

The Renaissance of Aluminum Chemistry†

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The preparation and reactions of stable monomeric and tetrameric organoaluminum(I) compounds are described. Especially, their conversion to the more stable oxidation state (III) is discussed. The synthesis of unusual and unique molecules such as $\text{Al}(\text{OH})_2$, $\text{Al}(\text{SH})_2$, $\text{Al}(\text{SeH})_2$, and $\text{Al}(\text{NH}_2)_2$ is reported. A new synthetic approach to organometallic hydroxides and amides was discovered, when N-heterocyclic carbenes are used as hydrogen chloride acceptors. The synthesis of LGeOH demonstrates that this method can also be applied for other elements in the periodic system. The successful preparation of carbaalanes and aluminum nitride clusters resulted in the generation of several model compounds for the fixation of organometal substituents on carbide and nitride surfaces. It is shown that $\text{AlH}_3 \cdot \text{NMe}_3$ is a powerful hydroalumination reagent for acetylenes, nitriles, and isonitriles.

*I don't know who discovered water but it probably
wasn't a fish.*

Marshall McLuhan

Introduction

The name aluminum was originally proposed by Humphry Davy and stems from the Latin word *alumen*, which refers to the alums, minerals containing aluminum. In 1855, this metal was shown next to the crown jewels at the Paris World Exhibition while Napoleon III used aluminum cutlery at state dinners. Jules Verne praised the properties of aluminum (from *Traveling to the Moon*, 1865):

*It is easy to work, wide-spread, for almost every
stone contains it, it is three times lighter than iron
and it seems that it has been specially created for
making projectiles.*

Today, materials science would be unthinkable without the use of aluminum, and for 100 years its price in the world market has remained below a dollar per kilogram. Aluminum is the most abundant metal in the earth's crust and the major constituent of many common minerals including feldspars and micas. A breakthrough in organoaluminum chemistry stems from the discovery of the alkene insertion reaction by Ziegler and the low-pressure polymerization of ethene and propene in the presence of organometallic mixed group 4 and 13 catalysts by Ziegler and Natta.

We followed the suggestions of Ralph Waldo in organoaluminum chemistry, who wrote:

*Research is the art of seeing what others see, but
thinking what others don't think.*

Preparation of Stable Tetrameric Aluminum(I) Compounds

The pentamethylcyclopentadienyl ligand is an important substituent due to its steric bulk and variable bonding modes in main group chemistry. Monoorganylaluminumhalides incorporating the Cp^* ($\text{Cp}^* = \text{C}_5\text{Me}_5$) ligand are interesting precursors for aluminum(I) compounds. The halides of composition $[\text{Cp}^*\text{AlX}(\mu\text{-X})_2]$ ($\text{X} = \text{Cl}$, **1**; Br , **2**; I , **3**) are prepared from AlX_3 and Cp^*SiMe_3 .^{1–3}

The reduction of $[\text{Cp}^*\text{AlX}(\mu\text{-X})_2]$ with a Na/K alloy results in the formation of $(\text{Cp}^*\text{Al})_4$ (**4**) in a 35%, 48%, and 53% yield, respectively. The decreasing aluminum–halide bond energy and the lower reaction temperature in the series AlCl (331 kJ/mol) > AlBr (256 kJ/mol) > AlI (172 kJ/mol) results in higher yields of the product **4** using the iodides in the reduction process. An alternative method for the preparation of $(\text{Cp}^*\text{Al})_4$ (**4**) is the reaction at low temperatures of Cp^*_2Mg and AlCl .⁴

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Herbert W. Roesky was born in 1935 in Laukischken. He obtained his Diplom and Dr.rer.nat. from the University of Göttingen. He spent one year of postdoctoral work at DuPont in Wilmington, DE. In 1971, he became full professor in Frankfurt, and in 1980, he joined the faculty of chemistry in Göttingen. Since 2004, he has been working as an emeritus professor in Göttingen and as an adjunct professor in DeKalb, IL. Presently, he is the president of the Göttinger Akademie der Wissenschaften. He has obtained several awards such as the ACS Award for Creative Work in Fluorine Chemistry and the ACS Award in Inorganic Chemistry. More than 900 research publications, patents, and books document his activity in the fields of inorganic chemistry, catalysis, and material science. Moreover, he is well-known for his contributions to public understanding of chemistry.

A key factor in the synthesis of aluminum(I) compounds of the general formula $(\text{RAl})_4$ is the R group. In the structurally characterized compounds $(\text{RAl})_4$, the ligands are Cp^* ,⁴ tris(trimethylsilyl)methyl,⁵ tris(trimethylsilyl)silyl,⁶ and tritert-butylsilyl.⁷ Moreover, the unsymmetrically substituted $[(\text{Cp}^*\text{Al})_3\text{AlN}(\text{SiMe}_3)_2]$ ⁸ and the exclusively N-based $[2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)\text{Al}]_4$ (**5**) have been prepared.⁹ The latter compound was obtained by reacting $[2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)\text{-AlI}_2]_2$ with Na/K alloy in hexane (Scheme 1).

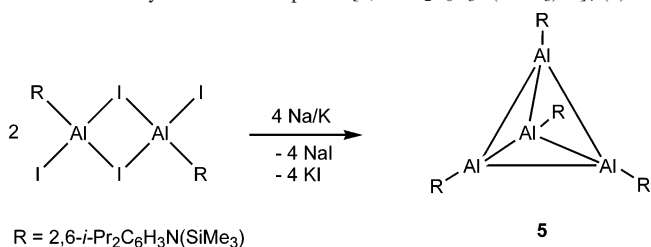
The examples $(\text{RAl})_4$ demonstrate that, independently of the R groups, the formation of the Al_4 cluster is favored. A monomeric species of composition RAl was not isolated.

Fantasy is more important than knowledge.

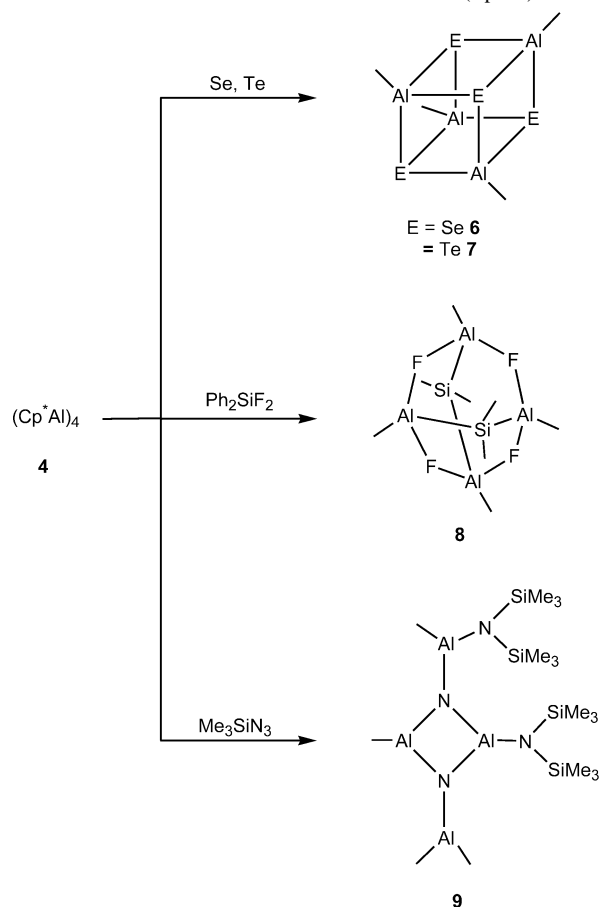
Albert Einstein

This is reflected by the reactions of $(\text{Cp}^*\text{Al})_4$ with selenium, tellurium, Ph_2SiF_2 , and Me_3SiN_3 , respectively, shown in Scheme 2. When a solution of **4** in toluene is treated with an excess of selenium and tellurium, respectively, yellow-green solutions are obtained. From these solutions, colorless crystals of $[\text{Cp}^*\text{AlSe}]_4$ (**6**) and pale green shiny

Scheme 1. Synthesis of Compound $[2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)\text{Al}]_4$ (**5**)



Scheme 2. Selected Products from the Reaction of $(\text{Cp}^*\text{Al})_4$ ^a



octahedral crystals of $[\text{Cp}^*\text{AlTe}]_4$ (**7**) can be obtained. Both compounds are tetrameric; the parent skeleton comprises an $(\text{Al-E})_4$ heterocubane (E = Se, Te).

The bond angles at Al, Se, and Te, respectively, deviate little from the ideal 90° (av Se-Al-Se 94.6° , Te-Al-Te 95.0° , Al-Se-Al 85.2° , Al-Te-Al 84.7°). The facile formation of compounds **6** and **7** under mild conditions illustrates the desire of aluminum to attain the more stable oxidation state (III).³ The reaction of **4** with Ph_2SiF_2 yielded the cage compound **8** with novel structural features. The expected formation of Cp^*AlF_2 was not observed; only two Al-Si-Al units were found. All fluorine atoms in **8** are in a bridging position. An unusual product **9** resulted from the reaction of **4** with Me_3SiN_3 .¹⁰ The central core of **9** is a four-membered, almost ideally planar Al_2N_2 ring. Moreover, the aluminum and nitrogen atoms are three-coordinate. Compound **9** may originate from an Al_4N_4 cube in which the top layer is broken open and the remaining ring represents the base. A silyl group migration and a rearrangement of a Cp^*

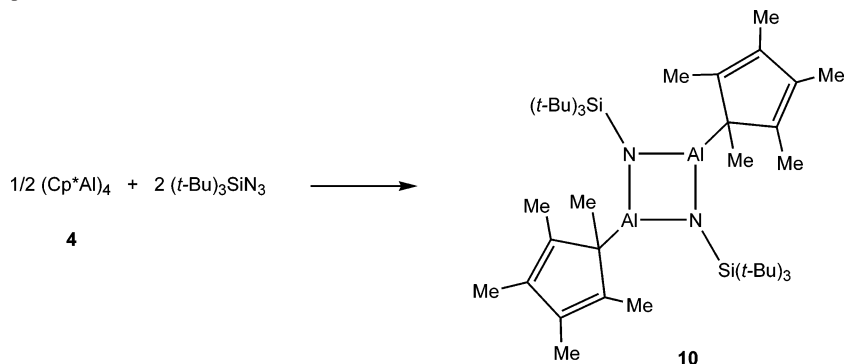
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Scheme 3. Reaction of $(\text{Cp}^*\text{Al})_4$ with $(t\text{-Bu})_3\text{SiN}_3$ 

group take place simultaneously.¹⁰ A comparable four-membered Al_2N_2 ring was obtained (**10**) when $(t\text{-Bu})_3\text{SiN}_3$ was reacted with $(\text{Cp}^*\text{Al})_4$ ¹¹ (Scheme 3).

The formation of a monomeric species with an $\text{Al}=\text{N}$ double bond was not observed.

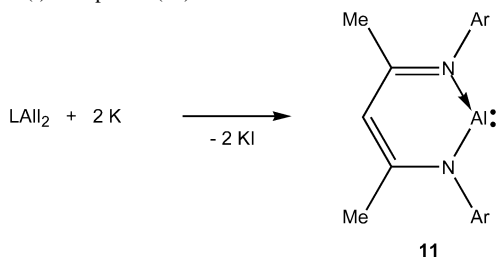
The Struggle for a Stable Monomeric Aluminum(I) Compound

There is no highway for science.

Karl Marx

From our previous experiments, we learned that, on one hand, aluminum(I) compounds can be prepared preferentially when iodides are employed as precursors for the reduction. On the other hand, the steric bulk of the ligands (R) Cp^* , $(\text{Me}_3\text{Si})_3\text{C}$, $(\text{Me}_3\text{Si})_3\text{Si}$, $(t\text{-Bu})_3\text{Si}$, and $2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{-N}(\text{SiMe}_3)$, respectively, is not sufficient enough to stabilize a monomeric RAl species. Subsequently, we became interested in the synthesis of aluminum diiodides with chelating monovalent ligands.

The first example of a room temperature stable aluminum(I) compound of composition $[\text{HC}(\text{CMeNAr})_2]\text{Al}$ (**11**) ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$) was synthesized by reacting the aluminum diiodide LAlI_2 ($\text{L} = \text{HC}(\text{CMeNAr})_2$) with potassium (Scheme 4).¹²

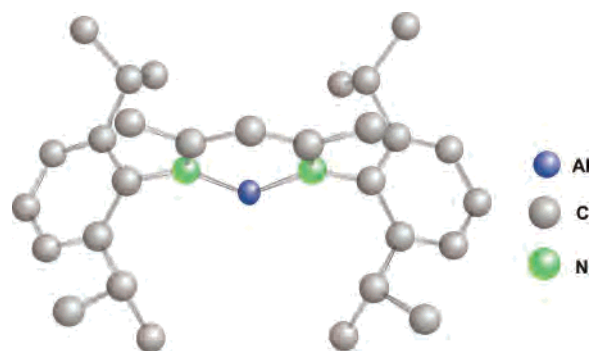
Scheme 4. Synthesis of a Room Temperature Stable Monomeric Aluminum(I) Compound (**11**)

Compound **11** is a red crystalline solid that is stable in organic solvents such as toluene, benzene, and hexane. It is stable both thermally and in an inert atmosphere. The decomposition point is above $150\text{ }^\circ\text{C}$.

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The single crystal X-ray structural analysis of **11** has been determined, and the molecular structure is shown in Figure 1.

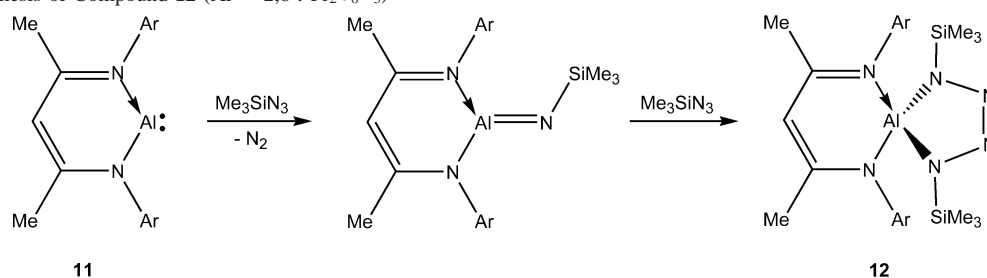
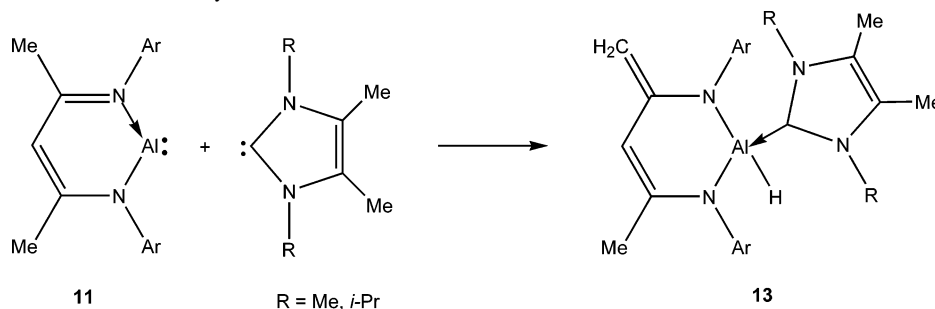
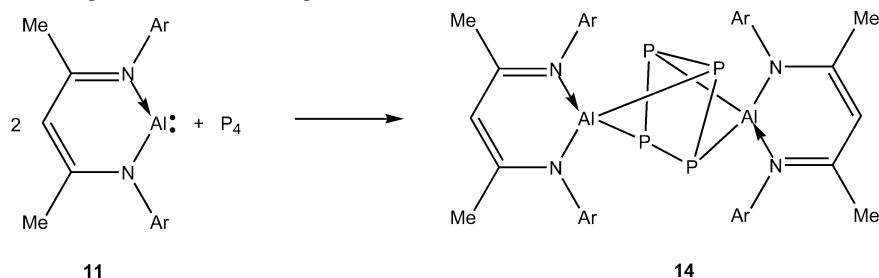
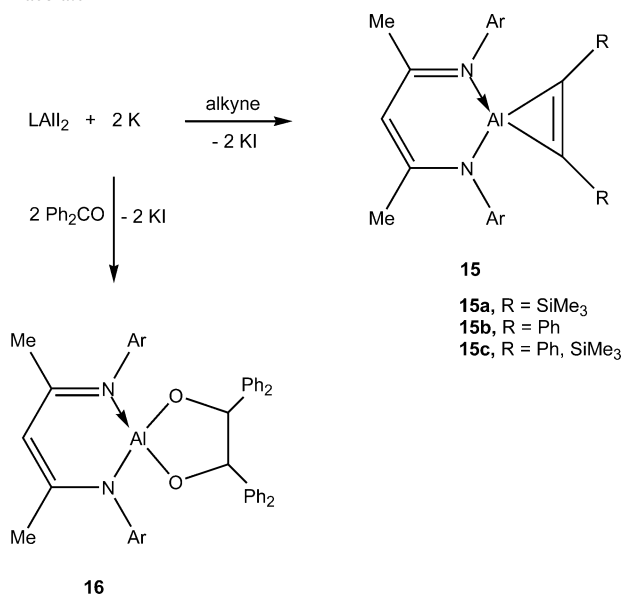
**Figure 1.** Molecular structure of $[\text{HC}(\text{CMeNAr})_2]\text{Al}$ (**11**). Hydrogen atoms have been omitted for clarity.

Compound **11** is monomeric, and no remarkable close contacts are found in the unit cell. This is the first dicoordinate aluminum(I) compound to be prepared and structurally characterized. The aluminum atom in **11** is part of a planar six-membered heterocycle with the skeletal atoms of the NCCCN ligand. The $\text{Al}-\text{N}$ bonds (1.957 \AA) are slightly longer than in comparable $\text{Al}(\text{III})$ compounds due to the larger ionic radius of $\text{Al}(\text{I})$ compared to $\text{Al}(\text{III})$.

On the basis of *ab initio* calculation, it was shown that the lone pair of $\text{Al}(\text{I})$ in **11** is stereochemically active and possibly has a quasi-trigonal-planar orientation. Charge depletion of the aluminum atom into the semiplane of the ring is also noticed. These features provide scope for observing both Lewis acid and Lewis base behavior of **11**.¹²

In the first step, compound **11** reacts with Me_3SiN_3 via the accepted intermediate $[\text{HC}(\text{CMeNAr})_2\text{Al}=\text{NSiMe}_3]$ in a $[2 + 3]$ cycloaddition to the tetrazole **12** (Scheme 5). No dimerization of the intermediate $[\text{HC}(\text{CMeNAr})_2\text{Al}=\text{NSiMe}_3]$ was observed, presumably due to the bulky chelating β -diketoinimate ligand preventing association. Interestingly, the AlN_4 five-membered ring in **12** is essentially planar. Ph_3SiN_3 reacts with **11** to yield the same five-membered AlN_4 ring like the one in compound **12**. However, the methyl groups at the silicon are replaced by phenyl groups.

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Scheme 5. Synthesis of Compound **12** (Ar = 2,6-*i*-Pr₂C₆H₃)**Scheme 6.** Reaction of **11** with an N-Heterocyclic Carbene**Scheme 7.** Preparation of a Phosphorus–Aluminum Compound with an Al₂P₄ Core**Scheme 8.** Cyclopropene Analogues of Aluminum and an Aluminum Pinacolate

Surprisingly, compound **11** reacts with an N-heterocyclic carbene to yield adduct **13** under migration of a hydrogen atom from one methyl group of the β -diketoiminate ligand to the aluminum (Scheme 6).¹⁴

The expected product with an Al=C double bond was not obtained. Likewise, the reaction of **11** with white

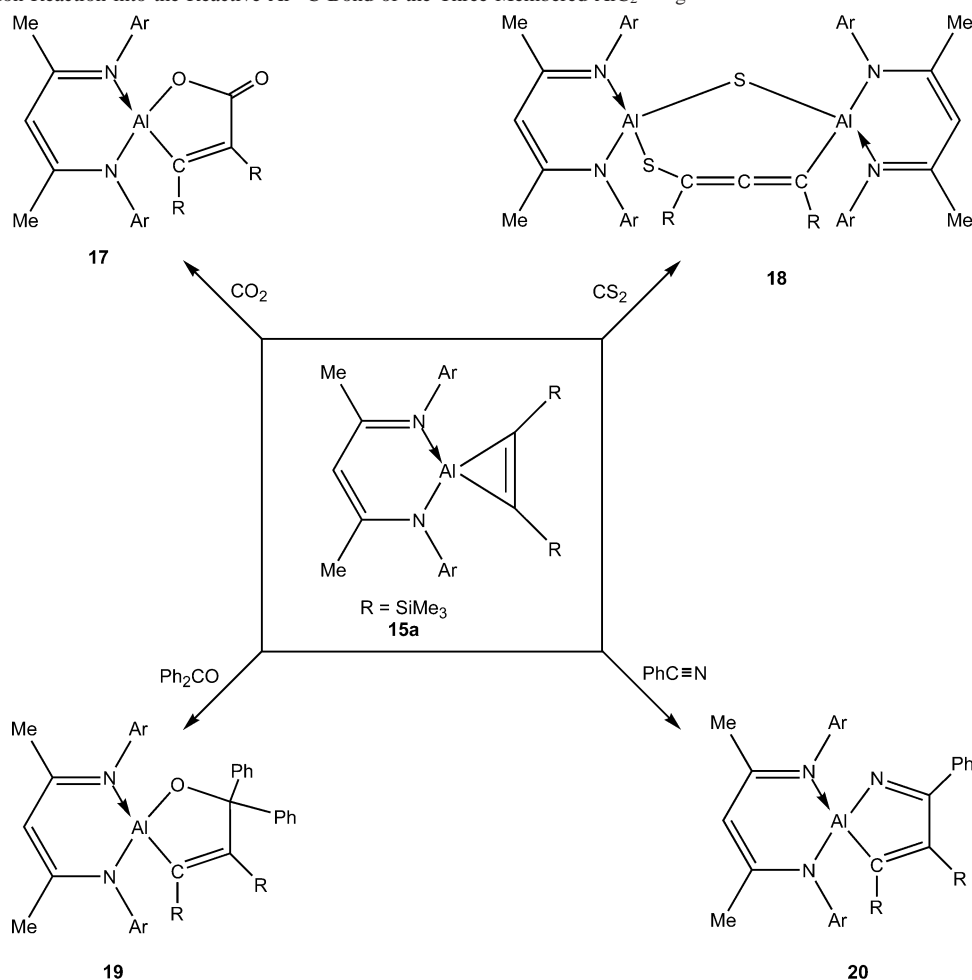
phosphorus resulted in the formation of compound **14** (Scheme 7).¹⁵

The single crystal structural analysis of **14** clearly indicates that two of the six P–P bonds of the P₄ tetrahedron are opened under formation of a four-membered highly puckered P₄ ring. In compound **14**, the two opened P–P edges of the tetrahedron have bond distances of 3.049(2) and 3.063(2) Å, thus showing the complete cleavage of two P–P bonds within the P₄ molecule. DFT calculations support a significant charge transfer from aluminum to the P₄ molecule, indicating an ionic Al–P bond rather than a dative bond as found in the corresponding transition metal complexes.¹⁵ The reason for the two different metal–P₄ bonds is expected to arise from the different ability to form a dative bond for transition and main group metals. The transition metal uses d electrons and can feed electron density back to the P atom to strengthen the dative bond, while for main group metals such feedback is not possible.

*The princes of Serendip are always making
discoveries by accident and sagacity of things
which they are not in quest of.*

Sir Horace Walpole (1754)

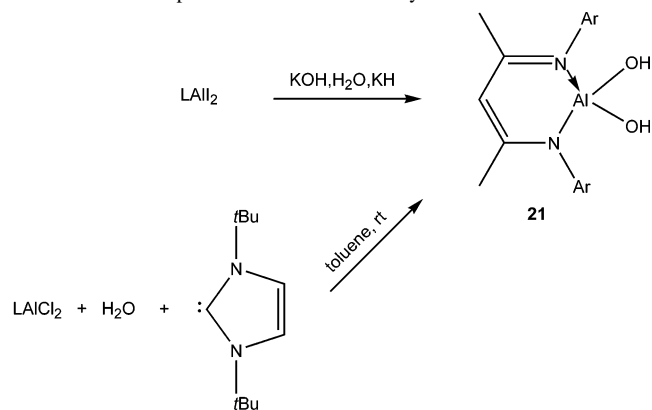
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Scheme 9. Insertion Reaction into the Reactive Al–C Bond of the Three-Membered AlC₂-Ring

By serendipity, we were able to prepare an AlC₂ three-membered ring (**15**) from the reaction of aluminum diiodide LAlI₂ (L = HC(CMeNAr)₂) and potassium in the presence of an alkyne. Previously, several attempts to react **11** with an alkyne in a [1 + 2] cycloaddition were not successful.

Therefore, we reasoned that the radicals [HC(CMeNAr)₂]-AlI[•] and K⁺(RCCR)^{•-} might be involved in the reductive coupling¹⁶ (Scheme 8). Compounds **15a** and **15b** have been characterized by single crystal X-ray structural analysis. In **15**, the two fused planes C–Al–C and N–Al–N are arranged nearly perpendicular to each other. The C–Al–C angle is very acute (42–43°).

The reduction of LAlI₂ with potassium in the presence of Ph₂CO resulted in the aluminum pinacolate **16** (Scheme 8). When a solution of benzophenone was added to a suspension of LAlI₂ and potassium, immediately a deep blue color was formed indicating the formation of the ketyl K⁺(OCPh₂)^{•-}. Therefore, it is assumed that this reaction mainly proceeds through the initial replacement of the iodide by the ketyl to form the radical LAl(OCPh₂)[•], which could easily couple

Scheme 10. Preparation of Aluminum Dihydroxide **21**

with another ketyl, followed by elimination of KI to yield **16**.¹⁶

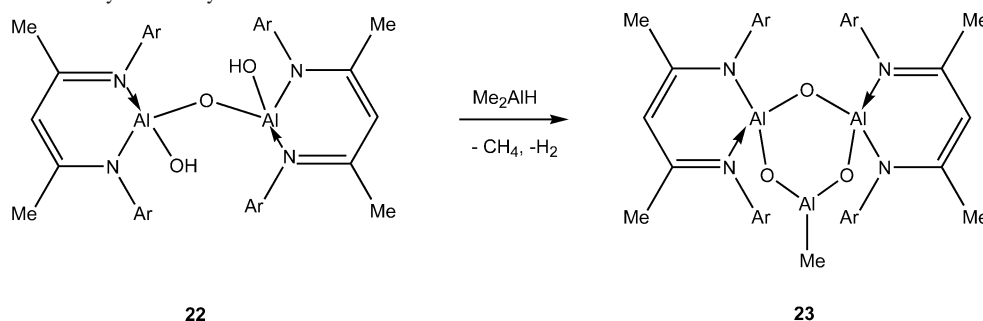
Insertion Reactions into the Reactive Al–C Bond of the Three-Membered AlC₂ Ring

Compounds **15a–c** are extremely sensitive to air and moisture. Compound **15a** is easily available and exhibits facile insertion reactions with CO₂ (**17**), CS₂ (**18**), ketones (**19**), and nitriles (**20**), respectively (Scheme 9).^{16,17}

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Scheme 11. Synthesis of Acyclic and Cyclic Alumoxanes

The reaction of **15a** with carbonyl-containing molecules including CO₂ resulted in the O=C insertion to give five-membered AlC₃O heterocyclic compounds.

Characteristic for the products (**17**, **19**, **20**) is the formation of a new carbon–carbon bond. The heteroatoms bind toward the aluminum so that all reactions are stereoselective. The reactions of thiocarbonyl substrates with organoaluminum reagents resemble closely those of their carbonyl counterparts. Thus, we anticipate that the reaction of **15a** with CS₂ involves in the initial step the formation of the five-membered sulfur analogue of **17**. Obviously, this intermediate interacts with a second molecule of **15a** under elimination of one molecule of Me₃SiCCSiMe₃ and migration of a SiMe₃ group. The dialuminumthioallenyl compound **18** is formed in 57% yield.

Organoaluminum Dihydroxides and Their Higher Congeners

Science is a collection of successful recipes.

Paul Valéry

Arylboronic acids RB(OH)₂ are quite well-known and have been well-studied in Suzuki coupling reactions.¹⁸ However, the corresponding aluminum compound LAI(OH)₂ was published only recently.¹⁹ The starting material for the preparation of LAI(OH)₂ (**21**) was LAlI₂ and KOH/KH due to the water content of KOH. The reaction was conducted in a liquid ammonia/toluene two phase system. Under these conditions, a complete removal of the iodines resulted, and aluminum dihydroxide **21** was formed (Scheme 10).

A more facile route to **21** is the reaction of LAlCl₂ with water in the presence of an N-heterocyclic carbene as a HCl acceptor.²⁰ For this procedure, the solvent is benzene instead of liquid ammonia/toluene. Compound **21** starts to decompose slowly in a closed system below 60 °C.

Reacting LAlI₂ with KOH, H₂O, and KH under the same conditions as those for the preparation of **21** but with a different ratio of KOH and KH resulted in the formation of the first terminal hydroxide containing alumoxane **22** (Scheme 11).²¹

Acyclic alumoxane **22** can be converted with Me₂AlH to cyclic alumoxane **23**. The structure of **23** contains two four-coordinate Al atoms and one three-coordinate Al atom linked by μ -oxo bridges to form a highly distorted six-membered (AlO)₃ ring. Moreover, compound **23** can be considered to consist of a trapped MeAlO species, the monomer of the well-known cocatalyst MAO. Although **23** contains a three-coordinate Al center, no catalytic activity was observed when **23** was used as a cocatalyst for the dimethylzirconocene polymerization of ethene in toluene solution at room temperature.²¹

The sulfur (**24**) and selenium (**25**) analogues of **21** have been prepared from aluminum dihydride (**26**) and sulfur in the presence of P(NMe₂)₃ and elemental selenium, respectively (Scheme 12).^{22,23}

The role of P(NMe₂)₃ in the synthesis of **24** has been investigated by ¹H and ³¹P NMR spectroscopy.

From the ¹H NMR kinetics, it is evident that the reaction proceeds via an unstable reactive intermediate, LAIH(SH). P(NMe₂)₃ is immediately oxidized to SP(NMe₂)₃. However, no reactions between **26** and SP(NMe₂)₃ occurred unless additional sulfur was added to form S₂P(NMe₂)₃. Formation of such a species is also favored by theoretical calculations. It is most likely that S₂P(NMe₂)₃ forms a complex with **26** by opening the S–S bond and, consequently, inserts into one of the Al–H bonds. In the latter step, a change of the hydridic to the protonic form of the hydrogen takes place. Finally, a proton transfer occurs from one sulfur atom to another, and thus, the catalyst is regenerated.²³

In contrast, the heterogeneous reaction of **26** with 2 equiv of selenium in toluene at room temperature proceeds smoothly to yield the aluminumdiselenol **25**. Compound **25** is stable in the solid state but undergoes condensation reaction in solution over prolonged periods to eliminate H₂-Se and yield compound **27** (Scheme 12). Compound **27**, however, is best isolated directly by carrying out the latter reaction at 60 °C. The X-ray structures of both **24** and **25** clearly show them to be well-separated monomers in the solid state excluding the presence of any intermolecular hydrogen bonds.²⁴

Digression

The easy access of aluminumdihydroxide **21** prompted us to use the N-heterocyclic carbene as a HCl acceptor for the

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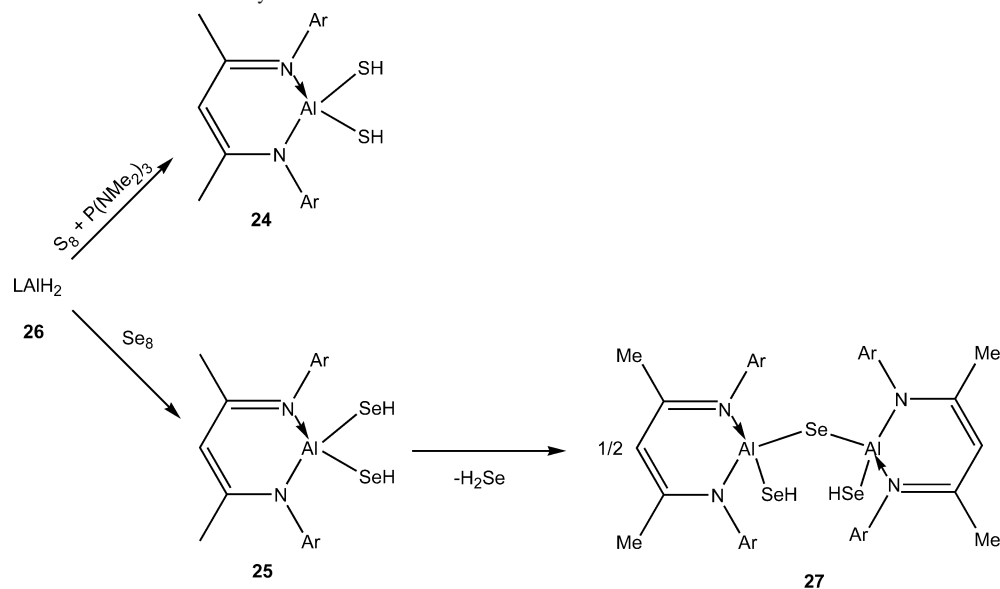
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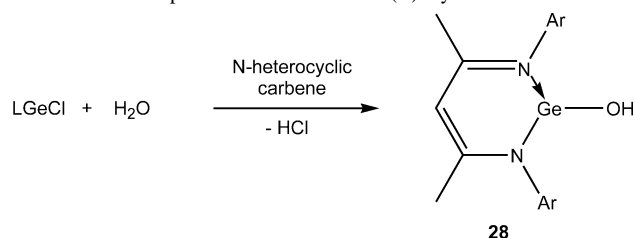
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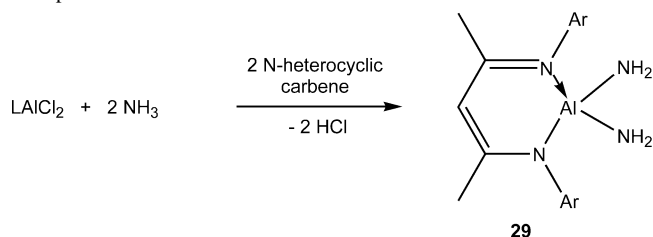
Scheme 12. Conversion of the Aluminumdihydride to the Dithiol and Diselenols

preparation of Ge(II) hydroxide **28** when water is used as a source for the OH moiety (Scheme 13).²⁵

Scheme 13. Preparation of a Germanium(II) Hydroxide

Compound **28** is stable at elevated temperatures. The carbon analogue of **28**, the carbene hydroxide, is so far not known. Obviously, such a compound would be extremely unstable and rearrange to the corresponding aldehyde. However, treatment of $LGeOH$ with elemental sulfur results in the formation of $LGe(S)OH$. It is the first analogue of a thiocarboxylic acid of group 14.²⁶

The successful story of the N-heterocyclic carbene as a HCl acceptor was further extended to the preparation of the first monomeric $LAI(NH_2)_2$, **29** (Scheme 14).²⁰ Com-

Scheme 14. Synthesis of an Aluminum Diamide with Terminal NH_2 Groups

ound **29** is a white crystalline solid with a melting point at 166 °C. According to the X-ray structural

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analysis, **29** is monomeric in the solid state. Consequently, the NH_2 groups are not involved in any hydrogen bonding.

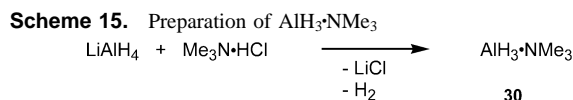
Now it is appropriate to ask about the function of the N-heterocyclic carbene in these reactions. Obviously, due to the high reactivity of **21** and **29** toward protons, amines commonly used in such reactions are not suitable as HCl acceptors. On one hand, there is always an equilibrium between the protonated amine and the free base, and thus, the proton causes side reactions. On the other hand, in the presence of the N-heterocyclic carbene, there is no such equilibrium of the free protons due to the favored C–H bond formation. Furthermore, the resulting imidazolium chloride is very sparingly soluble in hydrocarbon solvents such as hexane, toluene, or THF, which allows an easy separation from the reaction mixture by filtration. In addition, the imidazolium chloride can be easily recycled to the free carbene using a strong base. Finally, the new N-heterocyclic carbene route is obviously a powerful tool for acidic sensitive systems.²⁰

Hydroalumination Reactions Using $AlH_3 \cdot NMe_3$

Chance is the most essential part of discovery, but most people do not encounter chance.

Friedrich Nietzsche

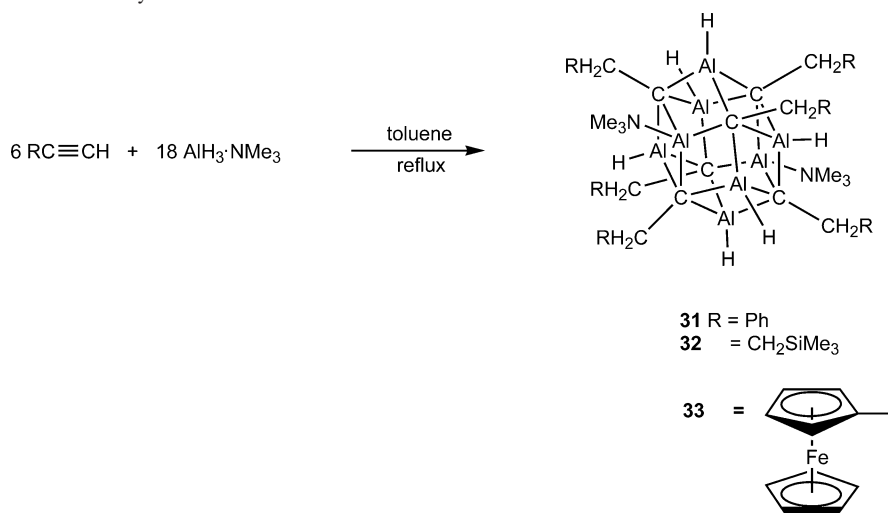
$AlH_3 \cdot NMe_3$ (**30**) is very easily accessible from the reaction of $LiAlH_4$ and $Me_3N \cdot HCl$ (Scheme 15).²⁷



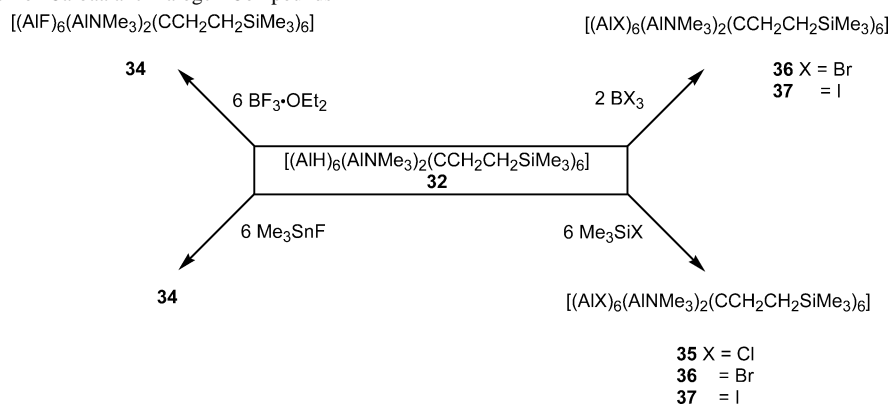
Compound **30** reacts with the CH acidic alkyne $HC \equiv CR$ in boiling toluene to yield the carbaalane $[(AlH)_6(AlNMe_3)_2(CCH_2R)_6]$ ($R = Ph$, **31**; CH_2SiMe_3 , **32**; $C_5H_4FeC_5H_5$, **33**) (Scheme 16).^{28,29}

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Scheme 16. Hydroalumination of Alkynes



Scheme 17. Preparation of Carbaalane Halogen Compounds



Compounds **31–33** are obtained in high yield. The molecular structure of **33** is shown in Figure 2.

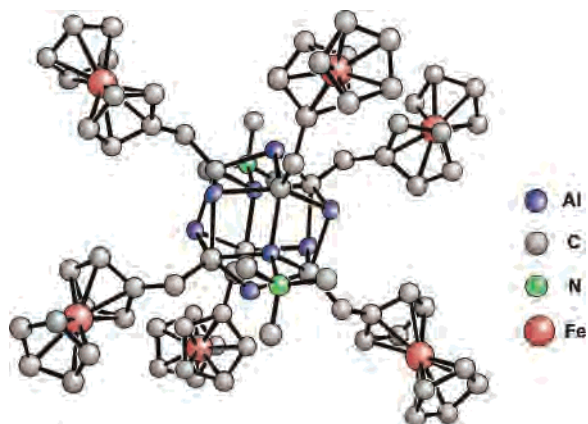


Figure 2. Molecular structure of $[(\text{AlH})_6(\text{AlNMe}_3)_2(\text{CCH}_2\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5)_6]$ (**33**).

Compound **33** is a model for the fixation of an organo-metallic fragment on a carbide surface. The structure is a rhombic dodecahedron containing a cube of eight aluminum

atoms with six carbon atoms and attached ferrocenylmethylene groups at each face of the cube. Each carbon atom of the cube is connected to three Al(H) units and one Al(NMe₃) group. The bonding properties in these cores can be regarded as three-dimensional surface aromaticity. The closed Al₄C faces of the cube are formed by four bonds using three electron pairs thus leading to a strong delocalization of the electrons. On the basis of ab initio (RHF and DFT) calculations, the orbital scheme localized at one cubic face

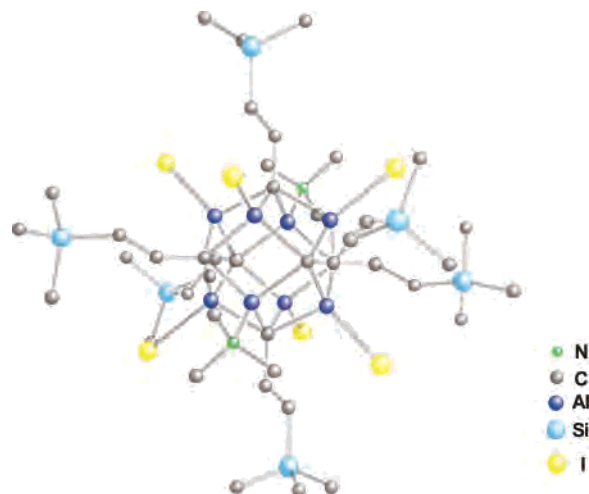
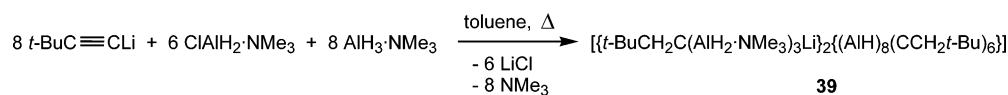


Figure 3. Molecular structure of $[(\text{AlI})_6(\text{AlNMe}_3)_2(\text{CCH}_2\text{CH}_2\text{SiMe}_3)_6]$ (**36**).

- (28) Stasch, A.; Ferbinteanu, M.; Prust, J.; Zheng, W.; Cimpoesu, F.; Roesky, H. W.; Magull, J.; Schmidt, H.-G.; Noltemeyer, M. *J. Am. Chem. Soc.* **2002**, *124*, 5441–5448.
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Scheme 18. Synthesis of Carbaalanate 39



has an orbital sextet with a large HOMO–LUMO gap (8.8 eV) consistent with the criteria of aromaticity. The reactive Al–H bonds can be used in **31** and **32** for substitution reactions. In fact, the halogen compounds $[(\text{AlX})_6(\text{AlNMe}_3)_2(\text{CCH}_2\text{CH}_2\text{SiMe}_3)_6]$ (X = F, **34**; Cl, **35**; Br, **36**; I, **37**) can be prepared from $[(\text{AlH})_6(\text{AlNMe}_3)_2(\text{CCH}_2\text{CH}_2\text{SiMe}_3)_6]$ (**32**) using $\text{BF}_3\cdot\text{OEt}_2$, BX_3 (X = Br, I), Me_3SnF , and Me_3SiX (X = Cl, Br, I), respectively^{28–31} (Scheme 17).

The molecular structure of the iodine derivative is shown in Figure 3. Treatment of compound **35** with an excess of BCl_3 resulted in the metathesis of one of the methyl groups of the SiMe_3 moiety by a chlorine atom to yield $[(\text{AlCl})_6(\text{AlNMe}_3)_2(\text{CCH}_2\text{CH}_2\text{SiMe}_2\text{Cl})_6]$ (**38**). This experiment clearly demonstrates the stepwise functionalization of **32** both within the inner (**35**) and outer (**38**) sphere of the molecule.

The reactions for the preparation of halogen compounds **34**–**38** show that on one hand metathesis of the hydrides is possible without decomposition of the core structure. On the other hand, it is quite surprising that especially the fluorine derivatives have still terminal and not bridging fluorine atoms.

The first carbaalanate (**39**) was prepared from $t\text{-BuC}\equiv\text{CLi}$, obtained in situ from $t\text{-BuC}\equiv\text{CH}$ and $n\text{-BuLi}$ in hexane with equivalent amounts of $\text{AlH}_3\cdot\text{NMe}_3$ and $\text{ClAlH}_2\cdot\text{NMe}_3$. The latter species was prepared by the addition of 1 equiv of Me_3SiCl to 3 equiv of $\text{AlH}_3\cdot\text{NMe}_3$ (Scheme 18).³²

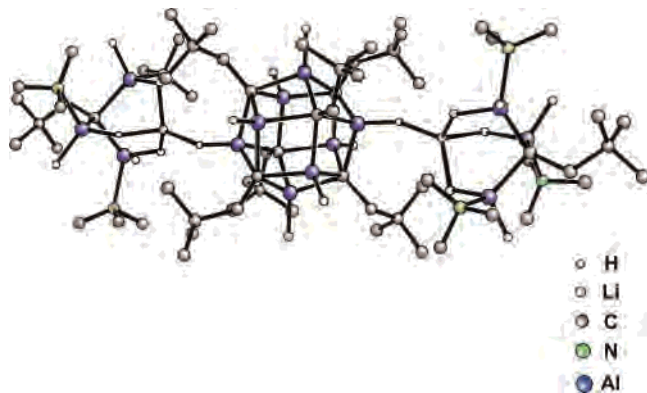


Figure 4. Molecular structure of the lithium carbaalanate cluster $\{[t\text{-BuCH}_2\text{C}(\text{AlH}_2\cdot\text{NMe}_3)_3\text{Li}]_2\{(\text{AlH})_8(\text{CCH}_2t\text{-Bu})_6\}\}$ (**39**).

The central part of **39** is a carbaalanate cluster $[(\text{AlH})_8(\text{CCH}_2t\text{-Bu})_6]^{2-}$ which is isoelectronic to the previously described **32**. Two lithium cations are each coordinated through hydride bridges to the neutral $[t\text{-BuCH}_2\text{C}(\text{AlH}_2\cdot\text{NMe}_3)_3]$ moiety in which three $\text{AlH}_2\cdot\text{NMe}_3$ groups are bound covalently to one carbon atom. The molecular structure of **39** is shown in Figure 4.

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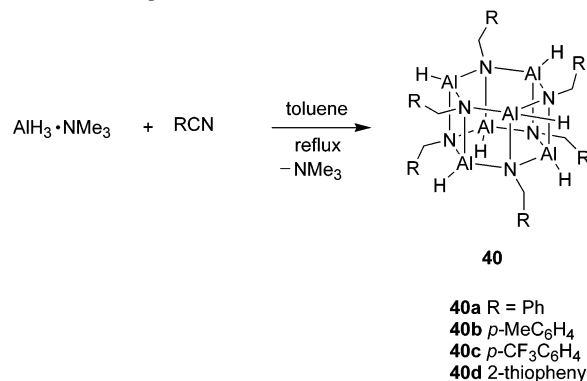
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Hydroalumination of $\text{RC}\equiv\text{N}$ with $\text{AlH}_3\cdot\text{NMe}_3$

Hydroalumination of $\text{RC}\equiv\text{N}$ with $\text{AlH}_3\cdot\text{NMe}_3$ in refluxing toluene resulted in $(\text{HAINCH}_2\text{R})_6$, **40** (Scheme 19).^{33,34}

Scheme 19. Preparation of Al–N Cluster



Compounds **40a**–**d** contain a hexagonal drum with the top and bottom faces of the polyhedron being made of two six-membered $(\text{AlN})_3$ rings, which are almost planar. These six-membered rings are joined by six Al–N bonds forming six rectangular side faces of the drum. The reactivity of Al–H bonds in **40** has been studied. Me_3SiBr reacts with **40a** to yield the corresponding bromine derivative **41**, where all six hydridic hydrogen atoms on the aluminum atoms are replaced by bromine. The reaction of **40a** with $\text{PhC}\equiv\text{CH}$ is straightforward with the evolution of hydrogen to yield the alkynyl derivative. A comparable reaction of compound **40d** and ferrocenylacetylene leads to the formation of compound **42** (Scheme 20). The molecular structure of **42** is shown in

Scheme 20. Fixation of Ferrocenyl Groups on an Aluminum Nitrogen Cluster

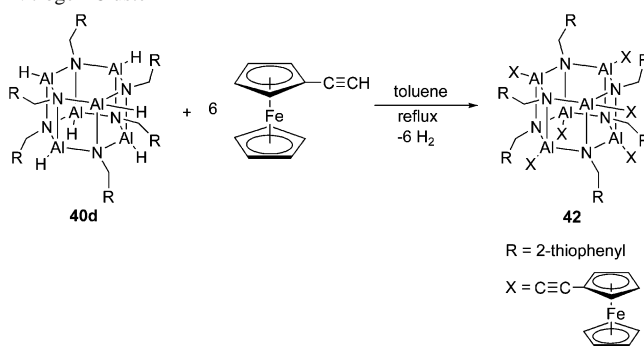


Figure 5. Compound **42** is the first model compound for the fixation of metal-containing ligands on an aluminum nitrogen cluster. The electrochemical behavior of this compound shows a single reversible oxidation wave, which suggests the electrochemical equivalence of the ferrocenylacetylene moieties.³⁵

(33) Reddy, N. D.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **2002**, *41*, 2374–2378.

(34) Reddy, N. D.; Kumar, S. S.; Roesky, H. W.; Vidovic, D.; Magull, J.; Noltemeyer, M.; Schmidt, H.-G. *Eur. J. Inorg. Chem.* **2003**, 442–448.

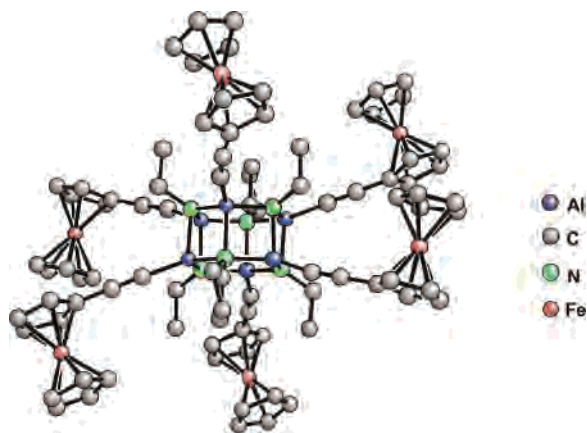


Figure 5. Molecular structure of $[\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{C}\equiv\text{CAICH}_2(\text{SH}_3\text{C}_4)]_6$ (42) in the crystal.

This molecule can also be viewed as a system acting as a multielectron source, electron-transfer mediator, and ion sensor. Moreover, this example initiates research for using metal nitrides as supports for catalysts. The hydroalumination with $\text{AlH}_3\cdot\text{NMe}_3$ was also successfully applied for isonitriles.³⁶

Finally, I have to mention that in recent years a number of colleagues contributed to the renaissance of aluminum chemistry: to name a few, A. R. Barron,³⁷ W. Kaminsky,³⁸ S. Pasynkiewicz,³⁹ W. Uhl,⁴⁰ H. Schnöckel,⁴¹ D. A. Atwood,⁴² J. L. Atwood,⁴³ P. P. Power,⁴⁴ R. F. Jordan,⁴⁵ N. Kuhn,⁴⁶ H. Nöth,⁴⁷ S. Schulz,⁴⁸ M. Veith,⁴⁹ N. Wiberg,⁵⁰ A. H. Cowley,⁵¹ and C. L. Raston.⁵²

Herein, we have summarized the recent contributions of our group to new aluminum systems. The chemistry of

monomeric aluminum(I) is still in its infancy, and the properties of the unusual compounds such as $\text{LAl}(\text{OH})_2$, $\text{LAl}(\text{SH})_2$, $\text{LAl}(\text{SeH})_2$, and $\text{LAl}(\text{NH}_2)_2$ toward transition metals have to be developed. Moreover, the search goes on for the so-called unstables in aluminum chemistry such as $\text{LAl}(\text{R})\text{OH}$ and $\text{LAl}=\text{O}$.⁵³ After all, there is plenty to do in this promising field for new materials and catalysts. I can recommend to follow Napoleon:

*On s'engage et puis on voit
(First start and then you will see)*

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