Reactions of the η^6-Benzene(η^5-ethyltetramethylcyclopentadienyl)-rhodium(III) Cation and Related Species with Nucleophiles; the Crystal Structure of $[Rh(\eta^5\text{-}C_5Me_4Et)\{\eta^5\text{-}C_6H_6P(O)(OMe)_2\}][PF_6]$ †

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The salt $[Rh(\eta^5\text{-}C_5Me_4Et)(\eta^6\text{-}C_6H_6)][PF_6]_2$ (1a) reacts with $Li[AlH(OBu^t)_3]$ to give $[Rh(\eta^5\text{-}C_5Me_4Et)(\eta^5\text{-}C_6H_7)][PF_6]$ which slowly loses hydride to regenerate the benzene complex; both hydride addition and hydride loss occur stereospecifically at the *exo* position. With Tl[acac] (acac = pentane-2,4-dionate) and phosphites $P(OR)_3$ (R = Me or Et, not Ph), (1a) gives the substituted-hexadienyl compounds $[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_6X)][PF_6]$ [X = $CH(COMe)_2$ or $P(O)(OR)_2$]; in both cases displacement of the co-ordinated benzene ligand is a competing reaction. An *X*-ray analysis of the dimethoxyphosphoryl derivative [X = $P(O)(OMe)_2$] has been carried out: the crystal is orthorhombic with a = 16.353, b = 21.847, c = 13.258 Å, Z = 8, and space group *Pbca*; the structure has been solved by the heavy-atom method from 903 observed reflections and refined to R 0.069 7. The cyclohexadienyl ring carries the phosphoryl group in an *exo* conformation. Phosphines (PBu^n_3 or PMe_2Ph, not PPh_3 or $PPhH_2$) and triethylamine react reversibly with $[Rh(C_5Me_4Et)(C_6H_6)][BF_4]_2$ to give the salts $[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_6L)][BF_4]_2$ (stability: L = $PBu_3 > PMe_2Ph \gg NEt_3$). In contrast, pyridine attacked the metal atom of (1a) to give $[Rh(C_5Me_4Et)(NC_5H_5)_3][PF_6]_2$. The corresponding benzene compounds $[M(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]Y_2$ react with tributylphosphine and methoxide ion to give $[M(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_6H_6L)]Y_n$ (M = Co, L = PBu_3, Y_n = $[BF_4]_2$; M = Ir, L = OMe, Y_n = PF_6). Infrared and ^1H, ^{13}C, and ^{31}P n.m.r. spectra are reported.

IT has long been recognised that co-ordination of an arene to a metal enhances the reactivity of the arene towards nucleophiles and this should be especially true of compounds of the type $[M(\eta^5\text{-}C_5Me_5)(arene)]X_2$ (X = BF_4 or PF_6; M = Co,[1] Rh or Ir[2-4]) which contain an arene co-ordinated to a metal in a formal oxidation state of III. Nucleophilic attack by $Na[BH_4]$ on $[M(C_5Me_5)(\eta^6\text{-}C_6Me_nH_{6-n})][PF_6]_2$ (M = Ir, n = 0, 5, or 6; M = Rh, n = 6) and by LiMe on $[Ir(C_5Me_5)(\eta^6\text{-}C_6Me_5H)][PF_6]_2$ has indeed been observed to give the corresponding cyclohexadienyl complexes.[2] We have extended these original studies and report herein the reactions of $[Rh(\eta^5\text{-}C_5Me_4Et)(\eta^6\text{-}C_6H_6)]X_2$ [X = PF_6 (1a) or BF_4 (1b)] with a wide range of both negatively charged and neutral nucleophiles; more limited studies on the pentamethylcyclopentadienyl complexes $[M(C_5Me_5)(C_6H_6)]X_2$ (M = Co, X = BF_4; M = Ir, X = PF_6) are also described.[5]

RESULTS AND DISCUSSION

(*i*) *Hydride Addition and Abstraction*.—The compound $[Ir(C_5Me_5)(\eta^6\text{-}C_6H_6)][PF_6]_2$ has been reported to react readily with sodium tetrahydroborate in water to give the cyclohexadienyl compound $[Ir(C_5Me_5)(\eta^5\text{-}C_6H_7)][PF_6]$.[2] Further nucleophilic attack by tetrahydroborate upon this product was not observed and reduction to the neutral η^4-cyclohexa-1,3-diene compound is only achieved by refluxing the cyclohexadienyl compound with $Li[AlH_4]$ in tetrahydrofuran (thf) for several hours.[6] In contrast, treatment of $[Co(C_5Me_5)(\eta^6\text{-}C_6H_6)][BF_4]_2$ or $[Rh(C_5Me_4Et)(\eta^6\text{-}C_6H_6)][PF_6]_2$ with $Na[BH_4]$ in either water or thf resulted in a vigorous reaction and the formation of a black intractable solid. The milder reducing agent $Li[AlH(OBu^t)_3]$ did, however, react smoothly with the rhodium–benzene compound (1a) to give the cyclohexadienyl compound $[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_7)][PF_6]$ (2). Hydride addition occurred stereospecifically in the *exo* position. This was demonstrated by reaction of $Li[AlH(OBu^t)_3]$ with the corresponding rhodium–hexadeuteriobenzene compound; the i.r. spectrum (KBr) of the resulting cyclohexadienyl compound $[Rh(C_5Me_4Et)(\eta^5\text{-}C_6D_6H)][PF_6]$ contained a characteristic[7] strong low-frequency $\nu(C\text{-}H_{exo})$ (2 825 cm^{-1}) whilst the ^1H n.m.r. spectrum ($CDCl_3$) contained only the high-field proton (*i.e. exo*[7]) of the methylene group (δ 2.57).

An interesting property of the cyclohexadienyl complex (2) is that it undergoes spontaneous loss of hydride to regenerate $[Rh(C_5Me_4Et)(\eta^6\text{-}C_6H_6)]^{2+}$. In trifluoroacetic acid this reaction went to completion in 12 d at 35 °C and the product was isolated by addition of HPF_6 (75%) and diethyl ether to the trifluoroacetic acid solution. The formation of the benzene complex also occurs in the solid state, albeit extremely slowly, and in acetone solution the cyclohexadienyl complex (2) decomposed at 35 °C over 7 d to liberate free benzene. This latter reaction is presumed to involve slow conversion of (2) into the benzene compound which is known to be unstable in acetone solution.[1]

The ^1H n.m.r. spectrum of the product isolated from the reaction of the *exo*-hydridohexadeuteriocyclohexadienyl compound with trifluoroacetic acid and HPF_6 corresponded to that of $[Rh(C_5Me_4Et)(C_6D_6)][PF_6]_2$; no trace of a pentadeuteriobenzene compound was detected. Thus the conversion of the cyclohexadienyl ligand into the benzene ligand is stereospecific (>95%) and involves the loss of the *exo*-hydrogen substituent. A mechanism involving the formation of a rhodium–hydride intermediate therefore appears unlikely.

Spontaneous loss of a hydride ligand is an unusual reaction although the related compound $[Fe(C_5H_5)(\eta^5\text{-}C_6H_7)]$ also reacts in this manner.[8]

(*ii*) *Reactions with Pentane*-2,4-*dionate Anion* (*acac*). Treatment of $[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$ with either

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† Recommended name: (1–5-η-6-dimethoxyphosphorylcyclohexadienyl)(1–5-η-ethyltetramethylcyclopentadienyl)rhodium(III) hexafluorophosphate.

TABLE 1

Proton and ^{31}P n.m.r. data (δ scale, J quoted in Hz)[a]

	^1H n.m.r.[b]								
Compound	$C_5\mathit{Me}_4Et$	C_5Me_4-$C\mathit{H}_2Me$	C_5Me_4-$CH_2\mathit{Me}$	H (1, *endo*)	H(2,6)	H(3,5)	H(4)	Other	^{31}P n.m.r.[c]
$[Rh(C_5Me_4Et)(\eta^6\text{-}C_6H_6)][PF_6]_2$ [d]	2.35(s), 2.36(s)	2.77(q) $J(CH_2\text{-}Me) = 8$	1.18(t)					C_6H_6, 7.39	
$[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_7)][PF_6]$ [e]	2.04(s), 2.08(s)	2.47(q) $J(CH_2\text{-}Me) = 7.5$	1.09(t)	2.89(m)	3.60(dd) $J[H_{endo}\text{-}H(2)] = 6$	5.27(dd) $J[H(2)\text{-}H(3)] = 5$	6.45(t) $J[H(3)\text{-}H(4)] = 5$	H(1,*exo*), 2.57(d) $J(H_{exo} - H_{endo}) = 17$	
$[Rh(C_5Me_4Et)\{\eta^5\text{-}C_6H_6CH(COMe)_2\}][PF_6]$	2.14(s)	2.65(q) $J(CH_2\text{-}Me) = 8$	1.14(t)	3.73(m)	4.14(dd) $J[H_{endo}\text{-}H(2)] = 6$	5.61(dd) $J[H(2)\text{-}H(3)] = 6$	6.66(t) $J[H(3)\text{-}H(4)] = 5$	$C\mathit{H}(COMe)_2$, 3.87 {d, $J[H\text{-}H(1)] = 7$} $CH(CO\mathit{Me})_2$, 2.20(s)	
$[Ir(C_5Me_5)(\eta^5\text{-}C_6H_6OMe)][PF_6]$ [f]	C_5Me_5 2.17(s)			3.79(t)	4.37(dd) $J[H_{endo}\text{-}H(2)] = 6$	5.48(dd)	6.51(t) $J[H(3)\text{-}H(4)] = 5$	OMe, 2.96(s)	
$[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_6PBu^n_3)][BF_4]_2$ [d]	2.15(s), 2.16(s)	2.58(q) $J(CH_2\text{-}Me) = 7.5$	1.12(t)	4.55(m) $J(H\text{-}P) = 6$	4.00(dd) $J[H_{endo}\text{-}H(2)] = 6$	5.70(dd) $J[H(2)\text{-}H(3)] = 6.5$	6.71(t) $J[H(3)\text{-}H(4)] = 5$	$P[(CH_2)_3\mathit{Me}]_3$, 0.91 [t, $J(Me\text{-}CH_2) = 7$] $P[CH_2(C\mathit{H}_2)_2Me]_3$, 1.35—1.62(m) $P(C\mathit{H}_2Pr)_3$, 1.90—2.15(m)	32.0(d) [d] $J(Rh\text{-}P) = 8$
$[Co(C_5Me_5)(\eta^5\text{-}C_6H_6PBu^n_3)][BF_4]_2$	C_5Me_5 2.06(s)			5.23(m) $J(H\text{-}P) = 9.5$	3.93(dd) $J[H_{endo}\text{-}H(2)] = 6$	5.66(dd) $J[H(2)\text{-}H(3)] = 8.5$	7.10(t) $J[H(3)\text{-}H(4)] = 5.5$	$P[(CH_2)_3\mathit{Me}]_3$, 0.91 [t, $J(Me\text{-}CH_2) = 6$] $P[CH_2(C\mathit{H}_2)_2Me]_3$, 1.40—1.60(m) $P(C\mathit{H}_2Pr)_3$, 1.95—2.20(m)	29.1(s)
$[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_6PMe_2Ph)][BF_4]_2$ [d]	2.11(s)	2.53(q) $J(CH_2\text{-}Me) = 7.5$	1.11(t)	4.53(m) $J(H\text{-}P) = 5$	3.99(dd) $J[H_{endo}\text{-}H(2)] = 6$	5.56(dd) $J[H(2)\text{-}H(3)] = 6$	6.39(t) $J[H(3)\text{-}H(4)] = 5$	$P\mathit{Me}_2Ph$, 2.03 [d, $J(P\text{-}H) = 13.5$] $PMe_2\mathit{Ph}$, 7.50—7.95(m)	22.3(d) [d] $J(Rh\text{-}P) = 10$
$[Rh(C_5Me_4Et)(PMe_2Ph)_3][BF_4]_2$	1.64(q), 1.73(q) $J(P\text{-}H) = 3$	[g] $J(CH_2\text{-}Me) = 8$	1.00(t)					PMe_2Ph, 2.19(m) $PMe_2\mathit{Ph}$, 7.55—7.83(m)	3.1(d) $J(Rh\text{-}P) = 129$
$[Rh(C_5Me_4Et)\{\eta^5\text{-}C_6H_6P(O)(OMe)_2\}][PF_6]$ [e]	2.08(s), 2.10(s)	2.50(q) $J(CH_2\text{-}Me) = 7.5$	1.11(t)	3.53	3.71 [g]	5.39(dd) $J[H(2)\text{-}H(3)] = 5$	6.56 $J[H(3)\text{-}H(4)] = 5$	$P(O)(OMe)_2$, 3.65(d) $J(P\text{-}H) = 10.5$	$P(O)(OMe)_2$, 20.3(s) [e] PF_6 −144.3(spt) $J(Rh\text{-}P) = 5$, $J(F\text{-}P) = 708$
$[Rh(C_5Me_4Et)\{\eta^5\text{-}C_6H_6P(O)(OEt)_2\}][PF_6]$	2.16(s,br)	2.61(q) $J(CH_2\text{-}Me) = 8$	1.12(t)	3.69(m) $J(H\text{-}P) = 13$	3.91 [g]	5.55(dd) $J[H(2)\text{-}H(3)] = 7$	6.66(t) $J[H(3)\text{-}H(4)] = 6$	$P(O)(OC\mathit{H}_2Me)_2$, 3.97 [m, $J(P\text{-}H) = 10$] $P(O)(OCH_2\mathit{Me})_2$, 1.22 [t, $J(Me\text{-}CH_2) = 8$]	$P(O)(OEt)_2$, 24.6(d) [d] PF_6, −144.4(spt) $J(F\text{-}P) = 708$, $J(Rh\text{-}P) = 5$
$[Rh(C_5Me_4Et)\{P(OEt)_3\}_3][PF_6]_2$	1.94(q) $J(P\text{-}H) = 5$	2.34(m) $J(CH_2\text{-}Me) = 7.5$	1.11(t)					$P(OCH_2\mathit{Me})_3$, 1.44(t), $J(Me\text{-}CH_2) = 7$ $P(OC\mathit{H}_2Me)_3$, 4.36(m)	
$[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_6NEt_3)]^{2+}$	1.99(s), 2.00(s)	2.43(q) $J(Me\text{-}CH_2) = 7$	1.02(t)	3.50(t)	3.78(dd) $J[H(1)\text{-}H(2)] = 5$	5.21(dd) $J[H(2)\text{-}H(3)] = 5.5$	6.21(t) $J[H(3)\text{-}H(4)] = 5.5$	$N(CH_2\mathit{Me})_3$, 1.17 [t, $J(Me\text{-}CH_2) = 8$] $N(C\mathit{H}_2Me)_3$, 3.08(q)	
$[Rh(C_5Me_4Et)(NC_5H_5)_3][PF_6]_2$	1.64(s), 1.65(s)	2.19(q) $J(Me\text{-}CH_2) = 7.5$	1.13(t)		8.66(d)	7.76(dd) $J[H(2)\text{-}H(3)] = 5$	8.25(t) $J[H(3)\text{-}H(4)] = 7.5$		

[a] Unless stated otherwise spectra were recorded in $[^2H_6]$acetone. [b] $SiMe_4$ internal standard. [c] 85% H_3PO_4 external reference. [d] Recorded in $[^2H_3]$nitromethane. [e] Recorded in $[^2H]$chloroform. [f] Recorded in $[^2H_6]$dimethyl sulphoxide. [g] Signal partly obscured.

TABLE 2

Carbon 13 n.m.r. data (δ scale, J quoted in Hz) [a]

Compound	$C_5Me_4CH_2Me$				C(1)	C(2,6)	C(3,5)	C(4)	Other
	C_5	Me_4	CH_2	Me					
$[Rh(C_5Me_4Et)(\eta^6\text{-}C_6H_6)][BF_4]_2$	114.7(9) [b] 115.6(8) 117.6(9)	10.9 {131} [c] 11.2 {132}	19.5 {137}	13.2 {129}					C_6H_6: 108.5(6) {185}
$[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_7)][PF_6]$ [d]	102.1(6) 103.1(4) 107.4(6)	9.9 10.2	19.3	14.3	25.9	52.3 (8)	95.4 (5)	91.4 (6)	
$[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_6PBu^n_3)][BF_4]_2$	105.6(6) 106.4(6) 110.4(8)	10.0 10.3	18.8	14.4	35.5 [26] [e]	49.1 (8)	98.0 (3)	94.3 (6)	PBu^n_3: 13.5, 17.1[41], 24.3[6], 24.9[15]
$[Co(C_5Me_5)(\eta^5\text{-}C_6H_6PBu^n_3)][BF_4]_2$ [f]	101.4	(Me_5 9.9)			g	50.0	97.9	93.5	PBu^n_3: 13.5, 16.9[43], 24.0[5], 24.6[15]
$[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_6PMe_2Ph)][BF_4]_2$	105.9(6) 106.7(8) 110.7(6)	10.1 10.4	19.0	13.2	37.1 [26]	48.5 (5)	98.0 (3)	94.1 (6)	$P\mathit{Me}_2Ph$: 3.6[50] $PMe_2\mathit{Ph}$: 129.7—136.4
$[Rh(C_5Me_4Et)\{\eta^5\text{-}C_6H_6P(O)(OMe)_2\}][PF_6]$ [d]	103.2(6) 104.1(6) 108.3(8)	9.9 10.1	19.2	14.5	35.4 [131]	50.2 (8)	95.4 (3)	92.3 (6)	$P(O)(OMe)_2$: 53.4[8]
$[Rh(C_5Me_4Et)\{\eta^5\text{-}C_6H_6P(O)(OEt)_2\}][PF_6]$	104.6(8) 105.4(8) 109.8(6)	10.2 10.4	19.2	14.9	37.1 (3) [131]	52.1 (8)	96.5 (6)	93.4 (6)	$P(O)(OC\mathit{H}_2Me)_2$ [g] $P(O)(OCH_2\mathit{Me})_2$: 17.0[5]
$[Rh(C_5Me_4Et)\{P(OEt)_3\}_3][PF_6]_2$ [f]	110.3 112.0 114.4	9.9 10.2	18.6	12.9					$P(O\mathit{C}H_2Me)_3$: 67.5 $P(OCH_2\mathit{Me})_3$: 16.1

[a] Recorded in [$^2H_3$]nitromethane unless specified. [b] $J(^{103}Rh-^{13}C)$ in parentheses. [c] $J(H-^{13}C)$ in braces. [d] Recorded in [^2H]-chloroform. [e] $J(^{31}P-^{13}C)$ in square brackets. [f] Recorded in [$^2H_6$]acetone. [g] Signal obscured by solvent.

Tl[acac] or a mixture of pentane-2,4-dione and sodium carbonate always gave a mixture of two products despite variations in solvent and reaction temperature. Attempts to separate the products by fractional crystallisation were only partially successful in that although the ^1H n.m.r. spectrum of each could be obtained neither complex could be isolated analytically pure. The major product in all reactions was unambiguously identified as $[Rh(C_5Me_4Et)\{\eta^5\text{-}C_6H_6CH(COMe)_2\}][PF_6]$ (3) from the ^1H n.m.r. spectrum (Table 1). The purest sample of the other compound was obtained as an orange oil by careful addition of diethyl ether to a dichloromethane solution of the mixture; attempts to crystallise this oil further failed. The ^1H n.m.r. spectrum ([$^2H_6$]acetone) contained signals characteristic of the ethyltetramethylcyclopentadienyl ligand [δ 1.13 (t, 3 H), 1.65, 1.68 (s, 12 H), and 2.13 (q, 2 H)] and the acac ligand [δ 2.11 (s, 6 H) and 3.91 (s, 1 H)] in addition to a signal due to dichloromethane (δ 5.58). Clearly the benzene ligand has been displaced and the ^1H n.m.r. spectrum is consistent with the formulation $[Rh(C_5Me_4Et)(acac)(CH_2Cl_2)][PF_6]$. It therefore appears that attack at the metal centre or the co-ordinated benzene ligand are competing pathways in the reaction of $[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$ with the pentane-2,4-dionato-anion.

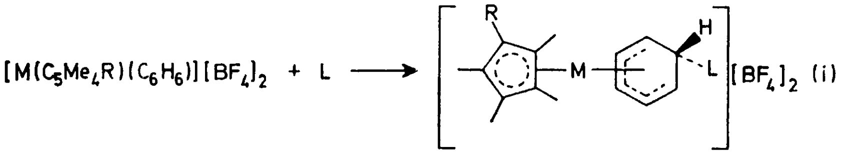
(*iii*) *Reactions with Methoxide and Cyanide*.—No stable compounds could be isolated from the reaction of $[Rh(C_5Me_4Et)(C_6H_6)][BF_4]_2$ with either sodium methoxide or potassium cyanide in nitromethane. It would appear, however, that nucleophilic attack occurred solely at the metal since it was shown by ^1H n.m.r. spectroscopy that rapid displacement of the benzene ligand occurred in both reactions. In contrast, the iridium compound $[Ir(C_5Me_5)(C_6H_6)][PF_6]_2$ reacted with sodium methoxide to give the *exo*-methoxycyclohexadienyl compound $[Ir(C_5Me_5)(\eta^5\text{-}C_6H_6OMe)][PF_6]$ (4). The i.r. spectrum of the product contained no characteristic $\nu(C-H_{exo})$ absorption at $<2\,850$ cm^{-1} in keeping with the proposed stereochemistry.

These results, together with the contrasting behaviour of the compounds $[M(C_5Me_4R)(C_6H_6)][PF_6]_2$ (M = Rh, R = Et; or M = Ir, R = Me) towards $Na[BH_4]$, confirm previous observations that the rhodium(III)–benzene bond is cleaved more readily than the iridium(III)–benzene bond by nucleophiles.[3]

(*iv*) *Reactions of Phosphorus-donor Ligands*.—Treatment of either $[Rh(C_5Me_4Et)(C_6H_6)][BF_4]_2$ or $[Co(C_5Me_5)(C_6H_6)][BF_4]_2$ with excess of tri-n-butylphosphine gave the corresponding *exo*-tributylphosphoniocyclohexadienyl compound (5) or (6) quantitatively [equation (i)]. The rhodium–benzene complex (1b) reacted similarly with dimethylphenylphosphine to give the adduct (7) although no reaction occurred with the less basic phosphines, triphenylphosphine and phenylphosphine.

Compounds (5)—(7) were formulated as shown on the basis of microanalytical, i.r., and ^1H, ^{13}C, and ^{31}P n.m.r. data (Tables 1 and 2). In particular, the observed small $J(^{103}Rh-^{31}P)$ [*i.e.* (5), J = 8 Hz; (7), J = 10 Hz] indicates that the phosphorus ligands are not directly bonded to the rhodium atom {*cf.* $[Rh(C_5Me_4Et)(PMe_2Ph)_3][BF_4]_2$, $J(^{103}Rh-^{31}P) = 129$ Hz}. The stereochemistry of the phosphonio-substituents was assigned on the basis of an absence of a characteristic $\nu(C-H_{exo})$ in the i.r. spectra and the low-field chemical shift of the H(1) proton in each of the three complexes.

All three phosphonium salts were isolated as crystalline solids which appeared to be quite stable in air at room temperature. In solution, however, these complexes were unstable; the rhodium complexes (5) and (7) decomposed within minutes in acetone at room temperature whereas under identical conditions the cobalt compound decomposed much more slowly (*ca.* 3 d). In nitromethane the tributylphosphine rhodium adduct decomposed more slowly than the dimethylphenylphosphine rhodium adduct ($t_{\frac{1}{2}} \approx 10$ and 4 h respectively at 35 °C) and in both cases decomposition was accompanied by the appearance of signals in the ¹H n.m.r. spectrum due to both co-ordinated and free benzene. Furthermore, the rates of decomposition were considerably reduced by addition of the respective phosphines to the solutions of the phosphonium compounds (5) and (7). Phosphorus-31 n.m.r. spectroscopy indicated that one of the decomposition products of the dimethylphenylphosphonium salt was $[Rh(C_5Me_4Et)(PMe_2Ph)_3][BF_4]_2$ (8). These results are all consistent with equilibria (ii) and (iii).



(5) M = Rh, R = Et, L = PBu_3
(6) M = Co, R = Me, L = PBu_3
(7) M = Rh R = Et L = PMe_2Ph

$$[Rh(C_5Me_4Et)(C_6H_6L)][BF_4]_2 \rightleftharpoons [Rh(C_5Me_4Et)(C_6H_6)][BF_4]_2 + L \quad (L = PBu_3 \text{ or } PMe_2Ph) \qquad \text{(ii)}$$

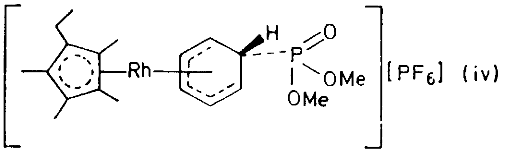
$$[Rh(C_5Me_4Et)(C_6H_6)][BF_4]_2 + L + \text{solvent} \rightleftharpoons [Rh(C_5Me_4Et)L_n(\text{solvent})_{3-n}][BF_4]_2 + C_6H_6 \quad (n = 0\text{—}3) \qquad \text{(iii)}$$

Reversible addition of phosphines to cyclic organic ligands [equation (ii)] may be a common reaction in organometallic chemistry since it has recently been demonstrated that both $[Mn(\eta^6-C_6H_6)(CO)_3][BF_4]$ [9] and $[Fe(\eta^4-C_4H_4)(CO)_2(NO)][PF_6]$ [10] also undergo reversible nucleophilic additions of this type. The observed order of stability of the phosphine adducts ($PBu_3 > PMe_2Ph \gg PPh_3, PPhH_2$) appears to correlate with the basicity of the phosphine. In common with the cyclohexadienyl compound (2), all three phosphine adducts (5)—(7) were converted back into the respective benzene complexes upon treatment with trifluoroacetic acid.

The reactions of $[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$ with phosphites proved to be more complex. With trimethyl phosphite the major product was the *exo*-dimethoxyphosphorylcyclohexadienyl derivative (9b) [equation (iv)]. This product was characterised by elemental analysis, i.r., and n.m.r. (¹H, ¹³C, and ³¹P) spectroscopy and also by *X*-ray crystallography. Bond lengths and angles, together with estimated standard deviation (where appropriate, see Experimental section), are collected in Table 3 and details of least-squares planes through molecular fragments are given in Table 4.

$$[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2 + P(OMe)_3 \longrightarrow [Rh(C_5Me_4Et)\{\eta^5-C_6H_6P(OMe)_3\}][PF_6]_2 \longrightarrow$$

(9a)



(9b)

TABLE 3

Molecular geometry and estimated standard deviations

(*a*) Bond lengths (Å)		(*b*) Bond angles (°)	
Rh(1)–C(1)	2.22(2)	O(1)–P(2)–O(2)	113.4(12)
Rh(1)–C(2)	2.19(2)	O(1)–P(2)–O(3)	117.3(12)
Rh(1)–C(3)	2.15(2)	O(2)–P(2)–O(3)	100.0(11)
Rh(1)–C(4)	2.15(2)	O(1)–P(2)–C(13)	113.2(13)
Rh(1)–C(5)	2.19(2)	O(2)–P(2)–C(13)	105.3(12)
Rh(1)–C(13)	2.73(3)	O(3)–P(2)–C(13)	106.1(12)
Rh(1)–C(14)	2.26(3)		
Rh(1)–C(15)	2.18(3)	P(2)–O(2)–C(11)	122.9(18)
Rh(1)–C(16)	2.15(3)	P(2)–O(3)–C(12)	119.4(17)
Rh(1)–C(17)	2.18(3)		
Rh(1)–C(18)	2.17(3)	C(1)–C(2)–C(3) [a,c]	108.0
P(1)–F(all) [a]	1.46	C(2)–C(1)–C(6) [b]	124.0(17)
		C(5)–C(1)–C(6) [b]	128.0(17)
P(2)–O(1)	1.51(2)	C(1)–C(2)–C(7) [b]	127.0(15)
P(2)–O(2)	1.60(2)	C(3)–C(2)–C(7) [b]	123.2(15)
P(2)–O(3)	1.56(2)	C(2)–C(3)–C(8) [b]	126.8(18)
P(2)–C(13)	1.86(3)	C(4)–C(3)–C(8) [b]	125.1(17)
		C(3)–C(4)–C(9) [b]	125.6(17)
O(2)–C(11) [a]	1.45	C(5)–C(4)–C(9) [b]	126.2(17)
O(3)–C(12) [a]	1.45	C(4)–C(5)–C(10) [b]	125.9(17)
C(1)–C(2) [a,c]	1.436	C(1)–C(5)–C(10) [b]	126.0(17)
C(1)–C(6) [b]	1.48(3)		
C(2)–C(7) [b]	1.51(2)	C(2)–C(7)–C(19) [a]	109.5
C(3)–C(8) [b]	1.53(3)		
C(4)–C(9) [b]	1.51(3)	P(2)–C(13)–C(14)	118.3(20)
C(5)–C(10) [b]	1.49(3)	P(2)–C(13)–C(18)	114.3(19)
C(7)–C(19) [a]	1.54	C(14)–C(13)–C(18)	105.6(22)
		C(13)–C(14)–C(15)	119.6(24)
C(13)–C(14)	1.46(4)	C(14)–C(15)–C(16)	119.5(25)
C(14)–C(15)	1.38(4)	C(15)–C(16)–C(17)	121.2(27)
C(15)–C(16)	1.42(4)	C(16)–C(17)–C(18)	114.6(26)
C(16)–C(17)	1.44(4)	C(17)–C(18)–C(13)	117.4(24)
C(17)–C(18)	1.47(4)		
C(13)–C(18)	1.52(4)		

[a] Geometrically constrained value. [b] Initially constrained value; allowed limited refinement in later stages. [c] Representative of five equivalent constrained values.

TABLE 4

Mean planes through planar fragments. The equation of each plane is $px + qy + rz = d$, where p, q, and r are the direction cosines of the normal to the plane referred to the orthogonal crystal axes a, b, and c. Deviations (Å) of atoms from planes are given in square brackets

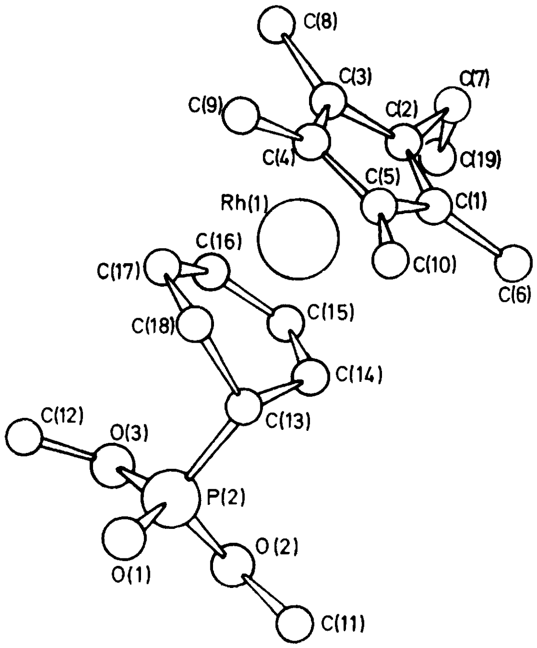
	p	q	r	d
Plane A: C(1)—C(5)	0.8781	0.1674	−0.4482	6.0521
[C(1)—C(5) 0.00, Rh(1) −1.80, C(6) 0.03, C(7) 0.31, C(8) 0.08, C(9) 0.09, C(10) 0.10, C(19) −1.01]				
Plane B: C(2), C(7), C(19)	−0.1125	−0.8848	−0.4523	−9.5092
Plane C: C(14)—C(18)	−0.8321	−0.2523	0.4939	−2.8303
[C(14) 0.02, C(15) −0.03, C(16) 0.01, C(17) 0.01, C(18) −0.02, Rh(1) −1.68, C(13) 0.62, H(14) 0.00, H(15) 0.73, H(16) 0.24, H(17) 0.82, H(18) 0.06]				
Plane D: C(13), C(14), C(18)	−0.8562	0.4421	0.2674	0.7897
[Rh(1) −0.69, P(2) 1.26, C(15) 0.90, C(16) 1.45, C(17) 1.03, H(13) −0.80, H(14) −0.33, H(18) −0.25]				

Selected interplanar angles (°): A–B 92.5; A–C 173.9; C–D 42.9.

The *X*-ray analysis confirms the *exo*-stereochemistry of the phosphoryl group and shows that the cyclohexadienyl ring is non-planar in an envelope conformation bent along the line C(14)–C(18) (see Figure) by an angle of 42.9°. Table 4 lists the deviations of the ring hydrogen atoms from the mean five-atom plane; all lie displaced from this plane on the side remote from the rhodium atom. The substituent carbon atoms on the cyclopentadienyl ring also lie out of the ring plane in a direction away from the metal: the plane of the ethyl group is almost perpendicular (92.5°) to that of the ring and the methyl carbon atom is bent back towards the rhodium atom. This contrasts with other structures containing the ethyltetramethylcyclopentadienyl ligand in which the methyl carbon atom of the ethyl group lies on the opposite side of the mean ring plane to the metal atom.[11] The position for this methyl group seems to represent the site of major occupancy only (the isotropic thermal vibrational parameter is very large) but no other site was detected from difference-Fourier syntheses for sites of minor occupancy either on the same carbon atom or on other carbon substituents of the cyclopentadienyl ring; it is likely that, apart from this major-occupancy site, several other sites are occupied but at too low a population to allow detection. In view of the constraints which were applied during refinement (see Experimental section), no further features of the molecular geometry can realistically be discussed.

From our studies with phosphine nucleophiles, it is reasonable to presume that formation of (9b) proceeds *via* the phosphonium salt (9a) which then undergoes a Michaelis–Arbuzov-type rearrangement reaction similar to that reported for $[W(C_5H_5)(AsMe_3)(CO)_2\{P(OMe)_3\}]I$.[12] Since only very basic phosphines gave stable phosphonium salts, one would not expect phosphites, which are relatively weak bases, to undergo this reaction readily and indeed there are only three previous reports of nucleophilic attack by a phosphite upon a co-ordinated ligand.[13,14] The driving force for the reaction must therefore come from the ease of rearrangement of the phosphonium intermediate (9a) to the phosphonate product (9b).

The reaction was monitored by ^1H n.m.r. spectroscopy. No phosphonium intermediate was detected although free benzene was identified; integration of the spectrum suggested that *ca.* 25% of the reaction proceeded *via* attack at the metal leading to displacement of the benzene ligand. Phosphorus-31 n.m.r. spectroscopy confirmed that the reaction was indeed complex; in addition to signals of the phosphonate product (9b), eight other signals were observed. Two of these corresponded to a doublet [δ + 113.3, J = 200 Hz (nitromethane)] and are assigned to $[Rh(C_5Me_4Et)\{P(OMe)_3\}_3][PF_6]_2$ by analogy with the spectrum of $[Rh(C_5Me_5)\{P(OMe)_3\}_3][PF_6]_2$ [δ + 113.1, J(Rh–P) = 200 Hz (acetone)].[15] Some of the other products are probably complexes of the type $[Rh(C_5Me_4Et)\{P(OMe)_3\}_nL_{3-n}][PF_6]_2$ (*e.g.* L = solvent).



Molecular structure and atom labelling for the ion $[Rh(\eta^5\text{-}C_5Me_4Et)\{\eta^5\text{-}C_6H_6P(O)(OMe)_2\}]^+$

The corresponding reaction of triethyl phosphite with $[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$ gave the two compounds $[Rh(C_5Me_4Et)\{\eta^5\text{-}C_6H_6P(O)(OEt)_2\}][PF_6]$ (10) and $[Rh(C_5Me_4Et)\{P(OEt)_3\}_3][PF_6]_2$ (11) in the ratio 1 : 1.35. In contrast to trimethyl phosphite, therefore, attack at the benzene ligand is a minor reaction pathway. This may be rationalised with the reduced tendency of triethyl phosphite, compared to trimethyl phosphite, to undergo Michaelis–Arbuzov rearrangement.

Triphenyl phosphite did not react with $[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$. Presumably nucleophilic attack at the rhodium atom does not occur for steric reasons and because triphenyl phosphite is a comparatively weak nucleophile. Arbuzov elimination of the phenyl carbonium ion only occurs under extreme conditions and consequently it is not surprising that $[Rh(C_5Me_4Et)\{C_6H_6P(O)(OPh)_2\}][PF_6]$ is not formed.

A feature of the i.r. spectra of the phosphonate compounds $[Rh(C_5Me_5Et)\{\eta^5\text{-}C_6H_6P(O)(OR)_2\}][PF_6]$ [R = Me (9b) or Et (10)] is the presence of several bands in the region 1 226—1 266 cm^{-1} (Experimental section) which are absent for the phosphite complexes $[Rh(C_5Me_4Et)\{P(OEt)_3\}_3][PF_6]_2$ and $[Co(C_5Me_5)\{P(OR)_3\}_3]$ (R = Me or Et).[16] These bands could be assigned to ν(P=O) if several spatial isomers of the dialkoxyphosphoryl substituents were present;[17] however, from *X*-ray crystallographic studies of the dimethoxyphosphoryl derivative (9b) the dimethylphosphoryl group seems to be fully ordered with no evidence for partial occupancy of methyl-group sites. Further, the i.r. spectra of the cyclohexadienyl compounds $[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_6L)]^{n+}$ contain bands in this region when $n = 2$, L = PBu_3 or PMe_2Ph but not when $n = 1$, L = H. It appears, therefore, that the absorptions at 1 226—1 266 cm^{-1} in the i.r. spectra of (9b) and (10) are not simply due to ν(P=O) but include ν(PCH) absorptions.

Reactions with N-*Donor Ligands.*—Triethylamine reacted with $[Rh(C_5Me_4Et)(C_6H_6)][BF_4]_2$ to give a product identified by ^1H n.m.r. spectroscopy as $[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_6NEt_3)][BF_4]_2$ (Table 1). Attempts to isolate this complex, however, failed due to its ready decomposition. Similar reactions were observed with diethylamine, piperidine, and *N*-methylpiperidine, but again no complexes could be isolated. It is obvious that, despite the greater basicity of these amines relative to phosphines and phosphites, the ammoniocyclohexadienyl adducts are less stable than the adducts (5), (7), (9b), and (10) formed by phosphorus donors. We note that the compound $[Fe(CH_2CH_2NMe_3)(C_5H_5)(CO)_2][BF_4]$ also readily loses trimethylamine whereas $[Fe(CH_2CH_2PPh_3)(C_5H_5)(CO)_2][BF_4]$ and $[Fe\{CH_2CH_2P(O)(OEt)_2\}(C_5H_5)(CO)_2]$ are stable.[13]

In contrast, pyridine displaced the co-ordinated benzene in $[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$ to give the *tris*(pyridine) complex $[Rh(C_5Me_4Et)(NC_5H_5)_3][PF_6]_2$ in 74% yield. We found no evidence to suggest that pyridine also attacked the ring to give a substituted-cyclohexadienyl compound.

EXPERIMENTAL

Reactions were carried out under a dry nitrogen atmosphere although all the products proved to be quite stable to air. Elemental analysis were carried out by the microanalytical department of this University. Proton n.m.r. spectra were recorded on a Perkin-Elmer R34 220 MHz spectrometer, and ^{13}C and ^{31}P n.m.r. spectra on a JEOL PFT 100 spectrometer. The compounds $[Co(C_5Me_5)(C_6H_6)][BF_4]_4$ [1] and $[Ir(C_5Me_5)(C_6H_6)][PF_6]_2$ [2] were prepared as previously described.

(η⁶-Benzene)(η⁵-ethyltetramethylcyclopentadienyl)rhodium(III) *Hexafluorophosphate.*—Silver hexafluorophosphate (1.57 g, 6.2 mmol) was added to a stirred solution of $[\{Rh(C_5Me_4Et)Cl_2\}_2]$ [18] (1.0 g, 1.55 mmol) in acetone (40 cm^3). After stirring for another 20 min, the mixture was filtered through a cellulose column (1 × 3 cm) and the residue was washed with acetone (20 cm^3). The combined filtrate and washings were concentrated to *ca.* 20 cm^3 and refiltered. Benzene (50 cm^3) was added to the filtrate and the solution was allowed to stand at *ca.* 0 °C for 4 h. The grey precipitate which had formed was filtered off and recrystallised from nitromethane and ether to give white crystals of $[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$ (1.44 g, 75%) (Found: C, 33.0; H, 3.5. $C_{17}H_{23}F_{12}P_2Rh$ requires C, 32.9; H, 3.7%).

The analogous tetrafluoroborate salt, $[Rh(C_5Me_4Et)(C_6H_6)][BF_4]_2$, was prepared as a white crystalline solid in a 78% yield by a similar method which employed $Ag[BF_4]$ in place of $Ag[PF_6]$ (Found: C, 40.7; H, 4.6. $C_{17}H_{23}B_2F_8Rh$ requires C, 40.5; H, 4.6%).

(η⁵-Cyclohexadienyl)(η⁵-ethyltetramethylcyclopentadienyl)rhodium(III) *Hexafluorophosphate.*—A solution of $Li[AlH(OBu^t)_3]$ (125 mg, 0.49 mmol) in thf (2 cm^3) was added dropwise to a stirred solution of $[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$ (200 mg, 0.32 mmol) in nitromethane (5 cm^3). After stirring for another 5 min, the solution was filtered and diethyl ether (20 cm^3) was added. The resultant precipitate was washed with ether, dissolved in chloroform, and then filtered through a short alumina column (0.5 × 1 cm). Addition of ether to the filtrate precipitated pale yellow crystals of $[Rh(C_5Me_4Et)(C_6H_7)][PF_6]$ (110 mg, 71%) (Found: C, 43.0; H, 5.2. $C_{17}H_{24}F_6PRh$ requires C, 42.9; H, 5.1%).

Reaction of $[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$ *with Penta*-2,4-*dionatothallium.*—The salt Tl[acac] (145 mg, 0.48 mmol) was added to a solution of $[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$ (300 mg, 0.48 mmol) in nitromethane (5 cm^3). The mixture was stirred for 5 min and then diethyl ether (20 cm^3) was added. The products were extracted from the resultant yellow oil into dichloromethane and this solution was filtered through alumina (0.5 × 2 cm). Addition of ether to the filtrate caused an orange oil to separate out. The ^1H n.m.r. spectrum (in $[^2H_6]$acetone) showed that the oil was a mixture of two products, believed to be $[Rh(C_5Me_4Et)\{C_6H_6CH(COMe)_2\}][PF_6]$ and $[Rh(C_5Me_4Et)(acac)(solvent)][PF_6]$. The former was less soluble in chloroform than the latter and this enabled them to be isolated as an orange solid and an orange oil, respectively. Neither of these products, however, could be obtained in an analytically pure form.

(η⁵-Methoxycyclohexadienyl)(η⁵-pentamethylcyclopentadienyl)iridium(III) *Hexafluorophosphate.*—Sodium (0.1 g, 4.3 mg atom) in methanol (50 cm^3) was added to a solution of $[Ir(C_5Me_5)(C_6H_6)][PF_6]_2$ (0.29 g, 0.42 mmol) in methanol (30 cm^3). The reaction mixture was stirred overnight, concentrated to 10 cm^3, and then poured into diethyl ether (50 cm^3). A white precipitate was formed and this was recrystallised from a mixture of methanol and ether to give $[Ir(C_5Me_5)(C_6H_6OMe)][PF_6]$ (221 mg, 91%) (Found: C, 34.7; H, 4.1. $C_{17}H_{24}F_6IrOP$ requires C, 35.1; H, 4.2%).

*(η⁵-Ethyltetramethylcyclopentadienyl)(2—6-η-1-*exo*-tri-butylphosphoniocyclohexadienide)rhodium*(III) *Tetrafluoroborate.*—Tri-n-butylphosphine (0.5 g, 2.47 mmol) was added to a solution of $[Rh(C_5Me_4Et)(C_6H_6)][BF_4]_2$ (200 mg, 0.4 mmol) in nitromethane (5 cm^3) and the golden-yellow solution was stirred for 5 min. Diethyl ether (50 cm^3) was added and the mixture was cooled to 0 °C and allowed to stand for 1 h. The yellow precipitate which had formed was filtered off and washed repeatedly with ether. Recrystallisation from dichloromethane and ether afforded yellow crystals of $[Rh(C_5Me_4Et)(C_6H_6PBu^n_3)][BF_4]_2$ (280 mg, 99%)

(Found: C, 49.1; H, 7.0. $C_{29}H_{50}B_2F_8PRh$ requires C, 49.3; H, 7.1%). Infrared spectrum (KBr): ν(PCH) at 1 301w, 1 284w, 1 252w, and 1 229w; BF_4 at 1 060vs,br cm^{-1}.

(η^5-*Pentamethylcyclopentadienyl*)(2—6-η-1-exo-*tributylphosphoniocyclohexadienide*)*cobalt*(III) *Tetrafluoroborate*.—The salt $[Co(C_5Me_5)(C_6H_6PBu^n_3)][BF_4]_2$ was prepared from $[Co(C_5Me_5)(C_6H_6)][BF_4]_2$ (400 mg, 0.9 mmol) and PBu^n_3 (1.5 g, 9.4 mmol) in a similar manner to that described above for the preparation of $[Rh(C_5Me_4Et)(C_6H_6PBu^n_3)][BF_4]_2$. The product was obtained as orange crystals (520 mg, 89%) (Found: C, 51.4; H, 7.1. $C_{28}H_{48}B_2CoF_8P$ requires C, 51.9; H, 7.5%). Infrared spectrum (KBr): ν(PCH) at 1 300w, 1 283w, 1 258w, and 1 230w; BF_4 at 1 050vs,br cm^{-1}.

(2—6-η-1-exo-*Dimethylphenylphosphoniocyclohexadienide*)-(η^5-*ethyltetramethylcyclopentadienyl*)*rhodium*(III) *Tetrafluoroborate*.—The salt $[Rh(C_5Me_4Et)(C_6H_6PMe_2Ph)][BF_4]_2$ was prepared from $[Rh(C_5Me_4Et)(C_6H_6)][BF_4]_2$ (300 mg, 0.6 mmol) and PMe_2Ph (0.6 g, 4.35 mmol) in a similar manner to that described above for the preparation of $[Rh(C_5Me_4Et)(C_6H_6PBu^n_3)][BF_4]_2$. The product was obtained as pale yellow crystals (355 mg, 93%) (Found: C, 47.0; H, 5.5. $C_{25}H_{34}B_2F_8PRh$ requires C, 46.8; H, 5.3%). Infrared spectrum (KBr): ν(PMe) at 1 318m and 1 301m; ν(PCH) at 1 261w and 1 244m cm^{-1}.

Tris(*dimethylphenylphosphine*)(η^5-*ethyltetramethylcyclopentadienyl*)*rhodium*(III) *Tetrafluoroborate*.—The compound $[\{Rh(C_5Me_4Et)Cl_2\}_2]$ (200 mg, 0.31 mmol) and $Ag[BF_4]$ (240 mg, 1.23 mmol) were stirred in nitromethane (10 cm^3) for 20 min. The resultant mixture was filtered through a cellulose column (1 × 2 cm) and the residue was washed with nitromethane (10 cm^3). Dimethylphenylphosphine (500 mg, 3.62 mmol) was added to the combined filtrate and washings and the solution was stirred for 5 min. Addition of diethyl ether (50 cm^3) precipitated a yellow solid which was recrystallised from acetone and ether to give yellow crystals of $[Rh(C_5Me_4Et)(PMe_2Ph)_3][BF_4]_2$ (395 mg, 76%) (Found: C, 49.8; H, 5.8. $C_{35}H_{50}B_2F_8P_3Rh$ requires C, 50.0; H, 6.0%). Infrared spectrum (KBr): ν(PMe) at 1 320m, 1 305(sh), and 1 293m cm^{-1}.

(2—6-η-1-exo-*Dimethoxyphosphorylcyclohexadienyl*)(η^5-*ethyltetramethylcyclopentadienyl*)*rhodium*(III) *Hexafluorophosphate*.—Trimethyl phosphite (500 mg, 4.0 mmol)was added to a solution of $[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$ (300 mg, 0.48 mmol) in nitromethane (10 cm^3). The solution was stirred for 30 min and then diethyl ether (50 cm^3) was added. The yellow oil, which separated out, was washed with ether (5 × 20 cm^3) and dissolved in dichloromethane. The dichloromethane solution was filtered through a short alumina column (0.5 × 2.0 cm) and addition of ether precipitated a yellow oily solid. Recrystallisation from nitromethane and ether yielded the product, $[Rh(C_5Me_4Et)\{C_6H_6P(O)(OMe)_2\}][PF_6]$, as a yellow crystalline solid (205 mg, 72%) (Found: C, 39.1; H, 4.8. $C_{19}H_{29}F_6O_3P_2Rh$ requires C, 39.1; H, 5.0%). Infrared spectrum (Nujol): ν(PCH), ν(P=O) at 1 266m, 1 258m, 1 240m, and 1 226w; ν(P–OMe) at 1 181w, 1 075m, and 1 025s; PF_6 at 835vs cm^{-1}.

(η^5-*Ethyltetramethylcyclopentadienyl*)*tris*(*triethyl phosphite*)-*rhodium*(III) *Hexafluorophosphate and* (2—6-η-1-exo-*Diethoxyphosphorylcyclohexadienyl*)(η^5-*ethyltetramethylcyclopentadienyl*)*rhodium*(III) *Hexafluorophosphate*.—Triethyl phosphite (1.0 g, 6.0 mmol) was added to a solution of $[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$ (700 mg, 1.13 mmol) in nitromethane and the resulting deep yellow solution was stirred for 1 h. Addition of diethyl ether precipitated a yellow solid which was extracted into dichloromethane. A small amount of a residual white solid which was insoluble in dichloromethane was identified by ^{1}H n.m.r. spectroscopy as unchanged $[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$. The dichloromethane solution was concentrated and upon addition of thf a white solid precipitated out. This was filtered off and recrystallised from acetone and ether to give white crystals of $[Rh(C_5Me_4Et)\{P(OEt)_3\}_3][PF_6]_2$ (580 mg, 49%) (Found: C, 35.5; H, 5.9. $C_{29}H_{62}F_{12}O_9P_5Rh$ requires C, 35.5; H, 6.0%).

The yellow filtrate was reduced to an oil *in vacuo* and this oil was dissolved in thf and filtered through an alumina column (0.5 × 3 cm). Addition of ether to the filtrate precipitated a yellow solid. Repeated recrystallisations of this solid from chloroform and ether gave a pale yellow solid which was identified by i.r. and ^{1}H, ^{13}C, and ^{31}P n.m.r. spectroscopy as impure $[Rh(C_5EtMe_4)\{C_6H_6P(O)(OEt)_2\}][PF_6]$ (240 mg, 36%). Attempts to purify this product further were unsuccessful. Infrared spectrum (Nujol): ν(P=O), ν(PCH) at 1 268m, 1 258m, and 1 244m; ν(P–OEt) at 1 161w, 1 043m, 1 030m, 975m, and 968m; PF_6 at 830s cm^{-1}.

Reaction of $[Rh(C_5Me_4Et)(C_6H_6)][BF_4]_4$ *with Triethylamine*.—A solution of triethylamine (60 mg, 0.6 mmol) in thf (1.4 cm^3) was cautiously added to a solution of $[Rh(C_5Me_4Et)(C_6H_6)][BF_4]$ (300 mg, 0.59 mmol) in nitromethane (10 cm^3) and an immediate colour change from pale yellow to red was observed. Addition of diethyl ether caused an orange-red oil to separate and this was washed with ether and dried *in vacuo* (1 h, 20 °C). The ^{1}H n.m.r. spectrum of this oil indicated that the major product was $[Rh(C_5Me_4Et)(C_6H_6NEt_3)][BF_4]_2$, but all attempts to purify the product resulted in decomposition. Similar results were obtained with diethylamine, piperidine, and *N*-methylpiperidine.

(η^5-*Ethyltetramethylcyclopentadienyl*)*tris*(*pyridine*)-*rhodium*(III) *Hexafluorophosphate*.—Pyridine (0.5 cm^3, 6.3 mmol) was added to a solution of $[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$ (200 mg, 0.4 mmol) in nitromethane (10 cm^3). An immediate colour change from pale yellow to a deep yellow was observed and addition of diethyl ether caused a yellow oil to separate out. This oil was washed with ether and recrystallised twice from acetone and ether to give yellow crystals of $[Rh(C_5Me_4Et)(NC_5H_5)_3][PF_6]_2$ (195 mg, 74%) (Found: C, 39.7; H, 4.4; N, 5.1. $C_{26}H_{32}F_{12}N_3P_2Rh$ requires C, 40.1; H, 4.1; N, 5.4%).

X-Ray Crystal-structure Determination of $[Rh(C_5Me_4Et)\{C_6H_6P(O)(OMe)_2\}][PF_6]$ (9b).—Recrystallisation of compound (9b) from nitromethane–diethyl ether gave, as described above, long thin needle-shaped crystals. One such crystal with dimensions 0.069 × 0.035 × 0.875 mm was chosen for *X*-ray study.

Crystal Data. $C_{19}H_{29}F_6O_3P_2Rh$, $M = 584.28$, Orthorhombic, $a = 16.353(26)$, $b = 21.847(35)$, $c = 13.258(14)$ Å, $U = 4\,737(12)$ Å^3, $D_m = 1.64$, $Z = 8$, $D_c = 1.638$ g cm^{-3}, $F(000) = 2\,368$, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 9.05 cm^{-1}, space group *Pbca* from systematic absences.

Three-dimensional *X*-ray data ($6.5 < 2\theta < 50°$) were collected on a Stoe Stadi-2 diffractometer by the moving-crystal, stationary-counter method and the 903 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz, polarisation, and absorption effects. The structure was solved by conventional Patterson and Fourier methods. In an attempt to counteract an ill determined refinement, which resulted from the rather limited data set and from the disturbing influence of the thermal motion of the hexafluorophosphate group, extensive geometric constraints were imposed during the later stages of least-squares refinement, as follows: (*a*) the cyclopentadienyl ring was constrained to have a pentagonal planar geometry (C–C 1.436 Å); (*b*) the substituent atoms on the cyclopentadienyl ring were constrained to lie approximately above or below the external bisector of the ring angle (*i.e.* positional refinement was restricted to one rotational parameter about an axis tangential to the ring through the atom to which the substituent was bonded, C–C 1.505 Å); (*c*) in addition to the above constraint, the ethyl substituent (which, in view of the high thermal parameter of the methyl carbon atom, may only represent the major-occupancy site for this atom) was allowed rotational refinement about the exocyclic carbon–carbon bond; (*d*) the methoxy-groups were refined (O–C 1.45 Å) rotationally about the site of the refined oxygen position; and (*e*) the hexafluorophosphate group was assigned O_h symmetry (P–F 1.46 Å) and positionally refined as a six-parameter group.

During constrained least-squares refinement the opportunity was taken to include the hydrogen atoms of all methylene and methyl groups in the structure-factor calculations (C–H 0.95 Å), those on the latter being approximated by six half-population hydrogen atoms distributed around the annulus (X–C–H 109.5°, X = C or O) since difference electron-density maps showed no evidence for localised sites. All constrained bond lengths were surveyed from ref. 19 and correspond to equivalent values found in comparable structures. This refinement with constraints produced a tight convergence with a chemically acceptable geometry at a final R 0.069 7 which was not significantly higher than that achieved with three positional parameters for each non-hydrogen atom (R 0.068 0). The final model allowed thermal anisotropy for the rhodium, phosphorus, fluorine, and oxygen atoms and for the carbon atoms excepting those of the substituents on the cyclopentadienyl group, for which isotropic thermal parameters were refined. Hydrogen atoms were assigned isotropic thermal parameters of 12.0 Å². Allowance was also made for the anomalous scattering of the rhodium and phosphorus atoms. The hydrogen atoms of the cyclohexadienyl ring, which were all detected on a difference-Fourier synthesis, were inserted at the correct carbon–hydrogen distance (0.95 Å) in a position to best satisfy the electron density in a plane perpendicular to the plane through the ring carbon atom and its immediate ring neighbours.

TABLE 5

Atomic positional parameters and estimated standard deviations

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Rh(1)	0.323 66(14)	0.371 28(10)	0.295 75(17)
P(1)	0.346 7(5)	0.097 8(4)	0.237 0(6)
P(2)	0.148 9(5)	0.256 1(4)	0.469 4(7)
F(1)	0.397 0(11)	0.120 5(12)	0.154 1(12)
F(2)	0.416 3(8)	0.103 2(12)	0.305 3(12)
F(3)	0.322 5(14)	0.160 5(5)	0.261 1(20)
F(4)	0.296 4(11)	0.075 2(12)	0.319 9(12)
F(5)	0.370 8(14)	0.035 2(5)	0.212 9(20)
F(6)	0.277 0(8)	0.092 5(12)	0.168 7(12)
O(1)	0.173 2(14)	0.221 6(9)	0.563 2(14)
O(2)	0.093 9(13)	0.216 9(9)	0.393 9(14)
O(3)	0.093 1(11)	0.313 2(8)	0.483 2(15)
C(1)	0.405 0(12)	0.342 3(9)	0.170 9(14)
C(2)	0.384 2(11)	0.405 9(10)	0.159 8(13)
C(3)	0.412 5(13)	0.437 7(7)	0.247 8(17)
C(4)	0.450 8(11)	0.393 9(10)	0.313 3(12)
C(5)	0.446 1(12)	0.334 9(8)	0.265 8(16)
C(6)	0.387 3(16)	0.294 9(2)	0.093 9(10)
C(7)	0.358 0(14)	0.438 1(4)	0.064 0(8)
C(8)	0.408 5(19)	0.506 7(2)	0.267 0(12)
C(9)	0.493 7(17)	0.408 5(3)	0.411 7(13)
C(10)	0.483 3(16)	0.277 4(3)	0.304 2(10)
C(11)	0.113 6(21)	0.154 5(6)	0.365 6(30)
C(12)	0.093 7(20)	0.345 6(16)	0.578 7(15)
C(13)	0.237 8(17)	0.282 1(12)	0.393 3(21)
C(14)	0.223 6(15)	0.300 0(11)	0.288 4(22)
C(15)	0.193 6(14)	0.357 6(14)	0.267 1(22)
C(16)	0.205 5(18)	0.405 9(12)	0.337 7(25)
C(17)	0.252 3(19)	0.396 6(14)	0.428 1(23)
C(18)	0.285 6(16)	0.334 4(14)	0.439 9(18)
C(19)	0.264 5(5)	0.446 6(28)	0.065 3(22)

Atomic scattering factors were taken from ref. 20 and unit weights were used throughout the block-diagonal least-squares refinement. Computer programs formed part of the Sheffield X-ray package.

Table 5 lists atomic positional parameters (with estimated standard deviations either directly obtained or converted from group translational and rotational parameters where appropriate). The predicted hydrogen positions, thermal vibrational parameters, and observed structure amplitudes and calculated structure factors are available as Supplementary Publication No. SUP 22714 (14 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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