

Arene Complexes of $\text{Al}(\text{C}_6\text{F}_5)_3$. Relationship to a Déjà Vu Silylium Ion

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Once somewhat of a curiosity,¹ the potent Lewis acid, $\text{B}(\text{C}_6\text{F}_5)_3$, has become a compound of practical importance due largely to its role as a cocatalyst for olefin polymerization.² However, information on the analogous aluminum compound, $\text{Al}(\text{C}_6\text{F}_5)_3$, is much more sparse,^{3,4} although Lewis acid behavior is manifested by the isolation of a THF complex³ and a titanium aluminate zwitterion.⁵

One of the noteworthy developments over the past 5–6 years has been the isolation and structural assay of silylium (silicinium) ions, $[\text{SiR}_3]^+$, the earliest examples of which feature $\text{R} = \text{Et}^6$ or $i\text{-Pr}^7$. In neither case, however, is the silylium ion “free,” being coordinated to toluene when $\text{R} = \text{Et}$ and to one of the bromines of the carboranyl gegenion in the other.⁸ Alanes are isoelectronic with silylium ions; moreover, aluminum is considerably more electropositive than silicon (Pauling electronegativities: Al, 1.61; Si, 1.90). Hence it occurred to us that $\text{Al}(\text{C}_6\text{F}_5)_3$ might coordinate to arenes in a fashion similar to $[\text{SiEt}_3]^+$.

Equimolar mixtures of $\text{B}(\text{C}_6\text{F}_5)_3$ and AlMe_3 were allowed to react anaerobically in either benzene or toluene solutions at 25 °C for 12 h, following which the reaction mixtures were filtered.⁹ Concentration of the filtrates afforded single crystals of $\text{Al}(\text{C}_6\text{F}_5)_3 \cdot \text{benzene}$ (**1**)¹⁰ and $\text{Al}(\text{C}_6\text{F}_5)_3 \cdot \text{toluene}$ (**2**)¹⁰ suitable for study by X-ray diffraction.¹¹ Compounds **1** and **2** both crystallize in the

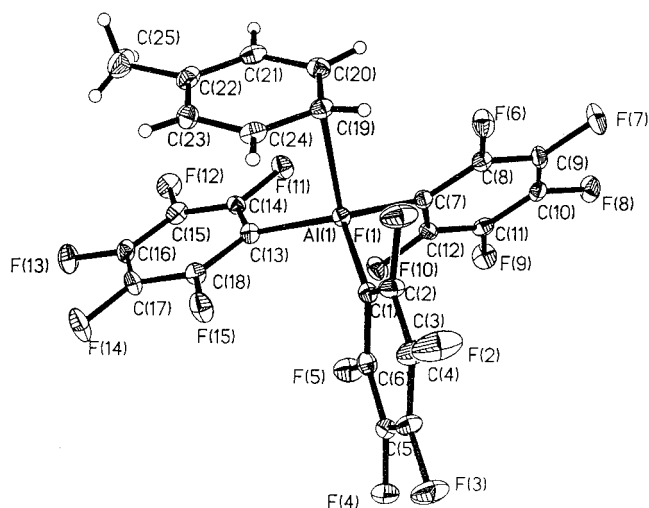


Figure 1. Molecular structure of $\text{Al}(\text{C}_6\text{F}_5)_3 \cdot \text{toluene}$ (**2**) showing the atom numbering scheme. Important parameters (with the corresponding parameters for $\text{Al}(\text{C}_6\text{F}_5)_3 \cdot \text{benzene}$ (**1**) shown in parentheses): $\text{Al}(1)-\text{C}(1)$, 1.9836(14) Å (1.976(7) Å); $\text{Al}(1)-\text{C}(7)$, 1.9812(14) Å (1.976(6) Å); $\text{Al}(1)-\text{C}(13)$, 1.988(2) Å (1.986(7) Å); $\text{Al}(1)-\text{C}(19)$, 2.366(2) Å (2.342(6) Å); $\text{C}(1)-\text{Al}(1)-\text{C}(7)$, 117.18(6)° (107.9(3)°); $\text{C}(1)-\text{Al}(1)-\text{C}(13)$, 108.44(6)° (117.0(3)°); $\text{C}(7)-\text{Al}(1)-\text{C}(13)$, 114.51(6)° (116.8(3)°); $\text{C}(1)-\text{Al}(1)-\text{C}(19)$, 107.98(6)° (105.4(3)°); $\text{C}(7)-\text{Al}(1)-\text{C}(19)$, 104.39(6)° (103.9(3)°); $\text{C}(13)-\text{Al}(1)-\text{C}(19)$, 103.12(6)° (104.2(2)°).

triclinic space group $P\bar{1}$. In the case of **1**, there is one crystallographically unique molecule of $\text{Al}(\text{C}_6\text{F}_5)_3 \cdot \text{benzene}$ per asymmetric unit, along with half a molecule of uncoordinated benzene; the crystalline state of **2** is similar but without the extra half molecule of solvent. There are no unusually close intermolecular contacts in **1** or **2**. All the hydrogen atoms were located in the structure of **2**; for **1**, the hydrogen atoms were placed in idealized positions.

In both **1** and **2** the arene is coordinated in an η^1 fashion, and the conformations of both molecules are very similar (Figure 1). As in the case of $[\text{SiEt}_3 \cdot \text{toluene}]^+$ (**3**),⁶ the toluene molecule in **2** is attached in the para position. The Al–C(arene) distances in **1** and **2** are 2.342(6) and 2.366(2) Å, respectively, which is 0.28–0.30 Å longer than the sum of covalent radii for these elements. For comparison, the Si–C(toluenes) distance in **3** is 0.24 Å longer than the sum of the Si and C covalent radii.⁶ Use of the Pauling bond length equation¹² gives an estimated bond order of 0.3 for the Al–C(arene) bonds in **1** and **2**. The nature of the arene bonding in **1** and **2** can be discussed in terms of two canonical forms, **A** and **B**, (Scheme 1) in a manner similar to that reported for **3**¹³ and the Ag^+ complex of benzene.¹⁴ Structure **A** is a π -arene complex¹⁵ and features an sp^2 carbon, while structure **B**, with an sp^3 carbon, is a σ complex or Wheland intermediate;¹⁶ the Al–C–C_{para} angles for **A** and **B** are 90 and 125°, respectively. The experimentally determined bond angles of 99.1 and 96.1° for **1** and **2**, respectively, are therefore closer to those for structure **A** which involves idealized sp^2 hybridization. A slight perturbation of the arene ring was detectable in the case of **2** in the sense that

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(2) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, 26, 345.

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(5) Cowley, A. H.; Hair, G. S.; McBurnett, B. G.; Jones, R. A. *Chem. Commun.* **1999**, 437.

(6) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, 260, 1917.

(7) Reed, C. A.; Xie, Z.; Bau, R.; Benesi, A. *Science* **1993**, 262, 402.

(8) For a free silylium ion, see the following: Lambert, J. B.; Zhao, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 400.

(9) Although we have not encountered any problems, caution should be exercised when handling $\text{Al}(\text{C}_6\text{F}_5)_3$ since detonations have been reported at elevated temperatures. See the following: Pohlmann, J. L. W.; Brinckman, F. E. Z. *Naturforsch. B: Anorg. Chem. Org. Chem.* **1965**, 20B, 5; Chambers, R. D. *Organomet. Chem. Rev.* **1966**, 1, 279. See also, ref 3.

(10) **1**: yield 70%; mp 118–119 °C; NMR data ¹⁹F NMR (282 MHz, C_6D_6) δ –123.1 (m, *o*-F, 6F), –150.8 (m, *p*-F, 3F), –160.6 (m, *m*-F, 6F); ²⁷Al NMR (78.21 MHz, C_6D_6) δ 52 (s, br, $w_{1/2} = 6257$ Hz). **2**: yield 74%; mp 120–122 °C; ¹⁹F NMR (282 MHz, C_6D_6) δ –121.2 (m, *o*-F, 6F), –149.0 (m, *p*-F, 3F), –158.8 (m, *m*-F, 6F); ²⁷Al NMR (78.21 MHz, C_6D_6) δ 61 (s, br, $w_{1/2} = 6400$ Hz).

(11) Crystal data for **1**: $\text{C}_{27}\text{H}_9\text{AlF}_{15}$, triclinic, $P\bar{1}$, $a = 7.408(1)$, $b = 1.378(1)$, $c = 15.606(1)$ Å, $\alpha = 73.70(1)$, $\beta = 78.49(1)$, $\gamma = 84.74(1)^\circ$, $V = 1236.3(2)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.734$ g cm^{–3}, μ (Mo K α) = 2.13 cm^{–1}. Crystal data for **2**: $\text{C}_{25}\text{H}_8\text{AlF}_{15}$, triclinic $P1$, $a = 7.427(2)$, $b = 11.612(3)$, $c = 13.822(4)$ Å, $\alpha = 92.08(2)$, $\beta = 102.61(2)$, $\gamma = 101.95(2)^\circ$, $V = 1133.9(5)$ Å³, $Z = 1$, $D_{\text{calcd}} = 0.908$ g cm^{–3}, μ (Mo K α) = 0.114 mm^{–1}. Suitable single crystals of **1** and **2** were covered with mineral oil and mounted on a Siemens P4 diffractometer at 173(2) K. Totals of 6355 and 7138 reflections were collected in the ranges $4.0 < 2\theta < 55.0^\circ$ and $3.04 < 2\theta < 60^\circ$ for **1** and **2**, respectively, using Mo K α radiation ($\lambda = 0.71073$ Å). Of these, 5463 and 5834 reflections were considered observed for **1** and **2**, respectively ($I > 2.0 \sigma(I)$). Both structures were solved by direct methods and refined by full matrix, least squares methods. Final R values: **1**, $R_{w2} = 0.1495$, $R = 0.0844$; **2**, $R_{w2} = 0.1076$, $R = 0.0347$.

(12) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 255.

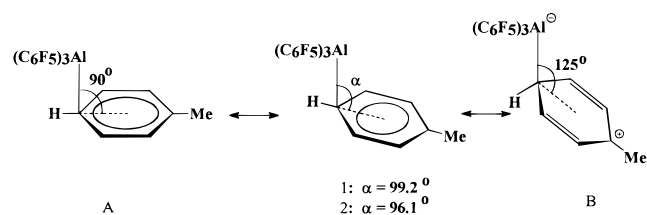
(13) Reed, C. A.; Xie, Z. *Science* **1994**, 263, 984.

(14) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, 107, 5955.

(15) For hexahapto π -type interactions between arenes and an iminophosphonium cation and related systems, see the following: Burford, N.; Clyburne, J. A. C.; Bakshi, P. K.; Cameron, T. S. *Organometallics* **1995**, 14, 1578, and references therein.

(16) For recent structural data on the chlorohexamethylbenzene cation, see Rathore, R.; Hecht, J.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, 120, 13278. Such cations were first observed by Olah and co-workers. See, for example: Olah, G. A.; Lin, H. C.; Mo, Y. K. *J. Am. Chem. Soc.* **1972**, 94, 3667.

Scheme 1



the average bond distance for C(20)–C(21) and C(23)–C(24) (1.386(2) Å) is shorter than that for the remaining C–C bonds (1.400(2) Å).

The interactions with the arene molecules are also evident from the metrical parameters of the $\text{Al}(\text{C}_6\text{F}_5)_3$ fragment. The sums of bond angles at aluminum are 341.7(3) and 340.13(6) $^\circ$ in **1** and **2**, respectively, thus indicating a significant tetrahedral distortion of the AlC_3 trigonal plane¹⁷ upon complexation. Interestingly, the average C–Al–C bond angles in **1** (113.9(3) $^\circ$) and **2** (113.38–(6) $^\circ$) are identical to that in $\text{Al}(\text{C}_6\text{F}_5)_3 \cdot \text{THF}$ (**4**)³ (113.58(10) $^\circ$), as are the average Al–C bond distances within experimental error

(17) The structure of uncomplexed $\text{Al}(\text{C}_6\text{F}_5)_3$ has not been reported. However, the structure of $\text{Al}(\text{mesityl})_3$ is known, and the AlC_3 unit is planar with the mesityl groups arranged in a propeller-like fashion around the trigonal axis. Jerius, J. J.; Hahn, J. M.; Magsudur Rahman, A. F. M.; Mois, O.; Ilsey, W. H.; Oliver, J. P. *Organometallics* **1986**, *5*, 1812.

(1.979(7), 1.984(2), and 1.995(3) Å in **1**, **2**, and **4**, respectively). The tetrahedral distortions in **1** and **2** are also very similar to that in **3**⁶ as reflected by the average C–Si–C bond angle of 114 $^\circ$.

The interactions between the arenes and $\text{Al}(\text{C}_6\text{F}_5)_3$ are sufficiently strong that complexes **1** and **2** persist in solution. Thus, the ^1H NMR spectrum of **1** in C_6D_6 solution exhibits a complex pattern in the aromatic C–H region (peaks observed at δ 6.99, 7.01, 7.05, 7.07, 7.11, and 7.13) as expected for an η^1 -benzene. Addition of approximately 5 equiv of THF to a solution of **1** in C_6D_6 results in displacement of the coordinated benzene and formation of the known³ complex, **4**. Interestingly, the coordinated benzene of **1** is not displaced by Et_2O as evidenced by ^1H NMR spectroscopy. These observations imply the sequence of donor strengths, $\text{THF} > \text{benzene} > \text{Et}_2\text{O}$, toward $\text{Al}(\text{C}_6\text{F}_5)_3$. Complexes **1** and **2** also retain their integrity in the vapor phase since peaks corresponding to the molecular ions are detectable at m/z 606.3 (**1**) and 620.3 (**2**) in the negative ion CI mass spectra.

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Supporting Information Available: X-ray experimental details with positional parameters and full bond distances and angles for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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