Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part 18.[1] The Reactions of $[M(C_5Me_5)(sol)_3][PF_6]_2$ (M = Rh or Ir; sol = MeCN, Me_2CO, or MeOH) with Mono-, Di-, and Tri-olefins †

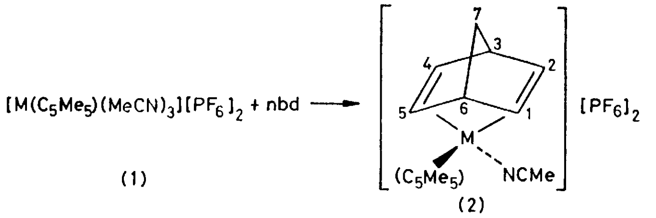
By **Colin White,* Stephen J. Thompson,** and **Peter M. Maitlis,*** Department of Chemistry, The University, Sheffield S3 7HF

Reaction of $[M(C_5Me_5)(MeCN)_3][PF_6]_2$ (1; M = Rh or Ir) with bicyclo[2.2.1]heptadiene (nbd) gave $[M(C_5Me_5)(nbd)(MeCN)][PF_6]_2$. Cyclo-octa-1,5-diene (cod) underwent deprotonation when treated with (1) or $[M(C_5Me_5)(Me_2CO)_3][PF_6]_2$, (3), to give the 1—3:5,6-η-cyclo-octadienyl complexes $[M(C_5Me_5)(C_8H_{11})][PF_6]$ (M = Rh or Ir); the iridium complex underwent hydride attack by $[BH_4]^-$ to give $[Ir(C_5Me_5)(cod)]$. Cyclopentadiene, dicyclopentadiene, and propene were all complexed with deprotonation on reaction with (3) to give $[M(C_5Me_5)(C_5H_5)][PF_6]$, the 1—3:5,6-η-(4,7-methano)-3a,4,7,7a-tetrahydroindenyl complexes, $[M(C_5Me_5)(C_{10}H_{11})][PF_6]$ (M = Rh or Ir) and $[Ir(C_5Me_5)(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_3H_6)][PF_6]$ respectively. In contrast, cycloheptatriene underwent nucleophilic attack by the solvent when treated with $[M(C_5Me_5)(YH)_x][PF_6]_2$ [3; YH = Me_2CO, M = Rh or Ir; YH = MeOH, M = Rh] to give the 6-*exo*-acetonyl- or 6-*exo*-methoxy-1—5-η-cycloheptadienyl complex $[M(C_5Me_5)\{C_7H_8(Y)\}][PF_6]$. The ^1H and ^{13}C spectra of the products are discussed.

THE tris-solvent complexes $[M(C_5Me_5)(sol)_3][PF_6]_2$ ‡ are readily prepared by the reaction of $[\{M(C_5Me_5)Cl_2\}_2]$ with $Ag[PF_6]$ in the appropriate solvent, sol. With acetonitrile, dimethyl sulphoxide, or pyridine well defined tris-solvent complexes have been isolated and characterised whereas complexes with less strongly co-ordinating solvents (*e.g.* acetone or dichloromethane) are only known in solution.[2] These solvent molecules are easily displaced by more strongly co-ordinating ligands and we have previously described the reactions of $[M(C_5Me_5)(sol)_3]^{2+}$ with arenes,[2] phosphorus donor ligands,[3] and phenol.[4] In this paper we report their reactions with mono-, di- and tri-olefins.

RESULTS AND DISCUSSION

(i) *Reactions involving only Co-ordination of the Olefin.*—An excess of bicyclo[2.2.1]heptadiene (norbornadiene, nbd) reacted with $[Ir(C_5Me_5)(MeCN)_3][PF_6]_2$ (1b) at room temperature to displace two of the acetonitrile ligands and give the bicyclo[2.2.1]heptadiene complex, $[Ir(C_5Me_5)(nbd)(MeCN)][PF_6]_2$ (2b). The complex $[Rh(C_5Me_5)(nbd)(MeCN)][PF_6]_2$ (2a) was prepared similarly but proved to be less stable in solution.



(1) (2)

a, M = Rh; b, M = Ir

The complexes (2a) and (2b) were formulated as shown on the basis of microanalyses and i.r. and ^1H n.m.r. spectroscopy (Table 1). In particular, the presence of co-ordinated acetonitrile was indicated by singlets at δ 2.88 (2a) and 3.14 (2b) in the ^1H n.m.r. spectra (*cf.* free acetonitrile δ 2.02) and by ν(CN) at 2 318 and 2 290 (2a) cm^{-1} and 2 308 and 2 280 (2b) cm^{-1} in the i.r. spectra. In the ^1H n.m.r. spectrum of uncomplexed bicyclo[2.2.1]heptadiene in acetone, the olefinic protons appear at δ 6.79; complexation to Rh^{III} or Ir^{III} results in an upfield shift (0.13—0.9 p.p.m.).

The ^1H n.m.r. spectrum of $[Rh(C_5Me_5)(nbd)(MeCN)][PF_6]_2$ recorded in $[^2H_6]$acetone was similar to that of the corresponding iridium complex (2b) (Table 1) but contained additional singlets at δ 2.50 (MeCN) and 1.82 (C_5Me_5) together with signals corresponding to those of free nbd. The two additional singlets are presumed to be those of $[Rh(C_5Me_5)(MeCN)\{(CD_3)_2CO\}_2][PF_6]_2$ since they disappeared upon addition of an excess of nbd and the singlets assigned to (2a) at δ 2.88 and 2.02 increased in intensity. Similar effects were observed when (2a) was dissolved in $MeNO_2$; approximately 30% of the complexed bicyclo[2.2.1]heptadiene was displaced in either of these solvents.

In the proposed structure (2) the 1 and 2 (or 4 and 5) positions of the norbornadiene ligand are inequivalent as are the positions 3 and 6. Although there are indications of this in the ^1H n.m r. spectra of (2a) and (2b) it is most clearly evident in the ^{13}C spectrum of (2a) (Table 2). This spectrum also confirmed that displacement of norbornadiene from (2a) occurred in acetone. The ^{13}C resonances were assigned with the aid of the proton-coupled spectrum; an interesting feature is that the norbornadiene CH_2 exhibits a small (3.1 Hz) but definite rhodium coupling; a similar effect was observed in the 1—3:5,6-η-(4,7-methano)-3a,4,7,7a-tetrahydroindenyl-rhodium complex (7) discussed below.

An excess of bicyclo[2.2.1]heptadiene was treated with $[Ir(C_5Me_5)(Me_2CO)_3][PF_6]_2$ (3b) in the hope that norbornadiene would displace the weakly co-ordinated

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† No reprints available.

‡ Unless specified M = Rh or Ir.

[1] Part 17, M. J. H. Russell, C. White, and P. M. Maitlis, *J.C.S. Dalton*, 1978, 849.

[2] C. White, S. J. Thompson, and P. M. Maitlis, *J.C.S. Dalton*, 1977, 1654.

[3] S. J. Thompson, C. White, and P. M. Maitlis, *J. Organometallic Chem.*, 1977, **136**, 87.

[4] C. White, S. J. Thompson, and P. M. Maitlis, *J. Organometallic Chem.*, 1977, **127**, 415.

acetone to give $[Ir(C_5Me_5)(\eta^4-C_7H_8)(\eta^2-C_7H_8)][PF_6]_2$. Although a white solid was isolated from this reaction it rapidly decomposed, even in the solid state, to give what appeared to be iridium metal.

TABLE 1

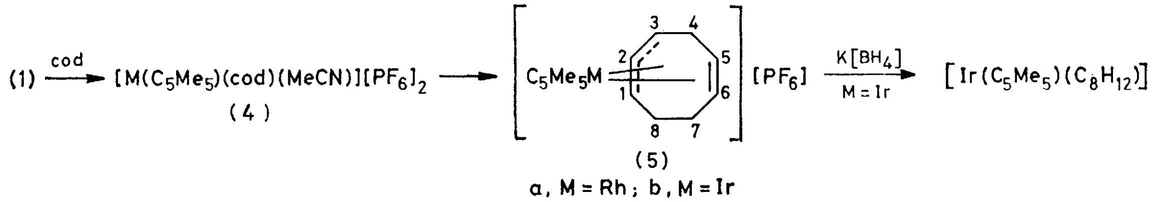
Analytical data and ^1H n.m.r. data (δ scale; coupling constants in Hz) [a]

	C	H	N	C_5Me_5	H(1) [b]	H(2)	H(3)	H(4)	H(5)	H(6)	Other
$[Rh(C_5Me_5)(nbd)(MeCN)][PF_6]_2$ (2a)	34.5 (34.5)	3.7 (3.7)	1.9 (2.1)	2.02(s) [c]	6.18(m) * J(1), (2) = 3	6.66(t) * J(2), (3) = 3	4.07(s, br) †	≡H(2)	≡H(1)	4.42(s,br) †	MeCN = 2.88(s) CH_2 = 1.92(s,br)
$[Ir(C_5Me_5)(nbd)(MeCN)][PF_6]_2$ (2b)	30.5 (30.4)	3.8 (3.5)	2.0 (1.9)	2.04(s) [e]	5.89(m) *	6.1(m) *	4.58(s,br) †	≡H(2)	≡H(1)	4.58(s,br) †	MeCN = 3.14(s) CH_2 = 1.60(s,br)
$[Rh(C_5Me_5)$(cyclo-octadienyl)]-$[PF_6]$ (5a)	44.1 (44.0)	5.3 (5.3)		2.05(s) [c]	4.99(m)	4.28(m)	4.53(m)	3.25(m)		4.11(m)	H(4′) = 3.25(m), H(7′) = 2.9(m), H(7) and H(8) = 2.6(m) H(8′) = 1.85(m)
$[Ir(C_5Me_5)$(cyclo-octadienyl)]-$[PF_6]$ (5b)	37.3 (37.3)	4.4 (4.5)		2.08(s) [e]	4.93(m) J(1),(2) = 7; J(1),(8) ≈ J(1), (8′) = 7.5	4.05(t) J(2),(3) = 7	4.29(m)	3.44(m) J(4), (4′) = 15	3.22(m) J(5), (6) = 6	3.93(t) J(6),(7) = 6	H(4′) = 3.32(m), H(7) = 2.44(m), H(7′) = 2.88(m), H(8) = 2.35(m), H(8′) = 1.61(m)
$[Rh(C_5Me_5)(C_{10}H_{11})][PF_6]$ (7)	47.6 (46.7)	5.2 (5.1)		1.83(s)	5.72(dd) J(1), (7a) = 3	4.70(t) J(1), (2) = 2	≡H(1)	3.29(s,br)	5.87(dd)	≡H(5)	H(3a) and H(7a) = 2.99(s,br), H(8) * = 2.14(dd), J(7), (8) = 2, J(8), (9) = 10; H(9) = 1.85 [d]
$[Ir(C_5Me_5)(C_3H_5)(C_3H_6)][PF_6]$ (8)	34.3 (34.6)	4.8 (4.7)		1.92, 1.98 [e]		4.1(m)					Me = 1.65(d, 6)
$[Rh(C_5Me_5)\{C_7H_8(CH_2COMe)\}]$-$[PF_6]$ (10a)	45.4 (45.1)	5.6 (5.3)		2.05(s)	4.48(m) J(1), (2) = 8.5	5.21(dd) J(2), (3) = 5.5	6.46(t) J(3), (4) = 5	5.59(t) J(4), (5) = 8	4.41(m)	3.26(m) J(6), (CH_2) = 8	$H(7_{endo})$,[d] $H(7_{exo})$ = 0.50(m), CH_2 = 2.32 and 2.47 (J = 18) Me = 2.09(s)
$[Ir(C_5Me_5)\{C_7H_8(CH_2COMe)\}]$-$[PF_6]$ (10b)	38.5 (38.6)	4.7 (4.5)		2.10(s)	4.27(m) J(1), (2) = 7	5.66(d) J(2), (3) = 5	6.67(t) J(3), (4) = 6.5	5.32(dd) J(4), (5) = 8.5	4.50(d,br)	2.90(m)	$H(7_{endo})$ = 1.94(m), $H(7_{exo})$ = 0.57 (m) CH_2 = 2.40(t), Me = 2.06(s)
$[Rh(C_5Me_5)\{C_7H_8(OMe)\}][PF_6]$ (11)	42.7 (42.7)	5.2 (5.2)		2.06(s)	4.05(m) J(1), (2) = 7	5.59(t) J(2), (3) = 6.5	6.45(t) J(3), (4) = 6.5	5.36(t) J(4), (5) = 9	4.40(d,br)	3.95(dt) J(6),(7_{endo}) ≈J(6),(7_{exo}) = 8	$H(7_{endo})$ = 2.35(m) $H(7_{exo})$ = 0.66(m) [J(1),(7_{exo}) = 5] OMe = 3.30(s)

[a] Calculated % composition in parentheses; unless stated otherwise spectra were recorded in $CDCl_3$ using $SiMe_4$ as internal standard. [b] For ring numbering system see text. [c] Recorded in $[^2H_6]$acetone. [d] Signal partially obscured by C_5Me_5 signal. [e] Recorded in $[^2H_3]$nitromethane at −20 °C; other signals observed as broad multiplets between δ 3.8—1.0.

*,† These assignments may be interchanged.

(ii) *Reactions involving Deprotonation of the Olefin*.—Co-ordination of a substituted alkene to a metal is known to increase its acidity; for example Pd^{II}–olefin complexes are known to deprotonate in the presence of a base to give the corresponding η^3-allyl-complexes;[5] in some cases this deprotonation occurs even in the absence of base.[5a,b] If, in contrast to nbd, the olefin contained an α-hydrogen which could be removed, then complexation to M^{III} in a dicationic complex might facilitate similar deprotonation reactions. As described below such behaviour was indeed observed.



(a) *Cyclo-octa-*1,5-*diene*. The addition of one equivalent of cyclo-octa-1,5-diene (cod) to a solution of $[Ir(C_5Me_5)(Me_2CO)_3][PF_6]_2$ (3b) in acetone resulted in the rapid formation of the 1—3:5,6-η-cyclo-octadienyl complex (5b). However, at least six equivalents of cod were required for the analogous rhodium reaction to go to completion. Reaction of cod with $[Ir(C_5Me_5)(MeCN)_3][PF_6]_2$ was much slower than with the tris-acetone complex (3b) and was monitored by ^1H n.m.r. spectroscopy. This allowed the detection of an intermediate complex which exhibited signals at δ 2.07 and 3.12, very close to those observed for $[Ir(C_5Me_5)(nbd)(MeCN)][PF_6]_2$ (at δ 2.04 and 3.14), and it is suggested that the intermediate is (4b) which subsequently undergoes spontaneous deprotonation to give (5).

The concentration of the intermediate (4b) reached a maximum after *ca*. 3 h at 35 °C and after a further 24 h only the complex (5b) was present. No such intermediate was detected in the formation of the rhodium complex, from either the acetone or acetonitrile solvent complexes.

The n.m.r. spectra of (5), particularly the ^{13}C n.m.r. spectrum of (5b), reflect the asymmetry of the cyclo-octadienyl ligand and clearly indicate that it bonds in a 1—3:5,6-η manner in these complexes. The ^1H n.m.r. spectra were assigned on the basis of spin-decoupling experiments on (5b). It may be noted that the assign-

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[5] (*a*) R. Hüttel and M. Bechter, *Angew. Chem.*, 1959, **71**, 456; (*b*) R. Hüttel, J. Kratzer, and M. Bechter, *Chem. Ber.*, 1961, **94**, 766; (*c*) A. D. Ketley and J. Braatz, *Chem. Comm.*, 1968, 169.

[6] J. Lewis and A. W. Parkins, *J. Chem. Soc.* (*A*), 1967, 1150.

ments differ from those reported for the 1—3:5,6-η-cyclo-octadienyl complexes $[M(C_5H_5)(C_8H_{11})][PF_6]$ (M = Co,[6] Rh, or Ir [7]).

Cyclo-octadienyl complexes are usually prepared either by hydride abstraction from a cyclo-octa-1,5-diene complex {*e.g.* $[Co(C_5H_5)(C_8H_{12})] + CPh_3BF_4$}[6] or by protonation of a cyclo-octatriene complex {*e.g.* $[M(C_5H_5)(C_8H_{10})]$ (M = Co, Rh, or Ir) + CF_3CO_2H}[7] and the reaction described above involving deprotonation of a cyclo-octadiene complex is rare, but not without precedent.[8]

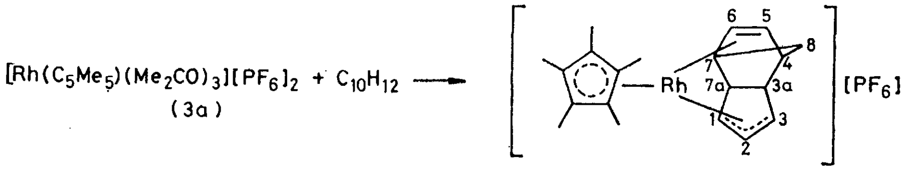
Reaction of KBH_4 at 20 °C with the cyclo-octadienyl complex cation, $[Ir(C_5Me_5)(C_8H_{11})]^+$, resulted in hydride attack to give the known cyclo-octa-1,5-diene complex $[Ir(C_5Me_5)(C_8H_{12})]$.[9]

(b) *Cyclopentadiene.* In view of the tendency of the cyclo-octadiene complex (4) to deprotonate spontaneously it is not surprising that the more acidic cyclopentadiene undergoes this reaction even more readily. Thus when freshly cracked cyclopentadiene was added to the metal–acetone complex (3), the cyclopentadienyl complexes (6) [10] were formed in high yields. No intermediate diene complexes were detected.

$$\underset{(3)}{[M(C_5Me_5)(Me_2CO)_3][PF_6]_2} + C_5H_6 \longrightarrow \underset{(6)}{[M(C_5Me_5)(C_5H_5)][PF_6]}$$

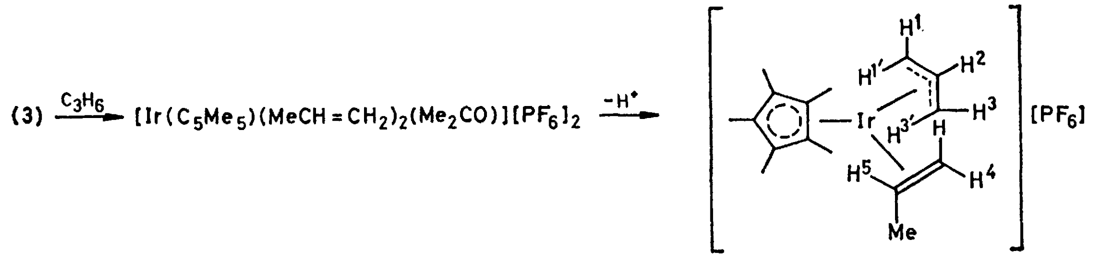
a, M = Rh; b, M = Ir

(c) *Dicyclopentadiene.* The rhodium tris-acetone complex (3a) reacted similarly with dicyclopentadiene in acetone to give the 1—3:5,6-η-(4,7-methano)-3a,4,7,7a-tetrahydroindenyl complex (7).



(7)

The proposed structure of (7) is fully consistent with the ^1H and ^{13}C n.m.r. data (Tables 1 and 2). The ^1H n.m.r. spectrum was assigned on the basis of spin-decoupling experiments and is comparable to the ^1H n.m.r. data reported for $[Co(C_5H_5)(C_{10}H_{11})]^+$ which was prepared from the corresponding Co^I–dicyclopentadiene complex by hydride abstraction.[11]



(8)

In common with $[Rh(C_5Me_5)(nbd)(MeCN)][PF_6]_2$ discussed above, the bridging methylene, C(8), exhibited a small (4.6 Hz) coupling to rhodium in the ^{13}C n.m.r. spectrum.

(d) *Propene.* When propene was bubbled into an acetone solution of $[Rh(C_5Me_5)(Me_2CO)_3][PF_6]_2$ no reaction was observed. However, reaction of propene did occur with the corresponding iridium–acetone complex (3b) to give η^3-allyl(η^5-pentamethylcyclopentadienyl)(η^2-propene)iridium(III) hexafluorophosphate. No intermediate was detected but this complex is probably formed by loss of a proton from a bis-η^2-propene complex.

Absorptions characteristic of the η^3-allyl ligand [12] were observed in the i.r. spectrum of (8) [*e.g.* $\delta(CH_2)_{sym}$, 1 460 cm^{-1}; $\nu(C-C-C)_{sym}$, 1 382 cm^{-1}; and $\nu(C-C-C)_{asym}$, 1 030 cm^{-1}].

^1H and ^{13}C n.m.r. studies revealed that complex (8) was stereochemically non-rigid. At +35 °C the C_5Me_5 signal could be seen as a clear singlet but other resonances were broad and complex. On cooling the solution to −20 °C the spectrum sharpened considerably but even then few of the signals could be assigned with any certainty. However, the C_5Me_5 signal was split into two singlets (δ 1.92 and 1.98, relative intensity 3 : 2) indicating that two isomers of this complex were present. The complexity of the ^1H n.m.r. spectrum therefore arises from the asymmetry of structure (8) and because the resonances of the two isomers overlap. The high temperature limiting ^1H n.m.r. spectrum could not be obtained because significant decomposition occurred above 80 °C.

The room temperature ^{13}C spectrum was broad, as expected, but at low temperatures the spectrum clearly

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[7] J. Evans, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 2668.

[8] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1964, 5002; W. C. Kaska and R. F. Reichelderfer, *J. Organometallic Chem.*, 1974, **78**, C47.

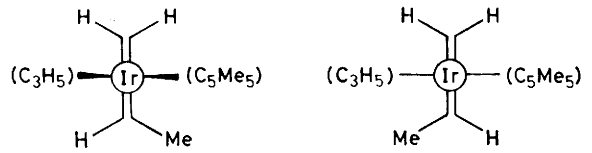
[9] H. B. Lee, K. Moseley, C. White, and P. M. Maitlis, *J.C.S. Dalton*, 1975, 2322.

[10] K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2875.

[11] J. Lewis and A. W. Parkins, *J. Chem. Soc.* (*A*), 1969, 953.

[12] D. C. Andrews and G. Davidson, *J.C.S. Dalton*, 1972, 1381.

showed the presence of two isomers with each signal being duplicated (Table 2).



Isomeric forms of $[Ir(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_3H_6)][PF_6]$

Two anticipated isomeric forms of (8) are shown in the Figure and they arise from complexing different faces of the prochiral propene to the iridium atom. At higher temperatures, free rotation about the iridium–propene bond would convert these two isomers into enantiomers which would not be distinguished by conventional n.m.r. spectroscopy. Other isomers could arise from different orientations of the η^3-allyl ligand; however, since only two isomers were observed we assume the allyl ligand adopts a single preferred orientation as in the complexes $[M(C_5Me_5)(\eta^3\text{-}C_3H_5)Cl]$ [10] and $[M'(C_5H_5)(\eta^3\text{-}C_3H_5)(CO)]$ (M' = Fe or Ru).[13]

TABLE 2

$^{13}C\{^1H\}$ N.m.r. data (δ scale); $J(^{103}Rh\text{-}^{13}C)$ in Hz in parentheses [a]

	C_5Me_5	$C_5\mathit{Me}_5$	C(1) [b]	C(2)	C(3)	C(4)	C(5)	C(6)	Other
$[Rh(C_5Me_5)(nbd)(MeCN)][PF_6]_2$	110.9(d) [c] (7.6)	9.9	94.9(d) * (4.6)	105.7(d) * (4.6)	47.0 †	≡C(4)	≡C(1)	51.2 †	C(7) = 70.5(d, 3.1) *Me*CN = 4.5
$[Ir(C_5Me_5)(cyclo\text{-}octadienyl)][PF_6]$	99.3	9.2	34.6 †	84.2	29.4 †	36.8 *	81.4 †	71.5 †	C(7) * = 19.5, C(8) * = 30.8
$[Rh(C_5Me_5)(C_{10}H_{11})][PF_6]$	104.3(d) [c] (4.6)	8.9	93.4(d) † (9.2)	99.7(d) (5.6)	≡C(1)	51.7 *	104.1(d) † (10.7)	≡C(5)	[C(3a) and C(7a) * = 60.3 C(7) ≡ C(4), C(8) = 58.9 (d, 4.6)
$[Ir(C_5Me_5)(C_3H_5)(C_3H_6)][PF_6]$	101.4, 101.8 [d]	8.4, 9.1	43.3, 45.5 *	86.0, 86.2	49.1, 49.9 *	51.0, 51.1 *	64.9, 72.3		Me = 19.2, 19.5
$[Rh(C_5Me_5)\{C_7H_8(CH_2COMe)\}][PF_6]$	104.5(d) (6.1)	10.0	86.7(d) * (12.2)	97.6(d) † (6.1)	101.5(d) (3.1)	98.8(d) † (6.1)	94.2 *(d) (12.2)	51.6	C(7) = 30.1, *C*H₂CO = 50.7 *Me*CO = 32.6, CO = 209.5
$[Ir(C_5Me_5)\{C_7H_8(CH_2COMe)\}][PF_6]$	99.1 [c]	9.5	67.7 *	88.4 †	98.2	88.8 †	76.5 *	51.7	C(7) = 31.6, *CH*₂CO = = 50.1 *Me*CO = [e], CO = 172.3
$[Rh(C_5Me_5)\{C_7H_8(OMe)\}][PF_6]$	104.9(d) (6.1)	9.9	74.8(d) * (10.7)	98.7(d) (4.6)	101.4(d)	98.7(d) (4.6)	87.5(d) * (13.7)	87.2	C(7) = 28.8, OMe = 56.8

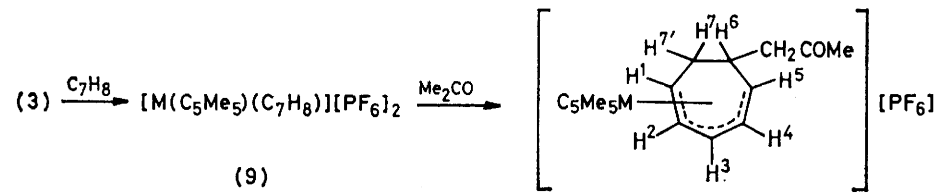
[a] Unless stated otherwise spectra recorded in $[^2H_3]$nitromethane with $SiMe_4$ as internal standard. [b] For ring numbering system see text. [c] Recorded in $[^2H_6]$acetone. [d] Recorded at −25 °C. [e] Obscured by the solvent signals.

*,† These assignments may be interchanged.

The $RhCl_3$-catalysed co-dimerisation of butadiene and ethylene in ethanol has been postulated to proceed *via* an (η^2-ethylene)(1-methylallyl)rhodium(III) intermediate.[14] This intermediate resembles the iridium complex (8) but preliminary experiments suggest that (8) does not catalyse dimerisation or oligomerisation of propene since g.l.c. analysis of the mother liquor from the reactions of the complex (8) in acetone with an excess of propene (at 20 °C/1—10 atm or 50 °C/1 atm) gave no indication of the formation of propene dimers or oligomers.

(iii) *Reactions involving Nucleophilic Attack at the Coordinated Olefin.*—The reaction of cycloheptatriene with $[M(C_5Me_5)(Me_2CO)_3][PF_6]_2$ (3) in acetone gave the 1—5-η-6-acetonylcycloheptadienyl complexes (10a) and (10b). These products are probably formed by nucleophilic attack of the solvent, acetone, on an intermediate η^6-cycloheptatriene complex (9).

The field desorption mass spectra of the reaction products contained parent peaks at *m/e* 387 (10a) and 477 (10b) corresponding to the relative atomic masses of the two respective cations, while the i.r. spectra indicated the presence of an aliphatic ketone [ν(CO), (10a) = 1 719, (10b) = 1 712 cm⁻¹]. Further evidence for the proposed structure (10) comes from the ¹H n.m.r. spectra (Table 1). The spectrum of the rhodium complex clearly shows the inequivalence of the methylene protons in the acetonyl group which arises because of the asymmetry of the complex. The spectra were assigned on the basis of decoupling experiments carried out on the rhodium complex (10a). In particular H(6) was readily assigned since this is the only signal which is significantly coupled to the methylene protons of the acetonyl group and H(1) and H(5) were differentiated by the fact that H(5) and not H(1) is coupled to H(6). The assignments and coupling constants are comparable to those reported for other cycloheptadienyl complexes.[15]



(10)

a, M = Rh; b, M = Ir

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It appears to be a general phenomenon in cycloheptadienyl complexes that the *exo*-protons occur at much higher fields than the *endo*-protons. For example, in the ^1H n.m.r. spectrum of 6-*exo*-methylcycloheptadienyl(tricarbonyl)manganese the *endo* H(6) and H(7) protons appear at δ 3.20 and 1.98 respectively whereas the H(7) *exo*-proton appears at δ 0.65.[15b,16] The ^1H n.m.r. spectra of (10a) and (10b) show very similar shifts (Table 1) and on this basis the acetonyl-substituent is assumed to be *exo* and the high-field resonances at δ 0.50 (10a) and 0.57 (10b) are assigned to the H(7) *exo*-protons of the two compounds.

The ^{13}C n.m.r. spectra (Table 2) confirm the proposed structures of (10a) and (10b). The asymmetry produced by introducing a substituent into the seven-membered ring is apparent in the spectra and the presence of an acetonyl-substituent is evident in both spectra despite the fact that in the iridium complex (10b) the methyl signal is obscured by the solvent. Five of the carbon signals of the seven-membered ring in (10a) exhibit rhodium coupling and to confirm the other assignments the proton-coupled spectrum of (10b) was recorded.

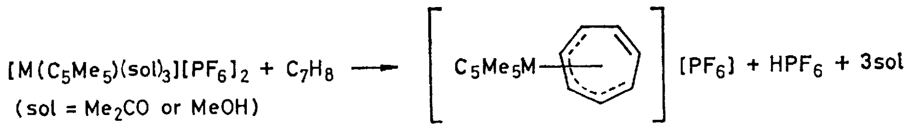
When the reaction of cycloheptatriene with the rhodium tris-solvent complex (3a) was carried out in [$^2H_6$]acetone at −5 °C and the reaction monitored by ^1H n.m.r. spectroscopy an intermediate product was observed. The C_5Me_5 region of the initial spectrum of the reaction mixture showed signals at δ 2.43 (60% intensity), 2.05 (15%), and 1.77 (25%). We propose that the first peak is due to the η^6-cycloheptatriene complex (9), and the peaks at δ 2.05 and 1.77 to complexes (10a) and $[Rh(C_5Me_5)\{(CD_3)_2CO\}_3][PF_6]_2$ respectively. After two hours at −5 °C all the starting complex and intermediate were converted into the final product, the cycloheptadienyl complex (10a).

All the data are consistent with the proposal that the complexes (10a) and (10b) result from *exo*-nucleophilic attack by the solvent acetone on the intermediate cycloheptatriene complex, although nucleophilic attack by acetone is unusual. We have shown, however, that the iridium complex (3b) can promote an aldol-condensation reaction and hence may readily generate the acetonyl ion.[17]

The experiment was repeated in methanol, using $[Rh(C_5Me_5)(MeOH)_3][PF_6]_2$; this reacted immediately with cycloheptatriene and yielded a bright yellow solid which was shown by elemental analysis, and ^1H and ^{13}C n.m.r. spectroscopy to be the expected 1—5-η-6-*exo*-methoxycycloheptadienyl(η^5-pentamethyicyclopentadienyl)rhodium hexafluorophosphate, (11), confirming that the intermediate cycloheptatriene complex is indeed susceptible to nucleophilic attack by the solvent. The ^{13}C n.m.r. spectrum of (11) was assigned with the aid of the proton-coupled spectrum and both it and the ^1H n.m.r. spectrum were very similar to the spectra of the acetonyl-derivative (10a) except that the C(4) and C(2) signals coincided in the ^{13}C n.m.r. spectrum of the methoxy-derivative.

Conclusion.—From this study it is clear that the rhodium–olefin complexes are not as stable in solution as the corresponding iridium–olefin complexes. For example, $[Rh(C_5Me_5)(nbd)(MeCN)][PF_6]_2$ undergoes extensive dissociation in both acetone and nitromethane whereas the corresponding iridium–bicyclo[2.2.1]heptadiene complex is stable in these solvents. Similarly although propene does not react with $[Rh(C_5Me_5)(Me_2CO)_3][PF_6]_2$, (3a), the iridium tris-acetone solvent complex does give a propene complex. Also six-equivalents of cyclo-octa-1,5-diene are required to ensure that all of (3a) reacts with the diene whereas the corresponding iridium reaction requires only one equivalent of ligand. It is not unexpected that the third-row transition metal should show a greater preference than rhodium to bond to π-acceptor ligands and indeed we have observed this effect with arene ligands.[2]

It is also clear that these cationic metal–olefin complexes bearing an overall charge of +2 are extremely reactive and will readily deprotonate or undergo nucleophilic attack. However, it is intriguing that although many cyclo-octa-1,5-diene complexes are known to undergo nucleophilic attack to give cyclo-octenyl complexes,[18] the reaction between cyclo-octa-1,5-diene and $[M(C_5Me_5)(sol)_3][PF_6]_2$ (sol = MeCN or Me_2CO) involves only a deprotonation reaction. Equally puzzling is the observation that the reaction between the solvent-complexes and cycloheptatriene in either acetone or methanol involves only nucleophilic attack by the solvent and no deprotonation of the ligand occurs. Such a deprotonation would be expected to lead to the corresponding η^5-cycloheptatrienyl complex:



In view of the ready deprotonation reactions of the other alkenes examined there does not appear to be any good reason why the above reaction should not occur, especially since similar η^5-cycloheptatrienyl complexes are known {*e.g.* $[Mn(C_7H_7)(CO)_3]$ [19] and $[Fe(C_7H_7)(CO)_3]BF_4$ [20]}. We can only presume that the reaction pathway is determined by the stability of the final products.

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EXPERIMENTAL

Reactions were carried out under a dry nitrogen atmosphere although all the products proved to be quite stable to air. Elemental analyses were carried out by the microanalytical department of this University. ^{1}H N.m.r. spectra were recorded on a Varian Associates HA 100 or Perkin-Elmer R34 220 MHz spectrometer and ^{13}C n.m.r. spectra were recorded on a JEOL PFT 100 spectrometer. Field desorption mass spectra were measured on a Varian combined FD/FI/EI source on a CH5 mass spectrometer linked to a Varian 620i data system. The complexes $[M(C_5Me_5)(MeCN)_3][PF_6]_2$ (M = Rh or Ir) were prepared as previously described.[2]

Acetonitrile(η^4-bicyclo[2.2.1]*heptadiene)(η^5-pentamethylcyclopentadienyl)rhodium*(III) *Hexafluorophosphate* (2a).—Bicyclo[2.2.1]heptadiene (0.7 cm^3, 6.88 mmol) was added to a stirred solution of $[Rh(C_5Me_5)(MeCN)_3][PF_6]_2$ (0.30 g, 0.46 mmol) in acetone (3 cm^3). Within 2 min a precipitate formed which was filtered off, washed with ether, and dried to give yellow crystals of the pure product (90 mg). A further crop of crystals (120 mg) was obtained from the filtrate by removing the solvent *in vacuo*, washing the orange residue with ether and recrystallising it from a mixture of acetone, ether, and bicyclo[2.2.1]heptadiene (total yield = 71%).

Acetonitrile(η^4-bicyclo[2.2.1]*heptadiene)(η^5-pentamethylcyclopentadienyl)iridium*(III) *Hexafluorophosphate*, (2b).—$[Ir(C_5Me_5)(MeCN)_3][PF_6]_2$ (0.05 g, 0.06 mmol) and bicyclo[2.2.1]heptadiene (0.04 g, 0.40 mmol) were stirred in acetone (2 cm^3) for *ca.* 10 min. The solvent was removed under reduced pressure to give a yellow solid. Recrystallisation from acetone–ether afforded the pure yellow complex (0.05 g, 67%).

1—3:5,6-η-*Cyclo-octadienyl(η^5-pentamethylcyclopentadienyl)rhodium*(III) *Hexafluorophosphate*, (5a).—$[\{Rh(C_5Me_5)Cl_2\}_2]$ (0.2 g, 0.32 mmol) and Ag[PF$_6$] (0.33 g, 1.34 mmol) were stirred in acetone (10 cm^3). An immediate exothermic reaction occurred to give a white precipitate of silver chloride and a yellow solution containing the rhodium tris-acetone species(3a). After being stirred for 15 min, the solution was filtered through a short column of cellulose powder and the column washed with acetone (5 cm^3). Cyclo-octa-1,5-diene (0.42 g, 3.9 mmol) was added to the combined filtrate and washings and the mixture stirred for 24 h. The solution was then filtered again and the solvent removed *in vacuo*. Crystallisation of the residue from acetone–ether gave yellow-green crystals of complex (5) (0.23 g, 73%).

1—3:5,6-η-*Cyclo-octadienyl(η^5-pentamethylcyclopentadienyl)iridium*(III) *Hexafluorophosphate*, (5b).—$[\{Ir(C_5Me_5)Cl_2\}_2]$ (0.4 g, 0.5 mmol) and Ag[PF$_6$] (0.5 g, 2.0 mmol) were stirred in acetone (10 cm^3) to give the iridium–acetone solvated species. The solution was then filtered and stirred with cyclo-octa-1,5-diene (0.11 g, 1.01 mmol) for 30 min. Removal of the solvent under reduced pressure and ether washing of the residue gave an off-white solid (0.48 g, 83%). Recrystallisation from acetone–ether afforded the pure white complex.

A sample of $[Ir(C_5Me_5)(C_8H_{11})][PF_6]$ (0.1 g) in tetrahydrofuran was stirred with an excess of K[BH$_4$] for 15 min before the solvent was removed *in vacuo*. The residue was then extracted with ether (2 × 10 cm^3) and removal of the ether *in vacuo* gave a yellow solid. The i.r. and ^{1}H n.m.r. spectra of the product were identical to those reported for cyclo-octa-1,5-diene(pentamethylcyclopentadienyl)iridium(I).[9] A parent peak at *m/e* 436 in the mass spectrum of the product also supported this formulation.

η^5-Cyclopentadienyl(η^5-pentamethylcyclopentadienyl)rhodium(III) *Hexafluorophosphate*, (6a).—The rhodium–acetone solvated species, prepared from $[\{Rh(C_5Me_5)Cl_2\}_2]$ (0.2 g, 0.32 mmol) and Ag[PF$_6$] (0.33 g, 1.34 mmol) in acetone (10 cm^3), was stirred with freshly cracked cyclopentadiene (0.06 g, 0.90 mmol) for *ca.* 30 min. Removal of the acetone under reduced pressure gave an off-white solid which was recrystallised from acetone and ether to give the pure white product (0.27 g, 93%) (Found: C, 40.5; H, 4.7. Calc. for $C_{15}H_{20}F_6PRh$: C, 40.2; H, 4.5%). The ^{1}H n.m.r. spectrum of the product was identical to that reported for $[Rh(C_5Me_5)(C_5H_5)][PF_6]$.[10]

η^5-Cyclopentadienyl(η^5-pentamethylcyclopentadienyl)iridium(III) *Hexafluorophosphate*, (6b).—This white complex was prepared in a 78% yield in the same way as its rhodium analogue (Found: C, 33.5; H, 3.8. Calc. for $C_{15}H_{20}F_6IrP$: C, 33.5; H, 3.8%). The ^{1}H n.m.r. spectrum of the product was identical to that reported for $[Ir(C_5Me_5)(C_5H_5)][PF_6]$.[10]

1—3:5,6-η-(4,7-*Methano*)-3a,4,7,7a-*tetrahydroindenyl(η^5-pentamethylcyclopentadienyl)rhodium*(III) *Hexafluorophosphate*, (7).—The rhodium–acetone solvated species, prepared from $[\{Rh(C_5Me_5)Cl_2\}_2]$ (0.2 g, 0.32 mmol) and Ag[PF$_6$] (0.33 g, 1.30 mmol) in acetone (10 cm^3) was stirred with dicyclopentadiene (0.09 g, 0.68 mmol) for 30 min. Removal of the solvent under reduced pressure gave a residue which was then washed with ether to give a yellow solid (0.23 g, 89%). This was recrystallised from acetone–ether to give the pure product.

η^3-Allyl(η^5-pentamethylcyclopentadienyl)(η^2-propene)iridium(III) *Hexafluorophosphate*, (8).—The iridium–acetone solvated species was prepared from $[\{Ir(C_5Me_5)Cl_2\}_2]$ (0.64 g, 0.80 mmol) and Ag[PF$_6$] (0.80 g, 3.20 mmol) in acetone (50 cm^3) as previously described. Propene was slowly bubbled into the stirred solution for 1 h after which, with continued stirring, it was left in an atmosphere of propene for 18 h. The solvent was removed under reduced pressure and the residue washed with ether to give the white product (0.67 g, 75%). Recrystallisation from acetone–ether gave the pure product.

1—5-η-6-*Acetonylcycloheptadienyl(η^5-pentamethylcyclopentadienyl)rhodium*(III) *Hexafluorophosphate*, (10).—$[\{Rh(C_5Me_5)Cl_2\}_2]$ (0.4 g, 0.64 mmol) and Ag[PF$_6$] (0.65 g, 2.58 mmol) were stirred in acetone (10 cm^3) to give the rhodium acetone solvated species. Cycloheptatriene (0.12 g, 1.3 mmol) was then added to the filtered solution. After the mixture had been stirred for 25 min the solvent was removed under reduced pressure and the residue was washed with ether to give a yellow solid (0.49 g, 77%). Recrystallisation from acetone–ether gave the pure product.

1—5-η-6-*Acetonylcycloheptadienyl(η^5-pentamethylcyclopentadienyl)iridium*(III) *Hexafluorophosphate*, (10b).—This white complex was prepared in a 59% yield in the same way as its rhodium analogue.

1—5-η-6-*Methoxycycloheptadienyl(η^5-pentamethylcyclopentadienyl)rhodium*(III) *Hexafluorophosphate*, (11).—$[\{Rh(C_5Me_5)Cl_2\}_2]$ (0.4 g, 0.64 mmol) and Ag[PF$_6$] (0.65 g, 2.58 mmol) were stirred in methanol (10 cm^3) to give the rhodium–methanol solvated species. Cycloheptatriene (0.12 g, 1.3 mmol) was added to the filtered, stirred solution and left for 25 min. The volume of solvent was then reduced *in vacuo* to *ca.* 2 or 3 cm^3 to give a yellow precipitate. This was then filtered off, washed with ether, and air-dried. Recrystallisation from methanol afforded yellow crystals of the pure product (0.41 g, 63%).

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