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Ferrocenylalanes: Solid-State and Solution Structures of Some New Aluminum-Bridged *ansa*-Ferrocenes

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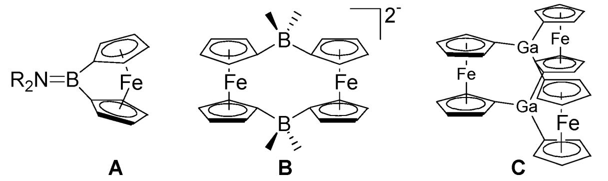
Addition of dilithiated ferrocene to $AlEt_2Cl$ and $Al(\kappa^2\text{-}C,N\text{NMe}_2\text{-}CH_2C_6H_4)Cl_2$ yields the trimeric ferrocenyl derivative **1** and the dimeric [1,1′]-ferrocenophane **2**, respectively. Solution spectroscopy is consistent with the solid-state structures, which reveal unusual and unprecedented bonding around the aluminum centers.

Substitution of the ferrocene unit by main group elements has recently been the subject of considerable attention.[1] Such systems are prized both as precursors to polymeric materials with ferrocenyl repeat units and as frameworks for new ferrocene-based ligands capable of important catalytic transformations when bound to a suitable transition metal.[2] Depending on the Lewis acidity of the main group element, "E", such systems can give rise to multinuclear metallocenophanes in which E bridges across the cyclopentadienyl ring to another ferrocene or spans the cyclopentadienyl rings bound to the same iron center to give an ansa bridge. Monomers, dimers, and trimers, with respect to ferrocene, are all possible outcomes and representative examples (**A**−**C**) incorporating group 13 elements are shown in Chart 1.

The examples shown incorporate either boron or gallium centers;[3−6] except for a very recent, rare exception,[7] aluminum-substituted metallocenophanes are conspicuously absent for iron and, indeed, for any other transition metal. From the point of view of reactivity, this is reasonable in that the Lewis-acidic aluminum center would be expected to draw any electron density toward itself and undergo exhaustive substitution to give oligomeric or intractable material. In fact, although a few examples of aluminum directly bound to a ferrocenyl group have been isolated,[8] in none of these cases is any degree of structural complexity exhibited. In this Communication, the isolation and structure of a multinuclear ferrocene derivative with aluminum substitution is reported by way of reaction between dilithiated ferrocene and the simple aluminum reagent $AlEt_2Cl$. In addition, an unprecedented and authentic [1,1′]-ferrocenophane is presented in which a based-stabilized aluminum is the bridging element.

Chart 1



Slow addition of stoichiometric $AlEt_2Cl$ (2 equiv) in hexanes to a slurry of $[Fe(\eta^5\text{-}C_5H_4)_2]Li_2\cdot$TMEDA (TMEDA = *N*,*N*,*N*,*N*-tetramethylethylenediamine) in toluene at −78 °C results in rapid dissolution of the starting material and the deposition of an insoluble white precipitate. Upon

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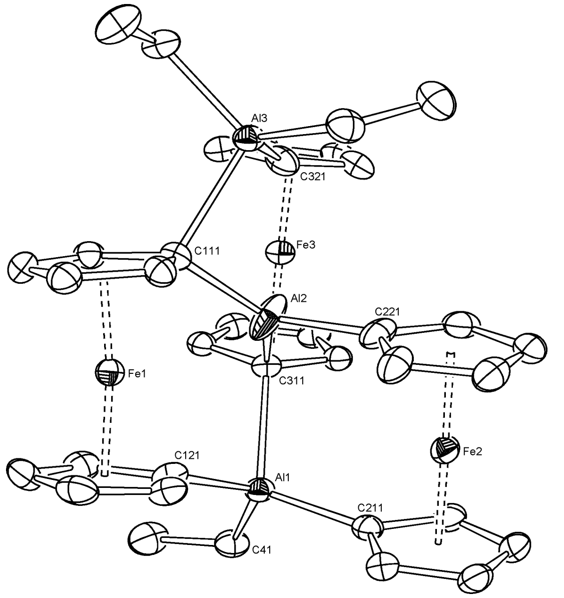
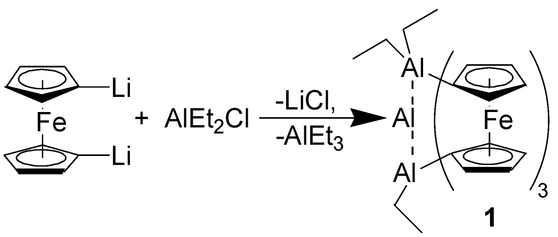


Figure 1. ORTEP representation of and numbering scheme for **1**.[13]

Scheme 1



workup, red-orange crystals of **1** can be obtained after filtration and crystallization from toluene or benzene (Scheme 1).

The presence of $AlEt_3$ is evidenced by observation of a first-order triplet and a quartet at $\delta = 1.24$ and 0.44 ppm, respectively, in the ^{1}H NMR spectrum of crude **1**; presumably, extrusion of $AlEt_3$ occurs after metathesis and elimination of LiCl.

An ORTEP representation of **1** appears in Figure 1. The trinuclear nature of the complex is clearly revealed, but the most interesting feature is the presence of the aluminum core, centrally located between the three ferrocenyl units with each bound to a pair of cyclopentadienyl rings in a 1,1′ fashion. Although the aluminum centers lie roughly along the same vector [$\angle$Al1−Al2−Al3 = 171.27(4)°], the two metal−metal separations [Al1−Al2 = 2.9653(15), Al2−Al3 = 2.9043(15) Å] are effectively too large to invoke any interaction. The central Al2 nucleus has one short contact to a neighboring iron center [Al2−Fe3 = 2.8179(13) Å], but this is again beyond reasonable limits of interaction [$\Sigma_{\text{atomic radii}}$(Fe, Al) = 2.65 Å],[9] as further supported by DFT calculations.[10] The interaction binding the trimer together likely arises from the short 1,1′ bonds from the formally anionic cyclopentadienyl positions to the aluminum centers [ipso-C−Al separations range from 1.9399(29) to 2.1544(26) Å]. This situation is reminiscent of the bonding in the classic dialane, Al_2Ph_6, which displays both bridging Al−C−Al and terminal Al−C interactions [Al−Al = 2.702(2) Å; Al−C_{bridging} = 2.184(5); Al−C_{terminal} = 1.956(5), 1.960(4) Å].[11] In **1**, the geometrical constraints of the cyclopentadienyl (Cp) rings enforce a rigid, tight enclosure of the ferrocenyl groups around the aluminum core, and the interaction between the Cp rings and the aluminum centers is reflected by the average Cp_{centroid}−Cp_{centroid} distance observed for the ferrocenyl groups of 3.31 Å. This is to be compared with the equivalent distance of 3.35 Å observed in ferrocene itself and the distance of 3.31 Å observed in the related tris(1,1′-ferrocenyl) uranium complex $[U(1,1'\text{-Fe}(\eta^5\text{-}C_5H_4)_2)_3(C_5H_5N)_3Li_2]\cdot C_5H_5N$ that also exhibits a linear trimetallic core;[12] the observed compression in **1** arguably derives from ipso-C−Al interactions along the aluminum core.

Regarding the solution structure of the molecule, ^{1}H NMR spectroscopy in methylene chloride-d_2 or benzene-d_6 reveals two sets of the familiar $[AX]_2$ pattern associated with singly substituted cyclopentadienyl rings in equal intensities and first-order patterns due to two nonequivalent ethyl groups in a ratio of 2:1. This is precisely in accord with the solid-state structure, if the three capping cyclopentadienyl groups bound to Al1 (i.e., C211, C121, and C311) are designated as equivalent and likewise the cyclopentadienyl groups are proximate to Al3. Such a scheme gives rise to two sets of cyclopentadienyl groups as observed in the ^{1}H NMR spectrum. In the same manner, the ethyl groups bound to Al3 and Al1 give rise to two absorptions in a 2:1 ratio as observed. Of course, under this regime, a dynamic process must be invoked that equates each set of cyclopentadienyl groups without interchanging the ethyl groups bound to aluminum; however, given the apparent coordinative unsaturation and Lewis acidity of Al2, the central aluminum

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(10) Calculations of the Wiberg bond indices for all Fe−Al pairs with values close to zero (0.002−0.027) show that there is no covalent bond between the metal centers; an electron localization function (ELF) study with no bond attractors among metal atoms supports this finding. The DFT/B3LYP-optimized structure of **1** agrees well with the X-ray data. The calculations employed the Wachters+f full-electron basis set for Fe and the 6-31G(d,p) set for other elements. The electronic structure of **1** was studied by means of the built-in NBO module of the Gaussian 03 (ref 10b) and TopMoD (ref 10c) packages. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian Inc.: Pittsburgh, PA, 2003. (c) Noury, S.; Krokidis, X.; Fuster F.; Silvi, B. *TopMoD*; Université Pierre et Marie Curie: Paris, 1997.

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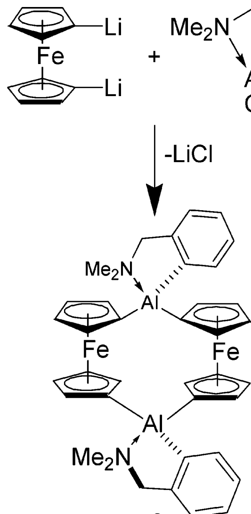
Scheme 2



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center in the trimer, such a process should be low in energy. It is therefore submitted that there is no difference between the solid-state and solution structures.

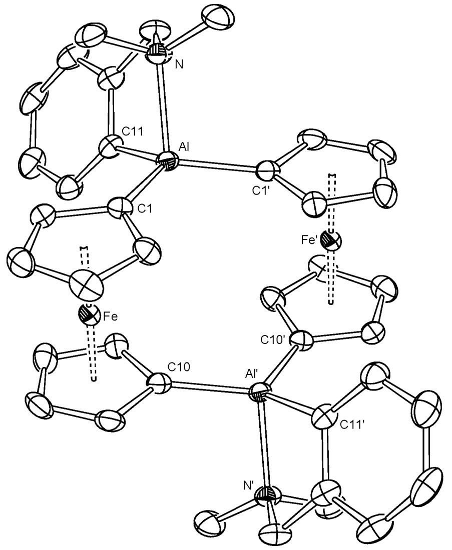

Figure 2. ORTEP representation of and numbering scheme for **2**.[15]

Reaction of $[Fe(\eta^5\text{-}C_5H_4)_2]Li_2{\cdot}TMEDA$ with a stoichiometric amount of the base-stabilized aluminum reagent $Al(\kappa^2\text{-}C,N NMe_2CH_2C_6H_4)Cl_2$[14] (Scheme 2) allows isolation of the [1,1′]-ferrocenophane derivative, $[Fe(\eta^5\text{-}C_5H_4)_2(AlNMe_2CH_2C_6H_4)]_2$ (**2**), whose X-ray structure appears in Figure 2. Given base stabilization by the CH_2NMe_2 pendant arm, each aluminum center participates in a symmetric [1,1′]-metallocenophane interaction, a bonding situation that has previously been unknown for aluminum. Curiously, the equivalent experiment in which $Al\{\kappa^2\text{-}C,N2\text{-}(C(SiMe_3)_2SiMe_2)C_5H_4N\}Cl_2$ is used as the aluminum source gives the [1]-ansa-aluminum compound, $Fe(\eta^5\text{-}C_5H_4)_2(AlC(SiMe_3)_2SiMe_2C_5H_4N)$; here, however, steric saturation around Al is much greater than in **2** and might act to stabilize the monomer.[7] Bond distances in **2** around the saturated aluminum center are unremarkable [Al−N = 2.0748(14) Å; Al−C1, −C10, −C11 = 1.9571(16), 1.9599(17), 1.9856(17) Å, respectively], and ∠C1−Al−C10 has a value of 116.74(7)°. Although there is no solution handle on molecularity, (i.e., the hypothetical ansa-Al-bridged species would give rise to a similar ^1H NMR spectrum), it is unreasonable to suppose that crystallization from solution would involve association of monomers, especially given that the dimer is relatively unstrained. Four unique cyclopentadienyl resonances of equal intensity (2H) are observed in the ^1H NMR spectrum of **2** in benzene-d_6 as required, and the spectrum is completed by four aryl (8H), one methylene (4H), and one *N*-methyl (6H) absorptions.

In conclusion, although limited examples of direct bonds between ferrocene and aluminum have so far been known, treatment of $[Fe(\eta^5\text{-}C_5H_4)_2]Li_2{\cdot}TMEDA$ by $AlEt_2Cl$ has allowed the isolation and structural characterization of **1**, a trimeric ferrocenyl derivative with an unusual core of aluminum nuclei. On the other hand, the base-stabilized aluminum reagent $Al(\kappa^2\text{-}C,N NMe_2CH_2C_6H_4)Cl_2$ affords a regular 1,1′-ferrocenophane with an unprecedented aluminum bridge in **2**. Efforts to extend this chemistry to other transition metal metallocenes and bis-arene complexes are ongoing.

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Supporting Information Available: X-ray crystallographic data (CIF) and details of experimental methods (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal data for **1**: $C_{36}H_{39}Al_3Fe_3{\cdot}1.5C_6H_6$, $M_r = 837.32$, orange blocks, 0.5 × 0.3 × 0.3 mm, triclinic, space group $P\bar{1}$, $a = 11.1136(14)$ Å, $b = 12.7965(16)$ Å, $c = 13.6370(17)$ Å, $\alpha = 84.901(2)°$, $\beta = 75.131(2)°$, $\gamma = 88.444(2)°$, $V = 1867.0(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.489$ g·cm^{-3}, $\mu = 1.254$ cm^{-2}, $F(000) = 870$, $T = 173$ K; Bruker APEX diffractometer with CCD area detector, graphite-monochromated Mo Kα radiation. The structure was solved by direct methods, refined with the SHELX software package, and expanded by Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. R1 = 0.0391, wR2 = 0.0982, 7380 independent reflections ($2\theta \leq 52.3°$), and 460 parameters.

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(15) Crystal data for **2**: $C_{38}H_{40}Al_2Fe_2N_2$, $M_r = 690.38$, orange-red blocks, 0.3 × 0.2 × 0.15 mm, monoclinic, space group P2(1)/c, $a = 10.3099(6)$ Å, $b = 11.6422(9)$ Å, $c = 14.0998(9)$ Å, $\alpha = 90°$, $\beta = 106.336(7)°$, $\gamma = 90°$, $V = 1624.07(19)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.412$ g·cm^{-3}, $\mu = 0.978$ cm^{-2}, $F(000) = 720$, $T = 193$ K; STOE-IPDS diffractometer with area detector, graphite-monochromated Mo Kα radiation. The structure was solved by direct methods, refined with the SHELX software package, and expanded by Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. R1 = 0.0380, wR2 = 0.0704, 3463 independent reflections ($2\theta \leq 53.78°$), and 201 parameters.