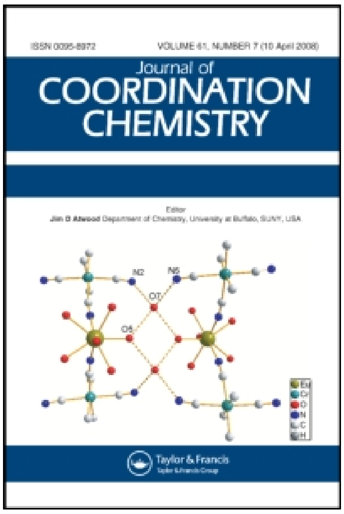

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Triethylaluminum-Based Ferrocenylalanes. Synthesis and Crystal Structure of (η^5-C_5H_5)Fe[η^5-$C_5H_4Al_2(C_2H_5)_4Cl$]

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TRIETHYLALUMINUM-BASED FERROCENYLALANES. SYNTHESIS AND CRYSTAL STRUCTURE OF $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4Al_2(C_2H_5)_4Cl]$.

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The trietheylaluminum based ferrocenylalane $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4Al_2(C_2H_5)_4Cl]$ was prepared from the reaction of triethylaluminum with chloromercuriferrocene in toluene and characterized by single crystal X-ray diffraction. The compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 9.353(3)$ Å, $b = 10.281(7)$ Å, $c = 11.599(9)$ Å, $\alpha = 79.64(7)°$, $\beta = 69.41(6)°$, $\gamma = 84.33(4)°$, and $Z = 2$ for $D_c = 1.27$ g cm^{-3}. Full-matrix least-squares refinement has led to a final R factor of 0.068 based on 1866 independent observed reflections. The two diethylaluminum units are bridged by a chlorine atom and one carbon atom of a cyclopentadienyl group, thus forming an Al-Cl-Al-C ring. The four-membered ring is planar to within 0.02 Å. The Al-Cl distances are 2.404(4) Å and 2.266(5) Å. The Al-Cl-Al angle is 78.9(1)° while the Al-C-Al angle is 91.3(4)°. No significant aluminum-iron interaction is observed (Al ... Fe = 3.137(4) Å).

Key words: aluminium alkyl, ferrocenylalane, synthesis, structure, bonding.

INTRODUCTION

Apart from Ziegler-Natta catalysts, the interaction of metallocene species with complexes of aluminum and its congeners has generated little attention. This is particularly surprising since the few metallocene-aluminum complexes reported have proved interesting in terms of structure and bonding, as is illustrated by the product of the reaction of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ with trimethylaluminum, $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)MoH]_2Al_3(CH_3)_5$.[1] Since the chemistry of ferrocenyl groups has been extensively studied, it is noteworthy that only two ferrocenylalanes have been characterized: $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)Al_2(CH_3)_3Cl]_2$ (I)[2] and $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4Al_2(CH_3)_4Cl]$ (II).[3,4]

The structure of **I** was interesting, but crystallographic difficulties precluded a detailed description of the bonding of the ferrocenyl units to the aluminum atoms. However, the structure of **II** afforded metrical details which were indicative of the bonding mode of the bridging cyclopentadienyl group. Since arguments rested on nonbonded interactions between methyl groups and the ferrocenyl unit, we sought the structure of the $Al(C_2H_5)_3$ derivative.

EXPERIMENTAL

The title compound is extremely air- and moisture-sensitive. The exclusion of oxygen from the synthesis and subsequent manipulations was achieved by using Schlenk techniques in conjunction with an inert atmosphere glove box (Vacuum Atmospheres HE-43 Dri-Lab). Toluene was distilled from sodium/benzophenone under an atmosphere of nitrogen immediately prior to use. Chloromercuriferrocene and triethylaluminum were purchased from Aldrich Chemical Company and both were used as received.

Inside the glove box, a 150 cm^3 Schlenk flask was charged with (η^5-C_5H_5)Fe[η^5-C_5H_4HgCl] (4.75 mmol), 20 cm^3 of toluene, and $Al(C_2H_5)_3$ (9.5 mmol). The flask was removed from the glove box and heated at 60°C for twelve hours. This produced a deep red solution. Removal of some solvent (and the $Hg(C_2H_5)_2$) and subsequent cooling produced large red rectangular crystals (mp 35–37°C) in *ca* 50% yield.

Single crystals of the title compound were mounted in thin-walled glass capillaries (under N_2) for X-ray structure determination.

Structure Solution and Refinement

A summary of data collection parameters and final lattice parameters as determined from the least-squares refinement of $(\sin \phi/\lambda)^2$ values for 24 reflections (2ϕ 25°) accurately centred on an Enraf-Nonius CAD-4 diffractometer are given in Table I. Data were collected by the ϕ-2ϕ scan technique as described previously.[5] The intensities were corrected for Lorentz, polarization, and absorption effects. Calculations were carried out using the SHELX system of computer programs.[6] Neutral atom scattering factors for Fe and Al were taken from Cromer and Waber,[7] and those stored within the SHELX program were used for other atoms. The scattering for all atoms was corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman.[8]

Structure solution was accomplished by means of the direct methods program MULTAN,[9] which gave the location of the Fe, Cl and Al atoms. Difference Fourier

TABLE I
Crystal data, summary of intensity data collection, and structure determination for (η^5-C_5H_5)Fe[η^5-$C_5H_4Al_2(C_2H_5)_4Cl$].

formula	$C_{18}H_{29}Al_2FeCl$
mol wt	390.44
space group	$P\bar{1}$
a, Å	9.353(3)
b, Å	10.281(7)
c, Å	11.599(9)
α, deg	79.64(7)
β, deg	69.41(6)
γ, deg	84.33(4)
cell vol. Å^3	1026
Z	2
D_c, g cm^{-3}	1.27
μ_c, cm^{-1}	9.49
max cryst. dimens, mm	0.40 × 0.50 × 1.0
scan width	$0.85 + 0.2 \tan\theta$
variation of stds.	< 2%
2θ range, deg	2–42
obsd. reflctns.	1866
no. of parameters varied	199
temp, °C	22
radiation	Mo$K\alpha$, $\lambda = 0.71069$ Å
GOF	1.42
R	0.068
R_w	0.072

TABLE II
Final fractional coordinates and their estimated standard deviations for $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4Al_2(C_2H_5)_4Cl]$.

Atom	*x/a*	*y/b*	*z/c*
Fe	1.1493(2)	0.1752(1)	0.1886(1)
Al(1)	0.8017(4)	0.2397(3)	0.2294(3)
Al(2)	0.7955(4)	0.3694(3)	0.4402(3)
Cl	0.5965(3)	0.3453(3)	0.3783(3)
C(1)	1.301(2)	0.031(1)	0.116(1)
C(2)	1.160(2)	0.001(1)	0.125(1)
C(3)	1.107(1)	0.104(1)	0.051(1)
C(4)	1.225(2)	0.196(1)	−0.0005(9)
C(5)	1.344(1)	0.151(1)	0.044(1)
C(6)	1.022(1)	0.156(1)	0.3715(8)
C(7)	1.172(1)	0.181(1)	0.3542(9)
C(8)	1.215(1)	0.302(1)	0.275(1)
C(9)	1.087(1)	0.351(1)	0.2461(8)
C(10)	0.960(1)	0.2668(9)	0.3043(7)
C(11)	0.724(2)	0.061(1)	0.266(1)
C(12)	0.588(2)	0.022(2)	0.270(2)
C(13)	0.809(1)	0.363(1)	0.0731(9)
C(14)	0.665(2)	0.402(2)	0.050(1)
C(15)	0.837(1)	0.556(1)	0.415(1)
C(16)	0.834(2)	0.644(1)	0.304(1)
C(17)	0.755(1)	0.264(1)	0.6075(8)
C(18)	0.644(2)	0.327(1)	0.712(1)

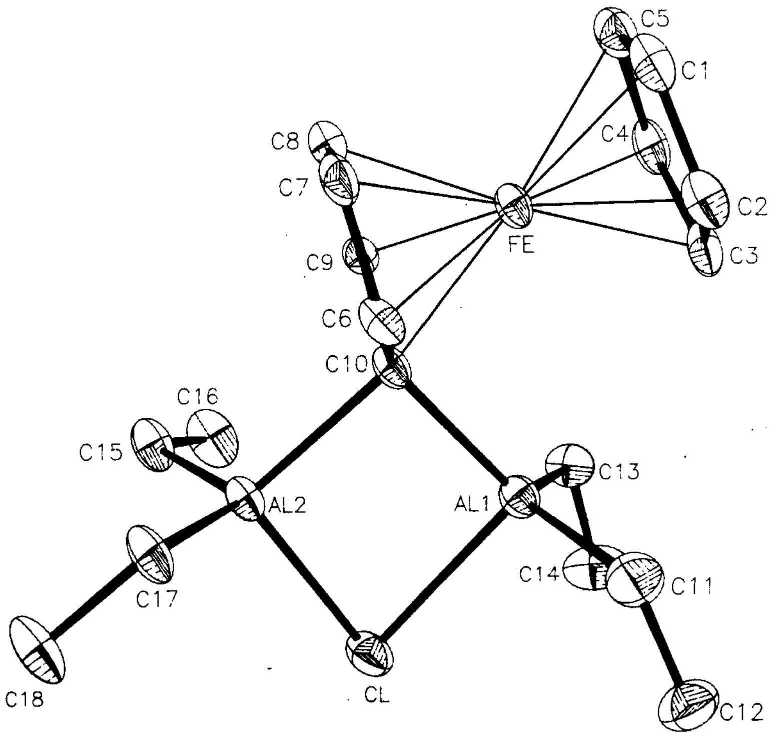

FIGURE 1 Structure of $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4Al_2(C_2H_5)_4Cl]$.

maps phased on these atoms readily revealed the positions of the remaining non-hydrogen atoms. Disorder was noted for one of the terminal ethyl carbons, C(12), and separate refinement of the positional and thermal parameters and the occupancy factors showed this to be in the ratio of 2:1. (The disorder involves a rotation of the ethyl group about the Al-C bond). Refinement of all non-hydrogen atoms except the disordered carbon with anisotropic thermal parameters led to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.088$, at which as many hydrogen atoms as possible were geometrically positioned and allowed to ride upon the relevant carbon atoms. Further refinement converged at $R = 0.068$, $R_w = 0.072$.

A final difference Fourier showed no feature greater than 0.3e/Å^3. The weighing scheme was based upon unit weights, and no systematic variation of $w(|F_o| - |F_c|)^2$ *vs* $|F_o|$ or $(\sin \phi/\lambda)$ was observed. The final fractional coordinates of the non-hydrogen atoms are given in Table II.

RESULTS AND DISCUSSION

The structure of the title compound, $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4Al_2(C_2H_5)_4Cl]$ **(III)**, is shown in Figure 1. Important bond distances and angles are presented in Table III. The low

TABLE III
Selected bond distances (Å) and angles (deg) for $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4Al_2(C_2H_5)_4Cl]$.

)Atoms	Distance	Atoms	Distance
Fe — C(1)	2.03(1)	Fe — C(2)	2.03(1)
Fe — C(3)	2.04(2)	Fe — C(4)	2.031(9)
Fe — C(5)	2.03(1)	Fe — C(6)	2.018(8)
Fe — C(7)	2.02(1)	Fe — C(8)	2.04(1)
Fe — C(9)	2.00(1)	Fe — C(10)	2.069(8)
Al(1) — Cl	2.404(4)	Al(1) — C(10)	2.02(1)
Al(1) — C(11)	1.97(1)	Al(1) — C(13)	2.00(1)
Al(2) — Cl	2.266(5)	Al(2) — C(10)	2.129(9)
Al(2) — C(15)	1.95(1)	Al(2) — C(17)	1.973(9)
C(1) — C(2)	1.35(2)	C(1) — C(5)	1.36(2)
C(2) — C(3)	1.40(2)	C(3) — C(4)	1.42(2)
C(4) — C(5)	1.39(2)	C(6) — C(7)	1.39(2)
C(6) — C(10)	1.45(1)	C(7) — C(8)	1.41(2)
C(8) — C(9)	1.38(2)	C(9) — C(10)	1.43(1)
C(11) — C(12)	1.35(3)	C(13) — C(14)	1.47(2)
C(15) — C(16)	1.44(2)	C(17) — C(18)	1.50(1)
Fe . . . . .Al(1)	3.137(4)	Al(1) . . .Al(2)	2.970(5)
Atoms	Angle	Atoms	Angle
Cl — Al(1) — C(11)	99.9(4)	Cl — Al(1) — C(10)	94.2(3)
Cl — Al(1) — C(13)	99.9(3)	C(10) — Al(1) — C(11)	116.4(6)
C(11) — Al(1) — C(13)	122.1(7)	C(10) — Al(1) — C(13)	115.6(5)
Cl — Al(2) — C(15)	109.8(5)	Cl — Al(2) — C(10)	95.5(3)
Cl — Al(2) — C(17)	107.3(4)	C(10) — Al(2) — C(15)	112.4(4)
C(15) — Al(2) — C(17)	119.34(5)	C(10) — Al(2) — C(17)	109.8(4)
C(2) — C(1) — C(5)	112(1)	Al(1) — Cl — Al(2)	78.9(1)
C(2) — C(3) — C(4)	106(1)	C(1) — C(2) — C(3)	107(1)
C(1) — C(5) — C(4)	106(1)	C(3) — C(4) — C(5)	109(1)
C(6) — C(7) — C(8)	110(1)	C(7) — C(6) — C(10)	108.9(9)
C(8) — C(9) — C(10)	113.2(9)	C(7) — C(8) — C(9)	105(1)
Al(1) — C(10) — Al(2)	91.3(4)	Al(2) — C(10) — C(6)	107.0(6)
Al(1) — C(10) — C(6)	121.2(8)	Al(1) — C(10) — C(9)	125.6(7)
Al(2) — C(10) — C(9)	106.1(6)	C(6) — C(10) C(9)	102.5(9)
Al(1) — C(11) C(12)	130(1)	Al(1) — C(13) C(14)	118.3(8)
Al(2) — C(15) — C(16)	121(1)	Al(2) — C(17) C(18)	115.1(8)

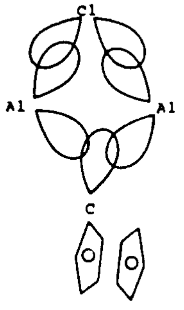

FIGURE 2 Proposed bonding scheme for the bridging groups in ferrocenylalane **II**.[4]

melting point of the compound gave rise to rather high thermal parameters for the atoms, which in turn led to higher standard deviations than were desired. However, several points of significance arise. First, the severe interaction of the C_5H_5 group with the nearby methyl groups in **II** was deduced from a study of the bond distances and angles together with a consideration of the ^1H NMR spectrum. For **III** the repulsion is clearly shown by the configuration of the ethyl groups; both C(12) and C(14) lie far from the C_5H_5 group.

Secondly, the close equivalence of the parameters of the core in **III** compared to **II** is interesting.[10] Indeed, the similarity can best be appreciated by a survey of the title compound in which the values in brackets are the related one for the methyl derivative: Al(1)-C(10) = 2.02(1) [2.026(8)] Å, Al(2)-C(10) = 2.129(9) [2.116(8)] Å, Al(2)-Cl = 2.266(5) [2.260(4)] Å, Al(1)-C(1) = 2.404(4) [2.410(4)] Å, Al(1)-C(10)-Al(2) = 91.3(4) [91.03(3)]°, and Al(1)-Cl-Al(2) = 78.9(1) [78.4(1)]°. Even the pattern of apparent bond localization in the bridging cyclopentadienyl ring in **II** is maintained in **III**.

In the discussion of the bonding in **II**[4] it was pointed out that the presence of the ferrocenyl group produces the situation depicted in Figure 2. Thus, the Al-C bond nearer the ferrocenyl unit is shorter. Related arguments concerning the Al-Cl bonds have been given.[4]

In order to further place the bond lengths in perspective, additional comparisons are necessary. The Al(1)-C(10) (bridging) distance, 2.02(1) Å, is just outside the range of the terminal Al-C lengths in this structure, 1.95–2.00 Å, and in others.[11] The Al(2)-C(10) (bridging) length, 2.129(9) Å, is near the Al-C (bridging) value in $[Al(CH_3)_3]_2$, 2.124(1) Å.[12] The Al(2)-Cl distance, 2.266(5) A, is as expected for a bridging situation (i.e., 2.25 Å in $[AlCl_2(CH_3)]_2$[13]). The remaining Al-Cl length, 2.404(4) Å, is unprecedented outside the realm of **I**, **II**, and **III**.

The Al-C-Al-Cl ring is planar to within 0.02 Å. In **II**, crystallographic symmetry constrained the analogous atoms to planarity. The Al... Fe separation of 3.137(4) Å is too long to be indicative of a metal-metal interaction.

The bond distances and angles in the ferrocenyl unit itself are near those found for ferrocene.[14] The angle of tilt of the two cyclopentadienyl rings is 6.6° in **III** compared to 8.3° in **II**.

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SUPPLEMENTARY MATERIAL

Tables of hydrogen atom coordinates, anisotropic thermal parameters, and structure factors are available from the Editor.

REFERENCES

1. M.L.H. Green, R.E. MacKenzie and J.S. Poland, *J. Chem. Soc., Dalton Trans.*, 1993 (1976); S.J. Rettig, A. Storr, B.S. Thomas and J. Trotter, *Acta Crystallogr.*, **B30**, 2312 (1974).
2. J.L. Atwood and A.L. Shoemaker, *J. Chem. Soc., Chem. Commun.*, 536 (1976).
3. J.L. Atwood, B.L. Bailey, B.L. Kindberg and W.J. Cook, *Aust. J. Chem.*, **26**, 2297 (1973).
4. R.D. Rogers, W.J. Cook and J.L. Atwood, *Inorg. Chem.*, **18**, 279 (1979).
5. J. Holton, M.F. Lappert, D.G.H. Ballard, R. Pearce, J.L. Atwood and W.E. Hunter, *J. Chem. Soc., Dalton Trans.*, 45 (1979).
6. SHELX, a system of computer programs for X-ray structure determination by G.M. Sheldrick, 1976.
7. D.T. Cromer and J.T. Waber, *Acta Cryst.*, **18**, 104 (1965).
8. D.T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
9. G. Germain, P. Main, M.M. Woolfson, *Acta Cryst.*, **A27**, 368 (1971).
10. The two compounds crystallize in different space groups, *Pnma* for **II** and *P*1 and **III**.
11. J.H. Medley, F.R. Fronczek, N. Ahmad, M.C. Day, R.D. Rogers, C.R. Kerr and J.L. Atwood, *J. Cryst. Spec. Res.*, **15**, 99 (1985).
12. J.C. Huffman and W.E. Streib, *J. Chem. Soc., Chem. Commun.*, 911 (1971).
13. G. Allegra, G. Perego and A. Immirzi, *Makromol. Chem.*, **61**, 69 (1963).
14. P. Seiler and J.D. Dunitz, *Acta Cryst.*, **B35**, 1068 (1979); F. Takusagawa and T.F. Koetzle, *Acta Cryst.*, **B35**, 1074 (1979).