

## RENAISSANCE OF ALUMINUM CHEMISTRY

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### Abstract

Aluminum is the third most abundant element in the earth's crust and therefore aluminum and its compounds have found a broad application in daily life. The most favored oxidation state in aluminum compounds is +3. In contrast stable aluminum(I) compounds are rare. Herein it is demonstrated that LAl (L =  $\beta$ -diketiminato ligand) can be isolated and a variety of reactions are shown. LAl functions as a Lewis base as well as a Lewis acid. This is demonstrated in the reaction with  $B(C_6F_5)_3$ . Preferentially LAl can be used as a reducing reagent in reactions with  $O_2$ ,  $P_4$ ,  $S_8$ ,  $HC\equiv CH$ , and  $Ph_2CN_2$  respectively.

*Key words:* Aluminum, Aluminum(I), Reactions of Al(I).

### Resumen

**Renacimiento de la química del aluminio.** El aluminio es el tercer elemento en abundancia en la corteza terrestre y por ello el elemento y sus compuestos han encontrado una amplia aplicación en la vida diaria. El estado de oxidación más favorecido del aluminio es +3 y, contrariamente, compuestos de aluminio(I) son raros. En este trabajo se demuestra que las especies del tipo LAl (L = ligando  $\beta$ -dicetiminato) pueden ser aisladas y se muestra una variedad de reacciones de las mismas. LAl pueden actuar como ácidos o bases de Lewis. Esto se demuestra en la reacción con  $B(C_6F_5)_3$ . Preferentemente, LAl puede ser usado como reactivo reductor en reacciones con  $O_2$ ,  $P_4$ ,  $S_8$ ,  $HC\equiv CH$ , y  $Ph_2CN_2$  respectivamente.

*Palabras clave:* Aluminio, Aluminio(I), Reacciones de Al(I).

### Introduction

Impure aluminum was first prepared by H. C. Oersted using the reduction of  $AlCl_3$  with potassium amalgam. Pure aluminum was obtained in 1827 by F. Wöhler by reduction of  $AlCl_3$  with potassium. Larger amounts of aluminum were obtained in 1834 by H. Sainte-Claire Deville, when he treated  $AlCl_3$  with sodium. So precious was the metal at that time that it was exhibited next to the crown jewels at the exposition of 1855 in Paris. Moreover, Napoleon III used aluminum cutlery on state occasions. The price of the aluminum, which is the most abun-

dant metal in the earth's crust dropped tremendously, when Paul-Lewis Toussaint Hérault in France and Charles Martin Hall in the USA used a smelting flux electrolysis of  $Al_2O_3$  (alumina) and cryolite ( $Na_3AlF_6$ ). This process is still today in operation, where cheap electricity is available. Bauxite, the raw material for alumina, is a mixed oxide hydroxide. Large deposits of bauxite are available in Australia, Guinea, Jamaica, Guyana, Surinam, Brazil, India, Greece, Cameroon, and France. Bauxite has its name from Les Baux in the south of France where it was discovered in 1821.

### Fascination by Gems

The fascination of gem materials is related to the beauty of the stone and the price. Many gems contain aluminum. A few well known are mentioned here.

Corundum	$\alpha\text{-Al}_2\text{O}_3$
Topaz	$\text{Al}_2(\text{SiO}_4)(\text{F}, \text{OH})_2$
Beryl	$\text{Al}_2\text{Be}_3(\text{Si}_6\text{O}_{18})$
Chrysoberyl	$\text{Al}_2\text{BeO}_4$
Spinel	$\text{MgAl}_2\text{O}_4$

The addition of some transition metals causes a change in the color of the gems. Both ruby and emerald are derivatives of corundum, where some of the  $\text{Al}^{3+}$  cations are replaced by  $\text{Cr}^{3+}$ . Especially surprising in this system is the red color of ruby, although  $\text{Cr}_2\text{O}_3$  is green. The reason is the different octahedral ligand field, due to the increasing ionic radius of  $\text{Cr}^{3+}$  (0.69 Å) compared to that of  $\text{Al}^{3+}$  (0.50 Å), which causes a shift of the light to the blue region. The result is a complete absorption of light within the green and yellow region while the red light passes through, the blue has only partly transmissivity. Another derivative of corundum is the sapphire. The blue color of this gem is due to a charge transfer of  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$ . These ions are partly replacing the aluminum atoms, which are octahedrally surrounded by oxygen atoms.

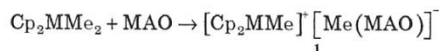
In Table 1 some properties of aluminum and of aluminum compounds are summarized.

### The role of $(\text{MeAlO})_x$ (MAO)

Organoaluminum compounds play an emerging role in modern chemistry. One of the most striking results was the discovery by Sinn et al. [9] that MAO, a hydrolysis product of  $(\text{Me}_3\text{Al})_2$ , is the co-catalyst of choice in Ziegler-Natta stereoregular alkene polymerization. Al-

though the structure of MAO is not known, it is widely accepted that it functions as a Lewis acid in abstracting an alkyl group or a chlorine atom from metallocenes of titanium and zirconium, respectively to generate a cationic vacancy on the metal center (Scheme 1). The

Scheme 1



resulting ion pair **1** is in an equilibrium between a contact one and a solvent separated ion pair. Although there are a number of structurally characterized model compounds of MAO known, none has been as active as MAO itself.

### Aluminum(I) Chemistry

$[\text{Cp}^*\text{AlCl}_2]_2$  ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) prepared from  $\text{Cp}^*\text{SiMe}_3$  and  $\text{AlCl}_3$  reacts under elimination of  $\text{Me}_3\text{SiCl}$  to the dimer  $[\text{Cp}^*\text{AlCl}_2]_2$ . The latter is reduced with potassium to yield  $[(\text{Cp}^*\text{Al})_2]$  (**2**) [8]. Previously compound **2** was prepared by Schnöckel et al. using  $\text{Cp}_2^*\text{Mg}$  and  $\text{AlCl}_3$  [3]. The yield of **2** was essentially improved when  $\text{Cp}^*\text{AlH}_2$  was used as a precursor instead of  $[\text{Cp}^*\text{AlCl}_2]_2$  [7].  $[(\text{Cp}^*\text{Al})_2]$  (**2**) exists as a monomer partly in solution and in the gas phase. The chemistry of **2** has been summarized in [6]. In general compound **2** exhibits a number of insertion reactions for example selenium and tellurium respectively give distorted cubes of composition  $[(\text{Cp}^*\text{AlE})_4]$  ( $\text{E} = \text{Se}$  (**3**),  $\text{Te}$ ). The  $[(\text{Cp}^*\text{AlSe})_4]$  (**3**) is shown in Figure 1.

A kinetically at room temperature stable aluminum(I) compound of composition  $\text{LAl}$  (**4**) ( $\text{L} = \text{HC}(\text{CMeNAr})_2$ ) was obtained when  $\text{LAlH}_2$  was reduced with potassium [2] in toluene (Scheme 2).

Table 1. Properties and Applications of Aluminum and Aluminum Compounds

Melting point of aluminum 660 °C
Density of aluminum 2.7 g/cm <sup>3</sup> (aeroplanes, cans, foils)
Human being contains 0.5 mg/kg
Beef 0.8 mg/kg
Addition of $\text{Al}^{3+}$ - salts retards withering of flowers
Catalysts and co-catalysts in polymerization of olefins
$\text{AlF}_3$ , $\text{Na}_2\text{AlF}_6$ in aluminum production
$\text{AlF}_3$ a molecule in the interstellar space
$\text{AlF}_3$ for surface modification the m.p. of $\text{AlF}_3$ is 1290 °C
$\text{Al-F}$ containing compounds are ingredients in tea
$\gamma\text{-AlF}_3$ is used for halogen exchange with HF in chlorocarbons
$\text{AlF}_4^-$ interferes with nucleotide binding proteins
$\text{PO}_4^{3-}$ has a similar size like that of $\text{AlF}_4^-$ and mimics the binding site of $\gamma$ -phosphate to nucleotide diphosphates

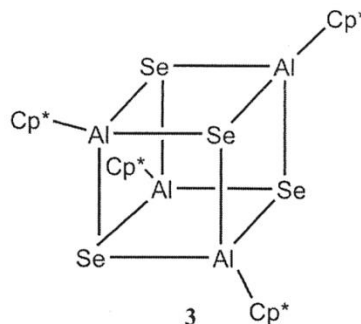
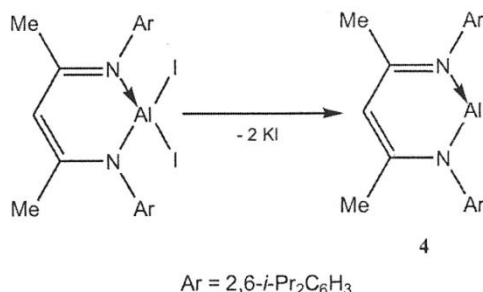
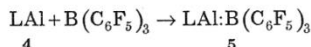


Figure 1

Scheme 2



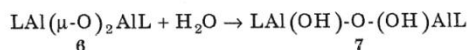
The aluminum atom in **4** is part of a six-membered ring. The Al-N bond lengths (1.937 Å) are slightly longer than those in the corresponding Al(III) compounds due to the larger ionic radius of Al(I) compared to that of Al(III). Compound **4** is the first stable compound that has both Lewis acid, due to its six electrons around aluminum, and Lewis base character according to its lone pair of electrons at aluminum. The Lewis base character of **4** can be demonstrated by adding B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to LAl.



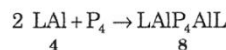
Moreover in compound **5** one of the fluorine atoms in the ortho-position of the phenyl rings simultaneously coordinates to the aluminum and thus is demonstrating the Lewis acid character of aluminum. In **5** the hybrid properties of an atom having Lewis base as well as Lewis acid properties is convincingly shown. This behavior for **4** is supported by ab initio calculations [2,10].

### Reactions of LAl

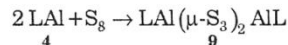
LAl reacts with molecular oxygen under oxidative addition to yield LAl(μ-O)<sub>2</sub>AIL (**6**) having a four-membered ring. We assume that the first step of this reaction is the formation of the peroxide LAlO<sub>2</sub>, which reacts with a second molecule of LAl to yield **6** [12]. The Al(I) atoms of two molecules of **4** are converted to Al(III) under the transfer of four electrons to the O<sub>2</sub> molecule, a process comparable to that in the respiration. Compound **6** reacts easily with water to yield the dihydroxide **7** [12].



Likewise the reaction of LAl with white phosphorus P<sub>4</sub> results in the formation of LAlP<sub>4</sub>AIL (**8**). Compound **8** contains a four-membered ring of composition P<sub>4</sub><sup>4+</sup>, thus during the transfer of four electrons from aluminum to phosphorus two edges of the tetrahedron have been opened [9]. The charge distribution in the Al<sub>2</sub>P<sub>4</sub> unit is investigated using DFT calculations with RI-BP86/TZVP within TURBO-MOLE. A net charge transfer from the aluminum atoms to P<sub>4</sub> is observed when calculated Mulliken charges on the P atom (-0.22) are taken into consideration, which clearly demonstrates the formation of an ionic Al-P bond.

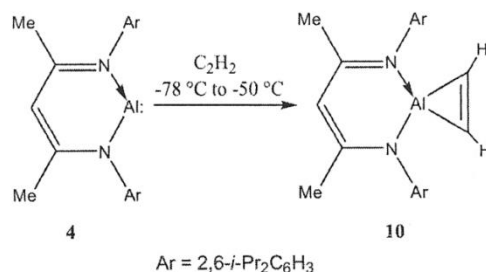


More complicated is the reaction of S<sub>8</sub> with LAl which yields LAl(μ-S<sub>3</sub>)<sub>2</sub>AIL (**9**). Compound **9** contains a puckered eight-membered Al<sub>2</sub>S<sub>6</sub> ring. Two sulphur atoms in the starting material have been replaced by two aluminum atoms. As a consequence for the formation of **9** the cleavage of four S-S bonds is necessary [4].

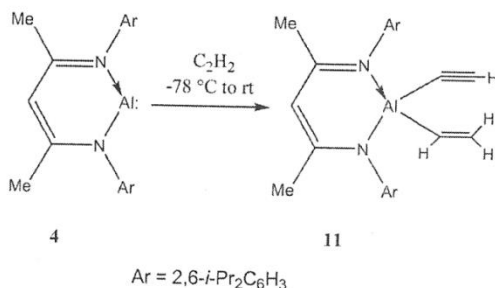


Quite interesting is the reaction of LAl with HC≡CH, which proceeds already at temperatures between -78 °C and -50 °C to yield the 1:1 adduct **10**. Compound **10** can be isolated and was characterized by single crystal X-ray structural analysis [11] (Scheme 3). Compound **10** reacts with an excess of HC≡CH under ring opening to yield **11**. We assume that the reaction proceeds through a donor-acceptor intermediate of HC≡CH with **10** due to the Lewis acidic center of aluminum. The X-ray structural analysis of **11** reveals that **11** has terminal acetylene and ethylene groups [11] (Scheme 4).

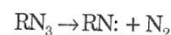
Scheme 3



Scheme 4

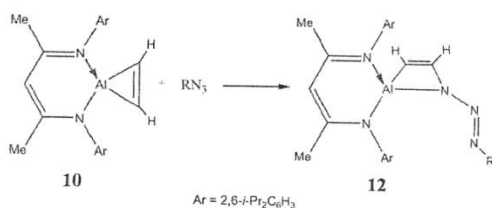


In general covalent azides react under formation of a nitrene with elimination of nitrogen, and the nitrene is the reactive species for the insertion into metal-non metal bonds. A different



route was however observed, when  $\text{Me}_3\text{SiN}_3$  and  $\text{LAl}$  were reacted at elevated temperature. The final product was the triazole **13**. We assume that the reaction proceeds through the intermediate **14** which reacts with another molecule of  $\text{Me}_3\text{SiN}_3$  to yield the [2+3] cycloaddition product **13** [1] (Scheme 6).

Scheme 5

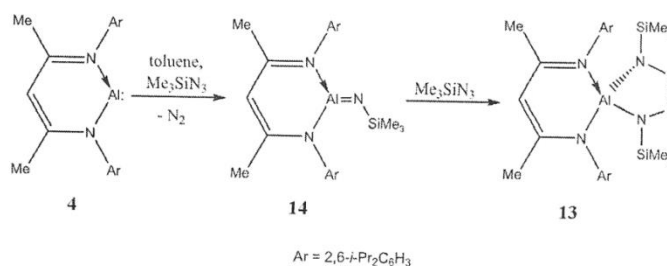


Particularly interesting is the reaction of **10** with a bulky azide  $\text{RN}_3$  to yield the end-on insertion product **12** [11] (Scheme 5).

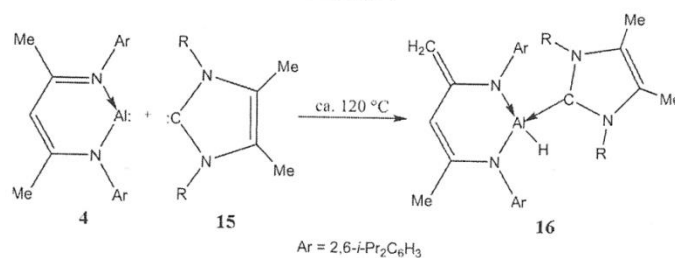
Moreover we observed another type of reactions with  $\text{LAl}$ , where hydrogen migration is involved. The N-heterocyclic carbene **15** reacts with  $\text{LAl}$  to yield **16**. The reaction was conducted at ca. 120 °C. Under these conditions a hydrogen atom migrated from a methyl group of **4** to aluminum in **16** undergoing simultaneously coordination of **15** at the aluminum in **16** [13] (Scheme 7).

Treatment of  $\text{LAl}$  at 80 °C with two equivalents of diphenyldiazomethane affords compound **18** under elimination of one molecule of  $\text{N}_2$  [13]. Compound **18** is the first diiminylaluminum derivative, which is obtained in quantitative yield (Scheme 8).

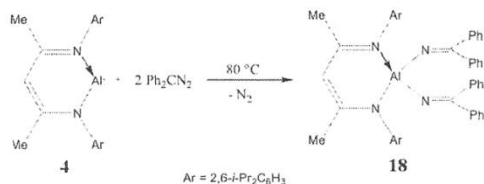
Scheme 6



Scheme 7



Scheme 8



In summary the chemistry of at room temperature stable aluminum(I) compounds is still in its infancy but it has already been demonstrated that a completely new field has been opened. In the near future many more unexpected results will be discovered using aluminum(I) compounds.

#### Acknowledgements

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