# Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part XII.[1] Tris(solvent) Complexes and Complexes of η6-Benzene, -Naphthalene, -Phenanthrene, -Indene, -Indole, and -Fluorene and η5-Indenyl and -Indolyl

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The tris(solvent) complexes $[M(C_5H_5)(s)_3][PF_6]_2$ (M = Rh, Ir; s = Me_2CN, Me_2SO, or pyridine) were prepared and characterised; evidence for less stable solvent complexes (M = Rh, Ir; s = Me_2CO, MeOH, or CH_2Cl_2) was obtained. The dicationic Rh^{III} and Ir^{III} η6-arene complexes $[M(C_5Me_5)(arene)][PF_6]_2$ (M = Rh; arene = benzene, toluene, m-xylene, mesitylene, fluorene, or indole; M = Ir, arene = toluene, m-xylene, naphthalene, phenanthrene, indene, indole, or fluorene) were synthesised from the acetone solvent complexes (IVa; M = Rh) (IVa; M = Ir). Both the naphthalene- and phenanthrene-iridium complexes were very labile, but showed no evidence of fluxional behaviour; phenanthrene is bonded by the terminal 6-membered ring. Reaction of (IVa) with indene gave the η5-indenyl complex, $[Rh(C_5Me_5)(C_9H_7)][PF_6]$, which was protonated, with rearrangement, to the η6-indene complex. Similar reversible protonation–deprotonation reactions occurred for the iridium complexes, $[Ir(C_5Me_5)(η^6-C_9H_8)]^{2+} \rightleftharpoons [Ir(C_5Me_5)(η^5-C_9H_7)]^+ + H^+$. The iridium (but not the rhodium)-indole complex $[Ir(C_5Me_5)(η^6-C_8H_6NH)]^{2+}$ also underwent reversible deprotonation to the η5-indolyl complex $[Ir(C_5Me_5)-(η^5-C_8H_6N)]^+$. From exchange studies with CF_3CO_2D on $[Ir(C_5Me_5)(η^6-C_7H_8)]^{2+}$ it is concluded that protonation/deprotonation is fast and that the rate-determining step in the overall reaction is the movement of the metal from the 5- to the 6-membered ring and vice versa. The η6-fluorene-rhodium complex is very labile but the iridium analogue is deprotonated by base to give a fluorenyl complex of undetermined structure. An order of stability of η5- and η6-arenes bonded to Rh^{III} and Ir^{III} is given.

SOME years ago we reported [2] on cationic rhodium and iridium complexes of the type $[M(C_5Me_5)(η^6\text{-arene})]^{2+}$ (M = Rh or Ir) arene = substituted benzenes) as well as $[M(C_5Me_5)(η^5\text{-pyrrolyl})][PF_6]$. We have now developed new routes to such complexes which allow their formation under very mild conditions and which has enabled us to extend greatly the types of arene that can be complexed and to investigate their chemistry.

Our initial work [2] involved the reaction of the appropriately substituted benzene with the trifluoroacetato-complexes in refluxing trifluoroacetic acid, the role of the trifluoroacetic acid presumably being to protonate and remove the co-ordinated trifluoroacetate and thereby to free co-ordination sites at the metal.

$$[M(C_5Me_5)(OCOCF_3)_2]\cdot H_2O + arene + 2CF_3CO_2H \longrightarrow$$
$$[M(C_5Me_5)(arene)][H(OCOCF_3)_2]_2$$
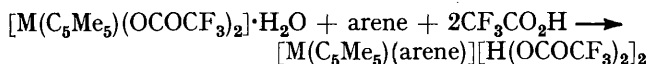
This procedure suffered from the disadvantage that only acid-insensitive compounds could be used and the necessity for carrying out the reactions at elevated temperature also meant that a number of less-stable complexes (e.g. $[Rh(C_5Me_5)(C_6H_6)]^{2+}$) could not be isolated.
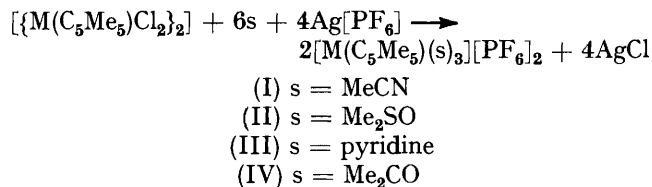
An alternative, related reaction, which involved refluxing the dimeric dichlorides and the arene in the presence of boron trifluoride etherate (as halide acceptor) allowed, for example, the synthesis of the naphthalene complex, $[Ir(C_5Me_5)(C_{10}H_8)][BF_4]_2$, but yields were poor and the work-up procedure was difficult.

By far the easiest route involved the in situ preparation of the solvent complexes $[M(C_5Me_5)(s)_3][PF_6]_2$ (s = MeCN, Me_2SO, Me_2CO, CH_2Cl_2, or MeOH) from the dimeric

dichlorides and the displacement of the solvent molecule by the arene. Both reactions occurred rapidly at room temperature and high yields of the desired arene complexes could be obtained particularly for s = acetone (Table 1). In order to check the stoicheiometry of the solvent complexes a number were actually isolated and characterised. Parts of this work have been published as Communications.[3]

RESULTS AND DISCUSSION

The Tris(solvent) Complexes $[M(C_5Me_5)(s)_3][PF_6]_2$.— The tris(acetonitrile), tris(dimethyl sulphoxide), and tris(N-pyridine) complexes (I)—(III) were all isolated in yields varying from 50 to 80% from the reaction of $[\{M(C_5Me_5)Cl_2\}_2]$ with $Ag[PF_6]$ in the appropriate solvent. These six compounds were relatively stable and in each case analytical and n.m.r. spectroscopic data agreed with the formulation that three solvent molecules were co-ordinated to the metal.

$$[\{M(C_5Me_5)Cl_2\}_2] + 6s + 4Ag[PF_6] \longrightarrow$$
$$2[M(C_5Me_5)(s)_3][PF_6]_2 + 4AgCl$$

$$\text{(I) s = MeCN}$$
$$\text{(II) s = Me_2SO}$$
$$\text{(III) s = pyridine}$$
$$\text{(IV) s = Me_2CO}$$

Similar reactions occurred in acetone, dichloromethane, or methanol and, by analogy, we formulate the compounds formed in solution as containing three molecules of these solvents. Attempts to isolate these materials failed; in the case of the acetone solvent complexes

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[2] C. White and P. M. Maitlis, *J. Chem. Soc. (A)*, 1971, 3322.

[3] (a) S. J. Thompson, P. M. Bailey, C. White, and P. M. Maitlis, *Angew. Chem. Internat. Edn.*, 1976, **15**, 490; (b) C. White, S. J. Thompson, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1976, 409.

(IVa) and (IVb) a series of complicated rearrangements occurred which we were able to elucidate.[3a,4]

The species could, however, be recognised by the characteristic ^{1}H n.m.r. resonances of their C_5Me_5 ligands as follows: [Rh(C$_5$Me$_5$)(Me$_2$CO)$_3$][PF$_6$]$_2$ (IVa), δ 1.79 (in [^{2}H$_6$]acetone); [Ir(C$_5$Me$_5$)(Me$_2$CO)$_3$][PF$_6$]$_2$ (IVb), δ 1.75 (in [^{2}H$_6$]acetone); [Rh(C$_5$Me$_5$)(MeOH)$_3$][PF$_6$]$_2$, δ 1.67 (in [^{2}H$_4$]methanol); and [Ir(C$_5$Me$_5$)(CH$_2$Cl$_2$)$_3$]-[PF$_6$]$_2$ δ 1.47 (in dichloromethane). Although we write them as tris(solvent) complexes and they behave as complexes containing loosely bound solvent molecules, we

mull) and 935 cm^{-1} in solution (acetone), whereas the iridium analogue (IIb) showed ν(SO) at 901 and 1 135 cm^{-1} in the solid but only at 1 128 cm^{-1} in solution. [These band assignments were confirmed from the Nujol mull spectra of the [^{2}H$_6$]dimethyl sulphoxide complexes which showed ν(SO) at 943 cm^{-1} (Rh) and 918 and 1 133 cm^{-1} (Ir) respectively.] Studies on dimethyl-sulphoxide complexes have shown that when ν(SO) > 1 040 cm^{-1} the ligand is S-bonded to the metal whereas when ν(SO) < 1 040 cm^{-1} it is O-bonded.[6,7]

We can, therefore, conclude that dimethyl sulphoxide

TABLE 1

Analytical data (%) (calculated values in parentheses)

Complex	C	H	N	% Yield [a]
[Rh(C$_5$Me$_5$)(MeCN)$_3$][PF$_6$]$_2$ (Ia)	29.1 (29.7)	4.0 (3.7)	6.7 (6.5)	65
[Ir(C$_5$Me$_5$)(MeCN)$_3$][PF$_6$]$_2$ (Ib)	25.9 (25.9)	3.3 (3.3)	4.7 (5.7)	84
[Ir(C$_5$Me$_5$)(Me$_2$SO)$_3$][PF$_6$]$_2$ (IIb)	22.3 (22.6)	4.5 (3.9)		51
[Rh(C$_5$Me$_5$)(C$_5$H$_5$N)$_3$][PF$_6$]$_2$ (IIIa)	39.3 (39.2)	4.1 (3.9)	5.6 (5.5)	81
[Ir(C$_5$Me$_5$)(C$_5$H$_5$N)$_3$][PF$_6$]$_2$ (IIIb)	35.4 (35.1)	3.7 (3.5)	5.0 (4.9)	51
[Rh(C$_5$Me$_5$)(benzene)][PF$_6$]$_2$ (V)	32.3 (31.7)	3.7 (3.5)		61
[Rh(C$_5$Me$_5$)(toluene)][PF$_6$]$_2$	32.9 (32.9)	4.0 (3.7)		82
[Ir(C$_5$Me$_5$)(toluene)][PF$_6$]$_2$	29.9 (28.8)	3.5 (3.3)		68
[Rh(C$_5$Me$_5$)(m-xylene)][PF$_6$]$_2$	34.1 (34.1)	4.0 (4.0)		71 [b]
[Ir(C$_5$Me$_5$)(m-xylene)][PF$_6$]$_2$	30.4 (29.9)	3.9 (3.5)		44 [c]
[Rh(C$_5$Me$_5$)(mesitylene)][PF$_6$]$_2$	35.5 (35.2)	4.3 (4.2)		75 [b]
[Ir(C$_5$Me$_5$)(naphthalene)][PF$_6$]$_2$ (VI)	32.7 (32.2)	3.3 (3.1)		58
[Ir(C$_5$Me$_5$)(phenanthrene)][PF$_6$]$_2$ (VII)	35.9 (36.2)	3.3 (3.2)		75
[Ir(C$_5$Me$_5$)(indene)][PF$_6$]$_2$ (VIIIb)	30.7 (31.1)	3.4 (3.1)		45 [d]
[Rh(C$_5$Me$_5$)(indenyl)][PF$_6$] (IXa)	45.5 (45.8)	4.8 (4.5)		93
[Ir(C$_5$Me$_5$)(indenyl)][PF$_6$] (IXb)	39.4 (38.8)	3.9 (3.8)		31 [d]
[Rh(C$_5$Me$_5$)(4,6-dimethylindenyl)][PF$_6$] (Xa)	48.0 (47.9)	4.2 (5.0)		91
[Ir(C$_5$Me$_5$)(4,6-dimethylindenyl)][PF$_6$] (Xb)	40.8 (41.0)	4.7 (4.3)		96
[Rh(C$_5$Me$_5$)(indole)][PF$_6$]$_2$ (XIa)	33.9 (33.5)	3.8 (3.4)	1.8 (2.2)	90
[Ir(C$_5$Me$_5$)(indole)][PF$_6$]$_2$ (XIb)	29.7 (29.4)	3.3 (3.0)	2.1 (1.9)	92
[Ir(C$_5$Me$_5$)(indolyl)][PF$_6$] (XII)	37.0 (36.7)	3.9 (3.6)	2.3 (2.4)	88
[Rh(C$_5$Me$_5$)(fluorene)][PF$_6$]$_2$ (XIIIa)	40.5 (39.8)	4.0 (3.6)		86
[Ir(C$_5$Me$_5$)(fluorene)][PF$_6$]$_2$ (XIIIb)	35.3 (35.7)	3.6 (3.2)		91

[a] Unless stated otherwise the arene complexes were prepared from [M(C$_5$Me$_5$)(Me$_2$CO)$_3$][PF$_6$]$_2$ (M = Rh or Ir). [b] Prepared from [Rh(C$_5$Me$_5$)(OCOCF$_3$)$_2$]$_n$. [c] Prepared from [{Ir(C$_5$Me$_5$)Cl$_2$}$_2$]–BF$_3$·OEt$_2$. [d] Both complexes isolated.

have no further evidence concerning either their stoicheiometry or the mode of binding involved. Weak co-ordination of [PF$_6$]$^-$ to the metal in the dichloromethane complex cannot, for example, be excluded.

The acetonitrile complexes (I) showed ν(CN) at 2 298 and 2 320 (Rh) cm^{-1}, and 2 300 and 2 330 (Ir) cm^{-1}, which are very close to ν(CN) observed for [M(cyclo-octa-1,5-diene)(MeCN)$_3$][BF$_4$] (M = Rh or Ir).[5] The observed increase in ν(CN) on co-ordination (free MeCN shows bands at 2 254 and 2 295 cm^{-1}) indicates that the ligand has a little π-acceptor ability and acts largely as a σ-donor. A [^{2}H$_3$]acetonitrile solution of (Ib) showed separate resonances in the ^{1}H n.m.r. spectrum for co-ordinated MeCN (δ 2.76) and solvent (δ 2.05) at 35 °C and therefore exchange must be very slow on the n.m.r. time scale.

The dimethyl sulphoxide complexes (II) are also of interest. The rhodium complex [Rh(C$_5$Me$_5$)(Me$_2$SO)$_3$]-[PF$_6$]$_2$ (IIa) showed ν(SO) at 926 cm^{-1} in the solid (Nujol

is *always* O-bonded to Rh in (IIa), but that it is S-bonded in solution and both O- and S-bonded in the solid to Ir. This suggests that C$_5$Me$_5$Rh^{III} is a harder centre than C$_5$Me$_5$Ir^{III}. Acetone solutions of the dimethyl sulphoxide complexes containing 3 equivalents of dimethyl sulphoxide showed only one resonance at ambient temperature in the ^{1}H n.m.r. spectrum, indicating that there was rapid exchange between co-ordinated and free dimethyl sulphoxide. For the iridium complex (IIIb) separate resonances due to co-ordinated and free dimethyl sulphoxide were clearly separated on cooling to −10 °C (coalescence temperature ca. +7 °C) whereas the rhodium complex (IIa) needed to be cooled to −40 °C to obtain two sharp signals (coalescence temperature ca. −25 °C).

The tris(pyridine) complexes (IIIa) and (IIIb) were N-bonded, as expected.

[M(η^5-C$_5$Me$_5$)(η^6-arene)][PF$_6$]$_2$ (*arene = benzene, toluene, m-xylene, mesitylene, naphthalene, and phenanthrene*).— A range of arene complexes (Table 1) was prepared from the tris(acetone) solvate complexes (IV). This

[4] S. J. Thompson, C. White, and P. M. Maitlis, *J. Organometallic Chem.*, in the press.
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[6] W. L. Reynolds, *Progr. Inorg. Chem.*, 1970, **12**, 10.
[7] F. A. Cotton, R. Francis, and W. Horrocks, *J. Phys. Chem.*, 1960, **64**, 1534.

TABLE 2

¹H N.m.r. data (δ scale) [a]

	C₅Me₅	Co-ordinated-ring protons	Other
[Rh(C₅Me₅)(MeCN)₃][PF₆]₂	1.85 (s)		MeCN, 2.53 (s)
[Ir(C₅Me₅)(MeCN)₃][PF₆]₂	1.89 (s)		MeCN, 2.76 (s)
[Ir(C₅Me₅)(Me₂SO)₃][PF₆]₂	1.74 (s)		Me₂SO, 3.13 (s)
[Rh(C₅Me₅)(C₅H₅N)₃][PF₆]₂	1.52 (s)		H(α), 8.64 (d, J = 6); H(β), 7.74 (dd); H(γ), 8.22 (t, J = 8)
[Ir(C₅Me₅)(C₅H₅N)₃][PF₆]₂	1.42 (s)		H(α), 8.70 (d, J = 6); H(β), 7.74 (dd); H(γ), 8.23 (t, J = 7)
[Rh(C₅Me₅)(benzene)][PF₆]₂	2.45 (s)	7.72 (s)	
[Rh(C₅Me₅)(toluene)][PF₆]₂	2.39 (s)	7.51 (s)	Me, 2.72 (s)
[Ir(C₅Me₅)(toluene)][PF₆]₂	2.47 (s)	7.56 (s)	Me, 2.77 (s)
[Rh(C₅Me₅)(m-xylene)][PF₆]₂ [b]	2.33 (s)	7.27 (m)	Me, 2.65 (s)
[Ir(C₅Me₅)(m-xylene)][PF₆]₂	2.46 (s)	7.55 (s)	Me, 2.77 (s)
[Rh(C₅Me₅)(mesitylene)][PF₆]₂	2.22 (s)	7.27 (s)	Me, 2.55 (s)
[Ir(C₅Me₅)(naphthalene)][PF₆]₂	2.10 (s)	H(5), H(8), 8.46 (m); H(6), H(7), 8.34 (m)	H(1), H(4), 8.37 (m); H(2), H(3), 7.82 (m)
[Ir(C₅Me₅)(phenanthrene)][PF₆]₂	1.97 (s)	H(4), H(5), 8.89 (m)	Others 7.75—8.63 (m)
[Rh(C₅Me₅)(indene)]²⁺ [c]	2.13 (s)	H(4), H(7), 7.50 (m); H(5), H(6), 7.18 (m)	H(1), H(1'), 3.48 (d); 3.97 (d, J = 26); H(2), 7.05 (d); H(3), 7.79 (d, J = 5.5)
[Ir(C₅Me₅)(indene)][PF₆]₂ [b]	2.30 (s)	H(4), H(7) 7.72 (m); H(5), H(6) 7.33 (m)	H(1), H(1'), 3.18 (d, J = 26); H(2), 7.00 (d, J = 6); H(3), 7.72 (m)
[Rh(C₅Me₅)(indenyl)][PF₆]	1.86 (s)	H(1), H(3) = 6.25 (d, J = 3); H(2) = 5.88 (m)	H(4), H(5), H(6), H(7) = 7.55 (s)
[Ir(C₅Me₅)(indenyl)][PF₆]	1.92 (s)	H(1), H(3) = 6.26 (d, J = 2.5); H(2) = 5.83 (t)	H(4), H(5), H(6), H(7) = 7.44 (s)
[Rh(C₅Me₅)(4,6-dimethylindenyl)][PF₆]	1.82 (s)	H(1), H(3) = 6.07 (m), 6.16 (m); H(2) = 5.74 (m)	H(5), H(7) = 7.06 (s), 7.19 (s); Me(4), Me(6) = 2.37 (s), 2.42 (s)
[Rh(C₅Me₅)(indole)][PF₆]₂	2.03 (s)	H(4), H(6) = 7.16 (m); H(5), H(7) = 7.96 (m)	H(1) = 11.65 (br), H(3) = 7.05 (d, J = 3); H(2) = 8.65 [dd, J(1)—(2) = 2]
[Ir(C₅Me₅)(indole)][PF₆]₂	2.09 (s)	H(4), H(6) = 7.22 (m); H(5), H(7) = 8.06 (m)	H(1) not observed; H(3) = 6.95 (d, J = 3); H(2) = 8.64 (d)
[Ir(C₅Me₅)(indolyl)][PF₆]	1.91 (s)	H(2) = 8.74 (d), H(3) = 6.38 (d, J = 3)	H(4), H(6) = 6.70 (m); H(5), H(7) = 7.50 (m)
[Rh(C₅Me₅)(fluorene)][PF₆]₂	1.94 (s)	H(1)—H(8), 7.50—8.30 (m)	H(9), H(9') = 4.17 (d), 4.47 (d, J = 24)
[Ir(C₅Me₅)(fluorene)][PF₆]₂	2.09 (s)	H(1)—H(8), 7.54—8.38 (m)	H(9), H(9') = 3.87 (d), 4.21 (d, J = 24)

[a] Spectra recorded in [²H₆]acetone with SiMe₄ as internal standard; J quoted in Hz. [b] Recorded in CF₃CO₂H. [c] Recorded in CF₃SO₃H with CH₂Cl₂ as internal standard.

TABLE 3

¹³C{¹H} N.m.r. data (δ scale) [a]

Complex	C₅Me₅	C₅Me₅					Others			
[Rh(C₅Me₅)(pyridine)₃][PF₆]₂	100.0 (d) (7.7)	8.5					C(α) = 154.0; C(β) = 128.8; C(γ) = 141.4			
[Ir(C₅Me₅)(pyridine)₃][PF₆]₂	88.1	8.9					C(α) = 152.3; C(β) = 128.5; C(γ) = 141.7			
[Rh(C₅Me₅)(benzene)][PF₆]₂ [b]	e	11.3	[J(C–H) = 132]				C₆H₆ = 108.7 [J(C–H) = 184; J(Rh–C) = 0.2]			
[Ir(C₅Me₅)(benzene)][PF₆]₂ [b]	108.5	10.7	[J(C–H) = 132]				C₆H₆ = 99.7 [J(C–H) = 188]			
[Rh(C₅Me₅)(toluene)][PF₆]₂ [b]	114.2 (d) (7.6)	10.9					C(1) = 125.0 (d); C(2) + C(6), C(3) + C(5) = 108.1 (d), 108.4 (d); C(4) = 106.5 (d); Me = 19.1 (4.6) (4.6) (3.0)			
[Rh(C₅Me₅)(mesitylene)][PF₆]₂ [b]	112.5 (d) (7.6)	10.1					C(1), C(3), C(5) = 124.0 (d); C(2), C(4), C(6) = 106.4 (d); Me = 18.7 (4.6) (4.6)			
[Ir(C₅Me₅)(phenanthrene)][PF₆]₂ [d]	104.8	8.8					C(1) = 141.4; C(2) + C(3) = 132.1; C(4) = 120.4; C(4a) = 124.1; C(4b), C(8a) = 104.1, 105.4; C(5) = 91.1; C(6), C(7), C(8) = 96.5, 97.4, 98.0; C(9), C(10) = 134.6, 127.7; C(10a) = 127.7			
[Ir(C₅Me₅)(fluorene)][PF₆]₂	105.1	8.9					C(1), C(2), C(3), C(4) = 134.6, 129.6, 127.1, 125.6; C(4a) = 146.0; C(4b), C(8a) = 131.0, 117.4; C(5), C(6), C(7), C(8) = 97.1, 96.7, 96.3, 90.9; C(9) = 36.4; C(9a) = 140.6			

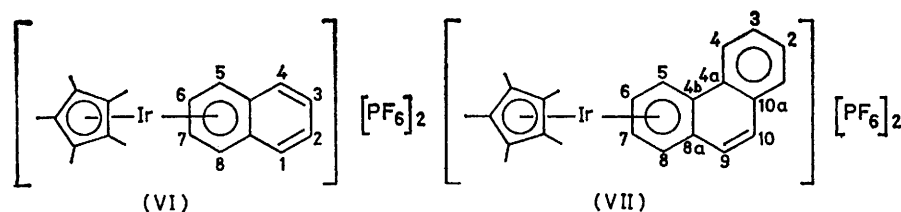| Complex	C₅Me₅	C₅Me₅	C(1)	C(2)	C(3)	C(3a)	C(4)	C(5)	C(6)	C(7)	C(7a)	Other
[Rh(C₅Me₅)(indene)]²⁺ [c]	112.4 (d) (9.1)	10.1	39.6	e	138.2	129.3 (d) (4.2)	101.1 (d) (3.1)	104.1 (d) (4.5)	105.2 (d) (4.2)	102.7 (d) (6.1)	125.7	
[Rh(C₅Me₅)(indenyl)][PF₆]	105.5 (d) (9.1)	9.2	82.6 (d) (6.1)	90.9 (d) (6.1)	82.6 (d) (6.1)	94.7 (d) (10.7)	129.6	123.6	123.0	129.6	94.7 (d) (10.7)	
[Rh(C₅Me₅)(4,6-dimethylindenyl)]-[PF₆]	105.1 (d) (6.1)	9.2	82.1 (d) * (6.1)	90.1 (d) (6.1)	80.4 (d) * (6.1)	105.1 (d) † (6.1)	141.4 ‡	116.9 §	133.0 ‡	130.6 §	102.6 (d) † (4.6)	Me = 18.5, 22.1
[Rh(C₅Me₅)(indole)][PF₆]₂	109.1 (d) (7.6)	9.2		144.2	102.7	111.9 (d) (9.2)	99.9 (d) (4.6)	99.1 (d) (6.1)	98.5 (d) (4.6)	93.0 (d) (6.1)	119.3 (d) (10.7)	
[Ir(C₅Me₅)(indole)][PF₆]₂	102.4	8.8		145.1	102.4	106.5	91.7 *	91.4 *	90.8 *	84.2	115.8	
[Ir(C₅Me₅)(indolyl)][PF₆]	99.7 *	8.3		161.3	98.5 *	110.0	86.0	87.0	87.0	88.6	123.3	

[a] Recorded in [²H₆]acetone wih SiMe₄ as inernal standard; J(¹⁰³Rh–¹³C) in Hz in parentheses. [b] Recorded in CD₃NO₂. [c] In CF₃SO₃H with CD₂Cl₂ as internal standard. [d] Assignment tentative. [e] Not observed.

*, †, ‡, § These assignments may be interchanged.

method allowed the convenient preparation of [Rh-$(C_5Me_5)(C_6H_6)][PF_6]_2$ (V), [Ir(C_5Me_5)(naphthalene)]-$[PF_6]_2$ (VI), and [Ir(C_5Me_5)(phenanthrene)][PF_6] (VII), which were not easily accessible by the other routes; some complexes which had already been obtained by the trifluoroacetic acid route were also prepared.

It may be noted from the [1]H n.m.r. spectra (Table 2) that the resonances of the co-ordinated arene are moved downfield with respect to the free ligand. This contrasts with arenetri(carbonyl)chromium complexes [8] and also for some monocationic complexes, e.g. [M(C_5Me_5)(C_6H_6)][+] (M = Fe or Ru) [9] where upfield shifts are observed on co-ordination. The shift is greater for the neutral complexes {δ 4.43 for [Cr(C_6H_6)(CO)$_3$]} than for the monocationic complexes {δ 6.49 for [Fe(C_5H_5)(C_6H_6)][+] compared with δ 7.37 for free C_6H_6}. A balance clearly exists between the upfield shift experienced by the arene protons on complexation and a downfield shift arising from the increasing positive charge which is tilted in favour of the charge for the dicationic complexes [δ 7.72 for C_6H_6 in (V)] described here.

The [13]C n.m.r. spectra (Table 3) show that the arene carbons directly bonded to the metal are shifted upfield

(VI) iridium complexes showed any sign of fluxional behaviour at ambient temperature. The ease of replacement of the ligands by solvent frustrated attempts to measure the spectra at higher temperatures, however the [1]H n.m.r. spectrum of a solution of [Ir(C_5Me_5)-(naphthalene)][PF_6]$_2$ in trifluoroacetic acid remained unchanged up to +70 °C; a similar result has been reported for [Cr(naphthalene)(CO)$_3$].[15]

A remarkable feature of these arene complexes is the ease with which the arenes are displaced by solvent. We had already noted that Ir complexes were more inert than Rh ones and whereas [Ir(C_5Me_5)(C_6H_6)][PF_6]$_2$ was stable in dimethyl sulphoxide solution, p-xylene was rapidly displaced from the analogous p-xylenerhodium complex at +20 °C; [2] to complete the picture, we have now found that benzene in the benzenerhodium complex is completely displaced by acetone within 30 min at 20 °C.

For the iridium–polycyclic aromatic complexes, we find that co-ordinated naphthalene in (VI) is displaced by dimethyl sulphoxide within 10 min and co-ordinated phenanthrene in (VII) in 23 h at +20 °C, while the benzeneiridium complex is stable.

These observations correlate with the calculations of

(VI) (VII)

with respect to the free ligand; similar phenomena have previously been noted.[10,11] J(C–H) for the metal-bonded carbons in arenetri(carbonyl)chromium compounds are rather larger than for the free ligand {e.g. 173 Hz for [Cr(C_6H_6)(CO)$_3$] as against 158 Hz for benzene itself}, an effect that has been ascribed to an increase in the effective nuclear charge on the carbons brought about by withdrawal of electron density from the ring.[12,13] This effect should be even larger for the dicationic complexes and indeed J(C–H) is 188 Hz for the benzene carbons in [Ir(C_5Me_5)(C_6H_6)][PF_6]$_2$.

The complexity of the [13]C n.m.r. spectrum of [Ir(C_5-Me_5)(phenanthrene)][PF_6]$_2$ (VII) clearly shows that the iridium is bonded to a terminal rather than to the central ring. This form of bonding was also found in tricarbonyl(η^6-phenanthrene)chromium [14] and is probably due to the bond-localisation energy being lowest for an end ring; i.e. less resonance energy is lost if this is taken out of conjugation and complexed.

Neither the phenanthrene- (VII) nor the naphthalene-

localisation energies [naphthalene (9.21β) > phenanthrene (9.02β) > benzene (8.00β)][16] since the greater the energy needed to localise the electrons of six carbon atoms, the less stable the resultant complex may be expected to be. A similar order of stability towards co-ordinating solvents has been observed for arenetri-(carbonyl)chromium complexes.[17]

In summary, the monocyclic benzene complexes are the most stable towards solvolysis and the stability can be markedly enhanced by alkyl substitution.

η^6-Indene and η^5-Indenyl Complexes.[3b]—Indene reacted with the tris(acetone)rhodium solvent complex (IVa) to give the deprotonated η^5-indenyl complex (IXa) in high yield. The tris(acetone)iridium complex (IVb), in contrast, gave a 1 : 1 mixture of the η^5-indenyl complex (IXb) and the η^6-indene complex (VIIIb); the two complexes were separable since (IXb) was soluble in dichloromethane (Scheme 1).

When the reaction of indene with (IVa) was followed by [1]H n.m.r. spectroscopy, the initial formation of

[8] B. Deubzer, E. O. Fischer, H. P. Fritz, C. G. Kreiter, N. Kubitzsch, H. D. Simmons, and B. R. Willeford, Chem. Ber., 1967, 100, 3084; W. Strohmeier and H. Hellman, ibid., 1964, 97, 1877.

[9] I. U. Khand, P. L. Pauson, and W. E. Watts, J. Chem. Soc. (C), 1968, 2257; R. A. Zelonka and M. C. Baird, J. Organometallic Chem., 1972, 44, 383.

[10] B. E. Mann, Chem. Comm., 1971, 976.

[11] F. H. Köhler, Chem. Ber., 1974, 107, 570.

[12] R. V. Emanuel and E. W. Randall, J. Chem. Soc. (A), 1969, 3002.

[13] G. M. Bodner and L. J. Todd, Inorg. Chem., 1974, 13, 360.

[14] H. Deuschl and W. Hoppe, Acta Cryst., 1964, 17, 800; K. W. Muir, G. Ferguson, and G. A. Sim, J. Chem. Soc. (B), 1968, 467.

[15] K. M. Nicholas, R. C. Kerber, and E. I. Stiefel, Inorg. Chem., 1971, 10, 1519.

[16] B. J. Nicholson, J. Amer. Chem. Soc., 1966, 88, 5156.

[17] G. Yagupsky and M. Cais, Inorg. Chim. Acta, 1975, 12, L27.

(VIIIa) was observed, which then deprotonated within 30 min at 20 °C to (IXa). The indeneiridium complex also deprotonated and rearranged, but more slowly (36 h at 20 °C).

In trifluoroacid acid 20% of (IXa) was converted into (VIIIa) but the iridium complex (IXb) was left unchanged. In the stronger acid CF_3SO_3H, however, (IXa) and (IXb) were converted into (VIIIa) (90%) and (VIIIb) (66%) respectively.

The structures of the complexes (VIIIa) and (IXa) are clearly shown by their ^{13}C $\{^1H\}$ n.m.r. spectra (Table 3); thus, in the spectrum of (IXa) three resonances, corresponding to the five carbons bound to rhodium C(1) [≡C(3)], C(2), and C(3a) [≡C(7a)], all show doubling due to coupling to ^{103}Rh (100%, $I = \frac{1}{2}$), while the remaining

(at δ 3.12 and 3.64, $J = 26$ Hz) collapsed to a singlet (at δ 3.17). This stereospecific H^+/D^+ exchange cannot be due to the transient formation of (IXb) since the latter is stable to CF_3CO_2H over several days. The most reasonable explanation is that exchange occurs rapidly at C(1) without movement of the iridium from the six-membered to the five-membered ring, possibly via Ir^V-hydrido-intermediates as shown in Scheme 2.

This is not implausible since the intermediates can be stabilised in the resonance forms (A) and (B). Support for this suggestion comes from recent work by Johnson and Treichel [19] who found that in the fluorenyl complexes $[M(C_{13}H_{10})]$ [M = $Fe(C_5H_5)$ or $Mn(CO)_3$] the metal was bonded to one of the six-membered rings [either η^6 as in (C) or η^5 as in (D)]; the manganese complex slowly
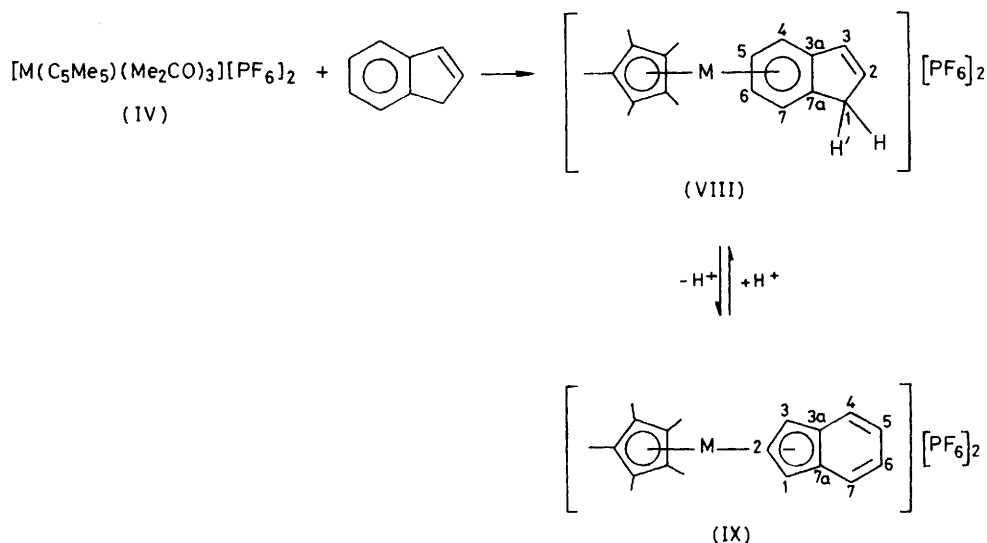
SCHEME 1

two resonances C(4) [≡C(7)] and C(5) [≡C(6)] do not. The pattern of the ^{13}C n.m.r. spectrum of the η^6-indene complex is quite different and shows the much greater asymmetry of the ligand and five of the six rhodium-bonded carbons show coupling to ^{103}Rh. Similar changes in the pattern of the ^{13}C spectra of η^3- and η^5-indenyl and of η^6-indene complexes of other metals have been noted.[18]

Attempts to stabilise the η^6-indene form by using the dimethylated derivative, 4,6-dimethylindene, as ligand in reaction with (IV) were only partially successful; the reaction products isolated were the η^5-4,6-dimethyl-indenyl complexes (X). In this case, however, the iridium complex (Xb) was more easily protonated (60%) in CF_3CO_2H than the rhodium complex (Xa) (<10%).

Although the protonation/deprotonation rearrangements of the iridium complexes (VIIIb) and (IXb) are slow, when the η^6-indene complex (VIIIb) was dissolved in CF_3CO_2D the double doublet due to H(1) and H(1')

rearranged on heating to the complex (E) in which the metal is bound to the central five-membered ring.

Clearly then, if stereospecific exchange of one hydrogen at C(1) occurs rapidly then protonation/deprotonation must be fast and, therefore, the rate-determining step in the overall arrangements (VIII) ⇌ (IX) is the movement of the metal from the six-membered to the five-membered ring or vice versa.

One other example of such a rearrangement has been observed, namely the protonation of bis(η^5-indenyl)iron to give the η^5-indenyl(η^6-indene)iron cation.[20] Stereospecific deuteriation was again observed (with CF_3CO_2D) which the authors suggested involved endo-attack at C(1) via an $[Fe^{IV}H(\eta^5-C_9H_7)_2]^+$ species. This reaction was not, however, reversed by base.

On the evidence we have at present we are unable to say whether the C(1) hydrogen which exchanges with D^+ in (VIIIb) is endo- or exo-, though in contrast to the bis(indenyl)iron complex it is the lower field resonance

[18] F. H. Köhler, *Chem. Ber.*, 1974, **107**, 570.
[19] J. W. Johnson and P. M. Treichel, *J.C.S. Chem. Comm.*, 1976, 688.

[20] C. C. Lee, R. G. Sutherland, and B. J. Thompson, *Chem. Comm.*, 1971, 1071; P. M. Treichel and J. W. Johnson, *J. Organometallic Chem.*, 1975, **88**, 207.

which disappears. Certainly the intermediacy of an Ir–H (Ir–D) species would imply that *endo*-exchange was occurring.

η^6-*Indole and* η^5-*Indolyl Complexes*.—Reaction of the tris(acetone) complexes (IVa) and (IVb) with indole gave

Neither of these dications deprotonated spontaneously in acetone in the manner of the η^6-indene complexes (VIII), but the iridium complex (XIb) lost a proton when it was reacted with base (Na_2CO_3 in H_2O, or KOBu^t in acetone) to give the η^5-indolyl complex (XII). This
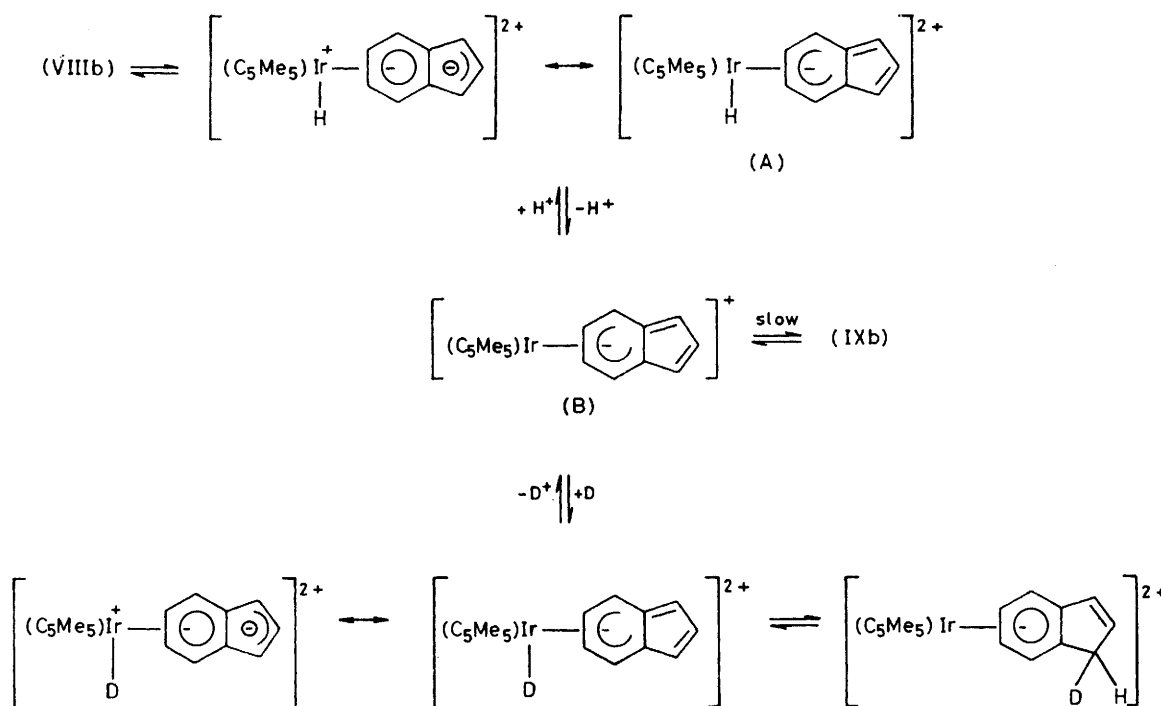
Scheme 2

the η^6-indole complexes (XIa) and XIb). The complexes are assigned the structures shown on the basis of their analyses and spectra, in particular the ^{13}C $\{^1H\}$ spectrum of the rhodium complex (XIa) (Table 3) where the doubling of six ring carbon atoms, arising from coupling to

reaction was easily reversed on addition of small quantities of CF_3CO_2H (Scheme 3). By contrast, reaction of the η^6-indole-rhodium complex with base caused decomposition. The η^5-indolyl iridium complex (XII) was completely characterised by analysis and spectroscopy
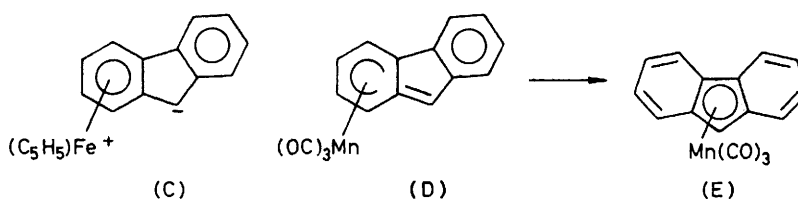
^{103}Rh, clearly shows that rhodium is bonded to six of the indole carbons. The spectrum of the iridium complex (XIb) is very similar but, of course, no coupling to the metal can be observed.

The NH proton was observed as a broad resonance at δ 11.65 in (XIa), and ν(NH) was also observed for both complexes [at 3 380 (XIa) and 3 395 (XIb) cm^{-1}] in the i.r. spectrum.

(see Tables); as expected, the ν(NH) in (XIb) was not present in (XII). Only one other η^6-indole complex, tricarbonyl(indole)chromium,[21] and one other η^5-indolyl complex tricarbonyl(2-methylindolyl)manganese,[22] appear to have previously been reported.

η^6-*Fluorene Complexes*.—Fluorene reacted with the acetone solvent complexes to give the η^6-bonded compounds (XIIIa) and (XIIIb). This is clearly evident from the analytical data (which show no loss of HPF$_6$ to

[21] E. O. Fischer, H. A. Goodwin, C. G. Kreiter, H. D. Simmons, jun., K. Sonogashira, and S. B. Wild, *J. Organometallic Chem.*, 1968, 14, 359.
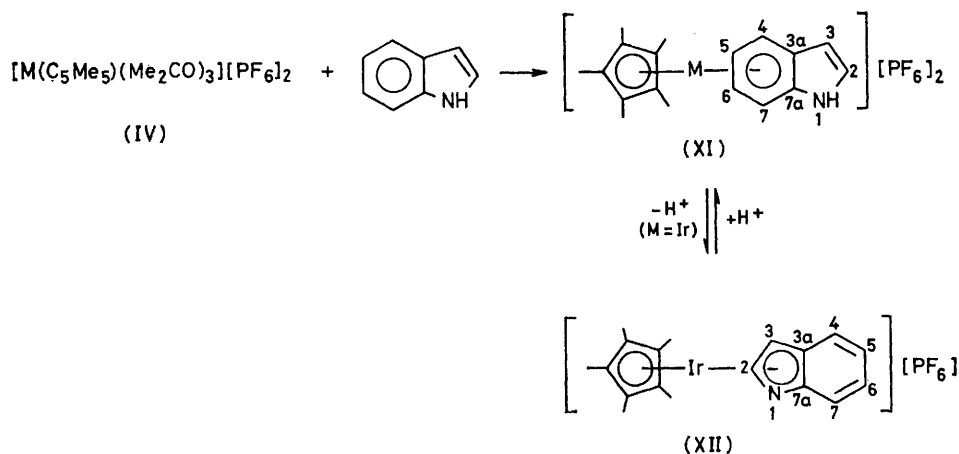
[22] P. L. Pauson, A. R. Qazi, and B. W. Rockett, *J. Organometallic Chem.*, 1967, 7, 325.

have occurred) and from the complexity of the ^{13}C $\{^1H\}$ n.m.r. spectrum of (XIIIb) where the six co-ordinated ring carbons [C(4b), C(5), C(6), C(7), C(8), and C(8a)] are also moved considerably upfield with respect to the

also failed. At least three bonding types are known for the fluorenyl ligand [15,19,23,24] and in the absence of further data we cannot tell what the bonding is in the fluorenyl-iridium complex we obtained in solution.
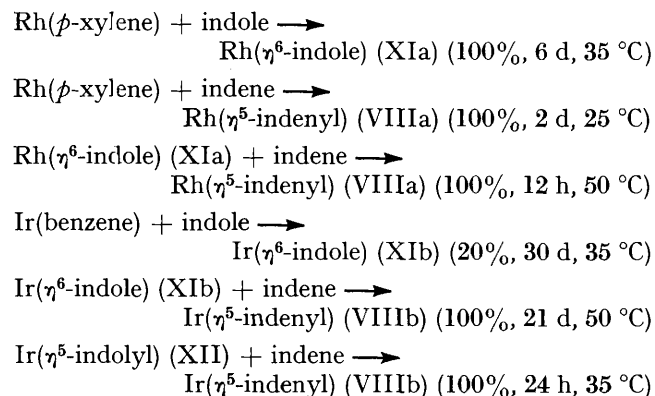
$$[M(C_5Me_5)(Me_2CO)_3][PF_6]_2 \quad + \quad \text{(IV)} \longrightarrow \text{(XI)} [PF_6]_2$$

$$\begin{array}{c} -H^+ \\ (M=Ir) \end{array} \Bigg\updownarrow \begin{array}{c} +H^+ \end{array}$$

(XII)

SCHEME 3

remainder. Acetone (and other donor solvents) completely and rapidly displaced fluorene from the rhodium complex (XIIIa), even at 0 °C.

$$[M(C_5Me_5)(Me_2CO)_3][PF_6]_2 \quad + \quad \text{(IV)}$$

$$\downarrow$$
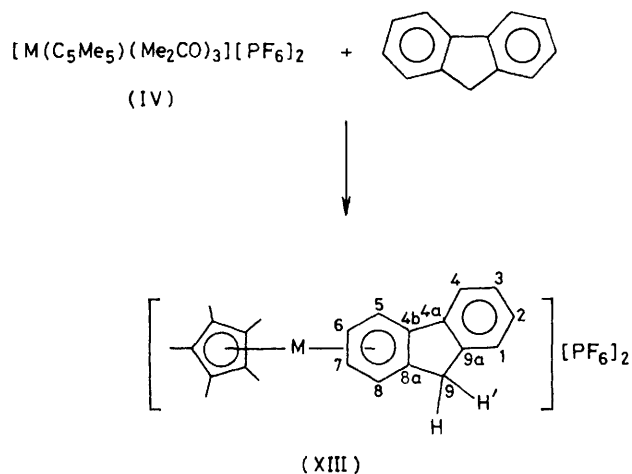
(XIII)

Neither complex showed any tendency to deprotonate spontaneously, but the iridium compound (XIIIb) reacted with base (Na$_2$CO$_3$ in H$_2$O, or KOBu^t in acetone) to give a mixture, the major component of which showed an ^1H n.m.r. resonance at $\delta\,1.8$ (s, C$_5$Me$_5$) and a singlet ($\delta\,3.9$) which may be ascribed to a single hydrogen on the five-membered ring [(XIIIb) shows a double doublet at $\delta\,3.87$ and 4.21, $J = 24$ Hz]. No complex was isolable from this mixture but since the ^1H n.m.r. spectrum of (XIIIb) was regenerated on the addition of CF$_3$CO$_2$H it is plausible to suppose that the reaction of (XIIIb) with base led to deprotonation at C(8) of the fluorene ring. Attempts to prepare a fluorenyliridium complex from Na[C$_{13}$H$_9$]

Exchange Reactions.—A number of reactions in which a co-ordinated arene was exchanged were investigated by ^1H n.m.r. spectroscopy. They were carried out by reacting 1.2—1.5 equivalents of the free ligand with the appropriate complex in nitromethane solution. The results are summarised below as follows.

Rh(p-xylene) + indole $\longrightarrow$
Rh(η^6-indole) (XIa) (100%, 6 d, 35 °C)

Rh(p-xylene) + indene $\longrightarrow$
Rh(η^5-indenyl) (VIIIa) (100%, 2 d, 25 °C)

Rh(η^6-indole) (XIa) + indene $\longrightarrow$
Rh(η^5-indenyl) (VIIIa) (100%, 12 h, 50 °C)

Ir(benzene) + indole $\longrightarrow$
Ir(η^6-indole) (XIb) (20%, 30 d, 35 °C)

Ir(η^6-indole) (XIb) + indene $\longrightarrow$
Ir(η^5-indenyl) (VIIIb) (100%, 21 d, 50 °C)

Ir(η^5-indolyl) (XII) + indene $\longrightarrow$
Ir(η^5-indenyl) (VIIIb) (100%, 24 h, 35 °C)

The greater lability of the arenerhodium compared to the areneiridium complexes has already been mentioned and these data emphasise this further. The high stability of the η^5-indenyl complexes (VIII) is not surprising since they may be regarded as substituted rhodicinium or iridicinium (analogous to cobalticinium) cations. It is, however, unexpected that indole should be so easily displaced by indene and particularly that the displacement occurs more readily for η^5-indolyl than for η^6-indole. In view of the low stability of the naphthalene and phenanthrene complexes (VI) and (VII) it is also surprising that indole will displace (albeit slowly) p-xylene from rhodium and benzene from iridium to give the η^6-indole complexes.

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

[24] C. Kowala, P. C. Wailes, H. Weigold, and J. A. Wunderlich, *J.C.S. Chem. Comm.*, 1974, 993.

An order of increasing stability of arene ligand may therefore be drawn up: η^6-naphthalene < η^6-phenanthrene < η^6-benzene < η^6-alkylbenzenes < η^6-indole < η^5-indenyl > η^6-indene, η^5-indolyl.

EXPERIMENTAL

All reactions were run under a protective atmosphere of nitrogen as a precaution but none of the complexes prepared showed any marked sensitivity to air. Analytical data are collected in Table 1, ^{1}H n.m.r. spectra in Table 2, and ^{13}C n.m.r. spectra in Table 3. Since the methods used to prepare the compounds were very similar only typical preparations are detailed; most of the compounds were prepared by method (c) below, the only variation being that in some cases diethyl ether was added to precipitate the product.

Tris(acetonitrile)pentamethylcyclopentadienylrhodium Hexafluorophosphate (Ia).—Silver hexafluorophosphate (1.3 g, 5.2 mmol) was added to a solution of [{Rh(C$_5$Me$_5$)Cl$_2$}$_2$] (0.8 g, 1.3 mmol) in acetonitrile (10 ml). An immediate exothermic reaction occurred with the precipitation of silver chloride. This was removed by centrifugation and the yellow supernatant solution was freed from any remaining silver salt by filtration through a short column packed with cellulose. The eluate was taken to dryness under reduced pressure and the residue crystallised from acetonitrile–diethyl ether to give crystals of the yellow complex (Ia) (1.09 g, 65%).

Preparation of η^6-Naphthalene(pentamethylcyclopentadienyl)iridium(III) Hexafluorophosphate (VIb).—(a) *From η^5-pentamethylcyclopentadienylbis(trifluoroacetato)iridium(III) hydrate.* [Ir(C$_5$Me$_5$)(OCOCF$_3$)$_2$]·H$_2$O (0.25 g, 0.45 mmol) and naphthalene (0.60 g, 0.46 mmol) were heated in trifluoroacetic acid (5 ml) under nitrogen for 48 h at 65 °C. The solvent was removed *in vacuo* and the residue dissolved in acetone (2 ml); this solution was treated with a saturated aqueous solution of ammonium hexafluorophosphate to yield a white solid which was filtered off, washed with a little water and then with diethyl ether, and finally dried to give the complex [Ir(C$_5$Me$_5$)(C$_{10}$H$_8$)][PF$_6$]$_2$ (0.06 g, 18%). The complex was crystallised as white needles from acetone–ether.

(b) *From di-μ-chloro-bis[chloro(η^5-pentamethylcyclopentadienyl)iridium(III)].* [{Ir(C$_5$Me$_5$)Cl$_2$}$_2$] (0.1 g, 0.12 mmol) and naphthalene (0.05 g, 0.41 mmol) were refluxed for 64 h under nitrogen in freshly distilled boron trifluoride etherate

(6 ml). The solvent was removed *in vacuo* at 80 °C and the residue washed with chloroform to give complex (VIb) (0.14 g, 48%).

(c) *From tris(acetone)(η^5-pentamethylcyclopentadienyl)iridium(III) hexafluorophosphate* (IVb). The acetone solvent complex was prepared by stirring together [{Ir(C$_5$Me$_5$)Cl$_2$}$_2$] (0.2 g, 0.25 mmol) and Ag[PF$_6$] (0.25 g, 1.0 mmol) in acetone (5 ml) for 10 min. The silver chloride precipitate was filtered off and the filtrate treated with naphthalene (0.3 g, 2.34 mmol). When set aside, a white precipitate formed which was filtered off, washed with dichloromethane and ether, and then dried to give (VIb) (0.22 g, 58%).

Preparation of η^6-Indene(η^5-pentamethylcyclopentadienyl)iridium Hexafluorophosphate (VIIIb) *and η^5-Indenyl(η^5-pentamethylcyclopentadienyl)iridium Hexafluorophosphate* (IXb).—Indene (0.2 g, 1.7 mmol) was added to a solution of the iridium acetone solvent species, (IVb), prepared from [{Ir(C$_5$Me$_5$)Cl$_2$}$_2$] (0.2 g, 0.25 mmol) in acetone (5 ml), and the solution was stirred at room temperature for 5 min. The solvent was removed *in vacuo* and the off-white residue was washed with diethyl ether and air-dried. This solid was then thoroughly triturated with dichloromethane to extract the monocationic species and leave [Ir(C$_5$Me$_5$)(C$_9$H$_8$)][PF$_6$]$_2$ (VIIIb) as a white solid (0.17 g, 45%). The dichloromethane washings were taken to dryness and the residue washed with ether. Recrystallisation from dichloromethane and ether gave white crystals of [Ir(C$_5$Me$_5$)(C$_9$H$_7$)][PF$_6$] (IXb) (0.09 g, 31%).

The reaction of indene with the rhodium acetone solvent species (IVa), or of 4,6-dimethylindene [25] and (IVa) or (IVb), yielded only the indenyl complexes (IXa), (Xa), or (Xb) respectively.

η^5-Indolyl(η^5-pentamethylcyclopentadienyl)iridium Hexafluorophosphate (XII).—Potassium t-butoxide (0.06 g, 0.53 mmol) was added to a stirred acetone solution (10 ml) of [Ir(η^5-C$_5$Me$_5$)(η^6-C$_8$H$_7$N)][PF$_6$]$_2$ (XIb) (0.25 g, 0.34 mmol) which immediately turned yellow. After the mixture had been stirred for a further 10 min, the solvent was removed *in vacuo*; the remaining yellow solid was then washed with ethanol, to remove excess of KOBu^t, and then with diethyl ether to leave the yellow product [Ir(C$_5$Me$_5$)(C$_8$H$_7$N)][PF$_6$] (XII) (0.18 g, 88%).

[25] R. G. Kadesch, *J. Amer. Chem. Soc.*, 1944, **66**, 1207; J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 1963, 590.