

## Iridium(III) Complexes of Diphenylphosphinous Acid and Secondary Phosphites ‡

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Treating  $[\text{IrCl}(\text{1,5-C}_8\text{H}_{12})_2]$  with  $\text{PPh}_2\text{Cl}$  and water gives  $[\text{IrHCl}(\text{1,5-C}_8\text{H}_{12})\{\text{(PPh}_2\text{O)}_2\text{H}\}]$  (1). Diene dissociation readily occurs; in the absence of added ligand polymeric materials are probably formed, but in the presence of bidentate ligands, complexes  $[\text{IrHCl}(\text{L-L})\{\text{(PPh}_2\text{O)}_2\text{H}\}]$  [ $\text{L-L} = \text{Ph}_2\text{AsCH}_2\text{CH}_2\text{-AsPh}_2$ ,  $\text{PhSCH}_2\text{CH}_2\text{SPh}$ , or  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ] are formed. Reaction with  $\text{BF}_3$  and  $\text{HBF}_4$  leads to the respective formation of  $[\text{IrHCl}(\text{L-L})\{\text{(PPh}_2\text{O)}_2\text{BF}_2\}]$  ( $\text{L-L} = \text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$  or  $\text{PhSCH}_2\text{CH}_2\text{SPh}$ ) and  $[\text{IrHCl}(\text{L-L})\{\text{(PPh}_2(\text{OH}))_2\}\text{BF}_4]$  ( $\text{L-L} = \text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$  or  $\text{PhSCH}_2\text{CH}_2\text{SPh}$ ). The latter compounds readily lose  $\text{HF}$  to give the  $\text{BF}_2$ -capped products. Structural characterisation is by i.r.,  $^1\text{H}$ , and  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectroscopy. A heterobimetallic compound  $[\text{PPh}_3(\text{CH}_2\text{Ph})][(\text{Et}_2\text{NCS}_2)\text{Pt}(\mu\text{-PPh}_2\text{S})_2\text{-IrHCl}\{\text{(PPh}_2\text{O)}_2\text{H}\}]$  has been isolated from  $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PPh}_2\text{S})_2]$  and  $[\text{IrHCl}(\text{1,5-C}_8\text{H}_{12})\{\text{(PPh}_2\text{O)}_2\text{H}\}]$  and heterobimetallic and trimetallic compounds can be prepared by substitution of the phosphinous acid proton by a second metal ion. Consequently, compounds  $[\text{IrHCl}(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)(\mu\text{-PPh}_2\text{O})_2\text{M}(\text{acac})]$  ( $\text{acac} = \text{acetylacetonate}$ ) and  $[\{\text{IrHCl}(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{-AsPh}_2)(\text{PPh}_2\text{O})_2\}_2\text{M}]$  ( $\text{M} = \text{VO}^{2+}$  or  $\text{Co}^{2+}$ ) have been isolated. Treating  $[\text{Ir}(\text{MeCN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$  with  $\text{P}(\text{OMe})_2(\text{O})\text{H}$  yields  $[\text{IrH}(\text{CO})(\text{PPh}_3)_2\{\text{P}(\text{OMe})_2\text{O}\}_2\text{H}]\text{ClO}_4$ . Finally, solution addition of  $\text{P}(\text{OR})_2\text{-}(\text{O})\text{H}$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ , or  $\text{Ph}$ ) and  $\text{PPh}_2(\text{O})\text{H}$  to  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$  yields unstable hydrides whose composition and stereochemistry have been deduced *in situ* using a combination of  $^1\text{H}$  and  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectroscopy.

In recent years a number of transition metal compounds containing the hydrogen-bonded  $\text{R}_2\text{POHOPR}_2$  ligands ( $\text{R} = \text{Ph}$ ,  $\text{OMe}$ , or  $\text{OEt}$ ) have been synthesised and some reactions of these compounds reported.<sup>1</sup> To date, however, the majority of these studies have been confined to complexes of palladium(II) and platinum(II). In this paper, the full details<sup>2</sup> of our research to synthesise and characterise related complexes of iridium are presented.

### Results and Discussion

Treatment of  $[\{\text{IrCl}(\text{C}_8\text{H}_{12})_2\}]$  with an excess of chlorodiphenylphosphine in methanol-water (7 : 1 v/v) solvent gives within 20 min a precipitate of the colourless microcrystalline complex  $[\text{IrHCl}(\text{C}_8\text{H}_{12})\{\text{(PPh}_2\text{O)}_2\text{H}\}]$  (1). Evidence for this formulation comes from its  $^1\text{H}$  n.m.r. spectrum in  $\text{CDCl}_3$  which shows resonances due to  $\text{IrH}$  and  $-\text{OH}$  at  $\delta -15.2$  (t,  $^2J_{\text{PH}} = 12.0$  Hz) and 10.3 p.p.m. (br) respectively. The latter resonance disappears on addition of  $\text{D}_2\text{O}$  and its position is both temperature and concentration dependent. The size of the phosphorus-hydrogen coupling constant indicates that the hydrido-group is *cis* to two magnetically equivalent phosphorus atoms and this is supported by the single resonance at  $\delta 48.2$  p.p.m. found in the  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectrum of (1). As further proof of this structure, the  $^1\text{H}$  n.m.r. spectrum also contains five distinct diene resonances (see Experimental section) in the range  $\delta 2.0$ – $5.0$  p.p.m. of relative intensity 2 : 2 : 4 : 2 : 2. This increased number of cyclo-octa-1,5-diene signals compared to those found in the  $^1\text{H}$  n.m.r. spectrum of the related iridium(I) cation  $[\text{Ir}(\text{C}_8\text{H}_{12})\{\text{PPh}_2(\text{OMe})\}_2]^+$  [ $\delta 4.85$  (olefinic) and 2.30 p.p.m. (methylene)]<sup>3</sup> is consistent with the presence of H and Cl axial ligands. Finally, the i.r.

spectrum of (1) shows a band due to  $\nu(\text{IrH})$  at  $2\,250\text{ cm}^{-1}$  and a strong band at  $1\,015\text{ cm}^{-1}$  assigned to  $\nu(\text{PO})$  in a  $(\text{PPh}_2\text{O})_2\text{H}$  ring.<sup>4,5</sup>

An additional complication here is that in  $\text{CDCl}_3$ , compound (1) slowly loses cyclo-octa-1,5-diene ( $^1\text{H}$  n.m.r. evidence) to give various species which are possibly polymeric in nature. The retention of triplet patterns in the several new low-frequency  $\text{IrH}$   $^1\text{H}$  n.m.r. signals suggests however that the hydrido and  $(\text{Ph}_2\text{PO})_2\text{H}$  ligands remain *cis* to each other in all these complexes.

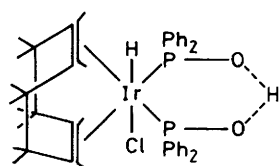
Although further speculation on the nature of these species is unwarranted at this juncture, this facile dissociation of  $\text{C}_8\text{H}_{12}$  from compound (1) allows the ready synthesis of a series of stable, monomeric complexes  $[\text{IrHCl}(\text{L-L})\{\text{(PPh}_2\text{O)}_2\text{H}\}]$  [ $\text{L-L} = \text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ , (2);  $\text{PhSCH}_2\text{CH}_2\text{SPh}$ , (3); and  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ , (4)]. These complexes are obtained as colourless solids by shaking chloroform solutions containing equimolar quantities of (1) and  $\text{L-L}$  for several hours, and for compounds (2) and (3),  $^{31}\text{P}$ - $\{^1\text{H}\}$  and  $^1\text{H}$  n.m.r. and i.r. spectral measurements (see Experimental section) confirm a single stereochemistry analogous to (1).

For the compound  $[\text{IrHCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\{\text{(PPh}_2\text{O)}_2\text{H}\}]$  two isomers are formed. The major isomer (4a) has the same stereochemistry as compounds (1)–(3) [ $\delta(\text{IrH}) -20.06$  p.p.m. (triplet of triplets),  $^2J_{\text{PH}} 11.0$  and 13.5 Hz]. Its  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectrum shows a complex AA'BB' spin pattern and this has been successfully simulated using the PANIC program routine<sup>6</sup> (see Experimental section).

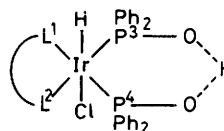
Phosphorus-31 and  $^1\text{H}$  n.m.r. spectral studies also show the presence of a minor isomer (4b) (ca. 5% yield) which, although impossible to isolate in a pure state, can be characterised spectroscopically. Thus, the  $^1\text{H}$  n.m.r. spectrum of (4b) in  $\text{CDCl}_3$  shows an  $\text{IrH}$  resonance centred at  $\delta -9.98$  p.p.m. split into a large doublet [ $^2J_{\text{PH}}(\text{trans}) = 151$  Hz] with three smaller doublet splittings [ $^2J_{\text{PH}}(\text{cis}) 17.9$ , 14.3, and 14.3 Hz] superimposed. The  $^{31}\text{P}$  proton coupled n.m.r. spectrum of (4b) confirms that it is a phosphorus atom in the  $\text{Ph}_2\text{PCH}_2\text{-CH}_2\text{PPh}_2$  group which is *trans* to the hydride ligand.

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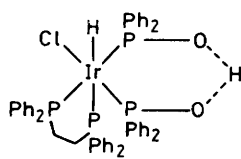
‡ Non-S.I. units employed:  $G = 10^{-4}$  T; B.M. =  $0.927 \times 10^{-23}$  A m<sup>2</sup>.



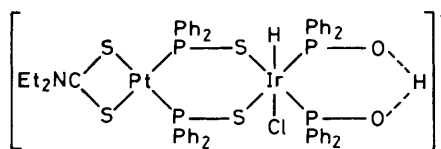
(1)



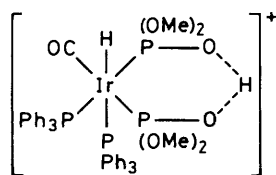
(2); L-L = Ph<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>AsPh<sub>2</sub>  
 (3); L-L = PhSCH<sub>2</sub>CH<sub>2</sub>SPh  
 (4a); L-L = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>



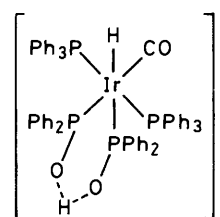
(4b)



(7)



(12)

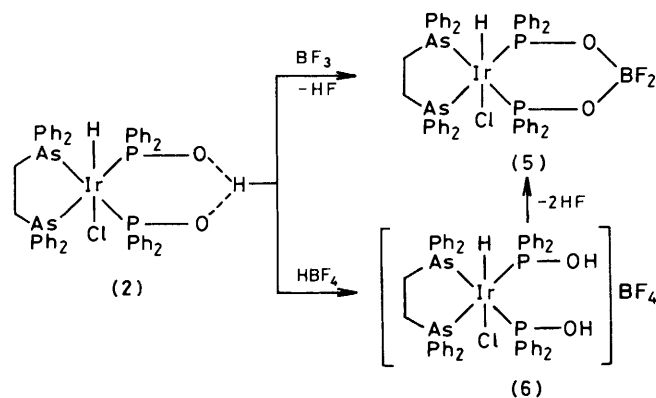


(13)

**Reactions with BF<sub>3</sub>·Et<sub>2</sub>O and HBF<sub>4</sub>.**—If [IrHCl(Ph<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>AsPh<sub>2</sub>){(PPh<sub>2</sub>O)<sub>2</sub>H}] (2) is shaken with an excess of BF<sub>3</sub>·Et<sub>2</sub>O, a new colourless non-conducting compound (5) is formed. The i.r. spectrum of (5) shows additional broad bands, ν(BF), in the region 7 1 000—1 100 cm<sup>-1</sup> and its <sup>1</sup>H and <sup>31</sup>P-<sup>1</sup>H} n.m.r. spectra in CDCl<sub>3</sub> show shifted but similar patterns to (2) with resonances at δ -20.29 (t, <sup>2</sup>J<sub>PH</sub> = 13.6 Hz, IrH) and 49.8 p.p.m. respectively. The latter <sup>31</sup>P n.m.r. resonance is broadened due to quadrupolar interaction with the boron nucleus<sup>8</sup> and hence complex (5) can be formulated as [IrHCl(Ph<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>AsPh<sub>2</sub>){(PPh<sub>2</sub>O)<sub>2</sub>BF<sub>2</sub>}]<sup>-</sup>. Further support for this conclusion is provided by the <sup>19</sup>F n.m.r. spectrum of (5) which shows an AB pattern with δ<sub>A</sub> -134.5, δ<sub>B</sub> -134.4 p.p.m., and <sup>2</sup>J<sub>FF</sub> = 8 Hz. Each of these lines is further broadened into an unresolved quartet by quadrupolar coupling. A similar product, [IrHCl(PhSCH<sub>2</sub>CH<sub>2</sub>SPh){(PPh<sub>2</sub>O)<sub>2</sub>BF<sub>2</sub>}]<sup>-</sup>, has been obtained using the same synthetic procedure.

If an aqueous solution of HBF<sub>4</sub> is added to a solution of compound (2) in CHCl<sub>3</sub>, a cationic complex, [IrHCl(Ph<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>AsPh<sub>2</sub>){(PPh<sub>2</sub>O)<sub>2</sub>H}]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (6), is formed. The <sup>1</sup>H and <sup>31</sup>P-<sup>1</sup>H} n.m.r. spectra in CDCl<sub>3</sub> show the expected resonances at δ -19.9 (t, <sup>2</sup>J<sub>PH</sub> = 13.7 Hz, IrH) and 55.0 (s) p.p.m. respectively. This compound is stable in both the solid state and in the presence of an excess of HBF<sub>4</sub>, but solutions in CHCl<sub>3</sub> readily convert to (5) by loss of HF (Scheme 1) and this conversion can be monitored either by <sup>1</sup>H or <sup>31</sup>P-<sup>1</sup>H} n.m.r. spectroscopy or by conductivity changes. The formation of a -BF<sub>2</sub>-capped complex by reaction with HBF<sub>4</sub> has been previously observed with [hydrogenbis(dimethylphosphito)nickel(II)] complexes.<sup>9</sup>

**Mixed-metal Complexes.**—An important property of these diphenylphosphinito and related complexes is that they can be used to prepare heterobimetallic compounds.<sup>1</sup> Thus, if equimolar quantities of [IrHCl(C<sub>8</sub>H<sub>12</sub>){(PPh<sub>2</sub>O)<sub>2</sub>H}] (1) and



Scheme 1.

[PPh<sub>3</sub>(CH<sub>2</sub>Ph)][Pt(S<sub>2</sub>CNEt<sub>2</sub>)(PPh<sub>2</sub>S)<sub>2</sub>]<sup>10</sup> are shaken in CHCl<sub>3</sub>, work-up of the resultant orange solution gives the unusual heterobimetallic complex [PPh<sub>3</sub>(CH<sub>2</sub>Ph)][(Et<sub>2</sub>NCS<sub>2</sub>)Pt(μ-PPh<sub>2</sub>S)<sub>2</sub>IrHCl((PPh<sub>2</sub>O)<sub>2</sub>H)] (7). Evidence for this formulation comes from its <sup>31</sup>P-<sup>1</sup>H} n.m.r. spectrum in CDCl<sub>3</sub> which shows separate resonances for the phosphorus nuclei bound to Ir and Pt, and for the PPh<sub>3</sub>(CH<sub>2</sub>Ph)<sup>+</sup> cation (see Experimental section). The <sup>1</sup>H n.m.r. spectrum shows the hydride resonance at δ -26.7 p.p.m. (t, <sup>2</sup>J<sub>PH</sub> = 18 Hz) as well as the expected ethyl and phenyl signals. The analogous compound with the NH<sub>2</sub>Et<sub>2</sub><sup>+</sup> cation can also be isolated.\*

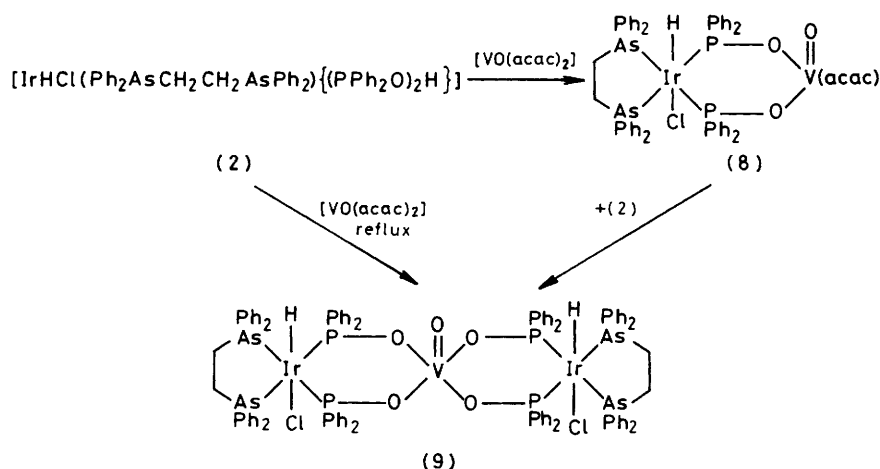
A more usual approach to the synthesis of heterobimetallic

\* In ref. 2 these complexes are correctly formulated as anions, but J. A. S. Duncan, D. Hedden, D. M. Roundhill, T. A. Stephenson, and M. D. Walkinshaw, *Angew. Chem.*, 1982, **94**, 463, formulate the complexes incorrectly as being uncharged.

complexes is the substitution of the hydroxylic hydrogen by a second metal ion.<sup>11-14</sup> Thus if the compound  $[\text{IrHCl}(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)\{(\text{PPh}_2\text{O})_2\text{H}\}]$  (2) is reacted with  $[\text{VO}(\text{acac})_2]$  or  $[\{\text{Co}(\text{acac})_2\}_4]$  (acac = acetylacetonate), substitution of this proton occurs by vanadium or cobalt. The green vanadyl complex (8) is paramagnetic [ $\mu_{\text{eff.}}(300 \text{ K}) = 1.87 \text{ B.M.}$ ]. The i.r. spectrum shows bands for  $\nu(\text{IrH})$  (2 200),  $\nu(\text{PO})$  (1 020 and 1 000),  $\nu(\text{VO})$  (985  $\text{cm}^{-1}$ ), and bands at 1 595 and 1 525  $\text{cm}^{-1}$  from co-ordinated acac.<sup>15,16</sup> Osmometric molecular weight measurements in benzene give a value of 1 222 (calc., 1 282.5) indicative of a heterobimetallic complex having a co-ordinated acac ligand. Using extended reaction times, further substitution occurs to give a pale blue compound in low (ca. 5%) yield. Higher yields of this very insoluble product [ $\mu_{\text{eff.}}(300 \text{ K}) = 1.87 \text{ B.M.}$ ] can also be obtained under reflux conditions. The i.r. spectrum now shows bands due to  $\nu(\text{IrH})$  (2 220),  $\nu(\text{PO})$  (1 025 and 1 005), and  $\nu(\text{VO})$  (988  $\text{cm}^{-1}$ ), but no bands due to co-ordinated acac, and therefore this compound is formulated as the trimetallic complex (9) (Scheme 2). Further evidence for these

and 1 520  $\text{cm}^{-1}$  for acetylacetonate complexed to Co in (10). For compound (10) the value for  $\mu_{\text{eff.}}$  is 4.38 B.M. at 303 K. The electronic spectrum of (10) in  $\text{CH}_2\text{Cl}_2$  shows bands at 19 801 ( $\epsilon = 38$ ), 18 018 (66), and 16 806  $\text{cm}^{-1}$  (66  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). The solid-state spectrum of (11) shows bands at 41 666 34 482, 18 691, 17 331, and 15 872  $\text{cm}^{-1}$ . The visible portion of these spectra corresponds to absorptions diagnostic of a tetrahedral cobalt(II) geometry.<sup>19</sup>

**Hydrides from P-H Addition.** The synthesis of  $[\text{IrHCl}(\text{C}_8\text{H}_{12})\{(\text{PPh}_2\text{O})_2\text{H}\}]$  by hydrolysis of chlorodiphenylphosphine most likely involves protonation from the HCl formed, rather than from  $\text{PPh}_2(\text{O})\text{H}$ . Hydrides of platinum(II) and iridium(III) have nevertheless been previously obtained from P-H addition reactions.<sup>7,20,21</sup> We have now carried out a series of reactions to show that such a pathway is a viable general route to iridium(III) hydrides, and have used i.r. and n.m.r. spectroscopy to elucidate the stereochemistry of the products. Thus,  $[\text{Ir}(\text{MeCN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$  has a labile MeCN ligand and addition of an excess of dimethyl phosphite



Scheme 2.

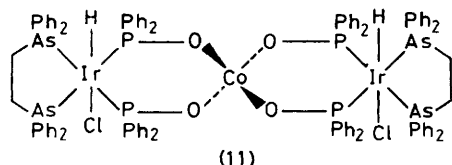
conclusions comes from e.s.r. studies. The e.s.r. spectrum of (8) at 303 K shows eight lines at  $g = 1.97$  [ $^{51}\text{V}$ ,  $I = \frac{7}{2}$ ,  $A = 100(\pm 5) \text{ G}$ ]. At 153 K two superimposed octets are observed due to  $g_{\perp}$  and  $g_{\parallel}$  differences ( $A_{\parallel} = 190 \text{ G}$ ,  $A_{\perp} = 60 \text{ G}$ ). These values are similar to those of  $[\text{VO}(\text{acac})_2]$ .<sup>17,18</sup> The e.s.r. spectrum of (9) at 303 K shows  $g = 2.00$  [ $^{51}\text{V}$ ,  $I = \frac{7}{2}$ ,  $A = 95(\pm 5) \text{ G}$ ].

A similar reaction occurs between  $[\text{IrHCl}(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)\{(\text{PPh}_2\text{O})_2\text{H}\}]$  (2) and  $[\{\text{Co}(\text{acac})_2\}_4]$  to sequentially give the bimetallic complex  $[\text{IrHCl}(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)(\mu\text{-PPh}_2\text{O})_2\text{Co}(\text{acac})]$  (10) and the very insoluble trimetallic complex  $[\{\text{IrHCl}(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)(\mu\text{-PPh}_2\text{O})_2\}_2\text{Co}]$  (11). The osmometric molecular weight of (10) in benzene is 1 339 (calc., 1 274.5). Relevant i.r. data are  $\nu(\text{IrH})$ , 2 195 (10), 2 165 (11);  $\nu(\text{PO})$  1 025, 1 010, and 1 000 (10), 1 035, 1 020, and 1 000  $\text{cm}^{-1}$  (11); and bands at 1 585

leads to P-H addition and formation of  $[\text{IrH}(\text{CO})(\text{PPh}_3)_2\{[\text{P}(\text{OMe})_2\text{O}]_2\text{H}\}]\text{ClO}_4$  (12). This complex, which is a 1 : 1 electrolyte in nitromethane, contains bands in its i.r. spectrum at 2 120 [ $\nu(\text{IrH})$ ], 2 080 [ $\nu(\text{CO})$ ], and 1 000  $\text{cm}^{-1}$  [ $\nu(\text{PO})$ ]. The  $^1\text{H}$  n.m.r. spectrum in  $\text{CDCl}_3$  shows resonances due to  $-\text{OH}$  at  $\delta$  11.05 p.p.m. (br) and for IrH at  $\delta$  -12.03 p.p.m. The latter is a double octet with  $^2J_{\text{PH}} = 108 \text{ Hz}$  for hydride *trans* to  $\text{PPh}_3$  and additional  $^2J_{\text{PH}}$  (*cis*) couplings of 12, 15, and 9 Hz. Assuming the smallest coupling of phosphorus to hydride ( $^2J_{\text{PH}} = 9 \text{ Hz}$ ) is from  $\text{PPh}_3$ , the stereochemistry of the product (12) is as shown with CO and  $\text{PPh}_3$  *trans* to the  $[\text{P}(\text{OMe})_2\text{O}]_2\text{H}$  ligand [*cf.* the minor isomer (4b)].

Reaction of either secondary phosphites or  $\text{PPh}_2(\text{O})\text{H}$  with *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$  also gives iridium(III) hydride complexes. Unfortunately, attempts to isolate products leads to formation of substantial quantities of  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ , indicating that these iridium(III) hydride adducts are stable only in the presence of an excess of ligand.

Therefore, attempts have been made to determine the stereochemistry of these products *in situ* using both  $^{31}\text{P}$ - $\{^1\text{H}\}$  and  $^1\text{H}$  n.m.r. (*IrH* region only) spectroscopic techniques. It must be admitted that unambiguous stereochemical assignment has not been achieved in all cases because invariably several geometric isomers of  $[\text{IrHCl}(\text{CO})(\text{PR}_2\text{O})_2]$



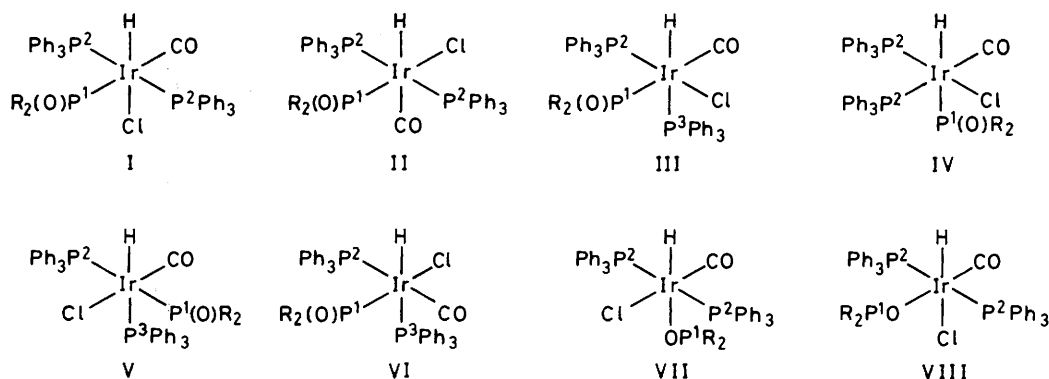


Figure. Geometrical (and linkage) isomers of  $[\text{IrHCl}(\text{CO})(\text{PR}_2\text{O})(\text{PPh}_3)_2]$

Table. Hydrogen-1 n.m.r. spectra in  $\text{CDCl}_3$  at 301 K [ $\delta(\text{IrH})$  region only] of the products from the reaction of *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$  with  $\text{P}(\text{OR})_2(\text{O})\text{H}$  or  $\text{PPh}_2(\text{O})\text{H}$

Reagent	Isomer of $[\text{IrHCl}(\text{CO})(\text{PR}_2\text{O})(\text{PPh}_3)_2]^a$	$\delta(\text{IrH})/\text{p.p.m.}$	$^2J_{\text{P}^1\text{H}}/\text{Hz}$	$^2J_{\text{P}^2\text{H}}/\text{Hz}$	$^2J_{\text{P}^3\text{H}}/\text{Hz}$
$\text{P}(\text{OMe})_2(\text{O})\text{H}$	I	-17.0	18 (d)	11 (t)	
$\text{P}(\text{OMe})_2(\text{O})\text{H}$	II	-7.9	16 (d)	14 (t)	
$\text{P}(\text{OEt})_2(\text{O})\text{H}$	I	-17.4	18 (d)	11 (t)	
$\text{P}(\text{OEt})_2(\text{O})\text{H}$	II	-8.3	18 (d)	11 (t)	
$\text{P}(\text{OPh})_2(\text{O})\text{H}$	I	-17.0	20 (d)	11 (t)	
$\text{P}(\text{OPh})_2(\text{O})\text{H}$	III, V, VI <sup>b</sup>	-9.2	10 (d)	6 (d)	154 (d)
$\text{P}(\text{OPh})_2(\text{O})\text{H}$	IV	-8.4	8 (d)	14 (d)	270 (d)
$\text{PPh}_2(\text{O})\text{H}$	I	-16.9	16 (d)	12 (t)	
$\text{PPh}_2(\text{O})\text{H}$	VII, VIII <sup>b</sup>	-15.8		12 (t)	
$\text{PPh}_2(\text{O})\text{H}$	VII, VIII <sup>b</sup>	-15.4		11 (t)	
$\text{PPh}_2(\text{O})\text{H}$	(13) <sup>c</sup>	-10.9	18 (d)	14 (t)	112 (d)
$\text{PPh}_2(\text{O})\text{H}$	IV, V, VI <sup>b</sup>	-8.8	18 (d)	11 (d)	123 (d)

<sup>a</sup> See Figure for diagrams of isomers. <sup>b</sup> Identification between alternatives uncertain. <sup>c</sup> Compound (13) is  $[\text{IrH}(\text{CO})(\text{PPh}_3)_2\{\text{PPh}_2\text{O}_2\text{H}\}]\text{Cl}$ .

$(\text{PPh}_3)_2]$  are produced. Percentage distribution of these isomers has been estimated by relative integration of their  $\text{IrH}$  resonances. The  $^1\text{H}$  n.m.r. data (hydride region) are listed in the Table and various possible isomers of  $[\text{IrHCl}(\text{CO})(\text{PR}_2\text{O})(\text{PPh}_3)_2]$  are given in the Figure.

Thus, the  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectrum in  $\text{CDCl}_3$  of  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$  and an excess of  $\text{P}(\text{OMe})_2(\text{O})\text{H}$  shows  $\delta$  41.7 (t) and -7.8 p.p.m. (d,  $^2J_{\text{P}^1\text{P}^2} = 34$  Hz) (isomer I);  $\delta$  25.9 (t) and 5.5 p.p.m. (d,  $^2J_{\text{P}^1\text{P}^2} = 20$  Hz) (isomer II). For  $\text{P}(\text{OEt})_2(\text{O})\text{H}$  we find  $\delta$  35.9 (t) and -7.1 p.p.m. (d,  $^2J_{\text{P}^1\text{P}^2} = 32$  Hz) (isomer I);  $\delta$  20.2 p.p.m. (t,  $^2J_{\text{P}^1\text{P}^2} = 19$  Hz) (isomer II) with the  $\text{PPh}_3$  resonance ( $\text{P}^2$ ) unresolvable from the intense signal of free  $\text{P}(\text{OEt})_2(\text{O})\text{H}$ . On immediate addition of  $\text{P}(\text{OMe})_2(\text{O})\text{H}$ , isomer I is formed in 90% yield, but after 48 h isomer II is present in excess. With  $\text{P}(\text{OEt})_2(\text{O})\text{H}$ , isomer II is present in 86% yield after 7 h. Solution i.r. measurements in  $\text{CDCl}_3$  with added  $\text{P}(\text{OMe})_2(\text{O})\text{H}$  give  $\nu(\text{CO}) = 2065$ ,  $\nu(\text{IrH}) = 2130$   $\text{cm}^{-1}$  (isomer I); and  $\nu(\text{CO}) = 2053$ ,  $\nu(\text{IrH}) = 2130$   $\text{cm}^{-1}$  (isomer II).

When diphenyl phosphite is added to  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$  three isomeric hydrides are formed. One minor isomer has stereochemistry I, and the second minor isomer (also in approximately 15% yield) has stereochemistry IV. This latter assignment is based on the premise that the large coupling ( $^2J_{\text{PH}} = 270$  Hz) results from *trans* coupling of the hydride to a diphenyl phosphito-ligand. The major solution isomer (70%) shows a *trans* coupling of hydride to triphenylphosphine ( $^2J_{\text{PH}} = 154$  Hz). The observed double doublet of doublets multiplicity does not unambiguously discriminate

between isomers III, V, and VI. Diphenylphosphinous acid will also undergo P-H oxidative addition to  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ . Five products are formed in relative amounts 1 : 2.7 : 1.1 : 0.6 : 13.5. These iridium(III) hydrides have  $^1\text{H}$  n.m.r. resonances centred at  $\delta$  -8.8, -10.9, -15.4, -15.8, and -16.9 p.p.m., respectively. The predominant isomer has structure I. The product having  $\delta$  -10.9 p.p.m. shows a double doublet of triplets spin multiplicity indicating spin coupling to four, rather than three, co-ordinated phosphorus nuclei. We believe that chloride substitution by diphenylphosphinous acid has occurred to give a complex  $[\text{IrH}(\text{CO})(\text{PPh}_3)_2\{\text{PPh}_2\text{O}_2\text{H}\}]\text{Cl}$ , analogous to complex (12). However, assuming magnetically equivalent  $\text{PPh}_3$  groups and a large *trans* diphenylphosphinito-coupling to the hydrido-ligand, structure (13) is proposed for this cation. The isomers centred at  $\delta$  -15.4 and -15.8 p.p.m. show triplet spin coupling to two, rather than three, co-ordinated phosphorus nuclei. It is probable that these are isomers with *O*-bonded diphenylphosphinito-ligands having been conceptually formed by *O*-H rather than *P*-H addition. We identify the isomers as VII and VIII but cannot unambiguously assign our spectral data to a particular isomer of the pair. The final isomer from diphenylphosphinous acid ( $\delta$  -8.8 p.p.m.) can be identified as having hydride and phosphorus mutually *trans*, but in the absence of additional information or coupling constant magnitudes several isomer assignments are possible.

In conclusion it appears that the reactions of secondary phosphites and diphenylphosphinous acid with iridium(I) complexes are dominated by the formation of iridium(III)

hydride complexes. Their formation is a likely consequence of an oxidative addition of the P-H bond, although in some cases hydride formation may be the result of HCl or O-H bond addition. In a separate publication we will report our results on the chemistry of rhodium(I) compounds with these types of phosphorus ligand. In this case both rhodium(I) and rhodium(III) complexes are obtained, but in no case has product hydride formation been observed. The greater ease of iridium(I) over rhodium(I) to undergo protonation to the metal(III) hydrides follows the general pattern for the chemistry of these metals, and the failure to observe rhodium(III) hydrides may reflect their greater instability to protolytic media.

## Experimental

Microanalyses were by the University of Edinburgh Chemistry Department, B.M.A.C., and Galbraith Laboratories Inc. Molecular weights were determined in benzene on a Perkin-Elmer-Hitachi (model 115) osmometer calibrated with benzil. Infrared spectra were recorded in the region 200–4 000  $\text{cm}^{-1}$  on Perkin-Elmer 557 (Edinburgh) or 283B (Washington) spectrometers either as Nujol mulls on caesium iodide plates, potassium bromide discs, or in  $\text{CDCl}_3$  solvent using balanced NaCl solution cells. Hydrogen-1 n.m.r. spectra were obtained on Varian Associates HA-100 (Edinburgh), T60 (Washington), Nicolet 200 (Washington), and Bruker WH-360 (Edinburgh) spectrometers. Phosphorus-31 n.m.r. spectra (proton noise decoupled) were obtained on a JEOL-FX60Q spectrometer (Edinburgh) operating in the pulse and Fourier-transform mode at 22.24 MHz. Chemical shifts are reported in p.p.m. to high frequency of 85%  $\text{H}_3\text{PO}_4$ . Fluorine-19 n.m.r. spectra were obtained on a Varian Associates XL100 spectrometer (Edinburgh) operating in the pulse and Fourier-transform mode at 94.15 MHz. Chemical shifts are reported in p.p.m. to high frequency of  $\text{CCl}_3\text{F}$ .

Magnetic susceptibility measurements were obtained by the Evans' method<sup>22</sup> over the temperature range 300–200 K using a Varian Associates HA100 spectrometer.

Electronic spectra, both in solution and in the solid state, were obtained on a Beckman Acta MIV spectrophotometer (Napier College, Edinburgh), and e.s.r. spectra in the Department of Biochemistry, University of Edinburgh on a Varian E4 spectrometer employing 100 kHz magnetic field modulation. Spectra were measured in  $\text{CH}_2\text{Cl}_2$  solvent at 303 and 153 K. Conductivity measurements were obtained on a Portland Electronics 310 conductivity bridge at 298 K. Melting points were determined with a Köfler hot-stage microscope and are uncorrected. Vanadium and cobalt analyses were measured by atomic absorption.

**Materials.**—Iridium trichloride (Johnson Matthey and Engelhard) and  $\text{P}(\text{OR})_2(\text{O})\text{H}$  (R = Me, Et, or Ph) (Aldrich) were used as supplied or distilled prior to use.  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  (BDH),  $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$  (Phase Separations Ltd.), cyclo-octa-1,5-diene (BDH), and  $\text{PPh}_2\text{Cl}$  (Aldrich) were used as supplied.

The compounds  $[\{\text{IrCl}(\text{1,5-}\text{C}_8\text{H}_{12})\}_2]$ ,<sup>23</sup>  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ ,<sup>24</sup>  $[\text{Ir}(\text{MeCN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ ,<sup>25</sup>  $\text{PhSCH}_2\text{CH}_2\text{SPh}$ ,<sup>26</sup>  $[\text{VO}(\text{acac})_2]$ ,<sup>27</sup>  $[\{\text{Co}(\text{acac})_2\}_4]$ ,<sup>28</sup> and  $\text{PPh}_2(\text{O})\text{H}$ <sup>29</sup> were prepared by published procedures.

**Chloro(cyclo-octa-1,5-diene)hydrido[hydrogenbis(diphenylphosphinito)]iridium(III) (1).**—Chlorodiphenylphosphine (0.30  $\text{cm}^3$ , 1.60 mmol) was hydrolysed in water-methanol (1 : 7 v/v) for one hour to give an *in situ* mixture of  $\text{PPh}_2(\text{O})\text{H}$  and HCl. This mixture was then added to a suspension of  $[\{\text{IrCl}(\text{1,5-}\text{C}_8\text{H}_{12})\}_2]$  (0.10 g, 0.15 mmol) in methanol (5  $\text{cm}^3$ ) and shaken at ambient temperature for 20 min until a white microcrystalline solid was deposited from the yellow solution. This was filtered off, washed with methanol and diethyl ether, and dried *in vacuo* at 60 °C, m.p. 142–145 °C (yield 0.20 g, 65%) (Found: C, 51.7; H, 4.7; Cl, 5.0. Calc. for  $\text{C}_{32}\text{H}_{33}\text{ClIrO}_2\text{P}_2$ : C, 51.9; H, 4.6; Cl, 4.8%). The compound is soluble in most common organic solvents.  $^1\text{H}$  N.m.r. ( $\text{CDCl}_3$ , 301 K):  $\delta$  10.3 (br,  $\text{Ph}_2\text{POHOPPh}_2$ ), 7.00–8.00 (m, Ph), 4.95 (br), 3.77 (br, olefinic), 2.65 (m), 2.50 (d), 2.10 (d, methylenic), –15.2 p.p.m. (t, IrH,  $^2J_{\text{PH}} = 12.0$  Hz).

**[1,2-Bis(diphenylarsino)ethane]chlorohydrido[hydrogenbis(diphenylphosphinito)]iridium(III) (2).**—The compound  $[\text{IrHCl}(\text{1,5-}\text{C}_8\text{H}_{12})\{(\text{PPh}_2\text{O})_2\text{H}\}]$  (0.35 g, 0.47 mmol) in  $\text{CHCl}_3$  (10  $\text{cm}^3$ ) was treated with an equimolar amount of  $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$  (0.25 g, 0.51 mmol) and shaken for 4 h. Concentration of the solution to ca. 2  $\text{cm}^3$  and addition of light petroleum (b.p. 40–60 °C) then gave the product as a sticky white solid. More product could be obtained by concentration of the remaining solution. After recrystallisation from  $\text{CHCl}_3$ –light petroleum (b.p. 40–60 °C), the product was washed with light petroleum (b.p. 40–60 °C), diethyl ether and dried *in vacuo* at 60 °C (0.35 g, 65%), m.p. 248–251 °C [Found: C, 53.5; H, 4.1%;  $M$  ( $\text{C}_6\text{H}_6$ , by osmometer), 1 122. Calc. for  $\text{C}_{50}\text{H}_{46}\text{As}_2\text{ClIrO}_2\text{P}_2$ : C, 53.7; H, 4.0%;  $M$ , 1 116.5]. The compound is soluble in most common organic solvents.  $^1\text{H}$  N.m.r. ( $\text{CDCl}_3$ , 301 K):  $\delta$  11.3 (br,  $\text{Ph}_2\text{OHOPPh}_2$ ), 6.80–7.80 (m, Ph), 2.47 (m), 1.71 (m,  $\text{CH}_2$ ), –21.02 p.p.m. (t, IrH,  $^2J_{\text{PH}} 13.5$  Hz).  $^{31}\text{P}$ - $\{^1\text{H}\}$  N.m.r. ( $\text{CDCl}_3$ , 301 K):  $\delta$  44.9 (s) p.p.m. I.r. (Nujol mull):  $\nu(\text{IrH})$  2 165,  $\nu(\text{PO})$  1 010 and 1 000  $\text{cm}^{-1}$ .

**[1,2-Bis(phenylthio)ethane]chlorohydrido[hydrogenbis(diphenylphosphinito)]iridium(III) (3).**—The method was as for compound (2), from  $[\text{IrHCl}(\text{1,5-}\text{C}_8\text{H}_{12})\{(\text{PPh}_2\text{O})_2\text{H}\}]$  (0.50 g, 0.68 mmol) and  $\text{PhSCH}_2\text{CH}_2\text{SPh}$  (0.18 g, 0.73 mmol) to give the product as a white powder (0.41 g, 75%), m.p. 210–211 °C (Found: C, 51.9; H, 4.2. Calc. for  $\text{C}_{38}\text{H}_{36}\text{ClIrO}_2\text{P}_2\text{S}_2$ : C, 52.0; H, 4.1%). The compound is slightly soluble in  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$ , and insoluble in other organic solvents.  $^1\text{H}$  N.m.r. ( $\text{CDCl}_3$ , 301 K):  $\delta$  8.0 (br,  $\text{Ph}_2\text{POHOPPh}_2$ ), 7.00–7.60 (m, Ph), 3.30 (m), 2.61 (m,  $\text{CH}_2$ ), –20.15 p.p.m. (t, IrH,  $^2J_{\text{PH}} 15.7$  Hz).  $^{31}\text{P}$ - $\{^1\text{H}\}$  N.m.r. ( $\text{CDCl}_3$ , 301 K):  $\delta$  43.7 (s) p.p.m. I.r. (Nujol mull):  $\nu(\text{IrH})$  2 250,  $\nu(\text{PO})$  1 000  $\text{cm}^{-1}$ .

**[1,2-Bis(diphenylphosphino)ethane]chlorohydrido[hydrogenbis(diphenylphosphinito)]iridium(III) (4).**—This was prepared as above using  $[\text{IrHCl}(\text{1,5-}\text{C}_8\text{H}_{12})\{(\text{PPh}_2\text{O})_2\text{H}\}]$  (0.50 g, 0.68 mmol) and  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  (0.28 g, 0.70 mmol). Concentration of the solution and addition of light petroleum (b.p. 40–60 °C) gave some of the white product as a mixture of two isomers (0.40 g, 55%) (see text). Filtration of this product and further concentration of the filtrate gave more white powder which was exclusively the isomer (4a) with hydride *trans* to chloride (0.10 g, 14%), m.p. 181–184 °C (Found: C, 57.6; H, 4.6. Calc. for  $\text{C}_{50}\text{H}_{46}\text{ClIrO}_2\text{P}_4$ : C, 58.3; H, 4.4%). Both isomers are soluble in most common organic solvents. Note that the minor isomer (4b) is not formed by isomerisation of the kinetic isomer (4a) since solutions of (4) are stable to isomerisation over a period of several weeks. The  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectrum of (4a) in  $\text{CDCl}_3$  at 301 K shows 22 well resolved lines, and two additional shoulders, in two symmetrical groups. The spectrum has been simulated using the PANIC program routine and assuming an AA'BB' spin system. All spectral line positions have been iteratively fitted to within 0.1 Hz to give the following parameters:

$\delta$  44.96 ( $\text{Ph}_2\text{POHOPPh}_2$ ), 17.31 p.p.m. ( $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ );  $J_{1,2}$  3.49,  $J_{1,3}$  21.17,  $J_{1,4} = -328.77$ ,  $J_{3,4} = 33.44$  Hz [see structure (4a) for numbering]. I.r. for (4a) (Nujol mull):  $\nu(\text{IrH})$  2 200,  $\nu(\text{PO})$  1 000  $\text{cm}^{-1}$ .

[1,2-Bis(diphenylarsino)ethane][bis(diphenylphosphinito)-difluoroborato]chlorohydroiridium(III) (5).—Boron trifluoride diethyl ether solvate (0.05  $\text{cm}^3$ , 0.40 mmol) was added to a  $\text{CHCl}_3$  solution (5  $\text{cm}^3$ ) of  $[\text{IrHCl}(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)\{(\text{PPh}_2\text{O})_2\text{H}\}]$  (0.10 g, 0.09 mmol) and the mixture shaken for 10 min. Concentration of the solution and addition of light petroleum (b.p. 40–60 °C) gave the product as a white crystalline solid which was washed with more light petroleum (b.p. 40–60 °C), methanol, and diethyl ether, and dried *in vacuo* at 60 °C (0.09 g, 86%), m.p. 222–226 °C. The compound is soluble in most common organic solvents.

[Bis(diphenylphosphinito)difluoroborato][1,2-bis(diphenylthio)ethane]chlorohydroiridium(III).—This was prepared as above using  $[\text{IrHCl}(\text{PhSCH}_2\text{CH}_2\text{SPh})\{(\text{PPh}_2\text{O})_2\text{H}\}]$  (0.10 g, 0.11 mmol) and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.05  $\text{cm}^3$ , 0.40 mmol) to give a white powder (0.085 g, 80%).  $^1\text{H}$  N.m.r. ( $\text{CDCl}_3$ , 301 K):  $\delta(\text{IrH})$  –19.87 p.p.m. (t,  $^2J_{\text{PH}}$  16.0 Hz).  $^{31}\text{P}$ - $\{^1\text{H}\}$  N.m.r. ( $\text{CDCl}_3$ , 301 K):  $\delta$  46.3 (br) p.p.m.

[1,2-Bis(diphenylarsino)ethane]chlorobis(diphenylphosphinous acid)hydroiridium(III) Tetrafluoroborate (6).—An aqueous solution of  $\text{HBF}_4$  (0.5  $\text{cm}^3$ ) was added to a  $\text{CHCl}_3$  solution (2  $\text{cm}^3$ ) of  $[\text{IrHCl}(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)\{(\text{PPh}_2\text{O})_2\text{H}\}]$  (0.10 g, 0.09 mmol) and the mixture shaken for 10 min. The two layers were separated and the lower organic layer collected. The aqueous layer was treated with more  $\text{CHCl}_3$  (2  $\times$  0.5  $\text{cm}^3$ ) to ensure all the product was extracted. The combined  $\text{CHCl}_3$  extracts were then treated with diethyl ether to precipitate the product as a white microcrystalline solid. This was washed with methanol and diethyl ether and dried *in vacuo* at 60 °C, m.p. 185–189 °C (0.09 g, 83%) (Found: C, 49.9; H, 4.0. Calc. for  $\text{C}_{50}\text{H}_{47}\text{As}_2\text{BClF}_4\text{IrO}_2\text{P}_2$ : C, 49.8; H, 3.9%).  $\Lambda_M$  ( $1.65 \times 10^{-3}$  mol  $\text{dm}^{-3}$  in  $\text{CH}_2\text{Cl}_2$ ) = 26.0  $\Omega^{-1}$   $\text{cm}^2$   $\text{mol}^{-1}$ . The product is soluble in most common organic solvents. I.r. (Nujol mull):  $\nu(\text{PO})$  885  $\text{cm}^{-1}$ .

[1,2-Bis(phenylthio)ethane]chlorobis(diphenylphosphinous acid)hydroiridium(III) Tetrafluoroborate.—This was prepared as above using  $[\text{IrHCl}(\text{PhSCH}_2\text{CH}_2\text{SPh})\{(\text{PPh}_2\text{O})_2\text{H}\}]$  (0.10 g, 0.11 mmol) and aqueous  $\text{HBF}_4$  (0.5  $\text{cm}^3$ ) to give a white powder (0.09 g, 82%) (Found: C, 46.9; H, 3.9. Calc. for  $\text{C}_{38}\text{H}_{37}\text{BClF}_4\text{IrO}_2\text{P}_2\text{S}_2$ : C, 47.2; H, 3.8%).

Benzyltriphenylphosphonium 2-chloro-1-(NN'-diethyldithiocarbamate)-2-hydrido-2-[hydrogenbis(diphenylphosphinito)]-bis[ $\mu$ -thiodiphenylphosphinito-P( $\text{Pt}^1$ )S( $\text{Ir}^2$ )]-platinum(II)iridate(III)(7).—The compound  $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PPh}_2\text{S})_2]$  (0.046 g, 0.04 mmol) was added to a  $\text{CHCl}_3$  (10  $\text{cm}^3$ ) solution of  $[\text{IrHCl}(1,5\text{-C}_8\text{H}_{12})\{(\text{PPh}_2\text{O})_2\text{H}\}]$  (0.031 g, 0.04 mmol) and the mixture shaken for 6 h. The solution, initially pale yellow, turned orange after *ca.* 1 h and was deep orange after 6 h. The solution was concentrated to *ca.* 1  $\text{cm}^3$  and addition of light petroleum (b.p. 40–60 °C) gave the product as a pale yellow powder which was recrystallised from  $\text{CHCl}_3$ –light petroleum (b.p. 40–60 °C) and washed with light petroleum (b.p. 40–60 °C), methanol, and diethyl ether, and dried *in vacuo* at 60 °C (0.05 g, 70%), m.p. 139–142 °C (Found: C, 53.4; H, 4.4; N, 0.7. Calc. for  $\text{C}_{78}\text{H}_{74}\text{ClIrNO}_2\text{P}_2\text{PtS}_4$ : C, 53.1; H, 4.2; N, 0.8%).  $\Lambda_M$  ( $1.8 \times 10^{-3}$  mol  $\text{dm}^{-3}$  in  $\text{CH}_2\text{Cl}_2$ ) 27.0  $\Omega^{-1}$   $\text{cm}^2$   $\text{mol}^{-1}$ . The compound is soluble in  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$ .  $^{31}\text{P}$ - $\{^1\text{H}\}$  N.m.r. ( $\text{CDCl}_3$ , 301 K):  $\delta$  57.7 (pseudo-triplet,  $^3J_{\text{PP}}$  2.2,  $\text{Ph}_2\text{POHOPPh}_2$ ), 26.8 (triplet of pseudo-triplets,

$^3J_{\text{PP}}$  2.2,  $^1J_{\text{PtP}}$  3 446 Hz,  $\text{Ph}_2\text{PS}$ ), 23.3 p.p.m. [s,  $\text{PPh}_3(\text{CH}_2\text{Ph})^+$ ].  $^1\text{H}$  N.m.r. ( $\text{CDCl}_3$ , 301 K):  $\delta$  7.00–8.00 (m, Ph), 5.41 (d,  $^2J_{\text{PH}}$  14.4,  $\text{PhCH}_2$ ), 3.48 [q,  $^3J_{\text{HH}}$  7.0,  $\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2$ ], 1.16 [t,  $^3J_{\text{HH}}$  7.0,  $\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2$ ], –26.7 p.p.m. (t,  $^2J_{\text{PH}}$  18.0 Hz, IrH). I.r. (Nujol mull):  $\nu(\text{IrH})$  2 210,  $\nu(\text{PO})$  1 030 and 1 000,  $\nu(\text{PS})$  598  $\text{cm}^{-1}$ .

$[\text{NH}_2\text{Et}_2][(\text{Et}_2\text{NCS}_2)\text{Pt}(\text{PPh}_2\text{S})_2\text{IrHCl}\{(\text{PPh}_2\text{O})_2\text{H}\}]$  was similarly prepared from  $[\text{NH}_2\text{Et}_2][\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PPh}_2\text{S})_2]$  (0.34 g, 0.4 mmol) and  $[\text{IrHCl}(1,5\text{-C}_8\text{H}_{12})\{(\text{PPh}_2\text{O})_2\text{H}\}]$  (0.3 g, 0.4 mmol) yield, 0.43 g (71%) (Found: C, 45.4; H, 4.0; N, 1.9. Calc. for  $\text{C}_{57}\text{H}_{64}\text{ClIrN}_2\text{O}_2\text{P}_4\text{PtS}_4$ : C, 46.1; H, 4.3; N, 1.9%). The product is only slightly soluble in  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$ , and is non-conducting in the latter due to strong ion-pair interactions.

2-Acetylacetonato-1-[1',2'-bis(diphenylarsino)ethane]-1-chloro-bis[ $\mu$ -diphenylphosphinito-P( $\text{Ir}^1$ )O( $\text{V}^2$ )]-1-hydrido-iridium(III)oxovanadium(IV) (8).—The compound  $[\text{VO}(\text{acac})_2]$  (0.04 g, 0.15 mmol) was added to a  $\text{CHCl}_3$  (10  $\text{cm}^3$ ) solution of  $[\text{IrHCl}(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)\{(\text{PPh}_2\text{O})_2\text{H}\}]$  (0.15 g, 0.14 mmol) and the mixture shaken at ambient temperature. After 30 s a green solution had formed and after 10 min, the solution was filtered, evaporated to dryness and diethyl ether (15  $\text{cm}^3$ ) added. The product was extracted into the ethereal layer and after filtering off unreacted starting material, solvent was removed *in vacuo* to precipitate out the product as a green microcrystalline solid. This was washed with light petroleum (b.p. 40–60 °C) and dried *in vacuo* at 60 °C (0.14 g, 81%), m.p. 210 °C (decomp.) [Found: C, 51.6; H, 4.0; V, 3.3%;  $M$  ( $\text{C}_6\text{H}_6$ , by osmometry), 1 222. Calc. for  $\text{C}_{55}\text{H}_{52}\text{As}_2\text{ClIrO}_5\text{P}_2$ : C, 51.5; H, 4.0; V, 4.0%;  $M$ , 1 282.5]. The compound is soluble in  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , benzene, and diethyl ether.

Bis[1,2-bis(diphenylarsino)ethane]chloro-bis[ $\mu$ -diphenylphosphinito-P( $\text{Ir}$ )O( $\text{V}$ )]-hydrido-iridium(III)-oxovanadium(IV)-chloroform (1/2) (9).—An equimolar mixture of  $[\text{IrHCl}(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)\{(\text{PPh}_2\text{O})_2\text{H}\}]$  (0.13 g, 0.12 mmol) and  $[\text{IrHCl}(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)(\mu\text{-PPh}_2\text{O})_2\text{VO}(\text{acac})]$  (0.15 g, 0.12 mmol) in  $\text{CHCl}_3$  was refluxed under nitrogen for 6 h during which time a pale blue solid precipitated out of solution. This was washed with  $\text{CHCl}_3$  and diethyl ether, and air-dried (0.24 g, 80%), m.p. >300 °C (Found: C, 48.1; H, 3.5; V, 1.9. Calc. for  $\text{C}_{102}\text{H}_{90}\text{As}_4\text{Cl}_2\text{Ir}_2\text{O}_5\text{P}_4\text{V}$ : C, 48.2; H, 3.6; V, 2.0%). This compound is insoluble in all solvents.

1-Acetylacetonato-2-[1',2'-bis(diphenylarsino)ethane]-2-chloro-bis[ $\mu$ -diphenylphosphinito-O( $\text{Co}^1$ )P( $\text{Ir}^2$ )]-2-hydridocobalt(II)iridium(III) (10).—Addition of  $[\text{Co}(\text{acac})_2]_4$  (0.035 g, 0.05 mmol) to a  $\text{CHCl}_3$  (15  $\text{cm}^3$ ) solution of  $[\text{IrHCl}(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)\{(\text{PPh}_2\text{O})_2\text{H}\}]$  (0.15 g, 0.14 mmol) produced immediately a purple colouration. The solution was shaken for 20 min at ambient temperature, filtered and then concentrated *in vacuo* to *ca.* 2  $\text{cm}^3$  volume. Addition of diethyl ether gave the product as a purple powder which was recrystallised from  $\text{CHCl}_3$ –diethyl ether, washed with diethyl ether, and dried *in vacuo* at 60 °C (0.13 g, 76%), m.p. >300 °C [Found: C, 51.6; H, 4.1; Co, 4.2%;  $M$  ( $\text{C}_6\text{H}_6$ , by osmometry), 1 339. Calc. for  $\text{C}_{55}\text{H}_{52}\text{As}_2\text{ClIrO}_5\text{P}_2$ : C, 51.8; H, 4.1; Co, 4.6%;  $M$ , 1 274.5]. The compound is soluble in most common organic solvents.

Bis[1,2-bis(diphenylarsino)ethane]chloro-bis[ $\mu$ -diphenylphosphinito-O( $\text{Co}$ )P( $\text{Ir}$ )]-hydrido-iridium(III)-cobalt(II) (11).—The compound  $[\text{Co}(\text{acac})_2]_4$  (0.02 g, 0.02 mmol) was added to a  $\text{CHCl}_3$  (15  $\text{cm}^3$ ) solution of  $[\text{IrHCl}(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)\{(\text{PPh}_2\text{O})_2\text{H}\}]$  (0.15 g, 0.15 mmol) and refluxed under nitrogen for 4 h to give a pale blue solution. The solution was concentrated to *ca.* 2  $\text{cm}^3$  and addition of light petroleum (b.p.

40–60 °C) precipitated the product as a pale blue powder which was washed with light petroleum (b.p. 40–60 °C), diethyl ether, and CHCl<sub>3</sub>, and dried *in vacuo* at 60 °C (0.13 g, 84%), m.p. >300 °C (Found: C, 52.1; H, 3.9; Co, 2.3. Calc. for C<sub>100</sub>H<sub>90</sub>As<sub>4</sub>Cl<sub>2</sub>CoIr<sub>2</sub>O<sub>4</sub>P<sub>4</sub>: C, 52.3; H, 3.9; Co, 2.6%). The same compound was obtained by refluxing [IrHCl(Ph<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>AsPh<sub>2</sub>){(PPh<sub>2</sub>O)<sub>2</sub>H}] with equimolar amounts of [IrHCl(Ph<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>AsPh<sub>2</sub>)(μ-PPh<sub>2</sub>O)<sub>2</sub>Co(acac)]. The product is virtually insoluble in all organic solvents.

*Carbonylhydrido[hydrogenbis(dimethylphosphito)]bis(tri-phenylphosphine)iridium(III) Perchlorate (12).*—To a solution of [Ir(MeCN)(CO)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> (0.10 g, 0.11 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) was added dropwise P(OMe)<sub>2</sub>(O)H (0.23 g, 2.10 mmol) and the mixture stirred under nitrogen for 21 h at ambient temperature. The solvent was removed *in vacuo*, diethyl ether added and the residual solid stirred with diethyl ether for 24 h until a colourless precipitate was produced. This was filtered off, washed with diethyl ether and dried *in vacuo* (0.11 g, 92%), m.p. 178–180 °C (Found: C, 46.3; H, 3.8; P, 11.6. Calc. for C<sub>41</sub>H<sub>44</sub>ClIrO<sub>11</sub>P<sub>4</sub>: C, 46.3; H, 4.1; P, 11.7%). Λ<sub>M</sub> (1 × 10<sup>-3</sup> mol cm<sup>-3</sup> in MeNO<sub>2</sub>) 75.5 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. I.r. (KBr disc): ν(CO) 2 080, ν(IrH) 2 120, ν(PO) 1 000 cm<sup>-1</sup>. <sup>1</sup>H N.m.r. (CDCl<sub>3</sub>, 301 K): δ 11.05 [br, (MeO)<sub>2</sub>POHOP(OMe)<sub>2</sub>]; 7.00–8.00 (m, Ph); 3.68 (d, <sup>3</sup>J<sub>PH</sub> 12.6), 3.26 (d, <sup>3</sup>J<sub>PH</sub> 9.8), 3.11 (t, <sup>3</sup>J<sub>PH</sub> 9.8), 2.81 (t, <sup>3</sup>J<sub>PH</sub> 12.4) [(MeO)<sub>2</sub>POHOP(OMe)<sub>2</sub>]; -12.03 p.p.m. [d, octet, <sup>2</sup>J<sub>PH</sub>(trans) 108 Hz, <sup>2</sup>J<sub>PH</sub>(cis) 12.0, 15.0, 9.0 Hz, IrH].

*Reactions of [IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] with P(OR)<sub>2</sub>(O)H (R = Me, Et, or Ph) and PPh<sub>2</sub>(O)H.*—Although <sup>1</sup>H and <sup>31</sup>P-{<sup>1</sup>H} n.m.r. studies reveal that *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] reacts readily with an excess of P(OR)<sub>2</sub>(O)H or PPh<sub>2</sub>(O)H in CDCl<sub>3</sub>, attempts to isolate products from these reactions only gave starting materials.

Solutions for n.m.r. studies were prepared by the addition of an excess of P(OR)<sub>2</sub>(O)H or PPh<sub>2</sub>(O)H to CDCl<sub>3</sub> solutions of *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>]. Sufficient ligand was added to produce homogeneity and decolourisation of the solution.

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