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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

Received October 1, 1999

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 studies² 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 $(\eta^5\text{-C}_5\text{Me}_5)\text{Al}$, 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 $(\eta^5\text{-C}_5\text{Me}_5)\text{Al} \rightarrow \text{B}(\text{C}_6\text{F}_5)_3$ (**1**), the first example of an aluminum(I)–boron donor–acceptor bond.

The addition of toluene (30 mL) to a mixture of $[\text{Al}(\eta^5\text{-C}_5\text{Me}_5)]_4$ (0.15 g, 0.93 mmol of $\text{Al}(\eta^5\text{-C}_5\text{Me}_5)$ units) and $\text{B}(\text{C}_6\text{F}_5)_3$ (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 data⁵ were consistent with the proposed Lewis acid–base adduct formulation. Moreover, the ¹¹B NMR chemical shift for **1**⁵ fell in the tetracoordinate boron region and the ¹⁹F chemical shifts of the (equivalent) C_6F_5 groups⁵ were similar to those observed for other Lewis base complexes of $\text{B}(\text{C}_6\text{F}_5)_3$.⁶ The ²⁷Al 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 GIAO method,⁷ and the equivalence of the methyl protons was suggestive of η^5 -attachment of the Me_5C_5

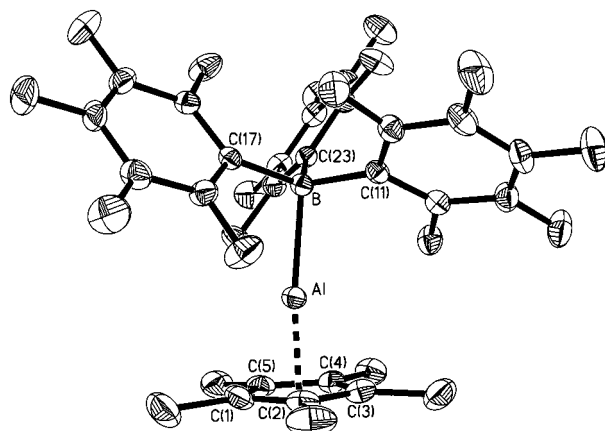


Figure 1. Molecular structure of $(\eta^5\text{-C}_5\text{Me}_5)\text{Al} \rightarrow \text{B}(\text{C}_6\text{F}_5)_3$ (**1**) showing the atom numbering scheme. Important distances (Å) and angles (deg): Al–B 2.169(3), Al–C(1) 2.164(3), Al–C(2) 2.185(3), Al–C(3) 2.179(3), Al–C(4) 2.160(2), Al–C(5) 2.166(2), 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 ²⁷Al chemical shifts for uncoordinated monomeric $\text{Al}(\eta^5\text{-C}_5\text{Me}_5)$ and tetrameric $[\text{Al}(\eta^5\text{-C}_5\text{Me}_5)]_4$ 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 $\text{Al}(\eta^5\text{-C}_5\text{Me}_5)$ (2.388(7) Å)⁹ and $[\text{Al}(\eta^5\text{-C}_5\text{Me}_5)]_4$ (2.344 Å).¹⁰ Such shortening

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(7) Ditchfield, R. *Mol. Phys.* **1974**, 27, 789; Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, 112, 8251. This single-point calculation employed the X-ray crystal structure parameters for **1**.

(8) Crystal data for **1**: $\text{C}_{28}\text{H}_{15}\text{AlBF}_3$, triclinic, $P\bar{1}$, $a = 9.534(2)$ Å, $b = 9.902(2)$ Å, $c = 15.658(3)$ Å, $\alpha = 91.04(3)^\circ$, $\beta = 104.10(3)^\circ$, $\gamma = 105.93(3)^\circ$, $V = 1372.9(5)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.631$ g cm^{–3}, $\mu(\text{Mo K}\alpha) 0.195$ mm^{–1}. A suitable single crystal 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 $5.9 < 2\theta < 55.0^\circ$ using Mo K α radiation ($\lambda = 0.71073$ Å). Of these, 6252 were considered observed ($I > 2.0 \sigma(I)$) 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**: $\text{C}_{22}\text{H}_{15}\text{AlF}_{10}$, orthorhombic, $Pnma$, $a = 9.049(2)$ Å, $b = 19.160(4)$ Å, $c = 11.902(2)$ Å, $V = 2063.6(7)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.598$ g cm^{–3}, $\mu(\text{Mo K}\alpha) 0.195$ mm^{–1}. 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 $6.04 < 2\theta < 73.32^\circ$ using Mo K α radiation ($\lambda = 0.71073$ Å). Of these, 2435 were considered observed ($I > 2.0 \sigma(I)$) 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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(2) For alanediyls, see (a) Ahlrichs, R.; Ehrig, M.; Horn, H. *Chem. Phys. Lett.* **1991**, 183, 227. (b) Schneider, U.; Ahlrichs, R.; Horn, H.; Schäfer, A. *Angew. Chem., Int. Ed. Engl.* **1992**, 31, 353. (c) Gauss, J.; Schneider, U.; Ahlrichs, R.; Dohmeier, C.; Schnöckel, H. *J. Am. Chem. Soc.* **1993**, 115, 2402. (d) Purath, A.; Dohmeier, C.; Ecker, A.; Schnöckel, H. *Organometallics* **1998**, 17, 1894.

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(5) **1**: MS (CI, CH_4) m/z 675 (0.93%) $[\text{M} + \text{H}]^+$; 512 (66.98%) $[\text{B}(\text{C}_6\text{F}_5)_3]^+$; 164 (2.02%) $[(\text{C}_5\text{Me}_5)\text{AlH}_2]^+$. HRMS (CI, CH_4) calcd for $\text{C}_{28}\text{H}_{16}\text{AlBF}_3$, 655.0859; found 655.0884. ¹H NMR (300.00 MHz, 295 K, C_6D_6) δ 1.39 (s, 15H, C_5Me_5). ¹⁹F NMR (282.72 MHz, 295 K, C_6D_6) δ –127.2 (s, $m\text{-C}_6\text{F}_5$), δ –154.9 (s, $p\text{-C}_6\text{F}_5$), δ –159.8 (s, $o\text{-C}_6\text{F}_5$). ¹¹B NMR (96.28 MHz, 295 K, C_6D_6) δ –32.9 (s). ²⁷Al NMR (78.21 MHz, 295 K, C_6D_6) δ –59.4 (br, $w_{1/2} = 1564$ Hz). **2**: MS (CI, CH_4) m/z 496 (17.95%) $(\text{M})^+$; 477 (36.71%) $[\text{M} - \text{F}]^+$; 329 (100%) $[\text{M} - \text{C}_6\text{F}_5]^+$. HRMS (CI, CH_4) calcd for $\text{C}_{22}\text{H}_{15}\text{AlF}_{10}$, 496.0829; found 496.0817. ¹H NMR (300.00 MHz, 295 K, C_6D_6) δ 1.63 (s, 15H, C_5Me_5). ¹⁹F NMR (282.78 MHz, 295 K, C_6D_6) δ –119.0 (s, $m\text{-C}_6\text{F}_5$), δ –149.0 (s, $p\text{-C}_6\text{F}_5$), δ –155.8 (s, $o\text{-C}_6\text{F}_5$). ²⁷Al NMR (78.21 MHz, 295 K, C_6D_6) δ 57.6 (br, $w_{1/2} = 4505$ Hz).

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 $\text{Me}_3\text{NAl}(\eta^2\text{-H}_2\text{BH}_2)_3$ ¹¹ and $[\eta^5\text{-C}_5\text{H}_5\text{-Ti}(\mu_2\text{-H})_2\text{Al}(\eta^2\text{-H}_2\text{BH}_2)]$ 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 calculation¹⁴ on the model compound $(\eta^5\text{-C}_5\text{Me}_5)\text{-AlBH}_3$ revealed that the global minimum possesses a “staggered” C_5 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 alanedyl, the geometry of $\text{B}(\text{C}_6\text{F}_5)_3$ 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 $(\text{C}_6\text{H}_5)_3\text{PB}(\text{C}_6\text{F}_5)_3$.^{6f}

The present results have a bearing on the current debate¹⁶ concerning the nature of the bonding between group 13 univalent ligands, RM, and transition metal carbonyl fragments, $\text{M}'(\text{CO})_n$. Much of the discussion has centered on whether the bonding is of the donor–acceptor type, viz. $\text{RM} \rightarrow \text{M}'(\text{CO})_n$, or whether M' -to-M back-bonding is important as reflected by the canonical forms $\text{RM} \rightleftharpoons \text{M}'(\text{CO})_n$ and $\text{RM} \rightleftharpoons \text{M}'(\text{CO})_n$. The isolation of **1** proves that an alanedyl 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 alanedyl fragment of **1**³ are very similar to those of the terminal alanedyl transition metal complexes $(\eta^5\text{-C}_5\text{Me}_5)\text{AlFe}(\text{CO})_4$ (av Al–C = 2.147(8) Å)¹⁷ and $(\eta^5\text{-C}_5\text{Me}_5)\text{AlCr}(\text{CO})_5$ (av Al–C =

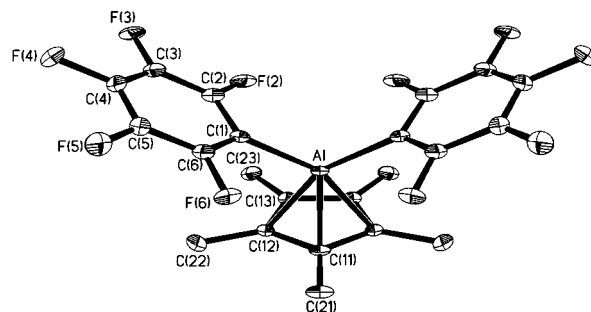


Figure 2. Molecular structure of $(\text{C}_6\text{F}_5)_2\text{Al}(\eta^3\text{-C}_5\text{Me}_5)$ (**2**) showing the atom numbering scheme. Important distances (Å) and angles (deg): Al–C(1) 2.018(3), Al–C(11) 1.672(3), Al–C(12) 2.067(3), C(1)–Al–C(11)* 103.5(2), C(11)–Al–C(12) 46.09(13).

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

Interestingly, when $[\text{Al}(\eta^5\text{-C}_5\text{Me}_5)]_4$ was treated with $\text{In}(\text{C}_6\text{F}_5)_3$ using the same procedure as that described above for the $\text{B}(\text{C}_6\text{F}_5)_3$ reaction, the product was colorless, crystalline $(\text{C}_6\text{F}_5)_2\text{Al}(\eta^3\text{-C}_5\text{Me}_5)$ (**2**) (mp 158 °C). The proposed formulation for **2** was consistent with mass spectral data⁵ and the presence of C_6F_5 and C_5Me_5 groups was evident from ¹⁹F and ¹H 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 $[(\eta^3\text{-C}_5\text{Me}_5)(\text{R})\text{Al-}\eta\text{-Cl}]_2$ (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 $\text{Al}(\text{C}_6\text{F}_5)_3$. It is possible that **2** was produced via C_6F_5 transfer from the adduct $(\eta^5\text{-C}_5\text{Me}_5)\text{Al} \rightarrow \text{In}(\text{C}_6\text{F}_5)_3$. Such a view would be consistent with the modest In–C bond energy and the relative stability of the In(I) oxidation state.

Acknowledgment. We are grateful to the National Science Foundation and the Robert A. Welch Foundation for support.

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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