

Ferrocenylalanes: Solid State and Solution
Structures of some New Aluminum-Bridged ansa-
Ferrocenes.

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SUPPLEMENTARY MATERIAL

Experimental

Unless otherwise stated all experiments were performed under an atmosphere of Ar by means of standard Schlenk techniques or in a MBraun Labmaster Glovebox. All solvents were distilled from molten alkali metal or alloy, degassed, and stored appropriately over 3Å molecular sieves or potassium mirror. $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2]\text{Li}_2\bullet\text{TMEDA}$ was prepared by a literature procedure and stored in the glovebox, as was AlArCl_2 .^{1,2} AlEt_2Cl was purchased from Aldrich as a 1.0 mol L⁻¹ solution in hexanes and titrated before use against EDTA.

1: To a slurry of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2]\text{Li}_2\bullet\text{TMEDA}$ (2.29 g, 7.29×10^{-3} mol) in toluene (50 mL) at -78 °C was added a hexanes solution of AlEt_2Cl (14.6 mL, 0.146 mol) over 40 minutes. Upon removal of the cooling bath the slurry went up to give an orange red solution and a white precipitate deposited. The red filtrate was reduced to 20 mL in volume and crops of orange red crystals of **1** appeared on standing (0.961 g, 55%). ¹H NMR (400 MHz, methylene chloride-*d*₂, 25 °C, TMS): δ 4.74, 4.33 (m, 30H, Cp), 0.47 (t, 6H, Et, JH-H' = 8 Hz), 0.40 (t, 3H, Et, JH-H' = 8Hz), -0.60 (q, 4H, Et, JH-H' = 8 Hz), -0.69 (q, 2H, Et, JH-H' = 8Hz); ¹³C{¹H} (50 MHz, methylene chloride-*d*₂, 25 °C): δ 79.9, 76.5 (Cp), 9.5 (CH₃), 4.2 (CH₂). Elemental analyses: calcd for C₃₀H₃₉Al₃Fe₃: C, 55.50; H, 6.06, found: C, 55.89; H, 6.40.

2: To a slurry of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2]\text{Li}_2\bullet\text{TMEDA}$ (0.500 g, 1.59×10^{-3} mol) in toluene (30 mL) was added dropwise a solution of $\text{Al}(\kappa^2\text{C}, N\text{-NMe}_2\text{CH}_2\text{C}_6\text{H}_4)\text{Cl}_2$ (0.387 g, 1.67×10^{-3} mol) in toluene (10 mL) at -78 °C. The reaction mixture was stirred for 1 h at this temperature and then allowed to warm to room temperature, during which time the reaction mixture turned dark red in color and a white precipitate deposited. After filtration, the volatiles were removed in high vacuum and the residue dissolved THF (4 mL). The product was precipitated by addition of hexanes, washed several times with hexanes, and dried (0.486 g, 86%). X-ray quality crystals were obtained by slow evaporation of a benzene solution of **2**. ¹H NMR (400 MHz, benzene-*d*₆, 25 °C, TMS): δ 8.68, 7.55, 7.41, 7.08 (m, 8H, aryl), 5.30, 4.64, 4.55, 4.10 (m, 16H, Cp), 3.44 (s, 4H, CH₂), 1.86 (s, 12H, NMe); ¹³C{¹H} (101 MHz, benzene-*d*₆, 25 °C): δ 145.2, 138.0, 127.3, 124.5 (aryl), 75.8, 75.5, 71.4, 71.2 (Cp), 66.5 (CH₂), 45.6 (NMe). EIMS: *m/z* (%); 690 (100) [M^+]; 529 (13) [$\text{M}^+ - \text{Al}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)$]; 395 (5) [$\text{M}^+ - \text{Al}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2) - \text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2$]; 345 (23) [M^{2+}]; 186 (65) [Fc^+]; 135 (31)

- (1) Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart J. C. *J. Organometallic Chem.* **1971**, 27, 241-249.
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$[\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2^+]$; 91 (23) $[\text{C}_7\text{H}_7^+]$; 58 (45) $[\text{Me}_2\text{NCH}_2^+]$; 56 (11) $[\text{Fe}^+]$. Elemental analyses were consistently low on C%, H%, N%.

- (1) Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart J. C. *J. Organometallic Chem.* **1971**, 27, 241-249.
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