Interaction of Hydridocarbonyltris(triphenylphosphine) Complexes of Iridium(I) and Rhodium(I) with Organic Acids †

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The interaction of the complexes $MH(CO)(PPh_3)_3$ [M = Rh or Ir] with organic acids such as *p*-nitrophenol, pyridine-2-thiol, trifluoroacetic, and trifluoromethylsulphonic acids have been studied. The new complexes $Ir(OC_6H_4NO_2)(CO)(PPh_3)_2$, $Ir(CF_3CO_2)(CO)(PPh_3)_2$, $[IrH_2(CO)(PPh_3)_3)]CF_3SO_3$, and $IrH(C_6H_4NS)(PPh_3)_2$ have been prepared; the latter complex has been found to insert ethylene to form the alkyl complex $Ir(C_2H_5)(C_6H_4NS)_2(PPh_3)_2$. More convenient routes to $Rh(CF_3CO_2)(CO)(PPh_3)_2$, $IrH(CF_3CO_2)_2(CO)(PPh_3)_2$, and the cationic complex $[Rh(CO)(PPh_3)_3]^+$ are given.

OXIDATIVE addition reactions with compounds of the type XY are common for d^8 iridium(I) and rhodium(I) complexes.[1-3] When the added molecule is an acid, HX, a metal(III) hydride may be obtained.[4,5] If the initial complex is a metal(I) hydride then a metal(III) dihydride is the expected product.[5,6] The present studies show that in certain cases iridium(III) and rhodium(III) dihydrides formed in this way are unstable with respect to loss of molecular hydrogen and may be formed only as transient intermediates in reactions which yield iridium(I) and rhodium(I) products. The situation is similar to that found in our previous studies [7] on the interaction of mono-substituted acetylenes (HA) with hydridocarbonyltris(triphenylphosphine) complexes of iridium(I) and rhodium(I) *i.e.*

$$MH(CO)(PPh_3)_3 \underset{(-PPh_3)}{\overset{HA}{\rightleftharpoons}} MH_2(A)(CO)(PPh_3)_2 \xrightarrow[(+PPh_3)]{-H_2} M(A)(CO)(PPh_3)_{2 \text{ or } 3}$$

There appears to be no direct correlation between the pK_a of acids, such as carboxylic acids,[8] and their propensity to add to complexes of the type *trans*-$IrCl(CO)(PR_3)_2$ and both the acidity and nephelauxetic effect of

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† No reprints available.

[1] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, 1965, **87**, 4008.

[2] R. F. Heck, *J. Amer. Chem. Soc.*, 1964, **86**, 2786.

[3] L. Vaska and J. W. Diluzio, *J. Amer. Chem. Soc.*, 1962, **84**, 679.

[4] H. Singer and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2516.

[5] D. Commereuc, I. Douek, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 1771.

[6] J. P. Collman, F. D. Vastine, and W. R. Roper, *J. Amer. Chem. Soc.*, 1968, **90**, 2282.

[7] C. K. Brown, D. Georgiou, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 3120.

[8] B. L. Shaw and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 3716.

the conjugate base may be important.[9] In the oxidative addition reactions of acetylenes where the pK_a of the acetylenic proton is *ca.* 22, the π-bonding of the group is clearly of importance.

We now report studies of the interaction of IrH(CO)(PPh$_3$)$_3$ and RhH(CO)(PPh$_3$)$_3$ with several acids. The iridium hydrido-complex has also been shown to react with 2,4-dinitrophenol, α-nitroso-β-naphthol, 2-aminothiophenol, benzothiazole-2-thiol, salicylaldehyde, *o*-allylphenol, and thiophenol but products giving consistently reliable analyses have not been isolated. No reaction has been observed at refluxing toluene temperatures between IrH(CO)(PPh$_3$)$_3$ or RhH(CO)(PPh$_3$)$_3$ and small excesses of *p*-fluorophenol, pentafluorophenol, nitromethane, *o*-cresol, *p*-cresol, ethylsalicylate, *o*-hydroxyacetophenone, 8-hydroxyquinoline, acetylacetone, benzyl α-dioxime, 1,1,1-trifluoroethanol, or hexafluoroacetone sesquihydrate.

p-Nitrophenol.—Although phenol is a much stronger acid than, say, methylacetylene (pK_a 9·9 and 22, respectively) neither the iridium nor the rhodium hydride complexes MH(CO)(PPh$_3$)$_3$ showed any reaction with phenol under the conditions studied. The interaction of *p*-nitrophenol (pK_a 7·2) with IrH(CO)(PPh$_3$)$_3$ in refluxing toluene, however, yields *p*-nitrophenolatocarbonylbis(triphenylphosphine)iridium(I), Ir(OC$_6$H$_4$NO$_2$)(CO)(PPh$_3$)$_2$. This complex may be isolated as yellow microcrystals and characterised by i.r. spectroscopy, analysis, and molecular weight measurements (see Table). According to the above scheme an intermediate complex, IrH$_2$(OC$_6$H$_4$NO$_2$)(CO)(PPh$_3$)$_2$, may be expected to be formed. In contrast to the reaction with phenol itself this intermediate would appear to be unstable with respect to the loss of molecular hydrogen rather than to the loss of the organic acid. This may suggest that the greater electron accepting properties increase the Ir–O bond strength and labilise one or both of the hydrogen atoms. Although small amounts of a corresponding phenolato-dihydrido-species may be formed with phenol itself the electron-attracting effect of the phenolato-group may be insufficient to labilise the hydrogen atoms.

The *p*-nitrophenolato-group in Ir(OC$_6$H$_4$NO$_2$)(CO)(PPh$_3$)$_2$ may be replaced by a stronger acid, *e.g.* HCl, and interaction in benzene yielded IrHCl$_2$(CO)(PPh$_3$)$_2$ [3] and free *p*-nitrophenol. This reaction presumably proceeds *via* a mechanism similar to that noted above, an intermediate IrHCl(OC$_6$H$_4$NO$_2$)(CO)(PPh$_3$)$_2$ being unstable to loss of *p*-nitrophenol.

$$\begin{tikzcd}
\mathrm{Ir(OC_6H_4NO_2)(CO)(PPh_3)_2} \arrow[r, "\mathrm{HCl}"] & \mathrm{IrHCl(OC_6H_4NO_2)(CO)(PPh_3)_2} \arrow[d, "-\mathrm{HOC_6H_4NO_2}"] \\
\mathrm{IrHCl_2(CO)(PPh_3)_2} & \mathrm{IrCl(CO)(PPh_3)_2} \arrow[l, "\mathrm{HCl}"']
\end{tikzcd}$$

p-Nitrophenol does not appear to react with the rhodium analogue RhH(CO)(PPh$_3$)$_3$ probably due to the lower tendency of rhodium(I) towards oxidative addition compared to iridium(I).

Pyridine-2-thiol (pySH).—Interaction of IrH(CO)(PPh$_3$)$_3$ with pyridine-2-thiol in refluxing toluene yields a yellow complex which may be crystallised by addition of ethanol. In the i.r. region, 2400—1800 cm^{-1}, the complex showed only a single band assigned as ν(IrH); no absorption attributable to a carbonyl stretching frequency was observed (Table). The yellow complex was found to be of the type IrH(pyS)$_2$(PPh$_3$)$_x$ [$x = 1$ or 2] and was normally obtained as a mixture. However, when the mixture was refluxed in toluene with a six-fold excess of triphenylphosphine for *ca.* 1 h crystallisation

Analytical (%), infra-red,[a] and n.m.r.[b] data for the rhodium and iridium complexes

Complex	Found				Required				ν(CO)s	ν(IrH)s	Other bands	τ Value	*J*/Hz
	C	H	Other	*M*	C	H	Other	*M*					
Ir(OC$_6$H$_4$NO$_2$)(CO)(PPh$_3$)$_2$	58·6	3·9	N, 1·6 P, 6·7	890	58·5	3·9	N, 1·6 P, 7·0	882	1941		ν(NO$_2$), 1581s 1290		
IrH(pyS)$_2$(PPh$_3$)									—	2143	*c*	32·3(d) [d] 31·2(d) [e]	22 22
IrH(pyS)$_2$(PPh$_3$)$_2$	58·6	4·0	N, 2·9 P, 7·0 S, 7·2	470	58·9	4·2	N, 3·0 P, 6·8 S, 6·6	937	—	2151	*c*	31·8(t) [d] 31·5(t) [e]	17 17
Ir(C$_2$H$_5$)(pyS)(PPh$_3$)$_2$												9·33(t) [e] 8·87(m) [e]	6·5
IrH(CF$_3$CO$_2$)$_2$(CO)(PPh$_3$)$_2$	49·4	3·4		960	50·6	3·2		971	2040	2243	1700s, 1678s [f,g]	27·09(t)	11
[IrH$_2$(CO)(PPh$_3$)$_3$]BPh$_4$	72·1	5·0	P, 7·3	650	71·4	5·1	P, 7·0	1327	2000	2139, 2108			
Ir(CF$_3$CO$_2$)(CO)(PPh$_3$)$_2$	55·3	3·5		445	54·6	3·5		857	1979	—	1710s, 1694s [f,g]		
Rh(CF$_3$CO$_2$)(CO)(PPh$_3$)$_2$	59·6	3·9			61·0	3·9			1990		1692s [f,g]		
[IrH$_2$(CO)(PPh$_3$)$_3$]CF$_3$SO$_3$	58·1	4·1	S, 2·8 P, 8·1	1157	58·5	4·0	S, 2·5 P, 7·7	1125	2005	2115, 2170	*g*, *h*	19·61 [e,i] 20·96(t) [e] 22·12(t) [e]	
[Rh(CO)(PPh$_3$)$_3$]CF$_3$SO$_3$,-CF$_3$SO$_3$H	56·0	3·8	S, 5·3		56·3	3·8	S, 5·3		2000		*g*, *h*		

[a] Nujol mulls, in cm^{-1}, all complexes show bands associated with co-ordinated triphenylphosphine. [b] At 100 MHz, 35°. [c] Bands associated with co-ordinated pyridine-2-thiol, *i.e.* 1582s, 1551m, 1148m, 1135s cm^{-1}. [d] In deuteriochloroform. [e] In deuteriobenzene. [f] Trifluoroacetate carboxylate stretch. [g] Strong ν(CF) bands in the 1200—1130 cm^{-1} region. [h] Bands in the 1450—1350 cm^{-1} region due to ν(SO$_3$). [i] Virtual quartet.

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[9] D. M. Roundhill, P. G. Tripathy, and B. W. Reave, *Inorg. Chem.*, 1971, **10**, 727.

from toluene–ethanol yielded the pure bis(triphenylphosphine) complex, $IrH(pyS)_2(PPh_3)_2$. N.m.r. studies show that this dissociates in solution:

$$IrH(pyS)_2(PPh_3)_2 \rightleftharpoons IrH(pyS)_2(PPh_3) + PPh_3$$

Recrystallisation of the mixture obtained initially from toluene–ethanol yielded the mono(triphenylphosphine) complex almost pure, only a high-field doublet (Table) being observed in the n.m.r. spectrum. On addition of a six-fold excess of triphenylphosphine the doublet slowly collapsed and a triplet due to $IrH(pyS)_2(PPh_3)_2$ grew in intensity. This reaction was very slow at 35°; a sharp triplet was obtained only after *ca.* 48 h, when no remaining doublet could be observed.

The formation of the $IrH(pyS)_2(PPh_3)_{1,2}$ complex is likely to occur *via* the intermediate $Ir(pyS)(CO)(PPh_3)_2$ formed in the same way as above. Addition of a further molecule of pyridine-2-thiol giving the hydride. It is likely that at some stage (either before, after, or during the addition of the second molecule of pySH) chelation of the pyridine-2-thiol occurs with loss of carbon monoxide. Chelation of pyridine-2-thiol is well known[10] and this reaction may be compared with that of *o*-aminobenzenethiol (abt) with $[Rh(CO)_2Cl]_2$ to give $Rh(abt)_3$,[5] in which chelation is also proposed to account for the loss of carbon monoxide.

$IrH(pyS)_2(PPh_3)_2$ failed to react with ethylene (*ca.* 3 atm) in benzene at room temperature even after 48 h, but on heating this system to 85° and holding it at that temperature for 16 h, the high-field triplet collapsed and was replaced by a lower-field ethyl resonance. Reaction is quantitative, the relative intensities of the final ethyl to the initial hydride being 5 : 1. The ethyl complex appears to be unstable with respect to loss of ethylene at atmospheric pressure and attempts to prepare solid $Ir(C_2H_5)(pyS)_2(PPh_3)_x$ failed.

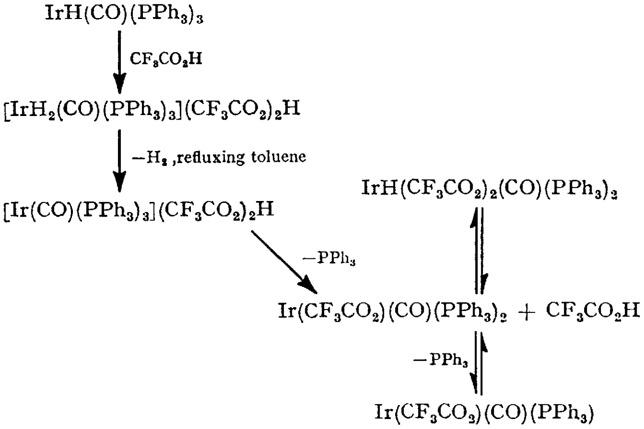
Trifluoroacetic Acid.—When $IrH(CO)(PPh_3)_3$ is refluxed in toluene with a large excess of trifluoroacetic acid a colourless solution is obtained from which a white complex may be precipitated by addition of light petroleum or ether. This complex, $IrH(CF_3CO_2)_2(CO)(PPh_3)_2$ (Table), is identical with that obtained earlier[4] by the reactions:

$$IrCl(CO)(PPh_3)_2 \xrightarrow{CF_3CO_2H} IrHCl(CF_3CO_2)(CO)(PPh_3)_2$$

$$IrHCl(CF_3CO_2)(CO)(PPh_3)_2 \xrightarrow{CF_3CO_2Ag} IrH(CF_3CO_2)_2(CO)(PPh_3)_2$$

Independent studies[11] of the reaction of $IrH(CO)(PPh_3)_3$ with trifluoroacetic acid in chloroform in the cold showed that a colourless salt, evidently $[IrH_2(CO)(PPh_3)_3](CF_3CO_2)_2H$ is formed. Although we have also obtained a similar complex, good analyses have not been obtained. However, the cation may be precipitated as the tetraphenylborate salt, $[IrH_2(CO)(PPh_3)_3]BPh_4$ (Table). If the salt $[IrH_2(CO)(PPh_3)_3](CF_3CO_2)_2H$ is refluxed in toluene for *ca.* 30 min $IrH(CF_3CO_2)_2(CO)(PPh_3)_2$ is formed and may be isolated from the solution. This suggests that the ion $[IrH_2(CO)(PPh_3)_3]^+$ may lose molecular hydrogen on heating to give the square d^8 cation $[Ir(CO)(PPh_3)_3]^+$ to which $(CF_3CO_2)_2H^-$ oxidatively adds forming $IrH(CF_3CO_2)_2(CO)(PPh_3)_2$, one molecule of triphenylphosphine being displaced.

Solutions of $IrH(CF_3CO_2)_2(CO)(PPh_3)_2$ are pale yellow when hot but colourless when cold. This suggests that dissociation of acid is occurring at high temperatures. Thus when $IrH(CF_3CO_2)_2(CO)(PPh_3)_2$ is refluxed in toluene with a large excess of triethylamine the solution remained yellow when cold and the complex, $Ir(CF_3CO_2)(CO)(PPh_3)_2$ was isolated. This shows a band in the i.r. at 1978 cm^{-1} assignable to ν(CO) but no ν(IrH) absorption; carboxylate bands and bands assignable to ν(CF) were observed indicating the presence of a trifluoroacetato-group. The molecular weight was found to be half that expected from the formula and as the complex is a non-electrolyte in dichloromethane and nitromethane solution dissociation of a triphenylphosphine ligand would appear to be indicated. The complete system $IrH(CO)(PPh_3)_3$–CF_3CO_2H known at present is shown in the following Scheme.



SCHEME

On bubbling oxygen through a benzene solution of $Ir(CF_3CO_2)(CO)(PPh_3)_2$ for *ca.* 10 h a yellow complex $Ir(O_2)(CF_3CO_2)(CO)(PPh_3)_2$ [ν(CO) = 2011, ν(O_2) = 860 cm^{-1}] is obtained. This is, however, contaminated with unconverted $Ir(CF_3CO_2)(CO)(PPh_3)_2$. The greater electron withdrawing effect of the trifluoroacetato-group compared to say, the chloride atom in *trans*-$IrCl(CO)(PPh_3)_2$ reduces the tendency of the complex oxidatively to add oxygen.

No reaction was observed between $IrH(CO)(PPh_3)_3$ and acetic acid. In an attempt to obtain the acetato-complex by reacting sodium acetate with $[IrH_2(CO)(PPh_3)_3]BPh_4$ only yellow $IrH(CO)(PPh_3)_3$ was recovered showing that the cationic complex $[IrH_2(CO)(PPh_3)_3]^+$ itself is a stronger acid than acetic acid.

When trifluoroacetic acid is added to a toluene solution of $RhH(CO)(PPh_3)_3$, immediate reaction took place with

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[10] J. D. Gilbert, D. Rose, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 2765; S. R. Fletcher and A. C. Skapski, *J.C.S. Dalton*, 1972, 635.

[11] I. Pi-Chiang and D. M. Roundhill, *Inorg. Chem.*, 1972, **11**, 1937.

liberation of hydrogen. The solution changed colour from deep yellow to a paler yellow. Precipitation by addition of light petroleum or ether yielded the complex, $Rh(CF_3CO_2)(CO)(PPh_3)_2$. This shows i.r. absorption attributable to $\nu(CO)$, $\nu(CO_2)$ (carboxylate), and $\nu(CF)$ (Table). A medium intensity sharp peak at 832 cm^{-1} was also observed. A similar complex has been prepared *via* a different route [12] and found to show an identical spectrum. It has been assumed that the peak at 832 cm^{-1} was associated with co-ordinated oxygen [13] but attempts to carry out the present reaction under completely oxygen-free conditions have failed to give a product with an i.r. spectrum which does not show absorption at 832 cm^{-1}. Further, bubbling oxygen, nitrogen, or carbon monoxide through a solution of the complex did not change the observed i.r. spectrum. In general rhodium complexes show a greater reluctance to add oxidatively than do the analogous iridium(I) complexes and it is concluded that the band at 832 cm^{-1} is not associated with co-ordinated oxygen.

Trifluoromethylsulphonic Acid.—At refluxing toluene temperatures $IrH(CO)(PPh_3)_3$ and trifluoromethylsulphonic acid interact to give a species [A] which we assign as $IrH(CF_3SO_3)_2(CO)(PPh_3)_2$ [$\nu(CO) = 2065$, $\nu(IrH) = 2285$ cm^{-1}] by comparison with $IrH(CF_3CO_2)_2(CO)(PPh_3)_2$. This species cannot, however, be obtained analytically pure and is contaminated, probably by small amounts of $Ir(CF_3SO_3)(CO)(PPh_3)_2$ which would be responsible for the consistently observed weak absorption at 1990 cm^{-1} [$\nu(CO)$] in the i.r. spectrum. The following equilibrium in solution would explain the isolation of a mixture of complexes [*cf.* $IrH(CO)(PPh_3)_3$–CF_3CO_2H Scheme].

$$IrH(CF_3SO_3)_2(CO)(PPh_3)_2 \rightleftharpoons Ir(CF_3SO_3)(CO)(PPh_3)_2 + CF_3SO_3H$$

The absence of a high-field hydridic, or a low-field acidic resonance in the n.m.r. at room temperature lends support to this proposed equilibrium; also, a high conductivity value (113 Ω^{-1} cm^2 mol^{-1}, 10^{-3}M solution in nitromethane) supports acid dissociation.

Only $IrH(CO)(PPh_3)_3$ could be isolated from a refluxing solution of [A] in ethanol containing triethylamine and triphenylphosphine; so that the $Ir(CF_3SO_3)(CO)(PPh_3)_2$ species, if formed, is probably converted to the hydride by hydrogen abstraction from solution. A precedent for this may be found in Robinson's synthesis [14] of platinum-metal hydrides which employs base–ethanol reaction media as reducing agents and sources of hydrogen.

$RhH(CO)(PPh_3)_3$ reacts with trifluoromethylsulphonic acid in cold toluene with effervescence to yield the pale yellow salt $[Rh(CO)(PPh_3)_3]CF_3SO_3,CF_3SO_3H$ (conductivity, 97·05 Ω^{-1} cm^2 mol^{-1}, 10^{-3}M in nitromethane) which contains an acid molecule of crystallisation according to the sulphur analysis, possibly as $(CF_3SO_3)_2H^-$. However, no low-field resonance owing to an acidic proton could be observed in the n.m.r. in deuteriochloroform or nitromethane solution. That the complex is not a hydride is confirmed by the absence of an appropriate band in the i.r. attributable to $\nu(RhH)$ and a high-field resonance in the n.m.r. The carbonyl cation may be obtained as the tetraphenylborate salt, $[Rh(CO)(PPh_3)_3]BPh_4$, by precipitation from methanol–acetone solution containing sodium tetraphenylbotate and this shows no bands attributable to trifluoromethylsulphonate in the i.r. spectrum. The prepared complex is similar to $[Rh(CO)(PPh_3)_3]BF_4$ previously obtained.[15]

EXPERIMENTAL

Microanalysis by the Microanalytical Laboratory, Imperial College. N.m.r. spectra were measured on a Perkin-Elmer model 257 spectrophotometer. M.p.s (uncorrected) were measured on an Electrothermal apparatus. Molecular weights were determined using a Hitachi–Perkin-Elmer 115 osmometer. Analytical and molecular weight data are collected in the Table.

Dried, degassed solvents of reagent grade were used throughout, light petroleum was of b.p. 60—80 °C fraction and all reactions were normally carried out under nitrogen. All samples were vacuum dried.

p-Nitrophenolato(carbonyl)bis(triphenylphosphine)iridium(I).—$IrH(CO)(PPh_3)_3$ (0·2 g) and *p*-nitrophenol (0·1 g) were refluxed in toluene (40 ml) for *ca.* 3 h. After cooling the volume was reduced to 15 ml and an approximately equal volume of ethanol added to precipitate the *complex* as yellow microcrystals which were filtered off and washed with ethanol (*ca.* 0·15 g, 85%, m.p. 210—214° decomp.).

Hydridobis(pyridine-2-thiolato)(triphenylphosphine)iridium(III).—$IrH(CO)(PPh_3)_3$ (0·2 g) and pyridine-2-thiol (0·2 g) were refluxed in toluene (40 ml) for *ca.* 3 h. After cooling the volume was reduced to 10 ml and ethanol (20 ml) was added to precipitate the *complex* as yellow microcrystals which were filtered off and washed with ethanol and ether (*ca.* 0·12 g, 90%).

Hydridobis(pyridine-2-thiolato)bis(triphenylphosphine)iridium(III).—$IrH(pyS)_2(PPh_3)$ (0·2 g) was refluxed in toluene (50 ml) containing triphenylphosphine (0·5 g) for *ca.* 1 h. After cooling the volume was reduced to 15 ml and the *complex* precipitated as yellow microcrystals by the addition of an equal volume of ethanol. The *complex* was filtered off and washed with ethanol and ether (*ca.* 0·25 g, 90%; m.p. 175—176 decomp.).

Hydridobis(trifluoroacetato)carbonylbis(triphenylphosphine) iridium(III).—$IrH(CO)(PPh_3)_3$ (0·2 g) was refluxed in toluene (50 ml) with trifluoroacetic (1 ml) acid for *ca.* 1·5 h. After cooling the solvent was removed and the colourless, sticky residue was treated with ether (35 ml). The *complex* was precipitated as white microcrystals, collected by filtration and washed with ether (*ca.* 0·2 g, 95%; m.p. yellow at 140° and then melts with decomp. at 210—215°).

Trifluoroacetato(carbonyl)bis(triphenylphosphine)iridium(I).—$IrH(CF_3CO_2)_2(CO)(PPh_3)_2$ (0·2 g) was refluxed in toluene (50 ml) with triethylamine (2 ml) for *ca.* 4 h; the solution turned yellow and remained yellow on subsequent

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[12] R. W. Mitchell, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 3224.

[13] S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, 1965, **87**, 2581.

[14] N. Ahmed, S. D. Robinson, and M. F. Uttley, *J.C.S. Dalton*, 1972, 843.

[15] P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 3322.

cooling. The volume was reduced to *ca.* 20 ml and the yellow *complex* was precipitated by addition of light petroleum (30 ml). The *complex* was filtered off, washed with petroleum and dried *in vacuo*. When dry the impure complex was washed with water and redried *in vacuo* (0·15 g, 90%; m.p. 200—203 decomp.). [If the complex was not washed in water it was contaminated with traces of $Et_3NHO_2CCF_3$ which caused partial reconversion to $IrH(CF_3CO_2)_2(CO)(PPh_3)_2$ after about 2 days.]

Trifluoroacetato(carbonyl)bis(triphenylphosphine)rhodium(I).—$RhH(CO)(PPh_3)_3$ (0·2 g) was stirred in toluene (40 ml) and 1 ml trifluoroacetic acid was added. Immediate effervescence occurred and the solution became a paler yellow. After stirring for 30 min the solvent was removed and the residue was treated with ether (30 ml). The yellow *complex* was collected by filtration and washed with ether (*ca.* 0·15 g, 90%; m.p. 184—187° decomp.).

Dihydridocarbonyltris(triphenylphosphine)iridium(III) *Hydrogen Bis(trifluoroacetate)*.—$IrH(CO)(PPh_3)_3$ (0·2 g) was stirred with trifluoroacetic acid (1 ml) in toluene in the cold for *ca.* 1 h. The colourless solution was evaporated to dryness and the colourless residue treated with ether (30 ml). White *microcrystals* were formed and were collected by filtration and washed with ether (*ca.* 0·23 g, 90%; m.p. turns yellow at 143—144° and then melts with decomp. at 200—205°).

Dihydridocarbonyltris(triphenylphosphine)iridium(III) *Tetraphenylborate*.—$[IrH_2(CO)(PPh_3)_3](CF_3CO_2)_2H$ (0·2 g), prepared as described above was dissolved in acetone (15 ml) and a solution of $NaBPh_4$ (0·14 g) in acetone (5 ml) was added; the mixture was stirred for *ca.* 30 min. Methanol (5 ml) and water (5 ml) were added and the volume of the solution reduced *slowly* to *ca.* 20 ml whereupon a white precipitate formed. The white *microcrystals* were filtered off and washed with acetone–water (1 : 1) (*ca.* 0·18 g, 90%; m.p. 175—178° decomp.).

Dihydridocarbonyltris(triphenylphosphine)iridium(III) *Trifluoromethylsulphonate*.—$IrH(CO)(PPh_3)_3$ (0·5 g) was stirred at room temperature in toluene (50 ml) with trifluoromethylsulphonic acid (0·5 ml) for *ca.* 1 h. The volume was reduced to *ca.* 15 ml and 35 ml diethyl ether was added to precipitate the cream-coloured complex which was filtered off, washed with a little ether, and dried *in vacuo*. The complex was washed with water until the washings were acid-free and then re-dried *in vacuo* at 95°. Dissolution of the complex in a minimum of ethanol, filtration, and crystallisation by careful addition of toluene and slow evaporation followed by cooling to −70° afforded the cream-coloured *microcrystals* which were filtered off, washed with a little cold toluene and ether, and dried *in vacuo* (0·35 g, 60% decomp. 198° and then melts at 203—204°).

Carbonyltris(triphenylphosphine)rhodium(I) *Trifluoromethylsulphonate*.—To a solution of $RhH(CO)(PPh_3)_3$ (0·2 g) in toluene (50 ml) was added *ca.* 0·5 ml trifluoromethylsulphonic acid. Immediate effervescence occurred and the solution was stirred for *ca.* 1 h. The toluene was removed by vacuum evaporation and the pale yellow residue dissolved in ether (30 ml). Pale yellow microcrystals of the complex precipitated out of solution upon standing overnight at −25°. The *microcrystals* were filtered off, washed with ether, and dried *in vacuo* (*ca.* 0·18 g, 85%: m.p. 159—163 decomp.).

Hydridobis(trifluoromethylsulphonato)carbonylbis(triphenylphosphine)iridium(III).—To a solution of $IrH(CO)(PPh_3)_3$ (0·5 g) in toluene (50 ml) was added 0·5 ml trifluoromethylsulphonic acid and the solution refluxed for *ca.* 6 h. The volume was reduced to *ca.* 10 ml and ether (15 ml) was added to complete precipitation of the pale yellow complex which was filtered off, washed with ether, and dried *in vacuo*. The complex was further washed with water until the washings were acid-free and dried *in vacuo* at 75°. Dissolution of the complex in a minimum of ethanol, filtration, and crystallisation by careful addition of toluene and slow evaporation followed by cooling to −70° afforded the pale yellow *complex* which was filtered off, washed with a little cold toluene and ether, and dried *in vacuo* (0·38 g, 73%; m.p. decomp. 247° then melts 252—255°). This complex could not be obtained analytically pure (Found: C = 47·6; H = 3·3; S = 6·8. $C_{39}H_{31}F_6IrO_7P_2S_2$ requires C = 44·8; H = 3·0; S = 6·1%. Molecular weight determined as being 557, requires 1043).

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