Synthesis and *X*-Ray Crystal Structure of the Novel Ferrocenylalane Dimer $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_3)Al_2Me_3Cl]_2$

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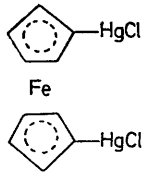
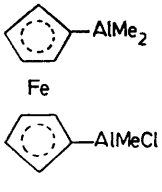
Summary The crystal structure of the novel ferrocenylalane dimer, $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_3)Al_2Me_3Cl]_2$, has revealed the presence of a unique type of bridging cyclopentadienyl group, and established a new type of ferrocenyl rearrangement.

FERROCENYL derivatives are well-known for a wide range of elements, but those of aluminium have been noteworthy in their absence. The only previously reported compound,

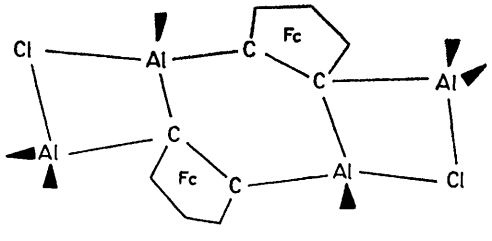


(I)



(II)

$(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)Al_2Me_4Cl$, was postulated on the basis of a ^1H n.m.r. study to possess electron-deficient methyl bridges.[1] In the course of further investigations of ferrocenylalanes a new member of the series has been isolated and characterized by *X*-ray techniques. $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_3)Al_2Me_3Cl]_2$ bears several features in common with



(III)

the electron-deficient transition metal cluster compounds $[MoH(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4)]_2Al_3Me_5$[2-4] and $[Mo(\eta\text{-}C_5H_4)_2Al_2Me_3]_2$.[2,3]

The extremely air-sensitive title compound was prepared in low yield from the reaction of trimethylaluminium with 1,1′-bischloromercuriferrocene (I) in toluene at 80 °C.

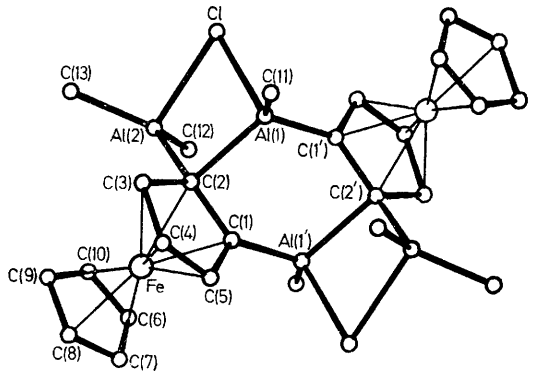


FIGURE. The molecular structure of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_3)Al_2Me_3Cl]_2$: interatomic distances (Å) not given in the text are Al(1)–Cl = 2·31(1), Al(2)–Cl = 2·48(1); angles (degrees) Al(1)–C(2)–Al(2) = 92(2), Al(1)–Cl–Al(2) = 77(1).

Compound (II) has not been isolated, but $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_3)Al_2Me_3Cl]_2$ (III) can be viewed as a rearranged dimer of (II).

$[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_3)Al_2Me_3Cl]_2$ is quite soluble in aromatic hydrocarbons, and crystals for the *X*-ray study were obtained by slow evaporation of a toluene solution. The compound was found to belong to the triclinic space group $P\bar{1}$. *Crystal data:* $a = 8.44(1)$, $b = 9{\cdot}07(1)$, $c = 11{\cdot}38(1)$ Å, $\alpha = 78{\cdot}61(6)$, $\beta = 68{\cdot}92(6)$, $\gamma = 62{\cdot}44(6)°$, $U = 706{\cdot}4$ Å^3, D_m not measured, $Z = 1$ (dimer at $\bar{1}$), $D_c = 1{\cdot}50$; 1027 reflections, $R = 0{\cdot}12$. Although five data sets were collected on five different crystals, in all cases the crystals were apparently multiple; the refinement reported is based on the data set which yielded the lowest R value (all atoms were refined with anisotropic thermal parameters, and the contributions of the hydrogen atoms were not included).

Compound (III), shown in the Figure, exhibits several interesting features. First, in the ferrocene portion of the molecule, a rearrangement has occurred such that there are now five hydrogen atoms on one cyclopentadienyl ring, and three on the other: initially in (I) there were four on each. The ferrocenyl unit itself is, however, normal in most respects: the two cyclopentadienyl rings are each planar to within 0·03 Å, and the angle of tilt of the rings is 2·4°.[5] The Fe–C bond lengths range from 1·94(2) to 2·12(2) Å and average 2·04 Å. Both of these are within the spread found in other structures,[5] and are close to the parameters for ferrocene itself.[6]

The portion of the dimer (III) involving the aluminium atoms is similar in many respects to that found in the previously reported molybdenum- and tungsten–aluminium compounds.[2–4] One carbon atom from a cyclopentadienyl ring, C(2), bridges two aluminium atoms together at distances of Al(1)–C(2) = 2·12(3) Å and Al(2)–C(2) = 2·01(3)Å. An adjacent carbon atom, C(1), is σ-bonded to Al(1) at a length of 1·98(3) Å, and completes the dimer.

Another point of comparison of (III) with $[MoH(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4)]_2Al_3Me_5$[2,4] and $[Mo(\eta\text{-}C_5H_4)_2Al_2Me_3]_2$[3] concerns the Al–metal interaction. In the latter compounds, the Al–Mo length is given as 2·66 Å. A comparison of the Mo–C lengths (2·28 average) with the Fe–C lengths (2·04 average) leads to an expected Al–Fe bond distance of 2·42 Å. In the present case the Al(2)–Fe contact is 3·15(1)Å: any significant Al–Fe bonding can be ruled out. Likewise, there is no evidence for any form of Al–H–Fe bond analogous to those found in $[(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4)TiHAlEt_2]_2$.[7]

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