η^6-Indene- and η^5-Indole-(pentamethylcyclopentadienyl)-rhodium(III) and -iridium(III) Hexafluorophosphates and their Reversible Deprotonation and Rearrangement Reactions to η^5-Indenyl- and η^5-Indolyl-complexes

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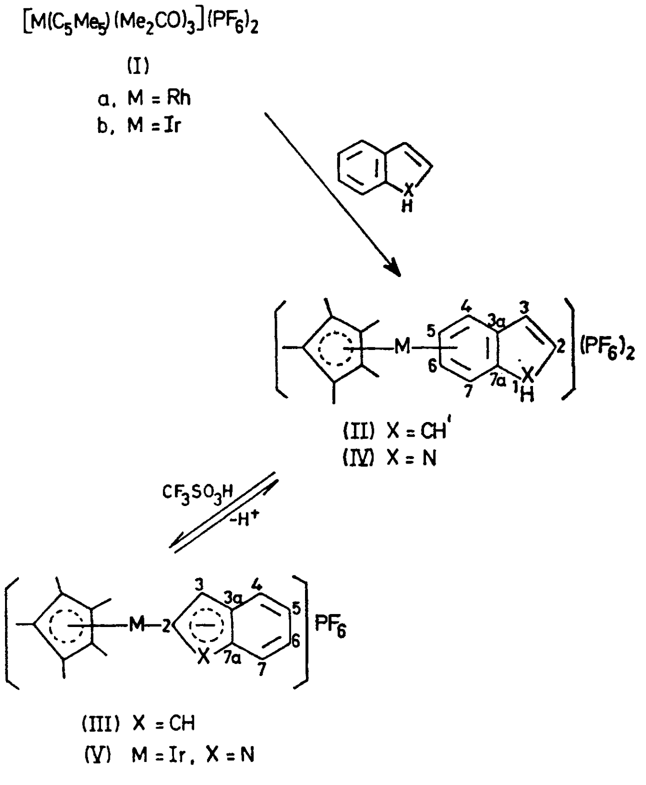
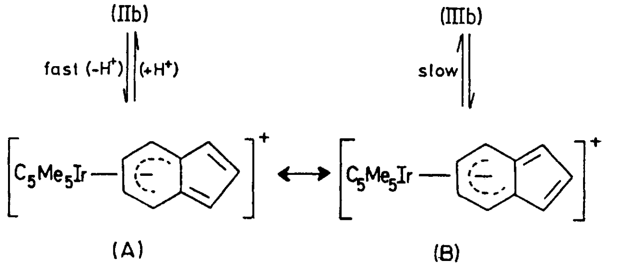
Summary The preparations of $[M(\eta^5\text{-}C_5Me_5)(\eta^6\text{-indene})](PF_6)_2$, (II), $[M(\eta^5\text{-}C_5Me_5)(\eta^5\text{-indenyl})](PF_6)$, (III), $[M(\eta^5\text{-}C_5Me_5)(\eta^6\text{-indole})](PF_6)_2$ (M = Rh or Ir), and $[Ir(\eta^5\text{-}C_5Me_5)(\eta^5\text{-indolyl})]PF_6$ are reported; in the interconversion (III) + $H^+ \rightleftharpoons$ (II), for M = Ir protonation–deprotonation is fast and the rate-determining step is the movement of the metal from the 5- to the 6-membered ring and *vice-versa*.

The dicationic pentamethylcyclopentadienyl-rhodium and -iridium acetone solvate complexes,[1] (I),† react with indene (in acetone at 20 °C) to give initially the η^6-indene complexes, (II), in which the metal is complexed to the 6-membered ring. These complexes deprotonate and quantitatively rearrange in solution (instantaneously for M = Rh, over 24 h for M = Ir) to the η^5-indenyl complexes, (III), in which the metal is bound to the 5-membered ring.

The structures of (II) and (III) follow from their n.m.r. spectra and in particular from the $^{13}C\{H\}$ spectra of (IIa) and (IIIa) in which the $J(^{13}C\text{–}^{103}Rh)$ coupling constants indicate the mode of attachment (Table). The complexes (IIa) (90%) or (IIb) (66%) were generated on dissolving (IIIa) or (IIIb) in CF_3SO_3H, and the iridium complex (IIb) was also isolated as a solid.





Closely related reactions occurred between indole and (I) to give (IVa) or (IVb), identified by n.m.r. and i.r. spectroscopy [ν(NH) at 3380 (IVa) and 3395 (IVb) cm^{-1}]. In base the η^6-indole–iridium complex (IVb) underwent deprotonation accompanied by migration of the metal from the 6- to the 5-membered nitrogen-containing ring, (V), a reaction that was easily reversed on addition of CF_3CO_2H to a solution of (V). The rhodium complex (IVa) decomposed in the presence of base. Only one η^6-indole-[2] and one η^5-indolyl-complex[3] had previously been reported.

When the η^6-indene-iridium complex (IIb) was dissolved in CF_3CO_2D the double-doublet [δ 3·12, 3·64, J(H-1–H-1′) 26 Hz] in the ^1H n.m.r. spectrum due to H-1 and H-1′ collapsed to a singlet at δ 3·17. Since (IIIb) was not converted back into (IIb) in CF_3CO_2H during several days, this implies that the observed stereospecific H^+/D^+ exchange of H-1 (or H-1′) in (IIb) does not occur through the intermediacy of (IIIb). Instead we propose that H^+/D^+

Table. ^1H and $^{13}C\{H\}$ n.m.r. spectra (δ) [J(H–H) and J(C–Rh) in Hz in parentheses]

Compound		Position										
		1/1′	2	3	3a	4	5	6	7	7a	C_5Me_5	C_5Me_5
(IIa)[c]	^1H	3·48d, 3·97d (26) (26)	7·05d (5·5)	7·79d (5·5)	—	7·50m	7·18m	7·18m	7·50m	—	—	2·13
(IIIa)[b]		6·25d (3)	5·88m	6·25d (3)	—	7·55s				—	—	1·86
(IIa)[c]	^{13}C	39·6	a	138·2	129·3d (4·2)	101·1d (3·1)	104·1d (4·5)	105·2d (4·2)	102·7d (6·1)	125·7	112·4d (9·1)	10·1
(IIIa)[b]		82·6d (6·1)	90·9d (6·1)	82·6d (6·1)	94·7d (10·7)	129·6	123·6	123·0	129·6	94·7d (10·7)	105·5d (9·1)	9·2

[a] Not observed. [b] In $[^2H_6]$-acetone. [c] In CF_3SO_3H.

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† The complexes (I) are obtained *in situ* by reaction of $[M(C_5Me_5)Cl_2]_2$ with $AgPF_6$ in acetone.

exchange occurs rapidly *via* an intermediate in which Ir is still bonded to the 6-membered ring (*e.g.* A $\leftrightarrow$ B). An Ir^V hydride, $[HIr(C_5Me_5)(C_9H_7)]^{2+}$, may be an additional intermediate or transition state and analogous species have been proposed to explain the H/D exchange in the protonation of $Fe(\eta^5\text{-indenyl})_2$.[4,5]

We therefore conclude that in the rearrangement (III) $\rightleftharpoons$ (II) the protonation/deprotonation step is fast and that the movement of the metal from the 5- to the 6-membered ring and *vice-versa* is rate-determining.

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[1] S. J. Thompson, P. M. Bailey, C. White, and P. M. Maitlis, unpublished results.

[2] E. O. Fischer, H. A. Goodwin, C. G. Krater, H. D. Simmons, K. Sonogashira, and S. B. Wild, *J. Organometallic Chem.*, 1968, **14**, 359.

[3] P. L. Pauson, A. R. Quazi, and B. W. Rockett, *J. Organometallic Chem.*, 1967, **7**, 325.

[4] C. C. Lee, R. G. Sutherland, and B. J. Thomson, *J.C.S. Chem. Comm.*, 1971, 1071.

[5] P. M. Treichel and J. W. Johnson, *J. Organometallic Chem.*, 1975, **88**, 207; P. M. Treichel, J. W. Johnson, and J. C. Calabrese, *ibid.*, p. 215.