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OXIDATIVE ADDITION OF DIALKYLPHOSPHITES TO COMPLEXES OF IRIDIUM(I) AND RHODIUM(I)

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Summary

The P–H bond of dialkylphosphites (dimethylphosphite, 5,5-dimethyl-1,3-dioxa-2-phosphorinane and 4,4,5,5-tetramethyl-1,3-dioxa-2-phospholane) oxidatively adds to $IrClL_2$($L = PPh_3$, $AsPh_3$) and $IrCl(PMe_2Ph)_3$ generated in situ to give six-coordinate hydrido(dialkylphosphonato)iridium(III) complexes, e.g. $IrHClL_2[\{(MeO)_2PO\}_2H]$ and $IrHCl(PMe_2Ph)_3[PO(OMe)_2]$. Addition of triphenylphosphine to a solution containing $[IrCl(C_8H_{14})_2]_2$ and dimethylphosphite in a 1 : 2 mol ratio gives a five-coordinate hydrido (dimethylphosphonato)iridium(III) complex $IrHCl(PPh_3)_2\{PO(OMe)_2\}$, from which six-coordinate pyridine and acetylacetonato complexes $IrHCl(PPh_3)_2(C_5H_5N)\{PO(OMe)_2\}$ and $IrH(PPh_3)_2(acac)\{PO(OMe)_2\}$ can be obtained. The ligand arrangements in the various complexes are inferred from IR, ^1H and ^{31}P NMR data.

Introduction

Dialkyl phosphites exist in tautomeric forms containing tricoordinate, trivalent phosphorus and tetracoordinate, pentavalent phosphorus (eq. 1), the equilibrium generally lying on the left-hand side.

$$(RO)_2P^V(O)H \rightleftharpoons (RO)_2P^{III}OH \qquad (1)$$

Metal complexes can be formed either from the neutral, tricoordinate molecule or from the dialkylphosphonate anion $[(RO)_2P^V(O)]^-$ derived by deprotonation of the neutral molecule [1], and dialkylphosphonato complexes can also be generated by dealkylation of coordinated trialkylphosphite [1–3]. In a preliminary note, we showed [4] that dimethylphosphite undergoes oxidative addition to complexes of rhodium(I) and iridium(I) to give hydrido-dimethylphosphonato complexes of

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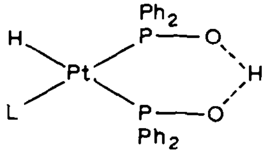
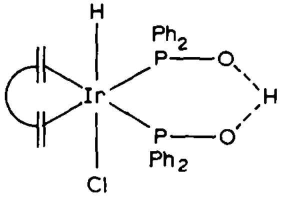
rhodium(III) and iridium(III), and full details of this work are reported here. Subsequently, oxidative addition of diphenylphosphinous acid, $Ph_2P(O)H$, to PtL_4 ($L = PPh_3$, $PMePh_2$) has been used to prepare hydrido-diphenylphosphinato complexes of platinum(II) (I) [5]. A similar reaction of diphenylphosphinous acid with the cycloocta-1,5-diene complex $[IrCl(COD)]_2$ gives the hydrido iridium(III) complex II, from which the diolefin can be displaced by bidentate P-, As- and S-donor ligands [6]. Oxidative addition of dimethylphosphite to $[Ir(NCMe)(CO)(PPh_3)_2]ClO_4$ to give complex III has also been reported briefly [6].

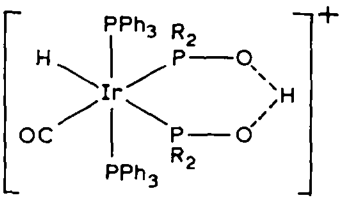


(L = PPh_3, $PMePh_2$)

(I)



(II)



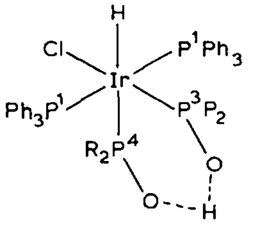
(R = OMe)

(III)

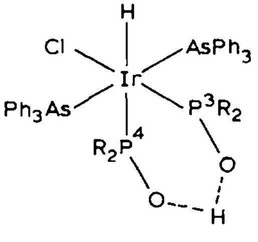
Results and discussion

When a solution of the dimeric chloro-iridium(I) cyclooctene complex $[IrCl(C_8H_{14})_2]_2$ in benzene or chloroform is treated successively with triphenylphosphine and dimethylphosphite (each 2 mols per mol Ir) and the mixture is heated under reflux, a colourless solid of formula $IrHCl(PPh_3)_2[\{(MeO)_2PO\}_2H]$ (IV) can be isolated in ca. 50% yield. The cycloocta-1,5-diene complex $[IrCl(COD)]_2$ can also be used as precursor. The ^1H NMR spectrum of IV in $CDCl_3$ (Table 1) shows complex multiplets at δ 7.35 and 7.65 ppm due to aromatic protons, a pair of doublets due to methoxyl protons at δ 2.53 ppm (J(PH) 11.6 Hz) and 3.04 ppm (J(PH) 11.0 Hz) and a hydride resonance centred at δ −9.49 ppm which consists of a widely spaced doublet of double triplets (J(PH) 208.1, 14.8, 12.5 Hz). No signal due to P–O*H* could be detected. The $^{31}P\{^1H\}$ NMR spectrum (Table 2) shows a doublet of doublets at δ 5.3 ppm (relative to 85% H_3PO_4) (J(PP) 24.4, 22.0 Hz) assigned to the triphenylphosphine ligands and two doublets of triplets at δ 43.7 ppm (J(PP) 22.0, 13.4 Hz) and 87.0 ppm (J(PP) 24.4, 13.4 Hz) due to inequivalent dimethylphosphonate phosphorus atoms. In the absence of proton decoupling, the last signal appears as a pair of multiplets separated by ca. 208 Hz, and can therefore be assigned to phosphorus *trans* to hydride, the magnitude of ^2J(PH) being similar to that observed for $P(OPh)_3$ *trans* to hydride in octahedral iridium(III) complexes [7,8]. It is noteworthy that the dimethylphosphonate phosphorus *trans* to hydride is the least shielded of the three different ^{31}P nuclei, an effect which has been noted previously in the case of the hydrogen bis(diphenylphosphinato) platinum(II) complex $PtH(PMePh_2)\{(Ph_2PO)_2H\}$ [9].

The IR spectrum of IV in Nujol (Table 1) shows a band due to ν(IrH) at 2180 cm^{-1} (2150 cm^{-1} in CH_2Cl_2), which is ca. 100 cm^{-1} higher than the values found in octahedral iridium(III) complexes containing hydride trans to $P(OPh)_3$ [7,8]. The spectroscopic data are consistent with structure IV, in which it is assumed that a hydrogen atom is located symmetrically between the oxygen atoms of the dimethylphosphite and dimethylphosphonate ligands. Such an arrangement has been found by X-ray crystallography in the hydrogen bis(diphenylphosphinato) complex $[Pd(\mu\text{-}SCN)\{(Ph_2PO)_2H\}]_2$ [10].



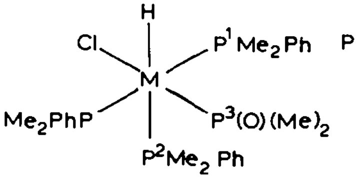
(IV : R = OMe ;
V : R_2 = $OCH_2CMe_2CH_2O$;
VI : R_2 = $OCMe_2CMe_2O$)



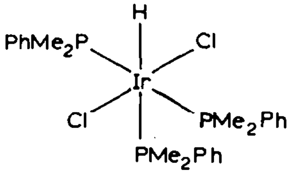
(VII : R = OMe)

The secondary phosphites 5,5-dimethyl-1,3-dioxa-2-phosphorinane, $\overline{OCH_2CMe_2CH_2O}P(O)H$, and 4,4,5,5-tetramethyl-1,3-dioxa-2-phospholane, $\overline{OCMe_2CMe_2O}P(O)H$, give complexes V and VI analogous to that obtained with dimethylphosphite, but diethylphosphite gives an inseparable mixture of products. Treatment of $[IrCl(C_8H_{14})_2]_2$ with triphenylarsine and dimethylphosphite gives the complex $IrHCl(AsPh_3)_2[\{(MeO)_2PO\}_2H]$ (VII), which appears to be structurally analogous to IV. As expected, its hydride resonance is a widely spaced doublet of doublets (J(PH) 210.2, 12.1 Hz) (Table 1). Attempts to prepare bis(dimethylphenylphosphine) or 1,2-bis(diphenylphosphino)ethane analogues of IV have been unsuccessful. We have also been unable to make hydrido-rhodium(III) analogues of complexes IV–VII starting from $[RhCl(C_8H_{14})_2]_2$.

When either $[IrCl(C_8H_{14})_2]_2$ or $[IrCl(CO)(C_8H_{14})_2]_2$ is treated with three mols per mol Ir of dimethylphenylphosphine and one mol per mol Ir of dimethylphosphite, a colourless solid of formula $IrHCl(PMe_2Ph)_3\{P(O)(OMe)_2\}$ is formed, for which structure VIII is proposed. In its ^1H NMR spectrum, the hydride resonance appears as a widely spaced doublet of double triplets at δ −9.7 ppm (J(PH) 142.6, 19.5, 14.6 Hz), showing that the hydride is *trans* to one of the P-donor ligands. The



(VIII : M = Ir ;
X : M = Rh)



(IX)

TABLE 1

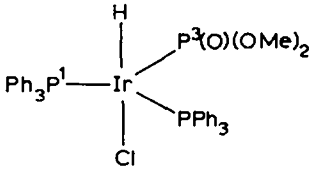
IR AND ^{1}H NMR DATA FOR RHODIUM AND IRIDIUM COMPLEXES DERIVED FROM SECONDARY PHOSPHITES[a]

Complex		IR		^{1}H NMR		
		ν(IrH) (cm^{-1})		δ(IrH) (ppm)	J(PH) (Hz)	Other
		Nujol	CH$_2$Cl$_2$			
IrHCl(PPh$_3$)$_2$[((MeO)$_2$PO)$_2$H]	(IV)	2180	2150	−9.5	208.1, 14.8, 12.5[b]	2. 53 (d, 11.6, OCH$_3$), 3.04 (d, 11.0, OCH$_3$)
IrHCl(PPh$_3$)$_2$(($\overline{\text{OCH}_2\text{CMe}_2\text{CH}_2\text{OP}}$O)$_2$H)	(V)	2170	2150	−9.5	215.8, 15.6, 13.7[b]	0.17, 0.31, 0.67, 1.11 (each s, CH$_3$) 2.34 (dd, 23.3, 12.0, CH$_2$), 3.12(dd, 19.5, 12.0, CH$_2$), 3.63 (dd, 12.0, 2.2, CH$_2$), 4.11 (dd, 12.0, 4.8, CH$_2$)
IrHCl(PPh$_3$)$_2$(($\overline{\text{OCMe}_2\text{CMe}_2\text{OP}}$O)$_2$H)	(VI)	2160	2170	−10.5	208.0, 15.6, 11.7[b]	0.26 (s, CH$_3$), 0.76 (s, 2CH$_3$), 1.21 (s, CH$_3$)
IrHCl(AsPh$_3$)$_2$[((MeO)$_2$PO)$_2$H]	(VII)	2110	2095	−9.5	210.2, 12.1[c]	2.56 (d, 11.6, OCH$_3$), 3.03 (d, 10.8, OCH$_3$)
IrHCl(PMe$_2$Ph)$_3${PO(OMe)$_2$}	(VIII)	2060	2090	−9.7	142.6, 19.5, 14.6	1.68 (d, 8.5, CH$_3$ on P^2), 1.69 (overlapping 1/2/1 triplets, 3.7, 2CH$_3$ on P^1)[e], 3.18 (s, 11.0, OCH$_3$)
RhHCl(PMe$_2$Ph)$_3${PO(OMe)$_2$}	(X)[d]	1960	1985	−9.1	181.6, 14.6, 14.6[f]	1.48 (d, 7.5, CH$_3$ on P^2), 1.61(overlapping 1:2:1 triplets, 3.5, 2CH$_3$ on P^1)[e], 3.19 (d, 11.2, OCH$_3$)
IrHCl(PPh$_3$)$_2${PO(OMe)$_2$}	(XI)	2210, 2170	2220	−20.0	17.6, 13.7[g]	3.06(d, 11.7, OCH$_3$)[h]
IrHCl(PPh$_3$)$_2$(C$_5$H$_5$N){PO(OMe)$_2$}	(XII)	2260	2250	−19.7[i]	20.5, 12.7[g,i]	2.62 (d, 10.8, OCH$_3$)[i]
				−20.4[j]	18.5, 12.7[j]	2.67 (d, 11.4, OCH$_3$)[j]
IrH(PPh$_3$)$_2${PO(OMe)$_2$}(acac)	(XIII)	2200	2200	ca. −22.3	*k*	0.77, 1.34 (each s, CH$_3$ of acac), 2.67 (d, 11.2, OCH$_3$) 4.22 (s, γ-H of acac)

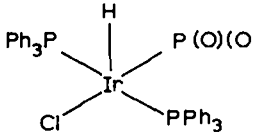
[a] Measured in CDCl$_3$, unless otherwise stated. [b] Widely spaced doublet of double triplets. [c] Widely spaced doublet of doublets. [d] In C$_6$D$_6$. [e] Coupling refers to spacing of outer lines, ^2J(PH)+^4J(PH). [f] Widely spaced doublet of quintets, J(Rh–H) 14.6 Hz. [g] Doublet of doublets. [h] In C$_6$D$_6$; sometimes accompanied by minor peak at δ 3.36 ppm (J 11.7 Hz) (see text). [i] Major isomer. [j] Minor isomer. [k] Unsymmetrical 8-line spectrum, not analysed.

magnitude of the largest PH coupling is similar to the value of 168 Hz observed in *mer*-$IrHCl_2(PMe_2Ph)_3$ (configuration IX) [11], and we therefore suggest that PMe_2Ph rather than $P(O)(OMe)_2$ is *trans* to hydride in VIII. The methyl resonance pattern of the dimethylphenylphosphine ligands comprises a doublet for the unique PMe_2Ph *trans* to hydride and an apparent quartet (actually overlapping 1/2/1 triplets) for the strongly coupled, mutually *trans* pair. This is as expected for the *mer*-arrangement, the methyl groups on each of the *trans*-PMe_2Ph ligands being inequivalent. In agreement, the $^{31}P\{^1H\}$ NMR spectrum shows a doublet of triplets due to the dimethylphosphonate phosphorus at high frequency relative to 85% H_3PO_4 and two resonances at low frequency in a 2/1 intensity ratio due to the ^{31}P nuclei of the dimethylphenylphosphine ligands (Table 2), the most highly shielded of the latter being that *trans* to hydride. The ν(IrH) values of 2060 cm^{-1} (Nujol) (2090 cm^{-1} (CH_2Cl_2)) are also consistent with the structure shown for VIII. The corresponding hydrido-rhodium(III) complex X can be made similarly to VIII from the cyclooctene-rhodium(I) complex $[RhCl(C_8H_{14})_2]_2$; its NMR spectroscopic parameters resemble those of VIII with the addition of coupling to ^{103}Rh (Tables 1 and 2).

When $[IrCl(C_8H_{14})_2]_2$ is heated under reflux in benzene with one mol of dimethylphosphite per mol Ir and two mols of triphenylphosphine per mol Ir is added to the cooled solution, an orange-brown, crystalline solid of formula $IrHCl(PPh_3)_2\{P(O)(OMe)_2\}$ (XI) is formed which is monomeric in chloroform. The



(XIa)



(XIb)

IR spectrum shows a split ν(IrH) band at 2210/2170 cm^{-1} (Nujol) and in the ^1H NMR spectrum the hydride resonance appears as a doublet of triplets at δ −20.0 ppm (*J*(PH) 17.6, 13.7 Hz) owing to coupling with the ^{31}P nuclei of two equivalent triphenylphosphine ligands and with one dimethylphosphonate. In agreement, the $^{31}P\ \{^1H\}$ NMR spectrum exhibits a triplet due to the dimethylphosphonate and a doublet due to triphenylphosphine (*J*(PP) 19 Hz) (Table 2); unusually the former is at lower frequency than the latter. The data are consistent with a five-coordinate hydrido-iridium(III) formulation for XI but do not distinguish between a trigonal bipyramidal structure XIa and a square pyramidal structure XIb containing axial hydride and *trans*-triphenylphosphine ligands. The monohydrido complex $RhHCl_2(P\text{-}t\text{-}Bu\text{-}n\text{-}Pr_2)_2$ has been shown by X-ray crystallography to have the latter structure, the bulky tertiary phosphine ligands being mutually *trans* [12], whereas for the dihydrido complex $IrH_2Cl(P\text{-}t\text{-}Bu_2Ph)_2$ a trigonal bipyramidal structure with axial phosphines was preferred on the basis of NMR spectroscopic data [13]. The ^1H NMR spectrum of XI in C_6D_6 shows a doublet due to the methoxyl protons at δ 3.06 ppm. Samples recrystallized from dichloromethane/ether showed sometimes an additional doublet of variable intensity (generally about one-sixth that of the main peak) at δ 3.36 ppm, an isomer of XI.

As expected for a five-coordinate d^6 complex, XI reacts readily with ligands, e.g. pyridine gives a colourless 1 : 1 adduct (XII) which exists in solution as a mixture of

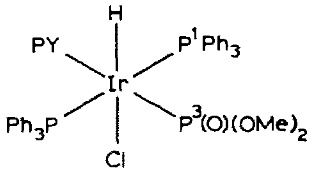
TABLE 2

^{31}P NMR SPECTRA OF RHODIUM AND IRIDIUM COMPLEXES DERIVED FROM SECONDARY PHOSPHITES[a]

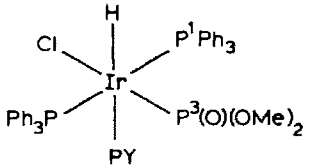
Complex		Phosphine		Phosphonate		J(PP)
		$\delta(P^1)$	$\delta(P^2)$	$\delta(P^3)$	$\delta(P^4)$	
$IrHCl(PPh_3)_2[((MeO)_2PO)_2H]$	(IV)	5.3		43.7	87.0	P^1P^3 22.0, P^1P^4 24.4, P^3P^4 13.4
$IrHCl(PPh_3)_2\{(\overline{OCH_2CMe_2CH_2OP}O)_2H\}$	(V)	5.6		42.3	82.0	P^1P^3 23.2, P^1P^4 24.4, P^3P^4 14.6
$IrHCl(PPh_3)_2\{(\overline{OCMe_2CMe_2OP}O)_2H$	(VI)	2.8		50.1	100.1	P^1P^3 23.5, P^1P^4 25.0 P^3P^4 10.3
$IrHCl(AsPh_3)_2[((MeO)_2)PO)_2H]$	(VII)			42.3	87.7	P^3P^4 13.4
$IrHCl(PMe_2Ph)_3(PO(OMe)_2)$	(VIII)[b]	−37.6	−43.0	31.1		P^1P^2 17.6, P^2P^3 16.2, P^1P^3 25.0
$RhHCl(PMe_2Ph)_3\{PO(OMe)_2\}$	(X)	−2.0	−17.8	81.9		P^1P^2 24.4, P^2P^3 22.0, P^1P^3 29.3[c]
$IrHCl(PPh_3)_2\{PO(OMe)_2\}$	(XI)	27.8		−15.0		P^1P^3 19.1
$IrHCl(PPh_3)_2(C_5H_5N)\{PO(OMe)_2\}$	(XII) (major)	5.7		16.4		P^1P^3 27.9
	(minor)	9.4		28.4		P^1P^3 23.5

[a] Measured in $CDCl_3$ unless otherwise stated. Chemical shifts (δ) are in ppm relative to 85% H_3PO_4, positive to high frequency, coupling constants (J) are in Hz. [b] In C_6D_6. [c] $J(RhP^1)$ 102.4, $J(RhP^2)$ 80.9, $J(RhP^3)$ 156.3.

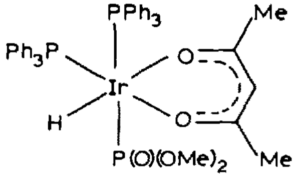
isomers in ca. 5/1 ratio. The hydride resonances in both isomers consist of a doublet of triplets at δ ca. −20 ppm arising from coupling with two equivalent triphenylphosphines and one dimethylphosphite (*J*(PH) ca. 20, 13 Hz); the magnitudes of these couplings show that the hydride in both isomers is *cis* to all three P-donor ligands. This is confirmed by the $^{31}P\{^1H\}$ NMR spectra of the two isomers, which, like XI, show a triplet due to $P(O)(OMe)_2$ and a doublet due to PPh_3 (*J*(PP) 28 Hz). In contrast to XI, the former is at higher frequency than the latter. These data are consistent with structures XIIa and XIIb, in which hydride is *trans* to chloride and to pyridine respectively, but do not allow a decision as to which structure corresponds to the major or minor isomer. The IR spectrum shows only one ν(IrH) band, both in Nujol (at 2260 cm^{-1}) and in CH_2Cl_2 (2250 cm^{-1}), values which are consistent with either XIIa or XIIb.



(XIIa)



(XIIb)



(XIII)

Complex XI also reacts with thallium acetylacetonate to give a colourless pentane-2,4-dionato derivative $IrH(PPh_3)_2(P(O)(OMe)_2)(acac)$ which is assigned structure XIII on the basis of spectroscopic data. The ^1H NMR spectrum shows two acac methyl singlets and a complex resonance centred at δ ca. −22 ppm, the chemical shift of which suggests that it arises from hydride *trans* to one of the acac oxygen atoms. The ^{31}P chemical shifts appear to be similar, leading to a non first-order pattern centred about δ −15 ppm which has not been analysed.

In view of the ability of dialkylphosphites to undergo oxidative addition of their P–H bonds to iridium(I) complexes, it was of interest to see whether phosphorous acid, $HP(O)(OH)_2$, would behave similarly. When $[IrCl(C_8H_{14})_2]_2$ in benzene is treated successively with two mols per mol Ir of triphenylarsine and two mols per mol Ir of phosphorous acid, a colourless, hygroscopic solid can be isolated which appears to analyze satisfactorily for $IrHCl(AsPh_3)_2(H_2PO_3)(H_3PO_3)$ (XIV) (Table 3). However, the spectroscopic data cannot be reconciled with this formulation. Thus the ^1H NMR spectrum shows a prominent singlet (i.e. no P–H coupling) at δ −20.6 ppm together with a weak doublet at δ −20.8 ppm (*J*(PH) 17.6 Hz), and there is a complex pattern at δ 6.7–7.7 ppm which may be due to cyclooctene. The peaks in the ^{31}P NMR spectrum at δ 6, 54, 58 and 59 ppm are weak and poorly defined and the IR spectrum shows a broad absorption at 2340 cm^{-1} which seems too high to be due to ν(IrH). At present the nature of this compound (or mixture of compounds) remains obscure and attempts to prepare analogous compounds containing triphenylphosphine have been unsuccessful.

Experimental

NMR spectra were recorded on a Bruker WH-90 spectrometer using TMS as internal standard for ^{1}H spectra and 85% H_3PO_4 as external standard for ^{31}P spectra (36.4 MHz). IR spectra were measured on a Perkin–Elmer 457 spectrometer. Microanalyses were carried out in the Microanalytical Unit of the Australian National University (Dr. Joyce Fildes, Miss Brenda Stevenson and their associates) and in the Chemistry Department, Queen's University (Mr. W.J. Swindall and associates); the data are in Table 3. Benzene was distilled from $LiAlH_4$ and ether was dried over sodium. All reactions were routinely carried out under dry nitrogen, although the products were air-stable once isolated. The complexes $[IrCl(C_8H_{14})_2]_2$ [14–16], $[IrCl(CO)(C_8H_{14})_2]_2$ [14,17] $[IrCl(COD)]_2$ [14,16,17] and $[RhCl(C_8H_{14})_2]_2$ [15], and the secondary phosphites 5,5-dimethyl-1,3-dioxa-2-phosphorinane, $\overline{\mathrm{OCH_2CMe_2CH_2OP}}\mathrm{(O)H}$, and 4,4,5,5-tetramethyl-1,3-dioxa-2-phospholane, $\overline{\mathrm{OCMe_2CMe_2OP}}\mathrm{(O)H}$, [18], were prepared by literature methods or slight variations thereof.

TABLE 3

ANALYTICAL DATA

Complex		Analysis (Found (calcd.) (%))			
		C	H	Cl	P
$IrHCl(PPh_3)_2[\{(MeO)_2PO\}_2H]$	(IV) [a]	49.2 (49.4)	4.7 (4.6)	4.05 (3.6)	12.7 (12.7)
$IrHCl(PPh_3)_2\{(\overline{\mathrm{OCH_2CMe_2CH_2OP}}\mathrm{O})_2H\}$	(V)	52.3 (52.5)	5.1 (5.0)		
$IrHCl(PPh_3)_2\{(\overline{\mathrm{OCMe_2CMe_2OP}}\mathrm{O})_2H\}$	(VI)	53.05 (53.4)	5.3 (5.2)		
$IrHCl(AsPh_3)_2[\{(MeO)_2PO\}_2H]$	(VII)	45.0 (45.3)	4.4 (4.2)	4.5 (4.2)	5.7 (5.8)
$IrHCl(PMe_2Ph)_3\{PO(OMe)_2\}\cdot 0.25(C_2H_5)_2O$	(VIII) [b]	41.4 (41.5)	5.3 (5.4)	5.1 (4.7)	16.65 (16.5)
$RhHCl(PMe_2Ph)_3\{PO(OMe)_2\}$	(X)	47.1 (47.1)	6.05 (6.1)	5.2 (5.35)	17.7 (18.7)
$IrHCl(PPh_3)_2\{PO(OMe)_2\}$	(XI) [c]	52.8 (52.9)	4.5 (4.3)	4.2 (4.1)	10.9 (10.8)
$IrHCl(PPh_3)_2(C_5H_5N)\{PO(OMe)_2\}$	(XII) [d]	53.65 (54.8)	4.7 (4.5)		
$IrHCl(PPh_3)_2(C_5H_7O_2)\{PO(OMe)_2\}$	(XIII)	56.2 (55.8)	4.95 (4.8)		
$IrHCl(AsPh_3)_2[\{(HO)_2PO\}_2H]$	(XIV)	42.8 (42.6)	3.7 (3.6)	3.45 (3.6)	6.0 (6.1)

[a] Mol wt(osmometry, $CHCl_3$, 37°C): Found: 932; calcd.: 972. [b] Ether confirmed by ^{1}H NMR spectroscopy. [c] Mol wt: Found: 853; calcd.: 862. [d] N(%): Found: 1.4; calcd.: 1.5.

Preparations. Chloro(hydrido)hydrogenbis(dimethylphosphonato)bis(triphenylphosphine)iridium(III), $IrHCl(PPh_3)_2[\{(MeO)_2PO\}_2H]$ *(IV)*

A mixture of $[\mathrm{IrCl(C_8H_{14})_2]_2}$ (0.315 g, 0.352 mmol) and triphenylphosphine (0.369 g, 1.408 mmol) in benzene (4 ml) was stirred and treated with dimethylphosphite (0.155 g, 1.408 mmol). The red solution was heated to reflux whereupon its colour faded to yellow. After 30 min at reflux the solution was allowed to cool and a few ml of ether added to complete precipitation of the solid product. This was taken up in dichloromethane (5 ml) and precipitated by addition of ether to give IV as a colourless solid (0.326 g, 47%). The compound was obtained in similar yield using $\mathrm{[IrCl(COD)]_2}$ in place of $\mathrm{[IrCl(C_8H_{14})_2]_2}$.

Similarly prepared were $\mathrm{IrHCl(PPh_3)_2\{(\overline{OCH_2CMe_2CH_2OP}O)_2H\}}$ (V), $\mathrm{IrHCl(PPh_3)_2\{(\overline{OCMe_2CMe_2OP}O)_2H\}}$ (VI) and $\mathrm{IrHCl(AsPh_3)_2[\{(MeO)_2PO\}_2H]}$ (VII) in yields of 62, 36 and 42% respectively. In the case of VI, the reaction mixture was evaporated to dryness and the residue was extracted with dichloromethane. The product was then precipitated by addition of ether.

Chloro(hydrido)(dimethylphosphonato)tris(dimethylphenylphosphine)iridium(III), $IrHCl(PMe_2Ph)_3\{PO(OMe)_2\}$ *(VIII)*

A mixture of $\mathrm{[IrCl(C_8H_{14})_2]_2}$ (0.455 g, 0.508 mmol) and dimethylphenylphosphine (0.42 g, 3.05 mmol) was stirred in benzene (5 ml) for 5 min to give a red solution and treated with dimethylphosphite (0.112 g, 1.017 mmol). After heating at reflux for 1–2 h the solution was pale yellow. Removal of solvent in vacuo gave a colourless solid which was recrystallized twice from dichloromethane/ether and dried in vacuo to give pure VIII (0.410 g, 54%). The same product was obtained starting from $\mathrm{[IrCl(CO)(C_8H_{14})_2]_2}$ in place of $\mathrm{[IrCl(C_8H_{14})_2]_2}$.

Chloro(hydrido)(dimethylphosphonato)tris(dimethylphenylphosphine)rhodium(III), $RhHCl(PMe_2Ph)_3\{PO(OMe)_2\}$ *(X)*

A mixture of $\mathrm{[RhCl(C_8H_{14})_2]_2}$ (0.521 g, 0.73 mmol) and dimethylphenylphosphine (0.601 g, 4.360 mmol) in benzene (5 ml) was treated with dimethylphosphite (0.160 g, 1.45 mmol). A purple-red solution was obtained after heating under reflux for 4 h. Addition of ether gave a colourless solid which was recrystallized from benzene/ether to give colourless X (0.450 g, 46%).

Chloro(hydrido)(dimethylphosphonato)bis(triphenylphosphine)iridium(III), $IrHCl(PPh_3)_2\{PO(OMe)_2\}$ *(XI)*

A mixture of $\mathrm{[IrCl(C_8H_{14})_2]_2}$ (0.475 g, 0.53 mmol) and dimethylphosphite (0.117 g, 1.06 mmol) in benzene (4.5 ml) was heated under reflux for 1 h. The pale brown solution was cooled and triphenylphosphine (0.555 g, 2.12 mmol) was added. After being stirred for a few minutes and allowed to stand overnight, a dark yellow solid precipitated, which was extracted with dichloromethane (1 ml). Addition of ether to the solution gave orange-yellow crystals of XI (0.365 g, 40%). Analytically pure, orange-yellow platelets were obtained by recrystallization from dichloromethane/ether (1/3).

Chloro(hydrido)(dimethylphosphonato)(pyridine)bis(triphenylphosphine)iridium(III), $IrHCl(PPh_3)_2(C_5H_5N)\{PO(OMe)_2\}$ *(XII)*

Addition of pyridine (0.1 ml) to a solution of XI (0.085 g) in benzene (4 ml) caused immediate decolorization. The residue obtained after solvents had been removed in vacuo was washed with ether (5 ml) to give XII (0.088 g, 95%) as a colourless solid.

Dimethylphosphonato(hydrido)(pentane-2,4-dionato)bis(triphenylphosphine)iridium(III), $IrH(PPh_3)_2(acac)\{PO(OMe)_2\}$ (XIII)

A mixture of XI (0.155 g, 0.18 mmol) and thallium(I) acetylacetonate (0.055 g, 0.18 mmol) was stirred in benzene (8 ml) for 6 h. Thallium(I) chloride was removed by centrifugation and ether (20 ml) was added to the pale orange solution to precipitate colourless XIII (0.098 g, 59%).

Attempted preparation of an iridium complex derived from phosphorous acid

A mixture of $[IrCl(C_8H_{14})_2]_2$ (0.352 g, 0.39 mmol), triphenylarsine (0.481 g. 1.57 mmol) and phosphorous acid (0.129 g, 1.57 mmol) in benzene (4 ml) was heated under reflux for 1.5 h, giving a white precipitate and a yellow solution. Addition of ether gave more precipitate. This was filtered off, washed with ether and dried in vacuo to give 0.603 g of a colourless, hygroscopic product which analysed satisfactorily for $IrHCl(AsPh_3)_2[\{(HO)_2PO\}_2H]$ (see Table 3 and text).

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