

Figure 6. Solution (a) and solid-state (b) electronic spectra for $[\text{Mn}(\text{C}_{22}\text{H}_{22}\text{N}_4)\text{NCS}]$. Spectrum (a) was taken in chloroform; spectrum (b) was taken in a Nujol mull between KBr plates. The intensity for (b) is recorded on an arbitrary scale.

$\pi-\pi^*$ and $d-\pi^*$ transition energies would show shifts relative to the nonaggregated solution spectra.

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Registry No. $[\text{Mn}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\text{NCS})]$, 56943-21-6.

Supplementary Material Available: A listing of the observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, University of Alabama, University, Alabama 35486

Ferrocenylalanes. 3. Synthesis and Crystal Structure of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{Al}_2(\text{CH}_3)_4\text{Cl}]$

ROBIN D. ROGERS, WILLIAM J. COOK, and JERRY L. ATWOOD*

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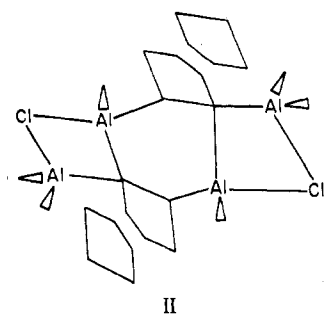
The crystal structure of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{Al}_2(\text{CH}_3)_4\text{Cl}]$ has been determined from three-dimensional X-ray data measured by counter methods. The compound crystallizes in the orthorhombic space group $Pnma$ with unit cell dimensions $a = 9.047$ (3) Å, $b = 11.944$ (4) Å, $c = 15.395$ (4) Å, and $Z = 4$ for $\rho_{\text{calcd}} = 1.34 \text{ g cm}^{-3}$. Full-matrix least-squares refinement has led to a final R factor of 0.041 based on 908 independent observed reflections. The molecule resides on a crystallographic mirror plane which contains the iron, aluminum, and chlorine atoms, and two of the cyclopentadienyl carbon atoms. The two dimethylaluminum units are bridged together by the chlorine atom and one carbon atom of a cyclopentadienyl group. Within the four-membered ring the bonding exhibits effects which may be attributed to the steric requirements of the ferrocenyl ligand: the aluminum-carbon (bridge) lengths are 2.026 (8) and 2.116 (8) Å, while the aluminum-chlorine distances are 2.260 (4) and 2.410 (4) Å. The angle of tilt of the two cyclopentadienyl rings is 8.3° . No significant aluminum-iron interaction is present ($\text{Al-Fe} = 3.100$ (3) Å).

Introduction

Recently a number of interesting compounds which contain both aluminum and transition-metal atoms have been prepared of which $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4)\text{MoH}]_2\text{Al}_3(\text{CH}_3)_5$ is an example. Ferrocenyl derivatives of group 3A metals, however, have received very little attention. There exist a few compounds containing one or more ferrocenyl units bonded to boron² but none of these has been fully characterized

structurally. Of the ferrocenylalanes, only two have been prepared: $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{Al}_2(\text{CH}_3)_3\text{Cl}]_2$ (I) and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{Al}_2(\text{CH}_3)_4\text{Cl}]$ (II).

X-ray crystallographic characterization of I revealed some interesting features of the bonding in these compounds. Of particular importance was the asymmetric manner in which the Cl atom was found to bridge the two Al atoms. One of the distances, 2.31 (1) Å, was typical for a chloro bridge, but

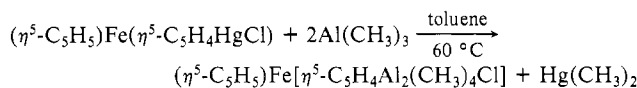


the other, 2.48 (1) Å, was the largest yet reported. This, together with the unusually sharp Al-Cl-Al angle of 77°, was sufficiently unique to warrant further study. Unfortunately, all of the crystals of I investigated proved to be badly twinned and severe limitations were therefore imposed upon the derived parameters. This problem also made it impossible to discern the detailed features of the bridging cyclopentadienyl group.

We have previously communicated⁴ the synthesis and preliminary ¹H NMR characterization of the other member of this series, (η⁵-C₅H₅)Fe[η⁵-C₅H₄Al₂(CH₃)₄Cl]. At room temperature, all methyl hydrogen atoms were equivalent while at -40 °C two signals in the ratio 1:1 were found. The upfield resonance, δ -0.31, was typical of an Al-CH₃ terminal resonance. The other signal, δ 0.05, was further downfield than any known Al-CH₃ terminal resonance and was in fact comparable to the methyl resonance in an electron-deficient Al-CH₃-Al situation. This led to the suggestion that the methyl groups might be involved in some type of bridging arrangement in II. The results reported herein show that in the solid state the two Al atoms are bridged by a Cl atom and one cyclopentadienyl group of the ferrocene unit.

Experimental Section

The title compound was prepared by the reaction of chloromercuriferrocene with trimethylaluminum in a sealed tube according to the overall equation



Dimethylmercury was not isolated but is included for a mass balance. Reaction began immediately and a dark green solution resulted. Twelve hours of heating at 60 °C produced a deep red solution. The liquid was separated, and the residue extracted with toluene. Concentration of the combined toluene solutions yielded red air-sensitive crystals of (η⁵-C₅H₅)Fe[η⁵-C₅H₄Al₂(CH₃)₄Cl], mp 108–109 °C.

Single crystals of the compound were sealed in thin-walled glass capillaries prior to X-ray examination. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections (2θ > 20°) accurately centered on an Enraf-Nonius CAD-4 diffractometer are given in Table I.

Data were collected on the diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω-2θ scan technique with a takeoff angle of 3.5°. The scan rate was variable and was determined by a fast 20° min⁻¹ prescan. Calculated speeds for the slow scan (based on the net intensity in the prescan) ranged from 7 to 0.4° min⁻¹. Other diffractometer parameters and the method of estimation of standard deviations have been previously described.⁵ As a check on the stability of the instrument and crystal, two reflections were measured after every 40 reflections; no significant variation was noted.

One independent octant of data was measured out to 2θ = 50°; a slow scan was performed on a total of 908 unique reflections. Since these data were scanned at a speed which should yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflections were subjected to a slow scan unless a net count of 30 was obtained in the prescan. On the basis of these considerations, the data set of 908 reflections (used in the subsequent structure determination and refinement) was considered observed and consisted of those for which I ≥ 3σ(I). The intensities were corrected for Lorentz

Table I. Crystal Data

compd	FeClAl ₂ C ₁₄ H ₂₁
mol wt	334.6
linear abs coeff, cm ⁻¹	11.79
calcd density, g cm ⁻³	1.34
max crystal dimensions, mm	0.20 × 0.20 × 0.20
space group	<i>Pnma</i>
molecules/unit cell	4
cell constants, Å	<i>a</i> = 9.047 (3) <i>b</i> = 11.944 (4) <i>c</i> = 15.395 (4)
cell vol, Å ³	1663.5

^a Mo Kα radiation, 0.710 69 Å. Ambient temperature of 22 °C.

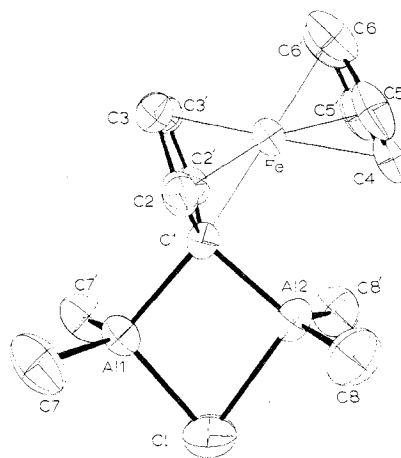


Figure 1. Molecular structure of (η⁵-C₅H₅)Fe[η⁵-C₅H₄Al₂(CH₃)₄Cl] with the atoms represented by their 50% probability ellipsoids for thermal motion.

and polarization effects but not for absorption (μ = 11.79 cm⁻¹).

The function w(|F_o| - |F_c|)² was minimized.⁶ No corrections were made for extinction. Neutral atom scattering factors were taken from the compilations of Cromer and Waber⁷ for Fe, Cl, Al, and C, and that of Fe was corrected for the real and imaginary components of anomalous dispersion.⁸ Scattering factors for H were from ref 9.

Structure Solution and Refinement

The position of the iron atom was deduced by the inspection of a Patterson map, and the subsequent calculation of a Fourier map allowed the location of the 17 remaining nonhydrogen atoms. Refinement with isotropic temperature factors led to a reliability index of R₁ = Σ(|F_o| - |F_c|) / Σ|F_o| = 0.108. Conversion to anisotropic thermal parameters and further refinement gave R₁ = 0.061. The hydrogen atoms of the cyclopentadienyl rings were placed at calculated positions 1.00 Å from the bonded carbon atoms and their parameters were refined for three cycles at a damping factor of 0.2. Those of the methyl groups were located on a difference Fourier map and their parameters were treated similarly. Additional cycles of refinement led to final values of R₁ = 0.041 and R₂ = {Σ(|F_o| - |F_c|)² / Σ|F_o|²}^{1/2} = 0.045. (Attempted refinement in the acentric space group *Pn2₁a* produced high correlations between parameters of atoms related by the mirror plane in *Pnma*.) The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. A final difference Fourier showed no feature greater than 0.3 e/Å³. The standard deviation of an observation of unit weight was 0.91. Unit weights were used at all stages; no systematic variation of w(|F_o| - |F_c|) vs. |F_o| or (sin θ)/λ was noted. The final values of the positional and thermal parameters are given in Table II.¹⁰

Discussion

The molecule, shown in Figure 1, resides on a crystallographic mirror plane which contains the Fe, Cl, and both of the Al atoms. The cyclopentadienyl rings are bisected by the plane and exist in an eclipsed configuration. The angle of tilt of the two rings is 8.3°. An angle of this magnitude is normally only found in situations in which the two rings are bridged together.¹¹ A value of 2° was found for [(η⁵-C₅H₅)Fe(η⁵-C₅H₃)Al₂(CH₃)₃Cl]₂. As discussed below, the origin of the

Table II. Final Fractional Coordinates and Anisotropic Thermal Parameters^a for $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{Al}_2(\text{CH}_3)_4\text{Cl}]$

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	1.0038 (1)	0.7500 (0)	0.0522 (1)	0.0104 (2)	0.0057 (1)	0.0027 (1)	0.0000 (0)	-0.0009 (1)	0.0000 (0)
Cl	0.4768 (3)	0.7500 (0)	-0.0688 (2)	0.0104 (4)	0.0187 (4)	0.0075 (2)	0.0000 (0)	-0.0012 (2)	0.0000 (0)
Al(1)	0.6880 (3)	0.7500 (0)	-0.1472 (2)	0.0126 (4)	0.0059 (2)	0.0035 (1)	0.0000 (0)	-0.0016 (2)	0.0000 (0)
Al(2)	0.6615 (3)	0.7500 (0)	0.0440 (2)	0.0124 (4)	0.0075 (2)	0.0041 (1)	0.0000 (0)	0.0018 (2)	0.0000 (0)
C(1)	0.8340 (9)	0.7500 (0)	-0.0398 (5)	0.0096 (10)	0.0059 (6)	0.0029 (4)	0.0000 (0)	0.0000 (6)	0.0000 (0)
C(2)	0.9357 (7)	0.6533 (5)	-0.0487 (4)	0.0132 (8)	0.0081 (6)	0.0034 (3)	0.0017 (6)	-0.0007 (4)	-0.0009 (4)
C(3)	1.0810 (6)	0.6912 (6)	-0.0636 (4)	0.0104 (8)	0.0137 (8)	0.0042 (3)	0.0037 (7)	0.0007 (4)	-0.0014 (4)
C(4)	0.9267 (12)	0.7500 (0)	0.1795 (6)	0.0176 (16)	0.0142 (12)	0.0024 (4)	0.0000 (0)	-0.0017 (7)	0.0000 (0)
C(5)	1.0194 (9)	0.6541 (6)	0.1625 (4)	0.0238 (14)	0.0086 (6)	0.0038 (3)	0.0005 (9)	-0.0035 (6)	0.0011 (4)
C(6)	1.1579 (8)	0.6899 (6)	0.1363 (4)	0.0182 (12)	0.0101 (7)	0.0055 (4)	0.0015 (8)	-0.0053 (6)	0.0001 (4)
C(7) [Al(1)]	0.7007 (9)	0.6092 (6)	-0.2096 (4)	0.0243 (15)	0.0070 (6)	0.0060 (4)	0.0007 (8)	-0.0048 (6)	-0.0016 (4)
C(8) [Al(2)]	0.6206 (9)	0.6055 (7)	0.0967 (5)	0.0212 (13)	0.0110 (8)	0.0072 (4)	-0.0057 (9)	0.0010 (6)	0.0016 (5)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> , Å ²	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> , Å ²
H(1) [C(2)]	0.900	0.576	-0.042	3.1	H(7) [C(7)]	0.604	0.593	-0.243	6.9
H(2) [C(3)]	1.169	0.642	-0.071	4.9	H(8) [C(7)]	0.810	0.596	-0.240	6.3
H(3) [C(4)]	0.833	0.750	0.197	6.2	H(9) [C(8)]	0.671	0.596	0.136	7.4
H(4) [C(5)]	0.974	0.578	0.166	4.0	H(10) [C(8)]	0.527	0.569	0.092	7.7
H(5) [C(6)]	1.259	0.642	0.116	4.7	H(11) [C(8)]	0.647	0.550	0.054	6.1
H(6) [C(7)]	0.692	0.561	-0.173	5.7					

^a Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

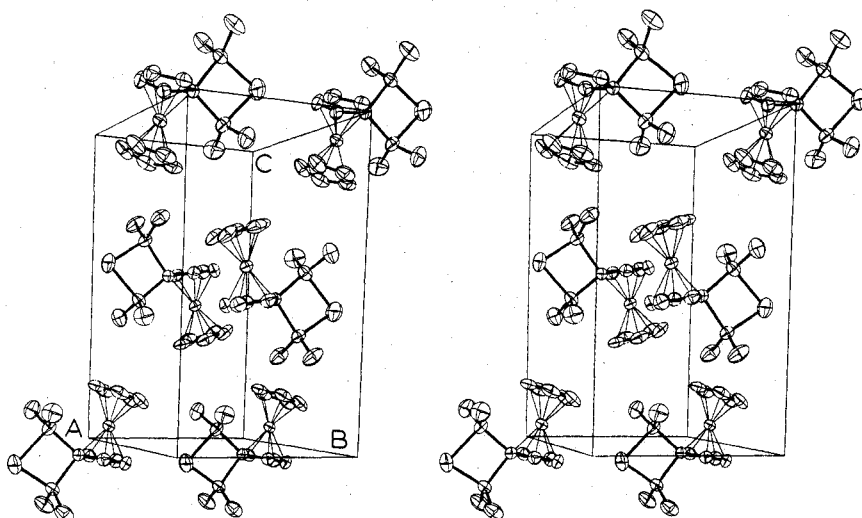


Figure 2. Stereoscopic view of the unit cell packing.

ring tilt appears to lie in steric rather than electronic effects.

The Al...Fe approach is 3.100 (3) Å. In $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4)\text{MoH}]_2\text{Al}_3(\text{CH}_3)_5$, the Al-Mo bond length is 2.66 Å.¹ Since Fe and Mo differ by 0.13 Å in single bond metallic radii,¹² one would predict an Al-Fe bond to be ca. 2.53 Å. Thus, the title compound presents no significant Al-Fe interaction.

Two features of the bridging Cl atom are of importance. The Al-Cl bond lengths are Al(1)-Cl = 2.260 (4) Å and Al(2)-Cl = 2.410 (4) Å (Table III). The Al-Cl terminal bond length is found to be 2.17 (1) Å in $\text{K}[\text{AlCl}_3(\text{CH}_3)]$ ¹³ and the Al-Cl (bridge) bond distance in $[\text{AlCl}_2(\text{CH}_3)_2]$ ¹⁴ is 2.25 Å. The Al(1)-Cl bond length is close to the expected value for an Al-Cl bridge, but the Al(2)-Cl distance is approximately 0.16 Å larger than the norm. These lengths are similar to those found in I, 2.31 and 2.48 Å, but are much more reliable because of the greater accuracy of the present structure determination. The Al-Cl-Al angle, 78.4 (1)°, compares favorably with the 77° found in structure I. A bonding pattern for the entire bridging situation which explains the observed bond lengths and angles is developed below.

The Al-C(cyclopentadienyl) bond lengths are 2.026 (8) and 2.116 (8) Å. In $[\text{Al}(\text{CH}_3)_3]_2$,¹⁵ the Al-C(terminal) distance is 1.952 (5) Å, while the Al-C (electron-deficient bridge) length is 2.124 (1) Å. The Al-C-Al angle is 91.0 (3)° in

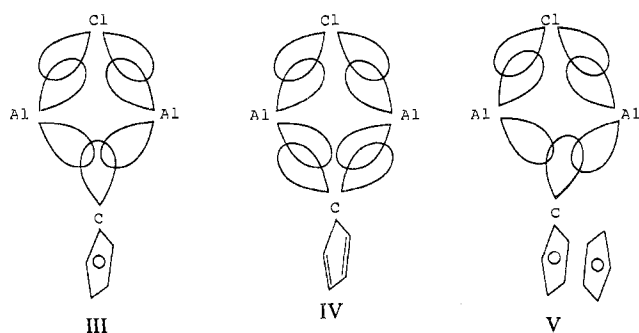
Table III. Interatomic Distances (Å) and Angles (deg) for $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{Al}_2(\text{CH}_3)_4\text{Cl}]$

Fe-C(1)	2.090 (8)	Fe-C(4)	2.081 (9)
Fe-C(2)	2.031 (6)	Fe-C(5)	2.054 (6)
Fe-C(3)	2.040 (6)	Fe-C(6)	2.034 (6)
Cl-Al(2)	2.410 (4)	Cl-Al(1)	2.260 (4)
Al(2)-C(1)	2.026 (8)	Al(1)-C(1)	2.116 (8)
Al(2)-C(8)	1.942 (8)	Al(1)-C(7)	1.940 (7)
C(1)-C(2)	1.482 (8)	C(4)-C(5)	1.444 (9)
C(2)-C(3)	1.409 (8)	C(5)-C(6)	1.385 (10)
C(3)-C(3) ^a	1.405 (15)	C(6)-C(6)'	1.435 (14)
Fe...Al(2)	3.100 (3)		
Al(2)-Cl-Al(1)	78.4 (1)	Cl-Al(2)-C(1)	94.3 (2)
Al(2)-C(1)-Al(1)	91.0 (3)	Cl-Al(1)-C(1)	96.3 (2)
Cl-Al(2)-C(8)	99.7 (3)	Cl-Al(1)-C(7)	108.3 (3)
C(1)-Al(2)-C(8)	114.4 (3)	C(1)-Al(1)-C(7)	110.5 (2)
C(8)-Al(2)-C(8)'	125.4 (5)	C(7)-Al(1)-C(7)'	120.2 (4)
C(2)-C(1)-C(2)'	102.3 (7)	C(5)-C(4)-C(5)'	105.0 (9)
C(1)-C(2)-C(3)	110.1 (6)	C(4)-C(5)-C(6)	109.5 (9)
C(2)-C(3)-C(3)'	108.7 (4)	C(5)-C(6)-C(6)'	108.0 (4)

^a Primed atoms are related to those in Table II by $(x, 1.5 - y, z)$.

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{Al}_2(\text{CH}_3)_4\text{Cl}]$.

Two possible descriptions for the bonding in the bridge emerge. In III the carbon atom would contribute one sp^2 hybrid orbital and one electron, while the aluminum atoms



would contribute two sp^3 hybrid orbitals and one electron. In IV, the carbon atom would give two essentially sp^3 hybridized orbitals and three electrons to produce two two-center bonds with the aluminum atoms. The chlorine atom would contribute two p orbitals and three electrons to construct two-electron, two-center bonds which would be weakened by the constraints of the four-membered ring system.

The presence of the ferrocenyl ligand rather than the cyclopentadienyl ring by itself produces via steric effects the situation shown as V. The five-membered cyclopentadienyl ring involved in the bridge is tilted with respect to the C(1)–Cl vector. This provides a direct measure of the contribution of III vs. IV. If III pertains, then the bond between the aluminum atom and the carbon atom must be stronger on the side which contains the remainder of the ferrocenyl unit. The bond away from the ferrocenyl group must therefore become weaker. If IV pertains, then the overlap will be greater for the orbital away from the ferrocenyl ligand and lesser for the orbital participating in the bond to the aluminum atom nearer the ferrocenyl moiety. Clearly from the bond distances shown in Table III, situation III pertains.

The effects upon the bonding of the chlorine atom are of two types, electronic and steric. Al(1) (involved in the weak Al–C interaction) is more electron deficient and therefore commands a greater overlap with a chlorine orbital. The Al(2)–Cl interaction is weakened by steric repulsion between the chlorine atom and the methyl groups bonded to the aluminum atom. This effect is seen most clearly in Figure 1 and in a comparison of angles. The C(1)–Al(1)–C(7) and Cl–Al(1)–C(7) angles are similar, 110.5 (2) and 108.3 (3)°, respectively. On the other hand, the C(1)–Al(2)–C(8) angle is expanded to 114.4 (3)° because of the nonbonded repulsion, and the Cl–Al(2)–C(8) angle is therefore contracted to 99.7 (3)°. The result of both effects is that the Al(2)–Cl distance is much larger than that of Al(1).

It should be noted that it is not possible to define the bonding as either that shown in III or that shown in IV. Indeed, there

is some evidence for IV in the pattern of bond distances in the bridging cyclopentadienyl ring. The carbon–carbon bond length for the atom involved directly in the bridge is 1.482 (8) Å, while the two remaining independent bond lengths are 1.409 (8) and 1.405 (15) Å. The results do show, however, that the bonding is predominantly as given in III and shown more specifically for the ferrocenylalane as V.

The low-temperature (–40 °C) ^1H NMR spectrum of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{Al}_2(\text{CH}_3)_4\text{Cl}]$ reveals two resonances in ratio 1:1. The one at δ –0.31 is normal for an Al–CH₃ terminal resonance, but the one at δ 0.05 is near the expected value for bridging methyl groups. With reference to Figure 1, it is clear that there are two different types of methyl protons, and it would appear that those attached to C(7) are in a normal terminal environment.

The unit cell packing, shown in Figure 2, presents no unusual intermolecular contacts.

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Registry No. $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{Al}_2(\text{CH}_3)_4\text{Cl}]$, 68200-85-1.

Supplementary Material Available: A listing of structure factor amplitudes and best plane results (7 pages). Ordering information is given on any current masthead page.

References and Notes

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