COMPLEXES CONTAINING PHOSPHORUS LIGANDS-16¹

NEW PHOSPHINITE, PHOSPHONITE AND PHOSPHITE DERIVATIVES OF RUTHENIUM, OSMIUM AND IRIDIUM

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Abstract—The complexes $[MHCl(CO)(PPh_3)_3]$ (M = Ru or Os) readily undergo substitution at the site *trans* to the hydride ligand to afford phosphinite-, phosphonite-, or phosphite-containing products $[MHCl(CO)(PPh_3)_2L]$ [L = P(OR)Ph₂, P(OR)₂Ph or P(OR)₃ respectively; R = Me or Et]. The ruthenium complexes alone undergo further substitution to afford complex cations $[RuH(CO)(PPh_3)_nL_{4-n}]^+$ [n = 2, L = P(OMe)₃; n = 1, L = P(OR)₃; n = 0, L = P(OR)₂Ph or P(OR)Ph₂] which were isolated and characterised as their tetraphenylborate salts. Synthesis of the cationic complexes $[IrHL_3][BPh_4]_2$ [L = P(OR)₃, R = Me or Et] is also reported. Stereochemical assignments based on NMR data are given, and second order ³¹P and high field ¹H NMR patterns are analysed.

In contrast to the tertiary phosphines, tertiary phosphite esters, $P(OR)_3$, and the closely related P(OR)₂Ph, phosphonites, and phosphinites $P(OR)Ph_2(R = alkyl)$ have attracted relatively little attention as ligands in platinum metal chemistry.² This situation has been corrected to some degree in recent years by the incorporation of these less common phosphorus donor ligands in a series of cationic complexes which can be readily isolated as tetraphenylborate, tetrafluoroborate or hexafluorophosphate salts of relatively low solubility. Much of the early work in this area originated from our own laboratory.³⁻⁵ We now report an extension of our studies and describe a new range of ruthenium, osmium, and iridium complexes containing phosphorus donor ligands of the type under discussion.

RESULTS AND DISCUSSION

The complexes $MHCl(CO)(PPh_3)_2L$ (M = Ru, Os) The hydrido complexes $[MHCl(CO)(PPh_3)_3]$ (M = Ru or Os) react with phosphorus donor ligands $[L = P(OR)_x Ph_{3-x}, R = Me \text{ or } Et, x = 1 - 3]$ in boiling benzene or alcohol (ROH) solution to afford the uncharged monosubstituted products [MHCl(CO) $(PPh_3)_2L$] as air-stable, white crystalline solids, soluble in most common organic solvents. The high field proton NMR spectra of these products each comprise a doublet of triplets pattern $[^{2}J(PH)_{trans} = ca.$ 120–180 Hz(Ru) or ca. 90–140 Hz(Os); $^{2}J(PH)_{cis} = ca.$ 20-22 Hz] indicative of stereochemistry (I). This assignment is similar to those made for other ruthenium complexes [RuHCl(CO)(PR'₃)₂L], prepared by analogous substitution processes, and is in accord with the known high trans labilizing influence of the hydride ligand.

The osmium complexes do not undergo further substitution when subjected to prolonged and/or vigorous treatment in the presence of excess ligand. However, their more labile ruthenium analogues, when similarly treated with a large excess of ligand, L, give solutions which upon addition of sodium tetraphenylborate deposit complex salts of the general stoichiometry $[RuH(CO)(PPh_3)_nL_{4-n}]$ [BPh₄](n = 0 - 2).

The complex salt [RuH(CO)(PPh₃)₂L₂][BPh₄] $[L = P(OMe)_3]$. This product was obtained as an air-stable, white, crystalline solid, soluble in acetone, chloroform and dichloromethane, but sparingly soluble in alcohols. The proton NMR spectrum displays aryl, methyl and hydride protons in the required ratio 50:18:1. The methyl resonance, consisting of two doublets of equal intensity $[{}^{3}J(PH) = ca. 10.25 Hz],$ establishes the presence of two non-equivalent P(OMe)₃ ligands. The absence of a large coupling ²J(PP')_{trans} from the ³¹P NMR spectrum implies that the P(OMe)₃ ligands are not trans to triphenylphosphine. These data establish stereochemistry (IIa) for the complex. The high field proton resonance consists of a broad second order pattern which does not directly afford stereochemical information, except to confirm the location of a phosphorus donor ligand trans to the hydride. However, iterative analysis of the ³¹P and high field ¹H NMR spectra gave the data shown below which are consistent with the proposed structure (IIa).

An isomeric product, present in small quantity (ca. 10%), displays a compact second order high field proton NMR pattern together with a virtual coupling triplet in the methyl region. The former implies the absence of a phosphorus donor ligand *trans* to the hydride and the latter indicates the presence of a *trans* pair of P(OMe)₃ ligands⁷ thus establishing stereo-chemistry (IIb) for this minor product.

The complex salts $[RuH(CO)(PPh_3)L_3][BPh_4]$ $[L = P(OR)_3]$. These products were obtained as airstable, white, crystalline solids soluble in acetone, chloroform and dichloromethane but sparingly soluble in alcohols. The proton resonance of the triethyl phosphite complex shows aryl, methylene, methyl

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 ${}^{2}J(HP^{1}) = 17.75 Hz$, ${}^{2}J(HP^{2}) = 37.9 Hz$, ${}^{2}J(HP^{3}) = -124.5 Hz$, ${}^{2}J(P^{1}P^{2}) = 43.45 Hz$, ${}^{2}J(P^{1}P^{3}) = 36.45 Hz$, ${}^{2}J(P^{2}P^{3}) = 38.35 Hz$.

and hydride protons in the required ratio 35:18:27:1. The methyl resonance, comprising three triplet of equal intensity, establishes the presence of three non-equivalent P(OEt)₃ ligands, and the broad, second order, high field proton NMR pattern betrays the presence of a *trans* coupling ²J(PH). On the basis of this evidence we assign stereochemistry (IIIa) to this product. In contrast, the proton NMR spectrum of the corresponding trimethyl phosphite complex establishes stereochemistry (IIIb). The methyl resonance comprises a doublet and a triplet (relative intensities 1:2) and the high field proton pattern consists of a complex pattern which when subjected to iterative analysis affords the following data

The complex salts $[RuH(CO)L_4][BPh_4]$ [L = P(OR)_xPh_{3-x}, R = Me or Et, n = 1 or 2]. These products were obtained as air-stable, white crystalline solids. Their high field proton NMR spectra each consist of a regular first order quintet pattern indicative of stereochemistry (IV). Virtual coupling patterns consistent with the presence of four equivalent P(OMe)_xPh_{3-x} ligands arranged in a square planar manner are observed for the methyl diphenylphosphinite and dimethyl phenylphosphonite derivatives.[§] The complex salts $[IrHL_3][BPh_4]_2$ $[L = P(OR)_3;$ R = Me or Et]. These air-stable, white crystalline solids are soluble in dichloromethane but only very sparingly soluble in chloroform and alcohols. Their proton NMR spectra show aryl, alkyl and hydride proton resonances with the correct intensity ratios, but do not distinguish between axial (*trans* to hydride) and equatorial P(OR)₃ ligands. The ³¹P and high field ¹H NMR spectra are second order and therefore do not provide stereochemical information directly. However, iterative analysis of the ³¹P and high field ¹H NMR spectra (mixed CDCl₃/d₆-DMSO solvent) gave the following data

High field proton NMR spectra recorded at 250 MHz were first order and yielded data for $[IrH{P(OEt)_3}_{J}]BPh_{4}_{2}$ in good agreement with those presented above $[\delta(IrH) = -12.3 \quad (\tau \ 22.3)$ $^2J(PH)_{trans} = 170$ Hz, $^2J(PH)_{cis} = 16$ Hz.

Attempts to prepare the carbonyl species $[IrH(CO){P(OEt)_3}_4[BPh_4]_2$ by carbonylation of $[IrH{P(OEt)_3}_3]_3[BPh_4]_2$ for $l_2^{\frac{1}{2}}$ hr in boiling ethylmethylketone gave only unchanged starting material.

The stereochemical assignments made for the ruthenium complexes (I)-(IV) establish that the ligand substitution reactions are accompanied by a carbonyl



 ${}^{2}J(HP^{1}) = 21.3 Hz$, ${}^{2}J(HP^{2}) = 19.25 Hz$, ${}^{2}J(HP^{3}) = 15.65 Hz$, ${}^{2}J(P^{1}P^{2}) = 64.2 Hz$, ${}^{2}J(P^{1}P^{3}) = 43.95 Hz$, ${}^{2}J(P^{2}P^{3}) = -330.3 Hz$





migration step. It appears that, in order to minimise the effect of the increasing number of strong π -acceptor phosphorus donor ligands, the carbonyl ligand migrates to the site *trans* to the strong σ -donor hydride ligand. The proposed substitution (S) and isomerisation (I) processes are collected in Scheme 1.

EXPERIMENTAL

Platinum metal salts and phosphorus donor ligands were obtained from Johnson Matthey and the Maybridge Chemical Co. Ltd., respectively. Platinum metal triphenylphosphine complexes were made as previously described. Reagent grade organic solvents were used as purchased. All reactions were performed under nitrogen but the products were worked-up in air. Analyses, by the microanalytical laboratory, University College, London, and melting points, taken in sealed tubes under nitrogen, are given in Table 1. IR spectra were taken for nujol mulls'using a Perkin-Elmer 457 grating spectrometer. Proton NMR spectra were obtained using a Perkin-Elmer R12B (60 MHz) and a Bruker HFX90 (90 MHz) spectrometer. ³¹P NMR spectra were obtained using the Bruker HFX90 spectrometer operating at 36.43 MHz and are referenced to external H₃PO₄ in the sense that positive values are to low field. Spectroscopic data are recorded in Table 2. Iterative analyses of second order NMR data were performed using an ITRCAL programme.10

Carbonylchlorohydrido (trimethylphosphite)bis(triphenylphosphine)ruthenium(II). Carbonyl chlorohydridotris(triphenylphosphine)ruthenium (0.34 g) and trimethyl phosphite (0.12 g) in a mixture of methanol (30 cm^3) and benzene (5 cm^3) were heated under reflux for *ca*. 1 hr. The resultant clear solution was filtered while hot, concentrated under reduced pressure and set aside overnight. The crystals which separated were filtered off, washed successively with methanol and light petroleum (60–80), then recrystallised from dichloromethane-methanol to yield the required product as colourless microcrystals (0.175 g, 61%).

Similarly prepared using the appropriate ligand and alcoholic solvent were: carbonylchlorohydrido(triethyl phosphite)bis(triphenylphosphine) ruthenium(II) as colourless microcrystals (61%); carbonylchlorohydrido(dimethyl phenylphosphonite)bis(triphenylphosphine) ruthenium(II) as colourless crystals (66%); carbonylchlorohydrido(diethyl phenylphosphonite)bis(triphenylphosphine)ruthenium(II) as white crystals (63%); and carbonylchlorohydrido(methyl diphenylphosphinite)bis(triphenylphosphine)ruthenium(II) as colourless crystals (63%);

Similarly prepared from carbonylchlorohydridotris(triphenylphosphine)osmium were: carbonylchlorohydrido(trimethyl phosphite)bis(triphenylphosphine)osmium(II) as colourless crystals (83%); carbonylchlorohydrido(triethyl phosphite)bis(triphenylphosphine) osmium(II) as colourless crystals (86%); carbonylchlorohydrido(dimethyl phenylphosphonite)bis(triphenylphosphine)osmium(II) as colourless crystals (75%); carbo-

Table 1. Analysis and melting point data

COMPLEX	%C*	8H*	M.p./°C	
{RuHC1 (CO) (PPh ₃) ₂ [P(OMe) ₃]}	59.88(59.00)	4.99(4.95)	156-158	
{RuHC1 (CO) $(PPh_3)_2 [P(OEt)_3]$ }	60.47(60.33)	5.42(5.42)	154-157	
$\{\text{RuHCl}(\text{CO}) (\text{PPh}_3)_2 [P(\text{OMe})_2\text{Ph}]\}$	62.64(62.8)	4.96(4.92)	157-158	
{RuHCl(CO)(PPh ₃) ₂ [P(OEt) ₂ Ph]}	62.98(63.54)	5.29(5.22)	159-162	
{RuHCl(CO)(PPh ₃) ₂ [P(OMe)Ph ₂]}	65.40(66.26)	5.1 (4.89)	141-143	
${RuH (CO) (PPh_3)_2[P(OMe_3)_2]}{BPh_4}$	65,99(65,85)	5.86(5.69)	169-171	
{RuH (CO) (PPh ₃) [P (OMe) $_{3}$] }{BPh ₄ }	57.7 (57.62)	5.97(5.86)	124-126	
{RuH(CO)(PPh ₃){ $P(OEt)_3$ }{BPh ₄ }	60.81 (60.59)	6.52(6.75)	174-176	
{RuH(CO) [P(OEt) $_{2}$ Ph] $_{4}$ {BPh $_{4}$ }	63.75(62.89)	6.52(6.57)	164-165	
{RuH(CO)[P(OMe)Ph ₂] ₄ }{BPh ₄ }	70.88(70.36)	5.76(5.61)	188-190	
{RuH (CO) [P (OEt) Ph ₂] $_{4}$ {BPh ₄ }	71.16(70.99)	6.00(5.97)	204-205	
{RuH(CO) $\{P(OMe)_2Ph\}_4$ {BPh ₄ }	60.63(60.87)	6.11(5.81)	192-193	
$\{O_{SHC1}(CO)(PPh_3)_2 \{P(OMe)_3\}\}$	52.87(52.9)	4.41(4.76)	198-201	
$\{OSHCl(CO)(PPh_3)_2[P(OEt)_3]\}$	54.93(54.4)	4.93(5.24)	207-209	
$\left\{ \text{OsHC1}(\text{CO})(\text{PPh}_3)_2[P(\text{OMe})_2\text{Ph}] \right\}$	57.52(57.36)	4.3 (4.56)	207-208	
$\left\{ OsHCl (CO) (PPh_3)_2 [P(OEt)_2Ph] \right\}$	57.87(57.76)	4.74(4.71)	177-178	
$\{\text{OsHCl}(\text{CO}), (\text{PPh}_3)_2[P(\text{OMe})Ph_2]\}$	58.9 (58.44)	4.36(4.33)	185-188	
$\{OSHC1(CO)(PPh_3)_2[P(OEt)Ph_2]\}$	62.41 (62.6)	4.8 (4.74)	178-179	
$\{IrH[P(OMe)_3]_5\}\{BPh_4\}_2$	52.02(52.17)	6.02(5.98)	202-204	
{IrH[P(OEt)3]5}{BPh4}2	56.46(56.4)	7.00(7.04)	208-209	

* Calculated figures in parentheses

nylchlorohydrido (diethyl phenylphosphonite)bis (triphenylphosphine)osmium(II) as colourless crystals (59%); carbonylchlorohydrido (methyl diphenylphosphinite)bis (triphenylphosphine)osmium(II) as colourless crystals (90%); and carbonylchlorohydrido (ethyl diphenylphosphinite)bis (triphenylphosphine)osmium(II) as colourless crystals (72%).

Carbonylhydridobis(trimethyl phosphite)bis(triphenylphosphine)ruthenium(II) tetraphenylborate-Carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.34 g) and trimethyl phosphite (0.2 g) in a mixture of methanol (20 cm³) and chloroform (10 cm³) were heated under reflux for 30 min. The resultant clear solution was filtered while hot, then treated with sodium tetraphenylborate (0.2 g) in methanol (5 cm³), and stirred until precipitation commenced. The white precipitate was allowed to stand overnight then filtered off, washed with methanol and light petroleum (60-80), recrystallised from dichloromethane-methanol and dried in vacuo to yield the required product as colourless crystals (0.25 g, 61%). NMR data (see Discussion) indicate the presence of a second isomer (ca. 10%).

Carbonylhydridotris(trimethyl phosphite)(triphenylphosphine)ruthenium(II) tetraphenylborate—Carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.34 g) and trimethyl phosphite (0.2 g) in a mixture of methanol (30 cm³) and benzene (5 cm³) were heated together under reflux for ca. 3 hr. The resultant clear solution was filtered while hot, treated with sodium tetraphenylborate (0.2 g) in methanol (5 cm³), then concentrated to a small volume on a water bath before being allowed to cool with gentle stirring. The white precipitate was allowed to stand for a few hours, then filtered off, washed with methanol and light petroleum (60–80), recrystallised from dichloromethane-methanol and dried *in vacuo* to yield the required product as colourless microcrystals (0.23 g, 64%).

Carbonylhydridotris(triethyl phosphite)(triphenylphosphine)ruthenium(II)tetraphenylborate. Similarly obtained as colourless crystals (62%) using triethyl phosphite and ethanol in place of trimethyl phosphite and methanol. Carbonylhydridotetrakis(diethyl phenylphosphonite)ruthenium(II) tetraphenylborate - carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.34 g) and diethyl phenylphosphonite (1.0 g) in a mixture of ethanol (20 cm³) and benzene (10 cm³) were heated under reflux for ca. 2 hr. The resultant clear solution was filtered while hot, treated with sodium tetraphenylborate (0.2 g) in ethanol (5 cm³), then concentrated to a small volume under reduced pressure and stirred until precipitation occurred. The precipitate was allowed to stand overnight then filtered off, washed thoroughly with ethanol and light petroleum (60-80), recrystallised from dichloromethane-ethanol and dried in vacuo as white crystals (0.25 g, 61%).

Carbonylhydridotetrakis (methyl diphenylphosphinite) ruthenium (II) tetraphenylborate — Carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.34 g) and methyl diphenylphosphinite (1.0 g) in a mixture of methanol (20 cm³) and benzene (5 cm³) were heated under reflux for 1 hr. The resultant clear solution was filtered, cooled to ambient temperature and treated with a solution of sodium tetraphenylborate (0.2 g) in methanol (5 cm³). The white precip-

Table 2. IR^a and proton NMR^b data

COMPLEX	v (CO)	vMHcma ⁻¹	т (СН ₃)	т (СШ ₂)	³ J (PH) Hz	³ ј(нн') Hz	1 (MB)	² J(PH) _{trans} Hz	² J(PH) Hz
{RuHC1(CO) (PPh ₃) ₂ [P(OMe) ₃]}	1938(s)	1815 (w)	6.75(đ)		10.3		15.52 (d of t	179.43	20.5
{RuHC1 (CO) (PPh3) 2 [P (OEt) 3] }	1955 (s)	1818(w)	9.01(t)	6.39(qn)		7.05	15.64 (d of t	174.28	21.3
${RuHC1(CO)(PPh_3)_2(P(OMe)_2Ph)}$	1955(s)	1820 (vw)	6.59(d)		10.7		15.6 (d of t	150.76)	20.7
{RuHC1 (CO) (PPh3) 2 [P(OEt) 2Ph] }	1950(s)	1822 (vw)	8.96(t)	(5.9-6.6) c p		7.05	15.7 (d of t.	, 147.9)	21.2
{RuHC1 (CO) (PPh 3) 2 [P (OMe) Ph 2] }	1950(#)	1820 (vw)	7.37(d)	-	10.6		16.3 (d of t	122.8)	21.3
$\{\operatorname{RuH}(\operatorname{CO})(\operatorname{PPh}_3)_2[\operatorname{P}(\operatorname{OMe})_3]_2\}\{\operatorname{BPh}_4\}^{\texttt{e}}$	2000(s)	1820 (w)	6.85(d) 7.14(d)		10.25 10.25		17.82 c.p.		
${\text{RuH}(\infty)(\text{PPh}_3)[P(\text{OMe}_3]_3]{\text{BPh}_4}$	2018(5)	1820 (w)	6.4(d) 6.78(t)		10.9 5.5		17.16 c.p.		
$\{RuH(OO) (PPh_3) [P(OEt)_3]_3\}\{BPh_4\}$	2019(5)	1818(v)	8.73(t) 8.81(t) 9.0(t)	(6.02-6.3) c p		7.05 7.05 7.05	18.28 c.p.		
{RuH(CO) [P(OEt) $_2$ Ph] $_4$ {BPh} }	2008(s)	1820 (vw)	8.9(t)	(6.42-7.1) c p			16.2{q	n)	21.3
${RuH(CO) [P(OMe)Ph_2]_4}{BPh_4}$	2008(s)	1820 (w)	7.39(vc)	f			14.7(g	n)	19.8
{RuH (CO) [P(OEt)Ph2]4} {BPh4}	1995(s)	1820 (w)	9.65(t)	(6.94-7.02 cp)	6.75	14.87(qn)	19.8
${\text{RuH(CO)}(P(OMe)_2Ph)_4}{\text{BPh}_4}$	1955(s)	1820 (vw)	7.4(vc)	9			16.37(qn)	20
{OsHC1 (CO) (PPh 3) 2 [P (OMe) 3] }	1938(s)	1820 (w)	6.78(d)		10.5		15.41 (d of t	138.25	21.3
{OsHC1(CO)(PPh3)2[P(OEt)3]}	1935(s)	1820 (w)	9.05(t)	6.45 (qn)		7.05	15.56 (diofit	134.57 :)	22.1
$\left\{ \text{OSHCl}\left(\text{CO}\right) \left(\text{PPh}_{3}\right)_{2} \left[P\left(\text{OHe}\right)_{2} Ph \right] \right\}$	1940(s)	1820 (w)	6.63(d)		10.5		15.55 (d of t	117	20.6
$\left\{ OSHC1(CO)(PPh_3)_2[P(OEt)_2Ph] \right\}$	1934(s)	1820	8.98(t)	(5.85-6.77)	7.1	15.67 (diofit	115	21.2
$\left\{ O_{SHC1}(CO) (PPh_3)_2 [P(OMe)Ph_2] \right\}$	1935(s)	1820 (w)	7.41(d)		10.6		16.14 {d of t	97.3	21.2
$\{OSHC1(CO)(PPh_3)_2[P(OEt)Ph_2]\}$	1930(s)	1820 (w)	9.33(t)	7.07(gn)		6.2	16.19 (d of t	∿98 :)	21
$\{IrH[P(OMe)_3]_5\}\{BPh_4\}_2^c$		2070 (m)	3.75(vc) ^h			22.35 C P		
$\{IrH[P(OEt)_3]_5\}\{BPh_4\}_2^d$		2082 (m)	8.59(t)	5.7(q)		7.1	22.36 cp		

a) I.r. spectra taken in CHCl₃ solution; w = weak, s = strong.

b) N.m.r. spectra run in CDCl₃ (c) DMSO or (d) $(CD_3)_2 CO$ solution.

d = doublet, t = triplet, q = quartet, qn = quintet, vc = virtual coupling pattern, cp = complex pattern.

(e) major isomer

(f) separation of outer satellite peaks, ca. 11.9 Hz.

(g) separation of outer satellite peaks, <u>ca</u>. 11 Hz.

(h) The methyl protons give rise to a complex asymmetrical signal, the shape of which is consistent with the presence

of a doublet, due to the axial P(OMe), partly submerged under a vc pattern due to the 4 equivalent P(OMe), ligands.

itate which rapidly deposited was filtered off, washed with methanol and hexane then dried *in vacuo* to yield the required product as white microcrystals (0.35 g, 76%).

Carbonylhydridotetrakis(ethyl diphenylphosphinite)ruthenium(II)tetraphenylborate. Similarly obtained as white microcrystals (0.41 g, 85%) using ethyl diphenylphosphinite and ethanol in place of methyl diphenylphosphinite and methanol.

Carbonylhydridotetrakis(dimethyl phenylphosphonite) ruthenium(II) tetraphenylborate—Carbon monoxide was bubbled through a refluxing solution of $\{RuH[P(OMe)_2Ph]_5\}$ $\{BPh_4\}$ (0.25 g) in ethylmethyl ketone (20 ml) for ca. l_2^1 hr. The solution was cooled to ambient temperature and concentrated to a small volume under reduced pressure, then diluted with methanol (10 cm³) to precipitate the product as a white solid. The precipitate was filtered off and washed with methanol and light petroleum (60-80). Recrystallisation from dichloromethane-methanol gave the required product as colourless microcrystals (0.22 g, 59%).

Hydridopentakis (trimethylphosphite) iridium (III) tetraphenylborate — Carbonyldichlorohydridobis (triphenylphosphine) iridium (0.27 g), trimethylphosphite (0.25 g), and sodium tetraphenylborate (0.4 g) suspended in a mixture of ethylmethylketone (20 cm³) and methanol (10 cm³) were heated under reflux for ca. 3 hr. The mixture was filtered to remove a quantity of undissolved material, evaporated under reduced pressure until crystallisation commenced, then diluted with methanol and set aside until crystallisation was complete. The white precipitate was filtered off, washed with methanol and light petroleum (60–80) then recrystallised from dichloromethane-methanol and dried *in vacuo* as white crystals (0.25 g, 52%).

Hydridopentakis(triethyl phosphite)iridium(III) tetraphenylborate. Was similarly obtained as white crystals (51%), using triethyl phosphite and ethanol in place of trimethyl phosphite and methanol.

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