The Reaction Chemistry of Aluminum(I, III) Compounds

Stabilized by Sterically Bulky Ligands

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Dedicated to my wife Qiaozhu Jiang

and my son Yicheng Zhu

for their love and affection
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1. Introduction

Aluminum, bound almost exclusively to oxygen in various combinations, is the most abundant metal in the earth’s crust. Once methods were developed to free useable quantities of the element from oxygen, applications for the element began developing rapidly. This growth has resulted in the ubiquity of the metal in today’s world.\cite{1}

The organoaluminum chemistry, due to the implications and potential, has been significant enough to excite widespread industrial interest. In 1859, ethylaluminum sesquiodide (a 1:1 mixture of EtAlI\(_2\) and Et\(_2\)AlI) was first prepared from ethyl iodide and aluminum by Hallwachs and Schafarik.\cite{2} The subsequent synthesis of aluminum alkyls from mercury alkyls and aluminum metal was reported by Buckton and Odling in 1865.\cite{3} The development of organoaluminum chemistry including the introductions of many new synthetic methods followed by researches on organomagnesium and organolithium reagents, the syntheses of a large number of new organoaluminum compounds, and the explorations of reactions of these compounds, however, started from the studies of Ziegler et al. in the early 1950’s. These studies open a wide insight into the organoaluminum chemistry which lies dormant for ca. one hundred years, and make the potential of organoaluminum reagents for organic synthesis and polymerization come to light. The most notable important discovery is the polymerization of ethylene by Ziegler through a stepwise addition to triethylaluminum.\cite{4,5} This directly leads to the generation of Ziegler’s catalysts based on transition-element compounds, which are normally formed by reaction of a transition-element halide or alkoxide or alkyl or aryl derivative with aluminum alkyl or alkyl halide.\cite{6} Correspondingly, the reactivity of the related organoaluminum compounds (Scheme 1) can be presented as follows:\cite{7}

a) The highest reactivity is observed if all three valences of Al are bound to C or C and H, respectively.

b) Many reactions are related to the electron deficiency of aluminum in its compounds of the type AlR\(_{3-n}\)X\(_n\) (n = 2 to 0).
c) Certain reversible relations exist between the Al–C and the Al–H bond.

d) Not only the Al–H group but also Al–C moiety can be added to C= C and C≡C bonds.

e) Organoaluminum compounds undergo a series of reactions more or less characteristic for many metal alkyls in which the aluminum is removed from carbon.

\[
\text{Scheme 1}
\]

In the following time, the organoaluminum chemistry was rapidly developed on the basis of Ziegler’s classic studies, and some new properties of organoaluminum compounds are found. For example, alumoxanes prepared from the controlled hydrolysis of organoaluminum compounds or alternatively by their reactions with oxygen-containing compounds can be used as active catalysts in the polymerization of epoxides, aldehydes, and olefins.\(^{[8-14]}\) In 1980, methylalumoxane (MAO) was found to be a highly active cocatalyst for group 4 metallocenes catalyzing ethylene and propylene polymerization by Kaminsky and Sinn.\(^{[15-16]}\) This has been of remarkable industrial importance.

In the meantime, the reactions of organoaluminum compounds towards unsaturated substrates, elements, or acidic hydrogen containing species are studied more systematically, comprehensively, and in detail, and many reaction types such as elimination, addition, insertion, reoxidation, C–H activation, dimerization (or oligomerization), and substitution are presented.\(^{[4]}\)

In comparison to the trivalent organoaluminum chemistry, the low valent aluminum(I, II) chemistry which is characterized by the restricted use of the valence electrons of Al in
compound formation is often invoked due to the roles of these Al(I, II) species as possible intermediates in photochemical and radical reactions. Although the pursuit of compounds of low valent aluminum has a long history of over 50 years, most of the fascinating progress occurs only in recent years, especially in the case of Al(I) which may prove to be of much importance in the near future (Scheme 2).\(^{[17-18]}\)

In view of the syntheses of organoaluminum compounds, some of formula $\text{AlR}_nX_{3-n}$ ($n = 1-3$) with simple $R$ groups ($R = \text{H, Me, Et, iPr, tBu}$) have been commonly employed as hydroalumination or carboalumination reagents. These compounds have been commercially available. Due to the strong Lewis acidity of the Al center in these compounds, their reaction products are often found in high degree of association, even for reagents with fairly large organic groups such as $t$Bu, Ph. A large number of clusters of alane or carboalane with two- or three-dimensional net or cage structures have been synthesized, exhibiting the extensive

\[ \text{Scheme 2} \]
organoaluminum chemistry. However, studies of this aspect often meet with challenges in detailed investigations of mechanism and stoichiometry.

The bulky organic ligand is usually employed to stabilize the metal center electronically and/or sterically. The introduction of a bulky organic ligand whether as a simple Lewis base donor, or in elimination reactions by gas (H₂, RH) or MXₙ salts to the Al center, in fact, can efficiently reduce the condensation of products, and meanwhile, result in the formation of unusual compounds. This has also been successfully applied for the synthesis of low valent aluminum compounds. Moreover, by the stabilization of these large ligands, we can selectively perform changes of the functionalities at Al, and intendedly control and design the reaction. All these help to understand organoaluminum chemistry and to investigate the possible reaction mechanisms.

![Scheme 3](image)

**Scheme 3**

In this thesis, the two types of bulky ligands (Scheme 3) are employed for the synthesis of aluminum monohydride, monohalide, and monoalkyl (using L’H₂), and aluminum(I) monomer, aluminum(III) dihydride and dihalide, and aluminacyclopentene (using LH), respectively. Subsequently, these compounds are further used as precursor to react with Lewis acidic species, fluorination agent, oxidation agents, carbene, water, unsaturated molecules, and so on. The sections 2.1.-2.8. will in detail point out the importance, recent research background, experimental results and discussion, and conclusion and remark of the chemistry
of the bulky ligands stabilized aluminum compounds and their reactions. Based on these
delineations, the objectives of the present work are:

(1) the chemical changes of aluminum functionalities in the stabilization of bulky
ligands at Al.

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

(3) the exploration of reaction chemistry of aluminacyclopene LAl(η²-C₂RR’).
2. Contents

2.1. A Bulky Chelating Diamide Aluminum Monohydride:
Synthesis, Structure, and Reactions with Me$_3$SnF
and Heavy Group 16 Elements

Abstract: A bulky chelating diamide aluminum monohydride \( \text{[ArN(CH}_2)_3\text{NAr]}\text{AlH(NMe}_3\text{)} \) (Ar = 2,6-iPr$_2$C$_6$H$_3$) (1) was prepared in excellent yield from the reaction of diamine ArNH \( (CH_2)_3HNAr \) with a small excess of AlH$_3$·NMe$_3$ in toluene. Subsequent fluorination of 1 with Me$_3$SnF resulted in the formation of an aluminum monofluoride \( \text{[ArN(CH}_2)_3\text{NAr]}\text{AlF(NMe}_3\text{)} \) (2), indicating the reactivity of 1 despite the bulk of diamido ArN(CH$_2$)$_3$NAr. Further reaction of 1 with elemental E (E = S, Se and Te) proceeded in toluene at elevated temperature to yield aluminum chalcogenide \( \{[\text{ArNH(CH}_2)_3\text{NAr]}\text{Al(µ-E)}\}_2 \) (E = S (3), Se (4), and Te (5)).

Compounds 1 and 2 are well-separated monomers with a central aluminum atom in a tetrahedral environment. Compound 4, however, is a dimer with a central Al$_2$Se$_2$ core bearing an ideal four-membered planar ring. The IR and $^1$H NMR spectral data of compounds 3–5 suggest that a migration of the hydrogen from selenium to one of the nitrogen atoms at the diamide ligand is involved in the course of the reaction.

Studies of aluminum hydrides have received considerable attention due to their scientific importance and numerous applications.$^{[4]}$ In recent years, much work has been devoted to aluminum hydrides in low aggregation, especially to the monomeric forms, since the synthetic process of monomeric aluminum hydride helps us to understand the reaction chemistry of surface-bound AlH$_n$ groups developed during thin film growth from organoaluminum sources.$^{[19-20]}$ Moreover, aluminum hydrides of low aggregation can be used as very effective precursors for preparing aluminum chalcogenides.$^{[21]}$ However, reactions involving aluminum hydrides of low aggregation with chalcogen or organochalcogenides have been reported to a lesser extent. Raston et al.$^{[22-25]}$ investigated the reaction of trimethylamine adduct of alane
Me₃N·AlH₃ with chalcogen or organochalcogenide. Power et al.²-six reported one example of the reaction of aluminum dihydride with organochalcogenide and our group discussed the reaction of a series of aluminum dihydrides with chalcogen,²-one,²-two,²-three,²-four where the isolation and structural characterization of some novel compounds (such as LAl(SeH)₂, LAl(SeH)Se(SeH)AlL,²-five,²-six LAl(SH)₂²-seven (L = N(Ar)C(Me)CHC(Me)N(Ar), Ar = 2,6-iPr₂C₆H₃); (RAIE)₂ (R = 2,4,6-iBu₃C₆H₂, E = S;²-eight R = N(SiMe₃)C(Ph)C(SiMe₃)₂,²-nine 2,6-(Et₂NCH₂)₂C₆H₃, 2-Et₂NCH₂-6-MeC₆H₃,²-ten E = Se, Te), trans-[[Me₃N(H)Al(μ-E)]₂] (E = Se, Te),²-eleven trans-[[Me₃N(PhTe)Al(μ-Se)]₂];²-twelve [(η¹⁻³,5-tBu₂pz(μ-Al)H)₂E (E = S, Se, Te);²-thirteen Me₃NAI(ER)₃ (E = Se, R = Et, Ph, CH₂Ph; E = Te, R = Ph)²-fourteen and Al₄Se₅(H)(NMe₃)₄²-fifteen showed a rich chemistry. Nonetheless, the reaction of monomeric bulky aluminum monohydrides with chalcogen, which might generate the corresponding monomeric Al–EH moieties, have not been reported so far. Therefore we became interested in finding the sufficiently bulky ligand to synthesize the intramolecularly stabilized aluminum monohydride, and further studies on its reactivity.

The divalent bulky chelating diamide ligand [ArN(CH₂)₃NAr]²- (Ar = 2,6-iPr₂C₆H₃) is currently exhibiting growing interests²-sixteen due to its special steric and electronic properties to control effectively the geometry at the metal center. The known complexes having this ligand include main group metal (Li, K, Al) and transition metal (Ti, Zr, Y, Lu) derivatives.²-seventeen-²-twenty The only reported aluminum complexes are a series of compounds containing alkyl and aryl groups [ArN(CH₂)₃NAr]AIr (R = Me, iBu, C₆F₅).²-twenty Herein we report on the synthesis and characterization of a bulky chelating diamide aluminum monohydride [ArN(CH₂)₃NAr]AlH(NMe₃) (Ar = 2,6-iPr₂C₆H₃) (1). The metathesis of 1 with Me₃SnF to give a monofluoride [ArN(CH₂)₃NAr]AlF(NMe₃) (2) and its reaction with heavy group 16 elements to afford dimeric aluminum chalcogenide {[ArNH(CH₂)₃NAr]Al(μ-E)}₂ (E = S (3), Se (4), and Te (5)) are also described.

Although the syntheses of aluminum hydrides have been reported in a number of publica
the use of AlH₃·NMe₃ as a precursor to react with N-substituted diamine, diimine and analogues containing NH groups or E(SiMe₃)₂ (E = P, As) under elimination of H₂ or HSiMe₃ has shown a facile route to aluminum hydrides of low aggregation. Reaction of the diamine [ArNH(CH₂)₃HNAr] with a small excess of AlH₃·NMe₃ in toluene under heating (80 °C) affords the intramolecularly stabilized diamide aluminum monohydride [ArN(CH₂)₃NAr]AlH(NMe₃) (1) in excellent yield. Subsequent fluorination of 1 with Me₃SnF either at room temperature or at elevated temperature (80 °C) results in the formation of an aluminum monofluoride [ArN(CH₂)₃NAr]AlF(NMe₃) (2, Scheme 4).

![Scheme 4](attachment:Scheme4.png)

Complexes 1 and 2 are characterized by NMR, MS (EI), IR spectroscopy and elemental analyses. The presence of hydride in 1 is evident from the IR spectrum. The broad IR band at 1799 cm⁻¹ can be assigned to the Al–H stretching absorption. In the IR spectrum of 2, this absorption disappears, indicating a complete fluorination of 1. The ¹⁹F NMR spectrum of 2 exhibits one singlet resonance (−175.4 ppm), which can be comparable to those terminal Al–F resonances in a series of compounds (ArN[Si(R)Me₂]AlF₂·THF: Ar = 2,6-iPr₂C₆H₃, R = Me, −178.1; R = iPr, −177.0; R = tBu, −175.1; Ar = 2,6-Me₂C₆H₃, R = tBu, −175.0; R = 2,4,6-Me₃C₆H₂, −175.9 ppm). In the ¹H NMR spectra of 1 and 2 the presence of the complex resonances for the backbone protons of the diamide ligand (two isopropyl methine (CHMe₂),
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Figure 1. Molecular structure of 1. H atoms are omitted for clarity except for the Al–H group.

Selected bond lengths (Å) and angles (º): Al(1)–N(1) 1.820(1), Al(1)–N(2) 1.828(1), Al(1)–N(3) 2.024(2), Al(1)–H(1) 1.52, N(1)–Al(1)–N(2) 106.52(6), H(1)–Al(1)–N(3) 96.0.

four isopropyl methyl (CHMe₂), two methene (NCH₂) and two methene (NCH₂CH₂) resonances) are consistent with a pseudotetrahedral geometry and Cs symmetry about Al. Similar resonances are observed in compounds [M{ArN(CH₂)₃NAr}η-C₅H₅]Cl (M = Zr, Y; Ar = 2,6-iPr₂C₆H₃). The resonance for the Al–H proton in 1 is not seen, which is, however, typical for amidoaluminum hydride species. Substitution of Al–H in 1 by Al–F has a stronger effect on the chemical shift of the NMe₃ group (1.66, 1; 1.75 ppm, 2), while a smaller effect is observed for the backbone protons of the ligand. The MS (EI) spectrum shows the molecular ion of [M⁺ – NMe₃] for 1, and [M⁺] and [M⁺ – NMe₃] for 2 and the single crystal X-ray structural determinations of 1 and 2 confirm the composition of [ArN(CH₂)₃NAr]AlR(NMe₃) (R = H, 1; F, 2), where the former contains half a molecule of n-hexane per molecule of complex 1 in the asymmetric unit.

Compounds 1 and 2 are well-separated monomers with a central aluminum atom both in a distorted tetrahedral environment (Figures 1 and 2 with selected bond lengths and angles). The terminal Al–H bond length (1.52 Å) is closer to those in compounds (2,4,6-tBu₃C₆H₂)₂AlH⁴⁷ (1.53(4) Å) and [HAl(NMe₂)₃]⁴⁸ (1.52(2) Å), but shorter than those in
AlH(Cl)(tBuNCH₂CH₂N(tBu)H)\(^{[37]}\) (1.60 Å), \(\text{Al}_2(\mu\text{-NET})_2\text{N(tPr)}_2\text{H}_2\)\(^{[49]}\) (1.67 Å) and (2,4,6-tBu\(_3\)C\(_6\)H\(_2\)Al(H)Cl·THF\(^{[50]}\) (1.73(5) Å). The terminal Al–F separation (1.678(1) Å) is in the range of 1.657–1.681 Å observed in compound \([(\text{Me}_3\text{Si})_3\text{CAIF}_2)_3\] \(^{[51]}\) and somewhat longer than those in \([(2,6-i\text{Pr}_2\text{C}_6\text{H}_3)\text{N(SiMe}_3\text{AlF}_2)_3\] \(^{[46]}\) (1.634–1.642 Å) and AlF\(_3\) \(^{[52]}\) (1.63 Å), as determined by electron diffraction. The diamide ligand chelates the Al atom to form an AlN\(_2\)C\(_3\) six-membered non-planar ring, in which Al(1) and C(2) occupy the head positions with distances to the quasi-plane N(1)–N(2)–C(3)–C(1) (the mean deviation \(\Delta = 0.0716\) Å) of 0.1034 and 0.6852 Å in 1 and the plane N(1)–N(2)–C(3)–C(1) (\(\Delta = 0.0316\) Å) of –0.0109 and 0.6730 Å in 2, respectively. It is obvious that the former displays a boat conformation and the latter a flattened chair conformation, as can be explained in terms of strain imposed by the Ar group. The F atom owns a stronger electron attractive tendency than the H atom. This generates different charge distribution for the central Al atom of 1 and 2, and gives rise to a small difference of the Al–N\(_{\text{diamide}}\) bond distance between 1 and 2 (average 1.824, 1; 1.807 Å, 2), as well as the Al–NMe\(_3\) bond distance (2.024(2), 1; 2.000(2) Å, 2) and the N(1)–Al(1)–N(2) chelating angle (106.52(6), 1; 107.45(7)°, 2). The Al–N\(_{\text{diamide}}\) distances in 1 and 2 can be
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compared with the terminal Al–N (amide) distances in \( \text{CH}_2(\text{CH}_2\text{CMe}_2)_2\text{NAI}_2\cdot\text{NMe}_3 \) \(^{[44]}\) (1.838(2) Å), \( \text{AlH(Cl)}[\text{tBuNCH}_2\text{CH}_2\text{N(tBu)}\text{H}] \) \(^{[37]}\) (1.80(1) Å) and \( \{\text{Al(µ-H)}[\text{N(CMe}_2\text{CH}_2)_2\text{CH}_2\text{]}\}_2 \) \(^{[53]}\) (1.836(3) Å), and are longer than the Al–N$_{\text{diamide}}$ bond lengths in the three coordinate aluminum compound \([\text{ArN(CH}_2\text{)}_3\text{NAr}]\text{AlMe}_3 \) \(^{[35]}\) (1.760(3), 1.766(3) Å). The Al–N$_{\text{NMe}_3}$ distances in 1 and 2 are as expected in a comparable range.\(^{[44,54-55]}\)

The successful fluorination of 1 using Me$_3$SnF is indicative of its reactivity despite the steric hindrance of the bulky ligand. Treatment of 1 with equivalent amounts of sulfur, selenium and tellurium proceeded in toluene at elevated temperature to afford solvated aluminum sulfide (3) as light yellow crystals, selenide (4) as yellow crystals and telluride (5) as green-yellow crystals, respectively. The former two compounds are obtained in good yield and the latter in moderate yield (Equation 1).

\[
2[\text{ArN(CH}_2\text{)}_3\text{NAr}]\text{AlH(NMe}_3\text{)} + 2\text{E} \rightarrow \{[\text{ArNH(CH}_2\text{)}_3\text{NAr}]\text{Al(µ-E)}\}_2 + 2\text{NMe}_3 \quad (1)
\]

\[\text{E} = \text{S (3), 80 ºC, 12 h}\]
\[= \text{Se (4), reflux, 12 h}\]
\[= \text{Te (5), reflux, 120 h}\]

Compounds 3–5 are air and moisture sensitive and soluble in hot toluene and benzene, while poorly soluble in THF, CHCl$_3$ and n-hexane. They were characterized by IR and NMR spectroscopy and MS (EI) spectrometry, as well as elemental analyses. The MS (EI) spectra of 3–5 show the dimeric molecular ion with the correct isotope pattern and their $^1$H NMR spectroscopies show the very similar characters of the ligand including the resonances of solvent toluene protons. The doublets in the range of $\delta$1.10–1.25, one septet centered at ca. $\delta$3.38 and a multiplet at $\delta$ 7.02–7.10 are corresponding to the protons of the 2,6-$i$Pr$_2$C$_6$H$_3$ group. One broad singlet at ca. $\delta$ 1.36 can be assigned to NH resonance\(^{[37,39]}\) with satisfied integral intensity indicating two protons. Two areas of unresolved multiplet resonances centered at ca. $\delta$1.78 and 3.00 arise from the six non-equivalent methylene protons, where the latter might be formed from overlapping proton resonances of the two amido NCH$_2$ and two
amine HNCH$_2$ groups. The IR spectra exhibit the NH absorption in the $\tilde{\nu}$$_{NH}$ region$^{[37-38]}$ (3190, 3; 3187, 4; 3185 cm$^{-1}$, 5). All these data indicate that compounds 3, 4 and 5 have the same structure corresponding to the formula of $\{[\text{ArNH}(\text{CH}_2)_3\text{NAr}]\text{Al(\mu-E)}\}_2$.

![Scheme 5](image)

**Scheme 5**

The reaction of aluminum dihydride with selenium has been discussed in our group,$^{[21,28-29]}$ where the formation of a dimeric compound might proceed through an Al–SeH intermediate.

In a similar way the reaction of aluminum monohydride 1 with selenium might involve the formation of intermediate $[\text{ArN(CH}_2)_3\text{NAr}]\text{Al(SeH)(NMe}_3)\$, which dimerizes to produce $\{[\text{ArN(CH}_2)_3\text{NAr}]\text{Al(\mu-SeH)}\}_2$ under elimination of gaseous NMe$_3$. However, with reference to related Al–SeH compounds LAl(SeH)$_2$ and LAl(SeH)Se(SeH)LAl (L = N(\text{Ar})C(\text{Me})CHC(\text{Me})N(\text{Ar}), \text{Ar} = 2,6-\text{iPr}_2\text{C}_6\text{H}_3),^{[56]}$ no absorptions in the range of 2000-2500 cm$^{-1}$ in the IR spectrum are observed to indicate the formation of an Al–SeH moiety. This suggests that the dimer $\{[\text{ArN(CH}_2)_3\text{NAr}]\text{Al(\mu-SeH)}\}_2$ is not stable under heating and the hydrogen atom attached to selenium atom migrates quickly to one of the nitrogen atoms at the diamide ligand to afford stable compound 4. The most likely mechanism is given in Scheme 5. The formation of compounds 3 and 5 might be similar to that of 4.

A suitable single crystal of compound 4 was measured by X-ray diffraction. The structure analysis of compound 4 shows a dimeric species containing two molecules of toluene.
Unfortunately, the quality of the crystal structure did not allow the location of the hydrogen atoms on the nitrogen atoms. Nevertheless, the presence of NH groups was established by IR and $^1$H NMR spectroscopy. The molecular structure is viewed in Figure 3 with selected bond lengths and angles. The Al(1)–N(1) (1.932(11) Å) and Al(1)–N(2) (1.916(11) Å) bond distances are midway between the Al–N_{amine} and Al–N_{amido} bond distances observed in complex AlH(Cl)[tBuNCH$_2$CH$_2$N(tBu)H]$^{[37]}$ (Al–N(1) (amine) (2.00(1) Å) and Al–N(2) (amido) (1.80(1) Å), and are longer than those Al–N distances found in compound Al[tBuNCH$_2$CH$_2$N(tBu)][tBuNCH$_2$CH$_2$NH(tBu)]$^{[38]}$ in which the unique amine nitrogen center is disordered over all four nitrogen centers (1.850(5), 1.870(5) Å), and much longer than Al–N_{amido} distances in 1 (1.820(1), 1.828(1) Å) and 2 (1.804(2), 1.810(2) Å). However, compared to compound AlH(Cl)[tBuNCH$_2$CH$_2$N(tBu)H]$^{[37]}$ where the remarkable difference (0.20 Å) between Al–N(1) (amine) and Al–N(2) (amido) was observed, the very slight difference (0.016 Å) between Al(1)–N(1) and Al(1)–N(2) in 4 may imply the disorder of the two hydrogen atoms over the sides of all four nitrogen centers. Moreover, the similar
coordinated environments and approximately planar co-ordination geometries at the N(1) and N(2) (at N(1), Al(1)–N(1)–C(1) 119.6(8)°, Al(1)–N(1)–C(16) 126.4(8)°, C(1)–N(1)–C(16) 113.2(9)°, \( \sum (C–N–Al, C) = 359.2° \); at N(2), Al(1)–N(2)–C(3) 121.1(9)°, Al(1)–N(2)–C(4) 130.1(7)°, C(3)–N(2)–C(4) 108.0(9)°, \( \sum (C–N–Al, C) = 359.2° \)) do not allow to distinguish between the amine nitrogen and the amido nitrogen centers. Overall, it is assumed that the almost equal possibility of the hydrogen migration from the selenium atom to any nitrogen atom at the diamide ligand is included in the course of the reaction.

The \( \text{Al}_2\text{Se}_2 \) core exhibits an ideal planar ring (the least-square deviation \( \Delta = 0.0005 \)) with Al(1)–Se(1) of 2.339(1) Å, Al(1)–Se(1A) of 2.381(1) Å and Al(1)–Se(1)–Al(1A) of 78.56(5)°, which are as expected in a range for \( \text{Al}_2\text{Se}_2 \) core compounds\(^{\text{[22-23,28-29]}} \), while the Al(1)–Se(1) and Al(1)–Se(1A) distances differ by ca. 0.042 Å probably due to steric effects of the backbone ligand toward the \( \text{Al}_2\text{Se}_2 \) ring. The ligand chelates the Al atom to fuse two six-membered \( \text{AlN}_2\text{C}_3 \) rings, which are arranged \textit{in trans} on each side of \( \text{Al}_2\text{Se}_2 \) core. The two \( \text{AlN}_2\text{C}_3 \) rings both display a boat conformation with Al(1) and Al(1A) at the bow and C(2) and C(2A) at the stern, respectively, and are almost arranged perpendicularly to the \( \text{Al}_2\text{Se}_2 \) ring (the dihedral angle between the ring (\( \text{Al}_2\text{Se}_2 \)) and the plane (N(1)–N(2)–C(3)–C(1), \( \Delta = 0.0238 \) Å) is 90.5°).

Thus, it has been shown that the \([\text{ArN(CH}_2)_3\text{NAr}]^2^-\) ligand forms a stable chelate with the aluminum hydride. The hydride functionally can be replaced by a fluorine atom or substituted by a chalcogen (S, Se, Te) under migration of the hydrogen to an adjacent nitrogen of the chelating ring. The latter reaction does not yield an aluminum chalcogen double bond system but rather a four-membered ring of composition \( \text{Al}_2\text{E}_2 \) (E = S, Se, Te).
2.2. The Stepwise Hydrolysis of Aluminum Chloride

Iodide LAlClI in the Presence of N-Heterocyclic Carbene as Hydrogen Halide Acceptor

Abstract: An aluminum chloride iodide LAlClI \((7, L = HC\[(CMe)(NAr)\], Ar = 2,6-iPr\_2C\_6H\_3)\) has been synthesized to study the stepwise hydrolysis of this compound in the presence of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene as hydrogen halide acceptor. The isolation and characterization of the aluminum chloride hydroxide \([\text{LAlCl(}\mu\text{-OH})\] \(8\)) and the dihydroxide \(\text{LAl(OH)}\_2 \(9\) demonstrate the realization of a controlled hydrolysis.

The controlled hydrolysis of organoaluminum compounds is of great interest since it can lead to the formation of alumoxanes which are used as active catalysts and cocatalysts for the polymerization of a wide range of organic monomers.\([8-16,57-59]\) Furthermore, it can be useful to generate organoaluminum hydroxides, oxides, or oxide hydroxides.\([12,57-58,60-65]\) On one hand, the reaction of AlR\(_3\) compounds (R = Me, tBu, Mes, or Ph)\([66-67]\) with water or hydrated inert salts afforded some aggregated alumoxanes [RAIO]\(_n\), aluminum hydroxides, and oxide hydroxides. On the other hand, it has been shown that aluminum hydrides,\([71-72]\) alkyls,\([73]\) or aluminum amino-amides\([74]\) stabilized by bulky organic ligands can be used as precursor for the synthesis of organoalumoxanes, organoalumoxane hydrides, and hydroxides by employing H\(_2\)O, or water-containing compounds (for example, H\(_2\)O-B(C\(_6\)F\(_5\))\(_3\)). In most cases the bulky ligand at the aluminum center hinders the aggregation of the hydrolysis products. However it has an effect on the stabilization of the metal whether electronically or sterically, and can result in the formation of unusual complexes, such as L’Al=O-B(C\(_6\)F\(_5\))\(_3\) (L’ = Et\(_2\)NCH\(_2\)CH\(_2\)NC(Me)CHC(Me)NCH\(_2\)CH\(_2\)NEt\(_2\)).\([73]\) More recently, we have reported the reaction of LAlI\(_2\) (L = HC\([(CMe)(NAr)]\), Ar = 2,6-iPr\_2C\_6H\_3) with KOH containing a small amount of H\(_2\)O and KH in a liquid ammonia/toluene two-phase system and successfully isolated the first terminal aluminum dihydroxide LAl(OH)\(_2\) supported by the bulky L ligand.\([75]\) An improved route to LAl(OH)\(_2\) was realized by using a strong nucleophilic
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In the course of the synthesis of LAl(OH)$_2$ from LAl(Hal)$_2$ (Hal = I, Cl), a stepwise process was proposed. However, there was no experimental evidence for the formation of LAl(OH)Cl or LAl(OH)I as an intermediate. In this context we report on the preparation of aluminum chloride iodide LAlClI (7) and its stepwise reaction with water by using a $N$-heterocyclic carbene as hydrogen halide acceptor, as well as isolation of the intermediate [LAlCl($\mu$-OH)$_2$]$_2$ (8).

Scheme 6

The toluene/$n$-hexane solution of LLLi prepared from LH and $n$-BuLi was directly used for the reaction with AlCl$_2$Me. Compound LAlClMe (6) was obtained as crystalline solid, its composition was confirmed by EI-mass and $^1$H NMR measurements as well as by elemental analysis. The reaction of 6 with one equiv of I$_2$ within 5 days at room temperature resulted in the formation of compound LAlClI (7) as very light yellow crystals (Scheme 6). Compound 7 melts at 200–203 °C and the EI-mass spectrum indicates its monomeric nature in the gas phase ($m/z$ (%): 606 (1, [M$^+$]), 571 (4, [M$^+$ – Cl]), 479 (100, [M$^+$ – I]). The $^1$H NMR spectrum of 7 shows two separated groups of septets (3.28, 3.64 ppm) and four groups of doublets (1.02, 1.12, 1.41, 1.42 ppm) for the respective isopropyl methine and methyl proton resonances of the Ar substituents, evidencing the asymmetric steric environment of the Ar isopropyl groups induced by Al–Cl and Al–I.
The X-ray crystal structural analysis of 7 showed a mononuclear compound with an aluminum center coordinated to the chelating \( \beta \)-diketiminato ligand and one Cl and one I atom in a distorted tetrahedral geometry. The molecular structure of 7 is shown in Figure 4 with selected bond lengths and angles. The terminal Al–I bond length (2.473(1) Å) is a little shorter than those in \( \text{LAlI}_2 \) (2.501(3), 2.543(3) Å),\(^{77}\) and close to those in \([\text{RAlI(\mu-I)}]_2 \) (R = \( \text{2,6-iPr}_2\text{C}_6\text{H}_3\text{N(SiMe}_3\text{)} \)) (2.464(2) Å).\(^{78}\) The Al–Cl distance (2.151(1) Å) is in good agreement with those in the terminal aluminum chlorides \([\text{3,5-tBu}_2\text{NCH=C(SiMe}_3\text{-pz)}\text{AlCl}_2 \) (2.135(1) Å), \( [\text{3,5-tBu}_2\text{NCH=C(SiMe}_3\text{-pz)}\text{AlCl(3,5-tBu}_2\text{pz)} \) (2.153(1) Å),\(^{79}\) and \( [(\text{C}_7\text{H}_13\text{N}_2\text{)}\text{AlCl}_2(\mu-O) \) (2.164(1) Å).\(^{65}\)

The stepwise hydrolysis of compound 7 was first carried out with one equiv of H\(_2\)O in the presence of one equiv of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (abbreviated as :C) in toluene solution from 0 °C to room temperature (Scheme 7). The removal of solvent in vacuo followed by extraction with \( n \)-hexane gave partial hydrolysis product \( [\text{LAlCl(\mu-OH)}]_2 \) (8) in 70% yield. The mass spectrum of 8 indicates the monomeric composition (m/z (%):
496.3 (50, [M^+]/2), 478.3 (16, [M^+]/2 – OH – 1), 461.3 (100, [M^+]/2 – Cl]). However the ^1H NMR spectrum of 8 recorded at 200.13 MHz shows one septet (3.40 ppm) for the isopropyl methine resonances of the Ar substituents, while two groups of incompletely separated septets (3.42, 3.47 ppm) were observed at 500.13 MHz. These are markedly different from those observed in the NMR spectrum of compound 7 (3.28, 3.64 ppm) and imply a possible oligomerization in solution. One singlet at 0.72 (in C$_6$D$_6$) alternatively 0.69 (in D$_8$-toluene) ppm could be assigned to the Al–μ-OH proton resonance comparable to the β-diketiminato aluminum dihydroxide LAl(OH)$_2$ (0.22 ppm).\[^{[76]}\] One broad absorption centered at 3459 cm$^{-1}$ corresponds to ν$_{OH}$ in the IR spectrum of 8.

The X-ray structural analysis unambiguously confirms compound 8 as a dimer in the solid state which is consistent with its solution behavior however in contrast to the EI-mass spectral results. The molecular structure of 8 is depicted in Figure 5 with selected bond lengths and angles. Each Al center is coordinated to one β-diketiminato ligand, one Cl, and two OH groups and adopts a distorted tetragonal-pyramidal geometry with the Cl atom located at the apical position and 2 N and 2 O atoms forming the basal plane (the least square plane Δ = 0.012 Å). The Al$_2$O$_2$ core is a perfectly planar four-membered ring due to the symmetry. The two H atoms of the OH groups are located within this plane (Δ = 0.009 Å). The Al–OH bond lengths (1.875(1), 1.886(1) Å) fall within the range of 1.787(3)–2.086(4) Å observed for
bridging aluminum hydroxides,[66-70] and are longer than the terminal ones in $\text{LAl(OH)}_2$ (1.697 (2) and 1.711 (2) Å)[75] and $[\text{LAl(OH)}]_2(\mu-\text{O})$ (1.738(3) and 1.741(3) Å).[80] The two Al–Cl bonds are in trans position arranged toward the $\text{Al}_2\text{O}_2\text{H}_2$ plane with bond distances (2.190(1) Å) slightly longer than that in 7.

Figure 5. Molecular structure of 8. H atoms in L are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.977(1), Al(1)–N(2) 1.984(1), Al(1)–Cl(1) 2.189(1), Al(1)–O(1) 1.875(1), Al(1)–O(1A) 1.886(1), N(1)–Al(1)–N(2) 90.05(6), O(1)–Al(1)–O(1A) 72.46(7), N(1)–Al(1)–Cl(1) 92.91(6), N(2)–Al(1)–Cl(1) 100.90(5).

Attempts to obtain monomeric 8 by recrystallization from THF or by the use of THF as a solvent during the preparation were not successful, only the dimer 8 being formed. This behavior demonstrates the strong Lewis-acidic Al center in the monomeric $\text{LAlCl(OH)}$ which leads to an association despite of the bulky ligand. This is in contrast to the monomeric species $\text{LAlMe}_2$,[81] $\text{LAlI}_2$,[77] $\text{LAl(NH}_2)_2$,[76] $\text{LAlMe(OH)}$, and $\text{LAlCI}_2$.

It is interesting to mention that a direct interaction between 7 and $N$-heterocyclic carbene $:\text{C}$ in THF solvent results in the generation of $[\text{H:C}]^+\text{T}$ as insoluble microcrystals, indicating the capability of proton abstraction of $:\text{C}$ from the $\beta$-diketiminato ligand. (Analytic data for
compound [H:C]^+T: M.p. 173-174 ºC; ^1H NMR (500.13 MHz, CD$_3$CN, 298 K, ppm): $\delta$ 1.51 (d, 4 x 3 H, $^3J_{HH}$ = 6.7 Hz, CH(CH$_3$)$_2$), 2.23 (s, 2 x 3 H, C(CH$_3$)$_2$), 4.49 (sept, 2 x 1 H, $^3J_{HH}$ = 6.7 Hz, CH(CH$_3$)$_2$), 8.63 (s, 1 H, H:C); EI-MS m/z (%): 181 (100, [H:C]^+), 128 (20, [I]); Anal. Calcd for C$_{11}$H$_{21}$IN$_2$ ($Mr$ = 308.1): C, 42.87; H, 6.87; N, 9.09; I, 41.17. Found: C, 43.19; H, 6.83; N, 8.95; I, 40.45. The proton source of [H:C]^+I might come from the $\beta$-methyl groups of the L ligand backbone.$^{[82-84]}$ Reference experiment of :C with H$_2$O in THF monitored by the $^1$H NMR spectrum shows no characteristic resonance for [H:C]^+, and therefore indicates the incapability of :C to abstract a proton from uncoordinated H$_2$O. Accordingly we assume that the formation of 8 from the reaction of 7, :C, and H$_2$O may proceed through the initial coordination of H$_2$O to aluminum (Scheme 8). This assumption is in accordance with the formation of Al(OH)$_2$Cl$_3$ from AlCl$_3$ by adding controlled amounts of water.$^{[85]}$ Comparable examples are the triarylaluminum water adduct Mes$_3$Al·OH$_2$·nTHF$^{[69]}$ and the structurally characterized (C$_6$F$_5$)$_3$Al·OH$_2$.$^{[86]}$ The coordinated H$_2$O in A is deprotonated by :C to give the cation [H:C]^+ which subsequently combines with I to form the insoluble [H:C]^+T. The generation of [H:C]^+T rather than [H:C]^+Cl$^-$ apparently indicates the easier removal of I compared to that of Cl$^-$. 

![Scheme 8](image)

$Ar = 2,6$-iPr$_2$C$_6$H$_3$, :C = [CN(iPr)C$_2$Me$_2$N(iPr)]

Further hydrolysis of 8 was accomplished with two equiv of H$_2$O and :C (Scheme 7). As expected the aluminum dihydroxide LAl(OH)$_2$ (9) was formed, however in a relatively low yield (25%). Such low yield might be due to the complete hydrolysis of partial 8, which resulted in an insoluble aluminum oxide or hydroxide, and HL.$^{[75]}$ Although a high yield was
achieved by the direct hydrolysis of LAICl₂ in the presence of :C. The hydrolytic procedure to 9 is similar to that for the conversion of 7 to 8, but undergoes during the reaction a dissociation from dimeric 8 to monomeric 9 compared to an association from monomeric 7 to dimeric 8 in the first step of the hydrolysis.

Thus, the synthesis of compound LAICII (7) and its stepwise hydrolysis in the presence of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (:C) has been described. The difference in the bond strength of Al–I and Al–Cl allows the controlled stepwise hydrolysis. The deprotonation of the coordinated H₂O by :C under the formation of the insoluble [H:C]⁺T or [H:C]⁺Cl⁻ salts leads to [LAICl(μ-OH)]₂ (8) and LAI(OH)₂ (9), respectively, and demonstrates the powerful acceptor properties of the N-heterocyclic carbene. Accordingly, we were able to confirm this stepwise process, since there are no structural characterized precedents known containing the Al(OH)Cl moiety, although this type of intermediate is assumed in any hydrolysis product of AlCl₃. However the stepwise hydrolysis from 7 to 8 and finally to 9 is accompanied by an association followed by a dissociation process of LAICl(OH) species. This observation is beyond our proposal during the direct hydrolysis of LAI(Hal)₂ (Hal = I, Cl) to 9, although it is not clear whether this pathway is involved in the latter formation. This may reflect the complexity of the stepwise hydrolysis process. Moreover the advantage of the [H:C]⁺X⁻ (X = Cl, I) is that it can be completely recovered by filtration and in the presence of a strong base such as tBuOK quantitatively recycled to the N-heterocyclic carbene. This method of hydrolysis in the presence of N-heterocyclic carbene will be further applied to the preparation of Brönsted acidic sensitive systems. Compound 8 contains Al–Cl and Al–OH functionalities, of which the former can react by metathesis, and the OH acting as a Brönsted acidic proton has been documented. Further investigations on the functional reactions of 8 are in progress.
2.3. The Oxidative Reaction of Aluminum(I) Monomer LAl with Molecular Oxygen: A New Approach to Alumoxane

Abstract: An alumoxane [(LAlO)]$_2$ (10) has been prepared from the oxidative reaction of aluminum(I) monomer LAl (L = HC[[(CMe)(NAr)]$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) with molecular oxygen. The intense contacts of the Al$_2$(μ-O)$_2$ unit bring the two oriented L closer together and causes a steric strain resulting in C–H···π interactions between one isopropyl group of one L and the aryl ring of another L. Further reaction of 10 with one equiv of H$_2$O resulted in the formation of an alumoxane hydroxide [(LAl(OH))$_2$(μ-O)] (11), indicating a strain releasing process of 10. An isomer of 10, a C–H activated aluminum hydroxide 13, however, was obtained from the hydrolysis of a C–H activated large bulky aluminium amide 12.

There is great interest in alumoxanes since they can be used as active catalysts in the polymerization of epoxides, aldehydes, and olefins.[8-14] Furthermore, methylalumoxane (MAO) functioning as a highly active cocatalyst for group 4 metallocenes catalyzing ethylene and propylene polymerization[15-16] has been of remarkable industrial importance. In general, alumoxanes of formula [RAIO]$_n$ or [R$_2$AlOAlR$_2$]$_n$ (R = organic group) can be synthesized by the controlled hydrolysis of organoaluminum(III) compounds using water, or water containing metal salts,[66-67] and alternatively by the reaction of those compounds with oxygen containing species such as CO$_2$,[62] RCONR$_2$,[67] MeCO$_2$H,[88] PbO,[89] and [Me$_2$SiO]$_3$.[63] The reaction of R$_2$AlAlR$_2$ (R = CH(SiMe$_3$)$_2$) with Me$_2$SO generates the alumoxane R$_2$AlOAIR$_2$.[90] Alkylaluminum(III) compounds reacting with O$_2$ often undergo insertion reaction into the Al–alkyl bond and result in the formation of aluminum alkoxides and alkylperoxides.[5,91-94] In contrast, the reaction of organoaluminum(I) compounds with O$_2$ could lead to the oxidation of the aluminum center to yield alumoxane. Herein, we report on the reaction of aluminum(I) monomer LAl (L = HC[[(CMe)(NAr)]$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) with molecular oxygen and the isolation of an alumoxane [(LAlO)]$_2$ (10). 10 is further hydrolyzed to form alumoxane hydroxide [(LAl(OH))]$_2$(μ-O) (11).
The toluene solution of LAl in the presence of O₂ between –78 °C and room temperature, under stirring, changed slowly the color from red to orange, to yellow, and finally to almost colorless. At ca. –15 °C 10 separated from the solution as a colorless crystalline solid (Scheme 9). The reaction of LAl with O₂ might proceed via an aluminum peroxide intermediate (LAIO₂), which further reacts with another molecule of LAl to afford 10. It has been demonstrated that in the photolytically induced reactions of AlX/O₂ and (AlX)₂/O₂, an aluminum peroxide XAlO₂ was mainly detected for the former and an oxide XAl(μ-O)₂AlX for the latter system by means of IR spectroscopy supported by quantum chemical calculations.¹⁹⁶-¹⁹⁷ The formation of XAl(μ-O)₂AlX was proposed via an Al(μ-X)₂AlO₂ intermediate. Moreover, peroxo complexes are also considered as potential intermediates or products during the oxidation of metals or metal clusters.¹⁹⁸-¹⁹⁹ The occurrence of this reaction at low temperatures indicates the high reactivity of LAl. The kinetic stabilization of LAl by ligand L allows its uncomplete oxidation in the range of –78 °C to room temperature and generates 10 rather than the inorganic aluminum oxide. Furthermore the sterical protection from the bulky Ar substituents at the N atoms of L allows the formation of the Al₂(μ-O)₂ unit instead of a higher condensed Al–O product.

Compound 10 was obtained in high yield (80%). It melts at 314–315 °C and the isotope distributed peaks at around m/z 920.4 (30%) in the EI-MS spectrum are assigned to the molecular ion [M⁺]. 10 is soluble in hot aromatic solvents (toluene and benzene), whereas its solubility is poor at room temperature.

Scheme 9
Quality X-ray single crystals were grown by cooling the hot toluene solution of 10 to room temperature within 24 h. The structural analysis reveals a dimer having crystallographic centro-symmetry (Figure 6). The central Al$_2$(μ-O)$_2$ core is formed in a nearly perfect square (Al–O: 1.760(1), 1.763(1) Å; O–Al–O: 90.89(1)°; Al–O–Al: 89.11(1)°), the two chelating L ligands at each Al atom are oriented with puckering Al(1)N(1)C(2)C(3)C(4)N(2) and Al(1A)N(1A)C(2A)C(3A)C(4A)N(2A) rings respectively almost perpendicular (89.3°) to the square. The Al–O bond lengths are shorter than the predicted one (1.96 Å).[100] This may be due to π-interaction between the oxygen p orbitals and acceptor orbitals on aluminum which is discussed in a considerable number of publications.[101-104] These bond lengths can be compared to those in compounds with four coordinate aluminum R$_2$AlOAlR$_2$(ONMe$_3$) (R = CH(SiMe$_3$)$_2$, 1.753(3) Å) and R$_2$(Me$_3$NO)AlOAlR$_2$(ONMe$_3$) (1.732(2)–1.739(2) Å).[105] However they are longer than those in L$^*$AlO-B(C$_8$F$_5$)$_3$ (L$^*$ = Et$_2$NCH$_2$CH$_2$NC(Me)CHC(Me)NCH$_2$CH$_2$NEt$_2$) (1.659(3) Å).[106] [(C$_7$H$_{13}$N$_2$)AlCl]$_2$(μ-O)
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(1.677(1) Å),\[107\] and \{{\textit{t}Bu}_{2}\text{Al}[\text{NH}(\text{Me})\text{CH}_{2}\text{CH}_{2}\text{NMe}_{2}]\}_{2}(\mu-\text{O}) (1.690(7)–1.714(7) Å),\[74\] as well as those in compounds 11 (1.694(3)–1.698(3) Å) and \{[\text{LA}l(\mu-\text{O})]_{2}(\mu-\text{O})\}\text{AlMe (1.712(2) Å).}\[80\] It is noteworthy that, based on the orientation of the two L, one isopropyl group of one L is facing toward the aryl ring of another L, and the two methyl substituents of this \textit{i}Pr group are arranged on the same side of the aryl plane. This arrangement is in sharp contrast to the other ones. Such structural feature is remarkable when compared with those closely related compounds 11, \{[\text{LA}l(\mu-\text{O})]_{2}(\mu-\text{O})\}\text{AlMe,}\[80\] [\text{LA}l\text{Cl}(\mu-\text{OH})]_{2} \[108\] and \text{LAl}(\mu-\text{S})_{2}\text{Al.}\[109\] Obviously, due to the strong electronic interaction of Al and O atoms, the Al\(_2\)(\mu-O)\(_2\) unit is prone to intense contacts. These contacts, however, bring the two oriented L closer together and cause a steric strain giving a stable minimum configuration and resulting in C–H····π interactions between one isopropyl group of one L and the aryl ring of another L (C(15)–H(15) (56%)····X\text{Ph(1A) 2.71 Å, C(15C)–H(15C) (44%)····X\text{Ph(1) 3.02 Å}). Similar structural features are discussed in compounds L\(_2\)M (M = Mg, Ca, Sr, Ba).\[110\] Accordingly, this indicates a considerable structural strain of 10, and this strain is also reflected in little longer Al–N bond lengths (1.929(1), 1.943(1) Å) compared to those in 11 (1.911(3)–1.928(3) Å) and \{[\text{LA}l(\mu-\text{O})]_{2}(\mu-\text{O})\}\text{AlMe (1.909(2)–1.930(3) Å).}\[80\] In section 2.2., we isolated compound [\text{LA}l\text{Cl}(\mu-\text{OH})]_{2} from the stepwise hydrolysis of \text{LA}l\text{ClI in the presence of N-}\text{heterocyclic carbene (abbreviated as :C) as hydrogen halide acceptor. [LA}l\text{Cl}(\mu-\text{OH})]_{2} presents a dimeric structure with Al–Cl and Al–\mu-OH functionalities and further treatment of this compound with two equiv of :C functioning as a HCl acceptor in an attempt to approach 10, or alternatively by the addition of \text{nBu}Li to eliminate LiCl and \text{nBuH} to the same target was not successful. The former resulted in no reaction and the latter led to an intractable mixture of products which was indicated by the EI mass spectrometry and proton NMR spectroscopy analysis. This may indicate the property of 10 that the functional changes using [\text{LA}l\text{Cl}(\mu-\text{OH})]_{2} as a precursor to approach 10 are energetically unfavored.

The NMR spectroscopic analysis of 10 clearly shows that this strained solid-state structure
is retained in solution. In the $^1$H NMR spectrum the isopropyl groups give rise to four separated septets and eight doublets, and two sets of aromatic signals and two singlets for the methyl group of the backbone are also observed, indicating different steric environments of two Ar groups of the LAl moiety. Moreover, one septet and one doublet of those appear at higher field (2.63 and 0.22 ppm) in comparison to the resonances in a series of related compounds $^{11}$, $^{[LAl(\mu-O)]_2(\mu-O)}AlMe$, and $^[LAlCl(\mu-OH)]_2$ (4.14–3.06, 1.58–0.72 ppm).$^{[80,109]}$ It is clearly seen that, in view of the structure of 10, the corresponding methine (CH) and methyl (CH$_3$) groups are shielded due to the ring current effect within the aryl groups,$^{[111]}$ and this is typical for groups involved in C–H···π interaction (Figure 6). The $^{13}$C$^{'1}$H NMR data also shows the methine carbon resonance at high field (71.4 ppm).

Scheme 10

It is interesting to note that when this sample was kept at room temperature for one month, the NMR analysis showed that the proton resonances at high field (one septet and one doublet) disappeared as well as the methine carbon resonance, and the data of the $^1$H NMR spectrum can be identified like that of compound 11 including a small amount of free ligand. The transformation of 10 to 11 could be considered as a further hydrolysis of 10 due to the possible penetration of small amounts of moisture to the sample through the seal (Scheme 10). Nevertheless, the reaction of 10 with stoichiometric amounts of water was performed, and colorless crystals of 11·1.5 $n$-hexane were obtained and confirmed by X-ray structural analysis.

The reaction of LAI with N$_3$Ar$^+$ in the presence of a small amount of H$_2$O resulted in the
formation of a C–H activated aluminum hydroxide 13, an isomer of 10. This reaction can be reproduced. The reaction of LAI with a large bulky azide N₃Ar which has shown two types of intramolecular addition to an Al=N multiple bond species will be detailed in section 2.8. The respective isolation of 12, 13, and H₂NAr’ indicates the partly hydrolysis of 12 to 13 at low temperature (Scheme 11). The Al–N bond imposed by the bulky Ar’ in 12 might preferentially react with H₂O to form 13, an isomer of 10. 12, 13 and H₂NAr’ are characterized by spectral analysis, and 12 and 13 are further confirmed by X-ray measurement.

The molecular structures of 12 and 13 are viewed in Figures 7 and 8. The structural analysis of 13 shows the same composition like that of 10 but with five coordinate Al and an Al₂(μ-OH)₂ non-planar core instead (Δ = 0.1009 Å). The parameters of Al–C (1.988(2) Å (av)) and C_{activated}–C (1.552(2) Å (av)) exhibit normal single bond distances, and those of Al₂(μ-OH)₂ (Al–O: 1.879(1) Å (av); O–Al–O: 73.88(6)° (av); Al–O–Al: 103.40(1)° (av)) are comparable to those in [LAlCl(μ-OH)]₂ (Al–O: 1.880(1) Å (av); O–Al–O: 72.46(7)° (av)). These data compared with those of 10 indicate less interference within 13 than in 10. The NMR (Al–CH₂: δ –1.69 (t), –0.35 (dd) ppm; Al–μ-OH: 0.29 (s) ppm) and IR spectral data
Figure 7. Molecular structure of 12. H atoms except for Al–CH$_2$ and Al–NH are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.930(1), Al(1)–N(2) 1.926(2), Al(1)–N(3) 1.840(1), Al(1)–C(25) 1.967(2), C(25)–C(24) 1.555(2), N(1)–Al(1)–N(2) 98.12(6), N(1)–Al(1)–N(3) 113.83(6), N(2)–Al(1)–N(3) 101.98(7), N(3)–Al(1)–C(25) 124.18(7).

Figure 8. Molecular structure of 13. H atoms except for Al–CH$_2$ and Al–OH are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.910(1), Al(1)–O(2) 1.850(1), Al(1)–C(13) 1.986(2), C(13)–C(12) 1.549(2), Al(2)–O(1) 1.852(1), Al(2)–O(2) 1.905(1), Al(2)–C(42) 1.989(2), C(42)–C(41) 1.554(3), Al(1)···Al(2) 2.950(1), O(1)–Al(1)–O(2) 73.84(6), Al(1)–O(2)–Al(2) 103.54(6), O(2)–Al(2)–O(1) 73.92(6), Al(2)–O(1)–Al(1) 103.25(6).
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(Al-µ-OH: ν 3400 (br) cm⁻¹) also confirm the functionalities of 13.

Although 10 does not contain three coordinate Al centers which are proposed to have strong Lewis acidity and are vital for catalytic activity, the notably structural character of 10 prompted us to test its cocatalytic property for the dimethylzirconocene polymerization of ethylene in toluene solution at either 25 or 80 °C. However, no activity was observed. Moreover, no reaction occurred between 10 and Cp₂ZrMe₂.

In conclusion, the oxidative reaction of aluminum(I) monomer LAI with molecular oxygen has been shown. This reaction type exhibits the O₂ oxidation of a central metal to yield alumoxane [LAlO]₂ (10), the hitherto unknown species, and represents a new synthetic approach to alumoxane. Compound 10 further reacts with one molecule of water to form alumoxane hydroxide [LAl(OH)]₂(µ-O) (11). Although 11 has been known and prepared by another route,[80] this reaction may proceed through the coordination of H₂O to the aluminum center. A further proton transfer from the coordinated H₂O molecule results in the ring opening of the Al₂(µ-O)₂ unit under the formation of terminal Al–OH functionalities, this implies a strain releasing process from 10 to 11. A further application of proton transfer using EHₙ (E = S, Se, Te, n = 2; E = N, P, As, Sb, n = 3) molecules and 10 to yield the unknown Al–EHₙ₋₁ species is currently under investigation in our group.
2.4. Reactions of Aluminum(I) Monomer LAl with Imidazol-2-ylidene and Diphenyldiazomethane: A Hydrogen Transfer of the L Ligand to the Aluminum Center and a Formation of a Diiminyl Aluminum Compound LAl(N=CPh$_2$)$_2$

Abstract: The solid-state reaction of LAl and imidazol-2-ylidene at elevated temperature (120 °C) yielded the aluminum monohydride $N$-heterocyclic carbene adduct [HC{C(CH$_2$)$_2$NAr}(CMeNAr)]AlH[CN(R)C$_2$Me$_2$N(R)] ($R = iPr$ (14), Me (15)). Compounds 14 and 15 have been characterized by spectroscopic (IR, $^1$H, and $^{13}$C NMR), mass spectrometric, and elemental analyses, and 14 was further characterized by X-ray structural analysis. These experimental data indicate that the Al–H bond is formed by hydrogen migration from one of the methyl groups of the $\beta$-diketiminato ligand backbone. The reaction of LAl with equivalent amounts of diphenyldiazomethane afforded the diiminyl aluminum compound LAl(N=CPh$_2$)$_2$ (16), while with an excess diphenyldiazomethane resulted in the formation of Ph$_2$C=N–N=CPh$_2$. This suggests that the Ph$_2$C=N–N=CPh$_2$ is initially generated and then further reacts under oxidative addition to yield 16.

Monovalent Group 13 species are of considerable interest not only due to their syntheses, structures, and theoretical investigations,[112-113] but more due to their reactivity.[114] In the last decade, a variety of new reactions has been intensively explored generating the tetrameric aluminum(I) compounds.[115-120] Compound (Cp*Al)$_4$ was reported to have a remarkable tendency to dissociate in solution and give a monomeric fragment in the gas phase.[121-122] The reactions involving such species have also been investigated to some extent and a number of novel compounds were isolated and structurally characterized.[123-127] Recently, we have prepared the first monomeric aluminum(I) LAl (L = HC[(CMe)(NAr)$_2$], Ar = 2,6-iPr$_2$C$_6$H$_3$) stable at room temperature.[95] Ab initio calculations show that this monomer possesses a nonbonded electron pair at the central two coordinated Al atom and is isoelectronic with a singlet carbene. Subsequent examination of LAl with organic azides at low temperature or with P$_4$ at room temperature indicates its reactivity, leading to the formation of a five-
membered AlN₄ heterocycle LAI[(NSiMe₃)₂N₂], a monomeric aluminum imide LAI(N-2,6-Trip₂C₆H₃) (Trip = 2,4,6-iPr₃C₆H₂), and a sandwich compound (LAl)₂P₄ containing a P₄⁺ unit. These results are markedly different from those in which (Cp*Al)₄ is used in related reactions. Obviously, the steric and electronic stabilization from the bulky β-diketiminato ligand enables its monomeric nature and therefore its unique chemical behaviour, and allows further investigation of its reactivity.

Imidazol-2-ylidene is a stable neutral N-heterocyclic carbene which has been prepared in recent years. The diphenyldiazomethane can be used as an effective precursor for the generation of transient :CPh₂. The reaction of imidazol-2-ylidene with monovalent Group 13 compounds is only reported for InBr, in which a disproportionation is observed. More recently, a handful of reactions involving imidazol-2-ylidene with trivalent Group 13 species have been investigated, and herein the N-heterocyclic carbene functions as a Lewis base. Corresponding reactions of diphenyldiazomethane with Group 13 element(I) species have not been described so far. We now report on the reaction of LAI with imidazol-2-ylidene and diphenyldiazomethane, respectively. The formation of the aluminum monohydride N-heterocyclic carbene adduct of composition [HC{C(CH₂)NAr}(CMeNAr)]AlH[CN(R)C₂Me₂N(R)] (R = iPr (14), Me (15)) indicates a hydrogen transfer from the L ligand to the aluminum center. The formation of a diminyl aluminum compound LAI(N=CPh₂)₂ (16) might proceed through the initial generation of Ph₂C=N=N=CPh₂ followed by its oxidative addition to LAI.

The initial reaction of LAI with 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene was conducted in toluene within the temperature range from 25 to 80 °C. However due to the low solubility of the N-heterocyclic carbene, this reaction was not successful. Therefore both starting materials were treated in the solid-state at 120 °C for 5 h. The softening of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene and a subsequent color change of LAI from red black to light yellow were observed. An extraction of the product with hot toluene and
keeping the eluate at room temperature afforded crystalline compound [HC\{C(CH_2)NAr\}(CMENAr)]AlH[CN(iPr)C_2Me_2N(iPr)] (14, Scheme 12).

**Scheme 12**

![Scheme 12](image)

**Figure 9.** Molecular structure of 14. H atoms in Ar and :C groups are omitted for clarity.

Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.853(2), Al(1)–N(2) 1.844(3), Al(1)–C(30) 2.088(3), Al(1)–H(1) 1.40, N(1)–C(2) 1.411(3), N(2)–C(4) 1.413(3), C(1)–C(2) 1.363(4), C(2)–C(3) 1.458(4), C(3)–C(4) 1.351(4), C(4)–C(5) 1.507(4), N(1)–Al(1)–N(2) 102.05(6), C(30)–Al(1)–H(1) 106.4.

Compound 14 is colorless and soluble in hot toluene and benzene while sparingly soluble in n-hexane and pentane. It has been characterized by spectroscopic and elemental analyses. The mass spectrum exhibits the molecular ion of 14 \{ m/z (\%) = 624 (5) [M^+]\}, 609 (40) [M^+ -
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Me], 581 (100) [M' - iPr]. The \(^1\)H and \(^{13}\)C NMR spectra recorded in C\(_6\)D\(_6\) are consistent with a pseudo tetrahedral geometry and C\(_s\) symmetry about aluminum, which give rise to six isopropyl CH resonances and twelve diastereotopic splitted isopropyl CH\(_3\) resonances due to the chiral environment of the Al center. It is noted that the proton resonance of \(\beta\)-CH\(_3\) (\(\delta 1.72\) ppm) at the L ligand backbone is indicative for 3H, while two other singlets are observed downfield (\(\delta 3.98\) and 3.30 ppm) for (1 + 1) H. The former corresponds to the normal terminal CH\(_3\)–C group, and the latter is assigned to the terminal CH\(_2\)=C group which gives rise to two non-equivalent protons due to the restricted rotation about the C=C double bond. One broad proton resonance centered at 4.80 ppm is characteristic for aluminum hydrides,\(^{29}\) and the IR spectrum exhibits a single band at 1809 cm\(^{-1}\) for Al–H absorption.\(^{142}\)

Complex 14 has also been characterized by X-ray structural analysis. The quality of the crystals by several recrystallizations from different solvents gave no improvement in the refinement of the structure. Nonetheless, the structural solution of 14 offers important structural informations which are in agreement with its spectral analysis. The molecular structure of 14 is shown in Figure 9 with selected bond lengths and angles. Compound 14 is monomeric and the central Al atom adopts a distorted tetrahedral geometry. The Al–N bond lengths (1.844(3), 1.853(2) Å) appear the shortest compared to those Al–N\(_{\beta\text{-diketiminato}}\) (1.875(4)–1.957(2) Å),\(^{21,75,80,95}\) and are closer to those found in diamide aluminum monohydride [ArN(CH\(_2\))\(_3\)NAr]AlH(NMe\(_3\)) (1.820(1), 1.828(1) Å).\(^{142}\) In the ligand backbone, the terminal C–C bond distances (C(4)–C(5), 1.507(4) Å; C(1)–C(2), 1.363(4) Å) are indicative for a single and double bond character, respectively, as well as the others within the backbone (C(2)–C(3), 1.458(4) Å; C(3)–C(4), 1.351(4) Å). The adjacent N–C bonds (1.411(3), 1.413(3) Å) are located between N–C double and single bonds.

Obviously, the Al–H hydrogen comes from one of the terminal methyl groups of the L ligand. However, such hydrogen transfer via proton, hydrogen radical, or hydride is not clear.

The reaction of the LAl with less bulky \(N\)-substituted 1,3,4,5-tetramethylimidazol-2-
ylidene was also performed in a similar manner (method A) like the preparation of 14 to investigate the steric bulk on the reaction product. As a result, 

\[
[HC\{C(CH_2)NAr\}(CMeNAr)]AlH[CN(Me)C_2Me_2N(Me)]
\]

(15) was obtained in a relatively low yield. All the spectroscopic (IR, EI mass, \(^1\)H and \(^{13}\)C NMR) data confirm the analogue structural arrangement like that of 14 with 1,3,4,5-tetramethylimidazol-2-ylidene as a ligand.

In the majority of organic and organometallic reactions, diphenyldiazomethane is used as an effective precursor for the generation of transient :CPh\(_2\) carbene.\(^{[133-135]}\) Therefore, it was selected as another electron-rich species for the reaction with LAl. However, treatment of LAl with 2 equivalents of N\(_2\)CPh\(_2\) under heating unexpectedly afforded LAl(N=CPh\(_2\))\(_2\) (16, Scheme 13), the first example of a diiminyl aluminum compound. When LAl was treated with an excess of N\(_2\)CPh\(_2\) under the same condition Ph\(_2\)C=N=N=CPh\(_2\) was isolated. The azine Ph\(_2\)C=N=N=CPh\(_2\) was obtained as colorless crystals with a melting point of 174 °C and the spectroscopic data (EI mass, IR, \(^1\)H and \(^{13}\)C NMR) and elemental analysis confirmed the composition. It is well-known that many salts and complexes of Cu(I) and Cu(II) are used as catalysts for the decomposition of diphenyldiazomethane. The reaction of LAl and diphenyldiazomethane to give Ph\(_2\)C=N=N=CPh\(_2\) may indicate that the LAl plays more likely a catalytic role.\(^{[143-144]}\) Therefore we assume that the formation of 16 might proceed via the initial generation of Ph\(_2\)C=N=N=CPh\(_2\) followed by its oxidative addition to LAl. In order to testify the possibility of the latter step, a toluene solution of LAl with equivalent amounts of Ph\(_2\)C=N=N=CPh\(_2\) was conducted under reflux and complex 16 was formed as expected in an almost quantitative yield. A reaction procedure is described here. A mixture of equivalent amounts of LAl and Ph\(_2\)C=N=N=CPh\(_2\) in toluene (20 mL) was allowed slowly to heat to reflux and kept for 3 h. After cooling to room temperature, the solution was dried in vacuum and the residue was washed with \(n\)-hexane (5 mL) to give an almost quantitative orange-yellow crystalline solid (yield, > 90%). The melting point and the spectroscopic data (EI mass and IR) are essentially the same as those of 16.
Scheme 13

Complex 16 is an orange-yellow crystalline solid and thermally stable as indicated by its high melting point (344-346 °C). The most intense ion in the EI mass spectrum appears at \( m/z \) 624 \( [M^+ - \text{NCPh}_2] \), and the peak at \( m/z \) 805 (20%) is assigned to the molecular ion \([M^+]\).

**Figure 10.** Molecular structure of 16. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.901(4), Al(1)–N(2) 1.899(4), Al(1)–N(3) 1.774(4), Al(1)–N(4) 1.785(4), N(3)–C(30) 1.249(6), N(4)–C(50) 1.269(6), N(1)–Al(1)–N(2) 97.23(18), N(3)–Al(1)–N(4) 116.1(2), C(30)–N(3)–Al(1) 169.4(4), C(50)–N(4)–Al(1) 163.4(5).

X-ray quality single crystals of 16 were grown in 1:1 solvent mixture (n-hexane, ether) at 4 °C for 2 d. The structural analysis unambiguously ascertains the composition of 16. The molecular structure is viewed in Figure 8 with selected bond lengths and angles. The central
Al atom is bound to two β-diketiminato nitrogen and two iminyl nitrogen atoms. The AlN$_4$ core exhibits a distorted tetrahedral geometry with trans N–Al–N angles ranging from 97.23(18)$^\circ$ to 117.6(2)$^\circ$. The Al–N$_{β}$-diketiminato bond lengths (1.899(4), 1.901(4) Å) are falling in the expected range (1.875(4)–1.957(2) Å). However, the Al–N$_{iminyl}$ distances (1.774(4), 1.785(4) Å) are the shortest among those found in four coordinated Al–N complexes.$^{[145]}$

Comparable Al–N bond lengths are only observed in three coordinated Trip$_2$AlN(H)Dipp (1.784(3) Å),$^{[146]}$ [MeAlNDipp]$_3$ (1.782(4) Å)$^{[147]}$ and Al[N(SiMe$_3$)$_2$]$_3$ (1.78(2) Å)$^{[148]}$. Surprisingly, the N–C distances of the iminyl group (1.249(6), 1.269(6) Å) are shorter compared to that of a carbon-nitrogen double bond.$^{[149]}$ The short Al–N$_{iminyl}$ bond can be considered to be highly ionic, and the shortening of the N=C bond may be due to a charge delocalization over the phenyl groups. The Al(1)–N(4)–C(50) (163.4(5)$^\circ$) and Al(1)–N(3)–C(30) (169.4(4)$^\circ$) angles show the less bent arrangement of the Al–N=C group. The observation of two sets of resonances for the iminyl phenyl rings in the $^1$H and $^{13}$C NMR spectra suggests a restricted rotation of phenyl rings around the N=C bond. This is confirmed by the high temperature proton NMR spectral analysis (40, 60, and 80 °C), where two corresponding sets of such resonances are always observed.

To sum up, the reaction of the aluminum(I) monomer LAl with imidazol-2-ylidene and diphenyldiazomethane, respectively, afforded the new compounds [HC{C(CH$_2$)$_2$NAr}(CMENAr)]AlH[CN(R)C$_2$Me$_2$N(R)] (R = iPr (14), Me (15)) and LAl(N=CPh$_2$)$_2$ (16). This further shows the unique reaction behaviour of LAl, and exhibits its properties of a carbene analogue. Inspired by these results, we are now exploring the reaction of LAl with metal carbonyl complexes to compare the electronic equivalence of LAl with CO.
2.5. A Rearrangement of Azobenzene by Interaction with an Aluminum(I) Monomer LAl

Abstract: Reaction of LAl or LAl[η²-C₂(SiMe₃)₂] (L = HC[(CMe)(NAr)]₂, Ar = 2,6-iPr₂C₆H₃) with azobenzene both afforded a five-membered ring compound LAl[N(H)-o-C₆H₄N(Ph)] (17). In the formation of 17 a three-membered intermediate LAl(η²-N₂Ph₂) (A) is suggested by [1 + 2] cycloaddition reaction. A is not stable and further rearranges to 17. The DFT calculations on comparable compounds with modified L’ (L’ = HC[(CMe)(NPh)]₂) show that the complexation energy of the reaction of L’Al with azobenzene to L’Al(η²-N₂Ph₂) is ca. –39 kcal/mol, and the best estimate of the energy difference between L’Al(η²-N₂Ph₂) and L’Al[N(H)-o-C₆H₄N(Ph)] is –76 kcal/mol.

The reactions of Group 13 metal(I) tetramers (RM)₄ (R = organic group, M = Al, Ga, In) with unsaturated molecules (H₂C=C(Me)–C(Me)=CH₂, PhC(O)–C(O)Ph, RN=C(H)=C(H)=NR, R = Me, iPr) evidence the trapping of the corresponding monomer RM, and meanwhile present an interesting oxidative addition of compounds with unsaturated bonds to low-valent metal centers. This leads to heterocyclic compounds containing novel heavier main group elements which have the potential application in pharmaceutical, agrochemical, and material science. We have recently prepared the aluminum(I) monomer LAl (L = HC[(CMe)(NAr)]₂, Ar = 2,6-iPr₂C₆H₃) which has a singlet carbene character. The reductive coupling reaction of LAlI₂ with potassium in the presence of alkynes has shown a [1 + 2] cycloaddition to yield aluminacyclopentene LAl[η²-C₂(R)R’] (R = R’ = SiMe₃, Ph; R = Ph, R’ = SiMe₂). A direct coupling reaction between LAl and alkyne (Me₃SiC≡CC≡CSiMe₃) is subsequently realized to form LAl[η²-C₂(SiMe₃)C≡CSiMe₃]). In this context we are interested in the interaction of the Al(I) center with compounds containing a N=N double bond. The reaction of LAl or LAl[η²-C₂(SiMe₃)₂] with azobenzene both unexpectedly resulted in the formation of a five-membered ring complex LAl[N(H)-o-C₆H₄N(Ph)] (17). Compound 17 contains a N(H)-o-C₆H₄N(Ph) moiety which presents an
isomerized azobenzene. Obviously, a rearrangement of azobenzene is occurring by interacting
with LAl.

Upon stirring a toluene solution of LAl and azobenzene at elevated temperature (80 °C) for 5 h, the red color changed to orange. Partial removal of the solvent in vacuum and addition of n-hexane led to the crystallization of 17 at 4 °C as orange crystals in good yield. An alternative route to 17 was investigated by the reaction of LAl[$\eta^2$-C$_2$(SiMe$_3$)$_2$] with azobenzene in the temperature range from −50 °C to room temperature. The result indicated that LAl[$\eta^2$-C$_2$(SiMe$_3$)$_2$] could be used as a good precursor for LAl.

**Figure 11.** Molecular structure of compound 17. The hydrogen atoms of the C–H bonds are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)–N(1) 1.862(1), Al(1)–N(2) 1.893(1), Al(1)–N(3) 1.807(2), Al(1)–N(4) 1.847(1), N(3)–C(31) 1.386(2), C(31)–C(36) 1.429(2), C(36)–N(4) 1.420(2), N(1)–Al(1)–N(2) 97.68(6), N(3)–Al(1)–N(4) 90.39(6), Al(1)–N(3)–C(31) 109.86(10), N(3)–C(31)–C(36) 115.57(14), C(31)–C(36)–N(4) 113.40(10), C(36)–N(4)–Al(4) 108.44(10).

Compound 17 is thermally stable, as indicated by its high melting point (260–261 °C) and its most intense molecular ion peak (m/z (%): 626 (100, [M$^+$]) recorded in EI-mass spectrum.
17 has been fully characterized by spectroscopic, analytical and X-ray single crystal measurements.

The molecular structure of 17 is viewed in Figure 11 with selected bond lengths and angles. The central Al atom is involved as part of two fused five- (AlN₂C₂) and six-membered (AlN₄C₃) rings. The corresponding AlN₄ core appears in a distorted tetrahedral geometry. The Al–N bond lengths within the AlN₂C₂ ring are 1.807(2) Å (Al–N(H)) and 1.847(1) Å (Al–N(Ph)), respectively, and can be compared with those of the AlN₄ ring complex (1.815(2), 1.851(2) Å).¹²⁹ The Al–Nβ-diketiminato bond lengths (1.893(1) and 1.862(1) Å) fall in the range (1.874(1)–1.959(3) Å) observed for four-coordinate β-diketiminato aluminum compounds,¹⁵⁵–¹⁵⁶ although one bond is a little shorter than these values. The AlN₂C₂ ring is nearly planar (Δ = 0.0719 Å) and this planar character can be extended to the adjacent disubstituted phenyl group (Δ = 0.0816 Å). It is interesting to note that, within the AlN₂C₂ ring, the C(31)–C(36) bond length (1.429(2) Å) is longer compared to the remaining ones of the phenyl ring (1.382(2)–1.393(2) Å). This obviously contributes to a ring formation of AlN₂C₂. The phenyl groups involved in different structural environments (disubstituted C₆H₄, N(Ph), Ar) exhibit diverse resonances for the aromatic protons in the ¹H NMR spectrum of 17. An unambiguous assignment of the resonances was not possible. The NH resonates at δ 3.06 (s) and in the IR spectrum the absorption at 3220 cm⁻¹ is assignable to ν₉H.

![Scheme 14](image)

**Scheme 14**

The reaction of LAI with azobenzene may initially proceed through a LAI(η²-N₂Ph₂) (A) intermediate which was formed by [1 + 2] cycloaddition reaction. A is not stable due to the
high strained metal containing three-membered AlN$_2$ ring, and therefore rearranges by cleaving the N–N bond under migration of a hydrogen from an ortho position of one adjacent phenyl ring to yield 17 (Scheme 14). Similar structural compounds like A are known for transition and lanthanide metals, in which the different electronic interaction modes ($\pi$ bonds and one electron transfer) are discussed.$^{[157-159]}$ A three-membered AlN$_2$ heterocycle bearing an exocyclic N=C double bond at one of the two N atoms has also been reported.$^{[160]}$ Correspondingly, an easy cleavage of the N–N bond and the rearrangement of the adjacent ortho phenyl hydrogen of azobenzene were also observed in the reaction of an FeH-containing active site with azobenzene,$^{[161-162]}$ in a cyclometalation$^{[163-166]}$ and a substitution$^{[167]}$ reaction.

A further insight into this proposed mechanism is gained from theoretical calculation.$^{[168]}$ The DFT (Density Functional Theory) calculations are performed by analyzing the energy difference of products and reactants in reaction system of L’Al and PhNNPh to L’Al($\eta^2$-N$_2$Ph$_2$), and then to L’Al[N(H)-$\sigma$-C$_6$H$_4$H$_2$N(Ph)], where L’ is modified as HC[(CMe)(NPh)$_2$] for simplicity of calculation and their corresponding geometries are optimized according to the real structures or related ones at BP86/TZVP level with RI approximation (L’Al to LAl, PhNNPh in cis position, L’Al($\eta^2$-N$_2$Ph$_2$) to LAl($\eta^2$-C$_2$Ph$_2$) but a N–N single bond, and L’Al[N(H)-$\sigma$-C$_6$H$_4$N(Ph)] to LAl[N(H)-$\sigma$-C$_6$H$_4$N(Ph)]) using TURBOMOLE 5.5 program. The computed results show that the complexation energy of the initial reaction of L’Al with azobenzene to L’Al($\eta^2$-N$_2$Ph$_2$) (here L’ is modified as HC[(CMe)(NPh)$_2$] for simplicity of calculation) is ca. $-39$ kcal/mol (that is $D_{298}^\circ$ (Al–$\eta^2$-N$_2$) = 39 kcal/mol). This indicates a reasonable possibility of A as an intermediate in the reaction of LAl with azobenzene. The value of $-39$ kcal/mol is even lower than that calculated for the complexation energy of LAl with alkyne (ca. $-21$ kcal/mol) using the same method.$^{[156]}$ When L’Al($\eta^2$-N$_2$Ph$_2$) is further converted to L’Al[N(H)-$\sigma$-C$_6$H$_4$N(Ph)], a best estimate of the energy difference between these two isomers is $-76$ kcal/mol. This suggests an energetically favored stable rearrangement, and
is also in agreement with the rearrangement of a three- to five-membered ring. Furthermore, the $D_{298}^{\text{Al-} \eta^2\text{-N}_2}$ value is comparable to that of the Al–N bond strength in donor-acceptor H$_3$Al:NH$_3$ species predicted by *ab initio* studies with zero-point vibrational energy correction ($D_{298}^{\text{Al–N}} = 26$ kcal/mol). This implies a somewhat strong Al–$\eta^2$-N$_2$ bonding. Therefore the cleavage of the corresponding N–N bond in the rearrangement of A to 17 is highly favored although no such bond dissociation energy data are available for comparison.

Thus, the reaction of aluminum(I) monomer LAI with azobenzene has been investigated. The formation of a five-membered AlN$_2$C$_2$ ring (17) shows the difference in comparison with that of the [1 + 2] cycloaddition product by the reaction of LAI with alkyne, and indicates an interesting rearrangement of azobenzene via a possible three-membered AlN$_2$ intermediate (A) by interacting with LAI.
2.6. A Stable Aluminacyclopropene \( \text{LAl}(\eta^2\text{-C}_2\text{H}_2) \) and Its End-on Azide Insertion to an Aluminaazacyclobutene

Abstract: A stable aluminacyclopropene \( \text{LAl}(\eta^2\text{-C}_2\text{H}_2) \) (18) has been isolated from the temperature controlled reaction of \( \text{LAl} \) with excess of \( \text{C}_2\text{H}_2 \). 18 further reacts with one molecule of \( \text{C}_2\text{H}_2 \) under ring opening and formation of terminal \( \text{C}≡\text{CH} \) and \( \text{CH}≡\text{CH}_2 \) groups at aluminum to yield \( \text{LAl(C≡CH)(CH}≡\text{CH}_2) \) (19). The reaction of \( \text{LAl}(\eta^2\text{-C}_2\text{Ph}_2) \) with one equiv of \( \text{HCCPh} \) smoothly afforded compound \( \text{LAl(C≡CPh)(C(Ph)=CH(Ph))} \) (20). This reaction was further monitored by \(^1\text{H} \) NMR spectral analysis, clearly disclosing the hydrogen migration of terminal \( \text{HCCPh} \) under the ring opening of \( \text{Al(} \eta^2\text{-C}_2 \) ). The end-on azide insertion in the \( \text{Al(} \eta^2\text{-C}_2 \) ) ring of 18 results in the first aluminaazabutene \( \text{LAl[CH=CHN(=NAr*)]} \) (21).

Heavier main group elements containing cyclopropenes have received considerable attentions due to their strained structure and remarkable reactivity. These compounds are often involved in reactions such as ring-opening, insertion, substitution, dimerization, and [1,2]-hydrogen migration,[171] and therefore are of great interest in syntheses, especially in the preparation of main group elements containing larger heterocycles with C–C unsaturated bonds.

These three-membered ring compounds with organic substituents at the two olefinic carbon atoms have been known.[155,160,171-175] However species with the simplest \( \text{M(} \eta^2\text{-C}_2\text{H}_2 \) moiety are either discussed on the basis of theoretical calculations,[176-180] or observed in metal vapor deposition reactions at 12 K.[181] \( \text{Et(solvent)Al(} \eta^2\text{-C}_2\text{Ph}_2 \) (solvent: \( \text{Et}_2\text{O}, \text{THF} \) and \( \text{ClAl(} \eta^2\text{-C}_2\text{R}_2 \) (R = Me, Et) were assumed as intermediates in the respective formation of 1,4-(dialumina)cyclohexadiene and \( \text{(ClAl-RC=CR)}_4 \).[182-185] Subsequently the bulky \( \beta \)-diketiminato ligand \( \text{L} \) stabilizes the \( \text{Al(} \eta^2\text{-C}_2\text{R}_1\text{R}_2 \) (L = \( \text{HC}[(\text{CMe})(\text{NAr})]_2 \), \( \text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3 \); \( \text{R}_1 \), \( \text{R}_2 \): \( \text{SiMe}_3 \), Ph) rings. Such compounds have been prepared by the reductive coupling reaction of \( \text{LAlI}_2 \) and potassium in the presence of \( \text{R}_1\text{C}≡\text{CR}_2 \).[155] Correspondingly,
XAl(η²-C₂H₂) (X = H, Cl) are suggested by calculations, however, they are unstable, as indicated by IR and ESR data on matrix isolated species at low temperatures. Herein, we show the reaction of the aluminum(I) monomer, LAl[95] with C₂H₂ in the range from low to room temperature, and the successful isolation of the first stable aluminacyclopentene LAl(η²-C₂H₂) (18) and its subsequent reaction product LAl(C=CH)(CH=CH₂) (19). The reaction of 18 with a large bulky organic azide leads to an unusual insertion product, an aluminaazacyclobutene LAl[CH=CH(N=NAr*)] (21, Ar* = 2,6-Ar′₂C₆H₃, Ar′ = 2,4,6-Me₃C₆H₂).

Scheme 15

The reaction of LAl with excess of carefully dried C₂H₂ in toluene was initially carried out in the range from –78 °C to room temperature. The instant color change of the solution from red to orange and then the slow change to almost colorless were clearly observed, and compound LAl(C=CH)(CH=CH₂) (19) was formed. Obviously, the formation of 19 indicated that LAl reacted with two molecules of C₂H₂. When this reaction was controlled in the temperature range from –78 to –50 °C, the red solution only changed to orange (this color change even occurred when this reaction was performed at ca. –100 °C). By removal of unreacted C₂H₂, a 1:1 adduct LAl(η²-C₂H₂) (18) was isolated (Scheme 15). It is noted that when this reaction was continued without removing excess of C₂H₂, the corresponding ¹H NMR spectrum has shown the formation of small amounts of 19, whereas the reaction solution remained orange in color.
The formation of 18 essentially follows \([1 + 2]\) cycloaddition with respect to the characters of LAl (one nonbonded electron pair at Al) and \(\text{C}_2\text{H}_2\) (\(\text{C}==\text{C}\) \(\pi\) electrons). The interaction between \(\text{C}_2\) and Al, in view of the theoretical molecular collision mechanism, gives the two extreme types: \(\text{C}_2\) center to Al (channel a), and one of the C atoms of \(\text{C}_2\) to Al (channel b). The DFT calculations by analyzing the total potential energy of LAl plus \(\text{C}_2\text{H}_2\) system versus Al···C distance show that channel a has an energy barrier (the most height at ca. 145 kJ/mol), while b has almost no barrier (Figure 10). Obviously, the reaction kinetically takes channel b, which means that reaction can occur almost without any energy supporting. This is in good agreement with our experimental observations. Moreover, the final calculations of the reaction energy of LAl and \(\text{C}_2\text{H}_2\) to 18 (ca. 155 kJ/mol) imply a stronger Al–\(\eta^2\)-\(\text{C}_2\text{H}_2\) bond in comparison to that of the disubstituted one (Al–\(\eta^2\)-\(\text{C}_2\text{R}_1\text{R}_2\), ca. 88 kJ/mol).\(^{[155]}\)

![Figure 10](image)

**Figure 10.** The total potential energy curve of LAl and \(\text{C}_2\text{H}_2\) versus the Al···C distance.

![Scheme 16](image)

**Scheme 16**

Further reaction of 18 with \(\text{C}_2\text{H}_2\) may proceed through a donor-acceptor intermediate due to the Lewis acidic Al center of 18. This mechanism has been extensively discussed in the
reaction of alkylaluminum(III) or alkylaluminum hydride compounds with alkynes, and further evidenced by some experimental data. The ring opening of Al(η²-C₂) may occur with concomitant hydrogen migration from the π-coordinated C₂H₂ to result in 19 (Scheme 16). The latter ¹H NMR monitored reaction of LAl(η²-C₂Ph₂) with a little excess of HCCPh to compound LAl(C≡CPh)[C(Ph)=CH(Ph)] (20) may clearly give a similar insight into this process.

Figure 12. Molecular structure of 18. H atoms in L are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.875(1), Al(1)–N(2) 1.884(1), Al(1)–C(6) 1.885(2), Al(1)–C(7) 1.878(2), C(6)–C(7) 1.358(2), C(6)–H(6) 1.000, C(7)–H(7) 1.021, N(1)–Al(1)–N(2) 97.98(5), C(6)–Al(1)–C(7) 42.30(7), Al(1)–C(6)–C(7) 68.57(10), Al(1)–C(7)–C(6) 69.13(10), H(6)–C(6)–C(7) 126.4, H(7)–C(7)–C(6) 127.1.

Compound 18 was obtained as an orange crystalline solid in quantitative yield. 18 is extremely air-sensitive. Its solution, once exposed to air, immediately changes its orange color to colorless. However, it is stable in an inert gas atmosphere. 18 is readily soluble in aromatic solvents and sparingly soluble in n-hydrocarbons. Compound 19 is a colorless crystalline
solid and is well soluble in hydrocarbons. 18 and 19 were characterized by mass spectrometry, $^1$H and $^{13}$C NMR spectroscopy, and by X-ray crystallography.

The structural analyses clearly reveal that compound 18 has a three-membered Al($\eta^2$-C$_2$H$_2$) ring (Figure 11), while 19 contains terminal C=CH and CH=CH$_2$ groups at the Al atom (Figure 12). The latter is the first crystallographic authenticated example with terminal C=CH and CH=CH$_2$ groups at the same Al atom. In 19, the X-ray reflection data indicate that both C=CH and CH=CH$_2$ groups are disordered in two positions (C(6)H(6)C(7)H(7)H(8), C(8)C(9)H(9), 62.2%; C(6A)H(6A)C(7A)H(7A)H(8A), C(8A)C(9A)H(9A), 37.8%). Thus, the central Al atom appears in a disordered tetrahedral geometry with N–Al–N bond angle of

**Figure 13.** Molecular structure of 19, the C=CH and CH=CH$_2$ groups both in 62.2% occupation. H atoms in L are omitted for clarity. Selected bond lengths (Å) and angles (°): 

Al(1)–N(1) 1.910(2), Al(1)–N(2) 1.895(1), Al(1)–C(6) 1.944(11), Al(1)–C(8) 1.962(11), C(6)–C(7) 1.325(17), C(8)–C(9) 1.173(11), N(1)–Al(1)–N(2) 96.99(6), C(6)–Al(1)–C(8) 110.8(4), Al(1)–C(6)–C(7) 124.6(12), Al(1)–C(8)–C(9) 173.9(13), 96.99(6)° and C–Al–C angles of 111.6(5)° (av). The Al–N bond lengths in 18 (1.875(1), 1.884(1) Å) are close to those in 19 (1.895(1), 1.910(2) Å), and are comparable to those
observed in compounds with four coordinate \( \beta \)-diketiminato aluminum(III) (1.888(2)–1.935(2) Å). However, they are shorter, in contrast to the longer Al–N bonds in LAl (1.957(2) Å) due to the larger radius of the Al(I)\(^{[95]} \) compared to that of Al(III).

In 19, the Al–C bond lengths (Al–C\(_{\text{C=C}}\), 1.941(14) Å (av); Al–C\(_{\text{C=C}}\), 1.954(14) Å (av)) are comparable to those in related compounds LAlMe\(_2\) (1.955(4)–1.961(3) Å) and L’AlMe\(_2\) (L’ = HC\([(\text{CMe})(\text{N–}\text{p-tol})]\)\(_2\), 1.958(3)–1.970(3) Å). The C=C (1.170(14) Å (av)) and C=C bond distances (1.323(18) Å (av)) are indicative of characteristic C–C triple and double bonds, while the Al–C\(_{\text{C=C}}\) (175.4(19)º (av)) and Al–C\(_{\text{C=C}}\) (124.6(14)º (av)) angles deviate from the ideal 180º and 120º, respectively.\(^{[189]} \) The \( ^1 \)H and \( ^{13} \)C NMR spectra of 19 confirm the functional CH=CH\(_2\) and C=CH groups at Al. In CH=CH\(_2\), the corresponding protons resonate at \( \delta \) 5.70–6.20 ppm and carbons at \( \delta \) 125.4 (=CH\(_2\)) and 138.0 (br, Al–CH=) ppm, respectively, and are within the typical alkenyl range. Three groups of double doublets are indicative for three non-equivalent protons. While the latter exhibits the proton resonance at \( \delta \) 1.55 (s) ppm and carbon resonances at \( \delta \) 94.6 (br, \( \equiv \)CH) and 137.3 (br, Al–C\(_{\text{C}}\)) ppm. The absorptions at 1996 and 3270 cm\(^{-1}\) in the IR spectrum of 19 are tentatively assigned to the stretching frequencies of C=C and \( \equiv \)C–H bonds.

In 18, the parameters within Al(\( \eta ^2\)-C\(_2\)H\(_2\)) moiety (Al–C 1.882(2) Å (av), C–C 1.358(2) Å, C–H 1.010 Å (av); C–Al–C 42.30(7)º, Al–C–C 68.85(10)º (av), H–C–C, 126.6º (av)) fit well when compared with those of Al(\( \eta ^2\)-C\(_2\)) in LAl(\( \eta ^2\)-C\(_2\)R\(_1\)R\(_2\)) (R\(_1\), R\(_2\): SiMe\(_3\), Ph) (Al–C 1.889(2)–1.899(3) Å, C–C 1.356(5)–1.382(4) Å; C–Al–C 42.02(14)–42.57(11)º, Al–C–C 68.39(15)–68.80(19)º),\(^{[155]} \) and are also much closer to those in the calculated HAl(\( \eta ^2\)-C\(_2\)H\(_2\)) (Al–C 1.844–1.852 Å, C–C 1.362–1.384 Å, C–H 1.076–1.089 Å; H–C–C, 126.8–127.3º).\(^{[179]} \) It is noteworthy that in the Al(\( \eta ^2\)-C\(_2\)H\(_2\)) ring of 18 the average Al–C and C–C bond lengths are respectively shorter and longer than those in 19 (deviation of 0.072 and 0.036 Å). This may indicate a conjugated ring system in Al(\( \eta ^2\)-C\(_2\)). Furthermore, the \( ^1 \)H and \( ^{13} \)C NMR spectra recorded in C\(_6\)D\(_6\) show the proton (\( \delta \) 8.82 (s) ppm) and carbon resonances (177.2 (br) ppm) of
the Al(η²-C₂H₂) moiety in the low-field region characteristic for the alkenyl system. The results are indicative for a certain aromatic character of the Al(η²-C₂) ring.

Figure 14. Molecular structure of 20. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.894(2), Al(1)–N(2) 1.895(2), Al(1)–C(6) 1.941(2), Al(1)–C(8) 1.971(2), C(6)–C(7) 1.217(2), C(8)–C(9) 1.343(3), N(1)–Al(1)–N(2) 97.04(6), C(6)–Al(1)–C(8) 111.15(8)

The reaction of LAl(η²-C₂Ph₂) with one equiv of HCCPh smoothly afforded compound LAl(C≡CPh)[C(Ph)=CH(Ph)] (20). The molecular structure of 20 is presented in Figure 14.

Figure 15. The ¹H NMR spectra monitored reaction of LAl(η²-C₂Ph₂) with HCCPh
This reaction was further monitored by $^1$H NMR spectral analysis (Figure 15). (I) clearly shows the gradual consumption of starting material LAI($\eta^2$-C$_2$Ph$_2$) and formation of product 20 by the indication of $\gamma$-CH of LAI moiety with reaction time. (II) reflects the gradual generation of olefinic proton corresponding to AlC(Ph)=CH(Ph) moiety, indicating the hydrogen migration from HCCPh molecule.

![Diagram of reaction](image)

**Scheme 17**

**Figure 16.** Molecular structure of 21. H atoms in L are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.866(2), Al(1)–N(2) 1.867(2), Al(1)–N(3) 1.892(2), Al(1)–C(6) 1.932(3), C(6)–C(7) 1.342(4), C(7)–N(3) 1.410(3), N(3)–N(4) 1.320(3), N(4)–N(5) 1.284(3), N(1)–Al(1)–N(2) 99.8(1), C(6)–Al(1)–N(3) 72.6(1), Al(1)–N(3)–C(7) 88.2(2), Al(1)–C(6)–C(7) 88.5(2), C(6)–C(7)–N(3) 110.7(2), N(3)–N(4)–N(5) 112.4(2).
The reaction of 18 with a large bulky azide N₃Ar* exhibits an unusual end-on azide insertion, resulting in a four-membered aluminaazacyclobutene 21 (Scheme 17). There are a handful of reactions known between monovalent organo-group 13 compounds and organic azides. The initial N₂ elimination is generally accepted, and supported by the experimental observation. The formation of a five-membered AlN₄ ring in LAl[(NSiMe₃)₂N₂] was suggested proceeding through a [2 + 3] cycloaddition of an Al=N intermediate and N₃SiMe₃. While the disubstituted aluminacyclopene LAl[(η²-C₂(SiMe₃))₂] reacted under disassociation and N₂ elimination with a similar bulky azide to an Al=N compound. Accordingly, the end-on N₃Ar* insertion in the Al(η²-C₂) ring unambiguously reveals the initial interaction between an Al center and the end-on N atom of the azide group. This type of reaction is, to the best of our knowledge, so far unknown. Compound 21 has been well characterized by spectroscopic, analytical, and X-ray crystal measurements. The molecular structure of 21 is viewed in Figure 16.

In general, the first stable aluminacyclopene LAl(η²-C₂H₂) (18) has been prepared by the direct reaction of LAl with C₂H₂ and structurally characterized. The crystallographic and NMR spectral data of 18 indicate a delocalized Al(η²-C₂) heterocycle, which can be described as a Hückel 2π aromatic system. The subsequent reaction of 18 with C₂H₂ to 19 shows its high reactivity. The end-on N₃Ar* insertion in the Al(η²-C₂H₂) ring of 18 to the aluminaazacyclobutene 21 exhibits a novel reaction pattern of aluminacycloprenes, and reflects the unusual trapping ability of 18. Further investigation of the reactivity of 18 is underway.
2.7. A Seven-membered Aluminum Allenyl Sulfur Heterocycle

**Arising from the Conversion of an Aluminacyclopropene with CS$_2$**

*Abstract:* The reaction of an aluminacyclopropene LAI[$\eta^2$-C$_2$(SiMe$_3$)$_2$] (L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) with CS$_2$ in the temperature range from –78 ºC to room temperature affords the first seven-membered aluminum sulfur containing heterocyclic compound [LAl$_2$(μ-S)[$\eta^2$-SC(SiMe$_3$)=C=C(SiMe$_3$)]] (24) bearing an allenyl group. The structural characterization of 24 and the analogous compound LAI[OC(O)C$_2$R$_2$] (R = Ph (22), SiMe$_3$ (23)) of the proposed intermediate A and the variable-temperature $^1$H NMR kinetic study of this reaction may give a better understanding on this unusual conversion.

There is a widespread interest in main group heterocyclic compounds due to their applications in pharmaceutical, agrochemical, and material science.$^{[154]}$ In recent years, the number of group 13 metal heterocycles has increased. Within the heterocycles those containing multiple bonds have shown interesting structural features and properties. The M$_n$N$_2$C$_2$ (M = Al, Ga, In, n = 2; M = Ga, n = 1, 3)$^{[193-198]}$ and MC$_3$N$_2$ (M = Al, Ga)$^{[95,199]}$ heterocycles with C=C or C=N double bonds are exhibiting high electron density. The three-membered AlC$_2$ ring with a C=C bond shows a highly strained structure and good reactivity.$^{[155]}$ Nonetheless, such species are rare, and the heteroatoms within cycle are limited to C, N, and O elements due to the lack of appropriate synthetic routes. Herein we report on a seven-membered Al$_2$C$_3$S$_2$ heterocycle bearing a C=C=C allenyl group prepared from the reaction of an aluminacyclopropene, LAI[$\eta^2$-C$_2$(SiMe$_3$)$_2$] (L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) with carbon disulfide. Interestingly, the unusual formation of the allenyl group, to the best of our knowledge, is hitherto unknown in organoaluminum chemistry.

The addition of neat carbon disulfide to the solution of LAI[$\eta^2$-C$_2$(SiMe$_3$)$_2$] in toluene was carried out at –78 ºC. In the course of warming the solution to room temperature, the color changed from red-black to green, to yellow green, and finally to yellow. An additional stirring for 12 h resulted in the formation of 24.
The initial reaction of \( \text{LAl}[\eta^2-C_2(SiMe_3)_2] \) with \( \text{CS}_2 \) resembles closely to that of \( \text{LAl}[\eta^2-C_2R_2] \) (\( R = \text{Ph, SiMe}_3 \)) with \( \text{CO}_2 \) (Scheme 18),\(^{155}\) resulting in the generation of the five-membered heterocycle \( \text{LAl}[\text{SC(S)C}_2(\text{SiMe}_3)_2] \) (A). Obviously, A further interacts with a second molecule of \( \text{LAl}[\eta^2-C_2(\text{SiMe}_3)_2] \) at the donor exocyclic S atom in A and the acceptor Al center in \( \text{LAl}[\eta^2-C_2(\text{SiMe}_3)_2] \) to give intermediate (B). The fact whether one equivalent or excess of \( \text{CS}_2 \) was employed, only product 24 was isolated, indicates the stronger competitive reaction of A with \( \text{LAl}[\eta^2-C_2(\text{SiMe}_3)_2] \) than with \( \text{CS}_2 \). B reacts further under elimination of one molecule of \( \text{Me}_3\text{SiCCSiMe}_3 \) due to the weak Al–\( \eta^2 \)-C\(_3\)-alkyne bonding (the bond dissociation energy of Al–\( \eta^2 \)-C\(_2\) is only 95.8 kJ/mol and therefore much less than that of Al–C\(_{\text{methyl}}\) in \( \text{AlMe}_3 \)\(^{[4]}\) (\( D_{\text{average}} \), 281.4 kJ/mol). The free \( \text{Me}_3\text{SiCCSiMe}_3 \) is detected in the latter \(^1\text{H}\) NMR
kinetic study. An easy migration of one Me$_3$Si group$^{[200]}$ and rearrangement of C=S$_{\text{ex}}$ and $\mu$-S–C bonds lead to the unique formation of the thioallenyl functional group and the final product 24. A proposed mechanism for the formation of 24 is given in Scheme 19. A parallel investigation of LAl[$\eta^2$-C$_2$(SiMe$_3$)$_2$] with S$_8$ resulted in the formation of a dimer [LAlS]$_2$.

Evidently, the bulky $\beta$-diketiminato ligand with the steric and electronic stabilizing properties acts as an optimal skeleton for the aluminum center throughout the reaction process.

![Molecular structure of 24](image)

**Figure 17.** Molecular structure of 24 (without H atoms). Selected bond lengths (Å) and angles (°): Al(1)–S(1) 2.2298(11), Al(1)–C(56) 1.990(3), Al(2)–S(1) 2.2188(11), Al(2)–S(2) 2.2270(11), S(2)–C(54) 1.809(3), C(54)–C(55) 1.325(4), C(55)–C(56) 1.316(4); Al(1)–S(1)–Al(2) 122.57(4), C(54)–C(55)–C(56) 178.0(3).

Compound 24 was obtained as yellow crystals, which were characterized by spectroscopy and by X-ray crystallography. The structural analysis of 24 reveals a novel heterocyclic molecule (Figure 17), which is in sharp contrast to those of known dinuclear aluminum sulfides or thiolates. Each aluminum atom is chelated by a $\beta$-diketiminato ligand to form LAl moieties. Between the two LAl, one S atom and one SC(SiMe$_3$)CC(SiMe$_3$) group are forming
The bond lengths of Al–S$_{\text{bridge}}$ (2.2188(11), 2.2298(11) Å) and Al–S$_{\text{thioallenyl}}$ (2.2270(11) Å) are in the range (2.10–2.30 Å) of dinuclear aluminum sulfides. However, the bond angle of Al(1)–S(1)–Al(2) (122.57(4)°) is the widest among those of dinuclear aluminum sulfides or thiolates (78.1–117.5°)\cite{201-202}. The two central Al atoms, the μ-S atom and the SCC group constitute one seven-membered Al$_2$C$_3$S$_2$ ring, of which S(2), Al(2), S(1), Al(1) and C(56) are arranged within a plane (mean deviation $\Delta = 0.0375$ Å), while the C(56)C(55)C(54) group is located outside of this plane. The remarkable feature of 24 is the SC(SiMe$_3$)CC(SiMe$_3$) group. The similar adjacent C–C bond distances (1.316(4), 1.325(4) Å) and the almost linear C–C–C angle (178.0(3)°) indicate the C=C=C allenyl functionality. A comparable example is only observed in trans-Rh[η-C(CH=CH$_2$)=C=CPH$_2$](CO)(P-iPr)$_3$] (1.308(6), 1.332(6) Å and 177.5(5)°)\cite{203}. The IR spectrum shows one weak band (1840 cm$^{-1}$) assignable to this bridged thioallenyl group. The deliberate $^{13}$C NMR spectral studies give an unambiguous assignment of such allenyl (Al-C(SiMe$_3$)=C=C(SiMe$_3$)S) carbon resonances ($\delta$ 212.70 (=C=); 80.60, broad (Al–C=); 59.94 ppm (=C–S)).

![Molecular structure of 22 (without H atoms). Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.776(3), Al(1)–C(7) 1.987(5), C(12)–O(1) 1.328(5), C(12)–O(2) 1.213(6), C(12)–C(19) 1.513(6), C(19)–C(7) 1.362(6); O(1)–C(12)–O(2) 122.5(4).](image)
The crystal structure evidence of 22 and 23 may approach to that of A (Figures 18 and 19). As expected, the CO\textsubscript{2} was inserted into one of the Al–C bonds to form a five-membered AlC\textsubscript{3}O planar ring with an \textit{exo} C=O group ($\Delta = 0.0199$ Å). The longer bond distances and weaker bond strength of CS\textsubscript{2} than those of the corresponding CO\textsubscript{2}\cite{204-205} might give rise to the further interaction of A with LAl[$\eta^2$-C\textsubscript{2}(SiMe\textsubscript{3})\textsubscript{2}] and rearrangement of the C=S\textsubscript{exo} unit.

**Figure 19.** Molecular structure of 23 (without H atoms). Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.7696(12), Al(1)–C(3) 1.9891(17), C(1)–O(1) 1.331(2), C(1)–O(2) 1.218(2), C(1)–C(2) 1.530(2), C(2)–C(3) 1.364(2); O(1)–C(1)–O(2) 121.78(15).

The variable-temperature \textsuperscript{1}H NMR spectroscopy regarding the reaction of LAl[$\eta^2$-C\textsubscript{2}(SiMe\textsubscript{3})\textsubscript{2}] and excess of CS\textsubscript{2} in [D\textsubscript{8}]toluene was monitored. The assignments of Ib, Ic, IIf and IIg were referenced to the \textsuperscript{1}H NMR spectra of 24. The assignment of free Me\textsubscript{3}SiCCSiMe\textsubscript{3} (Id) was referenced to the \textsuperscript{1}H NMR spectrum of the commercially available Me\textsubscript{3}SiCCSiMe\textsubscript{3} in [D\textsubscript{8}]toluene at room temperature ($\delta_{\text{SiMe}} = 0.14$ ppm). From -20 °C to 80 °C, that the gradual completion of (IIf) and (IIg) proceeds the coalescence to separation is temperature-dependant. The less than 1:1 integral intensity of 24 to the free Me\textsubscript{3}SiCCSiMe\textsubscript{3} might be due to excess of CS\textsubscript{2}, since traces of CS\textsubscript{2} are difficult to control in the \textsuperscript{1}H NMR experiment.
This variable-temperature $^1$H NMR kinetic study of this reaction (Figure 20) reveals the gradual consumption of LAl[$\eta^2$-C$_2$(SiMe$_3$)$_2$] (a) and formation of 24 (b and c) including the byproduct Me$_3$SiCCSiMe$_3$ (d) in (I). While in (II), this process is accompanied by the occurrence and quick disappearance of some resonances, indicating that this conversion proceeds via the proposed intermediates A and B to completion.

Figure 20. Variable-temperature $^1$H NMR kinetic studies of the reaction of LAl[$\eta^2$-C$_2$(SiMe$_3$)$_2$] with excess CS$_2$ in [D$_8$]toluene. (I) records the resonances of SiMe$_3$ (0.10–0.55 ppm) which correlate with changes of $\eta^2$-C$_2$(SiMe$_3$)$_2$ group and (II) shows those of $\gamma$-CH protons (4.4–5.1 ppm) directly with the changes of LAl moieties (a and e correspond to LAl[$\eta^2$-C$_2$(SiMe$_3$)$_2$], b,c,f and g to 24, d to free Me$_3$SiCCSiMe$_3$).

Thus, an unusual conversion of LAl[$\eta^2$-C$_2$(SiMe$_3$)$_2$] with CS$_2$ to 24 has been shown, where the search of sterically and energetically favored unsaturated substrate CS$_2$ is crucial. The investigation on such selenium or tellurium containing heterocycles is in progress.
2.8. Two Types of Intramolecular Addition of an Al=N Multiple

**Bonded Monomer LAl=NAr’ Arised from the reaction of LAI with N₃Ar’**

Abstract: The reaction of β-diketiminated aluminum(I) monomer LAI with a large bulky azide $N_3Ar’$ ($L = HC(CMeNAr)_2$, $Ar’ = 2,6$-$Ar_2C_6H_3$, $Ar = 2,6$-$iPr_2C_6H_3$) 25 and 26, which have been characterized by spectroscopic and X-ray structural analyses, as well as elemental analysis. The variable-temperature $^1H$ NMR kinetic studies of this reaction indicate the existence of the monomer LAlNAr’ (A) at low temperature and the thermal stability of the compounds increases in the order of $A < 25 < 26$.

Considerable attention has been attracted to the heavier group 13 imides, since they can be used as single-source precursors for metal nitrides, which have interesting electronic properties and therefore important applications for technological materials. In recent years, studies of the syntheses and characterization of such compounds have shown that they have a strong tendency to associate, even to oligomerize. However, the modification of the substituents on both metal and nitrogen of the (MN)$_n$ core have a great effect on their aggregation. The preparation of di- and tri-coordinate imido monomers Ar’MNL’’ (M = Ga, In; Ar’ = 2,6-$Ar_2C_6H_3$, Ar = 2,6-$iPr_2C_6H_3$, L’’ = 2,6-(4-$t$Bu-Xyl)$_2C_6H_3) and LMNL’ (M = Al, Ga; L = HC[(CMe)(NAr)]$_2$, L’ = 2,6-Trip$_2C_6H_3$, Trip = 2,4,6-$iPr_3C_6H_2)$, which have the lowest degree of association and the unique M-N multiple bond, demonstrates the stabilization of Al (Ga or In) imido monomers by the large bulky ligands. Nonetheless, the syntheses of compounds containing a Ga$_2$N$_2$ or a AlN$_4$ ring, which are proposed to proceed through the monomeric Al(Ga) imide, in the absence of steric protection, suggests the high reactivity of such monomers. Herein we show that the latent reactivity of a monomeric Al-N multiple bonded species initiates further intramolecular addition. The reaction of the β-diketiminated LAI with the bulky $N_3Ar’$ can afford two different isomers 25 and 26 derived from their parent imide LAlNAr’ (A). Also of great interest is the thermal conversion of 25 into 26. This indicates the difference of the thermal stability between 25 and 26.
The reaction of LAl with N$_3$Ar’ was carried out at -78 °C and allowed to warm to room temperature. Partial removal of toluene and addition of $n$-hexane led to crystallization of compounds 26 (colorless crystals in 24% yield) and 25 (yellowish crystals in 42% yield), one after the other. Crystals of 25 are of X-ray quality, while single crystals of 26 were obtained when 25 was treated by dissolving in a hot toluene/$n$-hexane mixture and then kept at 4 °C to allow to crystallize. This suggests that a thermal conversion of 25 to 26 is occurring.

Scheme 20

The LAl reacting with N$_3$Ar’ may proceed through an intermediate LAlNAr’ (A) with elimination of N$_2$. A similar reaction of LM (M = Al, Ga) with N$_3$L’ has been reported to afford LMNL’ containing a M=N multiple bond.$^{[191]}$ The latter $^1$H NMR kinetic study also suggests the existence of A at low temperature. Compound 25 is formed as a result of a [2 + 2] cycloaddition of a phenyl ring of the Ar’ substituent on nitrogen (route b, Scheme 20), while the formation of 26 might occur by an intramolecular C–H activated addition involving the methyl group of the isopropyl substituent on the $\beta$-diketiminato ligand (route a).

Compounds 25 and 26 are thermally stable. They change with color at ~320 °C and finally melt at 381–382 °C. Both of them show the molecular ion [M$^+$ - 1] at m/z 855. They have been characterized by spectroscopic, analytical and X-ray crystal measurements.
Figure 21. Molecular structure of 25. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.915(2), Al(1)–N(2) 1.926(2), Al(1)–N(3) 1.876(2), Al(1)–C(48) 1.998(3), C(48)–C(49) 1.536(4), C(49)–C(50) 1.520(4), C(50)–C(51) 1.348(4), C(51)–C(52) 1.469(4), C(52)–C(53) 1.336(4), C(53)–C(48) 1.475(4), N(3)–C(49) 1.537(3), N(1)–Al(1)–N(2) 96.92(10), N(3)–Al(1)–N(1) 127.76(10), N(3)–Al(1)–C(48) 78.53(10), Al(1)–N(3)–C(30) 138.71(17).

The structure of 25 (Figure 21) exhibits a [2 + 2] cycloaddition product. The four-membered AlNC$_2$ ring is quasi-planar ($\Delta = 0.0680$ Å) with Al–N bond length (1.876(2) Å) longer than those in the AlN$_4$ ring complex (1.851(2), 1.8152(15) Å)\cite{127} and Al–C distance (1.998(3) Å) similar to that in the AlC$_3$O ring compound (1.9852(16) Å).\cite{155} The phenyl ring involved in the [2 + 2] cycloaddition becomes non-planar, where C(50), C(51), C(52) and C(53) are in plane ($\Delta = 0.0430$ Å), C(48) and C(49) are away from this plane by 0.1813 and –0.2827 Å. The C–C bond lengths for C(50)–C(51) and C(52)–C(53) are 1.348(4) and 1.336(4) Å and are typical of C=C double bonds,\cite{207} while the remaining four C–C distances are in the range (1.469(4)–1.536(4) Å) and are indicative for C–C single bonds. The structural features of this phenyl ring are in good agreement with the proton NMR spectrum. The resonances at $\delta$
6.08 (dd), 5.41 (d), and 2.43 (d) ppm are assigned to $H_e$, $H_f$ and $H_d$, respectively, reflecting the extent of (un)saturation at the carbons where these protons are attached.

**Figure 22.** Molecular structure of 26. Selected bond lengths (Å) and angles (˚): $\text{Al(1)}–\text{N(1)}$ 1.940(2), $\text{Al(1)}–\text{N(2)}$ 1.913(2), $\text{Al(1)}–\text{N(3)}$ 1.858(2), $\text{Al(1)}–\text{C(222)}$ 1.961(3), $\text{C(222)}–\text{C(221)}$ 1.556(3), $\text{N(1)}–\text{Al(1)}–\text{N(2)}$ 95.69(10), $\text{N(3)}–\text{Al(1)}–\text{N(1)}$ 115.78(9), $\text{N(3)}–\text{Al(1)}–\text{N(2)}$ 103.44(10), $\text{N(3)}–\text{Al(1)}–\text{C(222)}$ 122.34(10), $\text{Al(1)}–\text{N(3)}–\text{C(51)}$ 138.72(16)

The X-ray crystal structure of 26 is shown in Figure 22. Compound 26 is monomeric and contains a tetra-coordinate Al (3N, 1C) center. The Al atom is involved as part of two fused six-membered rings (AlN$_2$C$_3$ and AlNC$_4$). The $\text{Al(1)}–\text{C(222)}$ (1.961(3) Å) and $\text{C(222)}–\text{C(221)}$ (1.556(3) Å) bond lengths are consistent with experimental values observed for Al–C and C–C single bonds. This suggests the absence of strain within the AlNC$_4$ ring formed as a result of Al–C ligation. The $\text{Al–NH(\text{Ar}^\prime)}$ bond length (1.858(2) Å) falls within the range (1.75–1.85 Å) of terminal Al–N single bonds and a little shorter than that of $\text{Al(1)}–\text{N(3)}$ in 25. The NH and the CH$_2$ protons ($H_a$ and $H_b$) resonate at $\delta$ 3.41 (s), $\delta$ 0.28 (dd) and $\delta$ 1.75 (t), respectively. The assignment of these Al–CH$_2$ ($H_a$ and $H_b$) protons in the $^1$H NMR spectrum of 26 is viewed in the following figure 23. The different dihedral angles between H(22B)—C(222)—
C(221)–H(22A) and H(22C)–C(222)–C(221)–H(22A) give rise to different coupling constants as $^3J_{H(22B)H(22A)} = 13.8$ Hz and $^3J_{H(22C)H(22A)} = 3.0$ Hz according to the Karplus formula of $^3J_{HH} = A - B \cos \phi + C \cos^2 \phi$ ($A = 7$, $B = -1$, $C = 5$). While $^2J_{H(22B)H(22C)} = -13.8$ Hz, therefore, the resonances at $\delta -0.28$ (dd) and $-1.75$ (t) are assigned to H(22B) ($H_b$) and H(22C) ($H_a$), respectively. The characteristic absorption at 3298 cm$^{-1}$ is assignable to $v_{NH}$ in the IR spectrum of 26.

![Figure 23](image)

Now we gain further insight into the reaction process between LAl and $N_3Ar'$ carried out by a variable-temperature $^1H$ NMR study (Figure 24). To a mixture of equivalent LAl and $N_3Ar'$ at $-78 \, ^\circ$C, pre-cooled D$_8$-toluene was added. At $-70 \, ^\circ$C, the proton NMR spectrum only presents the features indicated for those of $N_3Ar'$. This shows the only dissolving of $N_3Ar'$ in D$_8$-toluene at this temperature. From $-50$ to $-10 \, ^\circ$C, the occurrence of a singlet at $\delta 5.05-4.60$ ppm assigned for that of $\gamma$-CH proton in L indicates the starting and proceeding of this reaction, which initiate the dissolving of LAl species. The changes of the chemical shift of this singlet in this area are temperature-dependent. The sample was kept at $50 \, ^\circ$C for 1 h and the corresponding proton NMR spectrum showed that there were no remarkable changes of resonances compared to those in the previous one at 50 °C. While for 24 h the measurement on the sample showed the great changes of resonances in the spectrum.

Therefore, the $\gamma$-CH of the starting material LAl resonates at $\sim 5.10$ ppm (the low temperature $^1H$ NMR spectrum of the starting material LAl was measured as a reference. The resonances of $\gamma$-CH at $\delta 5.11, 5.13, 5.14,$ and $5.15$ ppm correspond at $-50, -30, -10, 25 ^\circ$C),
its change is a good indicator for the progress of the reaction. Thus in I, from −50 to −10 °C, the occurrence of one singlet may indicate the formation of A. From −10 to 50 °C, this singlet was gradually transformed into two other singlets, suggesting the further reaction of A and the concomitant formation of compounds 25 and 26. This is further evidenced by the corresponding presence of the characteristic proton resonances in II indicative for 25 and 26, respectively. The almost same integral intensity of 25 and 26 shows the equiponderance of the intramolecular addition of A via routes a and b. Keeping this reaction at 50 °C for 24 h, the final spectrum shows the disappearance of the characteristic resonances for 25 and the growing in of those for 26. This experiment confirms the result of recrystallization of 25 from a hot solution to yield 26.

**Figure 24.** Variable-temperature $^1$H NMR kinetic studies of the reaction of LAl with N$_3$Ar’ in [D$_8$]toluene. (I) records the resonances of γ-CH proton (δ 5.05–4.60 ppm) which correlate with changes of LAl moiety and (II) shows those of 25 ($H_f$ and $H_g$, δ 6.20–5.20 ppm) and 26 ($H_a$ and $H_b$, δ 0.00–−2.00 ppm). 50* means the available $^1$H NMR data by keeping the sample at 50 °C for 24 h.
The strained structure of 25 (torsional AlC₂N and C₆ rings) compared to that of 26 may energetically favor this thermal rearrangement. While the deliberate ¹H NMR kinetic studies of this reaction unambiguously reveal the thermal stability of these three isomers in the order of A < 25 < 26.

At last, an unprecedented reaction, which occurs by an intramolecular addition to an Al–N multiple bonded species LAInAr’ and furthermore by rearrangement of 25 to 26 without changing the monomeric nature of the products, has been shown. Presently we are involved in the low temperature synthesis of A and especially its X-ray structural analysis.
3. Summary and Outlook

In this thesis, the sterically bulky diamido L’ and β-diketiminato L ligands are employed as supporting moieties in aluminum compounds. Compounds 1–26 have been isolated and characterized (Schemes 21, 22, and 23). The experimental results demonstrate that a number of functional reactions involving an Al(I) or Al(III) center are realized exhibiting diverse reaction types and rich organoaluminum chemistry.

Moreover, organoaluminum chemistry has emerged as a more and more relatively mature field: new syntheses are being developed, much of its basic chemistry is being explored, and many of the prevailing structural types are in delineation. The motivating force for such fundamental studies has been the widespread industrial importance of these organometallic compounds in stoichiometric and catalytic processes.
The Reaction Chemistry of Aluminum(I, III) Compounds Stabilized by Sterically Bulky Ligands

Scheme 21

Scheme 22
The Reaction Chemistry of Aluminum(I, III) Compounds Stabilized by Sterically Bulky Ligands

Scheme 23
4. Experimental Sections

4.1. General Procedures

All manipulations were carried out under a dry nitrogen atmosphere using Schlenk techniques or inside a Mbraun MB 150-GI glovebox filled with nitrogen, where the O₂ and H₂O level were strictly maintained below 1 ppm. All solvents were distilled from Na/benzophenone ketyl prior to use.

4.2. Physical measurements.

The melting points of all compounds described in this thesis were measured in sealed glass tubes on a Bühler SPA-1 apparatus and are not corrected.

Mass spectra were obtained on a Finnigan MAT 8230 or a Varian MAT CH5 instrument by EI-, FI-, and FAB-MS techniques.

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 (middle), w (weak). In most cases only the characteristic absorptions are listed.

¹H, ¹³C, ¹⁹F, ²⁷Al, ²⁹Si, and ⁷⁷Se NMR spectra were recorded on a Bruker-Avance-500, Avance-200, MSL-400, AM-250, and AM-200 spectrometers. The chemical shifts are reported in ppm (positive shifts being downfield) with reference to external standards (SiMe₄ for ¹H, ¹³C, and ²⁹Si, CFCl₃ for ¹⁹F, AlCl₃ for ²⁷Al, and Me₂Se for ⁷⁷Se nuclei). If not otherwise stated, the operation temperature was at ca. 298 K. The symbols (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, dd = double doublet, m = multiplet) are used.

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

X-ray structure determinations and refinements. The crystallographic data for 1, 2, 4, 16, and 17 were collected on a Stoe AED2, for 7, 8, 14, 18, 19, 20, 21, 25, and 26 on IPDS II-
array detector system with four-circle instrument using graphite-monochromated Mo/Kα radiation \((\lambda = 0.71073 \ \text{Å})\), and for 10, 12, 13, 22, 23, and 24 on a bruker three-circle diffractometer equipped with a SMART 6000 CCD detector using monochromated Cu-Kα radiation \((\lambda = 1.54178 \ \text{Å})\). All structures were solved by direct methods (SHELXS-97)\(^{[212]}\) and refined with all data by full-least-squares against \(F^2\).\(^{[213]}\) The non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically. The hydrogen atoms were included in geometrically idealized positions with the \(U_{iso}\) tied to that of the parent atoms and were refined with the riding model, or by difference Fourier synthesis and refined isotropically. Crystal data, data collection details, structural solution and refinement procedures for all the compounds are summarized in the tables.

4.3. Starting materials

Commercially available chemicals were purchased from Fluka or Aldrich and used as received. The gas phase chemicals such as \(\text{O}_2\), \(\text{HCCH}\), \(\text{CO}_2\), \(\text{CO}\), \(\text{H}_2\text{CCH}_2\) are predried by \(\text{P}_4\text{O}_{10}\) perior to use. The other compounds used in the syntheses were prepared according to published references: \(\text{L'} (\text{L'} = \text{ArNH(CH}_2)_3\text{HNAr}, \text{Ar} = 2,6-\text{iPr}_2\text{C}_6\text{H}_3)^{[31]}\) \(\text{AlH}_3\cdot\text{NMe}_3^{[209]}\) \(\text{Me}_3\text{SnF}^{[210]}\) \([\text{ArN(CH}_2)_3\text{NAr}]\text{AlMe}^{[35]}\) \(\text{L} (\text{L} = \text{HC([CMe](NAr)]}_2)^{[81]}\) \(\text{LAII}_2^{[95]}\) \([\text{CN(R)C}_2\text{Me}_2\text{N}(\text{R})] (\text{*:C, R} = \text{Me, iPr})^{[132]}\) \(\text{N}_2\text{CPh}_2^{[133]}\) \(\text{N}_3\text{R} (\text{R} = \text{Ar, Ar'})^{[211]}\)
4.4. Syntheses

**[ArN(CH\textsubscript{2})\textsubscript{3}NAr]AlH(NMe\textsubscript{3}) (1)**

A solution of diamine ArNH(CH\textsubscript{2})\textsubscript{3}HNAr (4.03 g, 10.24 mmol) (Ar = 2,6-iPr\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) in toluene (20 mL) was added to a solution of AlH\textsubscript{3}·NMe\textsubscript{3} (1.18 g, 13.24 mmol) in toluene (30 mL). While stirring, gas evolution was observed. The mixture was slowly heated to 80 °C and stirred for 5 h. All volatiles were removed in vacuo and the residue was extracted with n-hexane. Filtered through Celite, the extract was evaporated to dryness to afford [ArN(CH\textsubscript{2})\textsubscript{3}NAr]AlH(NMe\textsubscript{3}) as a white solid. X-ray quality crystals were grown from n-hexane.

Yield: 4.41 g, 90%. M.p. 196–197 °C.

\(^1\)H NMR (200.13 MHz, 300 K, C\textsubscript{6}D\textsubscript{6}, ppm): δ = 1.22, 1.37, 1.47, 1.66 (d, 24H, CH\textsubscript{Me}\textsubscript{2}), 1.66 (s, 9H, NMe\textsubscript{3}), 2.10, 3.00 (m, 2H, NCH\textsubscript{2}C\textsubscript{H}\textsubscript{2}), 3.25–3.45 (m, 4H, NCH\textsubscript{2}), 3.63, 4.25 (sept, 4H, CHMe\textsubscript{2}), 7.10–7.16 (m, 6H, Ar–H).

MS (EI): \(m/z = 420 [M^+ - NMe\textsubscript{3}]\).

IR (KBr plate, Nujol mull, cm\textsuperscript{-1}): \(\tilde{\nu} = 1799 \) (sh, Al–H).

C\textsubscript{33}H\textsubscript{57}AlN\textsubscript{3} (522.02) (1·1/2n-hexane): calcd. C 75.93, H 11.00, N 8.05; found C 75.44, H 10.64, N 8.26.

**[ArN(CH\textsubscript{2})\textsubscript{3}NAr]AlF(NMe\textsubscript{3}) (2)**

**Method 1:** A suspension of 1 (1.44 g, 3 mmol) and Me\textsubscript{3}SnF (0.55 g, 3 mmol) in toluene (30 mL) was heated to 80 °C and stirred for 12 h. After filtration, the filtrate was concentrated to ca. 10 mL in vacuum and kept at 4 °C for 48 h to afford colorless block-shaped crystals of 2.

Yield: 1.20 g, 80%. M.p. 220-222 °C.

\(^1\)H NMR (200.13 MHz, 300 K, C\textsubscript{6}D\textsubscript{6}, ppm): δ = 1.22, 1.35, 1.47, 1.71 (d, 24H, CHMe\textsubscript{2}), 1.75 (s, 9H, NMe\textsubscript{3}), 2.00, 3.00 (m, 2H, NCH\textsubscript{2}CH\textsubscript{2}), 3.27, 3.40 (m, 4H, NCH\textsubscript{2}), 3.63, 4.29 (sept, 4H, CHMe\textsubscript{2}), 7.10–7.32 (m, 6H, Ar–H).

\(^{19}\)F NMR (188.29 MHz, 300 K, C\textsubscript{6}D\textsubscript{6}, ppm): δ = –12.4 (adjusted value, –175.4).

MS (EI): \(m/z = 497 [M^+], 438 [M^+ - NMe\textsubscript{3}]\).

C\textsubscript{30}H\textsubscript{49}AlFN\textsubscript{3} (497.72): calcd. C 72.40, H 9.92, N 8.44; found: C 72.31, H 9.71, N 8.28.

**Method 2:** A suspension of 1 (1.44 g, 3 mmol) and Me\textsubscript{3}SnF (0.55 g, 3 mmol) in toluene (30 mL) was stirred for 4 d at room temperature till Me\textsubscript{3}SnF was almost consumed. After filtration, the filtrate was concentrated to ca. 10 mL in vacuum and kept at 4 °C for a week to
afford colorless crystals. All spectroscopy confirmed the same compound as that obtained from method 1.

\[\{[\text{ArNH(CH}_2\text{)}_3\text{NAr}]\text{Al(µ-S)\}_2}\ (3)\]

A suspension of 1 (1.48 g, 3 mmol) and elemental S (0.096 g, 3 mmol) in toluene (30 mL) was heated to 80 °C and stirred for 12 h. After filtration, the orange-red filtrate was concentrated to ca. 10 mL and kept at 4 °C for 48 h to afford light yellow crystals of 3-toluene.

Yield: 1.00 g, 67%. M.p. 278−279 °C (> 250 °C, decompose).

\[{}^1\text{H NMR (200.13 MHz, 300 K, C}_6\text{D}_6, \text{ppm): } \delta = 1.17, 1.22 (d, 48H, CHMe_2), 1.36 (s, 2H, NH), 1.78 (m, 4H, NCH(CH}_2\text{)_2}), 2.1 (s, 3H, MePh), 3.00 (t, 8H, NCH(CH}_2\text{)_2}), 3.38 (sept, 8H, CHMe_2), 6.96−7.04 (m, 5H, MePh), 7.02−7.10 (m, 12H, Ar−H).\]

\[\text{MS (EI): } m/z = 904 [M^+].\]

\[\text{IR (KBr plate, Nujol mull, cm}^{-1}\text{: } \nu = 3190 (NH).\]

\[\text{C}_{61}\text{H}_{90}\text{Al}_2\text{N}_4\text{S}_2\ (996.8) (3-toluene): calcd. C 73.50, H 9.10, N 5.62; found: C 73.25, H 8.90, N 5.07.}\]

\[\{[\text{ArNH(CH}_2\text{)}_3\text{NAr}]\text{Al(µ-Se)\}_2}\ (4)\]

A suspension of 1 (1.44 g, 3 mmol) and elemental gray Se powder (0.24 g, 3 mmol) in toluene (30 mL) was refluxed for 12 h and almost all the selenium was consumed. In the course of hot filtration, the yellowish crystals were grown from the orange filtrate, which were collected by filtration. (0.10 g). The mother liquor was concentrated to ca. 10 mL and kept at 4 °C for 24 h to afford another crop of yellowish crystals of 4·2 toluene (1.00 g).

Total yield: 1.10 g (62%). M.p. 291 °C (> 259 °C, decompose).

\[{}^1\text{H NMR (200.13 MHz, 300 K, C}_6\text{D}_6, \text{ppm): } \delta = 1.17, 1.22 (d, 48H, CHMe_2), 1.36 (s, 2H, NH), 1.78 (m, 4H, NCH(CH}_2\text{)_2}), 2.1 (s, 6H, MePh), 3.00 (t, 8H, NCH(CH}_2\text{)_2}), 3.38 (sept, 8H, CHMe_2), 6.94−7.04 (m, 10H, MePh), 7.02−7.10 (m, 12H, Ar−H).\]

\[{}^{77}\text{Se NMR (500 MHz, 300 K, C}_6\text{D}_6, \text{CDCl}_3, \text{or C}_7\text{D}_8, \text{ppm): no resonances were observed.}\]

\[\text{MS (EI): } m/z = 998 [M^+].\]

\[\text{IR (KBr plate, Nujol mull, cm}^{-1}\text{: } \nu = 3187 (NH).\]

\[\text{C}_{68}\text{H}_{98}\text{Al}_2\text{N}_4\text{Se}_2\ (1182.9) (4·2toluene): calcd. C 69.04, H 8.35, N 4.74; found: C 68.79, H 8.22, N 4.63.}\]

\[\{[\text{ArNH(CH}_2\text{)}_3\text{NAr}]\text{Al(µ-Te)\}_2}\ (5)\]
A suspension of 1 (1.44 g, 3 mmol) and elemental Te powder (0.39 g, 3 mmol) in toluene (40 mL) was refluxed for 5 d and there still remained small amounts of unreacted Te powder. After filtration, the green-yellow filtrate was concentrated to ca. 10 mL and to it n-hexane (5 mL) was added. The solution was kept at 4 °C for 24 h to afford green-yellow crystals of 5-toluene.

Yield: 0.85 g, 48%. M.p. 320 ºC (decompose).

$^1$H NMR (200.13 MHz, 300 K, $C_6D_6$, ppm): $\delta = 1.17, 1.22$ (d, 48H, CH$_2$Me$^2$), 1.35 (s, 2H, NH), 1.75 (m, 4H, NCH$_2$CH$_2$), 2.1 (s, 3H, MePh), 3.00 (t, 8H, NC$_2$H$_2$), 3.37 (sept, 8H, C$_2$HMe$^2$), 6.94–7.04 (m, 5H, MePh), 7.02–7.10 (m, 12H, Ar–H).

MS (EI): $m/z$ = 1096 [$M^+$].

IR (KBr plate, Nujol mull, cm$^{-1}$): $\tilde{\nu} = 3185$ (NH).

C$_6$H$_90$Al$_2$N$_4$Te$_2$ (1188.1) ($5\cdot$toluene): calcd. C 61.67, H 7.63, N 4.71; found: C 61.72, H 7.61, N 4.76.

To a toluene solution (80 mL) of LH (8.36 g, 20 mmol) at 0 ºC n-BuLi (2 M, 10 mL, 20 mmol) was added dropwise. The mixture was stirred and allowed to warm to room temperature. After additional stirring for 12 h, the solution was cooled to −78 ºC and AlCl$_2$Me (1 M, 20 mL, 20 mmol) was added. The resulting suspension was allowed to warm to room temperature and stirred for 12 h. After workup, the insoluble LiCl was removed by filtration and the filtrate was dried in vacuo and washed with n-hexane to yield crystalline solid of 6.

Yield: 9.1 g, 92%. M.p. 191–192 ºC.

$^1$H NMR (300.13 MHz, 298 K, $C_6D_6$, ppm): $\delta = –0.64$ (s, 3 H, Al–Me), 1.00 (d, 2 x 3 H, $^3J_{HH} = 6.8$ Hz, CH(CH$_3$)$_2$), 1.19 (d, 2 x 3 H, $^3J_{HH} = 6.8$ Hz, CH(CH$_3$)$_2$), 1.28 (d, 2 x 3 H, $^3J_{HH} = 6.8$ Hz, CH(CH$_3$)$_2$), 1.46 (d, 2 x 3 H, $^3J_{HH} = 6.8$ Hz, CH(CH$_3$)$_2$), 1.54 (s, 2 x 3 H, $\beta$-Me), 3.21 (sept, 2 x 1 H, $^3J_{HH} = 6.8$ Hz, CH(CH$_3$)$_2$), 3.77 (sept, 2 x 1 H, $^3J_{HH} = 6.8$ Hz, CH(CH$_3$)$_2$), 4.98 (s, 1 H, $\gamma$-CH), 7.00–7.10 (m, 6 H, Ar–H).

MS (EI): $m/z$ (%): 494.3 (3, [$M^+$]), 479.3 (100, [$M^+ –$ Me]).

C$_{30}$H$_{44}$AlClI$_2$ (495.13): calcd. C 72.77, H 8.96, N 5.66; Found: C 72.32, H 8.74, N 5.71.

A toluene solution (80 mL) of 6 (7.43 g, 15 mmol) and I$_2$ (3.81 g, 15 mmol) was stirred for 5 d. The solution was concentrated (ca 20 mL) and kept at 4 °C for 24 h. The very light yellow crystals of 7 were formed and collected (5.5 g). The mother liquor was concentrated (ca 5 mL...
to afford a second crop of 7 (1.7 g).
Total yield: 7.2 g (79%). M.p. 200–203 °C.

\[^{1}H\text{ NMR (300.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 1.02 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{1}H\text{ NMR (300.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 1.02 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{1}H\text{ NMR (300.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 1.02 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{1}H\text{ NMR (300.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 1.02 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{1}H\text{ NMR (300.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 1.02 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{1}H\text{ NMR (300.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 1.02 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{1}H\text{ NMR (300.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 1.02 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{1}H\text{ NMR (300.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 1.02 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{1}H\text{ NMR (300.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 1.02 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{1}H\text{ NMR (300.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 1.02 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{27}Al\text{ NMR (78.20 MHz, 298 K, C}_6\text{D}_6, \text{ppm): no resonances were observed.}\]

MS (EI): \text{m/z }(%): 606 (1, [M\text{+}]^+), 571 (4, [M\text{+} – Cl]^+), 479 (100, [M\text{+} – I]^+).

C\text{_{29}H\text{_{41}AlClIN}_2 (606.97): calcd. C 57.34, H 6.81, Cl 5.32, I 20.91, N 4.62; Found: C 58.00, H 6.86, Cl 5.14, I 19.23, N 4.70.}\n
\[\text{[LAlCl(\mu-OH)]}_2 (8)\]

To a mixture of 7 (0.61 g, 1 mmol) and \[\text{[CN(\text{iPr})C}_2\text{Me}_2\text{N(\text{iPr})]} \text{:C, 0.18 g, 1 mmol}\] in toluene (40 mL) at 0 °C, distilled H\text{\textsubscript{2}}O (18 \text{ mL}, 1 mmol) was added. The suspension was allowed to warm to room temperature and stirred for 12 h. The insoluble solid was removed by filtration and the filtrate was dried in vacuo and extracted with \text{n-hexane (10 mL). The extract was kept at 4 °C to afford colorless crystals of 8. X-ray quality crystals of 8 were grown from \text{n-hexane and contained one molecule of \text{n-hexane.}\n
Yield: 0.35 g, 70%. M.p. > 177 °C (decomp.).

\[^{1}H\text{ NMR (500.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 0.72 \text{ (s, 2 H, OH)}, 1.12 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{1}H\text{ NMR (500.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 0.72 \text{ (s, 2 H, OH)}, 1.12 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{1}H\text{ NMR (500.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 0.72 \text{ (s, 2 H, OH)}, 1.12 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{1}H\text{ NMR (500.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 0.72 \text{ (s, 2 H, OH)}, 1.12 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{1}H\text{ NMR (500.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 0.72 \text{ (s, 2 H, OH)}, 1.12 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{1}H\text{ NMR (500.13 MHz, 298 K, C}_6\text{D}_6, \text{ppm):} \delta = 0.72 \text{ (s, 2 H, OH)}, 1.12 \text{ (d, 2 x 3 H, }^{3}J_{\text{HH}} = 6.8 \text{ Hz, CH(CH}_3\text{)_2)},\]

\[^{27}Al\text{ NMR (78.20 MHz, 298 K, C}_6\text{D}_6, \text{ppm): no resonances were observed.}\]

MS (EI): \text{m/z }(%): 496.3 (50, [M\text{+}/2]^+), 478.3 (16, [M\text{+}/2 – OH – 1]^+), 461.3 (100, [M\text{+}/2 – Cl]^+).

IR (KBr plate, Nujol mull, cm\textsuperscript{-1}): \nu = 3459 (broad, OH).

C\text{_{58}H\text{_{84}Al}_2Cl}_2\text{N}_4\text{O}_2 (994.21): calcd. C 70.07, H 8.52, N 5.64; Found: C 69.34, H 8.69, N 5.34.

\[\text{LAi(OH)}\text{\textsubscript{2} (9)}\]
The synthetic procedure for 9 resembled that of 8 with the starting materials 8, [CN(iPr)C2Me2N(iPr)], and H2O in molar ratio of 1 : 2 : 2. After workup, by filtration to remove insoluble solids and drying in vacuo the n-hexane extract was kept at 4 °C for 3 d to afford colorless crystals of 9 (25%). The spectrometric and spectroscopic data (EI-MS, IR, 1H NMR) are almost the same as those described in literature. The characteristic data for the Al–OH functionality are listed here: 1H NMR (300.13 MHz, 298 K, D8-toluene, ppm): δ = 0.27 (s, 2 x 1 H, OH); IR (KBr plate, Nujol mull, cm⁻¹): ν = 3448 (broad, OH). The X-ray single crystal diffraction analysis confirms the same set of data reported for complex 9.

\[
\text{[LAIO]_2 (10)}
\]

A toluene solution (20 mL) of LAl (0.44 g, 1 mmol) in 100 mL Schlenk flask was cooled to –78 °C. The N2 atmosphere in the flask was exchanged to O2 (O2 gas was predried with P4O10). In the course of stirring and warming to room temperature the color of the solution slowly changed from red to orange, to yellow, and finally to very light yellow, and at ca. –15 °C a colorless crystalline solid started to form from the very light yellow solution. After additional stirring for 2 h, the solvent was removed in vacuo and the residue was washed with n-hexane (2 mL) to give crystalline 10.

Yield: 0.37 g (80%). M.p. 314–315 °C.

1H NMR (C6D6, 298 K, 500.13 MHz, ppm): δ = 0.22 (d, 3J_HH = 6.7 Hz, 2 x 3H, CHMe2), 1.07 (d, 3J_HH = 6.7 Hz, 2 x 3H, CHMe2), 1.21 (d, 3J_HH = 6.7 Hz, 2 x 3H, CHMe2), 1.27 (d, 3J_HH = 6.7 Hz, 2 x 3H, CHMe2), 1.39 (d, 3J_HH = 6.7 Hz, 2 x 3H, CHMe2), 1.45 (d, 3J_HH = 6.7 Hz, 2 x 3H, CHMe2), 1.49 (d, 3J_HH = 6.7 Hz, 2 x 3H, CHMe2), 1.52 (s, 2 x 3H, β-CH3), 2.63 (sept, 3J_HH = 6.7 Hz, 2 x 1H, CHMe2), 3.22 (sept, 3J_HH = 6.7 Hz, 2 x 1H, CHMe2), 3.57 (sept, 3J_HH = 6.7 Hz, 2 x 1H, CHMe2), 3.83 (sept, 3J_HH = 6.7 Hz, 2 x 1H, CHMe2), 4.71 (s, 2 x 1H, γ-CH), 6.98–7.10, 7.15–7.31 (m, 12H, Ar−H).

13C NMR (C6D6, 298 K, 125.8 MHz, ppm): δ = 22.2, 23.4, 24.2, 24.5, 25.0, 25.7, 26.4, 26.8, 27.2, 27.7, 29.1, 31.5, 32.4 (CHMe2 and β-CH3), 71.4 (CHMe2), 97.8 (γ-C), 122.7, 124.2, 125.3, 125.7, 126.9, 127.7, 128.9, 142.0, 143.7, 145.7, 146.2, 148.1 (Ar−C6H3), 168.1 (CN).

MS (EI) (m/z (%)): 920.4 (30) [M+], 403.3 (100) [L − Me].

C₅₈H₈₂Al₂N₄O₂ (921.29) (%): calcd. C 75.62, H 8.97, N 6.08; found C 75.20, H 9.02, N 6.21.

\[
\text{[LAl(OH)]_2(µ-O) (11)}:
\]

To a suspension of 10 in toluene (30 mL) one equiv of H2O was added at 0 °C. The mixture
was allowed to warm to room temperature and stirred for 12 h to give a clear solution. All volatiles were removed and the residue was recrystallized in toluene/n-hexane at –26 °C. The colorless crystals of 11·1.5 n-hexane were obtained and determined by X-ray structural analysis. The cell parameters are almost the same as those for 11-n-hexane·0.5 toluene. 11·1.5 n-hexane: a = 13.677(1), b = 21.289(1), c = 23.014(1) Å, \( \beta = 104.69(1)° \), \( V = 6482(1) Å^3 \); 11·n-hexane·0.5 toluene: a = 13.731(3), b = 21.352(4), c = 22.877(5) Å, \( \beta = 103.58(3)° \), \( V = 6520(1) Å^3 \).

\[
\text{[HC][(CMe)(NAr)][(CMe)(N-C}_6\text{H}_3\text{-2-iPr-6-CH(CH}_2\text{)(Me)]}Al(NHAr'') \rightleftharpoons 12,}
\]

\[
\text{[HC][(CMe)(NAr)][(CMe)(N-C}_6\text{H}_3\text{-2-iPr-6-CH(CH}_2\text{)(Me)]}Al(\mu^2-\text{OH})]_2 \rightleftharpoons 13
\]

The reaction procedure is the same as that in the preparation of 25 and 26, and LAl (0.47 g, 1.07 mmol) and N\text{\textsubscript{3}}Ar' (0.38 g, 1.07 mmol) are used. After workup, the solution was dried in vacuum and the residue was washed with n-hexane (2 mL) to afford colorless crystalline solids. The melting point is 218–219 °C, however, the proton NMR spectrum indicates two sets of resonances, which may correspond to different compounds. By recrystallization in n-hexane/toluene, compounds 12 and 13 are isolated one by one both as colorless crystals.

12: yield: 0.48 g, 56%. M.p. 194−195 °C.

\(^1\text{H NMR (300.13 MHz, C}_6\text{D}_6, 298 K, ppm): } \delta = -0.94 (dd, 1 H, \text{ } \beta^2J_{HH} = -15.1 \text{ Hz, } \text{ } \gamma^2J_{HH} = 7.7 \text{ Hz, } \text{Al–C}_2\text{H}_2), -0.19 (dd, 1H, \beta^2J_{HH} = -15.1 \text{ Hz, } \text{ } \gamma^2J_{HH} = 2.0 \text{ Hz, } \text{Al–C}_2\text{H}_2), 0.66, 0.90, 0.97, 1.14, 1.18, 1.19, 1.22 (d, 7 \times 3 \text{ H, } \text{ } \gamma^3J_{HH} = 6.6 \text{ Hz, } \text{C}_3\text{H}_7\text{C}_2\text{H}_2), 1.44, 1.52 (s, 2 \times 3 \text{ H, } \text{ } \beta\text{-C}_2\text{H}_3), 1.59, 1.76, 2.13, 2.19, 2.25, 2.34 (s, 6 \times 3 \text{ H, Ar’’–Me}), 2.50, 2.79, 3.33 (sept, 3 \times 1 \text{ H, } \text{ } \beta^3J_{HH} = 6.6 \text{ Hz, } \text{C}_3\text{H}_7\text{C}_2\text{H}_2), 3.04 (m, 1 H, CH(CH}_3\text{)(C}_2\text{H}_2), 3.47 (s, 1 H, NH), 4.83 (s, 1 H, \gamma\text{-C}_2\text{H}_3), 6.62–7.20 (m, 13 H, Ar–H).

\(^{13}\text{C NMR (125.76 MHz, C}_6\text{D}_6, 298 K, ppm): } \delta = 20.25, 21.06, 21.13, 21.17, 22.16, 22.25, 23.00, 24.31, 24.77, 24.83, 24.84, 24.95, 25.13, 26.05, 26.90, 27.66, 28.08, 28.72, 31.91, 40.37 (\beta\text{-C}_2\text{H}_3, \text{CH(CH}_3\text{)(C}_2\text{H}_2), \text{CH(CH}_3\text{)(C}_2\text{H}_2), Ar’’–Me), 98.66 (\gamma\text{-C}_2\text{H}_3), 116.28, 118.60, 124.64, 124.72, 125.22, 127.43, 129.00, 129.40, 136.88, 137.04, 140.46, 141.46, 144.44, 144.80, 146.06, 146.27, 148.89 (Ar–C), 131.2 (br, Al–C), 169.97 (CN).

IR (KBr plate, Nujol mull, cm\(^{-1}\)): \( \nu = 3265 \text{ (NH).} \)

MS (EI): \( m/z \) (%): 771.7 (10, [\text{M}^+]), 443.4 (100, [\text{M}^+–NHAr’’ – 1]).

C\text{\textsubscript{53}}H\text{\textsubscript{60}}AlN\text{\textsubscript{3}} (771.743): calcd. C 82.45, H 8.62, N 5.44. Found: C 82.32, H 8.55, N 5.51.

13: yield: 0.23 g, 23%. M.p. 333–335 °C.
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$^1$H NMR (300.13 MHz, C$_6$D$_6$, 298 K, ppm): δ = −1.69 (t, 1 H, $^2$J$_{HH}$ = −14.2 Hz, $^3$J$_{HH}$ = 14.2 Hz, Al–CH$_2$), −0.35 (dd, 1 H, $^2$J$_{HH}$ = −14.2 Hz, $^3$J$_{HH}$ = 3.5 Hz, Al–CH$_2$), 0.29 (s, 2 x 1 H, O–H), 0.74, 0.86, 0.90, 1.03, 1.17, 1.28, 1.32 (d, 7 x 3 H, $^3$J$_{HH}$ = 6.6 Hz, CH(CH$_3$)$_2$), 1.42, 1.59 (s, 2 x 3 H, β–CH$_3$), 2.47, 2.78, 2.99 (sept, 3 x 1 H, $^3$J$_{HH}$ = 6.6 Hz, CH(CH$_3$)$_2$), 2.60 (m, 1 H, CH(CH$_3$)(CH$_2$)), 4.93 (s, 1 H, γ–CH$_3$), 6.80–7.20 (m, 12 H, Ar–H).

$^{13}$C NMR (125.76 MHz, C$_6$D$_6$, 298 K, ppm):


IR (KBr plate, Nujol mull, cm$^{-1}$): ν = 3400 (br., O–H).

MS (EI): m/z (%): 920.6 (2, [M$^+$]), 887.6 (100, [M$^+$ – 2 Me – 2 H – 1]).

C$_{58}$H$_{80}$Al$_4$N$_4$O$_2$ (921.234): calcld. C 75.62, H 8.97, N 6.08. Found: C 75.48, H 8.85, N 6.11.

After the collection of crystals of 12 and 13, the mother liquor was kept at 4 °C for three weeks. A small amounts of colorless crystals of H$_2$NAr’ were obtained and collected by filtration.

$^1$H NMR (500.13 MHz, C$_6$D$_6$, 298 K, ppm): δ = 1.35 (s, br, 2 H, N–H$_2$), 2.06 (s, 4 x 3 H, o–Ar’–Me), 2.20 (s, 2 x 3 H, p–Ar’–Me), 6.84–6.87, 7.07–7.10 (m, 7 H, Ar–H).

$^{13}$C NMR (125.76 MHz, C$_6$D$_6$, 298 K, ppm): δ = 20.53 (o–Ar’–Me), 21.19 (p–Ar’–Me), 128.88, 129.03, 130.26, 135.33, 136.43, 137.17, 142.53, 147.95 (Ar–C).

IR (KBr plate, Nujol mull, cm$^{-1}$): ν = 3468, 3472 (NH).

Correct elemental analysis.

[HC{C(CH$_2$)NAr}(CMeNAr)]AlH[CN(iPr)C$_2$Me$_2$N(iPr)] (14)

**Method A:** The suspension of LAIl$_2$ (2.08 g, 3.0 mmol) and finely divided potassium (0.25 g, 6.3 mmol) in toluene (50 mL) was stirred violently for 3 d at room temperature till all the potassium disappeared. After filtration the dark-red filtrate was slowly dried in vacuum and some red microcrystals of LAI were observed depositing on the wall of the flask. To the remaining solid [CN(iPr)C$_2$Me$_2$N(iPr)] (0.36 g, 2 mmol) was added. The mixture was allowed slowly to heat to ca. 120 °C and kept for 5 h. After cooling to room temperature, the yellow product was extracted with hot toluene (30 mL) and the extract was kept at room temperature for 24 h to afford X-ray quality colorless block crystals of 14, which were collected by filtration (0.42 g). The mother liquor was concentrated (ca. 5 mL) and kept at 4 °C for 24 h to give another crop of colorless crystals (0.25 g).

Total yield of 14: 0.67 g (47%, based on [CN(iPr)C$_2$Me$_2$N(iPr)]). M.p. 298–300 °C (> 250 °C
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$^1$H NMR (300.13 Hz, 300 K, C$_6$D$_6$, ppm): $\delta = 0.38, 0.50, 0.76, 0.82, 1.19, 1.32, 1.46, 1.50, 1.53, 1.55, 1.57, 1.59$ (d, 12 $\times$ 3H, CHMe$_2$ and N(CHMe$_2$)), 1.38, 1.62 (s, 2 $\times$ 3H, C$_2$Me$_2$), 1.72 (s, 3H, $\beta$-CH$_3$), 3.30, 3.98 (s, 2 $\times$ 1H, $\beta$-CH$_2$), 3.28, 3.62, 4.18, 4.26 (sept, 4 $\times$ 1H, CHMe$_2$), 4.80 (br, 1H, Al–H), 5.60 (s, 1H, $\gamma$-C), 7.10 – 7.38 (m, 6H, Ar–H).

$^{13}$C NMR (300.13 Hz, 300 K, C$_6$D$_6$, ppm): $\delta = 9.9, 10.0$ (C$_2$Me$_2$), 20.7, 21.1, 21.4, 22.0, 23.3, 23.7, 23.8, 24.4, 24.5, 24.7, 25.6, 25.7, 26.4, 27.1, 27.7, 28.4, 28.9 (N(CHMe$_2$), CHMe$_2$, CHMe$_2$ and $\beta$-CH$_3$), 50.9, 53.0 (N(CHMe$_2$)), 80.8 ($\beta$-CH$_2$), 106.6 ($\gamma$-C), 123.0, 124.5, 124.7, 124.9, 125.6, 126.6, 127.8, 128.5, 129.3, 143.4, 144.7, 145.6, 146.1, 147.2, 148.4, 149.0 (Ar–C, CN and C$_2$Me$_2$), 154.5 (Al–C).

$^{27}$Al NMR (79.2 Hz, 300 K, toluene-d$_8$, ppm): no resonances were observed.

IR (KBr plate, Nujol, cm$^{-1}$): $\nu = 1809$ (m, Al–H), $\nu = 1619$ (m, C=C).

MS (EI) ($m/z$ (%)): 624 (5) [M$^+$], 609 (40) [M$^+$ – Me], 581 (100) [M$^+$ – iPr].

C$_{40}$H$_{61}$AlN$_4$ (624.94): calcd. C 76.87, H 9.84, N 8.97; found C 77.07, H 9.55, N 8.86.

**Method B:** The suspension of LAII$_2$ (2.08 g, 3.0 mmol), [CN(iPr)C$_2$Me$_2$N(iPr)] (0.54 g, 3 mmol) and finely divided potassium (0.25 g, 6.3 mmol) in toluene (50 mL) was stirred intensively for 3 d at room temperature till all the potassium disappeared. After filtration the orange filtrate was concentrated (ca. 20 mL) and $n$-hexane (20 mL) was added. The solution was kept at 4 °C for one week to afford colorless block crystals (0.72 g). The mother liquor was further concentrated (ca. 5 mL) and kept at 4 °C for 2 d to give another crop of colorless crystals (0.32 g). Total yield of 14-toluene: 1.04 g (48%). The IR, $^1$H and $^{13}$C NMR spectral data are essentially the same as those of 14 except for one extra molecule of toluene.

[HC{C(CH$_2$)NAr}(CMeNAr)}AlH[CN(Me)C$_2$Me$_2$N(Me)] (15)

Compound 15 was prepared in a similar manner (method A) as 14. LAII$_2$ (2.08 g, 3.0 mmol), finely divided potassium (0.25 g, 6.3 mmol) and [CN(Me)C$_2$Me$_2$N(Me)] (0.24 g, 2.0 mmol) were used. The extract (10 mL) was added to $n$-hexane (10 mL) and kept at –26 °C for 48 h to afford colorless crystals of 15.

Yield: 0.42 g, 25%, based on [CN(Me)C$_2$Me$_2$N(Me)]. M.p. 252–253 °C.

$^1$H NMR (300.13 Hz, 300 K, toluene-d$_8$, ppm): $\delta = 1.45, 1.47$ (s, 2 $\times$ 3H, C$_2$Me$_2$), 0.29, 0.30, 1.16, 1.46, 1.58, 1.60, 1.61, 1.62 (d, 8 $\times$ 3H, CHMe$_2$), 1.69 (s, 3H, $\beta$-CH$_3$), 3.70, 3.75 (s, 2 $\times$ C$_2$Me$_2$), 5.60 (s, 1H, $\gamma$-C), 7.10 – 7.38 (m, 6H, Ar–H).
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\[ 3H, N(Me), 3.10, 3.85 \ (s, \ 2 \times 1H, \ \beta-CH_2) \], 3.21, 3.25, 4.15, 4.21 \ (sept, \ 4 \times 1H, \ CHMe_2), 4.80 \ (br, \ 1H, Al–H), 5.39 \ (s, \ 1H, \ \gamma CH), 7.04–7.38 \ (m, \ 6H, \ Ar–H).

\[ ^{13}C \ \text{NMR} \ (300.13 \ \text{Hz}, \ 300 \ \text{K}, \ \text{toluene-d}_8, \ \text{ppm}): \delta = 7.9, \ 8.0 \ (C_3Me_2), 23.6, 24.0, 24.2, 24.3, 24.8, 24.9, 25.4, 25.8, 26.0, 26.4, 26.5, 27.1, 27.8, 28.7, 29.0 \ (N(Me), \ CHMe_2, \ CHMe_2 \ and \ \beta-CH_3), \ 80.1 \ (\beta-CH_2), 102.3 \ (\gamma C), 122.9, 123.7, 124.2, 124.6, 124.9, 125.1, 125.3, 127.7, 128.0, 143.2, 143.8, 145.4, 146.3, 147.4, 148.2, 149.0 \ (Ar–C, \ CN \ and \ C_3Me_2), 155.2 \ (Al–C).

\[ \text{MS} \ (\text{EI}) \ (m/z \ (%)): \ 568 \ (15) \ [M^+], \ 553 \ (100) \ [M^+ – Me]. \]

\[ \text{IR} \ (\text{KBr \ plate, \ Nujol, cm}^{-1}): \nu = 1810 \ (\text{m, Al–H}), \nu = 1616 \ (\text{m, C=C}). \]

\[ C_{36}H_{53}AlN_4 \ (568.83): \ \text{calcd.} \ C 76.01, \ H 9.29, \ N 9.85; \ \text{found} \ C 76.50, \ H 9.60, \ N 9.40. \]

\[ \text{LAl(N=CPh}_2\text{)}_2 \ (16) \]

A solution of N_2CPh_2 \ (0.37 \ g, 1.90 \ mmol) in toluene \ (15 \ mL) was added to a solution of LAl \ (0.42 \ g, 0.94 \ mmol) in toluene \ (25 \ mL) at room temperature. The mixture was slowly heated to 60 °C and kept for 12 h, and a yellow colored solution developed. All volatiles were removed in vacuum. The residue was washed with \text{n}-hexane \ (5 \ mL) to afford an orange-yellow crystalline solid of 16. X-ray quality crystals were obtained by recrystallization from a 1:1 \text{n}-hexane/ether solution at 4 °C for one week.

Yield: 0.36 \ g, 48%. M.p. 344–346 °C.

\[ ^1H \ \text{NMR} \ (300.13 \ \text{Hz}, \ 300 \ \text{K}, \ C_6D_6, \ \text{ppm}): \delta = 0.82, 1.02 \ (d, \ 8 \times 3 \ H, \ CHMe_2), 1.64 \ (s, \ 2 \times 3 \ H, \ \beta-CH_3), 3.21 \ (sept, \ 4 \times 1H, \ CHMe_2), 5.28 \ (s, \ 1 \ H, \ \gamma CH), 6.92–7.00 \ (m, \ 2 \times 5 \ H, \ Ph), 7.00–7.08 \ (m, \ 2 \times 5 \ H, \ Ph), 7.18–7.32 \ (m, \ 6H, \ Ar–H).

\[ ^{13}C \ \text{NMR} \ (300.13 \ \text{Hz}, \ 300 \ \text{K}, \ C_6D_6, \ \text{ppm}): \delta = 23.8, 24.4, 24.9, 28.5 \ (CHMe_2, \ CHMe_2, \ \beta-CH_3), 98.8 \ (\gamma C), 124.5, 126.9, 127.6, 127.6, 127.9, 128.1, 128.3, 129.4, 142.4, 143.1, 144.7 \ (Ar–C, \ Ph), 166.9 \ (NCPh_2), 171.0 \ (CN).

\[ \text{MS} \ (\text{EI}) \ (m/z \ (%)): \ 805 \ (20) \ [M^+], \ 790 \ (30) \ [M^+ – Me], \ 624 \ (100) \ [M^+ – NCPh_2]. \]

\[ \text{IR} \ (\text{KBr \ plate, \ Nujol, cm}^{-1}): \nu = 1667 \ (\text{w, C=C}), \nu = 1624, 1554 \ (\text{w, C=N}). \]

\[ C_{55}H_{61}AlN_4 \ (805.10): \ \text{calcd.} \ C 82.05, \ H 7.64, \ N 6.96; \ \text{found} \ C 82.11, \ H 7.74, \ N 7.05. \]

\[ \text{LAl[N(H)-o-C}_6\text{H}_4\text{N(Ph)]} \ (17) \]

Method A. A toluene solution \ (30 \ mL) of LAl \ (0.22 \ g, 0.5 mmol) and PhNNPh \ (0.09 \ g, 0.5 mmol) was stirred and allowed to heat slowly to 80 °C for 5 h. The color of the solution changed from red to orange. The solution was reduced in vacuum \ (ca 10 \ mL) and \text{n}-hexane was added \ (10 \ mL). Keeping this solution at 4 °C for one week the orange X-ray quality
crystals of 17 were obtained (0.15 g) and collected. The mother liquor was concentrated again (ca. 4 mL) and n-hexane added (8 mL). Another crop of orange crystals (0.10 g) was obtained by keeping the solution at –26 °C for 24 h.

Total yield: 0.25 g, 81%. M.p. 260–261 ºC.

1H NMR (300.13 MHz, 298 K, C6D6, ppm): δ = 0.90 (d, 3JHH = 6.8 Hz, 2 x 3 H, CH(CH3)2), 0.92 (d, 3JHH = 6.8 Hz, 2 x 3 H, CH(CH3)2), 1.07 (d, 3JHH = 6.8 Hz, 2 x 3 H, CH(CH3)2), 1.23 (d, 3JHH = 6.8 Hz, 2 x 3 H, CH(CH3)2), 1.47 (s, 2 x 3 H, β-CH3), 3.05 (sept, 3JHH = 6.8 Hz, 2 x 1 H, CH(CH3)2), 3.06 (s, 1 H, NH), 3.14 (sept, 3JHH = 6.8 Hz, 2 x 1 H, CH(CH3)2), 5.12 (s, 1 H, –C), 6.31–6.34 (m, 1 H), 6.58–6.66 (m, 2 H), 6.82–6.92 (m, 3 H), 6.94–7.02 (m, 4 H), 7.22–7.30 (m, 4 H), 7.48–7.52 (m, 1 H) (Ar–H and Ph–H).

13C {1H} NMR (125.77 MHz, 298 K, C6D6, ppm): δ = 23.4, 24.2, 24.5, 24.9, 25.1, 28.3, 29.2 (CH(CH3)2, β-CH3), 99.2 (γ-C), 112.3, 114.0, 115.1, 118.8, 124.0, 125.1, 127.9, 128.2, 129.0, 139.5, 143.1, 143.7, 145.3, 148.8 (Ar–C, Ph–C), 171.5 (CN).

IR (KBr plate, Nujol mull, cm–1): v 3220 (NH).

MS (EI): m/z (%) 626 ([M]+,100).


**Method B.** To a toluene solution (20 mL) of LAl[η2-C2(SiMe3)2] (0.62 g, 1 mmol) at –50 ºC was added a toluene solution (5 mL) of PhNNPh (0.18 g, 1 mmol). The mixture was allowed to warm to room temperature under stirring. The solution changed from black to orange. After continuing the stirring for 12 h the solution was dried in vacuum and washed with n-hexane (10 mL) to afford an orange crystalline solid, which was characterized as 17 by m.p. and EI-mass measurements.

LAl(η2-C2H2) (18)

A toluene solution (30 mL) of LAl (0.22 g, 0.5 mmol) at reduced pressure was cooled to –78 ºC and exposed to dried C2H2. This mixture was kept in the temperature range of –78 ºC to –50 ºC for 2 h. An instant color change of the solution from red to orange was observed. All volatiles were removed and an orange crystalline solid of 18 was afforded. The X-ray single crystals of 18 were obtained by keeping the n-hexane/toluene solution of 18 at –26 ºC for one week.

Yield: > 95%. M.p. 219 ºC.

1H NMR (500.13 MHz, 298 K, C6D6, ppm): δ = 1.12 (d, 3JHH = 6.9 Hz, 4 x 3 H, CH(CH3)2), 1.46 (d, 3JHH = 6.9 Hz, 4 x 3 H, CH(CH3)2), 1.53 (s, 2 x 3 H, β-CH3), 3.33 (sept, 3JHH = 6.9
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Hz, 4 x 1 H, CH(CH$_3$)$_2$, 4.89 (s, 1 H, $\gamma$-CH), 7.02–7.12 (m, 6 H, Ar–H), 8.82 (s, 2 x 1 H, Al–$\eta^2$-CH$_2$).

$^{13}$C NMR (125.77 HMz, 298 K, C$_6$D$_6$, ppm): $\delta$ = 23.4, 24.4, 24.6, 28.9 (CH(CH$_3$)$_2$, $\beta$-CH$_3$), 96.5 ($\gamma$-C), 124.4, 138.8, 143.9 (Ar–C), 172.8 (CN), 177.2 (broad, Al–$\eta^2$-C$_2$).

$^{27}$Al NMR (77.13 MHz, 298 K, C$_6$D$_6$, ppm): the signal is too broad to be observed.

IR (KBr plate, Nujol mull, cm$^{-1}$): $\tilde{\nu}$ 442.7(w), 529.1(w), 589.8(m), 613.5(w), 647.4(w), 712.7(m), 748.3(w), 778.2(w), 801.0(s), 867.7(w), 893.9(w), 936.7(w), 1026.0(m), 1055.6(w), 1100.6(m), 1177.4(w), 1260.7(m), 1304.9(w), 1318.7(w), 1410.5(s), 1485.6(s), 1532.8(m), 1653.7(w).

MS (EI): m/z (%) 429.3 (100, [M$^+$ – Me – C$_2$H$_2$]), 455.3 (30, [M$^+$ – Me]), 469.3 (20, [M$^+$ – 1]).

C$_{31}$H$_{43}$AlN$_2$ (470.68): calcd. C 79.10, H 9.21, N 5.95; Found: C 79.43, H 9.18, N 6.03.

LAl(C≡CH)(CH≡CH$_2$) (19)

The initial procedure (LAl (0.22 g, 0.5 mmol), C$_2$H$_2$ (excess), and toluene (30 mL)) is the same as the synthesis of 19. At –50 ºC, the mixture was stirred and warmed to ambient temperature within 48 h, the color of the solution slowly turned to almost colorless. Then all volatiles were removed in vacuum and the residue was washed with $n$-hexane (2 mL) to afford colorless crystalline solid of 19. The X-ray single crystals of 19 were grown from the $n$-hexane solution of 19 at 4 ºC within one week.

Yield: 0.22 g, 90%. M.p. 163–164 ºC.

$^1$H NMR (500.13 MHz, 298 K, D$_8$-toluene, ppm): $\delta$ = 1.08 (d, $^3$J$_{HH}$ = 6.8 Hz, 2 x 3 H, CH(CH$_3$)$_2$), 1.25 (d, $^3$J$_{HH}$ = 6.8 Hz, 2 x 3 H, CH(CH$_3$)$_2$), 1.28 (d$^3$J$_{HH}$ = 6.8 Hz, 2 x 3 H, CH(CH$_3$)$_2$), 1.44 (d, $^3$J$_{HH}$ = 6.8 Hz, 2 x 3 H, CH(CH$_3$)$_2$), 1.55 (s, 2 x 3 H, $\beta$-CH$_3$), 1.73 (s, 1 H, C≡CH), 3.23 (sept, $^3$J$_{HH}$ = 6.8 Hz, 2 x 1 H, CH(CH$_3$)$_2$), 3.81 (sept, $^3$J$_{HH}$ = 6.8 Hz, 2 x 3 H, CH(CH$_3$)$_2$), 5.79 (dd, $^3$J$_{HH}$(trans) = 20.9 Hz, $^2$J$_{HH}$ = 6.4 Hz, 1 H), 6.04 (dd, $^3$J$_{HH}$(cis) = 16.5 Hz, $^2$J$_{HH}$ = 6.4 Hz, 1 H), 6.12 (dd, $^3$J$_{HH}$(trans) = 20.9 Hz, $^3$J$_{HH}$(cis) = 16.5 Hz, 1 H), (CH=C=CH$_2$), 6.97–7.12 (m, 6 H, Ar–H).

$^{13}$C NMR (125.76 HMz, 298 K, D$_8$-toluene, ppm): $\delta$ = 23.4, 24.5, 24.7, 24.8, 27.2, 28.2, 28.6 (CH(CH$_3$)$_2$, $\beta$-CH$_3$), 94.6 (broad, =CH), 98.4 ($\gamma$-C), 124.1, 124.8, 127.5, 128.8, 129.2, 137.1, 140.3, 143.7, 145.4 (Ar–C), 125.4, (=CH$_2$), 137.3 (broad, Al–C=), 138.0 (broad, Al–C=), 170.6 (CN).

IR (KBr plate, Nujol mull, cm$^{-1}$): $\tilde{\nu}$ 1992 (C=C), 3277 (=CH).

MS (EI): m/z (%) 469.4 (100, [M$^+$ – CH=CH$_2$]), 496.4 (15, [M$^+$]).
C₃₃H₄₅AlN₂ (496.72): calcd. C 79.80, H 9.13, N 5.64; Found: C 79.26, H 9.18, N 5.56.

**LAl(C≡CPh)(CPh=CHPh) (20)**

To a toluene solution (30 mL) of LAl(η²-C₂Ph₂) (1.24 g, 2 mmol) was added a toluene solution (10 mL) of a little excess of HC≡CPh (0.33 mL, 3 mmol). The mixture was stirred for 12 h at room temperature and dried in vacuum, and then extracted with n-hexane (10 mL). The extract was kept at 4°C for a week to afford colorless crystals of 20·0.5 n-hexane.

Yield: 1.12 g, 73%. M.p. 187–190 ºC.

1H NMR (300.13 MHz, 298 K, C₆D₆, ppm): δ = 0.86–0.90 (m, 7 H, n-hexane), 1.11 (d, 2 x 3 H, 3J_HH = 6.8 Hz, CH(CH₃)₂), 1.24 (d, 2 x 3 H, 3J_HH = 6.8 Hz, CH(CH₃)₂), 1.35 (d, 2 x 3 H, 3J_HH = 6.8 Hz, CH(CH₃)₂), 1.61 (s, 2 x 3 H, β-CH₃), 3.44 (sept, 2 x 1 H, 3J_HH = 6.8 Hz, C₆H(CH₃)₂), 4.01 (sept, 2 x 1 H, 3J_HH = 6.8 Hz, C₆H(CH₃)₂), 5.08 (s, 1 H, γ-CH), 6.72 (broad, 1 H, C=CH), 6.40–6.52, 6.80–7.00 (m, 10 H, C(Ph)=CH(Ph)), 7.08–7.24, 7.42–7.54 (m, 6 H, Ar–H).

13C NMR (125.76 MHz, 298 K, C₆D₆, ppm): δ = 14.3 (n-hexane), 23.0, 24.5, 24.8, 24.9, 26.1, 28.7, 29.2, 31.9 (CH(CH₃)₂), 99.5 (γ-C), 106.6 (broad, =CPh), 124.1, 124.2, 125.4, 126.4, 127.1, 127.4, 128.0, 129.6, 131.4, 132.0, 139.1, 141.3, 143.2, 145.9, 146.7 (Ph–C, Ar–C, =C), 144.4, 153.8 (broad, Al–C≡, Al–C≡), 171.1 (CN).

IR (KBr plate, Nujol mull, cm⁻¹): ν 2124 (C≡C).

MS (EI): m/z (%) 545 (100, [M⁺ – C(Ph)=CH(Ph)]), 724 (2, [M⁺ – 1]).

C₅₄H₆₄N₂Al (20·0.5n-hexane, 768.102): calcd. C 84.44, H 8.40, N 3.65; Found: C 84.81, H 8.42, N 3.61.

**LAl[η-C(H)=C(H)-η-]_2[(NN=NAr') (21)**

To a mixture of 18 (0.25 g, 0.5 mmol) and N₃Ar* (0.18 g, 0.5 mmol) at –50 ºC toluene (25 mL) was added. The suspension was stirred and allowed to warm to room temperature. After stirring for 12 h, the removal of solvent and washing with n-hexane (2 mL) afforded 21 as orange crystalline solid. The X-ray quality single crystals of 21·0.5n-hexane were grown from the n-hexane/toluene solution of 21 at 4 ºC within 5 d.

Yield: 0.37 g, 90%. M.p. 215–216 ºC.

1H NMR (300.13 MHz, 298 K, C₆D₈, ppm): δ = 1.02 (d, 3J_HH = 6.8 Hz, 2 x 3 H, CH(CH₃)₂), 1.05 (d, 3J_HH = 6.8 Hz, 2 x 3 H, CH(CH₃)₂), 1.16 (d, 3J_HH = 6.8 Hz, 4 x 3 H, CH(CH₃)₂), 1.50 (s, 2 x 3 H, β-CH₃), 2.23 (s, 2 x 3 H), 2.27 (s, 4 x 3 H) (Me(in Ar*)), 2.83 (sept, 3J_HH = 6.8 Hz, 2 x 1 H, CH(CH₃)₂), 3.03 (sept, 3J_HH = 6.8 Hz, 2 x 1 H, CH(CH₃)₂), 4.92 (s, 1 H, γ-CH), 5.03
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\[
\text{(d, } \delta \text{J}_{HH}\text{(cis)} = 7.6 \text{ Hz, 1 H), 7.51 (d, } \delta \text{J}_{HH}\text{(cis)} = 7.6 \text{ Hz, 1 H) } (HC=CH), 6.83, 6.97-7.12 \text{ (m), 7.15 (14 H, Ar}-H, \text{ Ar}^*-H, \text{ Ar}^*H).}
\]

\[
\text{13C NMR (75.47 HMz, 298 K, C}_{6}\text{D}_{6}, \text{ ppm): } \delta = 21.3, 22.3, 23.0, 23.2, 24.4, 24.7, 25.0, 25.8, 26.7, 29.1, 31.9 (\text{CH(CH}_{3})_{2}, \beta-CH_{3}, Me(\text{Ar})), 100.5 (\gamma-C), 114.8 \text{ (broad, Al–C=)}, 123.5, 123.8, 125.1, 130.9, 134.2, 136.0, 138.5, 141.6, 146.2, 147.3 (\text{Ar–C, Ar}^*-C, \text{ Ar}^*-C), 162.4 \text{(N–C(H)=), 171.9 (CN).}
\]

\[
\text{MS (EI): m/z (\%)} 417 \text{ (100, [M}^+\text{– N}_{3}\text{Ar}^*-\text{C}_{2}\text{H}_{2}–\text{Al]), 825 (5, [M}^+\text{– 1]).}
\]

\[
\text{C}_{55}\text{H}_{68}\text{AlN}_{5} \text{(826.17): calcd. C 79.96, H 8.30, N 8.48; Found: C 79.28, H 8.38, N 8.42.}
\]

\[
\text{LAl}[\text{OC(O)C}_{2}\text{(Ph)}_{2}] (22)
\]

A toluene solution (30 mL) of LAl[\text{OC(O)C}_{2}\text{(Ph)}_{2}] (0.62 g, 1 mmol) was exposed to predried CO \text{ and stirred for 12 h. After workup, all volatiles were removed in vacuum and the residue was washed with n-hexane (10 mL) to give a colorless solid of 22.}

Yield: 0.47 g, 70%. M.p. 341–343 ºC (decomp.).

\[
\text{1H NMR (300.13 MHz, 298 K, C}_{6}\text{D}_{6}, \text{ ppm): } \delta = 0.82 \text{ (d, } \delta \text{J}_{HH} = 6.7 \text{ Hz, 2 x 3 H, CH(C}_{6}\text{H}_{3})_{2}), 0.93 \text{ (d, } \delta \text{J}_{HH} = 6.7 \text{ Hz, 2 x 3 H, CH(C}_{6}\text{H}_{3})_{2}), 1.10 \text{ (d, } \delta \text{J}_{HH} = 6.7 \text{ Hz, 2 x 3 H, CH(C}_{6}\text{H}_{3})_{2}), 1.52 \text{ (d, } \delta \text{J}_{HH} = 6.7 \text{ Hz, 2 x 3 H, CH(C}_{6}\text{H}_{3})_{2}), 1.53 \text{ (s, 2 x 3 H, } -\text{C}_{6}\text{H}_{3}), 2.90 \text{ (sept, } \delta \text{J}_{HH} = 6.7 \text{ Hz, 2 x 1 H, CH(CH}_{3})_{2}), 3.60 \text{ (sept, } \delta \text{J}_{HH} = 6.7 \text{ Hz, 2 x 1 H, CH(CH}_{3})_{2}), 5.00 \text{ (s, 1 H, } \gamma\text{-CH}), 6.26–6.28 \text{ (m), 6.78–7.20 (m) (16 H, Ar–H and Ph–H).}
\]

\[
\text{13C } \{\text{1H} \} \text{ NMR (125.77 HMz, 298 K, C}_{6}\text{D}_{6}, \text{ ppm): } \delta = 20.7, 23.3, 23.6, 28.6 (\text{CH(CH}_{3})_{2}, \beta-CH_{3}), 94.2 (\gamma-C), 123.6, 125.8, 127.7, 128.2, 129.3, 141.2, 142.8, 143.0, 145.8 (\text{Ar–C, Ph–C, Al(Ph)=C(Ph)}, 143.4 (\text{Al–C}), 161.5 (C=O), 172.8 (CN).}
\]

\[
\text{MS (EI): m/z (\%)} 666.3 ([M}^+\text{], 15), 651.3 ([M}^+\text{– Me}], 100).}
\]

\[
\text{C}_{44}\text{H}_{51}\text{AlN}_{2} \text{O}_{2} (666.89): \text{calcd. C 79.25, H 7.31, N 4.20; Found: C 79.28, H 7.38, N 4.26.}
\]

\[
\text{LAl[OC(O)C}_{2}\text{(SiMe}_{3})_{2}] (23)
\]

Compound 23 was prepared in a similar manner as that of 22. The spectral data are recorded in reference 155. The X-ray quality crystals of 23 were obtained by crystallizing the crude product from a mixture of solvents (toluene : ether : n-hexane = 0.2 : 1 : 1).

\[
\text{LAl(} \mu\text{-S)}(\eta\text{-SC(SiMe}_{3})=\text{C=C(SiMe}_{3})-\eta\text{-)}\text{Al} (24)
\]

Neat carbon disulfide (0.038 g, 0.5 mmol) was added to a solution of LAl[\eta^2\text{-C}_{2}\text{(SiMe}_{3})_{2}] (0.62 g, 1 mmol) in toluene (20 mL) at –78 ºC. In the course of warming to room temperature, the color of the reaction mixture changed from red-black to green, to yellow green, and finally
to yellow. After additional stirring for 12 h, all volatiles were removed under vacuum and the residue was washed with n-hexane (20 mL) to give a yellow solid. The yellow solid was dissolved in a hot mixture of solvents (2 toluene : 1 ether) (15 mL) and then kept at r.t. for 72 h to afford X-ray suitable single crystals of $\text{24}$-0.55toluene-0.45ether.

Yield: 0.35 g, 57%. M.p. 281–283 °C.

$^1\text{H}$ $^{13}\text{C}$ NMR ([D$_8$]toluene, 500.13 MHz, 300 K, ppm): $\delta$ = 0.39, 0.47 (s, 2 × 9 H, SiMe$_3$), 0.88, 0.70, 0.83, 0.68, 1.19, 0.58, 1.39, 1.15, 1.31, 1.08 (d, $^3J_{\text{HH}}$ = 6.7 Hz, 10 × 3 H, CHMe$_2$), 1.15 (t, $^3J_{\text{HH}}$ = 6.9 Hz, 2.70 H, (CH$_3$CH$_2$)$_2$O), 1.25, 0.54, 1.33, 1.05 (d, $^3J_{\text{HH}}$ = 6.8 Hz, 4 × 3 H, CHMe$_2$), 1.14, 1.68 (d, $^3J_{\text{HH}}$ = 6.5 Hz, 2 × 3 H, CHMe$_2$), 1.48, 1.41, 1.40, 1.37 (s, 4 × 3 H, $\beta$-CH$_3$), 2.10 (s, 1.65 H, MePh), 3.17, 3.17, 3.10, 2.96, 2.93 (sept, $^3J_{\text{HH}}$ = 6.7 Hz, 5 × 1 H, CHMe$_2$), 3.13 (sept, $^3J_{\text{HH}}$ = 6.5 Hz, 1 H, CHMe$_2$), 3.26 (quartet, $^3J_{\text{HH}}$ = 6.9 Hz, 1.80 H, (CH$_3$CH$_2$)$_2$O), 3.29, 2.98 (sept, $^3J_{\text{HH}}$ = 6.8 Hz, 2 × 1 H, CHMe$_2$), 4.95, 4.96 (s, 2 × 1 H, $\gamma$-CH), 6.82–7.21 (m, 12 H, Ar–H).

$^{13}\text{C}$ NMR ([D$_3$]CDCl$_3$, 500.13 MHz, 300 K, ppm): $\delta$ = 212.70 (C=C=C), 171.16, 170.66, 170.32, 168.54 (CN), 145.30, 145.16, 144.69, 144.29, 144.09, 143.72, 142.91, 142.50, 142.49, 142.42 141.46, 141.03, 126.58, 126.44, 126.10, 125.98, 124.84, 124.50, 124.42, 124.34, 124.27, 124.00, 123.95, 123.02 (Ar–C), 137.88, 129.04, 128.23, 125.30 (MePh), 100.18, 99.74 ($\gamma$-C), 80.60 (broad, Al-C=C=CS), 65.84 ((CH$_3$CH$_2$)$_2$O), 59.94 (C=C=CS), 30.04, 29.19, 28.73, 28.26, 28.20, 27.98, 27.81, 27.74, 27.57, 27.17, 25.93, 25.86, 25.69, 25.52, 25.35, 25.19, 25.05, 24.95, 24.94, 24.82, 24.81, 24.71, 24.54, 24.51, 24.39, 24.36, 23.71, 23.22 (CHMe$_2$, CHMe$_2$ and $\beta$-CH$_3$), 21.45 (MePh), 15.27 ((CH$_3$CH$_2$)$_2$O), 2.19, 0.89 (SiMe$_3$).

$^{29}\text{Si}$ NMR (C$_6$D$_6$, 500.13 MHz, 300 K, ppm): $\delta$ = -5.51, -4.62 (SiMe$_3$).

IR (KBr plate, Nujol mull, cm$^{-1}$): $\nu$ = 1822 (C=C=C).

MS (EI): $m/z$ (%): 1135 (60, [M$^+$]); 460 (100, [M$^+$] – {HC(CMeNAr)$_2$}Al – SC(SiMe$_3$)=C=C(SiMe$_3$) – Me – H).

C$_{72.63}$H$_{108.90}$Al$_2$N$_4$O$_{0.45}$S$_4$Si$_{22}$ (24)-0.55toluene-0.45ether, 1219.82): calcd. C 71.53, H 9.00, N 4.59; Found: C 71.29, H 9.09, N 4.69.

$\text{LAl}[\text{N-C}_6\text{H}_3\text{H}_2\text{-}(2,6\text{-iPr}_2\text{C}_6\text{H}_3\text{-})\text{-}6\text{-}(2,6\text{-iPr}_2\text{C}_6\text{H}_3\text{-})]$ (25) and

$\text{[HC[(CMe(NAr)][(CMe)\text{N-C}_6\text{H}_3\text{H}_2\text{-}(2,6\text{-iPr-6-CH(CH}_2\text{)Me})\text{]}\text{Al(NHAr)}]}$ (26)

Pre-cooled toluene (25 mL) was added to a mixture of LAI (0.25 g, 0.56 mmol) and N$_3$Ar' (0.25 g, 0.56 mmol) at –78 °C. The mixture was allowed to warm to room temperature and
stirred for 12 h. The light yellow solution was concentrated (5 mL), and to it n-hexane (10 mL) was added. The solution was kept at 4 ºC for three weeks to afford colorless crystals of 26.

Yield: 0.12 g (24%). M.p. 381–383 ºC (> 320 ºC, decomp.).

$^1$H NMR (500.13 MHz, C$_6$D$_6$, 298 K, ppm): $\delta = -1.75$ (t, 1 H, $^2$J$_{HH} = -13.8$ Hz, $^3$J$_{HH} = 13.8$ Hz, Al–CH$_2$), $-0.28$ (dd, 1 H, $^2$J$_{HH} = 13.8$ Hz, $^3$J$_{HH} = 3.0$ Hz, Al–CH$_2$), 0.36, 0.39, 0.50, 0.80, 1.15, 1.22, 1.30 (d, 7 x 3 H, $^3$J$_{HH} = 6.8$ Hz, CH(CH$_3$)$_2$), 0.93, 0.94, 1.08, 1.11 (d, 4 x 3 H, $^3$J$_{HH} = 6.7$ Hz, CH(CH$_3$)$_2$), 1.25, 1.34 (d, 2 x 3 H, $^3$J$_{HH} = 6.6$ Hz, CH(CH$_3$)$_2$), 1.31, 1.53 (d, 2 x 3 H, $^3$J$_{HH} = 6.9$ Hz, CH(CH$_3$)$_2$), 1.45, 1.50 (s, 2 x 3 H, $^3$J$_{HH} = 6.9$ Hz, CH(CH$_3$)$_2$), 2.30 (sept, 1 H, $^3$J$_{HH} = 6.7$ Hz, CH(CH$_3$)$_2$), 2.41, 2.80, 3.47 (sept, 3 x 1 H, $^3$J$_{HH} = 6.8$ Hz, CH(CH$_3$)$_2$), 2.99, 3.39 (sept, 2 x 1 H, $^3$J$_{HH} = 6.7$ Hz, CH(CH$_3$)$_2$), 3.07 (sept, 1 H, $^3$J$_{HH} = 6.6$ Hz, CH(CH$_3$)$_2$), 2.56 (m, 1 H, CH(CH$_3$)(CH$_2$)), 3.41 (s, 1 H, NH), 4.82 (s, 1 H, $\gamma$-CH), 6.65 (m, 1 H, Ph–H), 6.92–7.00 (m, 3 x 1 H, Ph–H), 7.04–7.20 (m, 6 x 1 H, Ph–H), 7.20–7.32 (m, 4 x 1 H, Ph–H), 7.34–7.38 (m, 1 H, Ph–H).

$^{13}$C NMR (125.76 MHz, C$_6$D$_6$, 298 K, ppm): $\delta = 18.50$ (br, Al–C), 21.64, 21.68, 22.10, 22.84, 22.98, 23.61, 23.83, 23.93, 24.41, 25.31, 25.45, 25.55, 26.31, 26.92, 26.98, 27.06, 27.25, 27.66, 28.53, 28.57, 29.97, 30.03, 31.23, 31.69, 34.04 (CH$_3$, CH(CH$_3$)$_2$, CH(CH$_3$)(CH$_2$)), 98.99 ($\gamma$-CH), 114.62, 122.23, 122.98, 123.08, 123.64, 124.65, 124.67, 125.06, 125.65, 125.93, 126.55, 126.88, 127.81, 127.92, 128.42, 131.23, 133.84, 138.21, 140.30, 141.50, 142.48, 143.51, 143.82, 145.58, 146.53, 147.62, 148.48, 148.53, 150.68, 150.94 (Ph–C), 169.40, 169.52 (CN).

IR (KBr plate, Nujol mull, cm$^{-1}$): $\nu = 3298$ (NH).

MS (EI): m/z (%): 855 (10, [M$^+$ – 1]); 443 (100, [M$^+$ – NHAr$^+$]).

C$_{59}$H$_{78}$AlN$_3$ (855.42): calcd. C 82.76, H 9.18, N 4.91. Found: C 82.60, H 9.28, N 4.98.

After the collection of crystals of 26, the mother liquor was kept at 4 ºC for additional three weeks. A crop of yellowish crystals of 25 were obtained and collected by filtration. Compound 25 has a similar decomposition temperature and melting point as those of 26. Its EI mass spectroscopic data is also similar to that of 26.

Yield: 0.21 g (42%).

$^1$H NMR (500.13 MHz, C$_6$D$_6$, 298 K, ppm): $\delta = 0.26$, 0.53, 0.54, 1.46 (d, 4 x 3 H, $^3$J$_{HH} = 6.8$ Hz, CH(CH$_3$)$_2$), 0.81, 0.93, 1.01, 1.06, 1.11, 1.30 (d, 6 x 3 H, $^3$J$_{HH} = 6.7$ Hz, CH(CH$_3$)$_2$), 0.86, 0.88, 1.14, 1.27, 1.39, 1.42 (d, 6 x 3 H, $^3$J$_{HH} = 6.9$ Hz, CH(CH$_3$)$_2$), 1.30, 1.40 (s, 2 x 3 H, $\beta$-CH$_3$), 2.34, 3.33 (sept, 2 x 1 H, $^3$J$_{HH} = 6.8$ Hz, CH(CH$_3$)$_2$), 2.64, 3.02, 3.18 (sept, 3 x 1 H, $^3$J$_{HH} = 6.7$ Hz, CH(CH$_3$)$_2$), 3.12, 3.33, 3.33 (sept, 3 x 1 H, $^3$J$_{HH} = 6.9$ Hz, CH(CH$_3$)$_2$), 2.43 (d, 1 H,
The Reaction Chemistry of Aluminum(I, III) Compounds Stabilized by Sterically Bulky Ligands

$J_{HH} = 6.4$ Hz, Al–CH), 4.88 (s, 1 H, $\gamma$-CH), 5.41 (d, 1 H, $J_{HH} = 9.4$ Hz, AlCH–CH), 6.08 (dd, 1 H, $J_{HH} = 6.4$ Hz, $J_{HH} = 9.4$ Hz, AlCH–CH), 6.86 (m, 2 x 1 H, Ph–H), 6.92 (m, 1 H, Ph–H), 6.99 (m, 1 H, Ph–H), 7.04–7.12 (m, 4 x 1 H, Ph–H), 7.28 (m, 2 x 1 H, Ph–H), 7.37 (m, 1 H, Ph–H), 7.49 (m, 1 H, Ph–H).

$^{13}$C NMR (125.76 MHz, C$_6$D$_6$, 298 K, ppm): $\delta = 14.28, 15.64, 18.58, 20.40, 22.99, 23.46, 23.75, 24.36, 24.47, 24.72, 24.72, 24.84, 24.84, 24.89, 24.96, 25.00, 25.49, 25.63, 26.31, 26.60, 27.40, 28.22, 29.00, 29.10, 29.84, 32.50, 32.93 (C–CH$_3$, CH(CH$_3$)$_2$, CH(CH$_3$)$_2$, NC(iPr), 73.99 (Al–C), 100.93 (γ-CH), 113.08, 118.25, 121.76, 123.88, 124.19, 124.21, 124.52, 124.56, 125.22, 127.05, 127.70, 128.00, 128.10, 128.20, 130.33, 132.06, 134.52, 136.42, 137.18, 141.52, 141.95, 143.21, 143.58, 145.54, 146.09, 146.79, 149.47, 153.54 (Ph–C, CH=CH–C(iPr)=C), 170.21 (CN).

Correct elemental analysis. Attempts to recrystallize the yellow crystalline material of 25 by dissolving it in a hot toluene/n-hexane mixture resulted in the formation of colorless solution which was kept at 4 °C for crystallization. Colorless rectangular crystals were obtained and were found by spectroscopic and X-ray crystallographic evidence to be 26.
4.5. Handling and Disposal of Solvents and Residual Waste

1. The recovered solvents were distilled or condensed into cold-traps under vacuum, collected in halogen-free or halogen-containing solvent containers, and stored for disposal.

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

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

4. Drying agents such as KOH, CaCl$_2$, MgCl$_2$, MgSO$_4$, and P$_4$O$_{10}$ were hydrolyzed and disposed as acid or base wastes.

5. Wherever possible, sodium metal used for drying solvents was collected for recycling. The non-reusable sodium metal was carefully treated with cold ethanol and potassium in cold isopropanol and collected into the base-bath cleaning glassware.

6. Ethanol and acetone used for cooling baths were subsequently used for cleaning glassware.

7. The acid bath for cleaning glassware was neutralized with Na$_2$CO$_3$ and the resulting NaCl solution was washed off in the water drainage system.

8. The residual of the base both for cleaning glassware was poured into the container for base wastes.

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

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<tr>
<th>Type of Wastes</th>
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<td>Halogen-containing wastes</td>
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<tr>
<td>Halogen-free solvent wastes</td>
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<td>Acid wastes</td>
<td>12 L</td>
</tr>
<tr>
<td>Base wastes</td>
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### 4.6. Crystal Data and Refinement Details

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<td>200(2)</td>
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<td>monoclinic</td>
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<td>$P2(1)/n$</td>
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### Compounds

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<td>Compounds</td>
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<tr>
<td>Formula</td>
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<td>C\textsubscript{55}H\textsubscript{61}AlN\textsubscript{4}</td>
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<td>orthorombic</td>
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<td>\textit{P}2(1)2(1)2(1)</td>
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<td>b (Å)</td>
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<td>c (Å)</td>
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<tr>
<td>γ (deg)</td>
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<tr>
<td>V (Å\textsuperscript{3})</td>
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<td>4784.4(16)</td>
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<td>(R\textsubscript{1}\text{a}, wR\textsubscript{2}\text{b} (I &gt; 2\sigma (I)) )</td>
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<td>0.271/-0.282</td>
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The Reaction Chemistry of Aluminum(I, III) Compounds Stabilized by Sterically Bulky Ligands

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<thead>
<tr>
<th>Compounds</th>
<th>17</th>
<th>18</th>
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<tr>
<td>Formula</td>
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<td>C_{31}H_{43}AlN_{2}</td>
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<td>P2(1)/n</td>
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<td>a (Å)</td>
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<td>b (Å)</td>
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<td>γ (deg)</td>
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<tr>
<td>V (Å³)</td>
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<td>2802(1)</td>
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<td>ρc (Mg/m³)</td>
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<tr>
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<td>largest diff peak/hole (e·Å⁻³)</td>
<td>0.210/-0.235</td>
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### Compounds

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<td>$\text{C}<em>{54}\text{H}</em>{64}\text{AlN}_2$</td>
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<td>133(2)</td>
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<td>monoclinic</td>
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<td>$P2(1)/n$</td>
<td>$P2(1)/n$</td>
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<td><strong>a (Å)</strong></td>
<td>18.844(4)</td>
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<td><strong>b (Å)</strong></td>
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<td><strong>$\gamma$ (deg)</strong></td>
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<td>largest diff peak/hole (e·Å⁻³)</td>
<td>0.478 / −0.470</td>
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## The Reaction Chemistry of Aluminum(I, III) Compounds Stabilized by Sterically Bulky Ligands

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<thead>
<tr>
<th>Compounds</th>
<th>25</th>
<th>26</th>
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<td>Formula</td>
<td>$\text{C}<em>{59}\text{H}</em>{78}\text{AlN}_3$</td>
<td>$\text{C}<em>{59}\text{H}</em>{78}\text{AlN}_3$</td>
</tr>
<tr>
<td>Fw</td>
<td>856.22</td>
<td>856.22</td>
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<tr>
<td>temp (K)</td>
<td>133(2)</td>
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<tr>
<td>crystal syst</td>
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<tr>
<td>space group</td>
<td>$P2(1)/n$</td>
<td>$P\overline{1}$</td>
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<tr>
<td>$a$ (Å)</td>
<td>12.350(1)</td>
<td>11.806(8)</td>
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<tr>
<td>$b$ (Å)</td>
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<td>$c$ (Å)</td>
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<td>19.718(8)</td>
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<tr>
<td>$\alpha$ (deg)</td>
<td>76.04(3)</td>
<td>76.04(3)</td>
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<tr>
<td>$\beta$ (deg)</td>
<td>104.05(1)</td>
<td>74.54(4)</td>
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<tr>
<td>$\gamma$ (deg)</td>
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<td>64.63(4)</td>
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<td>$V$ (Å$^3$)</td>
<td>5038(1)</td>
<td>2560(2)</td>
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<td>$Z$</td>
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<td>2</td>
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<tr>
<td>$\rho_c$ (Mg/m$^3$)</td>
<td>1.129</td>
<td>1.111</td>
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<td>$\mu$ (mm$^{-1}$)</td>
<td>0.081</td>
<td>0.079</td>
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<td>$F(000)$</td>
<td>1864</td>
<td>932</td>
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<tr>
<td>$\theta$ range (deg)</td>
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<td>1.08–24.81</td>
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<td>Index ranges</td>
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<td>$-13 \leq h \leq 13$</td>
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<td></td>
<td>$-30 \leq k \leq 31$</td>
<td>$-15 \leq k \leq 15$</td>
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<td></td>
<td>$-18 \leq l \leq 15$</td>
<td>$-22 \leq l \leq 23$</td>
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<tr>
<td>no. of reflns collected</td>
<td>24428</td>
<td>39096</td>
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<tr>
<td>no. of indep reflns ($R_{int}$)</td>
<td>8626 (0.0929)</td>
<td>8758 (0.0409)</td>
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<td>no. of data/restraints/params</td>
<td>8626 / 0 / 586</td>
<td>8758 / 0 / 270</td>
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<td>$GoF/F^2$</td>
<td>1.011</td>
<td>1.039</td>
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<td>$R1^a$, $wR2^b$ ($I &gt; 2\sigma(I)$)</td>
<td>0.0633, 0.1360</td>
<td>0.0595, 0.1415</td>
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<tr>
<td>$R1^a$, $wR2^b$ (all data)</td>
<td>0.1059, 0.1551</td>
<td>0.0751, 0.1496</td>
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<tr>
<td>largest diff peak/hole (e·Å$^3$)</td>
<td>0.433 / −0.251</td>
<td>0.644 / −0.527</td>
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</tbody>
</table>
5. References


The Reaction Chemistry of Aluminum(I, III) Compounds Stabilized by Sterically Bulky Ligands

Some spectroscopic data are listed for [LAl(SeH)$_2$] (reference 21): $^1$H NMR (500 MHz, C$_6$D$_6$), $\delta_{\text{SeH}} = -2.82$; IR (KBr, Nujol), $\nu_{\text{SeH}} = 2318 \text{ cm}^{-1}$ and [L(HSe)AlSeAl(SeH)L]: $^1$H NMR (500 MHz, C$_6$D$_6$), $\delta_{\text{SeH}} = -2.83$, $^{77}$Se NMR (500 MHz, C$_6$D$_6$), $\delta_{\text{Al-SeH}} = -341$ and $\delta_{\text{Al-Se-Al}} = -535$; IR (KBr, Nujol), $\nu_{\text{SeH}} = 2276, 2292 \text{ cm}^{-1}$.


The structural data for LAlI$_2$ are resulted in the PhD Thesis of C. Cui, Göttingen, 2001, 41.
The Reaction Chemistry of Aluminum(I, III) Compounds Stabilized by Sterically Bulky Ligands


[204] The bond lengths of gas phase CO$_2$ and CS$_2$ are 1.1600 and 1.5526 Å, respectively. See *Handbook of Chemistry and Physics* (Ed.: D. R. Lide,) 2003-2004, 84, 9-19.


### 6. Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>Ar</td>
<td>aryl, aromatic group</td>
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<tr>
<td>av</td>
<td>average</td>
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<tr>
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<td>boiling point</td>
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<td>tBu</td>
<td>tertiary butyl</td>
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<tr>
<td>d</td>
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<td>$d$</td>
<td>density</td>
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<td>decompose</td>
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<td>degree</td>
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<td>hapto</td>
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<td>EI</td>
<td>electron impact ionization</td>
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<td>IR</td>
<td>infrared</td>
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<td>coupling constant</td>
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<td>Kelvin</td>
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<tr>
<td>L</td>
<td>$\beta$-diketiminato groups (ligands)</td>
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<td>NMR</td>
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<td>$m/e$</td>
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<td>Me</td>
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<tr>
<td>min</td>
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<tr>
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<td>mass spectrum</td>
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<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
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<td>iPr</td>
<td>isopropyl</td>
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<td>R</td>
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<td>THF</td>
<td>tetrahydrofuran</td>
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<tr>
<td>$\mu$</td>
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<td>$V$</td>
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<td>$\nu$</td>
<td>wave number</td>
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<tr>
<td>$Z$</td>
<td>number of molecules in the unit cell</td>
</tr>
</tbody>
</table>
CURRICULUM VITAE

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Name: Hongping Zhu
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Family: Qiaozhu Jiang (Wife)
        Yicheng Zhu (Son)
Nationality: P. R. China

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