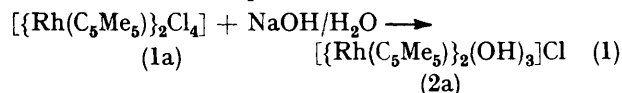


Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part 29.¹ Syntheses and X-Ray Structure Determinations of $[\{\text{Rh}(\text{C}_5\text{Me}_5)\}_2(\text{OH})_3]\text{OH}\cdot 11\text{H}_2\text{O}$ and $[\{\text{Ir}(\text{C}_5\text{Me}_5)\}_2(\text{OH})_3]\text{O}_2\text{CMe}\cdot 14\text{H}_2\text{O}$ † and Related Complexes

By Andrew Nutton, Pamela M. Bailey, and Peter M. Maitlis,* Department of Chemistry, The University, Sheffield S3 7HF

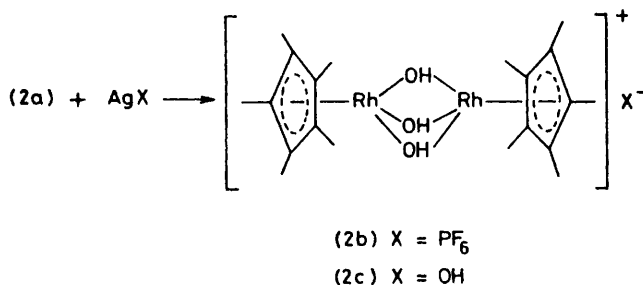
The complexes $[\{\text{M}(\text{C}_5\text{H}_5)\}_2(\text{OH})_3]\text{X}\cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Rh}$, $\text{X} = \text{PF}_6$ and OH ; $\text{M} = \text{Ir}$, $\text{X} = \text{O}_2\text{CMe}$, OH , and BPh_4) have been prepared. Single-crystal X-ray structure determinations have been carried out on $[\{\text{Rh}(\text{C}_5\text{Me}_5)\}_2(\text{OH})_3]\text{OH}\cdot 11\text{H}_2\text{O}$ (2c) and on $[\{\text{Ir}(\text{C}_5\text{Me}_5)\}_2(\text{OH})_3]\text{O}_2\text{CMe}\cdot 14\text{H}_2\text{O}$ (3a). Both show two metal atoms each η^5 -bonded to a C_5Me_5 ligand and bridged by three hydroxo-ligands with $\text{Rh}\cdots\text{Rh}$ 2.973 8(8) Å, $\text{Ir}\cdots\text{Ir}$ 3.070 9(7) Å, $\text{Rh}-\text{O}$ (mean) 2.109 Å, $\text{Ir}-\text{O}$ (mean) 2.120 Å, $\text{Rh}-\text{O}-\text{Rh}$ (mean) 89.6(1)°, and $\text{Ir}-\text{O}-\text{Ir}$ (mean) 92.8(3)°. Both (2c) and $[\{\text{Ir}(\text{C}_5\text{Me}_5)\}_2(\text{OH})_3]\text{OH}\cdot n\text{H}_2\text{O}$ are very strong bases in water. Reaction of $[\{\text{Rh}(\text{C}_5\text{Me}_5)\}_2\text{Cl}_4]$ (1) with Ag_2SO_4 gave $\text{Rh}(\text{C}_5\text{Me}_5)(\text{SO}_4)\cdot 2\text{H}_2\text{O}$ which probably exists in water as the dication $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{H}_2\text{O})_3]^{2+}$ and which is quantitatively carbonylated (20 °C, 1 atm, 48 h) to $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{CO})_2]$. The carbonato-complex $\text{Rh}(\text{C}_5\text{Me}_5)(\text{CO})_2\cdot 2\text{H}_2\text{O}$ was obtained from (1) and Ag_2CO_3 or by air-oxidation of $[\{\text{Rh}(\text{C}_5\text{Me}_5)\}_2(\text{CO})_2]$. Reaction of $[\{\text{Rh}(\text{C}_5\text{Me}_5)\}_2(\text{OH})_3]\text{Cl}$ with $\text{P}(\text{OMe})_3$ gave the unexpected methylrhodium complex $[\text{Rh}(\text{C}_5\text{Me}_5)\text{Me}\{\text{P}(\text{OMe})_3\}_2]^+$ as well as $[\text{Rh}(\text{C}_5\text{Me}_5)\{\text{P}(\text{OMe})_3\}_2]^{2+}$.

We originally reported, in 1971, the simple synthesis of the tri- μ -hydroxo-dirhodium complex (2a) by the action of aqueous base on complex (1a), reaction (1).² These compounds and their reactions have been of special interest because there are still relatively few stable and accessible hydroxo-complexes of the platinum metals. We here report the synthesis of a further range of these compounds, the X-ray crystal structures of one rhodium and one iridium complex, and some of their reactions.



RESULTS AND DISCUSSION

Syntheses.—The tri- μ -hydroxo-dirhodium complexes (2b) and (2c) were most conveniently prepared by a metathesis reaction of the chloride salt (2a) with AgPF_6 and moist Ag_2O in water, respectively (see below).



While the salts (2a) and (2b) gave aqueous solutions close to neutral (pH 8–9) the hydroxo-hydroxide (2c) gave a strongly alkaline solution (pH 12 for a 0.002 5 mol dm^{-3} solution).

Attempts to repeat the preparation of $[\text{Ir}(\text{C}_5\text{Me}_5)(\text{OH})_2]\cdot 4\text{H}_2\text{O}$ by hydrolysis of $[\text{Ir}(\text{C}_5\text{Me}_5)(\text{O}_2\text{CMe})_2]\cdot n\text{H}_2\text{O}$ as previously described² always led to a compound which still showed a carboxylate band in the i.r. spectrum

† Tri- μ -hydroxo-bis[(η -pentamethylcyclopentadienyl)rhodium] hydroxide 11-hydrate and tri- μ -hydroxo-bis[(η -pentamethylcyclopentadienyl)iridium] acetate 14-hydrate.

(see below). An X-ray crystal-structure determination was carried out on a crystal of this material and showed it to be the tri- μ -hydroxo-di-iridium acetate salt (3a). Addition of sodium tetraphenylborate to an aqueous solution of (3a) gave the tetraphenylborate salt (3b); the hydroxo-hydroxide (3c) (see below), analogous to (2c), was made by direct reaction of $[\{\text{Ir}(\text{C}_5\text{Me}_5)\}_2\text{Cl}_4]$ (1b) with moist silver oxide. Again, while (3a) and (3b) gave nearly neutral aqueous solutions, that of (3c) was strongly basic. The two hydroxo-hydroxide complexes (2c) and (3c) are only a little less basic in aqueous solution than is sodium hydroxide.

The salts of the tri- μ -hydroxo-cations showed high solubility in water and little in organic solvents less polar than dichloromethane. Further, the complexes reacted with many oxygen-containing organic solvents (such as alcohols, aldehydes, and ketones, and even tetrahydrofuran). The best solvent for spectroscopy and reaction studies was therefore water. The only exceptions were the tetraphenylborate salts $[\{\text{M}(\text{C}_5\text{Me}_5)\}_2(\text{OH})_3][\text{BPh}_4]$, which showed good solubility in most polar organic solvents and little in water. Analytical and spectroscopic data are collected in Table 1.

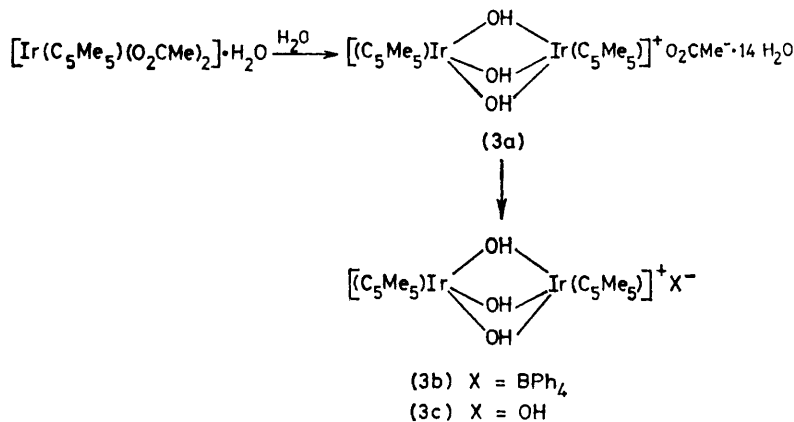
X-Ray Crystal Structures of $[\{\text{Rh}(\text{C}_5\text{Me}_5)\}_2(\text{OH})_3]\text{OH}\cdot 11\text{H}_2\text{O}$ (2c) and $[\{\text{Ir}(\text{C}_5\text{Me}_5)\}_2(\text{OH})_3]\text{O}_2\text{CMe}\cdot 14\text{H}_2\text{O}$ (3a).—Because of the ease with which crystals of both complexes lost water of crystallisation and then became amorphous, each of the chosen crystals was mounted in a capillary in the presence of mother-liquor, while the X-ray data were collected.

The structures of both (2c) and (3a) were similar (Figures 1 and 2; for further details see Experimental section). In each case, the two metal atoms are η^5 -bonded to the C_5Me_5 rings which are approximately parallel. The mean M–C distances are identical for (2c) and (3a) at 2.128 Å while the mean out-of-plane distances of the metal atoms to the C_5 rings are 1.744 Å for (2c) and 1.735 Å for (3a) (Tables 2 and 3). The dihedral angles between the planes of the C_5Me_5 rings are 3.1 and

4.9° respectively. In each case the metal atoms are bridged by three hydroxo-groups, mean distances Rh–O 2.109 Å, (2c), and Ir–O 2.120 Å, (3a).

In the case of the rhodium hydroxo-hydroxide complex (2c), the bridging hydroxo-groups are hydrogen-bonded to water molecules of crystallisation and to the

complex (3a). This is expected since numerous X-ray structure determinations have shown that Rh^{III} and Ir^{III} in C₅Me₅ complexes have the same size.⁴ However, the Rh···Rh separation of 2.973 8(8) Å in the rhodium hydroxo-hydroxide complex (2a) is significantly (0.0973 Å, 122σ) shorter than that in the iridium hydroxo-



ionic hydroxide. Although the diffractometer data were good enough to allow the positions of the methyl hydrogens on C₅Me₅ to be determined, no unambiguous positions could be assigned to hydrogen atoms attached to oxygen. We conclude that there is inherent disorder amongst these hydrogen atoms and that it is not possible to state which oxygen forms the hydroxide anion.

acetate (3a). It is certainly unrealistic to talk in terms of any significant degree of metal–metal interaction in any of these cations. Since the metal to bridging oxygen distances are essentially identical for (2c) and (3a), the difference in metal–metal separations is reflected in the more acute angle at oxygen in the rhodium hydroxo-hydroxide [mean Rh–O–Rh 89.6(1)°] than in the iridium

TABLE 1

Analytical, n.m.r., and i.r. data for the complexes

Complex	Microanalytical data ^a (%)		¹ H n.m.r. spectrum δ/p.p.m.			I.r. spectrum ν/cm ⁻¹	
	C	H	C ₅ Me ₅	H ₂ O	Other	ν(OH)	Other
(2b) [{Rh(C ₅ Me ₅) ₂ (OH) ₃][PF ₆]}·3H ₂ O	33.0 (33.1)	5.2 (5.4)	1.64 ^b	3.03 ^b		3 300vs,br 1 660m	ν(PF) 840vs
(2c) [{Rh(C ₆ Me ₆) ₂ (OH) ₃]}OH·11H ₂ O	<i>c</i>	<i>c</i>	1.61 ^d			3 250vs,br 1 670s,br	
(3a) [{Ir(C ₅ Me ₅) ₂ (OH) ₃]}O ₂ CMe·14H ₂ O	<i>c</i>	<i>c</i>	1.61 ^d		2.10 ^d (O ₂ CMe)	3 620, 3 200vs,br 1 730m, 1 682s	ν(CO ₂) 1 563vs 1 414s
(3b) [{Ir(C ₅ Me ₅) ₂ (OH) ₃]}[BPh ₄]	52.0 (51.6)	5.4 (5.2)	1.57 ^e	2.97 ^e	7.10 ^e (BPh ₄)	3 590, 3 540s	
(3c) [{Ir(C ₅ Me ₅) ₂ (OH) ₃]}OH· <i>n</i> H ₂ O	<i>c</i>	<i>c</i>	1.61 ^d			3 200vs,br 1 660s,br	
(4) Rh(C ₆ Me ₆)(SO ₄)·2H ₂ O ^f	31.8 (32.4)	5.3 (5.2)	1.67 ^e	4.15 ^e		3 200s,br 1 640w	ν(SO ₄) ^g 1 215s 1 060m, 1 028m 1 013m, 952w
(6) Rh(C ₆ Me ₆)(CO ₃)·2H ₂ O	39.2 (39.5)	5.7 (5.7)	1.62 ^d			3 200s,br 1 640s,br	ν(CO ₃) 1 605s 1 313s

^a Calculated values in parentheses. ^b In CDCl₃, relative to SiMe₄ = 0 p.p.m. ^c Variable water content made analysis meaningless. ^d In D₂O, Me₃SiCH₂CH₂CH₂SO₃Na as standard. ^e In [²H₆]acetone, relative to SiMe₄ = 0 p.p.m. ^f Analysis for S: 8.7 (8.7)%. ^g After crystallisation from CH₂Cl₂: ν(SO₄) 1 275w, 1 255m, 1 215s, 1 145s, 1 050s, 1 012s, 983m, 955w, 935w, 845s cm⁻¹.

In the structure of the iridium hydroxo-acetate complex (3a) the three bridging hydroxo-groups are hydrogen-bonded to the acetate anion which lies in the outer co-ordination sphere and is not bound to the metal (Figure 2).

The structure of [{Rh(C₅Me₅)₂(OH)₃}[BPh₄] (2d) has also been determined;³ the cation has the same structure as that found for (2c) but disorder amongst the tri-μ-hydroxo-groups limited the accuracy of the determination. The metal–metal distance of 3.030 Å in (2d) agrees well with that of 3.070 9(7) Å for the iridium

hydroxo-acetate [mean Ir–O–Ir 92.8(3)°]. We suggest that this arises because the bridging hydroxide in the rhodium complex is more basic than that in the iridium one. In general, more acute X–O–X angles are associated with greater basicity of the oxygen.

It is also of interest that all the three complexes which have had their structures determined are binuclear; there is no analogue of the tetranuclear complex, [{Ru(C₆H₆)₄(OH)₄][SO₄]₂, obtained in the benzene-ruthenium system.^{4,5}

Reactions of [M(C₅Me₅)₂(OH)₃]⁺.—A pH titration of

$[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{OH}]$, (2c), in water against hydrochloric acid showed two equivalence points, one after the addition of one mol of HCl per mol of (2c) and the other after the addition of four mol. We interpret this in

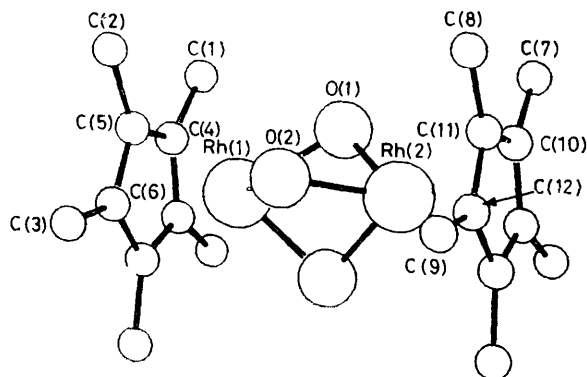
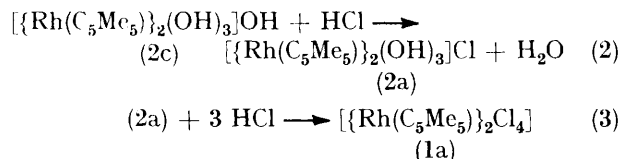


FIGURE 1 View of the cation of (2c), $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}]^+$ (hydrogen atoms and water of solvation omitted)

terms of the formation, first of the hydroxo-chloride salt (2a) and then of the chloride dimer (1a), equations (2) and (3).



Attempts to carry out the same titration on the iridium analogue (3c) were impeded by the precipitation of the water-insoluble $[\{\text{Ir}(\text{C}_5\text{Me}_5)_2\text{Cl}_4\}]$, (1b), but an equivalence point analogous to the first one for the rhodium

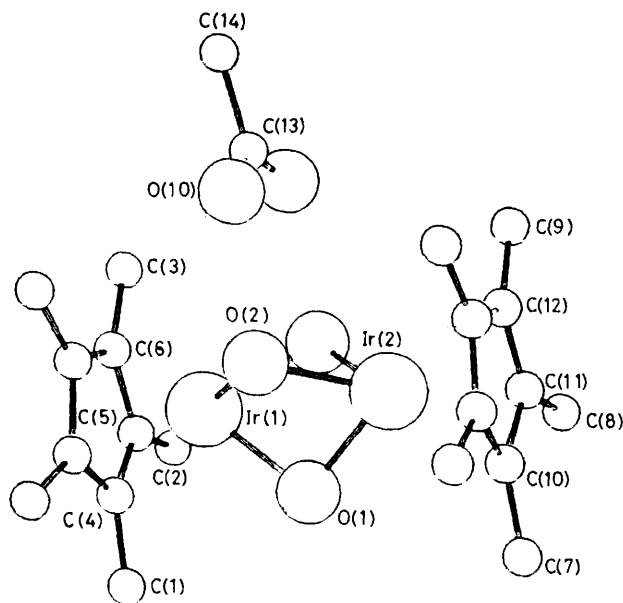


FIGURE 2 View of the cation and anion of (3a), $[\{\text{Ir}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}]_2^{2+} \text{O}_2\text{CMe}$ (hydrogen atoms and water of solvation omitted)

TABLE 2

Atomic co-ordinates for $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{OH}\cdot 11\text{H}_2\text{O}$ (2c), with estimated standard deviations in parentheses

Atom	X	Y	Z
Rh(1)	16 186(3)	25 000	-19 167(5)
Rh(2)	19 250(3)	25 000	9 085(5)
C(1)	3 012(5)	2 500	-3 996(8)
C(2)	1 933(4)	3 978(3)	-3 750(6)
C(3)	199(4)	3 404(4)	-3 257(6)
C(4)	2 152(4)	2 500	-3 769(6)
C(5)	1 675(3)	3 160(3)	-3 635(5)
C(6)	890(3)	1 905(3)	-3 428(4)
C(7)	3 675(5)	2 500(0)	2 001(9)
C(8)	2 614(4)	3 974(4)	2 426(7)
C(9)	887(4)	3 406(4)	3 006(6)
C(10)	2 821(4)	2 500	2 316(7)
C(11)	2 354(3)	3 160(3)	2 476(5)
C(12)	1 573(3)	2 916(3)	2 755(4)
O(1)	2 634(3)	2 500	-770(4)
O(2)	1 332(2)	3 228(2)	-371(3)
O(3)	551(3)	5 463(3)	-4 399(5)
O(4)	4 004(2)	4 496(3)	-3 452(4)
O(5)	438(2)	5 348(3)	-1 727(4)
O(6)	3 244(2)	4 057(3)	-1 048(4)
O(7)	1 692(3)	4 672(2)	-456(4)
O(8)	233(2)	6 671(3)	-118(4)

TABLE 3

Atomic co-ordinates for $[\{\text{Ir}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{O}_2\text{CMe}\cdot 14\text{H}_2\text{O}$ (3a)

Atom	X	Y	Z
Ir(1)	6 438(3)	25 000	37 259(6)
Ir(2)	8 817(3)	25 000	8 143(6)
C(1)	-765(9)	2 500	4 954(22)
C(2)	105(8)	999(8)	5 308(14)
C(3)	1 546(6)	1 580(8)	5 758(14)
C(4)	-63(9)	2 500	5 165(17)
C(5)	322(7)	1 831(7)	5 318(11)
C(6)	978(6)	2 087(7)	5 538(11)
C(7)	-257(10)	2 500	-1 263(24)
C(8)	626(10)	993(8)	-1 049(15)
C(9)	2 042(8)	1 575(12)	-480(16)
C(10)	439(11)	2 500	-975(18)
C(11)	854(7)	1 832(6)	-910(11)
C(12)	1 491(6)	2 086(8)	-658(12)
C(13)	2 573(9)	2 500	3 041(18)
C(14)	3 274(10)	2 500	3 525(29)
O(1)	79(5)	2 500	2 034(10)
O(2)	1 104(4)	3 227(4)	2 386(7)
O(3)	1 262(5)	5 701(5)	248(9)
O(4)	3 621(5)	4 539(8)	1 537(12)
O(5)	771(5)	4 716(5)	2 200(9)
O(6)	4 571(4)	3 980(5)	3 163(9)
O(7)	1 609(5)	5 461(5)	3 919(10)
O(8)	2 711(5)	4 549(5)	3 547(11)
O(9)	1 711(7)	6 699(6)	2 191(13)
O(10)	2 319(4)	3 136(5)	2 860(10)

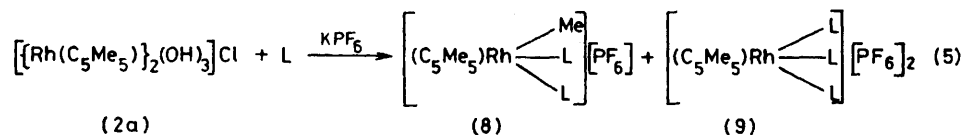
system (and probably corresponding to the formation of $[\{\text{Ir}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{Cl}]$) could be detected.

Results consistent with the above proposal were obtained when (2a) was titrated with aqueous hydrochloric or sulphuric acid. A sulphate complex of formula $\text{Rh}(\text{C}_5\text{Me}_5)(\text{SO}_4)\cdot 2\text{H}_2\text{O}$ (4), but of unknown structure, was also obtained by the action of silver sulphate on (1a) in water. The freshly prepared complex showed five bands in the i.r. which may be ascribed to bidentate sulphate⁶ but on crystallisation from dichloromethane-pentane a rather insoluble material was obtained which showed some twelve peaks in the region that could be ascribed to sulphate. These data suggest that some type of polymeric species had formed. The

formation of the polymer could be reversed on dissolving the material in hot water; evaporation of the solution regenerated the original material.

It seems likely that the aqueous solution of this sulphate complex contains the triaquo-cation $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{H}_2\text{O})_3]^{2+}$. This species showed a characteristic band in the visible spectrum at 375 nm (ϵ 3 130 dm³ mol⁻¹ cm⁻¹). Species with identical visible spectra were obtained from both the reaction of AgPF_6 with $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ in water and the addition of three equivalents of HPF_6 to an aqueous solution of $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3][\text{PF}_6]$. By contrast, the visible spectrum of $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{Cl}$, (2a), showed λ_{max} at 365 nm (ϵ 4 670), while a dilute sulphuric acid solution of (2a) or a solution of $\text{Rh}(\text{C}_5\text{Me}_5)(\text{SO}_4)\cdot 2\text{H}_2\text{O}$ containing one equivalent of LiCl showed λ_{max} at 377 nm (ϵ 3 700).

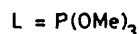
The large absorption coefficients of these bands suggest that they arise from charge transfer, probably from ligand to metal. Since their position varies with the precise nature of the ligands present it is tempting to suggest



(2a)

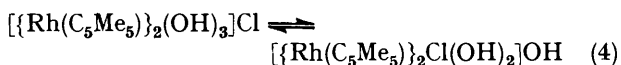
(8)

(9)



that they arise from transfer of an oxygen lone-pair electron to the metal.

However, these systems are all very labile and it may well be that equilibria, such as equation (4), play a



significant role in the chemistry of complex (2a). If chloride can easily displace a μ -hydroxo-ligand in a dynamic equilibrium then the difference between the visible spectrum of $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{H}_2\text{O})_3]^{2+}$ in the presence and in the absence of chloride may be due to the ability of chloride in part to replace an aquo ligand to give $[\text{Rh}(\text{C}_5\text{Me}_5)\text{Cl}(\text{H}_2\text{O})_2]^+$.

Further, if indirect, evidence for the existence of mononuclear cations in aqueous sulphuric acid comes from a study of the carbonylation reaction. Thus, carbonylation (20 °C, 1 atm, 48 h or 20 °C, 50 atm, 16 h) * of a dilute sulphuric acid solution of $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{Cl}$ (2a) gives $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{CO})_2]$ (5),⁷ in a clean and quantitative reaction; the same happens when an aqueous solution of $\text{Rh}(\text{C}_5\text{Me}_5)(\text{SO}_4)\cdot 2\text{H}_2\text{O}$ is carbonylated (20 °C, 1 atm, 48 h). However, when (2a) or (2b) is carbonylated in water under the same conditions a mixture of at least two components is obtained. One is the dicarbonyl (5) [$\nu(\text{CO})$ 1 965, 2 025 cm⁻¹] and another is a compound with $\nu(\text{CO})$ at 1 820 cm⁻¹, the nature of which is not clear. An even more complex mixture, as indicated by $\nu(\text{CO})$ at 1 790, 1 820, 1 965, and 2 025 cm⁻¹, is obtained on carbonylating an aqueous sodium hydroxide

* Throughout this paper: 1 atm = 101 325 N m⁻².

solution of (2a) (20 °C, 1 atm, 24 h). The lower-frequency bands in the i.r. can reasonably be assigned to bridging carbonyls and the tentative conclusion can therefore be drawn that a mononuclear starting complex gives the mononuclear dicarbonyl (5) whereas dinuclear starting complexes give (largely) dinuclear carbonyls.

A complex related to the sulphato-complex (4) is the carbonato-complex (6) which was prepared by reaction of (1) with silver carbonate. Microanalysis agreed with a formula $\text{Rh}(\text{C}_5\text{Me}_5)(\text{CO}_3)\cdot 2\text{H}_2\text{O}$ and the i.r. spectrum showed bands assigned to $\nu(\text{CO}_3)$ at 1 602 and 1 313 cm⁻¹. These are consistent with a bidentate carbonate, e.g. 1 604 and 1 268 cm⁻¹ for $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{Cl}$ ⁸ and 1 620 and 1 350 cm⁻¹ for $[\text{Rh}(\text{CO})_2(\text{CO})(\text{PPh}_3)_2]^+$,⁹ but whether (6) is mononuclear or dinuclear is not clear. A brown material similar to (6) was obtained by air oxidation of the dinuclear dicarbonyl $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{CO})_2]$ (7).¹⁰ When a solution of (7) in toluene was exposed to air for a few seconds the colour changed quickly from very dark blue to brown. Evaporation of

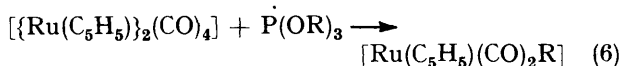
the solvent gave a brown solid which had $\nu(\text{CO}_3)$ bands identical to those found for (6) and which effervesced on addition of acid.

We have already described the reaction of complex (2a) with triphenylphosphine and with triethyl phosphite.¹¹ In the first case the complex catalysed the oxygenation of PPh_3 to PPh_3O . No significant oxidation of triethyl phosphite occurred, but the complex $[\text{Rh}(\text{C}_5\text{Me}_5)\{\text{P}(\text{OEt})_3\}_3]^{2+}$ was formed and some hydrolysis of $\text{P}(\text{OEt})_3$ to $\text{HP}(\text{O})(\text{OEt})_2$ was noted.

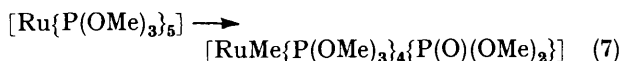
The reaction of (2a) with trimethyl phosphite in water proceeded rather differently. After addition of KPF_6 a 34% yield of the unexpected methylrhodium complex (8), as well as a 53% yield of the expected tris(trimethyl phosphite) complex (9), were isolated [reaction (5)].

The formation of complex (8) was indicated by the n.m.r. spectra which showed the rhodium methyl group as a double triplet in both the ¹H [δ 0.48, $J(\text{P}-\text{H})$ 4, $J(\text{Rh}-\text{H})$ 2 Hz] and the ¹³C spectra [δ -9.4, $J(\text{P}-\text{C})$ 14, $J(\text{Rh}-\text{C})$ 21 Hz].

The mechanism by which (8) arises is obscure but we note that ruthenium has been alkylated by trialkyl phosphites at 140 °C¹² [equation (6)], and that pentakis-



(trimethyl phosphite)ruthenium rearranges on heating to give a methylruthenium complex¹³ [equation (7)].



It therefore appears that trimethyl phosphite can, under suitable conditions, behave as an effective metal methylating agent, presumably by facilitating the normal high-temperature decomposition to give a compound containing a P-Me bond¹⁴ [equation (8)] which is the active methylating agent.



The reaction to form (8) is by no means the only unusual reaction that trimethyl phosphite undergoes; it also reacts with the iridium acetone complex $[\text{Ir}(\text{C}_5\text{Me}_5)(\text{Me}_2\text{CO})_3]^{2+}$ to give the hydride $[\text{Ir}(\text{C}_5\text{Me}_5)\text{H}\{\text{P}(\text{OMe})_3\}_2]^+$.¹⁵

EXPERIMENTAL

All experiments were routinely carried out under nitrogen even though none of the compounds showed any significant sensitivity to air. Hydrogen-1 n.m.r. spectra were recorded at 60 MHz (Perkin-Elmer R-12B) and i.r. spectra on a Perkin-Elmer 157G spectrometer. Microanalyses were carried out by the University of Sheffield Microanalysis service. Analytical and spectroscopic data are collected in Table 1.

$\{[\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3][\text{PF}_6] \cdot 3\text{H}_2\text{O}$ (2b).—Solutions of $\{[\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{Cl} \cdot 3\text{H}_2\text{O}$ (2a) (0.20 g, 0.32 mmol) in water (15 cm³) and AgPF_6 (0.08 g, 0.32 mmol) in water (2 cm³) were mixed and stirred (20 °C, 1 h). Silver chloride was removed by filtration through a short cellulose column and the yellow filtrate gave (2b) (0.21 g, 90%) on evaporation.

$\{[\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{OH}$ (2c).—Moist silver oxide [prepared from AgNO_3 (0.08 g, 0.46 mmol) and NaOH (0.04 g, 0.92 mmol) in water and washed free of NaOH] was added to a solution of (2a) (0.25 g, 0.39 mmol) in water (15 cm³) and stirred (20 °C, 0.5 h). Insoluble AgCl was removed by filtration and the yellow filtrate was evaporated to dryness on a rotary evaporator to give (2c) (0.21 g). Crystals of (2c) suitable for X-ray diffraction were grown from the minimum amount of hot water.

$\{[\text{Ir}(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{O}_2\text{CMe} \cdot 14\text{H}_2\text{O}$ (3a).—A freshly prepared sample of $[\text{Ir}(\text{C}_5\text{Me}_5)(\text{O}_2\text{CMe})_2(\text{H}_2\text{O})]^{2+}$ (0.20 g) was dissolved in water (30 cm³) and warmed (60 °C). The solution was then evaporated to dryness on a rotary evaporator to leave a solid, which was crystallised from the minimum volume of hot water to give crystals of (3a) (0.15 g).

$\{[\text{Ir}(\text{C}_5\text{Me}_5)_2(\text{OH})_3][\text{BPh}_4]$ (3b).—Addition of a solution of NaBPh_4 (0.10 g) in water (2 cm³) to a stirred solution of complex (3a) (0.20 g) in water (30 cm³) precipitated a solid, which was crystallised from chloroform-diethyl ether to give pale yellow crystals of (3b) (0.22 g).

$\{[\text{Ir}(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{OH} \cdot n\text{H}_2\text{O}$ (3c).—Moist silver oxide [prepared from AgNO_3 (0.26 g, 1.52 mmol) and NaOH (0.12 g, 3.05 mmol) in water and washed free of NaOH] was added to a stirred suspension of $\{[\text{Ir}(\text{C}_5\text{Me}_5)_2\text{Cl}_4]\}$ (0.25 g, 0.31 mmol) in water (10 cm³). After being stirred (20 °C, 1 h), the mixture was filtered through a short packed cellulose column to remove silver salts and the filtrate was evaporated to dryness to leave the yellow complex (3c) (0.20 g).

$\text{Rh}(\text{C}_5\text{Me}_5)(\text{SO}_4) \cdot 2\text{H}_2\text{O}$ (4).—Silver sulphate (0.60 g, 2.94 mmol) was added to a suspension of $\{[\text{Rh}(\text{C}_5\text{Me}_5)_2\text{Cl}_4]\}$ (0.25 g, 0.4 mmol) in water. The mixture was stirred (20 °C, 2 h), filtered, and the filtrate evaporated to dryness

to leave an orange solid which was crystallised from water to give complex (4) (0.21 g, 70%).

$\text{Rh}(\text{C}_5\text{Me}_5)(\text{CO})_2 \cdot 2\text{H}_2\text{O}$ (6).—A suspension of silver carbonate [prepared from K_2CO_3 (0.24 g, 1.74 mmol) and AgNO_3 (0.50 g, 2.94 mmol) in water and washed to remove K_2CO_3] was added to a suspension of complex (1) (0.35 g, 0.49 mmol) in water (15 cm³). The mixture was stirred (20 °C, 4 h) and then filtered to remove insoluble silver salts. The yellow solid obtained on removal of the water was extracted with CH_2Cl_2 , the solution was filtered and the CH_2Cl_2 removed to leave an orange solid which was crystallised from water to yield (6) (0.17 g, 63%).

$[\text{Rh}(\text{C}_5\text{Me}_5)(\text{CO})_2]$ (5).—A solution of $\{[\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{Cl}$ (2a) (0.10 g, 0.16 mmol) in sulphuric acid-water (0.5 cm³ in 20 cm³) was stirred under carbon monoxide (20 °C, 1 atm, 48 h). The yellow precipitate (0.09 g, 95%) was shown to be pure complex (5).

Reaction of Trimethyl Phosphite with $\{[\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{Cl}$ (2a).—Trimethyl phosphite (0.5 g, 4 mmol) was added to a solution of complex (2a) (0.25 g, 0.39 mmol) in water (7 cm³) and the mixture stirred vigorously (20 °C, 2 h). A solution of KPF_6 (0.1 g, 0.5 mmol) in water (5 cm³) was then added; a solid precipitated which was filtered off and dried. This solid was triturated with chloroform to leave the insoluble complex $[\text{Rh}(\text{C}_5\text{Me}_5)\{\text{P}(\text{OMe})_3\}_3][\text{PF}_6]_2$ (9) (0.27 g, 53%). Evaporation of the chloroform solution gave a solid which on crystallisation from chloroform-diethyl ether gave the colourless complex $[\text{Rh}(\text{C}_5\text{Me}_5)\text{Me}\{\text{P}(\text{OMe})_3\}_2][\text{PF}_6]$ (8) (0.24 g, 34%) (Found: C, 31.6; H, 5.6. $\text{C}_{17}\text{H}_{36}\text{F}_6\text{O}_6\text{P}_3\text{Rh}$ requires C, 31.6; H, 5.6%). ¹H n.m.r. (CDCl_3): δ 0.48 [dt, Rh-Me, $J(\text{Rh-H})$ 2, $J(\text{P-H})$ 4], 1.75 [t, C_5Me_5 , $J(\text{P-H})$ 5], 3.78 p.p.m. [dd, POMe , $^3J(\text{P-H})$, 7, $^5J(\text{P-H})$ 6 Hz]; ¹³C-¹H n.m.r. (CDCl_3): δ -9.4 [dt, Rh-Me, $J(\text{P-C})$ 14, $J(\text{Rh-C})$ 21], 9.0 (C_5Me_5), 54.4 (m, POMe), 103.4 p.p.m. [d, C_5Me_5 , $J(\text{Rh-C})$ 5 Hz]; ³¹P n.m.r. (CDCl_3): δ 125.8 [d, $\text{P}(\text{OMe})_3$, $J(\text{Rh-P})$ 230 Hz] and -144.0 p.p.m. (septet, PF_6).

X-Ray Structure Determinations of $\{[\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{OH} \cdot 11\text{H}_2\text{O}$ (2c) and $\{[\text{Ir}(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{O}_2\text{CMe} \cdot 14\text{H}_2\text{O}$ (3a).—*Crystal data*, (2c). $\text{C}_{20}\text{H}_{56}\text{O}_{15}\text{Rh}_2$, $M = 741.46$, Orthorhombic, $a = 17.206(8)$, $b = 17.547(9)$, $c = 10.352(16)$ Å (unit-cell parameters were obtained from a least-squares fit to the setting angles of 71 reflections centred manually), $U = 3.125(5)$ Å³, $D_m = 1.58$ (floatation), $Z = 4$, $D_c = 1.575$ g cm⁻³, $F(000) = 1540$. Systematic absences indicated the space group to be either $Pnma$ (D_{2h}^{16} , No. 62) or $Pna2_1$ (C_{2v}^9 , No. 33) (permuted axes), Mo-K_α radiation (graphite monochromator) $\lambda = 0.71069$ Å, $\mu(\text{Mo-K}_\alpha) = 10.98$ cm⁻¹. Crystal dimensions $0.10 \times 0.10 \times 0.40$ mm.

Crystal data, (3a). $\text{C}_{22}\text{H}_{64}\text{Ir}_2\text{O}_{19}$, $M = 1017.14$, Orthorhombic, $a = 21.114(20)$, $b = 17.395(16)$, $c = 10.405(20)$ Å (unit-cell parameters were obtained from a least-squares fit to the setting angles of 78 reflections centred manually), $U = 3.821(9)$ Å³, $D_m = 1.78$ (floatation), $Z = 4$, $D_c = 1.768$ g cm⁻³, $F(000) = 2008$. Systematic absences indicated the space group to be either $Pnma$ (D_{2h}^{16} , No. 62) or $Pna2_1$ (C_{2v}^9 , No. 33) (permuted axes), Mo-K_α radiation (graphite monochromator) $\lambda = 0.71069$ Å, $\mu(\text{Mo-K}_\alpha) = 69.96$ cm⁻¹. Crystal dimensions $0.03 \times 0.10 \times 0.40$ mm.

The crystals were mounted in Lindemann capillary tubes in the presence of mother-liquor to avoid physical decomposition. Three-dimensional X-ray data were collected with the crystal mounted along the c axis, using a Stoe STADI-2 diffractometer in the stationary-counter-moving-crystal mode $6.5 < 2\theta < 50^\circ$. Variable-width peak scans

were measured at 0.01° intervals with background counts accumulated at each end of the scan. 2 361 [for (2c)] and 2 254 [for (3a)] independent reflections were collected with $I_{\text{obs.}} > 3\sigma(I_{\text{obs.}})$ and background difference $\Delta < 4\sigma B$; data were corrected for Lorentz, polarisation, and absorption effects (integration by Gaussian quadrature).

In both cases, the three-dimensional Patterson function showed pairs of metal atoms with the same y co-ordinate, strongly indicative of the centric space group with mirror symmetry through the molecule; the structure was solved using the Patterson and further Fourier syntheses. Block-diagonal least-squares refinement in $Pnma$ reduced R to 0.039 for (2c) and 0.044 for (3a), at which stage the thermal parameters on all the atoms were anisotropic, and anomalous dispersion was included. A difference-Fourier synthesis at this stage did not give unambiguous positions for the hydrogen atoms attached to the oxygen atoms for either structure and it was not possible to ascertain in this way which of the oxygen atoms was the hydroxide ion in (2c). Since none of then on-bridging oxygens lies on the mirror plane there is inherent disorder of the hydrogen atoms in this situation. There was no evidence for disorder of the bridging oxygen atoms in either structure and we think that this may be due in part to hydrogen bonding. There is an extensive network of hydrogen bonding throughout the lattice, using the water molecules of crystallisation; this is indicated by a number of $O \cdots O$ contacts less than 3.0 Å.

TABLE 4

Important bond lengths (Å) and angles (°) for $\{[\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{OH} \cdot 11\text{H}_2\text{O}$ (2c), with estimated standard deviations in parentheses

(a) Co-ordination sphere of the rhodium atoms			
Rh(1)–O(1)	2.112(4)	Rh(2)–O(1)	2.124(4)
Rh(1)–O(2)	2.106(3)	Rh(2)–O(2)	2.104(3)
Rh(1)–C(4)	2.127(6)	Rh(2)–C(10)	2.122(6)
Rh(1)–C(5)	2.125(5)	Rh(2)–C(11)	2.127(5)
Rh(1)–C(6)	2.128(5)	Rh(2)–C(12)	2.135(5)
Rh(1)–C mean	2.127	Rh(2)–C mean	2.129
Rh(1) \cdots Rh(2)		2.974(1)	
O(1)–Rh(1)–O(2)	76.5(1)	O(1)–Rh(2)–O(2)	76.2(1)
O(2)–Rh(1)–O(2)'	74.6(1)	O(2)–Rh(2)–O(2)'	74.7(1)
C(4)–Rh(1)–C(5)	39.2(2)	C(10)–Rh(2)–C(11)	39.0(3)
C(5)–Rh(1)–C(6)	39.6(2)	C(11)–Rh(2)–C(12)	39.5(2)
C(6)–Rh(1)–C(6)'	39.0(2)	C(12)–Rh(2)–C(12)'	40.0(2)
(b) Bridging oxygen atoms			
Rh(1)–O(1)–Rh(2)	89.2(1)	O(2)–O(1)–O(2)'	58.6(1)
Rh(1)–O(2)–Rh(2)	89.9(1)	O(1)–O(2)–O(2)'	60.7(1)

The overall geometries of the molecules are shown in Figures 1 and 2. Atomic co-ordinates are in Tables 2 and 3; bond distances and angles are in Tables 4 and 5. Tables of structure factors, the anisotropic thermal parameters, and equations of planes are listed in Supplementary Publication No. SUP 23092 (127 pp).*

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

TABLE 5

Important bond lengths (Å) and angles (°) for $\{[\text{Ir}(\text{C}_6\text{Me}_6)_2(\text{OH})_3]\text{O}_2\text{CMe} \cdot 14\text{H}_2\text{O}$ (3a)

(a) Co-ordination sphere of the iridium atoms			
Ir(1)–O(1)	2.126(9)	Ir(2)–O(1)	2.117(9)
Ir(1)–O(2)	2.119(7)	Ir(2)–O(2)	2.121(7)
Ir(1)–C(4)	2.114(15)	Ir(2)–C(10)	2.084(17)
Ir(1)–C(5)	2.136(13)	Ir(2)–C(11)	2.139(13)
Ir(1)–C(6)	2.139(12)	Ir(2)–C(12)	2.126(9)
Ir(1)–C mean	2.133	Ir(2)–C mean	2.123
Ir(1) \cdots Ir(2)		3.071(1)	
O(1)–Ir(1)–O(2)	73.3(5)	O(1)–Ir(2)–O(2)	73.4(5)
O(2)–Ir(1)–O(2)'	73.3(5)	O(2)–Ir(2)–O(2)'	73.3(3)
C(4)–Ir(1)–C(5)	39.3(5)	C(10)–Ir(2)–C(11)	40.4(7)
C(5)–Ir(1)–C(6)	40.3(6)	C(11)–Ir(2)–C(12)	39.5(7)
C(6)–Ir(1)–C(6)'	39.3(5)	C(12)–Ir(2)–C(12)'	39.6(6)
(b) Bridging oxygen atoms			
Ir(1)–O(1)–Ir(2)	92.7(3)	O(2)–O(1)–O(2)'	59.9(5)
Ir(1)–O(2)–Ir(2)	92.8(3)	O(1)–O(2)–O(2)'	60.0(2)

Atomic scattering factors were taken from reference 16. Calculations were carried out on the University of Sheffield ICL 1906S computer using programs from the Sheffield X-ray system.

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