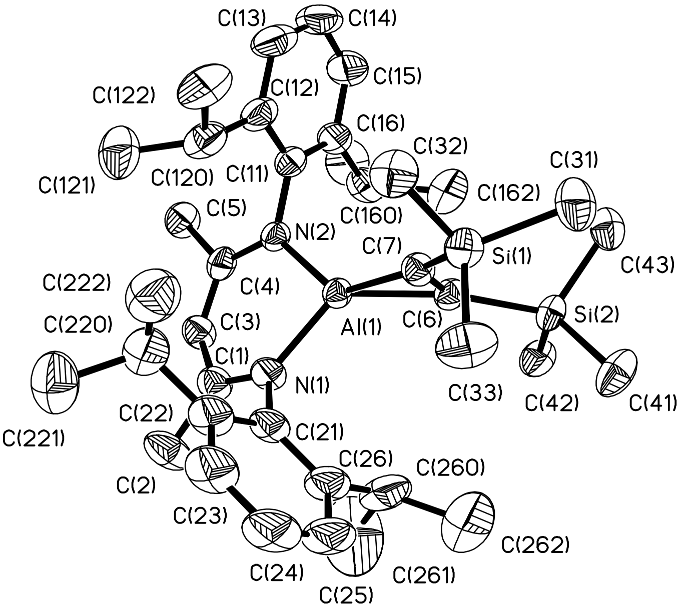


Figure 16. ORTEP drawing of **32** (50% thermal ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)-N(1) 1.889(2), Al(1)-N(2) 1.892(2), Al(1)-C(6) 1.899(3), Al(1)-C(7) 1.908(3), C(6)-C(7) 1.382(4); C(6)-Al(1)-C(7) 42.56(11), N(1)-Al(1)-N(2) 97.34, Al(1)-C(6)-C(7) 69.1(2), C(7)-C(6)-Si(2) 134.0(2), Al(1)-C(7)-C(6) 68.4(2), C(6)-C(7)-Si(1) 133.8(2).

Finally the structures of **32** and **33** were established unambiguously by single crystal X-ray structural analyses. The structures are shown in Figures 16 and 17 with important bond lengths and angles, respectively. The C(6)-C(7) bond length (1.382(4) Å) in **32** is consistent with a double bond character. The Al(1)-C(6) and Al(1)-C(7) distances (average 1.90 Å) are shorter than those of the corresponding dimethyl derivative $\{HC[(CMe)(NAr)]_2\}AlMe_2$ (average 1.95 Å)[64] and also much shorter than those of the aluminum alkynyl-bridging carbon distances (av 1.992 Å) in $[Ph_2Al(CCPh)]_2$[88a] and vinyl-bridging carbon distances (av 2.11 Å) in $\{i\text{-}Bu_2Al[(CHCH(t\text{-}Bu)]\}_2$.[88b] Similar short bond lengths have been found only in a few neutral organoaluminum compounds containing electron withdrawing as well as small groups.[89]. The angles C(6)-C(7)-Si(1) (133.8(2)°) and C(7)-C(6)-Si(2) (134.0(2)°) are comparable to those in η^2-silylalkyne Group 4 metallocene complexes.[86] The Al(1) atom resides outside of the β-diketiminato ligand backbone NCCCN (by 0.42 Å), the two fused planes (N(1)-Al(1)-N(2) and C(6)-Al(1)-C(7) (angle 93°) are arranged nearly perpendicular to each other. The C(6)-Al-C(7) angle (42.56(11)°) is very acute.

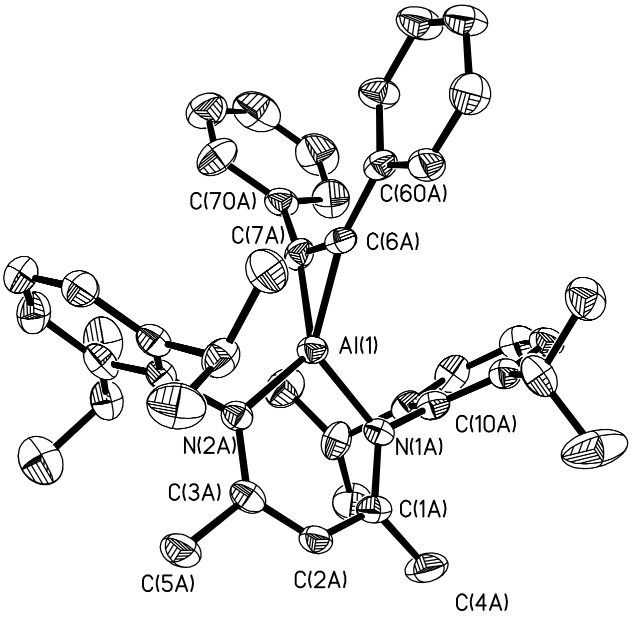


Figure 17. ORTEP drawing of **33** (50 % probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg) for one of the four independent molecules in the unit cell: Al(1)-N(1A) 1.885(3), Al(1)-N(2A) 1.875(4), Al(1)-C(6A) 1.889(4), Al(1)-C(7A) 1.894(3), C(6A)-C(7A) 1.356(5); C(6A)-Al(1)-C(7A) 42.02(14), C(7A)-C(6A)-Al(1) 69.2(2), C(6A)-C(7A)-Al(1) 68.80(19), N(2A)-Al(1)-N(1A) 97.03(13), Al(1)-C(6A)-C(60A) 160.0(2), Al(1)-C(7A)-C(70A) 160.9(3), C(6A)-C(7A)-C(70A) 129.8, C(7A)-C(6A)-C(60A) 130.4(3).

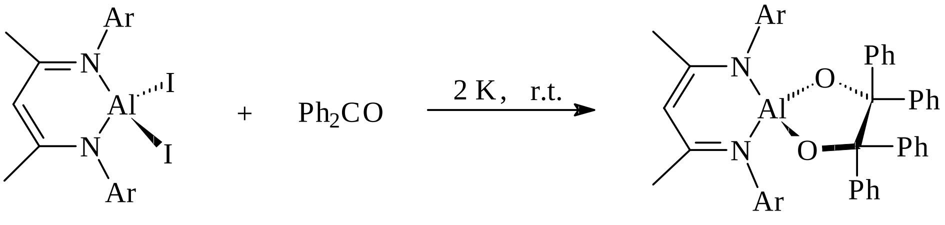
Compound **33** crystallizes in the monoclinic space group $P2_1$. The unit cell contains four molecules only marginally different in bond lengths and angles. Figure 17 shows one of the four independent molecules in the unit cell. The structure of **33** is similar to that of **32**. The Al(1)-C(6A) and Al(1)-C(7A) bond lengths are quite similar to those of **32**. The C(6A)-

C(7A) distances (1.356(5) Å) is slightly shorter than that of **32** (1.382(4) Å), consequently the C(6A)-Al(1)-C(7A) angle (42.02(14)°) is slightly smaller than that of **32** (42.56(12)°). The C(60A)-C(6A)-C(7A) and C(70A)-C(7A)-C(6A) angles (av 130°) are smaller than those of **32** (average 134°). We reason that compounds **32 - 34** should show high reactivities due to the highly strained three-membered C-C-Al ring, which is not only reactive but also makes the aluminum center accessible to other unsaturated molecules although the Al atom in this compound is four coordinated.

2.3.7 Reductive coupling reaction of $LAlI_2$ in the presence of Ph_2CO

Reduction of $LAlI_2$ (**27**) with potassium in the presence of benzophenone at room temperature unexpectedly afforded an aluminum pinacolate $LAl[O_2(CPh_2)_2]$ (**35**) despite of the fact that only a 1 : 1 molar ratio of $LAlI_2/Ph_2CO$ was employed. Coupling of two carbonyls has been well investigated with various reduction systems, in which either pinacols or alkenes (McMurry reaction) have been obtained depending on the reduction systems and carbonyls used.[90] Many examples of carbonyl coupling reactions have been demonstrated with electron-rich *d*-block metals, lanthanoides, and actinoides.[90] Organometallic compounds of early transition metals also have been used for reductive coupling of carbonyls in investigating the mechanism of carbonyl coupling and stereospecific carbonyl coupling reactions.[91] However, to the best of our knowledge the use of aluminum compounds for carbonyl coupling has not been reported to date. It is well known that benzophenone reacts with Na and K to form a stable radical anion (ketyl), which does not dimerize under normal conditions due to steric and electronic factors. It can be rationalized that the potassium ketyl formed reacts with **27** with concomitant potassium reduction to afford the η^2-ketone intermediate ($LAlOCPh_2$),[92] which is highly reactive and couples with another molecule of the ketone.

Scheme 12



27 **35**

Compound **35** has been characterized by NMR and EI-MS spectra, which are consistent with the proposed structure. The molecular array was finally established by single crystal X-ray structural analysis. The structure is shown in Figure 18 with selected bond distances and angles. The aluminum atom is four coordinated and acts as the center atom for the two fused rings. The Al-N distances (average 1.90 Å) are similar to those of LAl(SeH)$_2$ (**25**) (av 1.90 Å) and LAl[(NSiMe$_3$)$_2$N$_2$](**29**) (average 1.89 Å). The Al-O distances (av 1.73 Å) are among the shortest known Al-O distances (1.65 - 2.0 Å).[81] It is noteworthy that the C(6)-C(7) bond length (1.670(3) Å) is longer by 0.13 Å compared to normal C-C single bond distances (ca. 1.54 Å) due to the electronic and steric effects afforded by two phenyl groups on each carbon atom. The O(1)-Al(1)-O(2) angle (92.70(7)°) is the smallest among the internal angles of the five-membered AlOCCO cycle, consequently the Al-O-C angle (average 116 °) is larger than the average internal angle of a five-membered ring (108°). A smaller O-Al-O angle would increase the ionic character of the Al-O bonds.

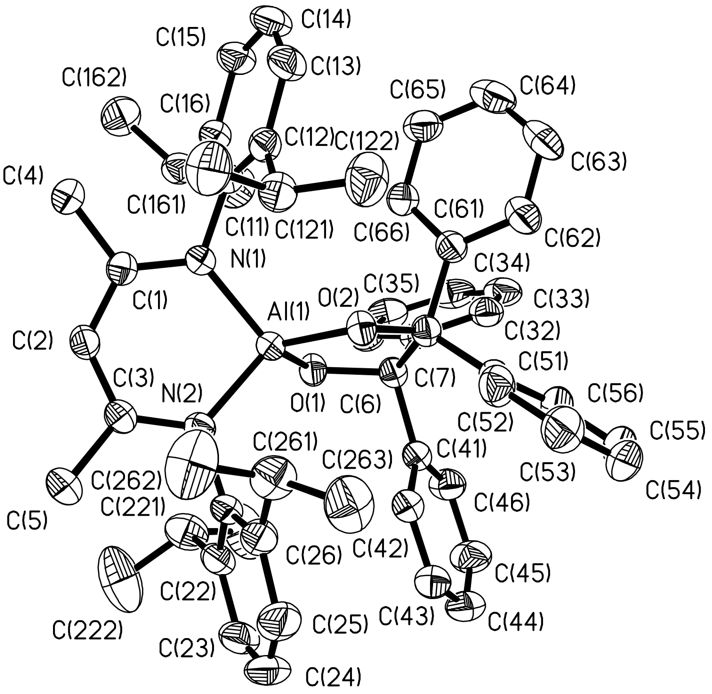


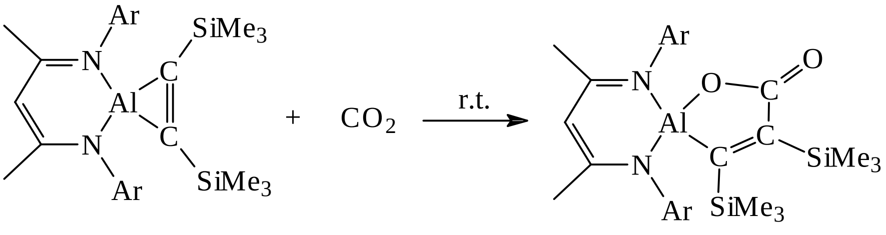
Figure 18. ORTEP drawing of **35** (50 % probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)-O(1) 1.7326(15), Al(1)-O(2) 1.7350(14), Al(1)-N(1) 1.8987(18), Al(1)-N(2) 1.9038(14), O(1)-C(6) 1.430(2), C(6)-C(7) 1.670(3); N(1)-Al(1)-N(2) 96.89(8), O(1)-Al(1)-O(2) 92.70(7), O(1)-Al(1)-N(1) 124.69(7), O(2)-Al(1)-N(1) 111.39(7), O(1)-Al(1)-N(2) 110.57(7), O(2)-Al(1)-N(2) 123.09(7).

2.3.8 Reaction of LAl[η^2-$C_2(SiMe_3)_2$] with CO_2, Ph_2CO, PhCN, and *t*-BuCN

Reductions of carbonyls by activated metals or metal complexes constitute a powerful strategy for C-C bond formation reactions.[90] We have shown that the LAl moiety can activate alkynes by forming strained ring systems. Therefore it is possible that the LAl moiety as a template allows unsaturated molecules to couple with each other and leads to organic chain growing reactions. It has been reported that aluminum alkyls or hydrides are excellent reducing reagents for carbonyls, nitriles and alkynes.[1b] Using strained ring systems for this reductions should result in different reaction patterns. In the first place, we examined the reaction of **32** with some selected unsaturated compounds.

Reaction of **32** with CO_2 at room temperature leads to C-C coupling with the formation of a new class of aluminum heterocycles, LAl[OC(O)C($SiMe_3$)C($SiMe_3$)] (**36**), in high yield (Scheme 13). The EI-MS spectrum shows the molecular ion with high intensity consistent with the formulation as a monomer. The ^{1}H, ^{13}C and ^{29}Si NMR spectra all gave two distinct singlets for the Me_3Si nuclei, indicating that CO_2 only inserts into one of the Al-C bonds. The IR spectrum shows a very strong band at 1666 cm^{-1}, suggesting the formation of an α,β unsaturated ketone unit. The ease of CO_2 insertion at a four-coordinated aluminum center may be attributed to the high strain of the three membered alumirene ring structure. CO_2 insertion reactions with aluminum trialkyls were studied by Ziegler *et al.* a few decades ago.[93] Subsequently it was found that CO_2 can insert selectively into vinylalanes. The insertion products can be converted to unsaturated acids with complete retention of the geometrical configuration through hydrolysis.[94] However, very little attention has been drawn to unsaturated ring systems for such transformations.[95]

Scheme 13

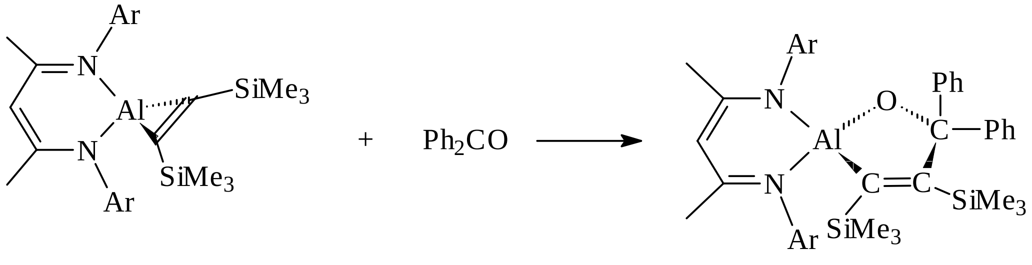


32 **36**

Reaction of **32** with Ph_2CO in diethyl ether at room temperature also led to C-C coupling with the formation of an aluminadihydrofuran LAl[OCPh_2C($SiMe_3$)C($SiMe_3$)] (**37**) despite of the bulkiness of the ketone (Scheme 14). It has been observed previously that trialkyl aluminum compounds can reduce carbonyls with either alkyl insertion or β-hydrogen insertion to form aluminum oxides.[1b] The neat insertion of carbonyls into an Al-C (vinyl) bond was observed in this case. This reaction pattern is different from that of zirconocene alkyne complexes in which displacement of the coordinated alkyne by the ketone afforded an zirconocene η^2-ketone complex.[92b] Compound **37** is the first example of an aluminum compound with a metalladihydrofuran ring structure.

Compound **37** has been characterized by spectroscopic methods and single crystal X-ray structure analysis. The structure is shown in Figure 19 with important bond distances and angles. The aluminum atom is four coordinated and has a distorted tetrahedral geometry as the angles N(1)-Al(1)-N(2) (98.16(6)° and O(1)-Al(1)-C(1) (93.68(6)°) are smaller than 109.28° for an ideal tetrahedral array. The Al(1)-O(1) distance (1.7278(12) Å) is comparable to those of **35** (av 1.73 Å) and shorter than the sum of covalent radii of Al and O, indicating increased ionic interaction between the two atoms. The bond length C(1)-C(2) (1.359(2) Å) is consistent with a C=C double bond character though shorter than that of **32** (C(6)-C(7) (1.382(2) Å) due to the strained three-membered Al(1) C(6)-C(7) ring in **32**. The Al(1)-C(1) bond length (1.9901(16) Å) is longer by ca. 0.09 Å than those of the parent compound **32** (av 1.90 Å).

Scheme 14



32 **37**

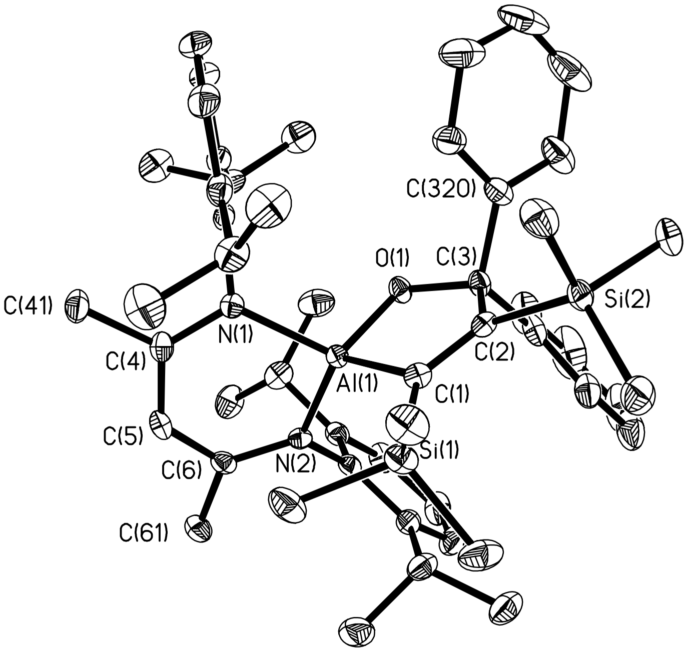
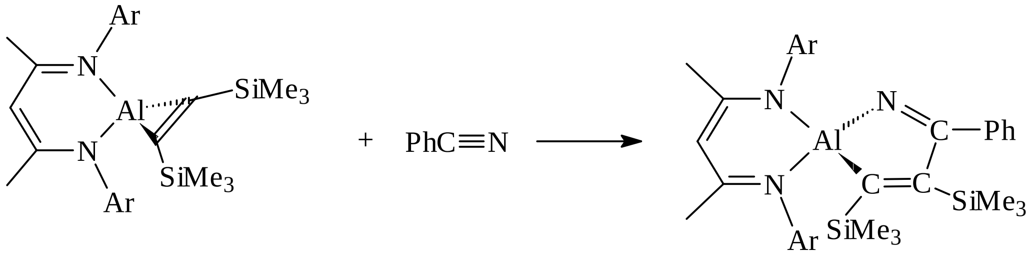


Figure 19. ORTEP drawing of **37** (50 % probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)-O(1) 1.7278(12), Al(1)-N(1) 1.9189(15), Al(1)-N(2) 1.9169(14), Al(1)-C(1) 1.9901(16), O(1)-C(3) 1.4287(11), C(1)-C(2) 1.359(2), C(2)-C(3) 1.578(2); O(1)-A(1)-C(1) 93.68(6), N(1)-Al(1)-N(2) 98.16(6), O(1)-Al(1)-N(2) 119.90(6), C(2)-C(1)-Al(1) 104.46(11).

Compound **32** also reacted with benzonitrile PhCN at room temperature to give a new aluminum containing unsaturated ring system LAl[NC(Ph)C($SiMe_3$)C($SiMe_3$)] (**38**) in moderate yield (Scheme 15). Compound **38** crystallized from diethyl ether as orange crystals, well soluble in aromatic solvents but only sparingly soluble in *n*-hexane. The EI-MS spectrum shows a peak of highest mass at (M^+ + H). The ^1H and ^{29}Si NMR spectra give two distinct singlets for the $SiMe_3$ nuclei respectively, indicating that PhCN inserts only into one of the Al-C bonds in **32**. The ^{13}C NMR spectrum of **38** shows a singlet (δ 183.8 ppm) corresponding to the unsaturated carbon of the Al-C unit.

Scheme 15



32 **38**

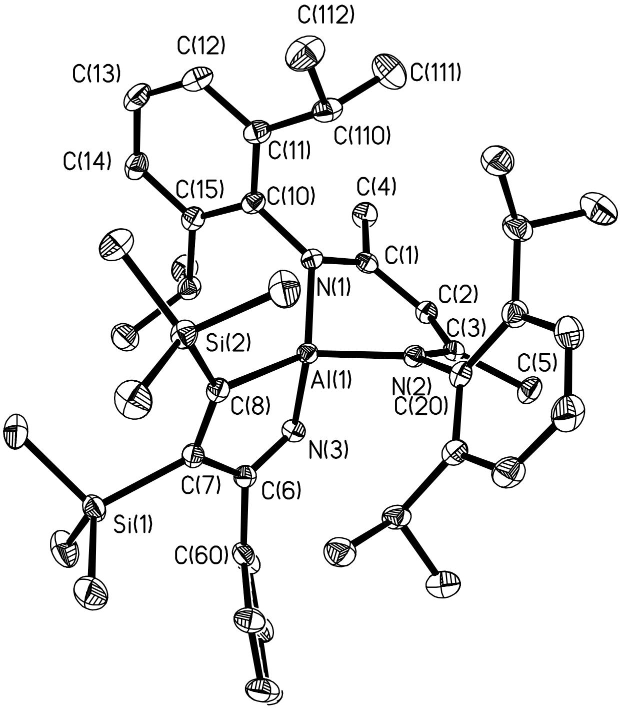


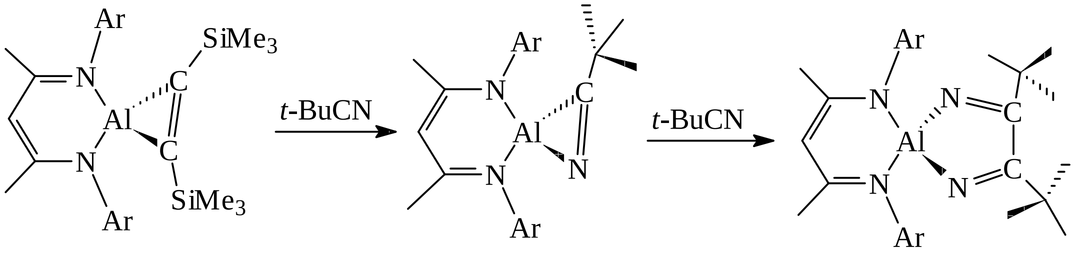
Figure 20. ORTEP drawing of **38** (50% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)-N(1) 1.9109(13), Al(1)-N(2) 1.8887(13), Al(1)-N(3) 1.8678(15), Al(1)-C(8) 1.9917, N(3)-C(6) 1.2741(19), C(6)-C(7) 1.552(2), C(7)-C(8) 1.366(2); N(1)-Al(1)-N(2) 96.39(6), N(3)-Al(1)-C(8) 93.33(7).

The X-ray structure determination of **38** (Figure 20) presents the detailed molecular array and important structural parameters. The aluminum atom is coordinated to a terminal iminato group and a vinyl group forming a planar five-membered AlNCCC ring (sum of internal angles 538.24°). The Al-N(3) distance (1.8678(15) Å) is significant shorter than those reported for the aluminum iminato complexes $\{(i\text{-Bu})_2\text{Al}[\mu^2\text{-N=C(H)(C}_6\text{H}_3\text{-2,6-Me}_2)]\}_2$ (1.248(7) Å),[96] and $\{\text{Me}_2\text{Al}[\mu^2\text{-N=CMe}(t\text{-Bu})]\}_2$ (1.96 Å),[97] in which the iminato groups are bridging two aluminum atom, due to the low coordination number (2) of the iminato moiety in **38**. The N(3)-C(6) (1.2741(19) Å) and C(7)-C(8) (1.366(2) Å) distances are consistent with N=C and C=C double bonds.

Unexpectedly, the reaction of **32** with equivalent of *t*-BuCN at room temperature led to the displacement of the alkyne moiety with the formation of the first aluminum bis(iminato) complex $\text{LAl}[\text{N}_2\text{C}_2(t\text{-Bu})_2]$ (**39**) (Scheme 16), which features an unprecedented aluminum containing imidazole ring. The detailed mechanism for the different reaction patterns of **32** towards PhCN and *t*-BuCN is currently not clear. It is possible that initial coordination of a nitrile molecule to **32** takes place, as a consequence of steric bulk and electron donation capacity of the *t*-Bu group, the carbon of the CN group is not easily attacked by the acetylene carbon as in the case of PhCN, instead, *t*-BuCN replaces $\text{Me}_3\text{SiCCSiMe}_3$ to give a metal η^2 nitrile intermediate (Scheme 16),[98] which is highly reactive and immediately couples with another molecule of *t*-BuCN to give **39**. The isolation of this interesting intermediate is under investigation.

Aluminum iminato complexes prepared by reduction of nitriles with trialkylalane or alkylaluminum hydrides have been employed as intermediates in the preparation of aldehydes, primary amines, Schiff-bases, and azacyclic compounds.[99,100] However, the utilization of unsaturated aluminum ring systems for the reduction of nitriles has not been reported to date. Here formally coupling of an unsaturated molecule with a nitrile induced by an aluminum complex was observed for the first time. Obviously, this is a new approach to synthesize novel cyclic aluminum iminato complexes.

Scheme 16



32 **39**

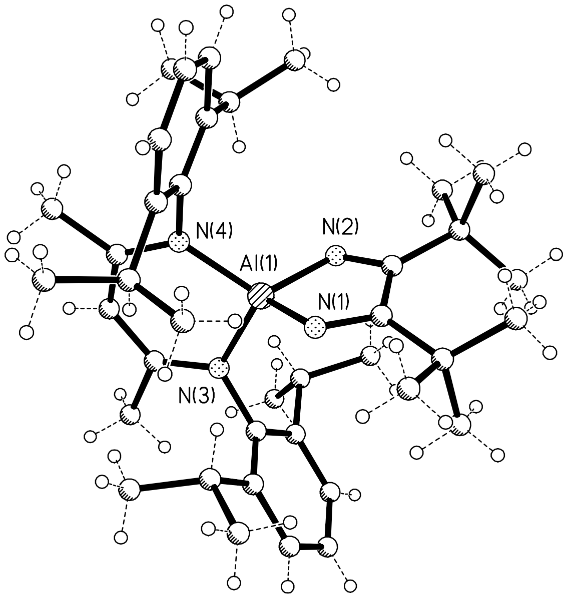


Figure 21. Molecular structure of **39** in the crystal. No exact bonding parameters are available due to the poor quality of the crystal investigated.

The ^{1}H NMR spectrum of **39** does not show low field singlets for SiMe$_3$ protons, a singlet (δ 1.25 ppm) can be assigned to *t*-Bu protons. The integration of all signals is consistent with the formulation of **39**. The EI-MS spectrum gives a peak of highest mass at [M$^+$–*t*–Bu]. The molecular structure of this unique compound was determined by single crystal X-ray structure analysis. Single crystals of **39** were obtained from diethyl ether. Unfortunately the quality of the crystal measured was not satisfactory to enable determination of precise bond parameters, however, the molecular array of **39** has been elucidated and is shown in Figure 21. The structure is consistent with the spectroscopic data of **39**.

2.3.9 Syntheses and characterization of L′AlI$_2$ (40) and L′GaCl$_2$ (41) (L′ = {HC[(CMe)(NAr′)]$_2$}$^-$, Ar′ = 2,6-Me$_2$C$_6$H$_3$)

A colorless product obtained from the reaction of L′H (L′ = {HC[(CMe)(NAr′)]$_2$}, Ar′ = 2,6-Me$_2$C$_6$H$_3$) with equivalent amount of AlMe$_3$ at room temperature followed by reaction with two equivalents of I$_2$ in refluxing toluene afforded the aluminum diiodide L′AlI$_2$ (**40**) in high yield. The L′GaCl$_2$ (**41**) was prepared by the reaction of LiL′ with GaCl$_3$ in diethyl ether. The EI-MS spectra of the two compounds both show the parent ions consistent with a monomeric nature in the gas phase.

Reductions of **40** and **41** with potassium in toluene afforded an orange powder and a red viscous oil, respectively, which could not be crystallized nor characterized to date.

2.4 Synthesis of aluminum methanediide complex (42)

It has been reported that the bis(iminophosphorano)methane CH$_2$(Ph$_2$PNSiMe$_3$)$_2$ can be doubly lithiated by MeLi or PhLi.[101] Several interesting Group 4 carbene complexes were obtained with the doubly lithiated ligand.[102] Being interested in employing various multidentate ligands in aluminum chemistry, we tried to use aluminum alkyls or hydrides to deprotonate the ligand. The reactions of AlMe$_3$ and AlMe$_2$H with CH$_2$(Ph$_2$PNSiMe$_3$)$_2$ in refluxing toluene both afforded the bimetallic compound **42** with the elimination of CH$_4$ and H$_2$, respectively. The ^{31}P NMR spectrum consists of one sharp singlet at δ 27.6 ppm substantially shifted downfield (ca. 33 ppm) relative to the free ligand. The ^{1}H NMR spectrum shows no signal for methylene protons, indicating that the ligand has been doubly deprotonated. Its molecular structure was determined by single crystal X-ray structure analysis. The structure is shown in Figure 22 with important bond lengths and angles. The compound has a spirocyclic dimetallic framework which consists of two nearly planar four-membered rings with a spirocyclic carbon atom connecting two dimethylaluminum units. The dihedral angle between these two planes is 75.28(5)°. The central carbon atom C(1) has a flattened tetrahedral environment. The Al-C bond lengths in the bridging carbene center (Al(1)-C(1) 2.122(3), Al(2)-C(1) 2.114(2) Å) are slightly longer than the Al-C (methyl) distances (average 1.963 Å).

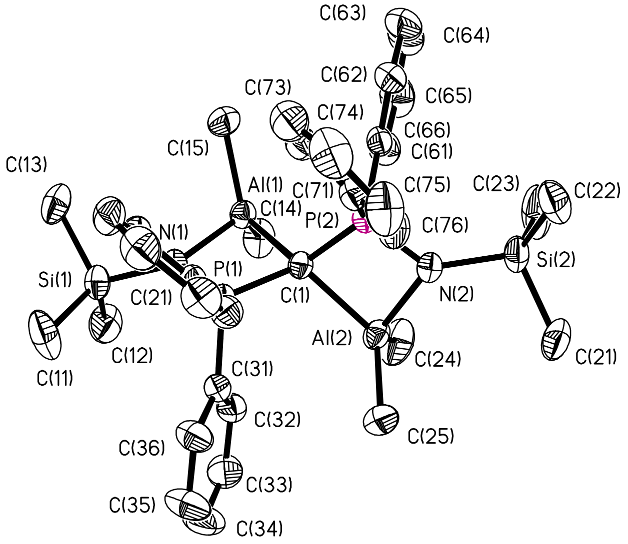


Figure 22. ORTEP drawing of **42** (50% probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)-C(1) 2.122(3), Al(2)-C(1) 2.114(2), Al(1)-N(1) 1.927(2), Al(2)-N(2) 1.926(2); Al(1)-C(1)-Al(2) 129.02(12), Al(1)-C(1)-P(1) 83.97(10), Al(2)-C(1)-P(2) 84.00(10), N(1)-Al(1)-C(1) 79.93(10), N(2)-Al(2)-C(1) 80.32(9).

2.5 Aluminum compounds with the bulky amidinato ligand *t*-BuC(NAr)$_2$

Jordan and co-workers have reported that dimethyl aluminum compounds incorporating bulky amidinate ligands can act as precursors for generating low-coordinate aluminum cationic species when they were reacted with $B(C_6F_5)_3$.[103] However, no stable three coordinated aluminum cations have been obtained with relatively bulky amidinato ligands.[104] We therefore prepared an extremely bulky amidinato ligand *t*-BuC(NAr)(NHAr) (Ar = 2,6-*i*-$Pr_2C_6H_3$) with the expectation of obtaining stable cationic systems. In addition, we have shown in earlier work that it is possible to generate species with low-valent aluminum by using very bulky bidentate ligands.

The synthesis of the aluminum complex *t*-BuC(NAr)$_2$AlMe$_2$ (**43**) was accomplished by the direct reaction of *t*-BuC(NAr)(NHAr) with equivalent amounts of $AlMe_3$ at room temperature. The compound has been characterized by NMR and EI-MS spectra. Its molecular structure was determined by single crystal X-ray structure analysis and is shown in Figure 23 with selected bond lengths and angles. The amidinato ligand is coordinated to the aluminum atom in a chelating mode and forms a planar four-membered heterocyclic AlNCN ring. The N(1)-Al(1)-N(2) angle (68.07(6)°) is acute and comparable to those of other known amidinato aluminum compounds.[105]

The reaction of **43** with 2 equivalents of I_2 in refluxing toluene afforded the corresponding diiodide compound *t*-BuC(NAr)$_2$AlI$_2$ (**44**) in high yield. It has been characterized by NMR, EI-MS spectra, and single crystal X-ray structure analysis. Its structure is shown in Figure 24 with important bond lengths and angles. The structure of **44** resembles closely to that of **43**. However, the core angle N(1)-Al(1)-N(2) (70.50(10)°) is more open than that of **43**. Consistently the Al-N bond lengths (average 1.897 Å) are shorter than those of **43** (average 1.933 Å). This is probably due to the fact that the halide ligand is more electrophilic than the methyl group, which leads to a more acidic aluminum center and increases the ionic character of the aluminum atom. The Al-I distances (average 2.50 Å) are only marginally shorter than those of $LAlI_2$ (**27**) (av 2.52 Å).

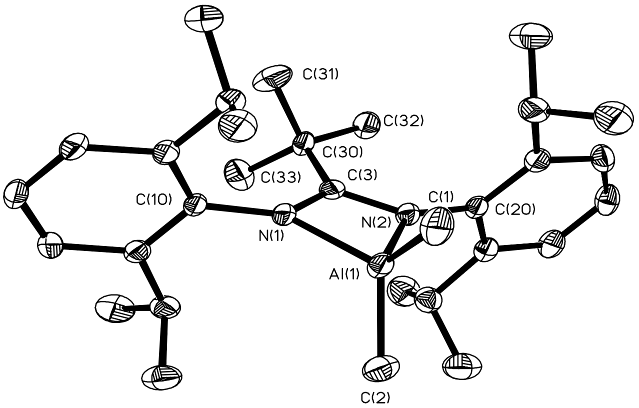


Figure 23. ORTEP drawing of **43** (50% probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)-C(1) 1.955(2), Al(1)-C(2) 1.952(2), Al(1)-N(1) 1.9386(15), Al(1)-N(2) 1.9277(15); N(1)-Al(1)-N(2) 68.07(6)

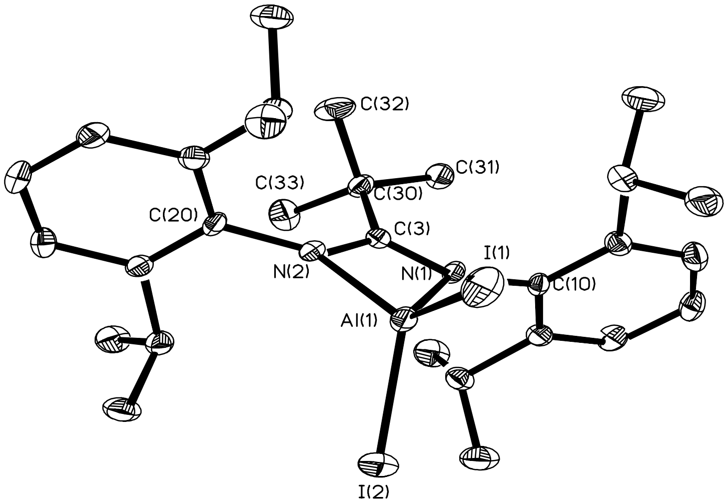


Figure 24. ORTEP drawing of **44** (50% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)-I(1) 2.5163(10), Al(1)-I(2) 2.4941(10), Al-N(1) 1.895(3), Al(1)-N(2) 1.898(2); N(1)-Al(1)-N(2) 70.50(10).

Reduction of **44** with potassium led to isolation of white crystals, which were characterized by EI-MS probably to be the potassium salt of the ligand.

2.6 Reactions of aluminum hydride and hydroaluminate with bulky amides

2.6.1 Reaction of $ArNH_2$ with $AlH_3 \cdot NMe_3$

Bulky aryl amide ligands of the type ArN[106]or Ar(R)N (Ar = 2,6-i-$Pr_2C_6H_3$)[107] have been employed for the stabilization of some interesting main group compounds.

The reaction of $ArNH_2$ with $AlH_3 \cdot NMe_3$ in refluxing toluene afforded the dimeric aluminum amide hydride $(ArNAlH)_2$ (**45**). Compound **45** has been characterized by ^1H and ^{27}Al NMR spectra and elemental analysis and its structure has been determined by single crystal X-ray structure analysis. Unfortunately some atoms are disordered. Tne Al-N (amide) distances (av 1.827 Å) are very short for a four coordinated aluminum center. The Al-N (NMe_3) distances (av 1.970 Å) are in the range of normal Al-N distances (1.8 - 2.0 Å).[106]

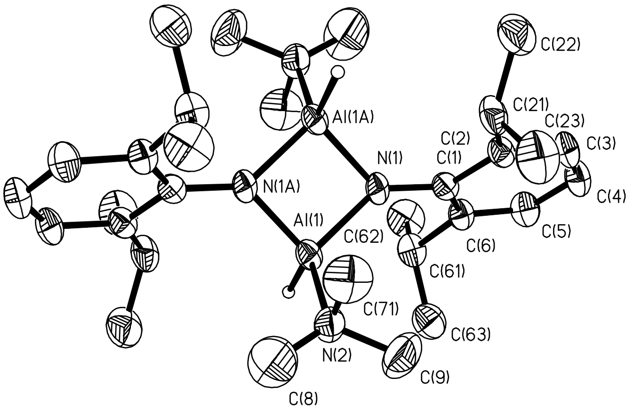


Figure 25. ORTEP drawing of **45**. No exact bonding parameters are available due to disorders.

2.6.2 Reactions of sterically demanding amides with $LiAlH_4$

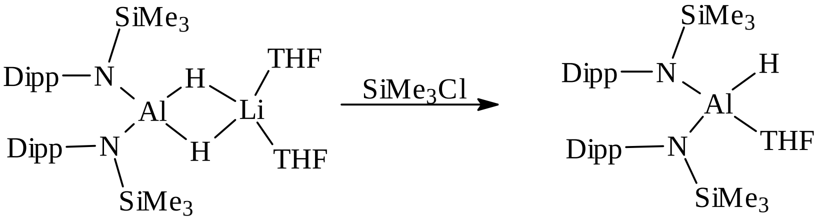
$LiAlH_4$ is a very important reducing reagent and has a polymeric structure in the solid state. Recent studies have demonstrated that dimeric or monomeric lithium hydridoaluminates can be obtained with bulky ligands. Furthermore, these ligands could render hydridoaluminates soluble in hydrocarbon solvents and increase the reactivities and selectivities of the hydrides as reducing agents. Substituted trihydridoaluminates are normally difficult to isolate because the species ($RAlH_3$) readily dissimulate in solution to give (R_2AlH_2) and (AlH_4) when the organic groups R are small.[108] Well characterized low-aggregated hydridoaluminates are rare.[109] In this section the reactions of $LiAlH_4$ with Mes^*NH_2 (Mes^* = 2,4,6-*t*-$Bu_3C_6H_2$) and Dipp($SiMe_3$)NH (Dipp = 2,6-*i*-$Pr_2C_6H_3$) are presented.

The reaction of Mes^*NH_2 with $LiAlH_4$ in THF at 40 °C gave $Mes^*NHAlH_3Li(THF)_3$ (**46**) in high yield. Additional refluxing does not promote further deprotonation. Its ^1H NMR spectrum shows a singlet for the NH proton (δ 3.49 ppm), and the IR spectrum a sharp band for the N-H vibration (ν = 3411 cm^{-1}) and a broad Al-H absorption (ν = 1691 cm^{-1}). These spectral data are consistent with the formulation of **46**.

The reaction of $LiAlH_4$ with 2 equivalents of amide Dipp($SiMe_3$)NH in refluxing THF afforded $[Dipp(SiMe_3)N]_2AlH_2Li(THF)_2$ (**47**) in modest yield. Compound **47** may have a monomeric structure as $[N(SiMe_3)_2]_2AlH_2Li(OEt)_2$ in the solid state.[109a]

47 was reacted with $SiMe_3Cl$ in *n*-hexane to afford solvated neutral aluminum hydride $[Dipp(SiMe_3)N]_2AlH(THF)$ (**48**, Scheme 17). It has been characterized by NMR spectra. Attempts to desolvate the coordinated THF at high temperature led to the decomposition of the hydride.

Scheme 17



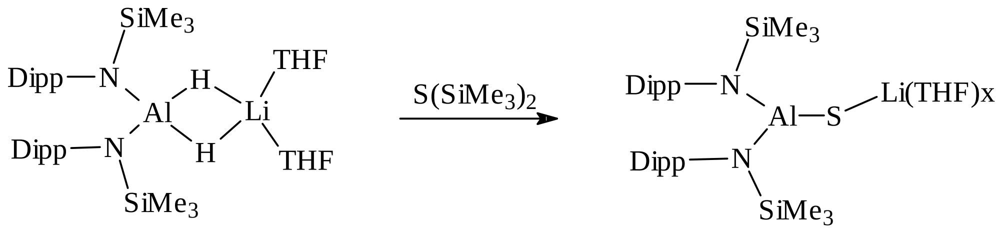
47 **48**

2.6.3 Synthesis of lithium hydridoaluminum chalcogenides

We have shown previously that neutral aluminum hydrides are excellent precursors for the preparation of aluminum chalcogenides by the reactions of elemental chalcogens with selected hydrides (Section 2.3). We reasoned that it is possible to prepare charged aluminum chalcogenides by the reactions of hydridoaluminates with elemental chalcogens (S, Se, Te) or $E(SiMe_3)_2$ (E = S, Se) by chalcogen insertion or elimination of $SiMe_3H$ molecules due to the increased reactivity of hydridoaluminates compared to neutral aluminum hydrides. In the quest for π-bonded systems anionic species seemed to be suited candidates to examine. Indeed, previously reported complexes $[Mes_2B{=}PRLi(Et_2O)_2]$[110] and $[Mes_2B{=}AsPhLi(THF)_3]$ (Mes = $2,4,6\text{-}Me_3C_6H_2$) and the corresponding complex with the lithium atom separated from the anion by complexion, $(Mes_2B{=}AsPh)^-[Li(TMEDA)_2]^+$,[111] have been shown to possess B=P and B=As multiple bonds, respectively. However, no analogues of binary group 13 - 16 systems have been reported to date.

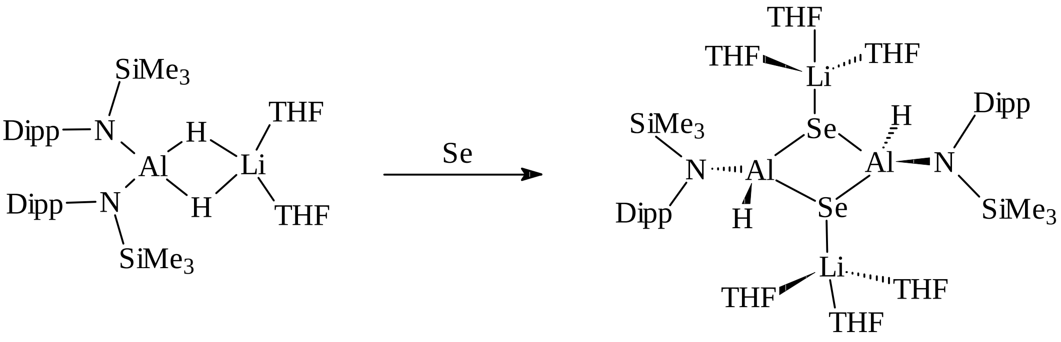
The dihydridoaluminate **47** reacted with $S(SiMe_3)_2$ in THF at 60 °C to give $[Dipp(SiMe_3)N]_2AlSLi(THF)_x$ (**49**) (Scheme 18), soluble in THF, less soluble in diethyl ether, and insoluble in hydrocarbon solvents. It could be crystallized from diethyl ether or THF/*n*-hexane as colorless crystals. The compound has been characterized by ^1H, ^7Li, ^{13}C, and ^{29}Si NMR spectra, the ^1H NMR spectrum in d_8-THF gives correct integration for the formulation as **49** except for the number of THF molecules. Unfortunately, the crystals obtained so far were not suited for single crystal X-ray structure analysis. Compound **49** might be a monomer as its EI-MS and FI-MS spectra only show fragments smaller than the molecular ion.

Scheme 18



47 **49**

Scheme 19



47 **50**

The reactions of **47** with elemental S, Se, Te proceeded smoothly at room temperature to afford colorless crystals after crystallization, respectively. However, only the selenium derivative $[Dipp(SiMe_3)NAlHSeLi(THF)_3]_2$ (**50**) (Scheme 19) was fully characterized by multinuclear NMR spectra and single crystal X-ray structure analysis. Compound **50** is the first example of a dilithiated dimeric aluminum chalcogenide. Interestingly, the reaction of **47** with selenium proceeds via elimination of one molecule of $Dipp(SiMe_3)NH$ and not of hydrogen. Its IR spectrum shows a typical Al-H absorption (ν 1776 cm^{-1}). The ^{77}Se NMR spectrum gives one high field singlet (δ -420.1 ppm) due to the increased negative charge on the selenium atoms.

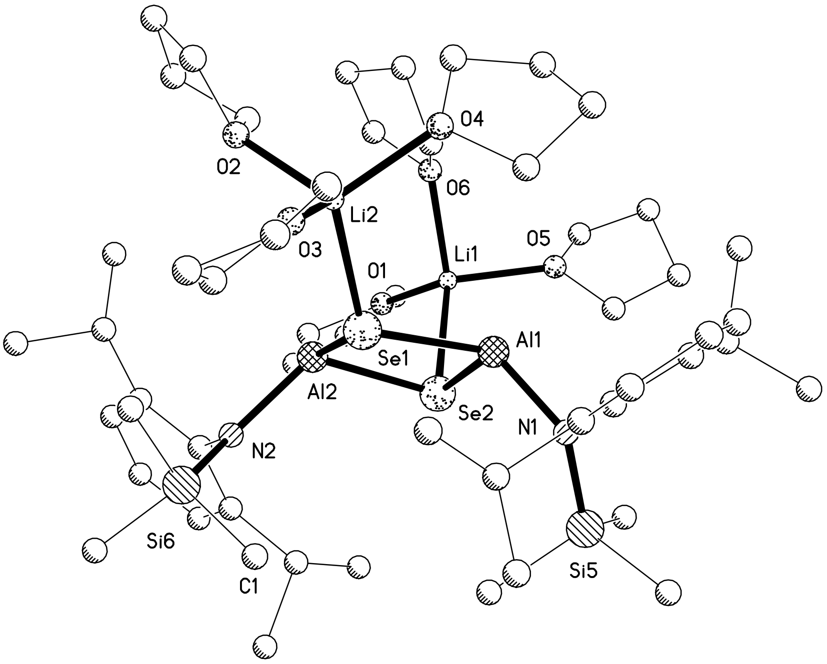


Figure 26. Molecular structure of **50** in the crystal. Hydrogen atoms have been omitted for clarity. Only a few bond lengths and angles are available due to THF disorder. Selected bond lengths (Å) and angles (deg) for central atoms: Al(1)-Se(1) 2.408 (2), Li(1)-Se(1) 2.48(5), Al(1)-N(1) 1.86 (7).

The molecular structure of **50** is shown in Figure 26.with important bond distances and angles. Despite the disorders of the coordinated THF molecules, the other heavy atoms can be refined and positioned. The Al-Se distances (average 2.40 Å) are slightly longer than those of dimeric Al_2Se_2 core compound $(RAlSe)_2$ (**16**) (av 2.36 Å) and longer by 0.08 Å than those of $LAl(SeH)_2$ (**25**) due to the higher coordination number (3) of the Se atoms. However they are shorter than those of $(Cp^*AlSe)_4$ (2.462 - 2.497 Å)[15] and $(Me_2EtCAlSe)_4$ (2.444 - 2.481 Å)[51] in which the Se atoms and Al atoms are three-coordinated and four-coordinated, respectively, similar to those of **50**. The shortening of the Al-Se distances is probably due to the increased negative charge on the Se atoms leading to an enhanced ionic bonding interaction between Al and Se atoms. The Li-Se distances (2.48 and 2.52 Å) are similar to that of $[\text{Mes}^*\text{SeLi(THF)}]_3$ (2.476(12) Å) (Mes^* = 2,4,6-t-$\text{Bu}_3\text{C}_6\text{H}_2$),[112] but little shorter than those of lithium-2,2,6,6-tetramethylpiperidinoselenolate (2.532(7) and 2.563(8) Å)[113] and $[\text{Li(bipy)SePh}]_2$ (2.552 and 2.588 Å).[114] The Al-N distances (average 1.86 Å) are in the range of known aluminum amides.[106]

The lithium aluminum oxides $[\text{Mes}_2\text{AlOLi(THF)}_2]_2$, $[\text{Ph}_2\text{AlOLi(THF)}_2]_3$ and $\{[\text{Me}_2\text{AlOLi}]_4\text{(THF)}_7\text{(LiCl)}\}$ have been prepared by careful hydrolysis of Mes_3Al and Ph_3Al, respectively.[115] The three compounds are the only known examples of lithium chalcogenaluminates so far. However, heavier group 16 element (S, Se, Te) aluminates have not been reported to date.

3 Summary

In this thesis, bulky bidentate 1-aza-allyls, β-diketiminates, amidinates, tridentate aryl and monodentate amido ligands have been employed as supporting moieties in aluminum compounds. The experimental results demonstrate that steric bulk and additional intramolecular coordination of these ligands could stabilize some unusual and unique aluminum compounds which otherwise are inaccessible. Another advantage is that these bulky ligands render aluminum compounds soluble in hydrocarbon solvents and as a result, more detailed characterization of these compounds is possible. In addition, these compounds may be useful as unique starting materials for further reactions in donor free solvents.

1-Aza-allyl aluminum dimethyl and dihalides $RAlX_2$ (R = $[N(SiMe_3)C(Ph)C(SiMe_3)_2]$, X = halides or methyl) were easily obtained from the reactions of RLi·THF and selected simple aluminum halide precursors. The difluoride $(RAlF_2)_2$ (**7**) and diiodide $RAlI_2$ (**8**) were prepared by the reaction of $RAlMe_2$ (**1**) with Me_3SnF and I_2, respectively. Reduction of $RAlCl_2$ (**3**) or $RAlBr_2$ (**4**) with $LiAlH_4$ gave the corresponding aluminum dihydride $(RAlH_2)_2$ (**14**). In $RAlCl_2$ (**3**) and $RAlCl_2$·THF (**6**), the 1-aza-ally1 ligand shows different bonding modes. $(RAlH_2)_2$ (**14**) was reacted with chalcogens (S, Se, Te) to afford aluminum chalcogenides $(RAlE)_2$ (E = S (**15**), Se(**16**), Te(**17**)). This reaction type is a new route for the preparation of aluminum chalcogenides. The molecular structures of **3**, **6**, **7**, **14**, **15**, **16**, and **17** have been determined by X-ray structure analysis.

Reduction of crude $RAlI_2$ with potassium afforded an unique divalent aluminum species R(I)Al-Al(Cl)R (**18**), in which the Al atoms bear one organic group and one halide ligand. The compound has the shortest Al-Al distance (2.59 Å) compared to other known neutral Al(II) species.

Reactions of the aryl aluminum dihydride $2,6\text{-}(Et_2NCH_2)_2C_6H_3AlH_2$ with Se and Te yielded dimeric $[2,6\text{-}(Et_2NCH_2)_2C_6H_3AlE]_2$ (E = Se (**21**), Te (**22**)). The molecular structure of **22** reveals that one amino substituent is coordinated to the Al atom and the other in a dangling position, indicating that the monomeric form ArAlE is energetically unfavorable over the dimeric one.

The reaction of the very bulky β-diketimine LH (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*-$Pr_2C_6H_3$) with $AlH_3{\cdot}NMe_3$ afforded a monomeric aluminum dihydride $LAlH_2$ (**24**). It reacted with elemental selenium to give the first examples of group 13 element SeH compounds, $LAl(SeH)_2$ (**25**) and L(HSe)AlSeAl(SeH)L (**26**), which were characterized by X-ray structure analysis.

As demonstrated by the unique protection of the ligand L, my attention was directed to the reduction of $LAlI_2$ (**27**) with the expectation to generate low-aggregated Al(I) species. As anticipated, this reaction afforded the first two-coordinated aluminum compound LAl (**28**). The molecular structure of this compound was determined by single crystal X-ray structure analysis. *Ab initio* calculations indicate the Al atom possesses one pair of electrons and an empty orbital, its electronic structure being similar to a singlet carbene.

Reaction of **28** with the organic azide Me_3SiN_3 afforded an aluminum containing tetrazole ring system $LAl[(NSiMe_3)_2N_2]$ (**29**). Its molecular structure shows a unique planar metallatetrazole cycle. The synthesis of this compound proceeds presumably through a [3 + 2] cycloaddition of an Al=N intermediate with Me_3SiN_3. This implies the possibility to generate stable Al=N compounds using bulkier azides. Indeed, the reaction of **28** with 2,6-$Trip_2C_6H_3N_3$ (Trip = 2,4,6-*i*-$Pr_3C_6H_2$) and Ph_3SiN_3 afforded the expected LAl=NC_6H_3-2,6-$Trip_2$ (**30**) and LAl=$NSiPh_3$ (**31**) as indicated by their spectroscopic data. Unfortunately, single crystals suitable for X-ray structure analysis for both compounds could not be obtained so far.

Reduction of **27** in the presence of alkynes ($SiMe_3CCSiMe_3$, PhCCPh, and $PhCCSiMe_3$) afforded aluminum cyclopropene analogues $LAl[\eta^2\text{-}C_2(SiMe_3)_2]$ (**32**), $LAl(\eta^2\text{-}C_2Ph_2)$ (**33**), and LAl[η^2-$C_2Ph(SiMe_3)$] (**34**). Reduction of **27** in the presence of Ph_2CO led to carbonyl coupling to give an aluminum pinacolate LAl[$O_2(CPh_2)_2$] (**35**) which is supposed to have formed through an intermediate LAl(η^2-$OCPh_2$), which is highly reactive and couples with another molecule of Ph_2CO despite the steric bulk of Ph_2CO.

The alumirene **32** features an Al-C-C three-membered ring and shows high reactivity toward carbonyls and nitriles. The reactions can be regarded as aluminum promoted coupling of unsaturated molecules, in which the LAl moiety acts as a template and opens up a new facet chemistry of aluminum. The reaction of **32** with CO_2 and Ph_2CO afforded the new aluminum heterocycles LAl[OC(O)C($SiMe_3$)C($SiMe_3$)] (**36**) and LAl[OC(Ph)$_2$C($SiMe_3$)C($SiMe_3$)] (**37**) via carbonyl insertion into the Al-C bond.

Interestingly, **32** displays different reaction patterns toward PhCN and *t*-BuCN. In the former case insertion of PhCN into one of the Al-C (alkyne) bonds was observed to give LAl[NC(Ph)C($SiMe_3$)C($SiMe_3$)] (**38**). In the latter, elimination of the alkyne took place, leading to unprecedented *t*-BuCN coupling at a *p*-block metal atom. The different reaction patterns may result from both steric and electronic factors inflicted by the Ph and *t*-Bu groups. Bulky azides 2,6-$Trip_2C_6H_3N_3$ and Ph_3SiN_3 also replace the alkyne in **32** to give aluminum imides **30** and **31**.

In order to prepare three-coordinated anionic aluminum chalcogenides, starting from [Dipp($SiMe_3$)N]$_2$AlH_2Li(THF)$_2$ (**47**) (Dipp = 2,6-*i*-$Pr_2C_6H_3$) and either S($SiMe_3$)$_2$, the ionic species [Dipp($SiMe_3$)N]$_2$AlSLi(THF)$_x$ (**49**) has been obtained. Compound **49** was supposed to be monomeric as suggested from its spectroscopic data. Compound **47** reacted with selenium with elimination of Dipp($SiMe_3$)NH instead of H_2 to give the charged group 13-16 dimeric species [Dipp($SiMe_3$)NAlHSeLi(THF)$_3$]$_2$ (**50**). The molecular structure of **50** shows relatively short Al-Se bond lengths compared to those of cubic core Al_4Se_4 compounds.

4 Experimental Section

4.1 General procedures

All experiments were carried out under an atmosphere of dry nitrogen or argon using Schlenk techniques or inside a MBraun MB 150-GI glove-box filled with dry nitrogen, where the O_2 and H_2O level were strictly maintained below 1 ppm. All solvents were dried using standard methods prior to use.[116] The samples for analytical measurements were prepared inside the glove box

4.2 Physical measurements

The *melting points* of all compounds described in this thesis were measured on a Bühler SPA-1 apparatus in sealed capillaries and are uncorrected.

^{1}H, ^{7}Li, ^{13}C, ^{19}F, ^{27}Al, ^{29}Si, and ^{77}Se *NMR spectra* were recorded on Bruker-Avance-500, Avance-200, MSL-400, AM-250 and AM-200 instruments. The chemical shifts are reported in ppm with reference to external standards, positive shifts being downfield, $SiMe_4$ for ^{1}H, ^{13}C and ^{29}Si nuclei, $CFCl_3$ for ^{19}F , LiCl for ^{7}Li, $AlCl_3$ for ^{27}Al NMR, and Me_2Se for ^{77}Se nuclei. Heteroatomic spectra were recorded ^{1}H-decoupled. If not otherwise stated, the operation temperature was in the range from 293 to 300 K. The single types are assigned as follows: s = singlet, d = dublet, t = triplet, q = quartet, m = mutiplet.

Mass spectra were obtained on a Finnigan MAT 8230 or a varian MAT CH5 instrument by EI-, FI- and FAB-MS techniques. Only the highest peak of an isotope distribution is given.

Elemental analysis were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

IR spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer as Nujol mulls on KBr plates. Intensities were abbreviated as follows: s (strong), m (medium), w (weak). Only the characteristic absorptions are listed.

*X-ray structure determinations and refinements***.** Data for crystal structures of **3**, **6**, **7**, **9**, **14**, **15**, **16**, **17**, **23**, **25**, **26**, **27**, **28**, **29**, **32**, **35**, **42**, **45**, **50** were collected on a Stoe-Siemens-Huber four-circle diffractometer and data for the structures of **18**, **21**, **33**, **36**, **38**, **39**, **43**, **44** were collected on a STOE-AED2 four circle diffractometer using Mo-Kα radiation (λ = 0.71073 Å). All structures were solved by direct methods (SHELXS-96)[117] and refined against F^2 using SHELXL-97.[118] All heavy atoms were refined anisotropically. Hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atom. Crystal data, data collection details, structural solution and refinement procedures for all compounds are summarized in the tables of section 6.

4.3 Starting materials

Commercially available chemicals were purchased from Fluka or Aldrich and used as received. The other compounds used in this thesis were prepared according to published procedures: Me_3SnF,[119] $[N(SiMe_3)C(Ph)C(SiMe_3)_2]Li\cdot THF$,[30] $AlH_3\cdot NMe_3$,[120] $\{[N(SiMe_3)C(t\text{-}Bu)CH(SiMe_3)]Li\}_2$,[29] 2,6-$(Et_2NCH_2)_2C_6H_3Br$ and its lithium salt,[58a] $H_2C\{(CMe)(NAr)\}_2$ (Ar = 2,6-*i*-$Pr_2C_6H_3$),[64,121] Ph_3SiN_3,[23b] 2,6-$Trip_2C_6H_3N_3$ (Trip = 2,4,6-*i*-$Pr_3C_6H_2$),[85] *t*-BuC(NAr)(HNAr) (Ar = 2,6-*i*-$Pr_2C_6H_3$),[122] $H_2C\{PPh_2)(NSiMe_3)\}_2$,[123] $Ar(SiMe_3)NH$ (Ar = 2,6-*i*-$Pr_2C_6H_3$).[124]

4.4 Synthesis of 1-aza-allyl complexes of aluminum, gallium and bismuth (R = [N(SiMe$_3$)C(Ph)C(SiMe$_3$)$_2$], R′ = [N(SiMe$_3$)C(*t*-Bu)CH(SiMe$_3$)])

RAlMe$_2$ (1): AlMe$_2$Cl (10 mL, 1M in *n*-hexane, 10 mmol) was added to a stirred suspension of RLi·THF (4.14 g, 10 mmol) in diethyl ether (30 mL) at -78 °C. The mixture was allowed to warm to room temperature and stirred for additional 15 h. The volatiles were removed *in vacuo*. The crude product was extracted with pentane (30 mL) and the extract evaporated to dryness *in vacuo*. Pure samples of **1** were obtained by sublimation (65 °C, 0.005 mbar) (3.5 g, 85 %). Mp: 60 - 62 ^{o}C. ^{1}H NMR (C$_6$D$_6$, 200.13 MHz): δ -0.19 (s, 6 H, Al*Me*$_2$), -0.06 (s, 9 H, NSi*Me*$_3$), 0.20 (s, 18 H, CSi*Me*$_3$), 6.90 - 7.00 (m, 3 H, Ph-*H*), 7.25 (d, 2 H, Ph-*H*). ^{13}C NMR (C$_6$D$_6$, 100.60 MHz): δ -5.50 (Al*Me*$_2$), 0.83 (NSi*Me*$_3$), 3.61(CSi*Me*$_3$), 49.5 (*C*Si$_2$), 127.1, 128.1, 130.3 (Ph), 143.1 (*ipso-C*), 208.5 (*C*N). ^{27}Al NMR (C$_6$D$_6$, 65.17 MHz): δ 161.2 ($\nu_{1/2}$ = 2920 Hz). ^{29}Si NMR (C$_6$D$_6$, 79.46 MHz): δ -4.11 (SiMe$_3$), 15.7 (NSiMe$_3$). EI-MS: *m/e* (%) 391 (M$^+$, 3), 376 (M$^+$ - Me, 36), 73 (SiMe$_3$$^+$, 100). Anal. Calcd for C$_{19}$H$_{38}$AlNSi$_3$ (391.75): C, 58.3; H, 9.8; N, 3.6 %. Found: C, 58.2; H, 9.4; N, 3.7 %.

RAlMeCl (2): AlMeCl$_2$ (3 mL, 1M in *n*-hexane, 3 mmol) was added to a suspension of RLi·THF (1.24 g, 3 mmol) in *n*-hexane (20 mL) at –78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 h. A colorless precipitate was filtered off and volatiles were removed. The crude product was sublimed (70 °C, 0.002 mbar) to give analytically pure **2** (0.96 g, 78 %). Mp: 120 - 122 ^{o}C. ^{1}H NMR (C$_6$D$_6$, 200.13 MHz) : δ –0.03 (s, 9 H, NSi*Me*$_3$), -0.01 (s, 3 H, Al*Me*), 0.18 (d, 18 H, CSi*Me*$_3$), 6.83-6.96 (m, 3 H, Ph-*H*), 7.22 (d, 2 H, Ph-*H*). ^{13}C NMR (C$_6$D$_6$, 100.60 MHz): δ -5.7 (Al*C*), 0.60 (NSi*Me*$_3$), 2.98 , 3.41 (CSi*Me*$_3$), 53.5 (*C*Si$_2$), 126.7, 128.0, 130.5 (Ph), 141.9 (*ipso-C*), 210.1 (*C*N). ^{27}Al NMR (C$_6$D$_6$, 65.17 MHz): δ 138.8 ($\nu_{1/2}$ = 2120 Hz). EI-MS: *m/e* (%) 411 (M$^+$, 8), 396 (M$^+$–Me, 36), 376 (M$^+$–Cl, 4), 73 (SiMe$_3$$^+$, 100). Anal. Calcd for C$_{18}$H$_{35}$AlClNSi$_3$ (412.17): C, 52.23; H, 8.56; N, 3.34. Found: C, 51.6; H, 8.6; N, 2.9.

RAlCl$_2$ (3): A solution of RLi·THF (0.83 g, 2 mmol) in *n*-hexane (20 mL) was added to a stirred suspension of AlCl$_3$ in *n*-hexane (10 mL) at -78 °C. The mixture was allowed to warm to room temperature and stirred for 15 h. After filtration from LiCl, the solvent was removed *in vacuo* and the residue was kept *in vacuo* (0.01 mbar) for 4 h. The crude product was crystallized from *n*-hexane (-8 °C) to give colorless crystals (0.73 g, 84 %). Mp: 170 °C dec.. ^{1}H NMR (C$_6$D$_6$, 200.13 MHz): δ 0.00 (s, 9 H, NSi*Me*$_3$), 0.24 (s, 18 H, CSi*Me*$_3$), 6.85 - 6.95 (m, 3 H, Ph-*H*), 7.23 (d, 2 H, Ph-*H*). ^{13}C NMR (C$_6$D$_6$, 100.60 MHz): δ 0.65 (NSi*Me*$_3$), 3.16 (CSi*Me*$_3$), 54.6 (*C*Si$_2$), 126.6, 128.4, 131.1 (Ph), 140.7 (*ipso-C*), 212.8 (*C*N). ^{27}Al NMR (C$_6$D$_6$, 65.17 MHz): δ 111.5 ($\nu_{1/2}$ = 772 Hz). ^{29}Si NMR (C$_6$D$_6$, 49.69 MHz): δ -1.14 (SiMe$_3$), 9.72 (NSiMe$_3$). EI-MS: *m/e* (%) 431 (M$^+$, 10), 416 (M$^+$–Me, 27), 73 (SiMe$_3^+$, 100). Anal. Calcd for C$_{17}$H$_{32}$AlCl$_2$NSi$_3$ (432.56): C, 47.20; H, 7.45; N, 3.24. Found: C, 47.5; H, 7.5; N, 3.2.

RAlBr$_2$ (4): This compound was prepared using the same procedure described for **3**, RLi·THF (0.62 g, 1.5 mmol) in *n*-hexane (15 mL) and AlBr$_3$ (0.40 g, 1.5 mmol) in *n*-hexane (5 mL). The crude product was crystallized from *n*-hexane to give colorless crystals (0.48 g, 61%). Mp: 105 °C. ^{1}H NMR (C$_6$D$_6$, 200.13 MHz): δ 0.02 (s, 9 H, NSi*Me*$_3$), 0.27 (s, 18 H, CSi*Me*$_3$), 6.80 - 6.95 (m, 3 H, Ph-*H*), 7.25 (d, 2 H, Ph-*H*). ^{13}C NMR (C$_6$D$_6$, 100.60 MHz): δ 0.85 (NSi*Me*$_3$), 3.54 (CSi*Me*$_3$), 41.0 (*C*Si$_2$), 126.6, 128.6, 131.2 (Ph), 140.7 (*ipso-C*), 212.4 (*C*N). ^{27}Al NMR (C$_6$D$_6$, 65.17 MHz): δ 107.8 ($\nu_{1/2}$ = 875 Hz). ^{29}Si NMR (C$_6$D$_6$, 79.46 MHz): δ -1.02 (SiMe$_3$), 10.3 (NSiMe$_3$). EI-MS: *m/e* (%) 521 (M$^+$, 10), 506 (M$^+$–Me, 30), 422 (M$^+$–Br, 15), 73 (SiMe$_3^+$, 100). Anal. Calcd for C$_{17}$H$_{32}$AlBr$_2$NSi$_3$ (521.48): C, 39.15; H, 6.18; N, 2.68. Found: C, 39.2; H, 6.5; N, 3.0.

RAlMeCl·THF (5): **2** (0.20 g, 0.48 mmol) was dissolved in THF (5 mL). After 30 min of stirring at room temperature, excess of THF was removed *in vacuo.* The crude product was crystallized from pentane to give colorless crystals (0.20 g, 85 %). Mp: 45 - 46 °C. ^{1}H NMR

(C_6D_6, 200.13 MHz): δ -0.14 (s, 3 H, AlCH_3), 0.12 (s, 9 H, NSi*Me*$_3$), 0.23 (br s, 18 H, CSi*Me*$_3$), 1.17 (m, 4 H, THF), 3.48 (m, 4 H, THF), 6.88 - 6.98 (m, 3 H, Ph-*H*), 7.28-7.35 (d, 2 H, Ph-*H*). ^{13}C NMR (C_6D_6, 100.60 MHz): δ -6.0 (AlCH_3), 0.81, 1.69 (NSi*Me*$_3$), 3.44 (CSi*Me*$_3$), 25.3 (THF), 41.2 (*C*Si$_2$), 69.6 (THF), 126.2, 128.8, 129.8 (Ph), 144.7 (*ipso-C*), 196.0 (*C*N). ^{27}Al NMR (C_6D_6, 65.17 MHz): δ 130.2 ($\nu_{1/2}$ = 980 Hz). Anal. Calcd for $C_{22}H_{43}AlClNOSi_3$ (484.17): C, 54.54; H, 8.88; N, 2.89. Found : C, 54.2; H, 8.6; N, 3.1.

RAlCl$_2$·THF (6): This compound was prepared using **3** (0.43 g, 1 mmol) and THF (10 mL) as described for **7.** After work-up, colorless crystals (0.45 g, 89%) were obtained from *n*-hexane at -8 °C. Mp: 88 - 89 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 0.16 (s, 9 H, NSi*Me*$_3$), 0.28 (s, 18 H, Si*Me*$_3$), 1.16 (m, 4 H, THF), 3.55 (m, 4 H, THF), 6.84 - 6.95 (m, 3 H, Ph-*H*), 7.32 (d, 2 H, Ph-*H*). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 1.00 (NSi*Me*$_3$), 2.96 (CSi*Me*$_3$), 25.7 (THF), 40.9 (*C*Si$_2$), 67.9 (THF), 126.2, 128.6, 129.9 (Ph), 147.3 (*ipso-C*), 182.1 (*C*N). ^{27}Al NMR (C_6D_6): δ 62.66 ($\upsilon_{1/2}$ = 5600 Hz). ^{29}Si NMR (C_6D_6): δ -6.18 (SiMe$_3$), 1.68 (NSiMe$_3$). Anal. Calcd for $C_{21}H_{40}AlCl_2NOSi_3$ (504.69): C, 49.98; H, 7.99; N, 2.77. Found: C, 49.4; H, 8.1; N, 2.7.

[RAlF(μ-F)]$_2$ (7): Toluene (20 mL) was added to a mixture of **1** (0.55 g, 1.4 mmol) and Me$_3$SnF (0.48 g, 2.8 mmol) at room temperature. The mixture was stirred for 15 h , resulting in a clear solution. All volatiles were removed *in vacuo* to leave a white solid, which was crystallized from toluene / *n*-hexane (1 : 10) and stored at -20 °C for 2 days to afford colorless crystals (0.35 g, 63 %). Mp: 185 °C dec. ^{1}H NMR (C_6H_6, 200.13 MHz): δ 0.14 (s, 9 H, NSi*Me*$_3$), 0.41 (br s, 18 H, Si*Me*$_3$), 6.87 - 7.00 (m, 3 H, Ph-*H*), 7.32 (d, 2 H, Ph-*H*). ^{1}H NMR (d$_8$-toluene, 200.13 MHz, 303 K): δ 0.13 (s, 9 H, NSi*Me*$_3$), 0.35 (s, 18 H, Si*Me*$_3$), 7.01-7.09 (m, 3 H, Ph-*H*), 7.32 (d, 2 H, Ph-*H*). ^{1}H NMR (d$_8$-toluene, 200.13 MHz, 213 K): δ 0.60 (s, Si*Me*$_3$), 0.28 (s, Si*Me*$_3$), 0.18 (s, NSi*Me*$_3$), 0.14 (s, NSi*Me*$_3$), Ph-*H* was not recorded. ^{1}H NMR(d$_8$-toluene, 200.13 MHz, 193 K), δ 0.15 (s, NSi*Me*$_3$), 0.20 (s, NSi*Me*$_3$), 0.31 (s, Si*Me*$_3$), 0.62 (s, Si*Me*$_3$), 6.81 (m, Ph-*H*), 6.93 (m, Ph-*H*), 7.27 (d, Ph-*H*), 7.34 (d, Ph-*H*). ^{13}C NMR (C_6H_6, 100.60 MHz): δ 0.63 (NSiMe$_3$), 2.98 (CSi*Me*$_3$), 40.9 (*C*Si$_2$), 125.7, 128.4, 131.1(Ph), 147.2 (*ipso-C*), 212.8 (*C*N). ^{19}F NMR (C_6D_6, 188.32 MHz): δ -160.2 (br s, $\nu_{1/2}$ = 400 Hz). ^{19}F NMR (d$_8$-toluene, 188.32 MHz, 293 K): δ -160.6 (br s, $\nu_{1/2}$ = 400 Hz). ^{19}F NMR (d$_8$-toluene, 188.32 MHz, 258 K): δ -160.3 (s), -159.5 (s), -140.4 (br s, $\nu_{1/2}$ = 180 Hz), -132.6 (br s, $\nu_{1/2}$ = 140 Hz), -120.5 (s br, $\nu_{1/2}$ = 180 Hz). ^{19}F NMR (d$_8$-toluene, 188.32 MHz, 213 K): δ -159.7 (t, 0.8 F, *J* = 15.0 Hz), -158.4 (t, 1.2 F, *J* = 13.4 Hz), -141.1 (d, 0.4 F, *J* = 82.4 Hz), -133.3 (s, 1.2 F), -120.6 (d, 0.4 F, *J* = 81.9 Hz). Anal. Calcd for $C_{34}H_{64}Al_2F_4N_2Si_6$ (799.34): C, 51.09; H, 8.07; N, 3.50. Found: C, 50.7; H, 7.7; N, 3.2.

RAlI$_2$ (8): A solution of **1** (4.02 g, 10.3 mmol) in toluene (20 mL) was added to a solution of I_2 (5.25 g, 20.6 mmol) in toluene (40 mL) at room temperature. The mixture was stirred for 18 h at room temperature, resulting in a slightly brown yellow solution. All volatiles were removed *in vacuo* and the residue was extracted with *n*-hexane (2 x 60 mL), and the extract was concentrated and stored at -20 °C overnight to give yellowish crystals, which were collected by filtration and dried (5.2 g, 92 %). Mp: 84 - 85 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 0.06 (s, 9 H, NSi*Me*$_3$), 0.30 (s, 18 H, Si*Me*$_3$), 6.85 - 6.94 (m, 3 H, Ph-*H*), 7.21 (d, 2 H, Ph-*H*). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 1.25 (NSi*Me*$_3$), 4.22 (CSi*Me*$_3$), 41.95 (*C*Si$_2$), 126.1, 128.4 and 131.3 (Ph), 140.8 (*ipso-C*), 211.7 (*C*N). ^{27}Al NMR (C_6D_6, 65.17 MHz): δ 80.1. ^{29}Si NMR (C_6D_6, 79.46 MHz): δ -0.96 (SiMe$_3$), 11.1 (NSiMe$_3$). MS: *m/e* (%) 615 (M$^+$, 1.6), 600 (M$^+$–Me, 21), 488 (M$^+$ –I, 75), 73 (SiMe$_3^+$, 100). Anal. Calcd for $C_{17}H_{32}AlI_2NSi_3$ (615.57): C, 33.14; H, 5.24; N, 2.27: Found: C, 32.7; H, 5.4; N, 2.0.

R′$_2$AlCl (**9**): (LiR′)$_2$ (0.75 g, 1.5 mmol) in diethyl ether (20 mL) was added to a suspension of AlCl$_3$ (0.40 g, 1.5 mmol) in diethyl ether (10 mL) at –78 °C. The reaction mixture was allowed to warm to room temperature and then stirred for 18 h. The volatiles were removed *in vacuo* and the residual was extracted with pentane (3 × 20 mL). The extract was concentrated and stored at –30 °C overnight to afford colorless crystals of **1** (0.72 g, 88%). Mp: 136-137 °C. ^{1}H NMR(C_6D_6, 200.13 MHz): δ 0.25, 0.29 (s, 9 H, NSi*Me*$_3$), 0.36, 0.47 (s, 9 H, Si*Me*$_3$), 1.07, 1.30 (s, 9 H, *t*-Bu), 2.33, 4.94 (s, 1 H, C*H*). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 1.99, 2.93 (NSi*Me*$_3$), 3.51, 4.12 (CSi*Me*$_3$), 29.04, 31.83 (*t*-Bu), 39.22, 42.38 (*t*-Bu), 119.1, 47.4 (*C*H), 172.8, 222.0 (*C*N). ^{29}Si NMR (C_6D_6, 79.46 MHz): δ -14.6, 0.81 (C*Si*Me$_3$), 3.20, 3.49 (N*Si*Me$_3$). EI-MS: *m/e* (%) 531 (M^+–Me, 8), 489 (M^+–*t*-Bu, 81), 304 (M^+–R´,100). Anal. Calcd for $C_{24}H_{56}AlClN_2Si_4$ (547.20): C, 52.65; H, 10.31; N, 5.11. Found: C, 52.4; H, 10.2; N, 5.1.

R′$_2$AlMe (**10**): This compound was prepared using (LiR′)$_2$ (2.00 g, 4 mmol) and $AlMeCl_2$ (3 mL, 1 M in *n*-hexane, 4 mmol) as described for **1**. After work-up, colorless crystals (1.90 g, 90%) were obtained. Mp: 115-116 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ -0.12 (s, 3 H, Al*Me*), 0.25-0.37 (m, Si*Me*$_3$), 1.07-1.29 (m, *t*-Bu), 2.32, 4.95(s, C*H*). ^{13}C NMR (C_6D_6, 100.60 MHz): δ -3.57 (Al*Me*), 1.37, 2.01, 2.25, 2.95, 3.53, 3.72, 4.13 (NSi*Me*$_3$ and Si*Me*$_3$), 29.25, 31.04 (*t*-Bu), 45.88, 42.39, 45.88 (*t*-Bu), 116.64 (*C*H), 174.4, 222.0 (*C*N). EI-MS: *m/e* (%) 526 (M^+, 5), 511 (M^+–Me, 20), 469 (M^+–*t*-Bu, 56), 284 (M^+–R′, 100). Anal. Calcd for $C_{25}H_{59}AlN_2Si_4$ (526.75): C, 56.95; H, 11.29; N, 5.32. Found: C, 56.2; H, 11.4; N, 5.4.

[(R′$_2$Al)AlCl$_4$] (**11**): A mixture of **1** (0.55 g, 1 mmol) and $AlCl_3$ (0.13 g, 1.0 mmol) in toluene (10 mL) was stirred at room temperature for 2 h. Two phases (a yellowish oil separated) developed upon complete consumption of $AlCl_3$. The volatiles were removed to leave a semi-solid product, which after tribulation with pentane (2 × 5 mL) gave compound **11** as a white solid (0.47 g, 69 %). ^{1}H NMR (CD_2Cl_2, 200.13 MHz): δ 0.30 (s, 18 H, NSi*Me*$_3$), 0.42 (s, 18 H, Si*Me*$_3$), 1.39 (s,18 H, *t*-Bu), 3.03 (s, 2 H, C*H*). ^{27}Al NMR(CD_2Cl_2): δ 103.0 (s, $AlCl_4^-$), 111.8 (br, R'_2Al^+).

RGaCl$_2$ (**12**): A solution of RLi·THF (0.83 g, 2 mmol) in toluene (15 mL) was added to a stirred suspension of $GaCl_3$ (0.35 g, 2 mmol) in *n*-hexane (10 mL) at –78 °C. The mixture was allowed to warm to room temperature and stirred for 15 h and then filtered. The filtrate was concentrated and stored at –30 °C for 2 d to afford colorless crystals (0.62 g, 65 %). Mp: 165 °C. ^{1}H NMR(C_6D_6, 200.13 MHz): δ -0.01 (s, 9 H, NSi*Me*$_3$), 0.24 (s, 18 H, Si*Me*$_3$), 6.82 -7.00 (m, 5 H, Ph-*H*). ^{13}C NMR (C_6D_6), 100.60 MHz): δ 0.69 (NSi*Me*$_3$), 2.55 (CSi*Me*$_3$), 63.6 (*C*Si$_2$), 126.4, 128.7, 130.8 (Ph), 139.3 (*ipso*-*C*), 207.3 (*C*N). ^{29}Si NMR (C_6D_6, 49.69 MHz): δ -0.42 (CSiMe$_3$), 9.73 (NSiMe$_3$). EI-MS: *m/e* (%) 475 (M^+, 90), 460 (M^+–Me, 100), 440 (M^+–Cl, 70). Anal. Calcd for $C_{17}H_{32}Cl_2GaNSi_3$ (475.04): C, 42.90; H, 6.78; N, 2.94. Found: C, 42.7; H, 6.5; N. 3.0.

RBiBr$_2$ (**13**): A solution of RLi·THF (0.83 g, 2 mmol) in toluene (20 mL) was added to a suspension of $BiBr_3$ (0.90 g, 2 mmol) in *n*-hexane (10 mL) at –78 °C. The mixture was allowed to warm to room temperature and stirred for 20 h, and then filtered. The filtrate was concentrated and stored at –30 °C overnight to give orange crystals (0.97 g, 69 %). Mp: 90 °C(dec.). ^{1}H NMR(C_6D_6, 200.13 MHz): δ -0.08 (s, 9 H, Si*Me*$_3$), 0.33 (s, 18 H, CSi*Me*$_3$), 6.82-7.00 (m, 5 H, Ph-*H*). ^{29}Si NMR(C_6D_6, 79.46 MHz): δ -2.17 (CSiMe$_3$), 4.00 (NSiMe$_3$). EI-MS: *m/e* (%) 703 (M^+, 4), 624 (M^+–Br, 90), 73 (Me_3Si^+, 100). Anal. Calcd for $C_{17}H_{32}BiBr_2NSi_3$ (703.22): C, 29.03; H, 4.59; N, 1.99. Found: C, 29.8; H, 4.9; N, 2.3.

[RAlH(μ-H)]$_2$ (**14**): A solution of RAlBr$_2$ (5.22 g, 10 mmol) in diethyl ether (30 mL) was added to a suspension of $LiAlH_4$ (1.14 g, 30 mmol) in diethyl ether (10 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred overnight. Volatiles were removed *in vacuo*, and the residue was extracted with toluene (30 mL). The extract was concentrated, and then stored at –30 °C overnight to give white crystals (3.4 g, 94 %). Mp: 82 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ -0.40 (s, 9 H, NSiMe$_3$), 0.25(s, 18 H, SiMe$_3$), 4.72 (s, 2 H, Al*H*), 6.9-7.0 (3 H, Ph-*H*), 7.3 (d, 2 H, Ph-*H*). ^{1}H NMR (d_8-toluene, 200.13 MHz, 295 K): δ -0.03 (s, 9 H, NSi*Me*$_3$), 0.22 (s, 18 H, Si*Me*$_3$), 4.61 (s, 2 H, Al*H*), 7.01, 7.20 - 7.30 (m, 5 H, Ph-*H*). ^{1}H NMR (d_8-toluene, 200.13 MHz, 233 K): δ 0.04 (s, 9 H, NSi*Me*$_3$), 0.35 (s, 18 H, Si*Me*$_3$), 4.75 (s, 2 H, Al*H*), 7.06, 7.20 - 7.30 (m, 5 H, Ph-*H*). ^{1}H NMR (d_8-toluene, 200.13 MHz, 193 K): δ 0.13 (s, 9 H, NSi*Me*$_3$), 0.48 (s br, 18 H, Si*Me*$_3$), 4.80 (s br, 2 H, Al*H*), 7.07, 7.27 (s br, 5 H, Ph-*H*). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 0.34 (NSi*Me*$_3$), 2.74 (Si*Me*$_3$), 48.8 (*C*Si$_2$), 127.0, 128.2, 130.6 (Ph), 142.9 (*ipso*-*C*), 209.8 (s, *C*N). ^{27}Al NMR (d_8-toluene, 296 K): δ 131.6 ($\nu_{1/2}$ = 2100 Hz). ^{29}Si NMR (C_6D_6, 49.69 MHz): δ 3.59 (CSi$_2$), 5.69 (NSiMe$_3$). Anal. Calcd for $C_{34}H_{68}Al_2N_2Si_6$ (726.91): C, 56.09; H, 9.42; N, 3.85. Found: C, 56.14; H, 9.56; N, 3.89.

[RAl(μ-S)]$_2$ (15): To a mixture of **14** (0.72 g, 1 mmol) and sulfur (0.064 g, 2 mmol) was added toluene (20 mL). The suspension was refluxed for 4 h. It was filtered, the filtrate was concentrated and stored at -30 °C to afford colorless crystals of **15** (0.40 g, 32 %). Mp: 220 °C. ^{1}H NMR (CDCl$_3$, 200.13 MHz): δ 0.24 (s, 18 H, NSi*Me*$_3$), 0.26 (s br, 36 H, Si*Me*$_3$), 7.2 (m, 10 H, Ph-*H*). ^{29}Si NMR (CDCl$_3$, 99.36 MHz): δ -2.71, -2.49 (s, SiMe$_3$), 7.57, 7.83 (s, NSiMe$_3$). EI-MS: *m/e* (%) 786 (M^+, 100), 771 (M^+–Me, 48), 713 (M^+–SiMe$_3$, 10). Anal. Calcd for $C_{34}H_{64}Al_2N_2S_2Si_6$ (787.00): C, 51.89; H, 8.20; N, 3.56. Found: C, 51.7; H, 8.2; N, 3.7.

[RAl(μ-Se)]$_2$ (**16**): To a mixture of **14** (0.64 g, 0.89 mmol) and selenium (0.14 g, 1.79 mmol) was added toluene (15 mL) at room temperature. After the mixture was heated to 80 °C and stirred for 8 h, it was filtered. The filtrate was concentrated (3 mL) and *n*-hexane (5 mL) was added. Cooling the solution to –30 °C overnight afforded colorless crystals, which were collected by filtration and dried (0.56 g, 71 %). Mp: 247 ºC (dec). ^{1}H NMR (C_6D_6, 200.13 MHz): δ 0.28 (d, 18 H, NSi*Me*$_3$), 0.48 (br s, 36 H, Si*Me*$_3$), 6.82 - 6.90 (m, 6 H, Ph-*H*), 7.35 (m, 4 H, Ph-*H*). ^{1}H NMR (d_8-toluene, 200.13 MHz, 295 K): δ 0.25 (d, 18 H, NSi*Me*$_3$), 0.44 (d, 36 H, Si*Me*$_3$), 7.01, 7.30 - 7.50 (m, 10 H, Ph-*H*). ^{1}H NMR (d_8-toluene, 200.13 MHz, 233 K): δ 0.27 (d, 18 H, NSi*Me*$_3$), 0.50 (br s, 36 H, Si*Me*$_3$), 7.06, 7.30-7.50 (m, 10 H, Ph-*H*).

^{1}H NMR (d$_8$-toluene, 200.13 MHz, 193 K): δ 0.29 (s, 18 H, NSi*Me*$_3$), 0.55 (s, 36 H, Si*Me*$_3$), 7.08, 7.35 (br s, 10 H, Ph-*H*). ^{29}Si NMR (C_6D_6, 79.46 MHz): δ -2.5, -2.2 (SiMe$_3$), 7.9, 8.4 (NSiMe$_3$). EI-MS: *m/e* 882 (M$^+$, 100%), 867 (M$^+$–Me, 4%), 441 (M$^+$ / 2, 5%). Anal. Calcd for $C_{34}H_{64}Al_2N_2Se_2Si_6$ (880.80): C, 46.34; H, 7.32; N, 3.18. Found: C, 45.9; H, 7.2; N, 3.3.

[RAl(μ-Te)]$_2$ (**17**): A mixture of **14** (0.56 g, 0.8 mmol) and tellurium (0.20 g, 1.6 mmol) in toluene (15 mL) was heated to 80 °C for 8 h and then refluxed for 4 h. After filtration the solvent was evaporated to dryness and the green residue crystallized from benzene/pentane (2 : 1) to give greenish crystals (0.60 g, 78.6 %). Mp: 176 ºC (dec). ^{1}H NMR (C_6D_6, 200.13 MHz): δ 0.34 (d, 18 H, NSi*Me*$_3$), 0.48 (d, 36 H, Si*Me*$_3$), 6.82 - 7.00 (m, 6 H, Ph-*H*), 7.30-7.40 (m, 4 H, Ph-*H*). ^{29}Si NMR (C_6D_6, 49.69 MHz): δ -2.7, -2.4 (Si*Me*$_3$), 8.6, 9.1 (NSi*Me*$_3$). EI-MS: *m/e* 976 (M$^+$, 100%), 488 (M$^+$/2, 10%). Anal. Calcd for $C_{34}H_{64}Al_2N_2Si_6Te_2$ (976.08): C, 41.70; H, 6.59; N, 2.86. Found: C, 41.0; H, 6.7; N, 3.1.

Synthesis of R(Cl)Al-Al(I)R (18): To crude RAlMe$_2$ (which contains RAlClMe, ca. 3.0 mmol) in toluene (10 mL) was added I_2 (1.52 g, 6 mmol) in toluene (30 mL). The solution was stirred at room temperature for 2d. It was filtered to remove residual amount of I_2 to yield a dark yellow solurion. This solution was added to a suspension of finely divided potassium (0.20 g, 5.6 mmol)in toluene (10 mL), and the suspension was vigorously stirred at room temperature for 3 d and additional 1 d at 60 °C to give a deep red solution containing a large amount of precipitate. After the mixture was filtered, the deep red filtrate was evaporated to dryness and the residual solid was recrystallized from diisopropyl ether at -30 °C to give bright yellow, almost orange crystals (0.20 g, 25%). Mp: 196 °C. ^{1}H NMR (C_6D_6, 200.13 MHz) : δ 0.12, 0.13, 0.14 (s, 18 H, NSi*Me*$_3$), 0.18, 0.28, 0.29, 0.33, 0.58, 0.66 (s, 36 H, Si*Me*$_3$), 6.8 - 7.0 (m, 6 H, Ph-*H*), 7.2 - 7.4 (m, 4 H, Ph-*H*). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ -3.9, -3.7, -3.1, -0.51, -0.17, 0.24, 1.5 (SiMe$_3$), 7.9, 8.2, 9.2 (NSiMe$_3$). EI-MS: *m/e* (%) 488 (RAlI$^+$, 52), 396 (RAlCl$^+$, 20), 73 (Me$_3$Si$^+$, 100). FI-MS: *m/e* (%) 722 (M$^+$–Cl–I, 1), 361

(M^+/2–Cl, 100). Anal. Calcd for $C_{34}H_{64}Al_2ClIN_2Si_6$ (885.73):C, 46.13; H, 7.29; Al, 6.11; N, 3.17. Found: C, 45.4; H, 7.3; Al, 6.2; N, 2.9.

4.5 Synthesis of aryl aluminum dihydrides and chalcogenides

2-(Et_2NCH_2)-6-MeC_6H_3Br (**a**): 2-(Et_2NCH_2)-6-(Me)C_6H_3Br was obtained as a by-product in the synthesis of 2,6-$(Et_2NCH_2)_2C_6H_3Br$ in ca.10 % yield. Bp: 76 °C/0.05 torr. ^1H NMR (C_6D_6): δ 0.78 (t, CH_2CH_3), 2.23 (q, CH_2CH_3), 2.60 (s, Me), 3.45(s, CH_2), 6.8 - 7.25 (m, Ph).

[2-(Et_2NCH_2)-6-MeC_6H_3]AlH_2 (**19**): A solution of [2-(Et_2NCH_2)-6-MeC_6H_3]Li prepared from **a** (0.76 g, 3 mmol) and BuLi (3 mL in *n*-hexane, 3 mmol) in diethyl ether (20 mL) was added to a solution of $AlCl_3$ (0.40 g, 3 mmol) in diethyl ether (10 mL) at -78 °C. The mixture was allowed to warm to room temperature and stirred overnight. After filtration the filtrate was added to a suspension of $LiAlH_4$ (0.30 g, 8 mmol) in diethyl ether (10 mL) at room temperature and stirred for 15 h. All volatiles were removed *in vacuo* and the residue was extracted with *n*-hexane (50 mL). The extract was concentrated to incipient crystallization at -30 °C to give white crystals of **19** (0.40 g, 65 %). Mp:92–93 °C. ^1H NMR (C_6D_6, 200.13 MHz): δ 0.62 (t, 6 H, J = 7.3 Hz, CH_2CH_3), 2.35 (q, 4 H, J = 6.2 Hz, CH_2CH_3), 2.57 (s, 3 H, Me), 4.60 (s br, 2 H, AlH_2), 7.02–7.23 (m, 3 H, Ar-*H*). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 8.75 (CH_2CH_3), 25.7 (Me), 45.8 (CH_2CH_3), 61.1 (CH_2), 121.1, 127.8, 128.3, 144.2, 146.5 (Ph), 149.3 (AlC). EI–MS: *m/e* 204 (M^+–H). Anal. Calcd for $C_{12}H_{20}AlN$ (205.29): C, 70.24; H, 9.76; N, 6.83. Found: C, 69.5; H, 9.8; N, 6.7.

[2,6–$(Et_2NCH_2)_2C_6H_3$]AlH_2 (**20**): [2,6–$(Et_2NCH_2)_2C_6H_3$]AlH_2 was prepared in a similar way as **19**. 2,6-$(Et_2NCH_2)_2C_6H_3Br$ (3.26 g, 10 mmol), BuLi (10 mL in *n*-hexane, 10 mmol), $AlCl_3$ (1.33 g , 10 mmol), and $LiAlH_4$ (0.85 g, 22.5 mmol) were used. The crude product was crystallized from toluene/pentane (1 : 1) to give white crystals (1.8 g, 65.2 %). Mp: 65–67 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 0.90 (t, 12 H, *J* = 7.2 Hz, CH_2CH_3), 2.75 (q, 8 H, *J* = 7.1 Hz, CH_2CH_3), 3.42 (s, 4 H, CH_2), 4.4 (s br, 2 H, AlH_2), 6.90 (d, 2 H, *J* = 7.3 Hz, Ar-*H*), 7.31 (t, 1 H, *J* = 7.2 Hz, Ph). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 9.27 (CH_2CH_3), 46.3 (CH_2CH_3), 60.0 (CH_2), 122.2, 128.3, 146.0 (Ph), 150.1 (Al*C*). EI–MS: *m/e* 275 (M^+–H). Anal. Calcd for $C_{16}H_{29}AlN_2$ (276.41): C, 69.53; H, 10.57; N, 10.13. Found: C, 69.4; H, 10.5; N, 9.9.

{[2-(Et_2NCH_2)-6-MeC_6H_3]AlSe}$_2$ (**21**): To a mixture of **19** (0.25 g, 1.2 mmol) and selenium (0.10 g, 1.3 mmol) was added toluene (20 mL) at room temperature. The mixture was stirred at 80 °C for 10 h, then it was filtered to remove small amounts of precipitate. The filtrate was concentrated and stored at–20 °C for 2 d to give colorless crystals of **21**·2 C_7H_8 , which easily lose solvents under vacuum to give **21** as a white solid (0.27 g, 78.2 %). Mp: 220-222 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 0.85 (t, 6 H, CH_2CH_3), 2.72 (q, 4 H, CH_2CH_3), 2.94 (s, 3 H, Me), 3.43 (s, 2 H, CH_2), 7.00–7.30 (m, 3 H, Ar-*H*). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 9.01 (CH_2CH_3), 25.1(Me), 46.6 (CH_2CH_3), 58.9 (CH_2), 121.6, 128.7, 129.3, 142.8, 146.2 (Ph), 147.7 (AlC). EI–MS: *m/e* 566 (M^+). Anal. Calcd for $C_{24}H_{36}Al_2N_2Se_2$ (564.40): C, 51.06; H, 6.38; N, 4.96. Found: C, 50.7; H, 6.3; N, 5.0.

{[2,6–(Et_2NCH_2)$_2C_6H_3$]AlSe}$_2$ (**22**): Compound {[2,6–(Et_2NCH_2)$_2C_6H_3$]AlSe}$_2$ was prepared in a similar way as **21**. Compound **20** (0.33 g, 1.2 mmol) and selenium (0.10 g, 1.2 mmol) were used for the preparation. Crystallization from hot toluene (10 mL) gave colorless crystals of **22** (0.28 g, 66 %). Mp: 160 - 162 °C. ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 1.08 (t, 12 H, *J* = 7.2 Hz, CH_2CH_3), 2.97 (q, 8 H, *J* = 7.1 Hz, CH_2CH_3), 3.96 (s, 4 H, CH_2), 7.2 (m, 3 H, Ar-*H*). ^{13}C NMR ($CDCl_3$, 100.60 MHz): δ 11.06 (CH_2CH_3), 47.29 (CH_2CH_3), 59.70 (CH_2), 124.2, 128.7, 145.5 (Ph), 145.8 (Al*C*). EI–MS: *m/e* 708 (M^+). Anal. Calcd for $C_{32}H_{54}Al_2N_4Se_2$ (706.69): C, 54.38; H, 7.70; N, 7.93. Found: C, 54.2; H, 7.7; N; 7.9.

{[2,6–$(Et_2NCH_2)_2C_6H_3$]AlTe}$_2$ (**23**): A suspension of **20** (0.28 g, 1.04 mmol) and tellurium (0.13 g, 1.04 mmol) in toluene (20 mL) was refluxed for 8 h. After filtration to remove small amounts of precipitate, the filtrate was concentrated and stored at room temperature for one week to give large plates of **23** suitable for X-ray single crystal analysis (0.33 g, 79 %). Mp: 233–235 °C. ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 1.20 (t, 12 H, J = 7.1 Hz, CH_2CH_3), 3.03 (q, 8 H, J = 7.2 Hz, CH_2CH_3), 3.96 (s, 4 H, CH_2), .23 (m, 3 H, Ar-*H*). ^{13}C NMR ($CDCl_3$, 100.60 MHz): δ 11.3 (CH_2CH_3), 47.4 (CH_2CH_3), 59.1(CH_2), 124.1, 128.6, 145.3 (Ph)., 144.6 (Al*C*). EI–MS: *m/e* 804 (M^+). Anal. Calcd for $C_{32}H_{54}Al_2N_4Te_2$ (803.97): C, 47.85; H, 6.78; N, 6.97. Found: C, 48.6; H, 6.8; N, 7.0.

2,6-[(*t*-Bu)(Me)NCH_2]$_2C_6H_3AlH_2$ (**b**): This compound was prepared similar to compound **19**. Mp: 91 - 92 °C. EI–MS: *m/e* 303 (M^+–H).

{2,6-[(*t*-Bu)(Me)NCH_2]$_2C_6H_3$AlSe}$_2$ (**c**) : This compound was prepared in a similar way as compound **21.** Mp: 322 - 323 °C. ^{1}H NMR ($CDCl_3$): δ 1.35 (s, 18 H, C*Me*$_3$), 2.57 (s, 6 H, Me), 4.04 (s, 4 H, CH_2), 7.21 (m, 3 H, Ar-*H*). ^{77}Se NMR ($CDCl_3$): δ -14.2, -13.8. EI–MS: *m/e* 764 (M^+).

4.6 Synthesis of β-diketiminato aluminum and gallium compounds (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*-$Pr_2C_6H_3$; L′= HC[(CMe)(NAr′)]$_2$, Ar′ = 2,6-$Me_2C_6H_3$)

$LAlH_2$ (24): To a solution of $AlH_3{\cdot}NMe_3$ (0.56 g, 6.3 mmol) in *n*-hexane (10 mL) was added a solution of LH (2.50 g, 6.0 mmol) in *n*-hexane (40 mL) at room temperature and the resulting mixture was stirred for 48 h. All volatile materials were removed *in vacuo*, and the crude product crystallized from *n*-hexane to afford colorless crystals of **24 (** 2.3 g, 86 % based on LH). Mp:194 °C. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.18 (d, 2 H, Ar-H), 7.10 (m, 1 H, Ar-H), 4.86 (s, 1 H, γ-CH), 3.42 (sept, 4 H, C*H*Me_2), 1.54 (s, 12 H, C*Me*), 1.37 (d, 12 H, CH*Me*$_2$), 1.12 (d, 12 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6, 125.75 MHz): δ 170.2 (CN), 144.6, 139.4, 124.8 (Ph), 96.2 (γ–CH), 28.48 (*C*HMe$_2$), 25.5, 24.5 (CH*Me*$_2$), 22.9 (C*Me*). EI-MS : *m/z* (%): 445 (M^+–H, 100). Anal. Calcd for $C_{29}H_{43}AlN_2$ (446.66): C, 78.0; H, 9.7; N, 6.3. Found: C, 78.2; H, 9.7; N, 6.7. IR (KBr, Nujol): $\tilde{\nu}$ = 1832, 1795 cm^{-1} (m, AlH);

LAl(SeH)$_2$ (25): To a mixture of **24** (0.45g, 1 mmol) and selenium (0.16 g, 2 mmol) was added toluene (20 mL). The mixture was stirred at room temperature for 15 h, and a light orange solution formed with trace amounts of unreacted selenium. After filtration, the solvent was removed and the residue was extracted with *n*-hexane (20 mL). The extract was stored at -30 °C for 2 days to give yellowish crystals of **25** (0.35 g, 58 %). Mp: 220 °C (dec.). ^{1}H NMR (C_6D_6, 500 MHz,): δ 7.15-7.09 (m, 6 H, Ar-H), 4.93 (s, 1 H, γ–CH), 3.52 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 1.51 (s, 6 H, C*Me*), 1.35 (d, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 1.10 (d, $^3J_{HH}$= 6.8 Hz, 6 H, CH*Me*$_2$), -2.82 (s, 2 H, SeH). ^{27}Al NMR (C_6D_6, 65.17 MHz): δ = 122 ($\nu_{1/2}$ = 260 Hz). EI-MS: *m/e* (%): 604 (M^+–H, 8), 525 (M^+–SeH, 20), 403 (L$^+$–Me, 100). Anal. Calcd for $C_{29}H_{43}AlN_2Se_2$ (604.58): C, 57.63; H, 7.21; N, 4.63. Found: C, 58.0; H, 7.5; N 4.6. IR (KBr, Nujol): $\tilde{\nu}$= 2318 cm^{-1} (w, SeH).

L(HSe)AlSeAl(SeH)L (26): This compound was prepared in a similar manner as **2** except that the mixture was stirred at 60 °C for 15 h. After removal of the solvent, the residual was recrystallized from THF at –30 °C to give pale yellow crystals of **26** (0.26 g, 46 %). Mp: 250 °C (dec). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.13, 7.03, 6.92 (m, 12 H, Ar-H), 5.17 (s, 2 H, γ–CH), 3.21 (sept, $^3J_{HH}$ = 6.7 Hz, 4 H, C*H*Me$_2$), 2.98 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 1.61 (s, 12 H, C*Me*), 1.10 (d, $^3J_{HH}$ = 6.75 Hz, 6 H, CH*Me*$_2$), 0.95 (d, $^3J_{HH}$ = 6.65 Hz, 6 H, CH*Me*$_2$), 0.90 (d, $^3J_{HH}$ = 6.82 Hz, 6 H, CH*Me*$_2$), 0.84 (d, $^3J_{HH}$ = 6.82 Hz, 6 H, CH*Me*$_2$), -2.83 (s, 2 H, SeH). ^{27}Al NMR ($CDCl_3$, 65.17 MHz): δ 116 ($\nu_{1/2}$ = 680 Hz). ^{77}Se NMR (C_6D_6, 500 MHz): δ = -341 (SeH, $\nu_{1/2}$ = 120 Hz), -535 (Al_2Se, $\nu_{1/2}$ = 90 Hz). EI-MS: *m/e* (%): 1126 (M^+–2 H, 7), 1048 (M^+–H–SeH, 90), 443 (LAl$^+$ + H, 100). Anal. Calcd for $C_{58}H_{84}Al_2N_4Se_3$ (1128.20):

C, 61.82; H, 7.54; N, 5.01. Found: C, 62.2; H, 7.1; N, 5.0. IR (KBr, Nujol): $\tilde{\nu}$ = 2276, 2292 cm^{-1} (w, SeH);

(LAlTe)$_2$ (**d**): A suspension of **24** (0.45 g, 1.0 mmol) and metallic tellurium (0.13 g, 1 mmmol) in toluene (20 mL) was refluxed for 10 h to develop a green colored solution. It was filtered to remove a small amount of precipitate and the green filtrate was concentrated (10 mL) and stored at -10 °C for 1 week to give green needles of **d**: Mp: 330 °C. EI-MS: *m/e* (%) 1144 (M$^+$, 8), 572 (M$^+$/2, 15), 445 (M$^+$/2–Te–H, 100).

LAlI$_2$ (27): To a mixture of [HC(CMeNAr)$_2$]AlMe$_2$ (4.74 g, 10 mmol) and I$_2$ (5.08 g, 20 mmol) was added toluene (60 mL) at room temperature. The deep red solution was stirred for 3 d to develop a slightly brown yellow solution. The solution was concentrated (ca. 20 mL) and stored at -30 °C in a freezer overnight to afford yellowish crystals of **27** (5.8 g, 83 %). Mp: 251 - 252 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.11 (m, 6 H, Ar-H), 5.05 (s, 1 H, γ–CH), 3.58 (sept, 4 H, *J* = 6.75 Hz, C*H*Me$_2$), 1.49 (s, 6 H, Me), 1.43 (d, 12 H, *J* = 6.80 Hz, CH*Me*$_2$), 1.08 (d, 12 H, *J* = 6.80 Hz, CH*Me*$_2$). ^{13}C NMR (C$_6$D$_6$, 100.60 MHz): δ 172.5 (CN), 144.9, 138.9, 125.1 (Ph), 100.4 (γ–C), 29.2 (*C*HMe$_2$), 26.6 (CH*Me*$_2$), 24.5 (CH*Me*$_2$), 24.3 (Me). ^{27}Al NMR (C$_6$D$_6$, 65.17 MHz): δ 83.2 ($\nu_{1/2}$ = 620 Hz). EI-MS: *m/e* (%) 571 ((M–I)$^+$, 100). Anal. Calcd for C$_{29}$H$_{41}$AlI$_2$N$_2$ (698.46): C, 49.87; H, 5.92; N, 4.01. Found: C, 50.1; H, 5.8; N, 3.9.

LAl (28): A solution of **27** (2.08 g, 3.0 mmol) in toluene (30 mL) was added to a suspension of finely divided potassium (0.25 g, 6.4 mmol) in toluene (10 mL) at room temperature. The mixture was vigorously stirred at room temperature for 3 d. The solution developed an orange-red color and almost all potassium was consumed. After filtration the orange red filtrate was concentrated (ca. 5 mL), and on standing overnight at -30 °C X-ray quality red crystals of **28** (0.28 g, 21 %) were obtained. Further products in the solution could not be characterized. Mp: >150 °C (dec.). ^{1}H NMR (C$_6$D$_6$, 200.13 MHz): δ 7.16 (m, 6 H, Ar-H), 5.18 (s, 1 H, γ–CH), 3.16 (sept, 4 H, *J* = 6.80 Hz, C*H*Me$_2$), 1.65 (s, 6 H, Me), 1.38 (d, 12

H, J = 6.80 Hz, CH*Me*$_2$), 1.13 (d, 12 H, J = 6.80 Hz, CH*Me*$_2$). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 165.3 (CN), 143.7, 142.3, 124.2 (Ph), 100.9 (γ-C), 29.0 (*C*HMe$_2$), 25.1 (CH*Me*$_2$), 23.9 (CH*Me*$_2$), 23.8(Me). ^{27}Al NMR (C_6D_6): could not be observed. EI–MS: *m/e* 444 (M$^+$, 12), 429 (M$^+$–Me, 100). Anal. Cacld for $C_{29}H_{41}AlN_2$ (444.62): C, 78.3; H, 9.3; N, 6.3. Found: C, 77.9; H, 9,7; N, 6.3.

LAl [(NSiMe$_3$)$_2$N$_2$] (29): To a solution of **28** (0.44 g, 1 mmol) in toluene (20 mL) was added neat Me_3SiN_3 (0.23 g, 2 mmol) at -78 °C and an immediate color change from red to orange yellow was observed. The mixture was allowed to warm to room temperature and stirred for 1 h. The yellow solution was concentrated (ca. 5 mL) and stored at -30 °C overnight to give yellow crystals of **29** (0.37 g, 58 %). Mp: 130 °C (dec). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.08 (m, 6 H, Ph), 5.04 (s, 1 H, γ-CH), 3.48 (sept, 2 H, J = 6.8 Hz, C*H*Me$_2$), 3.02 (sept, 2 H, J = 6.8 Hz, C*H*Me$_2$), 1.52 (s, 6 H, Me), 1.30 (d, 6 H, CH*Me*$_2$), 1.20 (d, 6 H, CH*Me*$_2$), 1.14 (d, 6 H, CH*Me*$_2$), 1.02 (d, 6 H, CH*Me*$_2$), 0.48 (s, 9 H, SiMe$_3$), -0.14 (s, 9 H, SiMe$_3$). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 172.49 (CN), 145.78, 142.68, 140.11, 125.67, 124.28 (Ph), 101.08 (γ-C), 28.91, 28.83, 25.22, 25.20 (CHMe$_2$), 24.07 (Me), 1.64, 0.62 (SiMe$_3$). ^{29}Si NMR (C_6D_6, 79.46 MHz): δ 4.89, 3.08 (SiMe$_3$). EI-MS: *m/e* (%) 646 (M$^+$, 20), 631 (M$^+$–Me, 100). Anal. Calcd for $C_{35}H_{59}AlN_6Si_2$ (646.86): C, 65.00; H, 9.19; N, 12.99. Found: C, 64.6; H, 9.4; N, 13.2.

{HC[(CMeNAr)$_2$]}AlNC$_6$H$_3$-2,6-Trip$_2$ (30): To a mixture of {HC[(CMe)(NAr)]$_2$}Al (**28**) (0.22 g, 0.5 mmol) and 2,6-Trip$_2$C$_6$H$_3$N$_3$ was added toluene (15 mL) at -60 °C. The mixture was allowed to warm to room temperature and a slow color change from orange red to yellow was observed during 1 h. After stirring at room temperature for additional 3 h, the solution was concentrated (ca. 5 mL) and stored at room temperature for 2 days to afford pale yellow solid of **30** (0.26 g, 52 %) (attempts to grow single crystals of this compounds in toluene, benzene, THF, CH_2Cl_2 were unsuccessful). Mp:342 °C . ^{1}H NMR (C_6D_6, 500 MHz): δ 7.21

(m, 1 H, Ph), 7.13 (m, 1 H, Ph), 7.08 (m, 6 H, Ph), 6.97 (m, 3 H, Ph), 6.95 (m, 1 H, Ph), 6.61 (t, 1 H, Ph), 4.82 (s, γ-C*H*), 3.51, 3.41, 3.10 (sept, 9 H, C*H*Me$_2$), 2.96-2.83 (m, 3 H, C*H*Me$_2$), 2.46, 2.32 (sept, 4 H, C*H*Me$_2$), 1.51, 1.45 (s, 12 H, β-Me), 1.38-1.14 (m, 36 H, CH*Me*$_2$), 0.95 (dd, 8 H, CH*Me*$_2$), 0.87 (d, 4 H, CH*Me*$_2$), 0.50 (d, 4 H, CH*Me*$_2$), 0.42 (dd, 8 H, CH*Me*$_2$). ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.35 (s, 1 H, Ph), 7.19 (t, 1 H, Ph), 7.14 (m, 1 H, Ph), 7.07 (m, 2 H, Ph), 7.00 (m, 2 H, Ph), 6.93 (m, 1 H, Ph), 6.86 (m, 1 H, Ph), 6.78 (d, 1 H, Ph), 6.71 (m, 1 H, Ph), 6.64 (d, 1 H, Ph), 6.56 (m, 1 H, Ph), 6.40 (t, 1 H, Ph), 5.02 (s, 1 H, γ-CH), 3.25 (sept, 1 H, C*H*Me$_2$), 2.94 (sept, 2 H, C*H*Me$_2$), 2.79 (sept, 1 H, C*H*Me$_2$), 2.62 (sept, 1 H, C*H*Me$_2$), 2.45 (sept, 1 H, C*H*Me$_2$), 2.29 (sept, 2 H, C*H*Me$_2$), 1.95 (sept, 1 H, C*H*Me$_2$), 1.70 (s, 3 H, Me), 1.64 (s, 3 H, Me), 1.44 (d, 3 H, CH*Me*$_2$), 1.34 (dd, 6 H, CH*Me*$_2$), 1.24 (dd, 6 H, CH*Me*$_2$), 1.20 (dd, 6 H, CH*Me*$_2$), 1.16 (d, 3 H, CH*Me*$_2$), 1.09 (d, 3 H, CH*Me*$_2$), 1.04 (d, 3 H, CH*Me*$_2$), 0.92 (m, 6 H, CH*Me*$_2$), 0.69 (d, 3 H, CH*Me*$_2$), 0.44 (d, 3 H, CH*Me*$_2$), 0.24 (d, 3 H, CH*Me*$_2$), 0.09 (d, 3 H, CH*Me*$_2$), 0.03 (d, 3 H, CH*Me*$_2$). ^{13}C NMR (CDCl$_3$, 500 MHz): δ 169.1 (CN), 168.9 (CN), 150.8, 149.9, 147.9, 147.6, 147.5, 146.7, 146.6, 146.1, 145.3, 143.7, 143.4, 142.3, 140.0, 138.4, 135.4, 133.4, 130.8, 127.5, 126.3, 125.9, 125.3, 125.2, 124.3, 122.9, 122.6, 122.1, 121.7, 120.7, 119.6, 113.7 (Ph), 98.8 (γ-C), 34.4, 33.9, 33.6, 31.4, 30.9, 29.6, 29.4, 28.3, 28.2, 27.4 (*C*HMe$_2$), 24.3, 24.2 (β-Me), 23.9, 23.7, 23.4, 23.3, 22.8, 22.7, 22.3, 22.0, 21.8, 21.1 (CH*Me*$_2$). ^{27}Al NMR (C_6D_6): not observable. EI-MS: *m/e* (%) 939 (M$^+$, 10), 443 (M$^+$–H–NC$_6$H$_3$-2,6-Trip$_2$, 100). Anal. Calcd for $C_{65}H_{90}AlN_3$ (940.43): C, 82.94; H, 9.65; N, 4.46. Found: C, 82.6; H, 9.5; N, 4.3. IR (KBr, Nujol): $\tilde{\nu}$ (cm^{-1}) 3296.8(w), 3068.7 (w), 1606.3 (m), 1558.5 (s), 1525.2 (s), 1408.5 (s), 1314.3 (m), 1264.0 (s), 1170.3 (m), 1100.6 (s), 1084.5 (s), 1021.2 (s), 985.6 (m), 937.5 (m), 867.2 (s), 804.8 (s), 765.7 (m), 757.7 (s), 723.0 (w), 708.6 (m), 665.4 (m).

LAlNSi(Ph)$_3$ (31): This compound was prepared similarly to compound **30**. **28** (0.22 g, 0.5 mmol) and N_3SiPh_3 (0.15 g, 0.5 mmol) were used. The compound was obtained as white solid

(0.28 g, 80 %). Mp: 203 °C. ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 7.32 - 6.88 (m, 21 H, Ar-H), 4.18 (s, 1 H, γ-C*H*), 3.40 (sept, 2 H, C*H*Me_2), 2.35 (sept, 2 H, C*H*Me_2), 1.47 (s, 6 H, Me), 0.85 (d, 6 H, CH*Me*$_2$), 0.68 (d, 6 H, CH*Me*$_2$), 0.56 (d, 6 H, CH*Me*$_2$), 0.49 (d, 6 H, CH*Me*$_2$). ^{13}C NMR ($CDCl_3$, 500 MHz): δ 172.0 (CN), 145.3, 143.6, 140, 4, 137.1, 136.5, 128.4, 127.3, 125.4, 124.8 (Ph), 102.3 (*γ-C*), 28.4, 28.1 (*C*HMe_2), 25.4 (*Me*), 24.8, 24.7, 24.6, 24.5 (CH*Me*$_2$). ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ -21.1. EI-MS: *m/e* (%) 717 (M^+, 100). Anal. Calcd for $C_{47}H_{56}AlN_3Si$ (717.96): C, 78.63; H, 7.86; N, 5.85. Found: C, 78.2; H, 8.0; N, 5.8.

LAl[η^2-$C_2(SiMe_3)_2$] (32): A solution of $[HC(CMeNAr)_2]AlI_2$ (**27**) (1.40 g, 2 mmol) and bis(trimethylsilyl)acetylene (0.34 g, 2 mmol) in toluene (20 mL) was added to a suspension of finely divided potassium (0.16 g, 4.1 mmol) at room temperature. The mixture was stirred at room temperature for 2 d. The solution developed a red-black color and all the potassium appeared consumed. Subsequently all volatiles were removed under vacuum, and the residue was extracted with *n*-hexane (20 mL). After filtration the red black filtrate was concentrated (ca 6 mL) and stored at -30 °C overnight affording red-black crystals of **32** (0.68 g, 55.4 %). Mp: 182 - 184 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 7.15 (m, 6 H, Ar-H), 4.79 (s, 1 H, *γ*–C*H*), 3.37 (sept, 4 H, *J* = 6.80 Hz, C*H*Me_2), 1.45 (d, 12 H, *J* = 6.80 Hz, CH*Me*$_2$), 1.41 (s, 6 H, Me), 1.10 (d, 12 H, *J* = 6.80 Hz, CH*Me*$_2$), 0.17 (s, 18 H, $SiMe_3$). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 174.1(CN), 143.5, 140.4, 124.3 (Ph), 97.2 (*γ*–C), 28.7 (*C*HMe_2), 25.6, 24.1 (CH*Me*$_2$), 24.0 (Me), 1.82 ($SiMe_3$). ^{27}Al NMR(C_6D_6): not observable. ^{29}Si NMR (C_6D_6, 79.46 MHz): δ -24.7. EI-MS: *m/e* (%) 541 (M^+–$SiMe_3$, 20), 444 (M^+–$C_2(SiMe_3)_2$, 25), 155 ($[C_2(SiMe_3)_2$–$Me]^+$, 100). Anal. Calcd for $C_{37}H_{59}AlN_2Si_2$ (614.88): C, 72.28; H, 9.67; N, 4.55. Found: C, 72.1; H, 9.8; N, 4.3. IR (Nujol, KBr): ν = 1663 cm^{-1}(m, C≡C).

LAl(η^2-C_2Ph_2) (33): Compound **33** was prepared in a similar way as **32**. $[HC(CMeNAr)_2]AlI_2$ (**27**) (1.4 g, 2 mmol), Ph_2C_2 (0.36 g, 2 mmol) and potassium (0.16 g, 4.1 mmol) were used. After filtration and partial removal of the solvents, storage at -30 °C overnight gave orange crystals of **33** (0.86 g, 70 %). Mp: 260 °C (dec). ^{1}H NMR (C_6D_6, 500 MHz): δ 6.8-7.15 (m, 16 H, Ar-H), 4.89 (s, 1 H, γ-C*H*), 3.39 (sept, 4 H, C*H*Me$_2$), 1.53 (s, 6 H, Me), 1.21 (d, 12 H, *J* = 6.8 Hz, CH*Me*$_2$), 1.11 (d, 12 H, *J* = 6.8 Hz, CH*Me*$_2$). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 173.1 (CN), 144.2, 144.0, 139.2, 131.9, 128.6, 128.4, 124.5, 124.0 (Ph), 97.3 (γ-C), 29.1 (*C*HMe$_2$), 25.0, 24.4 (CH*Me*$_2$), 23.5 (Me). ^{27}Al NMR (C_6D_6): not observable. EI-MS: *m/e* (%) 622 (M$^+$, 36), 607 (M$^+$–Me, 69), 579 (M$^+$–*i*Pr, 16). Anal. Calcd for $C_{43}H_{51}AlN_2$ (622.87): C, 82.92; H, 8.25; N, 4.50. Found: C, 82.5; H, 8.3; N, 4.7.

LAl[η^2-C$_2$Ph(SiMe$_3$)] (34): Compound **34** was prepared similarly to **32**: [HC(CMeNAr)$_2$]AlI$_2$ (1.4 g, 2 mmol) and 1-phenyl-2-(trimethylsilyl) acetylene (0.35 g, 2 mmol), and potassium (0.16 g, 4.1 mmol) were employed. Crystallization from toluene gave orange crystals of **34** (0.74 g, 60 %). Mp. 242 °C. ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 7.05-7.30 (m, 11 H, Ar-H), 5.50 (s, γ-CH), 3.41, 3.08 (sept, 2 H, C*H*Me$_2$), 1.85 (s, 6 H, Me), 1.27 (m, 12 H, CH*Me*$_2$), 1.20 (q, 6 H, CH*Me*$_2$), 1.05 (q, 6 H, CH*Me*$_2$), -0.36 (d, 9 H, SiMe$_3$). ^{13}C NMR ($CDCl_3$, 100.60 MHz): δ 211.9 (Al-C), 171.7 (CN), 144.97, 143.17, 139.46, 139.30, 128.73, 128.01, 127.80, 125.32, 124.12, 116.47, 115.60 (Ph), 99.56 (γ-C), 29.02, 27.96 (*C*HMe$_2$), 25.9 (Me), 24.75, 24.72, 23.86, 23.76 (CH*Me*$_2$), 0.008 (SiMe$_3$). EI-MS: *m/e* (%) 618 (M$^+$, 20), 603 (M$^+$–Me, 9), 545 (M$^+$–SiMe$_3$, 77), 429 (M$^+$–CPhCSiMe$_3$–Me, 100). Anal. Calcd for $C_{40}H_{55}AlN_2Si$ (618.88): C, 77.63; H, 8.96; N, 4.52. Found: C, 77.8; H, 9.0; N, 4.5.

LAl[O$_2$(CPh$_2$)$_2$] (35): A solution of [HC(CMeNAr)$_2$]AlI$_2$ (**27**) (1.4 g, 2 mmol) and Ph$_2$CO (0.36 g, 2 mmol) in toluene (15 mL) was added to a suspension of finely divided potassium (0.16 g, 4.1 mmol). Immediately a purple color was observed. The mixture was stirred at room temperature for 2 d and the solution finally developed a red color. After filtration the filtrate was concentrated and stored at -30 °C overnight to afford yellow crystals of **35** (0.56 g, 35 %). Mp: 272 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 7.01 - 6.58 (m, 26 H, Ar-H), 5.04 (s, 1 H, γ-CH), 3.55 (sept, 4 H, C*H*Me$_2$), 1.39 (s, 6 H, Me), 1.11 (d, 12 H, CH*Me*$_2$), 1.07 (d, 12 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6, 125.78 MHz): δ 174.17 (CN), 149.62, 143.94, 142.53, 130.36, 129.27, 128.51, 126.12, 125.64, 124.86, 124.75 (Ph), 99.26 (γ-C), 92.66 (CO), 28.77 (*C*HMe$_2$), 25.19, 24.57, 23.97 (CH*Me*$_2$), 23.06 (Me). EI-MS: *m/e* (%) 808 (M$^+$, 15), 626 (M$^+$–Ph$_2$CO, 100). Anal. Calcd for $C_{55}H_{61}AlN_2O_2$ (809.08): C, 81.65; H, 7.60; N, 3.46. Found: C, 81.0; H, 7.3; N, 3.4.

LAl[OC(O)C(SiMe$_3$)C(SiMe$_3$)] (36): When a solution of **32** (0.31 g, 0.5 mmol) in *n*-hexane (15 mL) was exposed to dry CO_2 at room temperature, the red-black color changed to yellow within 10 min. The solvent was removed under vacuum to give a slightly yellow powder, which was subsequently washed with cold pentane (5 mL) to give analytically pure **36** (0.30 g, 91 %). Mp: 258-260 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 7.03 (m, 6 H, Ar-H), 5.11 (s, 1 H, γ–C*H*), 3.10, 3.35 (sept, 4 H, C*H*Me$_2$), 1.51 (s, 6 H, Me), 1.23 (quad, 12 H, CH*Me*$_2$), 1.02 (quad, 12 H, CH*Me*$_2$), 0.49, -0.09 (s, 9 H, SiMe$_3$). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 178.1 (β–*C*SiMe$_3$), 172.9 (CN), 161.5 (CO), 145.4, 143.1, 142.8, 139.8, 125.8, 125.2, 124.2, 123.6 (Ph), 100.7 (γ–C), 29.0, 28.6, 28.1, 25.6, 24.9, 24.7, 24.5, 24.4, 23.8, 23.4 (CHMe$_2$ and Me), 2.37, 2.29 (SiMe$_3$). ^{27}Al NMR (C_6D_6): not observable. ^{29}Si NMR (C_6D_6, 79.46 MHz): δ -7.90, -12.04 (SiMe$_3$). EI-MS: *m/e* (%) 658 (M$^+$, 50), 643 (M$^+$–Me, 48), 585 (M$^+$–SiMe$_3$, 60), 429 (M$^+$–C(SiMe$_3$)C(SiMe$_3$)CO$_2$ –Me, 100). Anal. Calcd for $C_{38}H_{59}AlN_2OSi_2$ (658.89): C, 69.27; H, 9.03; N, 4.25. Found: C, 69.3; H, 9.1; N, 4.0. IR (Nujol, KBr): ν = 1665.6 cm^{-1} (s, C=O).

LAl[OC(Ph)$_2$C(SiMe$_3$)C(SiMe$_3$)] (37): To a mixture of **32** (0.61 g, 1 mmol) and Ph$_2$CO (0.18 g, 1 mmol) diethyl ether (20 mL) was added. The mixture was stirred at room temperature for 30 min. The solution was concentrated and stored at -30 °C overnight to give colorless crystals of **37**(0.59 g, 74 %). Mp: 215 °C . ^{1}H NMR (C_6D_6, 200.13 MHz): δ 7.70 (m, 2 H, Ar-H), 7.07-6.84 (m, 14 H, Ar-H), 4.91 (s, 1 H, γ-C*H*), 3.20 (sept, 4 H, C*H*Me$_2$), 1.38 (s, 6 H, Me), 1.33 (d, 6 H, CH*Me*$_2$), 1.20 (d, 6 H, CH*Me*$_2$), 1.12 (d, 6 H, CH*Me*$_2$), 1.02 (d, 6 H, CH*Me*$_2$), 0.64 (s, 9 H, SiMe$_3$), 0.14 (s, 9 H, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100.60 MHz): δ 190.8 (CO), 171.5 (CN), 165.8 (Al-C), 148.47, 144.71, 143.50, 141.75, 132.01, 130.16, 129.97, 127.26, 126.62, 125.57, 125.16, 124.31 (Ph), 99.88 (γ-C), 28.71, 28.55 (*C*HMe$_2$), 25.30, 25.22, 25.06, 24.74 (CH*Me*$_2$), 24.39 (Me) 5.72, 4.13 (SiMe$_3$). EI-MS: *m/e* (%) 781 (M$^+$–Me, 3), 626 (M$^+$–C$_2$(SiMe$_3$)$_2$, 100). Anal. Calcd for $C_{50}H_{69}AlN_2OSi_2$ (796.96): C, 75.36; H, 8.73; N, 3.51. Found: C, 74.9; H, 8.8; N, 3.3.

LAl [NC(Ph)C(SiMe$_3$)C(SiMe$_3$)] (38): To a solution of **32** (0.31 g, 0.5 mmol) in diethyl ether (20 mL) neat PhCN (0.052 g, 0.5 mmol) was added at room temperature, and the mixture was stirred at room temperature overnight. The solution was concentrated (ca 5 mL) and stored at -30 °C overnight to give orange crystals of **38** (0.22 g, 61 %). Mp: 235-236 °C. ^{1}H NMR (C$_6$D$_6$, 200.13 MHz): δ 7.65 (m, 2 H, Ar-H), 7.15-7.05 (m, 7 H, Ar-H), 5.27 (s, 1 H, γ-C*H*), 3.25 (sept, 4 H, C*H*Me$_2$), 1.60 (s, 6 H, Me), 1.34 (d, 6 H, CH*Me*$_2$), 1.31 (d, 6 H, CH*Me*$_2$), 1.13 (d, 6 H, CH*Me*$_2$), 1.06 (d, 6 H, CH*Me*$_2$), 0.09 (s, 9 H, SiMe$_3$), 0.03 (s, 9 H, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 500.13 MHz): δ 183.8 (Al-C), 181.5 (Ph*C*N), 177.3, 172.4 (CN), 149.7, 145.2, 143.5, 141.3, 127.4, 127.3, 127.2, 124.8, 124.4 (Ph), 102.0 (γ-C), 28.7, 28.2 (*C*HMe$_2$), 25.9, 25.1, 25.0 (CH*Me*$_2$), 24.0 (Me), 3.38, 3.20 (SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 99.36 MHz): δ -10.3, -11.8. EI-MS: *m/e* (%) 718 (M$^+$ + H, 5), 614 (M$^+$–PhCN, 15), 429 (M$^+$–PhCN–C$_2$(SiMe$_3$)$_2$–Me, 100). Anal. Calcd for $C_{44}H_{64}AlN_3Si_2$ (718.00): C, 73.61; H, 8.98; N, 5.85. Found: C, 73.3; H, 9.0; N, 5.4.

LAl{N$_2$[C(*t*-Bu)]$_2$} (39): To a solution of **32** (o.31 g, 0.5 mmol) in diethyl ether (20 mL) *t*-BuCN (0.042 g, 0.5 mmol) was added at room temperature. The black-red color disappeared during 2 h. The solution was stirred for additional 4 h. The solvents were partially removed (ca 10 mL) and stored at -5 °C for 2 days to give colorless crystals (0.10 g, 42 %). Mp: 249 - 250 °C. ^{1}H NMR (C$_6$D$_6$, 200.13 MHz): δ 7.01 (m, 6 H, Ar-H), 5.08 (s, 1 H, γ-CH), 3.42 (sept, 4 H, C*H*Me$_2$), 1.58 (s, 6 H, Me), 1.47 (d, 12 H, *J* = 6.7 Hz, CH*Me*$_2$), 1.25 (s, 18 H, *t*-Bu), 1.06

(12 H, *J* = 6.8 Hz, CH*Me*$_2$). EI-MS: *m/e* (%) 553 (M$^+$–*t*-Bu, 10), 470 (M$^+$–*t*-Bu–*t*-BuCN, 55), 461 (LAl$^+$ + Me, 100). Anal. Calcd for $C_{39}H_{59}AlN_4$ (610.90): C, 76.68; H, 9.73; N, 9.17. Found: C, 76.1; H, 9.7; N, 9.2.

L′H (e): This compound was prepared similarly to LH. 2,6–$Me_2C_6H_3NH_2$ and $H_2C(COCH_3)_2$ (2 : 1) were used. After work-up, a white powder of **e** was obtained. Mp: 78 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 12.2 (s, 1 H, NH), 7.03-6.98 (m, 6 H, Ar-H), 4.86 (s, 1 H, γ-CH), 2.16 (s, 12 H, Ar-Me), 1.70 (s, 6 H, Me).

L′AlI$_2$ (**40**): To a solution of compound **e** (3.06 g, 10 mmol) in *n*-hexane (60 mL) was added $AlMe_3$ (7 mL, 1.42 M in *n*-hexane, 10 mmol) at room temperature. The mixture was stirred at room temperature for 24 h. All solvents were removed and subsequently the white residue was dissolved in toluene (15 mL). This solution was transferred to a solution of I_2 (5.08 g, 20 mmol) in toluene (40 mL). The mixture was refluxed for 6 h and then filtered. The filtrate was concentrated (ca. 20 mL) and stored at -30 °C overnight to give off-white crystals of **40** (4.7 g, 81 %). Mp: 240-241 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 6.92 (m, 6 H, Ar-H), 4.95 (s, 1 H, γ-CH), 2.38 (s, 12 H, Ar-Me), 1.34 (s, 6 H, Me). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 171.53 (CN), 141.10, 134.12, 129.51, 127.39 (Ph), 99.73 (γ-C), 23.41 (Ar-Me), 21.11 (Me). ^{27}Al NMR (C_6D_6): δ 75.92 ($\nu_{1/2}$ = 980 Hz). EI-MS: *m/e* (%) 586 (M$^+$, 2), 459 (M$^+$–I, 100).

L′GaCl$_2$ (**41**): To a solution of **e** (1.53 g, 5 mmol) in diethyl ether (20 mL) was added MeLi (3.1 mL, 1.6 M in diethyl ether, 5 mmol). The solution was stirred at room temperature for 15 h. This solution was transferred to a solution of $GaCl_3$ (0.88 g, 5 mmoL) in diethyl ether (10 mL) at -78 °C. The mixture was allowed to warm to room temperature and stirred for 15 h. The solvent was removed under vacuum and the residue was extracted with toluene (2 x 10 mL). The extract was concentrated (10 mL) and stored at -30°C for 2 d to give colorless crystals of **41** (1.60 g, 72 %). Mp: 233-5 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 6.92 (s, 6 H, Ar-H), 4.74 (s, 1 H, γ-CH), 2.32 (s, 12 H, Ar-Me), 1.36 (s, 6 H, Me). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 171.09 (CN), 141.32, 134.07, 129.28, 127.37 (Ph), 96.63 (γ-C), 22.88 (Ar-Me), 19.02 (Me). EI-MS: *m/e* (%) 446 (M^+, 80), 411 (M^+–Cl, 35), 395 (M^+–Cl–Me, 100).

4.7 Synthesis of $C[(PPh_2)(NSiMe_3)]_2Al_2Me_4$ (42)

To a solution of $CH_2[(PPh_2)(NSiMe_3)]_2$ (0.58 g, 1 mmol) in toluene (20 mL) was added $AlMe_3$ (1.4 mL, 1.42 M in *n*-hexane, 2 mmol) or $AlMe_2H$ (2 mL, 1 M in *n*-hexane, 2 mmol), and the solution was refluxed for 6 h. Cooling the solution slowly to room temperature afforded colorless crystals of **42**. (0.38 g, 60 %): Mp: 265 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 7.35 (m, 4 H, Ar-H), 7.14 (m, 4 H, Ar-H), 7.02 (m, 8 H, Ar-H), 6.67 (m, 4 H, Ar-H), 0.28 (s, 6 H, AlMe), -0.11 (s, 18 H, $SiMe_3$), -0.75 (s, 6 H, AlMe). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 132.75, 131.44, 131.38, 129.27, 125.64 (Ph), 2.38 ($SiMe_3$), -2.49, -4.06 (Al-C). ^{29}Si NMR (C_6D_6, 79.46 MHz): δ 28.07.

4.8 Synthesis of aluminum compounds incorporating the bulky amidinato ligand [*t*-BuC(NAr)$_2$] (Ar = 2,6-*i*-$Pr_2C_6H_3$)

[*t*-BuC(NAr)$_2$]AlMe$_2$ (**43**): To a solution of *t*-BuC(NAr)(HNAr) (6.3 g, 15 mmol) in *n*-hexane (60 mL) was added $AlMe_3$ (10.6 mL, 1.42 M in n-hexane, 15 mmol). The mixture was stirred at room temperature overnight. All volatiles were removed under vacuum. The white solid was recrystallized from *n*-hexane to give colorless crystals of **43** (6.1 g, 85 %). Mp: 191 - 192 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 7.10 (m, 6 H, Ar-H), 3.6 (sept, 4 H, C*H*Me$_2$), 1.32 (d, 12 H, CH*Me*$_2$), 1.20 (d, 12 H, CH*Me*$_2$), 0.9 (s, 9 H, *t*-Bu), -0.2 (s, 6 H, Al-Me). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 180.5(CN), 144.8, 139.4, 126.3, 123.8 (s, Ph), 42.1

(*C*Me$_3$), 29.6, 28.7 27.2 (CHMe$_2$), 22.8 (CHMe$_2$), -8.1 (s br, AlMe). EI-MS: *m/e* (%) 461 (M$^+$–Me, 100).

[*t*-BuC(NAr)$_2$]AlI$_2$ (**44**): To a solution of **43** (4.76g, 10 mmol) in toluene was added a solution of I$_2$ (5.08g, 20 mmol) in toluene (50 mL). The mixture was stirred at room temperature for 1 day and subsequently refluxed for 10 h. The solution was concentrated and stored at -30 °C overnight to give pale yellow crystals of **44** (5.3 g, 76 %). Mp:236 °C. ^{1}H NMR (C$_6$D$_6$, 500.13 MHz): δ 7.0 - 7.08 (m, 6 H, Ar-H), 3.71 (sept, 4 H, C*H*Me$_2$), 1.35 (d, 12 H, CH*Me*$_2$), 1.27 (d, 12 H, CH*Me*$_2$), 0.82 (s, 9 H, *t*-Bu). ^{13}C NMR (C$_6$D$_6$, 100.60 MHz): δ 187.3 (CN), 145.5, 136.5, 127.7, 124.5 (s, Ph), 42.6 (CMe$_3$), 29.9, 29.5, 29.4, 28.9 (*C*HMe$_2$), 23.1 (CH*Me*$_2$). ^{27}Al NMR(C$_6$D$_6$): δ 85.6.

Reduction of **44** with potassium: To a mixture of **44** (1.4 g, 2 mmol) and finely divided potassium (0.16 g, 4.1 mmol) was added toluene (20 mL). The mixture was stirred at room temperature for 2 d during which time it developed a red color. After filtration, the filtrate was concentrated and stored at -30°C overnight to give colorless crystals, which were characterized as the potassium salt of the ligand by EI-MS spectrum.

4.9 Aluminum Compounds Incorporating the Bulky Amide Ligand

(DippNAlH)$_2$ (Dipp = 2,6-*i*-Pr$_2$C$_6$H$_3$) (**45**): To a solution of H$_2$NC$_6$H$_3$-2,6-*i*-Pr$_2$ (0.35 g, 2 mmol) in toluene (20 mL) was added a solution of AlH$_3$·NMe$_3$ (2 mL, 2 mmol) in benzene, and the mixture refluxed for 15 h. On cooling to room temperature, X-ray quality plates of **45** were obtained (0.32 g, 61 %). Mp: 258 °C. ^{1}H NMR (C$_6$D$_6$, 200.13 MHz): δ 7.25-6.90 (m, 6 H, Ar-H), 4.44 (sept, 4 H, C*H*Me$_2$), 3.54 (s br, 2 H, Al-H), 1.77 (s, H, NMe$_3$), 1.50, 1.35 (d, 12 H, *J* = 6.80 Hz, CH*Me*$_2$). Anal. Calcd for C$_{30}$H$_{54}$Al$_2$N$_2$: C, 68.70; H, 10.39; N, 10.69. Found: C, 68.6; H, 10.4; N, 10.5.

2,4,6-*t*-$Bu_3C_6H_2NHAlH_3$ Li(THF)$_3$ (**46**): To a solution of $LiAlH_4$ (0.114 g, 3 mmol) in THF (10 mL) was added a solution of 2,4,6-*t*-$Bu_3C_6H_2NH_2$ (0.78 g, 3 mmol) in THF (20 mL). The mixture was heated to 60 °C and stirred for 6 h. After removal of the solvent, the residue was crystallized from *n*-hexane to give white crystals of **46** (1.3 g, 81 %). ^1H NMR (C_6D_6, 200.13 MHz):δ 7.52 (s, 1 H, Ar-H), 7.15 (s, 1 H, Ar-H), 3.53 (m, 12 H, THF), 3.49 (s, 1 H, NH), 1.84 (s, 18 H, Ar-*o*-*t*-Bu), 1.82 (s, 9 H, Ar-*p*-*t*-Bu), 1.37 (m, 12 H, THF). ^7Li NMR (C_6D_6, 97.21 MHz): δ -0.25. ^{27}Al NMR (C_6D_6, 65.17 MHz): δ 110.35 ($\nu_{1/2}$ = 1100 Hz). IR (KBr, Nujol): $\tilde{\nu}$ = 3411.3 (m, NH), 1691.8 (br m, Al-H) cm^{-1}.

[Dipp(SiMe$_3$)N]$_2$AlH$_2$Li(THF)$_2$ (**47**): To a solution of $LiAlH_4$ (0.38 g, 10 mmol) in THF (50 mL) was added Dipp($SiMe_3$)NH (5.0 g, 20 mmol). The mixture was heated to 50 °C for 15 h. The solvent was removed and the residue crystallized from *n*-hexane to give white crystals of **47** (5.0 g, 74 %). ^1H NMR (C_6D_6, 500.13 MHz): δ 7.15 - 7.0 (m, 6 H, Ar-H), 4.12 (sept, 4 H, C*H*Me$_2$), 3.50 (m, 8 H, THF), 1.42 (d, 12 H, CH*Me*$_2$), 1.38 (m, 8 H, THF), 1.18 (d, 12 H, CH*Me*$_2$), 0.42 (s, 18 H, $SiMe_3$), 0.09 (s, 2 H, Al-H). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ -2.20.

[Dipp(SiMe$_3$)N]$_2$AlH(THF) (**48**): To a solution of **47** (0.68 g, 1 mmol) in *n*-hexane (15 mL) was added neat $SiMe_3Cl$ (0.11 g, 1 mmol). The mixture was stirred at room temperature overnight and subsequently filtered to remove white precipitate. The filtrate was concentrated and stored at -30 °C for 2 d to give white crystals of **48** (0.31 g, 52 %). Mp: 120 °C (dec). ^1H NMR (C_6D_6, 200.13 MHz): δ 7.30 - 7.10 (m, 6 H, Ar-H), 3.76 (sept, 4 H, C*H*Me$_2$), 3.55 (t, 4 H, THF), 1.32 (d, 12 H, CH*Me*$_2$), 1.21 (d, 12 H, CH*Me*$_2$), 1.02 (m, 4 H, THF), 0.26 (s, 18 H, $SiMe_3$). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 146.9, 146.8, 124.1, 123.5 (Ph), 27.69 (*C*HMe$_2$), 26.16, 25.56 (CH*Me*$_2$), 4.39 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 79.46 MHz): δ 0.83.

[Dipp(SiMe$_3$)N]$_2$AlSLi(THF)$_x$ (**49**): To a solution of **47** (0.68 g, 1 mmol) in THF (20 mL) was added $S(SiMe_3)_2$ (0.18 g, 1 mmol). The mixture was heated to 60 °C and stirred for

8 h. After removal of all volatile materials, the residue was crystallized from THF/*n*-hexane (1 : 4) at -30 °C to give colorless crystals (0.42 g). Mp: 103 - 105 °C. ^{1}H NMR (d$_8$-THF, 200.13 MHz): δ 6.75-6.55 (m, 6 H, Ar-H), 3.95 (sept, 4 H, C*H*Me$_2$), 3.60 (m, 9 H, THF), 1.75 (m, 9 H, THF), 1.07 (d, 12 H, CH*Me*$_2$), 1.00 (d, 12 H, CH*Me*$_2$), 0.09 (s, 18 H, SiMe$_3$). ^{7}Li NMR (d$_8$-THF): δ -0.34. ^{13}C NMR (d$_8$-THF): δ 152.5, 147.2, 122.5, 120.0 (Ph), 68.2, 67.8, 67.4, 67.0 (THF), 27.6 (*C*HMe$_2$), 26.2, 25.6 (CH*Me*$_2$), 26.3, 25.7, 25.3, 24.9 (THF). 4.06 (SiMe$_3$). ^{27}Al NMR (d$_8$-THF): δ 116.4 ($\nu_{1/2}$ = 630 Hz). ^{29}Si NMR (d$_8$-THF): δ -6.2.

{Dipp(SiMe$_3$)NAlHSeLi(THF)$_3$}$_2$ (**50**): To a mixture of **47** (0.68 g, 1 mmol) and selenium (0.08 g, 1 mmol) was added THF (15 mL) at room temperature. The selenium was completely consumed after 2 h. After removal of the solvent, the residue was crystallized from THF/*n*-hexane (1 : 4) at -30 °C to give colorless crystals of **50** (0.26 g, 45 %). ^{1}H NMR (d$_8$-THF, 200.13 MHz): δ 6.90 - 6.65 (m, 6 H, Ar-H), 4.13 (sept, 4 H, C*H*Me$_2$), 3.57 (m, THF), 1.68 (m, THF), 1.22 (d, 12 H, CH*Me*$_2$), 1.10 (d, 12 H, CH*Me*$_2$), 0.15 (s, 18 H, SiMe$_3$). ^{7}Li (d$_8$-THF): δ 0.39. ^{13}C NMR (d$_8$-THF): δ 149.5, 148.3, 123.2, 121.4 (Ph), 68.2, 67.8, 67.6, 67.4, 67.2, 67.1 (THF), 27.7 (*C*HMe$_2$), 26.9, 26.0 (CH*Me*$_2$), 26.4, 25.6, 25.5, 25.3, 25.1, 25.0 (THF), 5.0 (SiMe$_3$). ^{29}Si NMR (d$_8$-THF): δ -5.03 . ^{77}Se NMR (d$_8$-THF): δ -420.1. IR (KBr, Nujol): $\tilde{\nu}$ = 1776 cm^{-1} (br m, Al-H).

5 Handling and Disposal of Solvents and Residual Waste

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.

Used NMR solvents were classified into halogen-free or halogen-containing solvents and were disposed as heavy metal wastes and halogen-containing wastes, respectively.

The heavy metal residues were dissolved in nitric acid and after neutralization stored in the container for heavy metal wastes.

Drying agents such as KOH, $CaCl_2$, $MgCl_2$, and P_4O_{10} were hydrolyzed and disposed as acid or base wastes.

Wherever possible, sodium metal used for drying solvents was collected for recycling.[125] The non-reusable sodium metal was carefully hydrolyzed in cold ethanol and potassium in cold *iso*-propanol and collected into the base-bath for cleaning glassware.

Ethanol or acetone used for cooling baths were subsequently used for cleaning glassware.

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.

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:	6 L
Halogen-containing wastes:	5 L
Halogen-free solvent wastes:	40 L
Acid wastes:	12 L
Base wastes:	10 L.

6 Crystal Data and Refinement Details

Formula / Code	$C_{17}H_{32}AlCl_2NSi_3$ / **3**	$C_{37}H_{71}Al_2F_4N_2Si_6$ / **7**·0.5 C_6H_{14}
Fw	432.59	842.46
Temp (K)	150(2)	200(2)
Cryst syst	Orthorhombic	Triclinic
Space group	*P*bca	*P*-1
a , *b*, *c* (Å)	16.895(2),16.129(2), 17.769(2)	10.916(3),13.712(6), 242(6)
α, β, γ (°)	90, 90, 90	79.13(3), 80.207(13), 69.784(15)
V (Å^3), *Z*	4842.3(10), 8	2499.9(15), 2
d (calcd) Mg / m^3	1.187	1.119
Abs coeff (mm^{-1})	0.454	0.243
F (000)	840	906
Cryst size (mm)	0.70 × 0.40 × 0.20	0.50 × 0.50 × 0.50
θ range (deg)	3.56 - 25.05	3.55 - 20.04
No. Of reflns collected	10178	8628
No.of indep.reflns	4273 (R_{int} = 0.0502)	4653 (R_{int} = 0.0498)
Data/Restraints/Parameters	4266 / 0 / 226	4634 / 319 / 493
GOF/F^2	1.091	1.040
R indices [$I > 2\sigma(I)$]	*R*1 = 0.0380 *wR*2 = 0.0844	*R*1 = 0.0493, *wR*2 = 0.1130
R indices (all data)	*R*1 = 0.0590 *wR*2 = 0.1007	*R*1 = 0.0744 , *wR*2 = 0.1390
Largest diff peak/hole (eÅ^{-3})	0.1 / -0.231	0.272 / -0.323

Formula / Code	$C_{21}H_{40}AlCl_2NOSi_3$ / **6**	$C_{24}H_{56}AlClN_2Si_4$ / **9**
Fw	504.69	547.50
Temp (K)	203(2)	150(2)
Cryst syst	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$/n
a, b, c (Å)	14.290(2), 11,217(2), 18.358(3)	11.3848(13), 20.020(3), 5.355(2)
α, β, γ (°)	90, 98.268(11), 90	90, 102.647(12), 90
V (Å^3), Z	2912.1(9), 4	3414.9(9), 4
d (calcd) Mg / m^3	1.151	1.065
Abs coeff (mm^{-1})	0.389	0.292
F (000)	1080	-1200
Cryst size (mm)	0.60 × 0.60 × 0.50	1.00 x 1.00 x 0.70
θ range (deg)	3.63 – 21.95	3.56 to 25.02
No. Of reflns collected	3809	8721
No.of indep.reflns	3519 (R_{int} = 0.1363)	6010 (R $_{int}$ = 0.0231)
Data / Restraints / Parameters	3500 / 0 / 271	6001/ 0/ 307
GOF/F^2	1.063	1.068
R indices [$I > 2\sigma(I)$]	$R1$= 0.0518, $wR2$ = 0.1100	$R1$ = 0.0343, $wR2$ = 0.0854
R indices (all data)	$R1$ = 0.0518, $wR2$ = 0.1384	$R1$ = 0.0410, $wR2$ = 0.0937
Largest diff peak / hole (eÅ^{-3})	0.266 / -0.258	0.333 and –0.259

Formula / Code	$C_{34}H_{68}Al_2N_2Si_6$ / **14**	$C_{37.5}H_{68}Al_2N_2S_2Si_6$ / **15**·0.5 C_7H_8
Fw	727.40	833.56
Temp (K)	153 (2)	203 (2)
Cryst syst	Monoclinic	Triclinic
Space group	$P2_1/n$	P-1
a, b, c (Å)	14.014(2), 9.1980(13), 18.175(3)	10.969(4), 14.957(6), 16.240(6)
α, β, γ (°)	90, 106.760(15), 90	79.62(3), 81.07(2), 73.04(3)
V (Å^3), Z	2243.3(6), 2	2491.7(16), 2
d (calcd) Mg / m^3	1.077	1.111
Abs coeff (mm^{-1})	0.249	0.313
F (000)	792	898
Cryst size (mm)	0.90 × 0.70 × 0.40	0.80 × 0.40 × 0.40
θ range (deg)	3.67 - 22.52	3.51 - 25.04
Limiting indices	$-15 \leq h \leq 15$, $-8 \leq k \leq 9$, $-18 \leq l \leq 19$	$-12 \leq h \leq 7$, $-17 \leq k \leq 17$, $0 \leq l \leq 19$
No. Of reflns collected	3590	7345
No.of indep.reflns	2912 (R_{int} = 0.0449)	7252 (R_{int} = 0.0592)
Data / Restraints / Parameters	2911 / 0 / 216	7252 / 306 / 475
GOF/F^2	1.038	1.085
R indices [$I > 2\sigma(I)$]	$R1 = 0.0289$, $wR2 = 0.0733$	$R1 = 0.0513$, $wR2 = 0.1274$
R indices (all data)	$R1 = 0.0310$, $wR2 = 0.0757$	$R1 = 0.0708$, $wR2 = 0.1425$
Largest diff peak / hole (eÅ^{-3})	0.246 / -0.193	0.387 / -0.531

Formula / Code	$C_{34}H_{64}Al_2N_2Se_2Si_6$ / **16**	$C_{34}H_{64}Al_2N_2Si_6Te_2$ / **17**
Fw	881.29	978.57
Temp (K)	150(2)	213(2)
Cryst syst	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a, *b*, *c* (Å)	8.7959(10), 11.6070(15) 23.153(4)	9.0522(15), 11.666(2) 23.149(7)
α, β, γ (°)	100.984(10),92.014(13) 91.248(9)	99.55(3), 91.415(14) 92.158(12)
V (Å^3), *Z*	2318.1(6), 2	2407.8(9), 2
d (calcd) Mg / m^3	1.263	1.350
Abs coeff (mm^{-1})	1.813	1.421
F (000)	920	992
Cryst size (mm)	1.00 × 0.70 × 0.60	0.60 × 0.40 × 0.20
θ range (deg)	3.51 – 25.04	3.51 - 25.05
Limiting indices	$-10 \le h \le 10$, $-13 \le k \le 13$, $-24 \le l \le 27$	$-10 \le h \le 10$, $-13 \le k \le 13$, $-10 \le l \le 27$
No. of reflns collected	9658	8518
No.of indep.reflns	8160 (R_{int} = 0.0323)	8518 (R_{int} = 0.0000)
Data/ Restraints/Parameters	8160 / 0 /433	8518 / 0 / 435
GOF/F^2	1.047	1.032
R indices [$I > 2\sigma(I)$]	*R*1 =0.0363, *wR*2 = 0.0946	*R*1 = 0.0431, *wR*2 = 0.1050
R indices (all data)	*R*1 = 0.0422, *wR*2 = 0.1018	*R*1 = 0.0587, *wR*2 = 0.1190
Largest diff peak/hole (eÅ^{-3})	0.630 / -0.590	1.024 / -0.837

Formula / Code	$C_{34}H_{64}Al_2Cl_{0.86}I_{1.42}N_2Si_6$ / **18**	$C_{19}H_{26}AlNSe$ / (0.5 **21**)·C_7H_8
Fw	898.30	374.35
Temp (K)	133(2)	133(2)
Cryst syst	Monoclinic	Monoclinic
Space group	$P2_1$/n	$P2_1/n$
a, b, c (Å)	15.536(3), 18.201(4)	12.498(3), 11.556(2)
	17.155(3)	14.256(3)
α, β, γ (°)	90, 108.15(3), 90	90, 114.03(3), 90
V (Å^3), Z	4610(2), 2	1880.4(7), 4
d (calcd) Mg / m^3	1.294	1.187
Abs coeff (mm^{-1})	1.056	2.041
F (000)	1868	776
Cryst size (mm)	0.50 × 0.50 × 0.20	1.00 × 0.80 × 0.70
θ range (deg)	2.41 - 27.78	2.36 – 27.50
Limiting indices	$-20 \le h \le 20$, $-23 \le k \le 15$,	$-16 \le h \le 14$, $0 \le k \le 14$,
	$-22 \le l \le 22$	$0 \le l \le 18$
No. of reflns collected	70718	4301
No.of indep.reflns	10729 (R_{int} = 0.1281)	4301 (R_{int} = 0.0000)
Data/Restraints/Parameters	10727 / 0 / 453	4296 / 0 / 203
GOF/F^2	0.949	1.117
R indices [$I > 2\sigma(I)$]	$R1 = 0.0513$, $wR2 = 0.0868$	$R1 = 0.0435$, $wR2 = 0.1016$
R indices (all data)	$R1 = 0.1155$, $wR2 = 0.0985$	$R1 = 0.0627$, $wR2 = 0.1147$
Largest diff peak / hole (eÅ^{-3})	4.39 / -0.399	0.880 / -0.563

Formula / Code	$C_{16}H_{27}AlN_2Te$ / 0.5 **23**	$C_{29}H_{43}AlN_2Se_2$ / **25**
Fw	401.98	604.55
Temp (K)	203(2)	203(2)
Cryst syst	Monoclinic	Orthorhombic
Space group	$P2_1/c$	Pnma
a, b, c (Å)	10.542(2), 11.726(3), 14.580(4)	13.065(3), 22.049(4), 10.577(2)
α, β, γ (°)	90, 105.04(2), 90	90, 90, 90
V (Å^3), Z	1740.8(7), 4	3046.7(11), 4
d (calcd) Mg / m^3	1.534	1.318
Abs coeff (mm^{-1})	1.753	2.475
F (000)	808	1248
Cryst size (mm)	$0.60 \times 0.60 \times 0.20$	$1.00 \times 0.80 \times 0.40$
θ range (deg)	3.52 –25.01	3.63 – 25.01
Limiting indices	$-12 \leq h \leq 12$, $-13 \leq k \leq 13$, $-17 \leq l \leq 17$	$0 \leq h \leq 15$, $-21 \leq k \leq 26$, $0 \leq l \leq 12$
No. of reflns collected	9371	2769
No.of indep.reflns	3066 (R_{int} = 0.0479)	2760 (R_{int} = 0.0348)
Data / Restraints / Parameters	3066 / 0 / 185	2756 / 0 / 165
GOF/F^2	1.111	1.044
R indices [$I > 2\sigma(I)$]	$R1 = 0.0282$, $wR2 = 0.0759$	$R1 = 0.1020$, $wR2 = 0.2787$
R indices (all data)	$R1 = 0.0289$, $wR2 = 0.0768$	$R1 = 0.1282$, $wR2 = 0.3188$
Largest diff peak / hole (eÅ^{-3})	0.984 / -1.234	1.706 / -1.408

Formula / Code	$C_{58}H_{84}Al_2N_4Se_3$ / **26**	$C_{29}H_{41}AlI_2N_2$ / **27**
Fw	1128.13	698.42
Temp (K)	203(2)	200(2)
Cryst syst	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, b, c (Å)	12.255(3), 27.347(6), 17.753(4)	18.927(10), 8.690(5), 20.137(15)
α, β, γ (°)	90, 98.29(3), 90	90, 113.45(4), 90
V (Å^3), Z	5888(2), 4	3038(3), 4
d (calcd) Mg / m^3	1.273	1.527
Abs coeff (mm^{-1})	1.942	2.118
F (000)	2352	1392
Cryst size (mm)	1.00 × 0.80 × 0.40	0.80 × 0.40 × 0.40
θ range (deg)	3.53 – 22.53	3.71 – 25.04
Limiting indices	$-13 \leq h \leq 13$, $-2 \leq k \leq 29$, $-19 \leq l \leq 19$	$-22 \leq h \leq 22$, $-10 \leq k \leq 10$, $-23 \leq l \leq 23$
No. Of reflns collected	8425	8642
No.of indep.reflns	7712 (R_{int} = 0.0364)	5357 (R_{int} = 0.0184)
Data/Restraints/Parameters	7700 / 1 / 630	5351 / 0 / 317
GOF/F^2	1.076	1.088
R indices [$I > 2\sigma(I)$]	$R1$ = 0.0595, $wR2$ = 0.1253	$R1$ = 0.0248, $wR2$ = 0.0608
R indices (all data)	$R1$ = 0.894, $wR2$ = 0.1510	$R1$ = 0.0281, $wR2$ = 0.0647
Largest diff peak / hole (eÅ^{-3})	1.847 / -0.900	0.654 / -0.966

Formula / Code	$C_{29}H_{41}AlN_2$ / **28**	$C_{35}H_{59}AlN_6Si_2$ / **29**
Fw	444.62	647.04
Temp (K)	153(2)	200(2)
Cryst syst	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, b, c (Å)	12.576(3), 15.949(5), 13.962(3)	18.4571(11), 22.037(6), 14.136(2)
α, β, γ (°)	90, 104.84(2), 90	90, 91.358(11), 90
V (Å^3), Z	2707.1(12), 4	3879.3(12), 4
d (calcd) Mg / m^3	1.091	1.108
Abs coeff (mm^{-1})	0.093	0.145
F (000)	968	1408
Cryst size (mm)	0.50 × 0.30 × 0.20	0.70 × 0.60 × 0.20
θ range (deg)	3.54 – 25.03	3.51 – 25.05
Limiting indices	$-14 \leq h \leq 14$, $-1 \leq k \leq 18$, $-16 \leq l \leq 16$	$-14 \leq h \leq 14$, $-9 \leq k \leq 26$, $-16 \leq l \leq 16$
No. Of reflns collected	4978	10122
No.of indep.reflns	4759 (R_{int} = 0.0283)	6843 (R_{int} = 0.0510)
Data / Restraints / Parameters	4736 / 0 / 299	6835 / 0 / 413
GOF/F^2	1.128	1.050
R indices [$I > 2\sigma(I)$]	$R1$ = 0.0471, $wR2$ = 0.0914	$R1$ = 0.0436, $wR2$ = 0.1110
R indices (all data)	$R1$ = 0.860, $wR2$ = 0.1202	$R1$ = 0.0511, $wR2$ = 0.1201
Largest diff peak / hole (eÅ^{-3})	0.262 / -0.218	0.320 / -0.256

Formula / Code	$C_{37}H_{59}AlN_2Si_2$ / **32**	$C_{43}H_{51}AlN_2$ / **33**
Fw	615.02	622.84
Temp (K)	200(2)	133(2)
Cryst syst, Space group	Triclinic, *P*-1	Monoclinic, $P2_1$
a, *b*, *c* (Å)	11.160(4), 11.978(5), 16.460(7)	18.785(3), 20.832(4), 18.823(3)
α, β, γ (°)	85.68(3), 80.20(2), 64.11(2)	90, 90.08(3), 90
V (Å^3), *Z*	1950.6(13), 2	7366(2), 8
d (calcd) Mg / m^3	1.047	1.123
Abs coeff (mm^{-1})	0.138	0.086
F (000)	672	2688
Cryst size (mm)	1.00 × 0.60 × 0.30	0.70 × 0.40 × 0.15
θ range (deg)	3.51 – 25.12	2.23 – 27.50
Limiting indices	$-12 \le h \le 13$, $-14 \le k \le 14$, $-14 \le l \le 19$	$-23 \le h \le 23$, $-26 \le k \le 26$, $0 \le l \le 24$
No. of reflns collected	7806	143864
No.of indep.reflns	6894 (R_{int} = 0.0708)	32699 (R_{int} = 0.0839)
Data / Restraints / Parameters	6885 / 0 / 395	32699 / 1 / 1699
GOF/F^2	1.045	1.028
R indices [$I > 2\sigma(I)$]	$R1$ = 0.0698, $wR2$ = 0.1845	$R1$ = 0.0506, $wR2$ = 0.1045
R indices (all data)	$R1$ = 0.0849, $wR2$ = 0.2090	$R1$ = 0.0780, $wR2$ = 0.01177
Largest diff peak / hole (eÅ^{-3})	0.490 / -0.485	0.249 / -0.270

Formula / Code	$C_{59}H_{71}AlN_2O_3$ / **35**·OEt$_2$	$C_{54}H_{79}AlN_2O_2Si_2$ / **37**·OEt$_2$
Fw	883.16	871.35
Temp (K)	203(2)	133(2)
Cryst syst, Space group	Monoclinic, $P2_1/n$	Orthorhombic,$P2_12_12_1$
a, b, c (Å)	22.027(4), 11.4636(12), 20.857(4)	12.803(3), 17.176(3), 23.578(5)
α, β, γ (°)	90, 105.023(13), 90	90, 90, 90
V (Å^3), Z	5086.4(14), 4	5184.9(19), 4
d (calcd) Mg / m^3	1.153	1.116
Abs coeff (mm^{-1})	0.086	0.125
F (000)	1904	1896
Cryst size (mm)	$0.80 \times 0.60 \times 0.50$	$0.40 \times 0.30 \times 0.20$
θ range (deg)	3.52 – 25.03	2.10 – 27.86
Limiting indices	$-26 \le h \le 26$, $-13 \le k \le 13$, $-24 \le l \le 24$	$-16 \le h \le 16$, $0 \le k \le 22$, $0 \le l \le 30$
No. of reflns collected	12230	109910
No.of indep.reflns	8973 (R_{int} = 0.0434)	12113 (R_{int} = 0.0710)
Data / Restraints / Parameters	8973 / 577 / 598	12113 / 0 / 568
GOF/F^2	1.030	1.050
R indices [$I > 2\sigma(I)$]	$R1 = 0.0523$, $wR2 = 0.1161$	$R1 = 0.0394$, $wR2 = 0.0852$
R indices (all data)	$R1 = 0.0760$, $wR2 = 0.1325$	$R1 = 0.0485$, $wR2 = 0.0894$
Largest diff peak / hole (eÅ^{-3})	0.407 / -0.352	0.238 / -0.224

Formula / Code	$C_{44}H_{64}AlN_3Si_2$ / **38**	$C_{42}H_{58}Al_2N_2P_2Si_2$ / **42**
Fw	718.14	762.98
Temp (K)	133(2)	200(2)
Cryst syst, Space group	Triclinic, *P*-1	Triclinic, *P*-1
a, b, c (Å)	11.445(2), 12.591(3), 16.521(3)	11.787(3), 14.151(4), 14.454(4)
α, β, γ (°)	106.30(3), 90.82(3), 108.90(3)	83.47(2), 70.18(2), 79.501(13)
V (Å^3), Z	2147.3(7), 2	2226.6(10), 2
d (calcd) Mg / m^3	1.111	1.138
Abs coeff (mm^{-1})	0.135	0.221
F (000)	780	816
Cryst size (mm)	0.50 × 0.30 × 0.30	1.00 × 0.60 × 0.40
θ range (deg)	2.17 – 27.76	3.51 – 25.02
Limiting indices	$-14 \le h \le 14$, $-16 \le k \le 15$, $0 \le l \le 21$	$-12 \le h \le 14$, $-16 \le k \le 16$, $-17 \le l \le 17$
No. Of reflns collected	9997	13488
No.of indep.reflns	9997 (R_{int} = 0.0519)	7801 (R_{int} = 0.0662)
Data / Restraints / Parameters	9997 / 0 / 467	7791 / 645 / 446
GOF/F^2	1.065	1.036
R indices [$I > 2\sigma(I)$]	$R1 = 0.0437$, $wR2 = 0.1030$	$R1 = 0.0543$, $wR2 = 0.1550$
R indices (all data)	$R1 = 0.548$, $wR2 = 0.1084$	$R1 = 0.0600$, $wR2 = 0.1649$
Largest diff peak / hole (eÅ^{-3})	0.394 / -0.308	1.252 / -0.889

Formula / Code	$C_{31}H_{49}AlN_2$ / **43**	$C_{29}H_{43}AlI_2N_2$ / **44**
Fw	476.70	700.43
Temp (K)	133(2)	133(2)
Cryst syst, Space group	Triclinic, *P*-1	Orthorhombic, $Pna2_1$
a, b, c (Å)	10.138(2), 10.927(2), 14.344(3)	18.087(4), 10.241(2), 17.118(3)
α, β, γ (°)	74.44(3), 77.77(3), 74.27(3)	90, 90, 90
V (Å^3), *Z*	1456.8(5), 2	3170.7(11), 4
d (calcd) Mg / m^3	1.087	1.467
Abs coeff (mm^{-1})	0.090	2.030
F (000)	524	1400
Cryst size (mm)	$0.50 \times 0.40 \times 0.20$	$0.30 \times 0.20 \times 0.10$
θ range (deg)	2.11 – 27.72	2.25 – 27.96
Limiting indices	$-12 \le h \le 13$, $-13 \le k \le 14$, $0 \le l \le 18$	$0 \le h \le 23$, $0 \le k \le 13$, $-22 \le l \le 22$
No. Of reflns collected	22263	57704
No.of indep.reflns	6728 (R_{int} = 0.0495)	7456 (R_{int} = 0.0514)
Data/Restraints/Parameters	6728 / 0 / 320	7456 / 0 / 319
GOF/F^2	1.036	1.044
R indices [$I > 2\sigma(I)$]	*R*1 = 0.0548, *wR*2 = 0.1344	*R*1 = 0.0271, *wR*2 = 0.0657
R indices (all data)	*R*1 = 0.0711, *wR*2 = 0.1433	*R*1 = 0.0315, *wR*2 = 0.0680
Largest diff peak/hole (eÅ^{-3})	0.431 / -0.231	1.157 / -0.828

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8 Lebenslauf

Name: Chunming Cui

Geboren: 31. Juli 1967 in Shaanxi, China

Staatsangehörigkeit: chinesisch

Familienstand: verheiratet, ein Sohn.

Schulausbildung

02/1974 - 06/1979: Grundschule in Shaanxi, China

08/1979 - 06/1982: Wugong Middleschool in Shaanxi, China

09/1982 - 06/1985: Studium am *Shaanxi Chemical Engineering College*, Xi’an, China

Hochschulausbildung

09/1986- 07/1990: Studium Chemie am Fachbereich Chemie der Universität Northwest, Xi’an, China

07/1990: *Bachelor of Science*

09/1990 - 06/1993: Studium der Organische Chemie am Universität Nankai, Tianjin, China

06/1993: *Master of Science*

06/1993 - 10/1997: Forschungsmitarbeiter am *Research Institute of Petroleum Processing*, *SINOPEC*, Beijing, China

10/1997 - 12/1997: Äquivalenzprüfung zum Diplomexamen - Fach Chemie

01/1998 - 01/2001: Anfertigung der Dissertation unter Anleitung von Prof. Dr. Dr. h. c. mult. H. W. Roesky am Institut für anorganische Chemie der Georg August Universität zu Göttingen

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