Aluminum Complexes

DOI: 10.1002/ange.200502251

Janus-Faced Aluminum: A Demonstration of Unique Lewis Acid and Lewis Base Behavior of the Aluminum Atom in $[LAlB(C_6F_5)_3]$**

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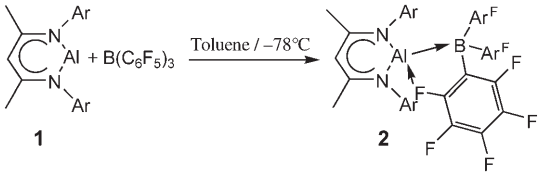
Compounds of aluminum with a formal +3 oxidation state on aluminum, such as trihalides, trialkyls, and triaryls, show classical behavior of Lewis acids.[1] In recent years, another class of compounds containing aluminum with the +1 oxidation state has attracted great interest.[2] These compounds, which have a nonbonding lone pair of electrons at the aluminum center, are proposed to have singlet, carbene-like character and they exhibit the potential for Lewis base behavior. In 2000, Cowley and co-workers reported the first example of an aluminum(I)–boron donor–acceptor bond, in $[Cp^*Al{\rightarrow}B(C_6F_5)_3]$ ($Cp^* = C_6Me_5$),[3] and one year later a corresponding Al–Al bond in $[Cp^*Al{\rightarrow}Al(C_6F_5)_3]$.[4] In neither of these systems did an aluminum center show both Lewis acid and Lewis base behavior.

The reduction of $[I_2AlL]$ ($L = HC(CMeNAr)_2$; $Ar = 2,6\text{-}iPr_2C_6H_3$) with potassium resulted in the formation of monomeric [LAl] (**1**).[5] This was the first stable two-coordinate aluminum(I) compound to be prepared and structurally characterized in the solid state. The fascinating aspect of **1** is its dual Lewis acid and Lewis base character. Ab initio calculations[6] with analysis of the Laplacian of the electron density[7] within the plane show a geometrically active lone pair of electrons on the aluminum atom with a probable quasi-trigonal-planar orientation of orbitals. This observation clearly indicates that **1** is Lewis basic. Moreover, charge depletion close to the aluminum atom in the semiplane of the six-membered ring indicates that **1** is Lewis acidic. Herein, we report the reaction of [LAl] (**1**) with $B(C_6F_5)_3$ to yield $[LAlB(C_6F_5)_3]$ (**2**), the first aluminum compound displaying both Lewis base and Lewis acid character at the metal center.

The reaction of a 1:1 molar ratio of [LAl] (**1**) and $B(C_6F_5)_3$ in toluene between −78 °C and room temperature resulted in the formation of **2** (Scheme 1). Compound **2** was characterized by ^1H, ^{13}C, ^{11}B, ^{19}F, and ^{27}Al NMR spectroscopy, as well as EI mass spectrometry and elemental analysis. ^1H, ^{13}C, ^{11}B, and ^{19}F NMR spectroscopic analysis was carried out at room temperature in $[D_6]$benzene or $[D_8]$toluene. No resonance signals were observed in the ^{27}Al NMR spectra of **2** in C_6D_6 or C_7D_8; consequently, the measurement was carried out in the solid state. The ^{19}F NMR spectrum of **2** exhibits nine partly overlapping resonances, and therefore an unambiguous assignment is not possible. However, this pattern indicates a distorted $B(C_6F_5)_3$ group caused by an Al–F interaction. The EI mass spectrum shows the molecular ion of **2** (*m*/*z* 956). Single crystals of **2** suitable for X-ray crystallographic analysis were obtained by keeping the hexane solution at room temperature for two weeks.[8] The solid-state structure consists of individual molecules of the Lewis acid/base adduct (Figure 1). An Al–F interaction arises from close intramolecular contact between one of the *ortho* fluorine atoms and the Al atom with the formation of an $AlBC_2F$ five-membered ring (Figure 2). There is a distorted tetrahedral geometry around the aluminum atom, with an average Al–N bond length of 1.892(6) Å. This distance is considerably shorter than the Al–N bonds in **1** (av 1.957(6) Å). This observation is consistent with the partial transfer of the lone pair of electrons on the aluminum center upon formation of the donor–acceptor bond. The Al–B bond in **2** (2.183(3) Å) is slightly longer than that in $[Cp^*Al{-}B(C_6F_5)_3]$ (2.169(2) Å). Also, the geometry of the $B(C_6F_5)_3$ group changes from trigonal planar to distorted tetrahedral in **2**. The extent of the geometrical change has been taken as an indication of the strength of the donor–acceptor interaction.[9] The sum of the C-B-C angles around the boron atom in **2** (330.3(2)°) is the smallest of those (333.5(2)–342.2(2)°) reported for $B(C_6F_5)_3$ compounds.[3,10,11] Thus, **1** appears to be a stronger base than {Cp*Al}. However it must to be considered that the relatively close Al–F contact in **2** (2.156(2) Å) changes the electron density on the aluminum center. The noticeable Al–F interaction is indicated by the lengthening of the C–F bond (1.414(6) Å) relative to the remaining 14 C–F bonds (av 1.355 Å). In addition, the C(41)-B(1)-Al(1) angle is clearly smaller



1 2

Scheme 1. Formation of **2**. $Ar = 2,6\text{-}iPr_2C_6H_3$, $Ar^F = C_6F_5$.

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[**] This work was supported by the Göttinger Akademie der Wissenschaften and the Fonds der Chemischen Industrie. $L = HC(CMeNAr)_2$, $Ar = 2,6\text{-}iPr_2C_6H_3$. The Roman god Janus has two faces looking in opposite directions. Herein, the aluminum is showing its two "faces" of Lewis acid and Lewis base properties.

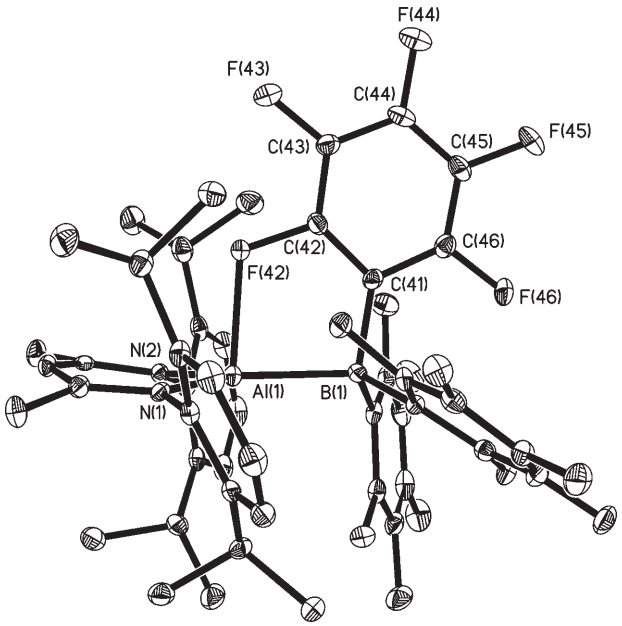

Figure 1. X-ray crystal structure of **2**. Selected bond lengths [Å] and angles [°]: Al(1)–B(1) 2.183(5), Al(1)–F(42) 2.156(3), C(42)–F(42) 1.414(4), Al(1)–N(2) 1.885(4), Al(1)–N(1) 1.900(3), C(33)–F(33) 1.371(5); C(41)-B(1)-Al(1) 100.4(3), C(51)-B(1)-Al(1) 115.1(3), C(31)-B(1)-Al(1) 110.1(3), F(42)-Al(1)-B(1)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

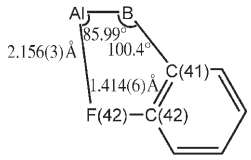

Figure 2. Depiction of Al-B-C(41)-C(42)-F(42) five-membered ring.

(100.4(3)°) than the C_{ipso}-B-Al angles (115.1(3)° and 110.1(3)°) of the two non-interacting perfluorophenyl rings. These data indicate that the lengthening of the C–F bond and the narrowing of the Al-B-C angle are due to the F→Al interaction and are consistent with a F→Al donor–acceptor behavior.

It is evident from the crystallographic data that there is a weak interaction between the aluminum and fluorine F(42) centers. To gain a better understanding of the bonding situation, **2** was examined by means of ab initio calculations. The first and crucial step in these calculations is to reproduce the crystallographic data with a reliable quantum-chemical method. Starting from this structure, the analysis of the molecular orbitals and bond order gives the most accurate picture of the electronic structure.

The calculated structural parameters (Al–F(42) 2.1626 Å, F(42)–C(42) 1.4384 Å, and F(42)-Al-B 85.236°) are in good agreement with the crystallographic data (Figure 1). The bond-order analysis reveals that the electron density of the fluorine atom is distributed between the carbon and aluminum centers with a (Al–F)/(F–C) ratio of 0.2930/0.7148, which indicates that there is a significant interaction between the fluorine and aluminum centers. The consequence of this interaction is the elongation of the C(42)–F(42) bond by 0.075 Å (calcd 1.4385 Å) relative to the other C–F bonds in the same ring (calcd range 1.3633–1.3636 Å). From natural bond order (NBO) analysis,[12] the bond between aluminum and fluorine can be described as the overlap of two hybrid orbitals of sp^n type with one located at Al (16.24% s and 83.76% p) and the other at F(42) (11.56% s and 88.44% p). The bonding orbital located on C(42) has $sp^{2.72}$ character, whereas the remaining carbon atoms in this ring have $sp^{2.22}$ character. This situation is also clearly visible in the corresponding orbital picture. Figure 3 shows the contour plots of two orbitals contributing to the formation of the Al–F bond.

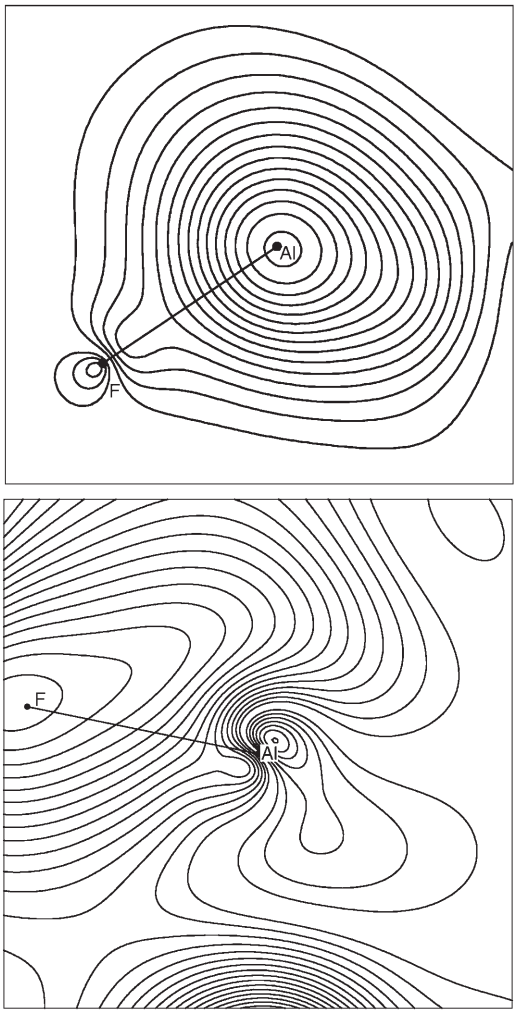

Figure 3. Schematic representation of the Al–F linkage resulting from the overlap of wave functions centered on aluminum and fluorine. The two relevant orbitals are shown here as contour plots. The clearly visible deformation in the second plot is due to the fact that there is a strong interaction with orbitals forming the Al–N bonds.

In conclusion, we have prepared $[LAlB(C_6F_5)_3]$, a unique compound of aluminum showing Lewis base and Lewis acid character at the aluminum center. There are no known precedents of this type of bonding in the literature.

Experimental Section

All manipulations were performed under a dry, oxygen-free atmosphere (N_2 or Ar) by using Schlenk and glove-box techniques.

2: Toluene (20 mL) was added to a mixture of **1** (0.223 g, 0.5 mmol) and $B(C_6F_5)_3$ (0.256 g, 0.5 mmol) at −78 °C. The mixture was stirred and slowly warmed to room temperature. After stirring the mixture for an additional 15 h, the solvent was removed under reduced pressure, and the solution was treated with hexane (30 mL). The solution was filtered and allowed to stand for two weeks at room temperature to afford colorless crystals of **2**. Yield: 0.09 g (19 %); m.p. 208–209 °C; EI-MS: *m/z* (%) 956 (10) [M^+], 403 (100) [L−Me]; ^{1}H NMR (300.13 MHz, C_6D_6): $\delta = 6.80$–6.75 (m, 6H, Ar-H), 4.91 (s, 1H, γ-H), 2.80 (sept, $^3J_{H,H} = 6.8$ Hz, 4H, C*H*Me$_2$), 1.61 (s, 6H, Me), 1.15 (d, $^3J_{H,H} = 6.8$ Hz, 12H, CH*Me*$_2$), 0.87 ppm (d, $^3J_{H,H} = 6.8$ Hz, 12H, CH*Me*$_2$); ^{13}C NMR (75.48 MHz, C_6D_6): $\delta = 173.33$ (CN), 142.75, 139.49, 129.27, 124.76 (Ar), 150.25, 147.13, 140.75, 138.63, 137.38, 134.95 (br, C_6F_5), 102.07 (γ-C), 24.53, 25.09(CH*Me*$_2$), 22.68 (CH*Me*$_2$), 20.74 ppm (Me). ^{11}B NMR (95.29 MHz, C_6D_6): $\delta = -26.52$ ppm; ^{19}F NMR (188.28 MHz, C_7D_8) $\delta = -124.28$ (br m), −128.26 (br m), −129.97 (d), −154.41 (t), −156.49 (br m), −157.27 (t), −158.86 (br m), −160.24 (t), −160.99 ppm (t); ^{27}Al NMR (400 MHz, 16 KHz, MAS, $AlCl_3$): $\delta = 0$–50 ppm; elemental analysis (%) calcd for $C_{47}H_{41}AlBF_{15}N_2$ ($M_r = 956.61$): C 59.01, H 4.32, N 2.93; found: C 58.66, H 4.67, N 2.70.

Details of ab initio calculations: The well-established B3LYP[13,14] method was employed for all the ab initio calculations because of the size of the system. Two different basis sets were used for the computations: a small one as the 3-21G basis set, and an extended one in which the aluminum atoms are described with functions taken from the 631-G basis set including double-diffuse functions.[15,16] The Gaussian G03[17] program suite was used to optimize the structure with the 3-21G basis first, and this structure was used as the starting geometry for a further optimization with the larger basis set to give an appropriate description of the aluminum atom and its binding situation. The resulting structure was used for visualization of the orbitals. The nature of the quantum-chemical method results in a wave function that produces molecular orbitals involving nearly every atom. Therefore, this method leads to a picture that, despite being mathematically correct, is difficult to interpret. A more descriptive picture is obtained by localizing the orbitals at those atoms according to the Boys Method.[18] Quantitative data about the bond between Al and F(42) was obtained by analyzing the bond order following a proposal of I. Mayer.[19]

Received: June 27, 2005
Published online: October 11, 2005

Keywords: aluminum · boron · fluorine · Lewis acids · Lewis bases

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