η^6-Fluorene and η^5-Fluorenyl Complexes of Iron and Manganese; *X*-Ray Structure of (η^5-Cyclopentadienyl)(η^6-fluorenyl)iron

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Summary Reversible deprotonation of $[Fe(C_5H_5)(\eta^6\text{-fluorene})]PF_6$ and $[Mn(\eta^6\text{-fluorene})(CO)_3]PF_6$ initially produces zwitterionic complexes wherein co-ordination to the six-membered ring is retained, and the manganese complex very slowly reverts to the isomeric η^5 complex, $[Mn(\eta^5\text{-fluorenyl})(CO)_3]$; the *X*-ray structure of the iron compound $[Fe(C_5H_5)(C_{13}H_9)]$ has been determined.

The complexes $[Mn(\eta^6\text{-fluorene})(CO)_3]PF_6$ and $[Fe(C_5H_5)(\eta^6\text{-fluorene})]PF_6$ can be prepared by standard routes, the former from $[Mn(CO)_5Br]$, $AlCl_3$, and fluorene, and the latter from $[Fe(C_5H_5)_2]$, $AlCl_3$, Al, and fluorene. Using t-butoxide we have deprotonated each of the species, producing neutral compounds wherein metal co-ordination to one of the six-membered rings is maintained. Structures were initially ascertained by ^1H n.m.r. data which showed the related protons on the two six-membered rings on each fluorenyl ligand to be non-equivalent; subsequently the structure of the iron compound, $[Fe(C_5H_5)(C_{13}H_9)]$, green crystals, m.p. 105 °C, was confirmed by a crystallographic study. *Crystal data:* space group $P2_1/c$, $a = 8{\cdot}944(3)$, $b = 14{\cdot}600(4)$, $c = 20{\cdot}201(5)$ Å, $\beta = 100{\cdot}08(2)^\circ$, $U = 2597(1)$ Å^3, $Z = 8$, $D_c = 1{\cdot}46$ g cm^{-3}, $D_m = 1{\cdot}45$ g cm^{-3}. A total of 2323 independent $[F > 2\sigma(F)]$ observations were collected by diffractometric techniques. The structure, solved by direct methods, was refined by anisotropic block-diagonal least-squares techniques to an R_1 value of 0·045. The molecular geometry of this compound is shown in the Figure.

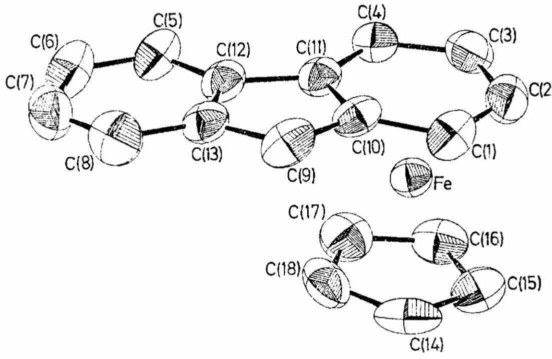


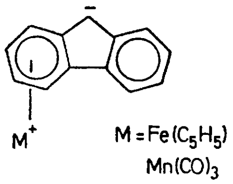
Figure. *X*-Ray structure of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{13}H_9)]$. Distances in the two crystallographically non-equivalent molecules (A) and (B) are: Fe–C(1), (A) 2·122(5), (B) 2·104(6); Fe–C(2), (A) 2·053(5), (B) 2·047(6); Fe–C(3), (A) 2·039(5), (B) 2·032(6); Fe–C(4), (A) 2·072(5), (B) 2·074(6); Fe–C(10), (A), 2·316(5), (B) 2·300(5); Fe–C(11), (A) 2·152(5), (B) 2·175(5); C(9)–C(10), (A) 1·372(7), (B) 1·397(7); C(9)–C(13), (A) 1·435(8), (B) 1·413(7) Å.

The metal atom remains co-ordinated to one six membered ring, slightly displaced from C(10) which also lies

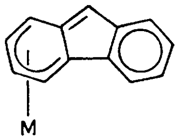
0·142(8) Å above a plane defined by the other co-ordinated carbon atoms. The best representation of bonding for the iron compound appears to be (i), wherein a positive charge is retained on the metal and negative charge remains substantially on C(9).

Reactions of the iron compound seem to be in accord with this representation of bonding. A reaction with $MeOSO_2F$ occurs in minutes giving stereospecifically the *exo*-9-methylfluorene-iron compound; similar reactions occur with MeI and *p*-$BrC_6H_4CH_2Br$. The product is protonated readily, but non-stereospecifically.

The chemistry of the analogous manganese complex, $[Mn(C_{13}H_9)(CO)_3]$, offers some interesting contrasts. It can be formed from $[Mn(\eta^6\text{-}C_{13}H_{10})(CO)_3]PF_6$ using weaker bases such as Et_3N, suggesting that $[Mn(C_{13}H_9)(CO)_3]$ is a weaker base than $[Fe(C_5H_5)(C_{13}H_9)]$. The complex is also a poorer nucleophile. Thus reaction with $MeOSO_2F$ at 25 °C requires 3 days rather than minutes to reach completion. Possibly, these data are better in accord with a structure represented by (ii).

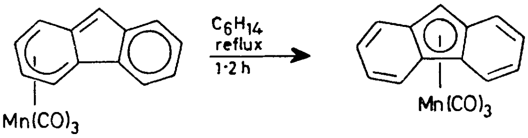


(i)



(ii)

After 2 weeks in the solid state or 1·2 h in refluxing hexane, the manganese compound rearranges to the known[1] isomeric species $[Mn(\eta^5\text{-}C_{13}H_9)(CO)_3]$ [equation (1)]. No rearrangement is found to occur with the iron compound. This second compound, $[Mn(\eta^5\text{-}C_{13}H_9)(CO)_3]$, does not undergo the reactions of its isomeric species.



(1)

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[1] R. B. King and A. Efraty, *J. Organometallic Chem.*, 1970, **23**, 527.