Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

(PENTAMETHYLCYCLOPENTADIENYL)RHODIUM AND -IRIDIUM COMPLEXES.
V*. COMPLEXES WITH OXY-LIGANDS AND THE EXCHANGE OF METHYL PROTONS BY DEUTERIUM UNDER BASIC CONDITIONS

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(Received January 25th, 1971)

SUMMARY

The (pentamethylcyclopentadienyl)rhodium and -iridium chlorides $(C_5Me_5MCl_2)_2$ reacted with silver acetate to give the acetates, $C_5Me_5M(OAc)_2 \cdot H_2O$, which in turn gave the trifluoroacetates, $C_5Me_5M(OCOCF_3)_2 \cdot H_2O$, with CF_3COOH. The rhodium acetate was relatively stable, but the iridium complex was readily hydrolyzed to the dihydroxo complex. Reaction of $(C_5Me_5RhCl_2)_2$ with aqueous base gave the complexes $[(C_5Me_5Rh)_2(OH)_3]^+X^-$, which are formulated with three bridging hydroxo groups. An analogous structure is proposed for $[(C_5Me_5Rh)_2Cl_3]BPh_4$. The complex $\{[C_5(CH_3)_5Rh]_2(OH)_3\}Cl$ gave $\{[C_5(CD_3)_5Rh]_2(OD)_3\}Cl$ on heating with OD^- in D_2O; this reaction was reversed in H_2O/OH^-. The complexes $[C_5(CD_3)_5RhCl_2]_2$ and $C_5(CD_3)_5Rh(C_2H_4)_2$ were also prepared.

INTRODUCTION

We have recently reported on the (pentamethylcyclopentadienyl)rhodium and -iridium dihalides and some related complexes[1]. Here we describe the extension of this work to the formation of hydroxo, acetato, and trifluoroacetato complexes, as well as the preparation of some novel triply bridged dimeric complexes and a very unusual reaction in which the methyl protons in some (pentamethylcyclopentadienyl)rhodium complexes are exchanged for deuterium in basic solution.

RESULTS AND DISCUSSION

Reaction of the dichlorides (I) with silver acetate in dry benzene, even at 25°, gave the diacetates (II). The rhodium complex, (IIa), was reasonably stable and has already been described[1]; the iridium complex, however, was exceedingly sensitive to moisture and was readily converted to a hydroxo complex, (IIIb), by water. This reac-

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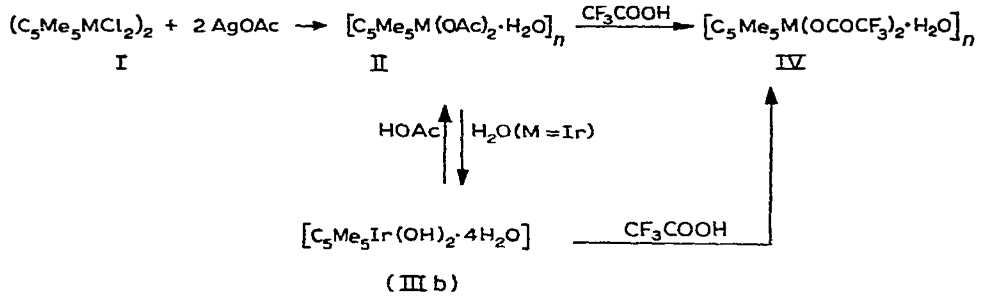
* For Part IV see ref. 8.

tion was reversed on dissolving the hydroxo complex in acetic acid. The hydrolysis reaction is rather unusual since the iridium acetate (IIb) itself is hydrated as can be seen both from the analysis and the NMR spectrum. The acetato complex was quite soluble in (dry) organic solvents, but reacted slowly with halogenated solvents such as chloroform or dichloromethane. In contrast, the hydroxo complex was readily soluble only in water and alcohols. We formulate it as $[C_5Me_5Ir(OH)_2 \cdot 4\ H_2O]_n$, in agreement with the analysis (Table 1), but the exact structure is not known.

Both the hydroxo complex (IIIb) and the acetato complexes (II) reacted with trifluoroacetic acid to give the trifluoroacetates (IV), in high yield. These again were hydrated.



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

TABLE 1

ANALYTICAL DATA (%)

Compound		Found			Calcd.		
		C	H	Other	C	H	Other
$[C_5Me_5Ir(OAc)_2 \cdot H_2O]_n$	(IIb)	35.61	5.00		36.27	5.00	
$[C_5Me_5Ir(OH)_2 \cdot 4H_2O]_n$	(IIIb)	31.59	5.33		31.66	5.01	
$[C_5Me_5Rh(OCOCF_3)_2 \cdot H_2O]_n$	(IVa)	33.65	3.19	F, 23.87	34.65	3.54	F, 23.67
$[C_5Me_5Ir(OCOCF_3)_2 \cdot H_2O]_n$	(IVb)	29.58	3.18	F, 19.15	29.48	2.81	F, 20.0
$[(C_5Me_5Rh)_2(OH)_3]Cl \cdot 4H_2O$	(Va)	37.89	6.82	Cl, 5.65	37.79	6.45	Cl, 5.67
$[(C_5Me_5Rh)_2(OH)_3]BPh_4$	(VIa)	62.93	6.64		62.39	6.26	
$[(C_5Me_5Rh)_2Cl_3]BPh_4$	(VIIa)	58.34	5.71	Cl, 12.02	58.54	5.54	Cl, 11.86

The hydroxorhodium complex, (IIIa), could not be obtained from (IIa) in a similar reaction to that which gave (IIIb). We discovered, however, that the dichlororhodium complex (Ia) was readily soluble in aqueous sodium hydroxide. On concentration of the aqueous solution large orange crystals (Va) were obtained. This was not the anticipated complex (IIIa) since it still contained chloride. Reaction of (Va) with sodium tetraphenylborate in methanol precipitated another orange crystalline complex, (VIa). This complex was shown by NMR to have one tetraphenylborate for every two C_5Me_5 groups and to have the stoichiometry $[(C_5Me_5Rh)_2(OH)_3]BPh_4$ by analysis (Table 2). The tetraphenylborate complex was soluble in more polar organic solvents, whereas the chloride (Va) was soluble only in water and alcohols.

A complex closely related to (VIa) was obtained by reaction of (Ia) with sodium

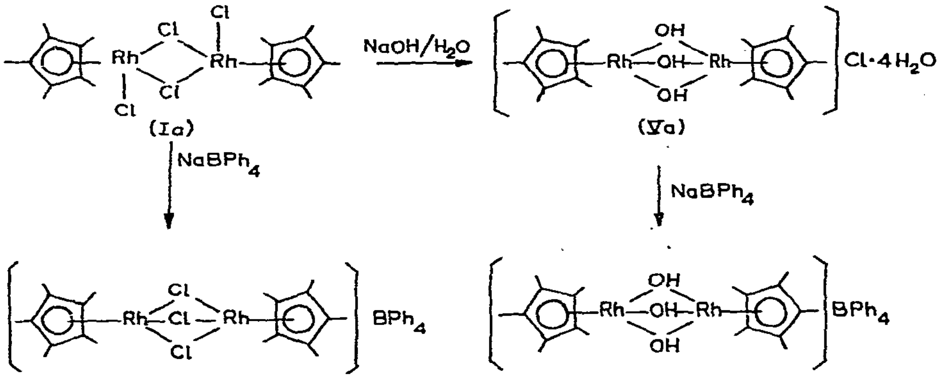
TABLE 2

NMR SPECTRA (IN $CDCl_3$)[a]

Compound		$\tau(C_5Me_5)$	$\tau(OH)$	τ(other)
$[C_5Me_5Rh(OAc)_2 \cdot H_2O]_n$	(IIa)	8.36 (s, 15 H)	5.02 (s, br, 2 H)	7.99 (s, 6 H; OAc)
$[C_5Me_5Ir(OAc)_2 \cdot H_2O]_n$	(IIb)	8.35 (s, 15 H)	5.05 (s, br, 2 H)	8.00 (s, 6 H; OAc)
$[C_5Me_5Ir(OH)_2 \cdot 4H_2O]_n$	(IIIb)[b]	8.43 (s, 15 H)	5.50 (s, 10 H)	
$[C_5Me_5Rh(OCOCF_3)_2 \cdot H_2O]_n$	(IVa)[c]	8.43 (s, 15 H)	3.45 (s, br, 2 H)	76.24[c] (s: CF_3)
$[C_5Me_5Ir(OCOCF_3)_2 \cdot H_2O]_n$	(IVb)[c]	8.46 (s, 15 H)	3.45 (s, br, 2 H)	75.35[c] (s; CF_3)
$[(C_5Me_5Rh)_2(OH)_3]Cl \cdot 4H_2O$	(Va)[b]	8.62 (s, 30 H)	5.50 (s, 11 H)	
$[(C_5Me_5Rh)_2(OH)_3]BPh_4$	(VIb)	8.57 (s, 30 H)	4.95 (s, br, 3 H)	2.8 (m, br, 20 H; BPh_4^-)
$[(C_5Me_5Rh)_2Cl_3]BPh_4$	(VIIa)	8.54 (s, 30 H)		2.84 (m, br, 20 H; BPh_4^-)

[a] Relative intensities given in parentheses; s, singlet; m, multiplet; br, broad. [b] In D_2O. [c] ^{19}F Spectrum, relative to $CFCl_3$ as internal standard. We are indebted to Dr. C. White of this laboratory for the observation that these bands remain singlets down to −60°.

tetraphenylborate in methanol. This complex, (VIIa), analyzed for $[(C_5Me_5Rh)_2Cl_3]BPh_4$, and the NMR spectrum agreed with this formulation. The far infrared spectrum showed only two rather broad bands at 246 and 253 cm^{-1}; by contrast (Ia), in which there are both bridging and terminal Rh–Cl bonds, showed bands at 243 and 286 cm^{-1}. The higher frequency peak for (Ia) arises from a terminal Rh–Cl bond, and that at lower frequency from the bridging bonds. In view of this we favor a structure for (VIIa) as shown, with three bridging Rh–Cl bonds in the cation and, by analogy then, the structures shown for (Va) and (VIa).



(Ia) (Va) (VIIa) (VIa)

An alternative formulation for (VIa) and (VIIa), which we can exclude, is one with two rhodium atoms π-bonded to two phenyls of the tetraphenylborate[2],

Complexes of this type are common for Rh^I and are distinguished by the presence of four strong bands at 1390, 1425, 1450 and 1480 cm^{-1}; in contrast, uncomplexed tetraphenylborate usually shows only two bands, at 1425 and 1480 cm^{-1}, in the infrared[3]. The complexes (VIa) and (VIIa) showed the typical BPh_4^- bands at 1425 and 1480 cm^{-1}; unfortunately the region around 1450 cm^{-1} was obscured by the C–Me deformation bands but there was no band around 1390 cm^{-1}. Furthermore, the complexes both showed only the normal multiplet centred at τ 2.8 for uncoordinated BPh_4^- in the NMR spectrum[3].

Reactions of this type, where a terminal M–Cl bond is either ionized off or becomes a bridge bond appear to be quite common though they have not, hitherto, been recognized. For example Pfrommer reported[4] that (tetramethylcyclobutadiene)-nickel chloride, which is a dimer in the solid[5] with two bridging and two terminal chlorines, forms complexes of the type $(C_4Me_4NiCl)_n \cdot n\, BPh_4$, or $(C_4Me_4NiCl)_2$-$SnCl_6$. It is tempting to propose that both of these contain the $(C_4Me_4NiCl_2C_4Me_4)^{2+}$ cation, with bridging chlorines and square planar Ni^{II}. Since in some cases the tetraphenylborates are more soluble than the parent halides, their preparation may often be advantageous. It is also tempting to suggest that in solution (Ia) exists as $(C_5Me_5RhCl_3RhC_5Me)^+Cl^-$; however, this does not appear to be the case in water, where the very high conductivity reported[6] probably arises from a complex aquation reaction rather than simple ionizaton.

Attempts to prepare the iridium analogs of the hydroxo compounds (Va) and (VIa) were unsuccessful. Complexes were isolated but their analyses did not agree with the formulations (Vb) and (VIb).

The hydroxo complex (Va) underwent a very unusual type of exchange reaction. When a solution of (Va) in D_2O was heated at 70° in the presence of a small amount of OD^- the NMR resonance of the methyl protons slowly decreased in size with time, until, after three days it had virtually disappeared (Fig. 1). This reaction was accompanied by a corresponding growth of the H_2O peak in the D_2O. Hence, exchange of the methyl protons in (Va) occurred under these conditions. This was confirmed by isolation of the solid, the infrared spectrum of which showed a broad strong band [ν(O–D)] at ca. 2450 cm^{-1} and bands [ν(C–D)] at 2220 and 2240 cm^{-1}. A strong band at 470 cm^{-1} in the hydroxo complex is seen at 460 cm^{-1} (with a shoulder at 445 cm^{-1}) in the deuteroxo complex (VIIIa) and may be due to ν[Rh–OH(D)].

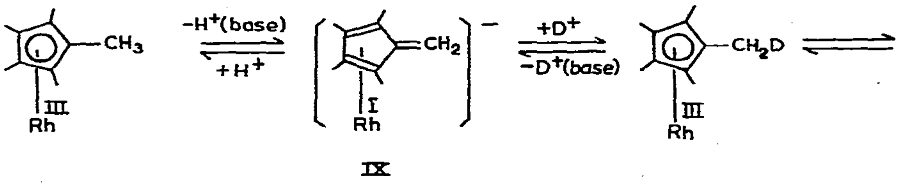
$$\underset{\text{(Va)}}{\{[C_5(CH_3)_5Rh]_2(OH)_3\}Cl} \xrightleftharpoons[H_2O/OH^-]{D_2O/OD^-} \underset{\text{(VIIIa)}}{\{[C_5(CD_3)_5Rh]_2(OD)_3\}Cl}$$

The reaction (Va)→(VIIIa) was reversed by heating (VIIIa) in water in the presence of hydroxide ion. All the complexes (II), (III), (IV) and (Va) were converted back into (I) on treatment with hydrogen chloride. This reaction was also carried out on (VIIIa) and gave $[C_5(CD_3)_5RhCl_2]_2$, without significant loss of deuterium on the methyls. This complex showed ν(C–D) at 2220 and 2245 cm^{-1} in the infrared and a small weak quintet arising from the presence of some CD_2H groups at τ 8.42 in the NMR spectrum ($CDCl_3$). The complex (VIIIa) was also formed, directly, on reaction of (Ia) with sodium deuteroxide in D_2O.

These reactions now make the fully deuterated (pentamethylcyclopentadienyl)-rhodium complexes readily available; for example, reaction of $[C_5(CD_3)_5RhCl_2]_2$ with ethylene in ethanol in the presence of sodium carbonate gave $C_5(CD_3)_5Rh$-$(C_2H_4)_2$[7], in which the deuterium was largely retained (NMR).

By contrast, the hydroxoiridium complex (IIIb) did not undergo exchange of the methyl hydrogens under these conditions.

The mechanism of this reaction is of considerable interest and we suggest that attack by $OH(D)^-$ may occur at a methyl group to give a Rh^I intermediate (IX) which then re-adds $H(D)^+$ to regenerate the Rh^{III} complex.



This reaction is very slow, however, and significant exchange does not occur under the conditions used to prepare the olefin complexes[7].

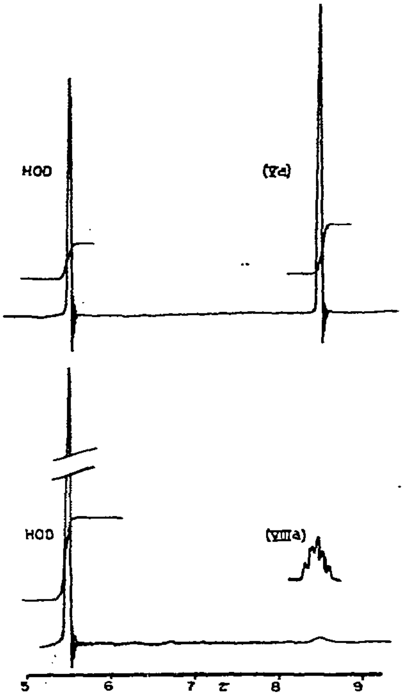


Fig. 1. NMR Spectra of $[(C_5Me_5Rh)_2(OH)_3]Ci$ (Va) (top), and after 72 h at 70° (bottom), in D_2O in the presence of NaOD.

EXPERIMENTAL

(Pentamethylcyclopentadienyl)rhodium and -iridium dichloride dimers were prepared as already described[1]. NMR spectra were measured on Varian A-60 (^1H) and DP-56 (^{19}F) spectrometers; infrared spectra were determined, usually as Nujol mulls or in KBr discs, on a Perkin–Elmer 337-G spectrometer; far infrared spectra were measured on a Perkin–Elmer 521 spectrometer. NMR and analytical data are presented in Tables 1 and 2. All reactions were carried out under nitrogen, even though none of the complexes prepared was appreciably air-sensitive.

Diacetato(pentamethylcyclopentadienyl)iridium hydrate (IIb)

A suspension of $(C_5Me_5IrCl_2)_2$ (1.0 g, 1.3 mmole) and silver acetate (0.9 g, 5.4 mmole) in dry benzene (50 ml) was stirred at 25° for 3 h. The yellow solution was filtered from a residue of silver chloride and excess silver acetate, and the filtrate was evaporated under reduced pressure to leave orange crystals of analytically pure (IIb) (1.15 g, 95%). This complex was readily hydrolyzed in moist air to (IIIb), but was soluble in dry organic solvents. With chloroform it slowly reacted to give (Ib); this reaction also occurred on treatment with HCl.

Dihydroxo(pentamethylcyclopentadienyl)iridium hydrate (IIIb)

The diacetato complex (IIb) (0.5 g) was dissolved in water (30 ml), with warming to 60°. The water was then removed in vacuo to give (IIIb) (0.4 g, 85%) as pale yellow crystals; these were recrystallized from acetone/water. The complex was also soluble in ethanol and methanol.

Bis(trifluoroacetato)(pentamethylcyclopentadienyl)rhodium and -iridium hydrates (IV)

The diacetato complex (IIa) (0.2 g) was dissolved in trifluoroacetic acid (5 ml) with warming to 50°. The solvent was removed *in vacuo* to leave an oily residue which was extracted with ether. The ether solution was concentrated to 5 ml and left at −20° for 18 h, when it deposited orange-red crystals (0.21 g, 80%) of (IVa).

The same complex was obtained in 66% yield by reaction of the hydroxo complex (Va) with trifluoroacetic acid, as described above.

The iridium complex (IVb) was prepared in the same manner from (IIb) and (IIIb) in 87% and 77% yield respectively.

Tri-μ-hydroxobis(pentamethylcyclopentadienyl)dirhodium chloride hydrate (Va)

The complex (Ia) (1.5 g) was dissolved, with warming to 60°, in a solution of sodium hydroxide (0.4 g) in water (30 ml) to give a homogeneous orange solution. This was filtered, concentrated to 10 ml and allowed to stand, when orange crystals of the complex (Va) (1.2 g, 78%) were deposited. The complex was recrystallized from water and was also soluble, though with slow decomposition, in methanol and ethanol.

Tri-μ-hydroxobis(pentamethylcyclopentadienyl)dirhodium tetraphenylborate (VIa)

A solution of sodium tetraphenylborate (150 mg) in methanol (10 ml) was added to a freshly prepared solution of (Va) (200 mg) in methanol (10 ml). After standing for 18 h at 25°, the solution deposited orange-red crystals of (VIa) (240 mg, 84%) which were collected and air-dried.

Tri-μ-chlorobis(pentamethylcyclopentadienyl)dirhodium tetraphenylborate (VIIa)

Sodium tetraphenylborate (700 mg) was added to a solution of complex (Ia) (300 mg) in methanol (50 ml), and the solution was stirred for 18 h at 25°. The red crystals which were slowly precipitated were filtered off and dried to give 380 mg (87%) of (VIIa). The complex reacted slowly with chloroform.

ACKNOWLEDGEMENT

We thank the National Research Council of Canada for supporting this work and Johnson, Matthey and Mallory for the loan of rhodium and iridium salts.

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