Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part VII.[1] Mono-, Di-, and Tri-μ-Hydrido-complexes

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The complexes $[M(C_5Me_5)Cl_2]_2$, $[M(C_5Me_5)X_2]_n$ (M = Rh or Ir; X = $OCOCH_3$ or $OCOCF_3$) are catalysts for the hydrogenation of olefins under ambient conditions. Reaction of these complexes with hydrogen has given the novel compounds $[\{M(C_5Me_5)\}_2HCl_3]$, $[\{M(C_5Me_5)\}_2HX_2]Y$, $[\{M(C_5Me_5)\}_2H_2X]Y$, and $[\{Ir(C_5Me_5)\}_2H_3]Y$ [X = $OCOCH_3$ or $OCOCF_3$; Y = PF_6, $H(OCOCF_3)_2$, or $H(OCOCH_3)_2$] which contain mono-, di-, and tri-μ-hydrido-ligands. The mono-μ-hydrido-complexes $[\{M(C_5Me_5)\}_2HX_2][HX_2]$ (M = Rh or Ir; X = $OCOCH_3$) can also be prepared from $[M(C_5Me_5)(OCOCH_3)_2]$ and isopropyl alcohol; in air the isopropyl alcohol is catalytically dehydrogenated to acetone. Hydrolysis of $[\{M(C_5Me_5)\}_2HX_2]^+$ (M = Rh, X = $OCOCH_3$ or $OCOCF_3$; M = Ir, X = $OCOCH_3$) leads to complexes which it is suggested contain μ-hydrido-μ-hydroxo-bridges $[\{M(C_5Me_5)\}_2H(OH)X]$.

In our study of the reactions of the pentamethylcyclopentadienyl-rhodium and -iridium chlorides (1) with a variety of olefins we were led to postulate the intermediacy of hydrido-complexes such as $[M(C_5Me_5)H(Cl)L]$

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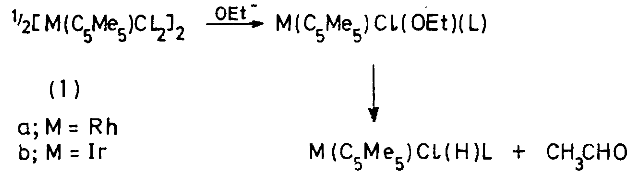
[1] Part VI, C. White and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1971, 3322.

(M = Rh or Ir, L = ligand or solvent).[2-4] These were presumed to arise from (1) in alcohol–base media by the following reaction sequence:



$$\tfrac{1}{2}[M(C_5Me_5)Cl_2]_2 \xrightarrow{OEt^-} M(C_5Me_5)Cl(OEt)(L) \longrightarrow M(C_5Me_5)Cl(H)L + CH_3CHO$$

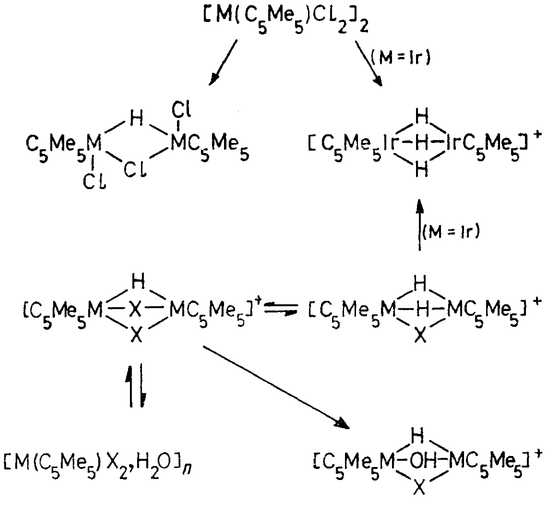
(1)

a; M = Rh

b; M = Ir

We have now isolated and characterised hydrido-complexes from such reactions in the absence of olefins from pentamethylcyclopentadienyl-rhodium and -iridium chloro-, acetato-, and trifluoroacetato-complexes. An outline is presented in the Scheme.

Mono-μ-hydrido-complexes.—In the absence of olefins the chloro-complexes (1) react with either (*a*), isopropyl alcohol (or, less conveniently, ethanol) and base or (*b*), sodium borohydride (on occasion lithium aluminium hydride has also been used successfully), or (*c*), hydrogen in a basic medium. These are all standard methods for preparing transition-metal hydrides from the chloro-complexes.[5] In each case the product obtained was the dinuclear hydride $[\{M(C_5Me_5)\}_2HCl_3]$ (2), formulated as such on the basis of analyses and molecular-weight measurements (see Table). The structure we propose has one bridging hydride, one bridging chloride, and two terminal chlorides, and is based on the i.r. and n.m.r. spectra.[6]



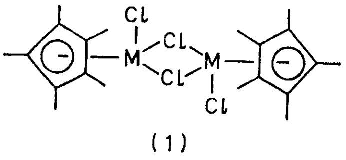
(M = Rh,Ir; X = OCOCH$_3$, OCOCF$_3$)

Scheme

The n.m.r. spectrum (CH_2Cl_2; 100 MHz) of the iridium complex (2b) showed a sharp doublet at τ 8·20 (J = 0·4 Hz), arising from the 30 equivalent methyl hydrogens coupled to the hydride, and a broader singlet at τ 23·72 owing to the hydride; the peak intensities were in the ratio expected, 30 : 1.

The rhodium complex (2a) showed a broadish singlet at τ 8·26 (30H, C_5Me_5) and a triplet at τ 21·54 (1H), owing to the hydride which is equally coupled to two equivalent rhodium atoms [^{103}Rh, $I = \tfrac{1}{2}$, 100% abundance; J(H–Rh) = 23 Hz].

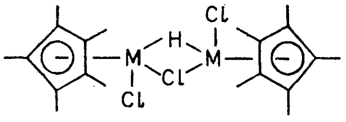
The n.m.r. spectra were temperature invariant down to −60°; solubility problems precluded measurements at even lower temperatures.



(1)

a;M = Rh

b;M = Ir



(2)

The presence of a high-field triplet in (2a) indicates that the hydride bridges the two metal atoms. Confirmation of this is provided by the i.r. spectra since no peak that can be ascribed to a terminal ν(M–H) is observed in the usual region for such vibrations, 1700—2200 cm^{-1}.[5] However, bands were observed at 1151 (2a) and 1155 cm^{-1} (2b) which were shifted to 812 (Rh) and 819 cm^{-1} (Ir) in the deuterio-complexes $[\{M(C_5Me_5)\}_2DCl_3]$ [ν(M–H)/ν(M–D) = 1·42] prepared from (1), $^2H_2$, and triethylamine in dichloromethane. These values are consistent with those reported by other workers for hydrides bridging two metal atoms.[5,7] In addition, the far-i.r. region showed bands at 255 and 280 cm^{-1} (2a) and 256 and 290 cm^{-1} (2b), which are ascribed to the presence of both bridging and terminal M–Cl bonds in the molecule.[8] *

When an equimolar mixture of the rhodium and iridium complexes (2a) and (2b) was dissolved in dichloromethane and the n.m.r. spectrum observed after the reaction had come to equilibrium (3 h at 35°) three high-field resonances with intensity ratios of 1 : 2 : 1 were found at τ 21·54, 22·97, and 23·72. The highest (triplet) and lowest (singlet) of these arose from (2a)

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* *Note added in proof:* Confirmation of the proposed structure for complex (2a) has been obtained from an *X*-ray determination (M. R. Churchill and S. W. Ni, *J. Amer. Chem. Soc.*, 1973, **95**, 2150).

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

[3] K. Moseley and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2884.

[4] P. M. Maitlis, *Trans. New York Acad. Sci.*, 1971, **33**, 87.

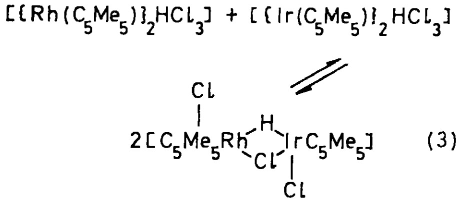
[5] R. A. Schunn in 'Transition Metal Hydrides,' ed. E. Muetterties, Marcel Dekker, New York, 1971, p. 203 *et seq.*

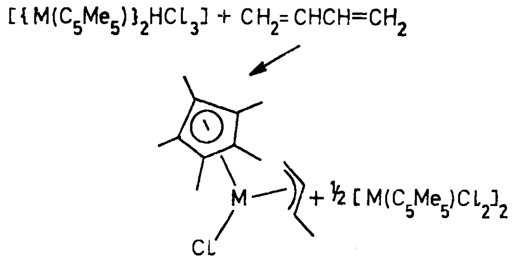
[6] A part of this work has been communicated: C. White, D. S. Gill, J. W. Kang, H. B. Lee, and P. M. Maitlis, *Chem. Comm.*, 1971, 734.

[7] J. Knight and M. J. Mays, *J. Chem. Soc.* (*A*), 1970, 711; B. F. G. Johnson, J. Lewis, and I. G. Williams, *ibid.*, p. 901.

[8] *Chem. Soc. Special Publ.*, 'Spectroscopic Properties of Inorganic and Organometallic Compounds,' vol. 1, p. 167; vol. 2, p. 281.

and (2b) respectively and the middle one is ascribed to the mixed hydride, (3). This resonance is a doublet ($J = 23$ Hz) in agreement with the proposed structure since the bridging hydride only couples to one ^{103}Rh atom. The intensity ratios found imply that a statistical redistribution has occurred.*


(3)


(4)

As we have mentioned previously[6] the hydrides (2a) and (2b) reacted with dienes to give π-allylic complexes [*e.g.* (4)] and were also active catalysts for the hydrogenation of olefins under ambient conditions. The iridium hydride (2b), but *not* (2a), also catalysed the isomerisation of olefins at 20°, and reacted stoicheiometrically with triphenylphosphine to give the known phosphine-dichloro and the phosphine-hydridochloride complexes.[2]*

$$[\{Ir(C_5Me_5)_2\}HCl_3] + 2PPh_3$$
$$\downarrow$$
$$Ir(C_5Me_5)(PPh_3)Cl_2 \quad + \quad Ir(C_5Me_5)(PPh_3)H(Cl)$$

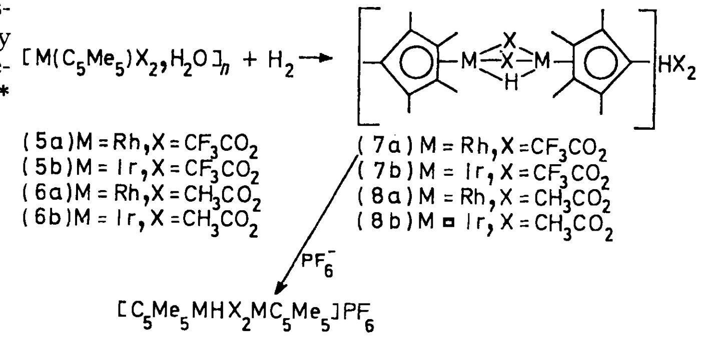
Details of this work will be published in due course.

The trifluoroacetato- and acetato-complexes (5) and (6)[9] were also active catalysts for olefin hydrogenation and here again it was reasonable to propose the intermediacy of a metal hydride. We therefore examined the interaction of (5) and (6) with hydrogen under a variety of conditions.

When the complexes (5) or (6) were exposed to hydrogen (20°, 1 atm, no base) in benzene or ether a rapid reaction occurred with the formation of new complexes of empirical formula $[\{M(C_5Me_5]\}_2X_4H_2]$. Their n.m.r. spectra (Table) showed, for example for $[\{Rh(C_5Me_5)\}_2(OCOCF_3)_4H_2]$, two equally intense ^{19}F resonances and, in the ^{1}H n.m.r. spectrum, a broad singlet at τ $-6{\cdot}43$ (1H), a doublet at τ $+8{\cdot}27$ (30H, $J = 0{\cdot}5$ Hz), and a triplet at τ $+18{\cdot}22$ [1H, J(H–Rh) = 26 Hz]. The spectra were temperature invariant down to −60°. The two ^{19}F resonances imply that the molecule has two pairs of inequivalent trifluoroacetates. The low field ^{1}H resonance is in the region of a very acidic hydrogen (H^+; it is at even lower field than in CF_3CO_2H), while the high-field resonance split into a triplet again implies a hydride bridging two rhodium atoms. The methyl doublet shows the two cyclopentadienyl rings to be equivalent and that the methyl hydrogens are coupled to the bridging hydride.

From these data we concluded that the correct structure was the ionic one, $[\{Rh(C_5Me_5)\}_2(H)(OCOCF_3)_2]^+$-$H(OCOCF_3)_2^-$ where the cation contains two C_5Me_5Rh groups bridged by one hydrido- and two trifluoroacetato-ligands. The anion is presumably proton bridged, $[CF_3CO_2 \cdots H \cdots OCOCF_3]^-$. Roundhill has also recently reported examples of complexes with a hydrogen-bis(trifluoroacetate) anion.[10]

The iridium trifluoroacetate (5b) and both the rhodium and iridium acetates (6a) and (6b) underwent very similar reactions. The reaction of the acetates (6a) and (6b) are particularly dramatic when they are carried out in an ether–light petroleum solvent mixture (2 : 1); the acetates are soluble in this solvent but on exposure to hydrogen (20°, 1 atm) the solution darkens and the hydrido-complexes (8) are rapidly precipitated. Overall, therefore, a heterolytic activation of hydrogen has occurred.



(5a) M = Rh, X = CF_3CO_2
(5b) M = Ir, X = CF_3CO_2
(6a) M = Rh, X = CH_3CO_2
(6b) M = Ir, X = CH_3CO_2
(7a) M = Rh, X = CF_3CO_2
(7b) M = Ir, X = CF_3CO_2
(8a) M = Rh, X = CH_3CO_2
(8b) M = Ir, X = CH_3CO_2
(9a) M = Rh, b; M = Ir, X = $OCOCF_3$
(10a) M = Rh, b; M = Ir, X = $OCOCH_3$

The reversibility of the reaction was tested for the rhodium hydridoacetate (8a); the stirring of (8a) in dichloromethane at 20° for 5 min resulted in a 10% conversion back into (6a). Although there was no difference in the rate when it was carried out under oxygen or nitrogen, the loss of hydrogen was much slower when ether was used as solvent. Virtually no decomposition occurred when (8a) was kept in solution for 24 h under 1 atm of hydrogen.

Further confirmation of the ionic structures of the complexes (7) and (8) came from their reactions with

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* We are indebted to Mr. D. S. Gill and Mr. H. B. Lee for these observations.

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

[10] P. C. Kong and D. M. Roundhill, *Inorg. Chem.*, 1972, **11**, 1437; K. Thomas, J. T. Daimler, B. W. Renoe, C. J. Nyman, and D. M. Roundhill, *ibid.*, p. 1795.

ammonium hexafluorophosphate to give the hexafluorophosphate salts (9) and (10). In this case the n.m.r. resonances owing to the HX_2^- anion were obviously absent but the cyclopentadienyl methyls, the hydride, and the bridging acetate or trifluoroacetate ligands were all in very similar positions to those found for the corresponding salts (7) or (8).

The mono-μ-deuterido-complexes $[\{M(C_5Me_5)\}_2DX_2]PF_6$ corresponding to (9a), (9b), and (10a) were obtained in the same manner from (5) and (6) using deuterium in place of hydrogen. The complex $[\{Rh(C_5Me_5)\}_2D(OCOCF_3)_2]PF_6$ did *not* undergo exchange with hydrogen in either dichloromethane or isopropyl alcohol–acetone solutions.

The complexes (7) and (8) were also produced very rapidly when (5) or (6) were dissolved in isopropyl alcohol. Neither hydrogen nor base was required (see also below).

The acetato-complexes (8) were also able to catalytically dehydrogenate isopropyl alcohol to acetone. When (8a) was stirred in isopropyl alcohol solution (3 days, 20°) it was recovered essentially unchanged and, on treatment of the mother liquors with 2,4-dinitrophenylhydrazine, acetone dinitrophenylhydrazone (a-dnph) was isolated. When the reaction was carried out in air 7 mol equiv. of a-dnph were obtained, whereas under nitrogen and in deoxygenated solvent the yield was only 0·7 mol equiv. The iridium complex (8b) was also active in air but only gave 2·6 mol equiv. of a-dnph and the rhodium complex is therefore more active. No reaction occurred in the absence of the catalyst.

This reaction is still under investigation but it is clear that in outline (if not in detail) the following catalytic cycle must be occurring.

$$[\{M(C_5Me_5)\}_2H(OCOCH_3)_2][H(OCOCH_3)_2]$$

(8)

$$\xrightarrow[Pr^iOH]{[O]} \frac{2}{n}[M(C_5Me_5)(OCOCH_3)_2]_n$$

(6)

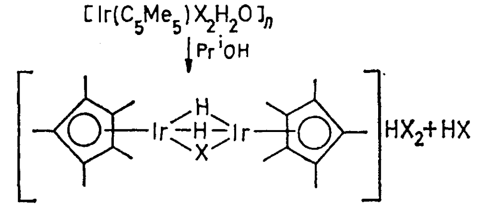
$$\frac{2}{n}[M(C_5Me_5)(OCOCH_3)_2]_n + Me_2CHOH$$

$$\downarrow$$

$$[\{M(C_5Me_5)\}_2H(OCOCH_3)_2][H(OCOCH_3)_2] + Me_2CO$$

Di-μ-hydrido-complexes.—When the complexes (5a), (5b), or (6a) [but *not* (6b)] were hydrogenated (1 atm, 20°) for longer times (2—3 days) in either isopropyl alcohol or benzene, the reaction proceeded one step further and a second molecule of hydrogen was activated. The products were now of the type $[\{M(C_5Me_5)\}_2H_3X_3]$ and these are formulated as $[\{M(C_5Me_5)\}_2H_2X][HX_2]$ with the cation having two equivalent bridging hydrido- and one bridging X ligand, while the anion is of the same form as in (7) and (8). Evidence for this comes again from the n.m.r. spectra; for example, the iridium trifluoroacetato-complex (11) shows two resonances (intensity ratio 2 : 1) in the ^{19}F n.m.r. spectrum, that at 75·4 p.p.m. arising from the $[H(OCOCF_3)_2]^-$ anion and that at 71·9 p.p.m. from the bridging trifluoroacetato-ligand. As in (7) the ^1H n.m.r. spectrum consists of three resonances: (i) a very low field rather broad resonance (τ −6·86, s, 1H) owing to the proton in the $[H(OCOCF_3)_2]^-$ anion, (ii) the C_5Me_5 resonance (τ 8·11, 30H) which is just resolved into a triplet (J = 0·4 Hz) owing to long range coupling to the two equivalent bridging hydrides, and (iii) a broadish high-field singlet (τ +22·67, 2H) arising from the two equivalent bridging hydrides.

On reaction with ammonium hexafluorophosphate the hexafluorophosphate salt, $[\{Ir(C_5Me_5)\}_2H_2(OCOCF_3)]PF_6$, was obtained which showed only the C_5Me_5 and high-field hydride resonances in the n.m.r. spectrum. The rhodium trifluoroacetate (5a) and the acetate (6a) reacted analogously but here it was only possible to obtain the hexafluorophosphate salts, $[\{Rh(C_5Me_5)\}_2H_2X]PF_6$ (12; X = $OCOCH_3$ or $OCOCF_3$). When an attempt was made to isolate the rhodium analogue of (11; X = $OCOCF_3$) from the solution which gave (12) with hexafluorophosphate, only the mono-μ-hydrido-complex (6a) could be detected. The reaction is therefore reversible.

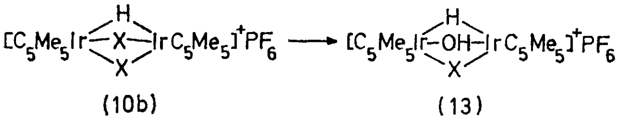


(11) X = $OCOCF_3$

$$[\{Rh(C_5Me_5)\}_2HX_2]HX_2 + H_2 \rightleftharpoons [\{Rh(C_5Me_5)\}_2H_2X]HX_2 + HX$$

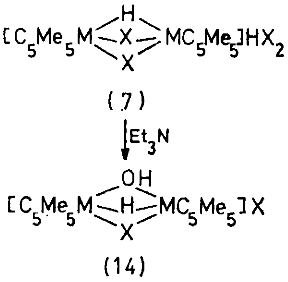
μ-Hydrido-μ-hydroxo-complexes.—It was also not possible to isolate the iridium complex (11; X = $OCOCH_3$) or its PF_6 salt from the above reaction, though when it was carried out in dry isopropyl alcohol complexes with high-field hydride resonances at τ 22·55 and 23·73 were obtained. It is thought that the latter may arise from (11; X = $OCOCH_3$) but no pure materials could be isolated.

When the hydrogenation of (6b) was carried out in moist isopropyl alcohol, a different complex (13), was obtained. This was prepared more conveniently by stirring the mono-μ-hydrido-complex (10b) in aqueous acetone for 3 days at 20°; longer reaction times (10 days) did not alter the product. This complex was characterised by the presence, in the i.r. spectrum, of a strong sharp band at 3585 cm^{-1} indicating the presence of a hydroxo-group. The presence of the hydroxo-ligand was not detectable in the n.m.r. spectrum which showed only the resonances of the μ-acetato, the μ-hydrido and the C_5Me_5 groups in the expected intensity ratios (Table). We formulate this complex as shown (13) with a bridging hydrido-, a bridging hydroxo-, and a bridging acetato-ligand; presumably it is formed from (10b) by hydrolysis of one of the bridging acetato-ligands:


(10b) (13)

X = OCOCH$_3$

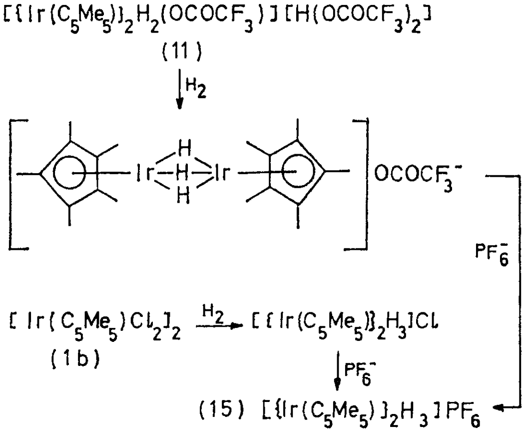
Two compounds which may well be analogous to (13) were obtained from (7a) or (7b) on treatment with triethylamine:


(7) (14)

M = Rh, Ir; X = OCOCF$_3$

The analytical and n.m.r. data are reasonably consistent with their formulation as (14) and it is certainly not surprising, in view of the formation of (13) from (10b) in the acetato-series, that a stronger base than water, alcohol, or acetone is able to remove trifluoroacetic acid from (7). Unfortunately, the presence of the hydroxo-hydrogen in (14) is not detectable in the n.m.r. spectrum nor, in this case, is it particularly clear in the i.r. spectrum where the evidence in its favour is only a broad low hump at 3550—3600 cm^{-1}; at present, however, the formulation (14) fits in best with available data.

Tri-μ-hydrido-complexes.—When the di-μ-hydrido-iridium complex (9b) is hydrogenated (1 atm, 20°, 38 h)


(11) (1b) (15)

in benzene in the presence of triethylamine a new complex is obtained which can be conveniently purified as the hexafluorophosphate salt (15). The same complex is also made by hydrogenating the dichloride dimer (1b) in isopropyl alcohol–aqueous acetone.

The complex (15) shows only two resonances in the ^{1}H n.m.r. spectrum, one at τ 7·91 (s, 30H, C_5Me_5) and one at 25·33 (s, 3H). From the integration it is evident that there are three hydrido-ligands per dimer unit and, even though the long-range coupling of the hydrides to the C_5Me_5 group is not detectable, by analogy with the other complexes this complex is most reasonably formulated as shown with three μ-hydrido-ligands.

The tri-μ-hydrido-complex (15) did *not* exchange with deuterium (3 days, 1 atm, 20°) *except* in the presence of triethylamine when the tri-μ-deuterido-complex $[\{Ir(C_5Me_5)\}_2D_3]PF_6$ was obtained. A peak at 936m cm^{-1} in the i.r. of the hydride is moved to 682m cm^{-1} in the deuteride and we therefore ascribe this band to a vibration of a bridging Ir–H(D) group [ν(Ir–H)/ν(Ir–D) = 1·37].

The tri-μ-hydrido-trifluoroacetate $[\{Ir(C_5Me_5)\}_2H_3][OCOCF_3]$, shows $\nu(CO)_{asym}$ at 1690s cm^{-1} and $\nu(CO)_{sym}$ at 1475s cm^{-1}. The $\Delta\nu$ of 215 cm^{-1} is in good agreement with that for the free trifluoroacetato-anion. The i.r. spectra of the other complexes are also in agreement with their structure, for example, $[\{Ir(C_5Me_5)\}_2H_2(OCOCF_3)]PF_6$ has ν(CO) at 1637s and 1457s cm^{-1}, and the $\Delta\nu$ here (180 cm^{-1}) is reasonable for a trifluoroacetate bridging two metal atoms.[11] There has been one other report of a tri-μ-hydrido-complex, namely the anion $[(OC)_3ReH_3Re(CO)_3]^-$.[12]

CONCLUSION

The dimeric pentamethylcyclopentadienyl-rhodium and -iridium complexes have, as has been remarked on before,[9] a tendency to become cationic with three bridging anionic ligands and this occurs here too. Overall then, the reactions which take place on hydrogenation of the chloro- or carboxylato-complexes, may be considered to involve successive replacements of a bridging Cl or OCOR by hydride (see Scheme).

Hydrides bridging two metal atoms are not uncommon but have not, up till now, been reported for rhodium and iridium except for the triply bridging hydride, $[Rh_3(\pi\text{-}C_5H_5)_4H]$.[13] The most usual description of the bonding in binuclear bridged hydrides is in terms of a two-electron three-centre bent $M\overset{H}{\diagup\diagdown}M$ bond and we suggest this to occur here too. An alternative view is that a protonated metal–metal bond is present but this is unlikely since we have found no evidence for deprotonation by base, despite the fact that the hydrido-ligands are in cationic complexes. Indeed, under such conditions hydrolysis of the carboxylato-ligand occurs in preference, *e.g.* (10b) ⟶ (13).

The reactions, particularly (5) or (6) ⟶ (7) or (8), are also remarkable examples of the heterolytic activation of molecular hydrogen to H$^-$H$^+$, and provide an

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[11] *Chem. Soc. Special Publ.*, 'Spectroscopic Properties of Inorganic and Organometallic Compounds,' vol. 2, p. 334; vol. 3, p. 326.

[12] A. P. Ginsberg and M. J. Hawkes, *J. Amer. Chem. Soc.*, 1968, **90**, 5930.

[13] E. D. Fischer, O. S. Mills, E. F. Paulus, and H. Wawersik, *Chem. Comm.*, 1967, 643.

unusually clear-cut example of this process, to the extent that we have been able to isolate ionic complexes with $[H(OCOCF_3)_2]^-$ and even $[H(OCOCH_3)_2]^-$ counter-ions.

EXPERIMENTAL

Although the hydride complexes, particularly in the solid state, were quite stable to air for considerable periods of time all work with them was carried out under a protective atmosphere and with use of deoxygenated solvents. The chloro- and carboxylato-complexes (1), (5), and (6) were prepared as previously described.[9,14] Typical experiments are described in detail; analytical and n.m.r. data are presented in the Table. Molecular weights of complexes (2a) and (2b) were determined osmometrically in benzene.

Analytical data (calculated values in parentheses)

		C	H	F	Other	Colour	N.m.r. data in CH_2Cl_2 [a] H⁺	OCOCH₃	C₅Me₅	H⁻	^{19}F [b]	
$[\{Rh(C_5Me_5)\}_2HCl_3]$	(2a)	41·0 (41·2)	5·1 (5·4)		Cl, 18·3 (18·2) M, 580 (584)	Purple			8·26	21·54 (t, J = 23) [d]		
$[\{Ir(C_5Me_5)\}_2HCl_3]$	(2b)	31·7 (31·5)	4·0 (4·1)		Cl, 13·3 (13·9) M, 756 (762)	Dark red			8·20 (d, J = 0·4) [c]	23·72		
$[\{Rh(C_5Me_5)\}_2H(OCOCF_3)_2][H(OCOCF_3)_2]$	(7a)	36·0 (36·1)	3·5 (3·5)	23·9 (24·5)		Orange	−6·43		8·27 (d, J = 0·5) [c]	18·22 (t, J = 26) [d]	73·6	75·4
$[\{Ir(C_5Me_5)\}_2H(OCOCF_3)_2][H(OCOCF_3)_2]$	(7b)	29·9 (30·3)	2·9 (2·9)	20·0 (20·6)		Yellow	−6·23		8·27 (d, J = 0·2) [c]	20·46	73·1	75·4
$[\{Rh(C_5Me_5)\}_2H(OCOCH_3)_2][H(OCOCH_3)_2]H_2O$	(8a)	45·7 (45·9)	6·3 (6·3)			Orange	2·45 [f]	7·96, 8·11	8·30	19·05 (t, J = 25) [d]		
$[\{Ir(C_5Me_5)\}_2H(OCOCH_3)_2][H(OCOCH_3)_2]$	(8b)	37·3 (37·7)	5·2 (5·0)			Yellow	2·60	7·85, 8·08	8·27	21·47		
$[\{Rh(C_5Me_5)\}_2H(OCOCF_3)_2]PF_6$	(9a)	33·5 (34·0)	3·5 (3·7)	26·7 (26·9)		Orange			8·24	18·24 (t, J = 26) [d]	72·6 (d, J = 710) [e]	73·5
$[\{Ir(C_5Me_5)\}_2H(OCOCF_3)_2]PF_6$	(9b)	28·0 (28·1)	3·0 (3·0)	24·0 (22·2)		Yellow			8·23	20·42	72·6 (d, J = 710) [e]	73·1
$[\{Rh(C_5Me_5)\}_2H(OCOCH_3)_2]PF_6$	(10a)	39·0 (38·9)	4·9 (5·0)			Orange-red		7·97	8·32	19·07 (t, J = 25) [d]		
$[\{Ir(C_5Me_5)\}_2H(OCOCH_3)_2]PF_6$	(10b)	31·6 (31·4)	4·3 (4·1)			Yellow		7·87	8·30	21·65		
$[\{Ir(C_5Me_5)\}_2H_2(OCOCF_3)][H(OCOCF_3)_2$	(11)	31·3 (31·3)	3·3 (3·3)	16·8 (17·2)		Red	−6·86		8·11 (t, J = 0·4) [c]	22·67	71·9	75·4
$[\{Rh(C_5Me_5)\}_2H_2(OCOCF_3)]PF_6$	(12)	35·9 (35·9)	4·4 (4·4)			Red			8·13	21·30 (t, J = 32·5) [d]		
$[\{Rh(C_5Me_5)\}_2H_2(OCOCH_3)]PF_6$	(12)	38·8 (38·8)	5·2 (5·2)			Dark red		7·80	8·13	21·78 (t, J = 33·5) [d]		
$[\{Ir(C_5Me_5)\}_2H_2(OCOCF_3)]PF_6$		28·9 (28·9)	3·6 (3·5)	18·0 (18·7)		Orange-brown			8·07	22·06	71·8	72·4 (d, J = 710)
$[\{Ir(C_5Me_5)\}_2H(OH)(OCOCH_3)]PF_6$	(13)	29·8 (30·1)	4·4 (4·0)			Orange		7·88	8·12	20·28		
$[\{Rh(C_5Me_5)\}_2H(OH)(OCOCF_3)][OCOCF_3]$	(14a)	40·5 (40·5)	4·5 (4·5)	15·1 (15·8)		Red			8·10	18·77 (t, J = 66) [d]	74·1	74·5
$[\{Ir(C_5Me_5)\}_2H(OH)(OCOCF_3)][OCOCF_3]$	14b)	32·1 (32·1)	3·7 (3·6)	13·4 (12·7)		Orange			8·07 (d, J = 70·4) [c]	20·26	74·3	74·7
$[\{Ir(C_5Me_5)\}_2H_3][OCOCF_3]2HCH_2Cl_2$		32·6 (32·9)	4·2 (4·3)	6·5 (6·5)		Yellow			7·91	25·57		
$[\{Ir(C_5Me_5)\}_2H_3]PF_6$	(15)	29·8 (29·8)	3·8 (4·1)			Yellow			7·91	25·33 [g]		

[a] τ scale; J quoted in Hz. [b] P.p.m. upfield from external reference of $CFCl_3$, higher-field resonance owing to anionic trifluoroacetate. [c] Long-range coupling to bridging hydride. [d] $^1J(H-^{103}Rh)$. [e] $^1J(^{19}F-^{31}P)$. [f] This peak is due to $[H(H_2O)]^+$ and has relative intensity 3. [g] In $CDCl_3$.

μ-Chloro-μ-hydrido-bis[chloro(pentamethylcyclopentadienyl)-rhodium] (2a).—(i) A solution of di-μ-chloro-bis[chloro-(pentamethylcyclopentadienyl)rhodium] (1a) (0·31 g) and potassium hydroxide (0·05 g) in isopropyl alcohol (10 ml) was stirred at 20° for 4 h. The solvent was removed on a rotary evaporator to leave a purple solid which was extracted with benzene (20 ml); the solution was then washed with water, dried (Na_2SO_4), filtered, and reduced to small volume. On addition of cyclohexane purple crystals of the hydrido-complex (2a), m.p. >155° (decomp.), were obtained (yield 90%). The analytical sample was recrystallised from benzene–cyclohexane.

(ii) Sodium borohydride (0·09 g) was added to a solution of the chloro-complex (1a) (0·33 g) in isopropyl alcohol (10 ml). The solution was stirred at 20° and the product was worked up as described above to give (2a) in 95% yield.

(iii) Hydrogen gas was slowly bubbled for 1 h at 20° through a solution of (1a) (0·62 g) in dichloromethane (25 ml) and triethylamine (3 ml). The product was then worked up as described above to give (2a) (76%). This was the least convenient method since side products were formed which were very difficult to remove completely.

The iridium complex (2b), m.p. >190° (decomp.), was also prepared by these methods in very similar yields.

Di-μ-trifluoroacetato-μ-hydrido-bis(pentamethylcyclopentadienylrhodium) Hydrogen Bis(trifluoroacetate) (7a) *and Hexafluorophosphate* (9).—A slow stream of hydrogen was bubbled through a solution of the rhodium trifluoroacetate (5a) (0·70 g) in benzene (35 ml) for 1·5 h at 20°. The solvent was removed on a rotary evaporator to leave an orange crystalline solid. This was recrystallised from dichloromethane–hexane to give the pure complex (7a) (0·54 g, 81%), m.p. 149—150°.

The complex (7a) (0·20 g) was dissolved in acetone (2 ml) and an equal volume of a saturated aqueous solution of ammonium hexafluorophosphate was added. A red precipitate formed immediately which was filtered off, washed with water (2 ml), and dried. Crystallisation from dichloromethane–ether gave orange crystals (0·13 g, 71%; m.p. 223°) of (9a).

The iridium complexes (7b) (83%; m.p. 169—171°) and (9b) (75%; m.p. 227—228°) were obtained in an identical manner.

Di-μ-acetato-μ-hydrido-bis(pentamethylcyclopentadienylrhodium) Hydrogen Diacetate Monohydrate (8a) *and Hexafluorophosphate* (10a).—(i) The rhodium acetate (6a) (0·10 g)

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

was dissolved in a mixture of ether (20 ml) and light petroleum (b.p. 30—60°; 10 ml) and hydrogenated (1 atm; 20°) for 0·5 h. The orange precipitate of (8a) (0·08 g, 82%) was filtered off, washed with light petroleum (5 ml) and dried. The presence of water in the complex was shown by the n.m.r. spectrum where the low-field resonance integrated for 3H (Table).

The hexafluorophosphate (10a) was prepared (80%) in the same manner as for (9a).

(ii) The complex (8a) was also formed almost immediately on dissolving the acetate (6a) in isopropyl alcohol, as determined by n.m.r. spectroscopy. Addition of ammonium hexafluorophosphate to this solution gave (10a) in high yield.

The iridium complexes (8b) (74%) and (10b) (88%) were prepared in the same manner as in (i).

Di-μ-hydrido-μ-trifluoroacetato-bis(pentamethylcyclopentadienyliridium) Hydrogen Bis(trifluoroacetate) (11) *and Hexafluorophosphate.*—A solution of the iridium trifluoroacetate (5b) (0·52 g) in benzene (20 ml) was hydrogenated (1 atm; 20°) for 36 h. The solvent was then removed *in vacuo* and the remaining red oil was crystallised from dichloromethane–ether at −60° to give red crystals of (11) (0·34 g, 75%; m.p. 145—146·5°).

The hexafluorophosphate salt (80%; m.p. 205°) was prepared in the same manner as (9a).

Di-μ-hydrido-μ-trifluoroacetato-bis(pentamethylcyclopentadienylrhodium) Hexafluorophosphate (12; X = $OCOCF_3$).—A solution of the rhodium trifluoroacetate (0·10 g) dissolved in isopropyl alcohol (20 ml) was hydrogenated (1 atm; 20°) for 3 days. Ammonium hexafluorophosphate (0·50 g) was added to the solution which was then stirred for 0·5 h; finally the solvent was removed *in vacuo*. The product was extracted with dichloromethane and crystallised from dichloromethane–ether to give red crystals of (12; X = $OCOCF_3$) (0·08 g, 77%).

When the solution was evaporated to dryness *without* addition of hexafluorophosphate, the only product was the mono-μ-hydrido-complex (7a).

Di-μ-hydrido-μ-acetato-bis(pentamethylcyclopentadienylrhodium) Hexafluorophosphate (12; X = $OCOCH_3$).—This complex was obtained (67%) in the same manner as for (12; X = $OCOCF_3$).

μ-Acetato-μ-hydrido-μ-hydroxo-bis(pentamethylcyclopentadienyliridium) Hexafluorophosphate (13; X = $OCOCH_3$).—The mono-μ-hydrido-di-μ-acetato-iridium complex (10b) (0·04 g) was stirred in aqueous acetone (50%, 20 ml) for 3 days at 20°. The solvent was removed *in vacuo* and the orange residue was crystallised from dichloromethane–ether–light petroleum (b.p. 30—60°) at 0° to give orange crystals of (13) (0·03 g, 82%).

μ-Hydrido-μ-hydroxo-μ-trifluoroacetato-bis(pentamethylcyclopentadienyl-rhodium and -iridium) Trifluoroacetates (14).—These compounds were both prepared by stirring a benzene (4 ml) solution of the mono-μ-hydrido-di-μ-trifluoroacetato-complexes (7a) or (8a) (0·6 g) with triethylamine (0·4 ml) for 15 min at 20°. No attempt was made to exclude moisture and, when the products were worked up in the usual manner, the complexes (14a) (red 72%) and (14b) (orange 76%; m.p. 159°) were obtained.

Tri-μ-hydrido-bis(pentamethylcyclopentadienyliridium) Chloride, Trifluoroacetate, and Hexafluorophosphate (15).—(i) A solution of the iridium dichloride (2b) (0·10 g) in an isopropyl alcohol (10 ml)–acetone (10 ml)–water (5 ml) solvent mixture was hydrogenated (1 atm; 20°) for 24 h. The solvent was evaporated to 1 ml when a yellow solid was precipitated. This was washed with water (1 ml) and ether (5 ml) to leave a very soluble and somewhat impure yellow chloride salt, $[\{Ir(C_5Me_5)\}_2H_3]Cl$ (0·044 g) (Found: C, 33·15; H, 5·2%. $C_{20}H_{33}ClIr$ requires C, 34·65; H, 4·8%) with resonances at τ 7·93 (s, 30H, C_5Me_5) and 25·50 (s, 3H, hydride) in the n.m.r. spectrum.

Addition of a saturated aqueous solution of ammonium hexafluorophosphate gave the yellow hexafluorophosphate (15) (82%), m.p. >228° (decomp.).

(ii) A solution of the di-μ-hydrido-μ-trifluoroacetato-complex (11) (0·20 g) and triethylamine (0·1 g) in benzene (10 ml) was hydrogenated (1 atm; 20°) for 38 h. The solvent was removed *in vacuo* to leave a yellow solid which was washed with benzene and ether and then recrystallised from dichloromethane–light petroleum (b.p. 30—60°) to give the yellow trifluoroacetate salt as a dichloromethane solvate [0·11 g, 72%; m.p. 141° (decomp.)] as indicated by the analysis and the n.m.r. spectrum in $CDCl_3$. This was also converted into the hexafluorophosphate (15, 77%).

Dehydrogenation of Isopropyl Alcohol to Acetone.—A solution of the mono-μ-hydrido-di-μ-acetatorhodium complex (8a) (0·025 g, 0·035 mmol) in isopropyl alcohol (20 ml) was stirred at 20° for 3 days. The solvent was distilled off and the residue was characterised as pure (8a) by n.m.r. spectroscopy. A solution of 2,4-dinitrophenylhydrazine (0·10 g) in hydrochloric acid (6N; 15 ml) and methanol (15 ml) was added to the distillate together with water (50 ml). After 24 h at 0° a fine crystalline precipitate of acetone 2,4-dinitrophenylhydrazone (0·056 g, 0·235 mmol) was isolated and identified by comparison with an authentic sample (m.p., n.m.r.). With a nitrogen atmosphere and nitrogen-saturated solvents a yield of 0·006 g (0·025 mmol) of the hydrazone was obtained. The analogous iridium complex (8b) on the same scale in air, gave 0·022 g (0·092 mmol) of the hydrazone. A blank run in the absence of catalyst gave no hydrazone.

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