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OXIDATIVE ADDITION OF DIALKYLPHOSPHINE OXIDES AND OF ALKYL ALKYLPHOSPHONITES TO IRIDIUM(I)

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Summary

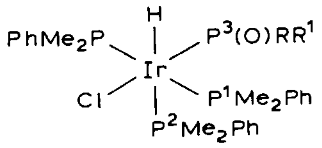
Dimethyl- and diethyl-phosphine oxide, methyl methylphosphonite and ethyl methylphosphonite all oxidatively add to $(Me_2PhP)_3IrCl$, generated in situ, to give hydrido(dialkylphosphinito)- or alkyl (alkylphosphonito)-iridium(III) complexes.

Introduction

A number of types of phosphorus-containing compounds can exist in tautomeric forms containing tricoordinate, trivalent phosphorus, (I) and tetracoordinate, pentavalent phosphorus (II) (eq.1) with form I usually predominating.

$$\underset{(I)}{RR^1POH} \rightleftharpoons \underset{(II)}{RR^1P(O)H} \qquad (1)$$

We have shown that the P–H bond of dialkylphosphites can oxidatively add to iridium(I) to give hydridodialkylphosphonatoiridium(III) species [1]. For example when the cyclooctene complex $[(C_8H_{14})_2Ir(CO)Cl]_2$ (III) was treated first with dimethylphenylphosphine (3 mols per mol Ir) and then with dimethylphosphite II ($R = R^1 = OCH_3$) (one mol per mol Ir), complex IVa was isolated.



(IV)

(IVa, $R = R^1 = OMe$,
IVb, $R = R^1 = Me$,
IVc, $R = R^1 = Et$,
IVd, $R = Me$, $R^1 = OMe$;
IVe, $R = Me$, $R^1 = OEt$;
IVf, $R = Ph$, $R^1 = OMe$)

Stephenson et al. recently reported [2] that diphenylphosphine oxide [3] II ($R = R^1 = Ph$), generated in situ from chlorodiphenylphosphine and water, reacts

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TABLE 1

^{1}H NMR SPECTRA [a] OF $IrHCl(Me_2PhP)_3$ (RR^1PO)

Complex	δ	Hydride [c]			Phosphine methyls	R, R^1	Aryl
		$J(HP^1)$	$J(HP^2)$	$J(HP^3)$			
IVa R = R^1 = OMe[b]	−9.7	142.6	19.5	14.6	1.62 (d,8.5,6H) 1.69 (2t,3.7,6H)	3.18 (d, 11.0, 6H)	7–8 (m, 15H)
IVb R = R^1 = Me	−11.4	136.0	20.6	14.0	1.50 (t, 3.5,6H) 1.75 (d, 8.2,6H) 1.87 (t, 4.1,6H)	0.84 (d, 10.0, 6H)	7–8 (m, 15H)
IVc R = R^1 = Et	−11.5	136.2	20.7	13.2	1.56 (t, 3.3,6H) 1.74 (d, 8.3,6H) 1.86 (t, 4.0,6H)	0.5–0.7 (m,6H) 1 –1.3 (m,4H)	7–7.9 (m, 15H)
IVd R = Me, R^1 = OMe	−11.4	137.2	19.7	17.2	1.40 (dd, 3.0,4.4,3H) 1.64 (d, 1.7,3H) 1.76 (dd,3.3,4.7,3H) 1.65–1.75 (m,9H)	0.34 (d,10.0,3H) 3.35 (d,10.6,3H)	7.2–7.9 (m, 15H)
IVe R = Me, R^1 = OEt [c]	−11.8	136.9	20.0	17.0	1.37 (t,3.6,3H) 1.64–1.81 (m,15H) [d]	0.29 (d,10.1,3H) 1.32 (t, 7.0,3H) 3.98 (d quin, 7,10,1H) 3.52 (d,quin, 7, 9,1H)	7.2–7.9 (m,15H)
IVf R = Ph, R^1 = OMe	−11.0	142.5	18.8	16.0	1.25 (d, 7.4, 3H) 1.35 (d, 7.0, 3H) 1.8–2 (m, 12H)	3.10 (d, 10.9, 3H)	6.8–8 (m, 20H)

[a] Measured in $CDCl_3$ at 250 MHz unless otherwise stated [b] Figures for IVa from ref. 1 [c] Widely spaced doublet of double triplets. In IVd–IVe the triplets overlap and appear as two quartets [d] When measured in C_6D_6 these protons appear as a three proton doublet at 1.75,(J(PH) 8.7 Hz) and two six proton multiplets.

with the cyclooctadiene complex $[IrCl(C_8H_{12})]_2$, to give $IrHCl(C_8H_{12})(Ph_2POHOPPh_2)$ containing a hydrogen-bonded ligand formed formally from diphenylphosphinous acid and diphenylphosphinite. The authors state that the hydride probably originates from the hydrochloric acid formed in the preparation of $Ph_2P(O)H$. They did however show that diphenylphosphine oxide will add to $IrCl(CO)(PPh_3)_2$ in solution to give five iridium(III) hydrides which were not isolated. Here and in our earlier work the hydrides must arise by P–H oxidative addition.

We now show that dialkylphosphine oxides II ($R = R^1$ = Me, Et) and alkyl alkylphosphonites II (R = Me, R^1 = OMe, OEt) can oxidatively add in a similar manner.

Results and discussion

When iridium(I) complex III in benzene was treated with dimethylphenylphosphine (3 mols per mol Ir) and then with dimethylphosphine oxide II ($R = R^1$ = Me) (1 mol per mol Ir) and the resulting solution heated at reflux, a colourless iridium(III) complex IVb could be isolated. The ^1H NMR spectrum ($CDCl_3$) of this complex shows a hydride resonance at -11.37 ppm consisting of a widely spaced doublet of overlapping double triplets (*J*(PH) 136.0, 20.6, 14.0 Hz) indicating that the hydride is *trans* to one phosphorus containing ligand and *cis* to three more, two of which are equivalent. The coupling constants are similar to those of IVa (see Table 1). A P–H coupling constant of 112 Hz has been observed for a cationic species made in solution in which hydride is probably *trans* to diphenyl phosphinite [2]. The $Me_2P(O)$ ligand in IVb appears as a doublet at 0.84 ppm (*J*(PH) 10.0 Hz) in the ^1H NMR spectrum while the signals due to the methyl groups of the phosphine ligands consist of a doublet at 1.75 ppm (*J*(PH) 8.2 Hz) for the ligand *trans* to hydride and two triplets at 1.50 ppm (*J*(PH) 3.5 Hz) and 1.87 ppm (*J*(PH) 4.1 Hz) for the strongly coupled mutually *trans* phosphines. The latter contain diastereotopic methyl groups and therefore give two signals. The $^{31}P\{^1H\}$ NMR spectrum of IVb shows a triplet (*J*(PP) 17 Hz) at 33.8 ppm due to two phosphorus atoms, an incompletely resolved signal at -42.2 ppm and a broad one at 17.0 each due to one phosphorus. The signal at -42.2 ppm appears as a broad doublet (*J*(PH) 135 Hz) in the undecoupled spectrum indicating that it is due to the ligand *trans* to hydride. It seems reasonable to assign the signal at 17.0 ppm to the dimethylphosphinito ligand since the other signals occur at chemical shifts typical of coordinated dimethylphenylphosphine and since oxygenated phosphorus ligands usually occur well to high field of orthophosphoric acid [1,2]. The addition of diethylphosphine oxide II ($R = R^1$ = Et) occurs in the same manner to give IVc which has very similar NMR spectral characteristics (see Tables 1 and 2). The $^{31}P\{^1H\}$ spectrum was however better resolved into a triplet and two quartets (pairs of overlapping triplets) indicative of two equivalent and two non-equivalent phosphorus ligands.

Next we turned to the addition of alkyl alkylphosphonites, compounds which seem to have been neglected as ligands [4]. When III was treated with dimethylphenylphosphine (3 mols per mol iridium) and methyl methylphosphonite II (R = Me, R^1 = OMe) (one mol per mol iridium) in benzene and the solution heated to reflux the brown-orange solution colour faded to pale yellow and a colourless complex could be isolated to which structure IVd has been assigned on the basis of its NMR

TABLE 2

^{31}P NMR SPECTRA [a] OF IrHCl $(Me_2PhP)_3(RR^1PO)$

	Complex	Phosphine R^1R^2PO			J(PP) (Hz)
		$\delta(P^1)$	$\delta(P^2)$ [e]	$\delta(P^3)$	
IVa	$R = R^1 = OMe$ [b]	−37.6	−43.0	31.1	$P^1P^2 = 17.6$, $P^2P^3 = 16.2$, $P^1P^2 = 25.0$
IVb	$R^2 = R^1 = Me$ [c]	−33.8	−42.2	17.0	$P^1P^2 = P^2P^3 = 17$
IVc	$R = R^1 = Et$	−34.4	−40.4	39.4	$P^1P^2 = P^2P^3 = P^1P^3 = 16$
IVd	$R = Me$, $R^1 = OMe$ [c]	−33.1	−41.6	50.8	$P^1P^2 = P^2P^3 = 19$
IVe	$R = Me$, $R^1 = OEt$ [c]	−33.4	−42.3	49.0	$P^1P^2 = P^2P^3 = 17$
IVf	$R = Ph$, $R^1 = OMe$ [c]	−36.5 [d]	−39.9	49.0	$P^1P^2 = P^2P^3 = 19$
		−37.0			$P^1P^2 = P^2P^3 = 20$

[a] Measured in $CDCl_3$, chemical shifts are in ppm relative to 85% H_3PO_4, positive to high frequency. Coupling constants are in Hz. [b] From ref. 1. [c] Signals for P^2 and P^3 not well resolved, therefore $J(P^2P^3)$ could not be measured. [d] Separate signals for *trans* phosphines (see text). [e] Appears as a broad doublet, when not proton decoupled, with same J(PH) as given by proton spectrum.

spectra. The ^{1}H NMR shows a hydride resonance similar to that in IVa–IVc (see Table 1) and the phosphonito ligand gives a doublet at 0.34 ppm (J(PH) 10.0 Hz) for the methyl joined directly to phosphorus and at 3.35 ppm (J(PH) 10.6 ppm) for the methyl joined to oxygen. Since the phosphonito ligand is chiral the signals due to the methyl groups of the phosphine ligands are more complex than in IVa–IVc. The methyl groups on the phosphine *trans* to hydride are diastereotopic in IVd and thus could appear as two doublets. One is apparent at 1.64 ppm (J(PH) 8.7 Hz), but the other is part of a multiplet at 1.65–1.75 ppm though it appears to be centred at 1.72 ppm (J(PH) 8.4 Hz). Similarly the methyl groups on the mutually *trans* phosphines could give up to four signals instead of two as in IVa–IVc. These should be triplets if the *trans* phosphorus atoms are strongly coupled. In practice this is not so and two three-proton double doublets rather than triplets appear at 1.40 ppm (J(PH) 3.0, 4.4 Hz) and 1.64 ppm (J(PH) 3.3, 4.7 Hz). The remaining two signals are in the multiplet at 1.65–1.75 ppm and seem to be coincident and centred at 1.69 ppm. The ^{31}P{^{1}H} NMR spectrum consists of a triplet (J(P–P) 19 Hz at −33.1 ppm due to two phosphorus atoms and unresolved signals at 50.8 and −41.6 ppm each due to one phosphorus. The signal at −41.6 ppm appears as a broad doublet (J(PH) 135 Hz) in the undecoupled spectrum showing it to be due to the ligand *trans* to hydride. As before the high field signal has been assigned to the oxygen containing ligand, the other signals having chemical shifts typical of coordinated alkylphosphines.

Compound IVe was made in a similar manner to IVd using ethyl methylphosphonite II ($R = Me$, $R^1 = OEt$) instead of methyl methylphosphonite. The ^{1}H and ^{31}P NMR spectra of the two compounds are similar (see Tables 1 and 2), but the phosphine-methyl resonances are less well resolved in the proton spectrum of IVe. The methylene protons of the ethoxy group in IVe are diastereotopic and give separate signals at 3.98 and 3.52 ppm which each appear as apparent double quintets as they are coupled to each other and to phosphorus and to the adjacent methyl protons.

When methyl phenylphosphonite II ($R = Ph$, $R^1 = OMe$) was used under the usual reaction conditions, IVf was the main product as judged by ^{1}H and ^{31}P NMR spectroscopy (see Tables 1 and 2), but it could not be isolated in an analytically pure state. The methyls on the phosphine *trans* to hydride show plainly as two doublets in

TABLE 3

ANALYTICAL DATA

Complex		Analyses (Found (calcd.) (%))	
		C	H
$IrHCl(Me_2PhP)_3(Me_2PO)$	(IVb)	43.89 (43.36)	5.80 (5.60)
$IrHCl(Me_2PhP)_3(Et_2PO)$	(IVc)	44.87 (44.95)	6.01 (5.93)
$IrHCl(Me_2PhP)_3[MeP(OMe)(O)]$	(IVd)	42.34 (42.42)	5.38 (5.48)
$IrHCl(Me_2PhP)_3[MeP(OEt)(O)]$	(IVe)	43.16 (43.23)	5.55 (5.64)

the proton spectrum consistent with their diastereotopic relationship. They also appear at higher field than in IVd and IVe presumably due to being close to the phenyl substituent on the phosphonite. That the phosphorus atoms of the mutually *trans* phosphines are diastereotopic is shown by the fact that they give separate signals in the $^{31}P\{^1H\}$ NMR spectrum. It is interesting that IVd and IVe do not show this effect.

Oxidative addition of P–H containing ligands to iridium(I) to give hydridoiridium(III) would appear to be a general process as we have shown that it occurs with ligands containing one, two or three P–O bonds [5].

Experimental

NMR spectra were recorded on a Bruker WM250 spectrometer at 250 MHz using TMS as internal standard for ^1H NMR spectra and at 101.27 MHz using 85% orthophosphoric acid as external standard for ^{31}P NMR spectra. Microanalyses were carried out at Queen's University by W.J. Swindall and associates. Benzene was dried by distillation from $LiAlH_4$ and ether was dried over sodium. Reactions were carried out under dry nitrogen. $[IrCl(CO)(C_8H_{14})_2]_2$ [6,7], $Me_2P(O)H$ [8,9] and $Et_2P(O)H$ [8] were made by literature methods. MeP(OMe)(O)H [10], MeP(OEt)(O)H [11] and PhP(OMe)(O)H [12] were made by the reaction of $MePCl_2$ [13] or $PhPCl_2$ with the appropriate alcohol by the method of Petrov et al. [11].

Preparations

To a solution of $[IrCl(CO)(C_8H_{14})_2]_2$ (0.200 g, 0.210 mmol) in benzene (6 ml) was added dimethylphenylphosphine (0.181 ml, 1.260 mmol) giving an orange solution. The appropriate oxygen containing ligand (0.420 mmol) was added and the solution heated at reflux for 1 h. The pale yellow solution which resulted was evaporated in vacuo and the residue washed with ether/pentane. The resulting solid was taken up in dichloromethane, the solution filtered and concentrated and ether added giving colourless solid (yield 30–40%). In the case of IVe, the product after benzene removal was triturated with cold ether and the resulting solid crystallized twice from dichloromethane ether.

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