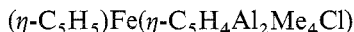


SHORT COMMUNICATIONS

FERROCENYLALANES. THE PREPARATION AND PROPERTIES OF



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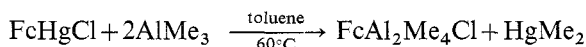
[Manuscript received 26 April 1973]

Abstract

The ferrocenylalane $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_4\text{Al}_2\text{Me}_4\text{Cl})$ has been synthesized and characterized by means of X-ray diffraction, nuclear magnetic resonance, and mass spectral studies. The structural implications of these studies are discussed.

Although ferrocenyl† chemistry is now in general a well developed area, compounds containing the Group III elements are notably lacking. Only a small number of ferrocenylboranes have been reported,¹⁻⁴ and ferrocenylalanes have been entirely absent. This is rather surprising in view of the number of ways the aluminium atom is suspected of being able to interact with the cyclopentadienyl group.^{5,6}

Of the several documented methods⁷ of preparing organoaluminum compounds, the one chosen for this study was the interaction of the organomercury halide with trimethylaluminum:



The reaction began immediately and produced a dark green solution. Heating at 60°C for several hours gave a deep red solution from which the red, air-sensitive crystals of $\text{FcAl}_2\text{Me}_4\text{Cl}$ were obtained, m.p. 108–109°C (Found: Fe, 17.0; Cl, 10.5; Al, 15.8; C, 50.1; H, 6.5. $\text{FcAl}_2\text{Me}_4\text{Cl}$ requires Fe, 16.7; Cl, 10.6; Al, 16.1; C, 50.3; H, 6.3%). Crystal data: orthorhombic, space group $Pna2_1$ or $Pnma$, $a = 9.03(1)$, $b = 11.88(1)$, $c = 15.36(1)$ Å, $\rho_c = 1.36$ g cm⁻³ for $Z = 4$.

The n.m.r. spectrum of $\text{FcAl}_2\text{Me}_4\text{Cl}$ in toluene at 30°C shows three resonances at 4.53 (4), 4.05 (5), -0.13 (12) p.p.m. The downfield peak is a singlet arising from the $\text{C}_5\text{H}_4\text{-}$ group, the peak at 4.05 p.p.m. is a sharp singlet arising from the C_5H_5 ring, and the upfield resonance is a broad doublet from the methyl protons. Thus, at room temperature the $\text{C}_5\text{H}_4\text{-}$ ring exhibits some type of fluxional behavior, while

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† The ferrocenyl group, $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_4\text{-})$, will be abbreviated as Fc.

¹ Kotz, J. C., and Post, E. W., *J. Am. chem. Soc.*, 1968, **90**, 4503.

² Kotz, J. C., and Post, E. W., *Inorg. Chem.*, 1970, **9**, 1661.

³ Post, E. W., Cooks, R. G., and Kotz, J. C., *Inorg. Chem.*, 1970, **9**, 1670.

⁴ Kotz, J. C., and Painter, W. J., *J. organomet. Chem.*, 1971, **32**, 231.

⁵ Drew, D. A., and Haaland, A., *Chem. Commun.*, 1972, 1300.

⁶ Haaland, A., and Weidlein, J., *J. organomet. Chem.*, 1972, **40**, 29.

⁷ Coates, G. E., Green, M. L. H., and Wade, K., "Organometallic Compounds," 3rd Edn, Vol. I, p. 295 *et seq.* (Methuen: London 1968).

the methyl groups on the aluminium atoms are undergoing slow exchange. At -40°C , the C_5H_4 -proton resonance is split into essentially two peaks separated by 0.05 p.p.m., and the methyl proton resonance is now likewise two peaks (0.05 and -0.31 p.p.m.) with area ratio 1 : 1. The C_5H_5 resonance remains a sharp singlet.

TABLE 1

COMPARISON OF METHYL PROTON CHEMICAL SHIFTS FOR BOTH BRIDGING AND TERMINAL METHYL GROUPS In toluene solution; δ to low field of tetramethylsilane, negative sign indicates a shift to high field

Compound	Chemical shift (p.p.m.)		Ref.	Compound	Chemical shift (p.p.m.)		Ref.
	Bridge	Terminal			Bridge	Terminal	
$\text{FcAl}_2\text{Me}_4\text{Cl}$	+0.05	-0.31		$\text{Et}_3\text{N}.\text{AlMe}_3$	—	-0.35	^d
$[\text{AlMe}_3]_2$	+0.07	-0.50	^a	$\text{Et}_2\text{O}.\text{AlMe}_3$	—	-0.35	^d
$\text{Al}_2\text{Me}_5\text{NPh}_2$	+0.59	-0.36	^b	$\text{C}_5\text{H}_5\text{N}.\text{AlMe}_3$	—	-0.24	^d
$\text{Be}[\text{AlMe}_4]_2$	-0.37	-0.62	^c				

^a Williams, K. C., and Brown, T. L., *J. Am. chem. Soc.*, 1966, **88**, 5460.

^b Magnuson, V. R., and Stucky, G. D., *J. Am. chem. Soc.*, 1969, **91**, 2544.

^c Atwood, J. L., and Stucky, G. D., *J. Am. chem. Soc.*, 1969, **91**, 2538.

^d Hatada, K., and Yuki, H., *Tetrahedron Lett.*, 1968, 213.

The structural implications of the n.m.r. behavior can be demonstrated with the aid of the data in Table 1. One intriguing explanation of the methyl portion of the spectrum can be found in terms of a system with electron deficient methyl bridges (A).



While this nicely accounts for the low-temperature n.m.r. spectrum, it seems more likely that the chloride ion would participate in the bridge. A structure such as (B) could be envisioned, but the solution behavior would then demand that an intramolecular exchange process make the two methyl groups attached to the Fc-Al unit equivalent at the temperatures examined. A single-crystal X-ray structural investigation now in progress should upon completion aid in the interpretation of the solution studies.

Attempted sublimation of $\text{FcAl}_2\text{Me}_4\text{Cl}$ yields ferrocene as the only identifiable product. The apparent non-volatility of the ferrocenylalane parent is also borne out by a mass spectral investigation. At 30 eV ionizing energy, the three major fragments correspond almost exactly to those reported⁸ for ferrocene: 186, $(\text{C}_5\text{H}_5)_2\text{Fe}^+$; 121, $\text{C}_5\text{H}_5\text{Fe}^+$; 56, Fe^+ . The next largest peak, comparable in size to that of Fe^+ , is 57, Me_2Al^+ .

Acknowledgment

We are grateful to the National Science Foundation for support of this work under Grant GP-24852.

⁸ Friedman, L., Irsa, A. P., and Wilkinson, G., *J. Am. chem. Soc.*, 1955, **77**, 3689.