Journal of Organometallic Chemistry, 325 (1987) 285–292
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

COMPLEXES OF PLATINUM(II) AND PALLADIUM(II) WITH HYBRID PHOSPHINE-PHOSPHINE OXIDE LIGANDS OF TYPE $Ph_2P(CH_2)_nP(=O)Ph_2$ (n = 1, 2, 3, OR 4) *

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(Received October 6th, 1986)

Abstract

Treatment of $[PtCl_2(NCBu^t)_2]$ or $[PtCl_2$(cyclo-1,5-octadiene)] with $Ph_2P(CH_2)_nP(=O)Ph_2$ ($n = 1$, dppmO; $n = 2$, dppeO; $n = 3$, dpppO; $n = 4$, dppbO) gives complexes of the type *cis*-$[PtCl_2\{Ph_2P(CH_2)_nP(=O)Ph_2\}_2]$, independently of mole ratio. Treatment of *cis*-$[PtCl_2(dppmO)_2]$ with LiBr or NaI gives $[PtX_2(dppmO)_2]$ (X = Br, *cis*; X = I, *cis/trans* mixture) and on treatment with $Hg(C{\equiv}CPh)_2$ in ethanol, *trans*-$[Pt(C{\equiv}CPh)_2(dppmO)_2]$ is formed. Treatment of these ligands with $[PtMe_2$(cyclo-octa-1,5-diene)] gives exclusively *cis*-$[PtMe_2\{Ph_2P(CH_2)_nP(=O)Ph_2\}_2]$. Coordination of the P=O group was achieved by treating $[PtCl_2\{Ph_2P(CH_2)_nP(=O)Ph_2\}_2]$ with either $AgNO_3$ or $TlPF_6$, whereupon *cis*-$[Pt\{Ph_2P(CH_2)_nP(=O)Ph_2\text{-}P,O\}_2]^{2+}$ ($n = 1$, or 2) is formed: these cations were also synthesized by treating $[PtMe_2\{Ph_2P(CH_2)_nP(\approx O)Ph_2\}_2]$ with HBF_4. Treatment of $[PdCl_2(NCPh)_2]$ with dppmO gives *trans*-$[PdCl_2(dppmO)_2]$ only and this reacts with $AgNO_3$ or $TlPF_6$ to form *cis*-$[Pd(dppmO\text{-}P,O)_2]^{2+}$. The complexes were characterized by microanalysis, IR and NMR spectroscopy.

Although the coordination chemistry of phosphine oxides has been examined for 3*d*-metals [1], lanthanides [2], and actinides [3] and for some 4*d*- and 5*d*-metals in higher oxidation states [4,5], relatively little has been reported on phosphine oxides as ligands for the platinum metals. The weakly coordinating perchlorate ligand in complexes of the type $[M(OClO_3)(C_6F_5)(AsPh_3)_2]$ (M = Pt or Pd) has been displaced by $Ph_3P{=}O$ [6,7], and complexes of the type $[Pt(X)(O{=}PPh_3)(PEt_3)_2]^+$ have been synthesized in a similar way [8,9]. Better defined palladium(II) complexes of the type $[PdX_2(O{=}PRR'_2)_2]$ (R = R′ = Ph; X = Br or I. R = Et, R′ = Ph; X = Cl or I) were reported as the products of heating the corresponding phosphine complexes in air [10]. A study of the extraction of $Pd(NO_3)_2$ from aqueous solutions, using

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* Dedicated to Professor G.E. Coates on the occasion of his seventieth birthday.

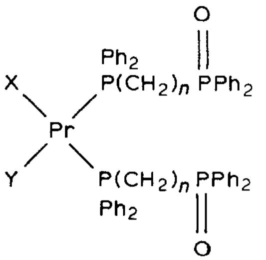
0022-328X/87/$03.50

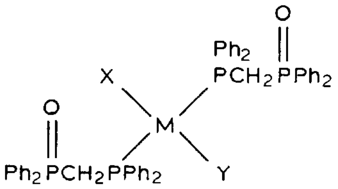
trialkylphosphine oxides, has been made [11] and there have been brief claims of the synthesis of paramagnetic Pd–Ph_3P=O complexes [12,13]. 2-Pyridyldiphenylphosphine oxide has been shown to act as a chelate for platinum(IV) in [$PtBr_4$(2-pyridyldiphenylphosphine oxide)] [14], which is the only structurally characterized phosphine oxide complex of a platinum metal. It seemed of interest to examine the behaviour of mixed tertiary phosphine/tertiary phosphine oxides as ligands towards platinum(II). We, of course, expected that the tertiary phosphine would bind strongly to the platinum but it was possible that the P=O might also be induced to coordinate because of the chelate effect, provided that the chelate ring was of a suitable size. Alternatively, the P=O group might interact only weakly with the platinum.

Results and discussion

We here report on a study of the four hybrid phosphine-phosphine oxides of type $Ph_2P(CH_2)_nP(=O)Ph_2$, $n = 1$, 2, 3, or 4 as ligands towards some platinum(II) moieties and the synthesis of one platinum complex. Recently a useful synthesis of such compounds has been reported which involves treatment of the diphosphines $Ph_2P(CH_2)_nPPh_2$ with benzyl bromide in benzene to give the monoquaternary salt, $[Ph_2P(CH_2)_nP(CH_2Ph)Ph_2]Br$, which when treated with aqueous alkali gives $Ph_2P(CH_2)_nP(=O)Ph_2$ and toluene [15]. In our hands this method gave good results for $n = 2$, 3, or 4 but a poor yield for $n = 1$. However, we devised a good method of synthesising $Ph_2PCH_2P(=O)Ph_2$ (dppmO) which was to treat the commercially available diphenyl(methyl)phosphine oxide with n-butyllithium in THF and treat the resultant carbanion with diphenylchlorophosphine. This gave dppmO in over 60% yield: details are in the Experimental.

Treatment of either $[PtCl_2(NCBu^t)_2]$ or $[PtCl_2(COD)]$ with dppmO (2/1, 1/1, 1/2 mole ratios) in $CDCl_3$, gave only *cis*-$[PtCl_2(dppmO)_2]$ (**1a**). The reactions were





1a : X = Y = Cl , n = 1
1b : X = Y = Br , n = 1
1c : X = Y = I , n = 1
1d : X = Y = Me , n = 1
1e : X = Y = Cl , n = 2
1f : X = Y = Me , n = 2
1g : X = Y = Cl , n = 3
1h : X = Y = Me , n = 3
1i : X = Y = Me , n = 4

2a : X = Y = I , M = Pr
2b : X = Y = C≡CPh , M = Pr
2c : X = Cl , Y = Me , M = Pr
2d : X = Y = Cl , M = Pd

TABLE 1

INFRARED [a] AND ANALYTICAL DATA

Complex	Analyses (Found (calcd.)(%)) [b]			ν(P=O) (cm^{-1}) [c]	Other bands (cm^{-1})
	C	H	Halogen		
1a·0.2 CH_2Cl_2	55.1(55.5)	4.25(4.1)	7.2(7.2)	1180m	320, 293, ν(Pt–Cl)
1b·1 $CHCl_3$	47.9(48.0)	3.7(3.8)	21.7 (20.3) [d]	1185m	
1c	48.0(48.0)	3.6(3.7)	20.2(20.3)	1195m	
1d·1 C_6H_6	63.1(63.1)	4.9(5.1)		1180m	
2b	64.4(64.4)	4.5(4.6)		1195s	2100m, ν(C≡C)
2c	58.6(58.5)	4.7(4.5)	3.6(3.4)	1190s	265, ν(Pt–Cl)
1e	56.6(57.0)	4.3(4.4)	6.7(6.5)	1195s	312, 290, ν(Pt–Cl)
1f	61.8(61.5)	5.2(5.2)		1200s	
1g	56.7(57.8)	4.5(4.7)	8.35(6.3)	1185s	314, 291, ν(Pt–Cl)
1h	62.1(61.2)	5.6(5.4)		1185br	
1i	see text			1185m	
2d	60.6(61.4)	4.5(4.5)	7.2(7.25)	1195m	343s, ν(Pd–Cl)
3a	49.5(50.2)	3.5(3.7)		1130s, 1120s	
3b	53.0(53.6)	4.0(4.0)	2.65(2.5) [e]	1108s, 1128s	
3d	46.5(47.5)	3.5(3.7)	16.9(17.4)		

[a] As Nujol mull. [b] The presence of some solvent of crystallization in some of the complexes was confirmed by ^{1}H NMR spectroscopy. [c] m = medium, s = strong, br = broad. [d] Halogen (total). [e] % nitrogen.

monitored by ^{31}P-{^{1}H} NMR spectroscopy and no evidence for chelation of the dppmO was found under these conditions. The product was isolated by precipitation with diethyl ether as a white solid. Its structure **1a** follows from (i) microanalytical data (Table 1) (ii) two strong IR absorbtion bands, at 293 and 320 cm^{-1}, assigned to ν(Pt–Cl) and absent from the spectra of the corresponding bromide or iodide complexes and a band at 1180 cm^{-1}, due to uncoordinated P=O, (iii) the ^{31}P-{^{1}H} NMR spectrum (Table 2), which shows ^1J(Pt–P) 3710 Hz, typical of P *trans* to Cl, and a resonance due to P^V at 25.4 ppm, shifted very little from the value for free dppmO (29.7 ppm). Interestingly, for **1a** the value of ^3J(Pt–P) is 103 Hz, whereas with [$PtBr_4$(2-pyridylphosphine oxide)], Pt–P^V coupling was not observed, even though the phosphine oxide is coordinated [14]. The ^{1}H-{^{31}P} NMR spectrum shows a singlet for the methylene protons, with platinum satellites, ^3J(Pt–H) 25.2 Hz. In the ^{1}H NMR spectrum, there is coupling to both *P* and *P*=O (Table 3). The corresponding dibromide is similar, see Tables and Experimental, but although the iodide was isolated as the *cis*-isomer, in solution it partially isomerized to the *trans*-isomer, as evidenced by ^{31}P-{^{1}H}, ^{1}H and ^{1}H-{^{31}P} NMR spectroscopy (Tables 2 and 3): equilibrium is reached after 3 h, in $CDCl_3$ at 20 °C, and the ratio of *trans*/*cis* is 7/3.

We have also prepared some organometallics containing dppmO ligands. Treatment of *cis*-[$PtCl_2$(dppmO-*P*)$_2$] with Hg(C≡CPh)$_2$ in hot ethanol gave *trans*-[Pt(C≡CPh)$_2$(dppmO)$_2$] (**2b**) in 65% yield. This formulation follows from (i) the analytical data (Table 1) and the *trans*-configuration from the single band due to ν(C≡C) at 2100 cm^{-1} (Table 1) (ii) the ^{31}P-{^{1}H} NMR spectrum, in which ^1J(Pt–P) is 2600 Hz, typical of *P trans* to *P* and (iii) the ^{1}H NMR spectrum, in which the methylene protons show a doublet of triplets with Pt satellites. The doublet (J(P–H) 12 Hz) is due to coupling to P=O and the triplet is a "virtual triplet" due

TABLE 2

^{31}P-{^{1}H} NMR DATA [a]

Complex	δ(P)	δ(PO)	^1J(PtP)	^3J(PtPO)	N [b]	Solvent [c]
1a	1.5	25.4	3710	103	12	A
1b	1.4	25.2	3664	95	17	A
1c	−2.3	26.6	3470	102	10	A
2a	−1.8	27.1	2497	49	n.r.	A
1d	13.6	25.4	1890	39	10	B
2b	5.5	24.9	2600	95	12	C
2c	18.3	25.5	3110	90	13	C
1e	10.0	32.9	3660	~ 0	57	C
1f	19.1	28.9	1880	~ 0	49	C
1g	70.5	32.6	3675	~ 0	~ 0	C
1h	16.6	30.6	1882	~ 0	~ 0	C
1i	17.4	31.5	1890	~ 0	~ 0	C
2a	11.8	24.4			~ 0	A
3a	36.0	59.2			d	D
3b	3.3	64.7	3877	72		C
3c	3.6	66.7	3850	76		C
3d	1.9	50.8	3655	~ 0	~ 0	C

[a] Chemical shifts (δ) in ppm ; ±0.1 ppm relative to 85% H_3PO_4 (positive shift to high frequency; coupling constants (J) in Hz (±2 Hz). Spectra were recorded at 25 °C, unless stated otherwise. [b] $N = |^2J(\text{PPO}) + {}^4J(\text{PP'O})|$. [c] A, $CDCl_3$; B, C_6D_6; C, CD_2Cl_2; D, $(CD_3)_2CO$. [d] $^2J(PPO)$ 5Hz.

to the mutually *trans* and strongly coupled Pt-bonded P-atoms (see Table 3). In this and other *trans*-isomers the methylene protons absorb at lower field than the methylenes of the *cis*-isomers.

TABLE 3

^{1}H AND ^{1}H-{^{31}P} NMR [a] DATA

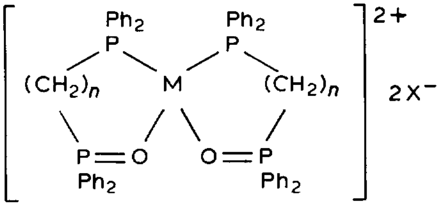
Complex	δ(CH_2)	$^3J(P\text{t}CH_2)$	$^2J(P\text{CH}_2)$	$J\{P(=\text{O})CH_2\}$	δ(CH_3)	$^2J(\text{PtCH}_3)$	N [b]	Solvent
1a	3.78	25.2	~ 6	~ 12				A
1b	3.82	24.6	12.0	12.0				A
1c	3.88	24.9	~ 12	~ 12				A
2a	4.49	26.1	~ 10 [d]	11.7				A
1d	3.54	16.1	7.8	12.0	0.51	69	14.0	B
2b	4.36	24.0	8.0 [d]	12.0				A
2c	4.22	18.1	7.8 [d]	11.0	−0.29	40	14.2	A
1e	2.64	n.r. [e]	n.r.	n.r.				A
1f	2.82	n.r.	n.r.	n.r.	1.33	68	13.8	B
1g	2.3–1.9m [f]							
1h	1.6–1.4m					65	13.8	B
1i	1.6–1.4m				0.43	65	13.2	A
2d	3.88	–	7.8 [d]	11.3				
3a	4.90		9.8	13.9				C
3c	4.76	28.8	9.8	13.4				C
3d	3.23m	–	–	–				C

[a] Spectra measured at 100 MHz. Chemical shifts (δ) in ppm (±0.01) to high frequency of $SiMe_4$ and coupling constants (J) in Hz. (±0.1) except for $^2J(P\text{t}CH_3)$ (±1 Hz). [b] $N = |^3J(\text{PCH}_3)_{trans} + {}^3J(\text{PCH}_3)_{cis}|$. [c] A = $CDCl_3$; B = C_6D_6; C = $(CD_3)_2CO$. [d] $|^2J(\text{PCH}_2) + {}^4J(\text{PCH}_2)|$. [e] n.r. = not resolved. [f] m = multiplet.

The action of dppmO on [PtMe$_2$(COD)] was studied by ^{31}P-{^{1}H} NMR spectroscopy in CDCl$_3$ or C$_6$D$_6$: in both cases only *cis*-[PtMe$_2$(dppmO-*P*)$_2$] (**1d**) was formed. This complex was prepared and isolated from toluene solution: characterizing data are in the Tables. When treated with dry HCl (1 mol) **1d** was converted into the *trans*-mono-methyl complex (**2c**), for which characterizing data are in the Tables. We hoped that the dimethyl complex (**1d**) would undergo oxidative addition reactions but when a solution of this complex (0.067 *M*) in dichloromethane was treated with MeI (0.27 *M*), no reaction occurred, even after 2 weeks at room temperature.

The homologous ligands dppeO and dpppO were also studied. These with [PtCl$_2$(NCPh)$_2$](dppeO) or [PtCl$_2$(COD)](dpppO) gave exclusively the *cis*-monodentate complexes **1e** and **1g**, respectively. Similarly the dimethylplatinum complexes **1f**, **1h** and **1i** were prepared by treating [PtMe$_2$(COD)] with dppeO, dpppO, or dppbO, respectively. These various complexes were more difficult to purify than the dppmO analogues and **1i** was only characterized by IR and NMR spectroscopy and not be elemental analysis.

Attempts to effect P=O coordination to platinum(II) or palladium(II) treating the halo complexes of type **1** with large coordinating anions such as BPh$_4$ or BF$_4$, failed. However, by treating the chloro complexes of type **1** with silver or thallium salts to remove chloride, P=O coordination was achieved. Thus treatment of a solution of the palladium complex **2d** with silver nitrate gave a precipitate of silver chloride and addition of ammonium hexafluorophosphate then gave the dppmO-*PO* chelate **3a**. The corresponding platinum bis-chelate was isolated as the nitrate salt **3b** and as the hexafluorophosphate salt **3c**, although the nitrate salt **3b** gave satisfactory elemental analytical data the carbon analysis for the hexafluorophosphate complex **3c** was low and the fluorine analysis high (Table 1), however, the ^{31}P-{^{1}H} NMR data indicate the cations to have the *cis*-structure shown in **3b** and **3c** in each case. The bis-chelated dppeO salt **3d** was also prepared. For the complexes **3b**, **3c** and **3d** the values of ^1J(PtP) are large, 3877, 3850 and 3655 Hz, respectively, and what one would expect for P *trans* to a hard donor such as O=P. The chemical shift of the coordinated P=O phosphorus is shifted downfield by ca. 35–40 ppm from the shift of the uncoordinated phosphorus. No coupling was observed between Pt and P=O for the dppeO-*PO* chelate **3d**, showing that $^2J(Pt\text{–}PO)$ is very small and suggesting that coupling between Pt and P in the dppmO chelate **3c** (76 Hz) or **3b** (72 Hz) is mainly a 3-bond coupling. As might be expected **3c** reacted with Et$_4$NI in CH$_2$Cl$_2$



(**3a** : M = Pd, n = 1, X = PF$_6$;
3b : M = Pr, n = 1, X = NO$_3$;
3c : M = Pr, n = 1, X = PF$_6$;
3d : M = Pr, n = 2, X = PF$_6$)

to give [PtI$_2$(dppmO-*P*)$_2$] (NMR evidence) although this could not be isolated pure.

Treatment of the dpppO chloro complex **1g** with either silver nitrate or thallium hexafluorophosphate gave only dark intractable oils, presumably because the seven-membered ring chelate produced is not stable. Treatment of the dimethyl compound **1h** with HPF$_6$ also led to decomposition; with **1d** or **1f**, treatment with HPF$_6$ gave **3c** or **3d**, respectively (^{31}P-{^{1}H} NMR spectroscopic evidence).

Experimental

The techniques and instrumentation used were as described in other recent papers from this laboratory [16].

Diphenylphosphino(diphenylphosphonyl)methane (dppmO). A solution of n-butyllithium in hexane (13.5 cm^3, 1.7 *M*, 23 mmol) was added at −78 °C with stirring to a solution of diphenylmethylphosphine oxide (4.9 g, 22.9 mmol). The solution was allowed to warm up to room temperature and then after 10 min recooled to −20 °C and diphenylchlorophosphine (5.08 g, 23 mmol) added to it, with stirring, over 20 min. The mixture was then warmed to ca. 20 °C and stirred for 2 h, after which it was hydrolysed with degassed aqueous ammonium chloride. The required product was isolated with ether and formed white prisms from propan-2-ol. Yield 6.0 g, 64%.

cis-[PtCl$_2$(dppmO-P)$_2$] (1a). A solution of dppmO (0.20 g, 0.25 mmol) in dichloromethane (5 cm^3) was added to a solution of [PtCl$_2$(NCBu^t)$_2$] (0.108 g, 0.25 mmol) in acetonitrile (10 cm^3). The mixture was then stirred for 30 min, after which it was evaporated under reduced pressure to ca. 4 cm^3 and diethyl ether added slowly; this gave the required product as white microcrystals. Yield 0.21 g, 79%.

cis-[PtBr$_2$(dppmO-P)$_2$] (1b). A mixture of *cis*-[PtCl$_2$(dppmO)$_2$] (0.20 g, 0.188 mmol) and lithium bromide (0.3 g) in acetone (30 cm^3) was stirred for 3 h and then evaporated to dryness. The required product was extracted into chloroform and formed yellow microcrystals from chloroform/propan-2-ol. Yield 0.18 g, 83%.

trans-[PtI$_2$(dppmO-P)$_2$] (2a). **2a** was prepared similarly and formed yellow microcrystals. Yield 83%.

trans-[Pt(C≡CPh)$_2$(dppmO-P)$_2$] (2b). A mixture of Hg(C≡CPh)$_2$ (0.075 g, 0.188 mmol) and *cis*-[PtCl$_2$(dppmO)$_2$] (0.20 g, 0.188 mmol) in ethanol (10 cm^3) was heated under reflux for 15 min. The mixture was then filtered to remove HgCl$_2$ and evaporated to dryness under reduced pressure, giving the required product, which formed yellow microcrystals from dichloromethane/diethyl ether. Yield 0.146 g, 65%.

cis-[PtMe$_2$(dppmO-P)$_2$] (1d). dppmO (0.20 g, 0.50 mmol) was added to a solution of [PtMe$_2$(COD)] (0.083 g, 0.25 mmol) in toluene (5 cm^3) at ca. 50 °C. The resultant yellow solution was slowly cooled to −20 °C, giving the required product as white prisms. Yield 0.224 g, 87%.

trans-[PtClMe(dppmO-P)$_2$] (2c). A solution of HCl (0.188 mmol) in methanol (1 cm^3) was generated by the addition of acetyl chloride (12.9 μl, 0.188 mmol). This solution was then added to a solution of *cis*-[PtMe$_2$(dppmO-*P*)$_2$] (0.193 g, 0.188 mmol) in dichloromethane (3 cm^3). The required product was isolated and formed a white powder from dichloromethane/n-hexane. Yield 0.16 g, 81%.

cis-[PtCl$_2$(dppeO-P)$_2$] (1e). dppeO (0.87 g, 2.1 mmol) and [PtCl$_2$(PhCN)$_2$] (0.47 g, 1.0 mmol) were heated together in refluxing benzene (25 cm^3) for 2 h. The mixture was then evaporated to dryness and the residue triturated with diethyl ether, to give the required product, which formed white microcrystals from chloroform/diethyl ether. Yield 0.91 g, 83%.

cis-[PtCl$_2$(dpppO-P)$_2$] (***1g***). dpppO (0.45 g, 1.05 mmol) was added to a suspension of [PtCl$_2$(COD)] (0.187 g, 0.5 mmol) in benzene (12 cm^3). The mixture was heated under reflux for 1 h, after which the resultant yellow solution was decanted from the sticky residue. The solution was evaporated to dryness and the residue triturated with diethyl ether and then dissolved in dichloromethane. n-Hexane was added, at intervals of 2 h to this solution, at 4 ° C, to give the required product as a white powder. Yield 0.32 g, 57%.

cis-[PtMe$_2$(dppeO-P)$_2$] (***1f***). A solution of dppmO (0.87 g, 2.1 mmol) in warm benzene (20 cm^3) was added to a solution of [PtMe$_2$(COD)] (0.353 g, 1.0 mmol) in benzene (20 cm^3). The mixture was stirred for 16 h, then evaporated to dryness and the residue triturated with pentane, giving the required product, which was obtained as a white powder from benzene/hexane. Yield 0.88 g, 84%.

cis-[PtMe$_2$(dpppO-P)$_2$] (***1h***). A mixture of dpppO (0.87 g, 2.05 mmol) and [PtMe$_2$(COD)] (0.37 g, 1.0 mmol) in benzene (25 cm^3) solution was warmed (40 ° C) for 30 min. The mixture was evaporated to dryness, giving a glass, which was triturated with diethyl ether/n-hexane and then stored under diethyl ether at −20 ° C. This produced the required product as a white powder. Yield 0.54 g, 48%. Attempts at recrystallization were unsuccessful.

cis-[PtMe$_2$(dppbO-P)] (***1i***). This was prepared similarly and formed white microcrystals from dichloromethane/cyclohexane. Yield 57%.

[Pd{Ph$_2$PCH$_2$P(=O)Ph$_2$}$_2$][PF$_6$]$_2$ (***3a***). A solution of silver nitrate (0.10 g, 0.6 mmol) in ethanol (5 cm^3)/water (0.5 cm^3), was added to a solution of **2d** (0.25 g, 0.25 mmol) in dichloromethane (2 cm^3). The resultant mixture was stirred for 1 h, in the dark, and then the silver salts were filtered off and the filtrate evaporated to ca. 3 cm^3. A solution of ammonium hexafluorophosphate (0.098 g, 0.6 mmol) in ethanol (18 cm^3) was then added to give a white precipitate. This was collected etc. and recrystallized from acetone/diethyl ether, to give the required product as white microcrystals. Yield 0.13 g, 42%.

[Pt{Ph$_2$PCH$_2$P(=O)Ph$_2$-PO}$_2$][NO$_3$]$_2$ (***3b***). A suspension of **1a** (0.27 g, 0.25 mmol) in acetone (20 cm^3) was treated with a solution of silver nitrate (0.10 g, 0.6 mmol) in methanol (9 cm^3)/water (1 cm^3). The resultant mixture was heated to ca. 50 ° C for 12 h and then evaporated to dryness. The required product was isolated with dichloromethane and formed white microcrystals from dichloromethane/diethyl ether. Yield. 0.20 g, 72%.

[Pt{Ph$_2$PCH$_2$P(=O)Ph$_2$-PO}$_2$][PF$_6$]}$_2$ (***3c***). A solution of TlPF$_6$ (0.128 g, 0.52 mmol) in acetone (10 cm^3) was added, with stirring to a solution of **1a** (0.25 g, 0.23 mmol) in dichloromethane (10 cm^3). After 2 h the solution was filtered from thallous salts and evaporated to dryness. The required product was extracted into acetone from which it was precipitated with diethyl ether. It formed white microcrystals from dichloromethane/chlorobenzene. Yield 0.21 g, 74%.

[Pt{Ph$_2$P(CH$_2$CH$_2$)P(=O)Ph$_2$-PO}$_2$][PF$_6$]$_2$ (***3d***). A solution of silver nitrate (0.20 g, 1.2 mmol) in ethanol (20 cm^3)/water (0.5 cm^3) was added to a solution of **1e** (0.55 g, 0.5 mmol) in dichloromethane (4 cm^3), in the dark. The mixture was then heated under reflux for 1 h, filtered and the filtrate evaporated to dryness. The residue was extracted with ethanol (15 cm^3) and the extract treated with a solution of NH$_4$PF$_6$ (0.19 g, 1.15 mmol) in ethanol (9 cm^3)/water (1 cm^3). The resultant

white precipitate was recrystallized from acetone/diethyl ether to give the required product. Yield 0.49 g, 75%.

Acknowledgements

We thank the S.E.R.C. for support and Johnson Matthey plc for the generous loan of platinum salts.

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