Pentamethylcyclopentadienyl-rhodium and -iridium complexes. Part 30.[1] Trimethylphosphine-chloro-, -acetato-, and -hydrido-complexes and Related Compounds of (Hexamethylbenzene)ruthenium

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Reaction of the η^5-pentamethylcyclopentadienyl-rhodium or -iridium complexes $[\{M(C_5Me_5)\}_2Cl_4]$ or the (η^6-hexamethylbenzene)ruthenium complex $[\{Ru(C_6Me_6)\}_2Cl_4]$ with PMe_3 gave $[M(C_nMe_n)Cl_2(PMe_3)]$ (2a; M = Rh, n = 5), (2b; M = Ir, n = 5), and (2c; M = Ru, n = 6) which with silver acetate gave the complexes $[M(C_nMe_n)(O_2CMe)_2(PMe_3)]$ (3a)—(3c). The structures of complexes (3) were determined, by i.r. and n.m.r. spectroscopy, to contain monodentate acetates in the solid and in aprotic solvents. This was confirmed by an *X*-ray crystal-structure determination on (3a). In water there was rapid exchange between co-ordinated and free acetate in (3a) and (3b) but this was slower on the n.m.r. time-scale for (3c). Exchange took place *via* $[M(C_nMe_n)(O_2CMe)(PMe_3)]^+$, the PF_6^- salts of which were obtained by reaction of (3) with KPF_6. The hydride complexes $[Ir(C_5Me_5)H(Cl)(PMe_3)]$ (6b) and $[M(C_nMe_n)H_2(PMe_3)]$ (7a)—(7c) were prepared from compounds (2); $[Ir(C_5Me_5)H_2(PMe_3)]$ was stable to oxygen in solution but the others all decomposed rapidly giving PMe_3O and other products. Reactions with olefins or acetylenes were slow and such complexes are unlikely to be intermediates in catalytic hydrogen-transfer reactions.

DURING the past few years we have developed complexes containing peralkylated π-ligands [*e.g.* $Rh(C_5Me_5)$, $Ir(C_5Me_5)$, or $Ru(C_6Me_6)$] as catalysts for a variety of hydrogen-transfer reactions.[2,3] In the cases where we have been able to carry them out, kinetic measurements have suggested that the active species are mononuclear even though the catalysts may well be introduced as dinuclear complexes, for example, $[\{M(C_nMe_n)\}_2Cl_4]$ (1a)—(1c), $[\{Rh(C_5Me_5)\}_2(OH)_3]^+$, or $[\{Ru(C_6Me_6)\}_2(OH)_3]^+$.[4,5] It was thus of interest to prepare and test for catalytic activity mononuclear complexes of the type $[M(C_nMe_n)Y(X)L]$ (X, Y = monoanionic ligand, L = neutral ligand; $n = 5$ for M = Rh or Ir, $n = 6$ for M = Ru). We have previously shown that the catalytic activity is generally low when L is large (*e.g.*, PPh_3 †)[4] and since small amines such as pyridine bind weakly,[7,8] we have now investigated trimethylphosphine complexes, the preparation and properties of which are reported here.

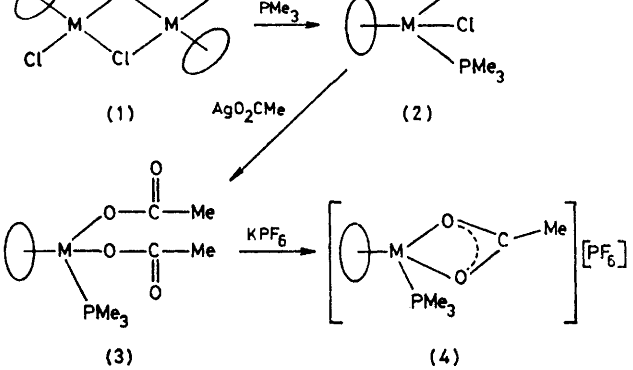
We have also taken advantage of the ready accessibility of $Ru(C_6Me_6)$ complexes[9,10] to prepare some of these for comparison with our $Rh(C_5Me_5)$ and $Ir(C_5Me_5)$ complexes.

RESULTS AND DISCUSSION

Chloro-, Acetato-, and Hydroxo-complexes.—The complexes (1a)—(1c) reacted readily with PMe_3 in dichloromethane to give the corresponding mononuclear complexes (2a)—(2c) in *ca.* 70% yield (Scheme). The latter were characterised by microanalysis, ^1H, ^{13}C, and ^{31}P n.m.r. spectroscopy (Tables 1 and 2). The far-i.r. spectra showed two strong ν(M-Cl) bands between 224 and 286 cm^{-1}, as expected.

On reaction with silver acetate (2a)—(2c) gave the acetate complexes (3a)—(3c), again characterised by analysis and spectroscopy. These complexes were remarkable in that they showed good solubility in solvents covering a wide range of polarities including water, alcohols, acetone, dichloromethane, benzene, and even cyclohexane. In the solid they are very hygroscopic.

The i.r. spectra of the complexes (3a)—(3c) showed very strong bands in the region 1 570—1 640 cm^{-1} arising from $\nu_{asym}(CO_2)$ together with somewhat weaker bands due to $\nu_{sym}(CO_2)$ in the region 1 300—1 370 cm^{-1}. This pattern is quite characteristic for monodentate carboxylate ligands.[11]



(a) M = Rh, ⬭ = η^5-C_5Me_5; (b) M = Ir, ⬭ = η^5-C_5Me_5; (c) M = Ru, ⬭ = η^6-C_6Me_6

SCHEME

Confirmation of this type of bonding comes from a single-crystal *X*-ray study of complex (3a) which showed the expected structure (Figure). The rhodium atom has the characteristic three-legged ‘piano-stool’ arrangement and is bound to one η^5-C_5Me_5 group [Rh–C (mean) 2.16(2) Å], two monodentate acetates [Rh–O 2.07(1),

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† However, catalytic activity has been claimed for $[Ru(C_6Me_6)H(Cl)(PPh_3)]$.[6]

TABLE 1

Microanalytical and i.r. spectroscopic data

Complex	Analysis * (%) C	H	Cl	M	Yield (%)	I.r. (cm^{-1})
						ν(M-Cl)
(2a) $[Rh(C_5Me_5)Cl_2(PMe_3)]$	40.6 (40.5)	6.2 (6.3)	18.4 (18.4)	434 (385)	74	224s, 268s
(2b) $[Ir(C_5Me_5)Cl_2(PMe_3)]$	33.0 (32.9)	5.1 (5.1)	15.3 (15.0)	560 (474)	71	266s, 286s
(2c) $[Ru(C_6Me_6)Cl_2(PMe_3)]$	44.2 (43.9)	6.8 (6.6)	17.4 (17.3)	449 (410)	68	236s, 250s, 278s
						$\nu(CO_2)$
(3a) $[Rh(C_5Me_5)(O_2CMe)_2(PMe_3)]$	47.4 (47.2)	6.9 (7.0)			61	1 315s, 1 365s, 1 577vs, 1 608vs, 1 622vs
(3b) $[Ir(C_5Me_5)(O_2CMe)_2(PMe_3)]$	38.7 (39.2)	6.1 (5.8)			73	1 300s, 1 320s, 1 370s, 1 590vs, 1 618vs, 1 638vs
(3c) $[Ru(C_6Me_6)(O_2CMe)_2(PMe_3)]$	48.6 (49.9)	7.3 (7.3)			82	1 315s, 1 365s, 1 570vs, br, 1 610vs, br
(4a) $[Rh(C_5Me_5)(O_2CMe)(PMe_3)][PF_6]$	35.2 (34.8)	5.4 (5.3)			73	1 410, 1 420m, 1 575m
$[Rh(C_5Me_5)(O_2CMe)(PMe_3)][BPh_4]$	67.1 (67.6)	7.1 (6.8)			93	1 427vs, 1 578vs
(4b) $[Ir(C_5Me_5)(O_2CMe)(PMe_3)][PF_6]$	29.3 (29.7)	4.6 (4.5)			86	1 410, 1 425m, 1 580m
(4c) $[Ru(C_6Me_6)(O_2CMe)(PMe_3)][PF_6]$	37.7 (37.6)	5.6 (5.6)			78	1 415m, 1 585m
(6b) $[Ir(C_5Me_5)H(Cl)(PMe_3)]$	35.3 (35.6)	5.5 (5.5)	8.7 (8.1)		68	ν(IrH) 2 057

* Calculated values in parentheses.

2.10(1) Å], and one trimethylphosphine [Rh–P 2.319(5) Å]. Although the difference between the two Rh–O distances is not significant, the two acetates are not quite equivalent as indicated by the two angles P–Rh–O(1) 90.7(3)° and P–Rh–O(3) 79.4(3)°. This presumably explains the larger than expected number of $\nu(CO_2)$ bands in the i.r. spectrum. The Rh–P distance is close to that found in $[Rh(C_5Me_5)H(PPh_3)_2]^+$ [2.308(5) Å]; [12] but while the Rh–O distances are insignificantly different from those in the O-dinitrato-complex $[Rh(C_5Me_5)(NO_3)_2(PPh_3)]$ [2.114, 2.152(2) Å],[13] the Rh–P distance there is slightly longer [2.383(1) Å]. This is presumably due to the greater size of PPh_3 and the larger non-bonded interactions compared with PMe_3.

The ^1H and ^{13}C n.m.r. spectra of (3a)—(3c) in chloroform showed that the acetate groups were equivalent on the n.m.r. time-scale. The spectra of (3a) and (3b) in D_2O were similar to those in chloroform, but on addition of sodium acetate the acetate resonance in the ^1H n.m.r. was displaced to a position between that of the free and the co-ordinated acetate, indicating that fast exchange was occurring.

The ^{13}C spectrum of the (hexamethylbenzene)ruthenium acetate complex (3c) in D_2O was, however, quite different to that in chloroform. While it showed single resonances for C_6Me_6 and one doublet for PMe_3, there were two resonances each for the acetate methyl and carbonyl carbons. These acetate resonances were significantly

TABLE 2

Hydrogen-1 and ^{13}C n.m.r. data [a]

	^1H N.m.r.			^{13}C N.m.r.				
	C_nMe_n	PMe_3	$MeCO_2$	$C_n\mathit{Me}_n$	C_nMe_n	PMe_3	$\mathit{Me}CO_2$	$Me\mathit{C}O_2$
(2a) $[Rh(C_5Me_5)Cl_2(PMe_3)]$ [b]	1.70 (d) (3.6)	1.63 (d) (11.8)		9.2 (s)	98.0 (dd) (6.5) [3.0]	14.6 (d) (33.0)		
(2b) $[Ir(C_5Me_5)Cl_2(PMe_3)]$ [c]	1.71 (d) (2.3)	1.67 (d) (11.1)		9.0 (s)	91.1 (s) [d]	13.9 (d) (39.7)		
(2c) $[Ru(C_6Me_6)Cl_2(PMe_3)]$ [e]	2.06 (d) (0.8)	1.48 (d) (10.3)		16.0 (s)	95.3 (d) (3.1)	15.3 (d) (33.6)		
(3a) $[Rh(C_5Me_5)(O_2CMe)_2(PMe_3)]$	1.66 (d) (3.7)	1.54 (d) (12.0)	2.07 (s)	9.8 (s)	96.4 (dd) (7.3) [3.4]	15.4 (d) (29.8)	25.1 (s)	177.3 (d) (1.5)
(3a) $[Rh(C_5Me_5)(O_2CMe)_2(PMe_3)]$ [f]	1.64 (d) (3.9)	1.53 (d) (11.0)	2.00 (s)	8.6 (s)	98.5 (dd) (7.6) [2.3]	12.5 (d) (29.7)	23.5 (s)	181.5 [d]
(3b) $[Ir(C_5Me_5)(O_2CMe)_2(PMe_2)]$	1.65 (d) (1.9)	1.57 (d) (11.2)	2.10 (s)	9.9 (s)	89.1 (d) (3.8)	15.1 (d) (36.6)	24.2 (s)	177.1 (d) [d]
(3b) $[Ir(C_5Me_5)(O_2CMe)_2(PMe_3)]$ [f]	1.62 (d) (2.2)	1.59 (d) (11.2)	2.03 (s)	10.3 (s)	92.4 (d) [d]	14.4 (d) (39.7)	25.2 (s)	169.0 [d]
(3c) $[Ru(C_6Me_6)(O_2CMe)_2(PMe_3)]$	2.13 (d) (1.0)	1.36 (d) (10.7)	2.03 (s)	16.3 (s)	94.1 (d) (3.1)	15.5 (d) (29.0)	25.1 (s)	178.1 (d) (3.1)
(3c) $[Ru(C_6Me_6)(O_2CMe)_2(PMe_3)]$ [f]	2.16 (d) (0.8)	1.42 (d) (10.9)	1.94 (s) 2.03 (s)	15.4 (s)	95.1 (s) [d]	12.7 (d) (30.5)	22.7 (s) 23.8 (s)	190.8 [d] 212.2 [d]
(4a) $[Rh(C_5Me_5)(O_2CMe)(PMe_3)][PF_6]$	1.68 (d) (3.2)	1.53 (d) (11.1)	1.96 (s)	9.3 (s)	98.3 (dd) (7.6) [2.3]	12.8 (d) (30.5)	23.9 (s)	188.3 [d]
(4b) $[Ir(C_5Me_5)(O_2CMe)(PMe_3)][PF_6]$	1.68 (d) (1.8)	1.64 (d) (11.3)	1.99 (s)	9.3 (s)	92.3 (d) (3.1)	12.9 (d) (37.4)	25.1 (s)	190.6 [d]
(4c) $[Ru(C_6Me_6)(O_2CMe)(PMe_3)][PF_6]$	2.16 (d) (0.9)	1.43 (d) (10.6)	1.87 (s)	16.0 (s)	95.1 (d) (3.1)	13.3 (d) (30.5)	24.0 (s)	231.9 [d]

[a] In $CDCl_3$, δ(p.p.m.), $SiMe_4$ = 0 p.p.m. Coupling J(P–H), J(P–C) to ^{31}P in round brackets (Hz); coupling J(Rh–C) to ^{103}Rh in square brackets (Hz). [b] $^{31}P-\{^1H\}$ n.m.r., δ −91.7 (d) (H_3PO_4 as reference), J(P–Rh) 136.6 Hz. [c] $^{31}P-\{^1H\}$ n.m.r., δ −91.6 (s). [d] Coupling not detected or not resolved. [e] $^{31}P-\{^1H\}$ n.m.r., δ −89.4 (s). [f] In D_2O ($Me_3SiCH_2CH_2CH_2SO_3Na$ as reference).

broader than the others, indicating that the two acetates were exchanging at an intermediate rate. The two different acetates in (3c) were also evident in the ^1H n.m.r. spectrum which showed two equal resonances, at δ 1.94 and 2.03 p.p.m. On addition of sodium acetate the peak at δ 1.94 p.p.m. increased in intensity and was therefore due to free acetate.

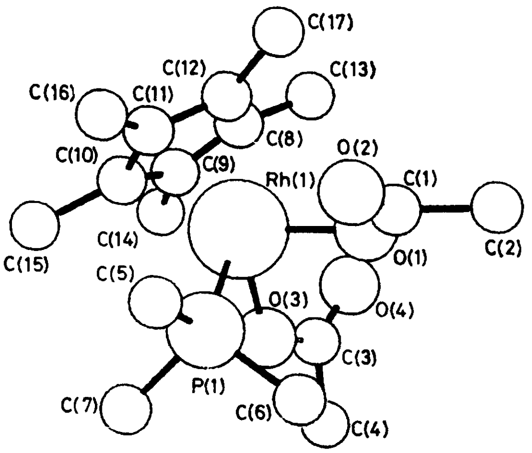
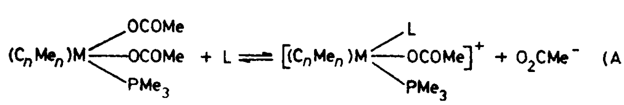


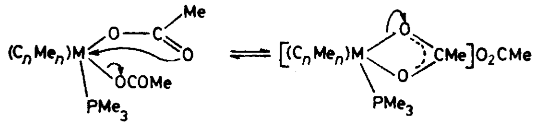
FIGURE Molecular structure of $[Rh(C_5Me_5)(O_2CMe)_2(PMe_3)]$, (3a), with hydrogen atoms omitted for clarity

Two mechanisms can be advanced for the exchange: one (A) in which co-ordinated acetate is reversibly displaced by another ligand such as water, and the other (B) in which one monodentate acetate is displaced formally by the other which becomes bidentate.



$$(C_nMe_n)M(OCOMe)_2(PMe_3) + L \rightleftharpoons [(C_nMe_n)M(L)(OCOMe)(PMe_3)]^+ + O_2CMe^-$$

(A)



(B)

Although both may well occur, we favour the latter since we have been able to synthesise the salts (4a)—(4c) containing the cation in (B) simply by reaction of (3a)—(3c) with KPF_6 in water. The bidentate nature of the acetate in (4) is clearly shown by the i.r. spectra which have lost the strong high-frequency bands arising from the monodentate acetates characteristic of (3). Instead, they show medium-intensity bands in the regions 1 410—1 425 and 1 575—1 585 cm^{-1} typical of bidentate chelating acetates.[11] An analogous complex $[Rh(C_5Me_5)(O_2CMe)(PMe_3)][BPh_4]$ was obtained from (3a) and $NaBPh_4$ but the acetate bands in the i.r. were obscured by the very strong BPh_4 bands and are only assigned tentatively. The ^1H and ^{13}C n.m.r. spectra of (4a)—(4c) confirmed the structures.

Reaction of $[\{Rh(C_5Me_5)\}_2Cl_4]$ with aqueous base gives $[\{Rh(C_5Me_5)\}_2(OH)_3]Cl$[14] and a wide variety of related and quite stable rhodium and iridium complexes are known.[1] When complex (2b) was reacted with silver oxide or with sodium hydroxide in water a material was obtained which has properties (*e.g.* the ^1H n.m.r. spectrum) consistent with those expected for $[Ir(C_5Me_5)(OH)_2(PMe_3)]$ (5b). It appeared to be stable in aqueous solution but on evaporation of the solvent only an extremely hygroscopic solid could be obtained, which could not be analysed.

When the same reactions were carried out on the rhodium complex (2a) and the ^1H n.m.r. spectrum was run immediately, resonances were observed that were consistent with the presence of (5a). However, these rapidly diminished in size to zero and were replaced by a singlet resonance which was due to $[\{Rh(C_5Me_5)\}_2(OH)_3]OH$.[1] The fate of the trimethylphosphine is obscure; significant amounts of PMe_3O were not formed but a number of small resonances did appear in the methyl region. The overall reactions are as shown below.

$$\underset{(2)}{[M(C_5Me_5)Cl_2(PMe_3)]} \xrightarrow{OH^-/H_2O} \underset{(5)}{[M(C_5Me_5)(OH)_2(PMe_3)]} \xrightarrow[M = Rh]{} [\{Rh(C_5Me_5)\}_2(OH)_3]OH$$

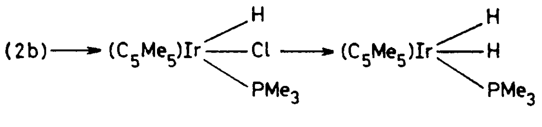
(a) M = Rh; (b) M = Ir

Hydrido-complexes.—Reaction of $[Ir(C_5Me_5)Cl_2(PMe_3)]$ (2b) with 1.5 equivalents of $NaBH_4$ in propan-2-ol gave the monohydride (6b); when a larger excess of $NaBH_4$ was used, the dihydride (7b) was also formed (see below). The dihydrides (7a) and (7c) were also obtained by reduction of (2a) or (2c) with $NaBH_4$ in propan-2-ol; all three dihydrides (7a)—(7c) were most conveniently made by Red-al $\{Na[AlH_2(OCH_2CH_2OMe)_2]\}$ reduction in benzene.

The rhodium and ruthenium hydrides were all extremely air-sensitive; the iridium monohydride (6b) was also air-sensitive in contrast to the reasonably air-stable $[Ir(C_5Me_5)H(Cl)(PPh_3)]$.[15] However, the iridium dihydride (7b) was, rather surprisingly, quite stable to oxygen in solution in the presence of excess hydride reducing agent.

The complexes were characterised by ^1H n.m.r. spectroscopy but only the chlorohydridoiridium complex (6b) could be isolated pure and microanalysed. They all showed hydride signals in the range δ −10 to −18 p.p.m., as well as resonances due to C_5Me_5 (or C_6Me_6) and PMe_3 in the expected intensity ratios. The hydride resonances showed coupling to phosphorus (32—48 Hz) and to rhodium (30.7 Hz) and they were also coupled to the ring methyls in the rhodium and iridium complexes. The latter was seen as a small splitting in the C_5Me_5 resonances of 0.7—1.0 Hz. As a consequence of coupling to P, Rh, and H the C_5Me_5 signal of the rhodium complex (7a) appeared as a complicated but easily analysed and highly characteristic 12-line multiplet.

It may also be noted that the C_5Me_5 resonances of the iridium complexes appeared at progressively lower field as the number of hydrides increased, δ (benzene): 1.36 (2b), 1.76 (6b), and 2.15 p.p.m. (7b).



(6b) (7b)

The effect of air on (6b) and (7b) was studied by exposing a benzene solution of a mixture [obtained by borohydride reduction of (2b)] to air while monitoring the ^1H n.m.r. spectrum. The monohydride reacted rapidly to give (2b) and trimethylphosphine oxide, which

$$(6b) + O_2 \longrightarrow (2b) + [\{Ir(C_5Me_5)\}_2(OH)_3]OH + PMe_3O$$

were identified by their characteristic spectra. In addition, a precipitate was formed which was shown to be the known $[\{Ir(C_5Me_5)\}_2(OH)_3]OH$.[1] By contrast, the resonances of the iridium dihydride remained quite unchanged and stayed the same even when oxygen was bubbled through the benzene solution.

By contrast, the rhodium and ruthenium dihydrides (7a) and (7c) reacted with air to give trimethylphosphine oxide; the ruthenium complex (7c) also decomposed to give hexamethylbenzene. The relative stabilities to air under these conditions decreased sharply in the order (7b) $\gg$ (7c) $>$ (7a).

The rhodium complex (7a) also reacted with methyl iodide at 20 °C to give $[Rh(C_5Me_5)I_2(PMe_3)]$. However, reactions with olefins and acetylenes only proceeded very slowly and required heating (to 65 °C) before reasonable rates were achieved. This low activity is presumably because no vacant site is readily accessible. One further point comes out of these experiments. Since the complexes (7a), (7b), and (7c) were all stable under argon in benzene solution and remained unchanged to at least 65 °C this implies that these complexes cannot be intermediates in the homogeneous hydrogenation of benzene.[6,16,17] It is therefore doubtful whether any of these complexes will exhibit significant activity in any catalytic hydrogen-transfer reaction without preliminary loss of either the phosphine or the π-ligand.

EXPERIMENTAL

Reactions were generally carried out under nitrogen except for the very sensitive hydrido-complexes, where argon was used. Solvents were distilled under argon before use. The details for some typical experiments are given below; yields, microanalytical and spectroscopic data are collected in Tables 1 and 2. Microanalytical data were determined by the University of Sheffield Microanalytical Service; n.m.r. spectra were determined on Perkin-Elmer R-12B (60-MHz, ^1H), R-34 (220-MHz, ^1H), and JOEL PFT-100 (^{13}C and ^{31}P) spectrometers, and far-i.r. spectra on a PE-180 spectrometer. The starting complexes (1a), (1b), and (1c) were prepared by standard methods.[7,10] Reactions involving benzene were carried out wholly within a good fume-cupboard.

$[Rh(C_5Me_5)Cl_2(PMe_3)]$, (2a).—Trimethylphosphine was liberated from a boiling solution of $[Ag(PMe_3)(NO_3)]$ (0.80 g, 3.2 mmol) in water (20 cm^3) by the slow addition of thiourea (1.0 g, 13 mmol) in water (15 cm^3) and was led by a stream of nitrogen into a stirred solution of $[\{Rh(C_5Me_5)\}_2Cl_4]$ (1a) (0.50 g, 0.8 mmol) in CH_2Cl_2 (50 cm^3) maintained at *ca.* 0 °C. The solution was slowly (2 h) allowed to warm up to 20 °C; the dichloromethane layer was separated from some water which was also extracted with CH_2Cl_2. The combined extracts were dried and evaporated to dryness to leave a residue which was crystallised to give dark red crystals of (2a) (0.46 g, 74%). The pale orange-yellow (2b) and the deep red-brown (2c) were prepared analogously. The complexes are all air-stable, and are soluble in dichloromethane, chloroform, benzene, and toluene, sparingly soluble in water or ether, and insoluble in petroleum ether.

$[Rh(C_5Me_5)(O_2CMe)_2(PMe_3)]$ (3a).—Silver acetate (0.48 g, 2.9 mmol) was added to a solution of complex (2a) (0.50 g, 1.3 mmol) in dry benzene (80 cm^3) and the mixture was stirred (20 °C, 20 h). The precipitated AgCl was filtered off and the solvent removed *in vacuo* to leave a residue which on crystallisation from hot cyclohexane gave orange crystals of complex (3a) (0.34 g, 61%).

Complexes (3a), (3b), and (3c) were air-stable but very hygroscopic and were soluble in water, methanol, acetone, chloroform, dichloromethane, benzene, and hot cyclohexane and were even sparingly soluble in petroleum ether.

$[Rh(C_5Me_5)(O_2CMe)(PMe_3)][PF_6]$ (4a).—A solution of KPF_6 (0.26 g, 1.4 mmol) in water (30 cm^3) was added to a solution of complex (3a) (0.30 g, 0.7 mmol) in water (20 cm^3), and the solution was stirred (20 °C, 1 h). Some crystals appeared and these and the solution were extracted with CH_2Cl_2 (2 × 20 cm^3), which was evaporated down to leave a residue. This was crystallised from dichloromethane–cyclohexane to give red-orange crystals of complex (4a) (0.26 g, 73%).

Reaction of $[M(C_5Me_5)Cl_2(PMe_3)]$ (2a) *or* (2b) *with Silver Oxide*.—A suspension of $[Ir(C_5Me_5)Cl_2(PMe_3)]$ (2b) (0.32 g, 0.66 mmol) and Ag_2O [from $AgNO_3$ (1.32 mmol) and NaOH] in water (5 cm^3) was stirred (20 °C, 0.5 h). Filtration gave a stable pale-yellow solution; the ^1H n.m.r. spectrum of this was consistent with the presence of $[Ir(C_5Me_5)(OH)_2(PMe_3)]$ (5b), δ 1.50 [d, PMe_3, *J*(PH) 11] and 1.64 p.p.m. [d, C_5Me_5, *J*(PH) 2 Hz]. Removal of solvent *in vacuo* gave a pale greenish yellow material but further analysis proved impossible owing to the extremely hygroscopic nature of the product.

When the solution from the corresponding reaction of $[Rh(C_5Me_5)Cl_2(PMe_3)]$ was examined by ^1H n.m.r. spectroscopy, two main sets of resonances were observed arising from (i) $[Rh(C_5Me_5)(OH)_2(PMe_3)]$ (5a), δ 1.44 [d, PMe_3, *J*(P–H) 11] and 1.62 p.p.m. [d, C_5Me_5, *J*(P–H) 2 Hz], and (ii) a material subsequently identified as $[\{Rh(C_5Me_5)\}_2(OH)_3]OH$, δ 1.60 p.p.m. (s). The mol ratio of $[Rh(C_5Me_5)(OH)_2(PMe_3)]$: $[\{Rh(C_5Me_5)\}_2(OH)_3]OH$ was about 1 : 1 but on standing, the resonance due to the former decreased rapidly while that of the latter increased until, after 40 min, there was little of the first material present.

Similar results were obtained when either complex (2a) or (2b) was dissolved in D_2O–NaOD.

$[Ir(C_5Me_5)H(Cl)(PMe_3)]$ (6b).—Sodium tetrahydroborate (57 mg, 1.5 mmol) was added to a stirred solution of $[Ir(C_5Me_5)Cl_2(PMe_3)]$ (2b) (0.43 g, 0.9 mmol) in propan-2-ol (20 cm^3). The resultant brown-yellow solution was stirred (20 °C, 17 h) and then evaporated to dryness. The residue was extracted with petroleum ether (40 cm^3) which gave the brown-yellow complex (6b) (0.27 g, 68%) on removal of solvent. The complex is fairly air-sensitive; ^1H n.m.r. (C_6H_6), δ (p.p.m.) -13.76 [d, hydride, J(P–H) 40.0], 1.43 [d, PMe_3, J(P–H) 10.1], and 1.76 [dd, C_5Me_5, J(P–H) 1.9, J(H–H) 0.8 Hz]; in $(CD_3)_2CO$, -14.12 [d, hydride, J(P–H) 40.0], 1.61 [d, PMe_3, J(P–H) 10.7], and 1.88 [dd, C_5Me_5, J(P–H) 2.1, J(H–H) 0.9 Hz].

$[M(C_nMe_n)H_2(PMe_3)]$ (7a)—(7c).—A benzene solution of Red-al {containing 2.8 mmol of $Na[AlH_2(OCH_2CH_2OMe)_2]$} was added to a stirred solution of $[Rh(C_5Me_5)Cl_2(PMe_3)]$ (2a) (0.42 g, 1.1 mmol) in benzene (5 cm^3) under argon. After stirring (20 °C, 3 h) a sample was removed and examined by ^1H n.m.r. spectroscopy (C_6H_6) which showed the quantitative formation of $[Rh(C_5Me_5)H_2(PMe_3)]$ (7a), δ (p.p.m.) -13.45 [dd, hydride, J(P–H) 41.3, J(Rh–H) 30.7], 1.12 [dt, PMe_3, J(P–H) 9.6, J(H–H) 1.3], and 2.11 [ddt, C_5Me_5, J(P–H) 2.8, J(Rh–H) 0.5, J(H–H) 1.0 Hz]. The complexes $[Ir(C_5Me_5)H_2(PMe_3)]$ (7b), mass spectrum, strongest peaks are molecular ions at m/e 404 (^{191}Ir, 37%) and 406 (^{193}Ir, 63%); ν(IrH) 2 080vs cm^{-1}; ^1H n.m.r. (C_6H_6), δ (p.p.m.) -17.42 [d, hydride, J(P–H) 32.0], 1.33 [d, PMe_3, J(P–H) 10.3], and 2.15 [dt, C_5Me_5, J(P–H) 2.0, J(H–H) 0.7 Hz] and $[Ru(C_6Me_6)H_2(PMe_3)]$, (7c), ^1H n.m.r. (C_6H_6), δ (p.p.m.) -10.80 [d, hydride, J(P–H) 48.5], 1.22 [d, PMe_3, J(P–H) 8.8 Hz], and 2.20 (s, C_6Me_6) were obtained similarly. Complexes (7a) and (7c) were extremely air-sensitive.

Oxygenation of $[Ir(C_5Me_5)H(Cl)(PMe_3)]$ (6b) and $[Ir(C_5Me_5)H_2(PMe_3)]$ (7b).—Sodium tetrahydroborate (86 mg, 2.3 mmol) was added to $[Ir(C_5Me_5)Cl_2(PMe_3)]$ (2b) (0.43 g, 0.9 mmol) in propan-2-ol (20 cm^3). The solvent was removed *in vacuo* and the residue dissolved in benzene (10 cm^3); the ^1H n.m.r. spectrum of this solution showed the presence of complexes (6b) and (7b) in a 7 : 1 molar ratio. The solution was stable under argon (even at 65 °C) but on exposure to oxygen it was found by n.m.r. spectroscopy that, while (7b) was quite stable, (6b) rapidly reacted to give $[Ir(C_5Me_5)Cl_2(PMe_3)]$ (2b), ^1H n.m.r. (C_6H_6), δ (p.p.m.) 1.34 [d, PMe_3, J(P–H) 10.8] and 1.36 [d, C_5Me_5, J(P–H) 2.2 Hz] and PMe_3O, δ (p.p.m.) 1.00 [d, J(P–H) 12.9 Hz]. A precipitate was also formed which was identified as $[\{Ir(C_5Me_5)\}_2(OH)_3]OH\cdot nH_2O$ by comparison with an authentic sample.[1]

X-*Ray Crystal Structure Determination of* $[Rh(C_5Me_5)(O_2CMe)_2(PMe_3)]$ (3a).—A crystal of (3a) grown from cyclohexane was mounted and rapidly coated with epoxy-resin to reduce exposure to air.

Crystal data. $C_{17}H_{30}O_4PRh$, $M = 432.4$, Monoclinic, $a = 8.331(6)$, $b = 9.463(7)$, $c = 25.92(2)$ Å, $\beta = 84.58(6)°$, $U = 2\,034$ Å^3, $Z = 4$, $D_c = 1.41$ g cm^{-3}, $F(000) = 896$. Systematic absences are consistent with space group $P2_1/c$ (C^5_{2h}, No. 14), Mo-K_α radiation (graphite monochromator) $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 9.1 cm^{-1}.

Single-crystal X-ray data in the range $3.5 < 2\theta < 50°$ were collected on a Nicolet Instruments Syntex R-3 four-circle diffractometer. Omega was scanned for each reflection at a rate (between 4.0 and 29.3° min^{-1}) dependent on prescan intensity. 1 816 Independent reflections with $I > 3\sigma(I)$ and background $\Delta < 4\sigma(B)$ were corrected for Lorentz and polarisation effects but not for absorption or extinction. A set of standard reflections which were monitored every 50 reflections showed slight decomposition of the crystal (less than 5%; this has not been corrected by scaling).

TABLE 3

Atomic co-ordinates (× 10^5 for Rh, × 10^4 for others) for $[Rh(C_5Me_5)(O_2CMe)_2(PMe_3)]$ (3a), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Rh	34 408(15)	23 759(13)	11 798(4)
P	4 929(6)	4 040(5)	1 587(2)
O(1)	1 693(12)	2 370(14)	1 805(4)
O(2)	3 291(16)	1 779(17)	2 409(5)
O(3)	2 360(14)	4 252(12)	952(4)
O(4)	−9(18)	3 357(16)	792(7)
C(1)	1 982(25)	2 046(20)	2 264(7)
C(2)	442(29)	1 995(31)	2 649(8)
C(3)	936(21)	4 346(20)	842(7)
C(4)	−433(29)	852(23)	4 270(10)
C(5)	6 682(24)	3 542(22)	1 958(7)
C(6)	3 691(24)	5 145(20)	2 046(7)
C(7)	5 852(25)	5 386(22)	1 115(8)
C(8)	2 644(20)	538(19)	753(7)
C(9)	3 543(22)	1 381(19)	420(6)
C(10)	5 043(27)	1 557(19)	571(8)
C(11)	5 263(22)	729(20)	1 048(7)
C(12)	3 660(29)	126(19)	1 146(8)
C(13)	1 023(32)	8(27)	807(12)
C(14)	3 032(40)	2 077(26)	−61(7)
C(15)	6 546(41)	2 333(32)	287(14)
C(16)	6 670(35)	523(34)	1 266(11)
C(17)	3 369(42)	−907(25)	1 617(9)

The Patterson function showed the ambiguity of Harker Section and Inversion peaks associated with a y co-ordinate for the rhodium atom of approximately 0.25; but successive structure factor and Fourier synthesis calculations gave a successful solution. Block diagonal-matrix least-squares refinement using anisotropic thermal parameters for all atoms reduced R to 0.069.

Calculations were computed on the Nicolet-Syntex XTL package and the University of Sheffield ICL 1906S computer using programs from the Sheffield X-Ray System.

Atomic co-ordinates are given in Table 3, key bond lengths are quoted in the text, and a diagram of the complex is given in the Figure. Tables of structure factors, anisotropic thermal parameters, and a complete listing of bond angles and bond lengths are in Supplementary Publication No. SUP 23093 (22 pp.).*

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REFERENCES

[1] Part 29, A. Nutton, P. M. Bailey, and P. M. Maitlis, preceding paper.

[2] P. M. Maitlis, *Acc. Chem. Res.*, 1978, **11**, 307.

[3] P. M. Maitlis, *Chem. Soc. Rev.*, 1981, **10**, 1.

[4] D. S. Gill, C. White, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1978, 617; K. Hirai, J. Hamlin, V. Gibson, and P. M. Maitlis, unpublished work.

[5] J. Cook, J. E. Hamlin, A. Nutton, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1980, 144.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans*, 1980, Index issue.

[6] M. A. Bennett, T. N. Huang, A. K. Smith, and T. W. Turney, *J. Chem. Soc., Chem. Commun.*, 1978, 582.

[7] J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5970.

[8] W. Rigby, P. M. Bailey, J. A. McCleverty, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 371.

[9] M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 233.

[10] M. A. Bennett, T. N. Huang, T. W. Matheson, and A. K. Smith, *Inorg. Synth.*, in the press.

[11] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1967, **29**, 2122; T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.

[12] D. M. P. Mingos, P. C. Minshall, M. B. Hursthouse, K. M. A. Malik, and S. D. Willoughby, *J. Organomet. Chem.*, 1979, **181**, 169.

[13] M. B. Hursthouse, K. M. A. Malik, D. M. P. Mingos, and S. D. Willoughby, *J. Organomet. Chem.*, 1980, **192**, 235.

[14] J. W. Kang and P. M. Maitlis, *J. Organomet. Chem.*, 1971, **30**, 127.

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

[16] M. A. Bennett, T. N. Huang, and T. W. Turney, *J. Chem. Soc., Chem. Commun.*, 1979, 312.

[17] M. J. H. Russell, C. White, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1977, 427; A. Millan and P. M. Maitlis, unpublished work.