Communications to the Editor

## A Lewis Acid Adduct of an Alanediyl: An Aluminum(I)−Boron Donor−Acceptor Bond

John D. Gorden, Andreas Voigt, Charles L. B. Macdonald, Joel S. Silverman, and Alan H. Cowley*

Department of Chemistry and Biochemistry
The University of Texas at Austin
Austin, Texas 78712

Despite a recent surge of interest in the lower oxidation state chemistry of the group 13 elements,[1] much less is known about monomeric species of the type RM(I) (M = B, Al, Ga, In) than the more familiar carbenes, nitrenes, and their heavier congeners. Theoretical studies[2] indicate that, regardless of the nature of the substituent R, the ground state of each four-valence-electron RM-(I) species is a singlet. In the particular case of $(\eta^5\text{-}C_5Me_5)Al$, the DFT-calculated singlet−triplet energy gap is between 67.6 and 70.9 kcal/mol, depending on the basis set employed.[3] Moreover, the a_1-symmetry HOMO of this alanediyl possesses distinctly lone pair character suggestive of potential Lewis base behavior. We report the synthesis and X-ray crystal structure of $(\eta^5\text{-}C_5Me_5)Al \rightarrow B(C_6F_5)_3$ (**1**), the first example of an aluminum (I)−boron donor−acceptor bond.

The addition of toluene (30 mL) to a mixture of $[Al(\eta^5\text{-}C_5\text{-}Me_5)]_4$[4] (0.15 g, 0.93 mmol of $Al(\eta^5\text{-}C_5Me_5)$ units) and $B(C_6F_5)_3$ (0.47 g, 0.92 mmol) resulted in a yellow-colored solution. After being stirred for 16 h at room temperature, the reaction mixture was filtered, and the solvent and volatiles were removed from the filtrate to afford a purple oil from which a 40% yield of colorless crystals of **1** (mp 126−129 °C dec) deposited over a period of days. Mass spectral data[5] were consistent with the proposed Lewis acid−base adduct formulation. Moreover, the ^{11}B NMR chemical shift for **1**[5] fell in the tetracoordinate boron region and the ^{19}F chemical shifts of the (equivalent) C_6F_5 groups[5] were similar to those observed for other Lewis base complexes of $B(C_6F_5)_3$.[6] The ^{27}Al NMR chemical shift of the broad singlet resonance of **1** (δ −59.4) was reasonably close to the value of δ −71.5 computed by the GAIO method,[7] and the equivalence of the methyl protons was suggestive of η^5-attachment of the Me_5C_5
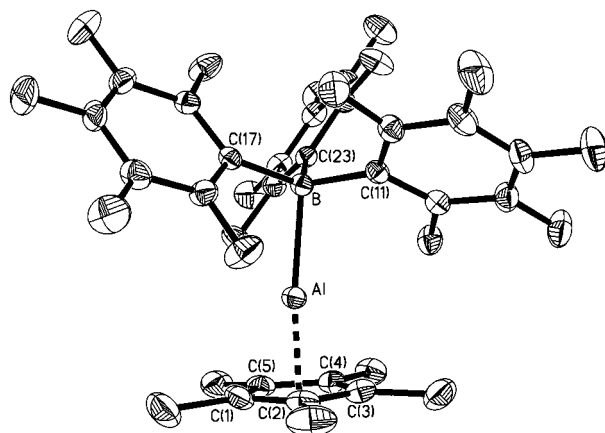
Figure 1. Molecular structure of $(\eta^5\text{-}C_5Me_5)Al \rightarrow B(C_6F_5)_3$ (**1**) showing the atom numbering scheme. Important distances (Å) and angles (deg): Al−B 2.169(3), Al−C(1) 2.164(3), Al−C(2) 2.185(3), Al−C(3) 2.179-(3), Al−C(4) 2.160(2), Al−C(5) 2.166(2), Al−(ring centroid) 1.802(3), B−C(11) 1.633(3), B−C(17) 1.634(3), B−C(23) 1.637(3), B−Al−X (ring centroid) 172.9(1), C(11)−B−C(17) 114.7(2), C(11)−B−C(23) 111.3-(2), C(17)−B−C(23) 113.8(2).

group to aluminum.[5] For comparison, the [27]Al chemical shifts for uncoordinated monomeric $Al(\eta^5\text{-}C_5Me_5)$ and tetrameric $[Al-(\eta^5\text{-}C_5Me_5)]_4$ are δ = −80 and −150, respectively.[1c] The foregoing spectroscopic conclusions were confirmed by X-ray crystallography.[8] Compound **1** crystallizes in the $P\bar{1}$ space group with Z = 2; the solid state consists of individual molecules of the Lewis acid−base adduct (Figure 1) and there are no unusually short intermolecular contacts. The C_5Me_5 group is attached in an η^5 fashion and ring centroid−Al−B moiety is essentially linear (172.9(1)°). The average Al−C distance of 2.171(3) Å is considerably shorter than those determined for $Al(\eta^5\text{-}C_5Me_5)$ (2.388(7) Å)[9] and $[Al(\eta^5\text{-}C_5Me_5)]_4$ (2.344 Å).[10] Such shortening

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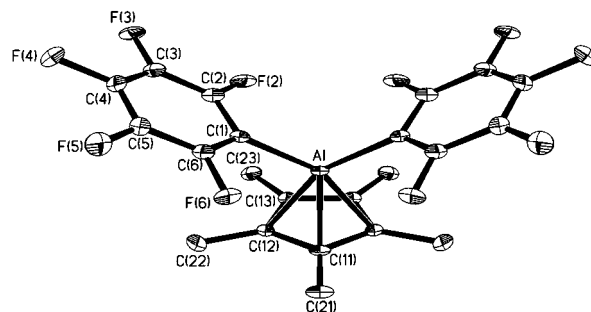
(3) Macdonald, C. L. B.; Cowley, A. H. *J. Am. Chem. Soc.* **2000**, in press.

(4) Prepared by the method of Schulz, S.; Roesky, H. W.; Koch, H. J.; Sheldrick, G. M.; Stalke, D.; Kuhn, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1729.

(5) **1**: MS (CI, CH₄) *m/z* 675 (0.93%) [M + H]⁺; 512 (66.98%) [B(C₆F₅)₃]⁺; 164 (2.02%) [(C₅Me₅)AlH₂]⁺. HRMS (CI, CH₄) calcd for C₂₈H₁₆AlBF₁₄, 655.0859; found 655.0884. ¹H NMR (300.00 MHz, 295 K, C₆D₆) δ 1.39 (s, 15H, C₅Me₅). ¹⁹F NMR (282.72 MHz, 295 K, C₆D₆) δ −127.2 (s, *m*-C₆F₅), δ −154.9 (s, *p*-C₆F₅), δ −159.8 (s, *o*-C₆F₅). ¹¹B NMR (96.28 MHz, 295 K, C₆D₆) δ −32.9 (s). ²⁷Al NMR (78.21 MHz, 295 K, C₆D₆) δ −59.4 (br, w₁/₂ = 1564 Hz). **2**: MS (CI, CH₄) *m/z* 496 (17.95%) (M⁺); 477 (36.71%) [M − F]⁺ 329 (100%) [M − C₆F₅]⁺. HRMS (CI, CH₄ calcd for C₂₂H₁₅AlF₁₀, 496.0829; found 496.0817. ¹H NMR (300.00 MHz), 295 K, C₆D₆) δ 1.63 (s, 15H, C₅Me₅). ¹⁹F NMR (282.78 MHz, 295K, C₆D₆) δ −119.0 (s, *m*-C₆F₅), δ −149.0 (s, *p*-C₆F₅), −155.8 (s, *o*-C₆F₅). ²⁷Al NMR (78.21 MHz, 295 K, C₆D₆) δ 57.6 (br, w₁/₂ = 4505 Hz).

(6) For a selection of structurally characterized donor adducts of B(C₆F₅)₃, see: (a) Bradley, D. C.; Hursthouse, M. B.; Motevalli, M.; Zheng, D. H. *J. Chem. Soc., Chem. Commun.* **1991**, 7. (b) Röttger, D.; Erker, G.; Fröhlich, R.; Kotila, S. *J. Organomet. Chem.* **1996**, *518*, 17. (c) Bradley, D. C.; Harding, I. S.; Keefe, A. D.; Motevalli, M.; Zheng, D. H. *J. Chem. Soc., Dalton Trans.* **1996**, 3931. (d) Parks, D. J.; Piers, W. *J. Am. Chem. Soc.* **1996**, *118*, 9440. (e) Parks, D. J.; Piers, W.; Parvez, M.; Atencio, R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 1369. (f) Jacobsen, H.; Berke, H.; Döring, S.; Kehr, G.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 1724.

(7) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789; Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *122*, 8251. This single-point calculation employed the X-ray crystal structure parameters for **1**.

(8) Crystal data for **1**: C₂₈H₁₅AlBF₁₅, triclinic, $P\bar{1}$, *a* = 9.534(2) Å, *b* = 9.902(2) Å, *c* = 15.658(3) Å, α = 91.04(2), β = 104.10(3), γ = 105.93(3)°, *V* = 1372.9(5) Å³, Z = 2, D_calcd = 1.631 g cm⁻³, μ(Mo Kα) 0.195 mm⁻¹. A suitable single of **1** was covered with mineral oil and mounted on a Nonius-Kappa CCD diffractometer at 153 K. A total of 11 088 independent reflections were collected in the range 5.9 < 2θ < 55.0° using Mo Kα radiation (λ = 0.71073 Å). Of these, 6252 were considered observed (*I* > 2.0 σ(*I*)) and were used to solve (direct methods) and refine (full-matrix, least-squares on *F*²) the structure of **1**; wR2 = 0.1372, R = 0.0549. Crystal data for **2**: C₂₂H₁₅-AlF₁₀, orthorhombic, *Pnma*, *a* = 9.049(2) Å, *b* = 19.160(4) Å, *c* = 11.902(2) Å, *V* = 2063.6(7) Å³, Z = 4, D_calcd = 1.598 g cm⁻³, μ(Mo Kα) 0.195 mm¹. A suitable single crystal of **2** was covered with mineral oil and mounted on a Nonius-Kappa CCD diffractometer at 153 K. A total of 4469 independent reflections were collected in the range 6.04 < 2θ < 73.32° using Mo Kα radiation (λ = 0.71073 Å). Of these, 2435 were considered observed (*I* > 2.0 σ(*I*)) and were used to solve (direct methods) and refine (full-matrix, least-squares on *F*²) the structure of **2**; wR2 = 0.1948, R = 0.0684.

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is anticipated as the aluminum lone pair is transformed into the donor−acceptor bond with the concomitant development of partial positive and negative charges on aluminum and boron, respectively. There is a very little information in the literature with which to compare the Al−B bond distance of **1** (2.169(3) Å). In the hydride-bridged complexes $Me_3NAl(\eta^2\text{-}H_2BH_2)_3$[11] and $[\eta^5\text{-}C_5H_5]\text{-}Ti(\mu_2\text{-}H)_2]_2Al(\eta^2\text{-}H_2BH_2)$[12] the average Al−B separations are 2.18-(2) to 2.27(3) Å, respectively, while in a variety of aluminum-substituted carboranes, these distances range from ~2.13 to 2.24 Å.[13] A DFT calculation[14] on the model compound $(\eta^5\text{-}C_5Me_5)\text{-}AlBH_3$ revealed that the global minimum possesses a "staggered" C_s geometry similar to that observed for **1** with a computed Al−B bond distance of 2.127 Å. As a consequence of donor action on the part of the alanediyl, the geometry of $B(C_6F_5)_3$ changes from trigonal planar to distorted tetrahedral. The sum of bond angles at boron is 339.8(2)°, and to the extent that this geometrical change is a measure of the strength of the donor−acceptor interactions, it is interesting to note an almost identical sum of bond angles in $(C_6H_5)_3PB(C_6F_5)_3$.[6f]

The present results have a bearing on the current debate[16] concerning the nature of the bonding between group 13 univalent ligands, RM, and transition metal carbonyl fragments, $M'(CO)_n$. Much of the discussion has centered on whether the bonding is of the donor−acceptor type, viz. $RM \rightarrow M'(CO)_n$, or whether M'-to-M back-bonding is important as reflected by the canonical forms $RM \rightleftharpoons M'(CO)_n$ and $RM \rightleftarrows M'(CO)_n$. The isolation of **1** proves that an alanediyl can function as a pure donor ligand because there is no question of back-bonding in this particular case. Moreover, the experimental structural parameters and the DFT computed charge distribution and orbital occupancy for the alanediyl fragment of **1**[3] are very similar to those of the terminal alanediyl transition metal complexes $(\eta^5\text{-}C_5Me_5)AlFe(CO)_4$ (av Al−C = 2.147(8) Å)[17] and $(\eta^5\text{-}C_5Me_5)AlCr(CO)_5$ (av Al−C =

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Figure 2. Molecular structure of $(C_6F_5)_2Al(\eta^3\text{-}C_5Me_5)$ (**2**) showing the atom numbering scheme. Important distances (Å) and angles (deg): Al−C(1) 2.018(3), Al−C(11) 1.672(3), Al−C(12) 2.067(3), C(1)−Al−C(1)* 103.5(2), C(11)−Al−C(12) 46.09(13).

2.183(2) Å),[10] suggesting the existence of the same donor−acceptor bonding mode in both cases.

Interestingly, when $[Al(\eta^5\text{-}C_5Me_5)]_4$ was treated with $In(C_6F_5)_3$ using the same procedure as that described above for the $B(C_6F_5)_3$ reaction, the product was colorless, crystalline $(C_6F_5)_2Al(\eta^3\text{-}C_5\text{-}Me_5)$ (**2**) (mp 158 °C). The proposed formulation for **2** was consistent with mass spectral data[5] and the presence of C_6F_5 and C_5Me_5 groups was evident from ^{19}F and ^{1}H NMR spectroscopic data;[5] however, to establish for example the hapticity of the cyclopentadienyl ring it was necessary to perform an X-ray crystal structure.[8] Individual molecules of **2** crystallize in the orthorhombic space group *Pnma* with $Z = 4$; there are no unusually short intermolecular contacts (Figure 2). The C_5Me_5 group is attached to aluminum in an η^3 fashion, a coordination mode that has been seen previously only in the case of the dimers $[(\eta^3\text{-}C_5\text{-}Me_5)(R)Al\text{-}\eta\text{-}Cl]_2$ (R = Me, *i*-Pr).[18] The Al−C(11) and Al−C(12) distances are 1.672(3) and 2.067(3) Å, respectively while the Al-(1)...C(13) distance is 2.687 Å. The Al−C(1) distance of 2.018-(3) Å in **2** is slightly longer than those in the THF (1.995(3) Å),[19] benzene (1.979(7) Å),[20] and toluene (1.984(2) Å)[20] complexes of $Al(C_6F_5)_3$. It is possible that **2** was produced via C_6F_5 transfer from the adduct $(\eta^5\text{-}C_5Me_5)Al \rightarrow In(C_6F_5)_3$. Such a view would be consistent with the modest In−C bond energy and the relative stability of the In(I) oxidation state.

Supporting Information Available: X-ray experimental details with positional parameters and full bond distances and angles for **1** and **2** and a summary of the DFT calculations (PDF). An X-ray crystallographic file, in CIF format is also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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