# SUBSTITUTION REACTIONS OF (DIPHOSPHINE)PALLADIUM(II) AND -PLATINUM(II) CHLORIDE AND TRIFLATE COMPLEXES

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Abstract—The triflate complexes  $[Pd(OTf)_2L_2]$  ( $L_2 = dppm$ , dppe, dppp) and  $[Pt(OTf)_2(dppp)]$  are prepared by reaction of the corresponding chloride with methyl triflate. The chloropalladium complexes  $[PdCl_2L_2]$  do not react with PPh<sub>3</sub>, but with PBu<sub>3</sub> substitution of one chloride takes place, whereas  $[PtCl_2(dppp)]$  reacts with either PPh<sub>3</sub> or PBu<sub>3</sub>. The triflate complexes  $[M(OTf)_2L_2]$  (M = Pd, Pt;  $L_2 = dppm$ , dppe, dppp) react with either PPh<sub>3</sub> or PBu<sub>3</sub> by substitution of one or both triflate ligands, although in CDCl<sub>3</sub> the system is complicated by reaction with the solvent.  $[Pt(cod)(dppp)][OTf]_2$  reacts with PPh<sub>3</sub> or PBu<sub>3</sub> by attack of the phosphine on one of the double bonds of cyclooctadiene.

We have described previously the substitution reactions of chloroplatinum(II) complexes containing bis(diphenylphosphino)methane (dppm) or 1,2-bis(diphenylphosphino)ethane (dppe) ligands.<sup>1</sup> Complexes of the type  $[PtCl_2L_2](L_2 = dppm, dppe)$ react with tertiary phosphines to give ionic species of the form  $[PtCl(PR_3)L_2]Cl$ . When  $L_2 = dppm$ , substitution of the second chloride by PR<sub>3</sub> occurs to generate  $[Pt(PR_3)_2(dppm)]Cl_2$ , whereas removal of the second chloride from the dppe complexes requires the addition of a silver salt. Also, the reactions of platinum(II) carboxylate complexes with tertiary phosphines in chlorinated solvents are complicated by the reaction of the displaced carboxylate ion with the solvent, and subsequent formation of chloroplatinum species of the type  $[PtCl(PR_3)]$ (dppe)]<sup>+</sup>.<sup>2</sup> Palladium and platinum complexes of the type  $[MCl(PR_3)L_2]ClO_4$ , formed by addition of  $PR_3$  to  $[MCl_2L_2]$  in the presence of silver perchlorate, have also been reported.<sup>3</sup>

We have reported recently the preparation of the triflate complexes  $[Pd(OTf)_2(dppe)]$  and  $[Pt(OTf)_2L_2]$  ( $L_2 = dppm$ , dppe;  $OTf = SO_3CF_3$ ).<sup>4</sup> In this paper we extend this series to  $[Pd(OTf)_2L_2]$ ( $L_2 = dppm$ , dppp) and  $[Pt(OTf)_2(dppp)]$ [dppp = 1,3-bis(diphenylphosphino)propane] and continue our studies on the substitution reactions of palladium and platinum complexes containing diphosphine ligands by investigating the reactions of the chloride and triflate compounds with tertiary phosphines.

### **RESULTS AND DISCUSSION**

We have shown that  $[PdCl_2(dppe)]$  and  $[PtCl_2L_2]$ ( $L_2 = dppm$ , dppe) react with AgOTf to give the corresponding triflate complexes. The dppe derivatives are actually isolated as diaquo species, whereas the triflates act as counter-ions and the dppm complex is obtained as  $[Pt(OTf)_2(dppm)]$ . The diaquo complex  $[Pt(H_2O)_2(dppe)][OTf]_2$  has been characterized by X-ray diffraction.<sup>4</sup> As an alternative to the use of silver salts, we have employed methyl triflate as a reagent for the synthesis of palladium or platinum triflates [eq. (1)].

$$[MCl_2L_2] + 2MeOTf \longrightarrow$$

$$[M(OTf)_2L_2] + 2MeCl \quad (1)$$

This has the advantage that the only by-product is methyl chloride, which is removed readily by evaporation along with the solvent. The reactions with  $[PdCl_2L_2]$  ( $L_2 = dppm$ , dppp) are complete within minutes, but the reaction of  $[PtCl_2(dppp)]$ is much slower, requiring almost 2 days to reach

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completion. The use of methyl triflate has limitations, however, and treatment of  $[PtCl_2(dppe)]$ with excess MeOTf gives virtually no reaction even after 2 days, whereas with AgOTf the reaction is complete within 2 h.

We have investigated the reactions of  $[MCl_2L_2]$ and  $[M(OTf)_2L_2]$  with one or two equivalents of PBu<sub>3</sub> or PPh<sub>3</sub>, as well as some reactions with diphosphines. The chloropalladium complexes do not react with PPh<sub>3</sub>, but with PBu<sub>3</sub> a complex of the form [PdCl(PBu<sub>3</sub>)L<sub>2</sub>]Cl is obtained in each case (Table 1). Addition of a second equivalent of PBu<sub>3</sub> results in no further reaction. For [PdCl<sub>2</sub>(dppm)] displacement of dppm by PBu<sub>3</sub> occurs also to give [PdCl<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub>] ( $\delta$ P 10.6), and this is more pronounced when a second PBu<sub>3</sub> is added [eq. (2)].

 $[PdCl_2(dppm)] + PBu_3 \longrightarrow$ 

## [PdCl(PBu<sub>3</sub>)(dppm)]Cl

+ $[PdCl_2(PBu_3)_2]$ +dppm (2)

We have reported that  $[PtCl_2(dppe)]$  reacts with PBu<sub>3</sub>, PEt<sub>3</sub>, PMePh<sub>2</sub> or PPh<sub>3</sub> to give  $[PtCl(PR_3)$  (dppe)]Cl, and  $[PtCl_2(dppm)]$  yields  $[PtCl(PR_3)$  (dppm)]Cl with PBu<sub>3</sub> or PMePh<sub>2</sub>.<sup>4</sup> The reaction of  $[PtCl_2(dppp)]$  with PPh<sub>3</sub> exhibits an unfavourable equilibrium; even with 2 equivalents of PPh<sub>3</sub> after 3 days the major species in solution are the reactants, although the central resonances for the  $[PtCl(PPh_3)(dppp)]^+$  cation could be detected (Table 1). The analogous reaction with PBu<sub>3</sub> produces  $[PtCl(PBu_3)(dppp)]Cl$ , but no further reaction takes place with excess PBu<sub>3</sub>.

The  ${}^{31}P{}^{1}H$  NMR spectrum of each of the complexes of the type  $[MCl(PR_3)L_2]Cl$  is characterized by three resonances, due to the three non-equivalent phosphorus atoms, with additional signals due to coupling with <sup>195</sup>Pt in the platinum complexes. For both palladium and platinum the <sup>31</sup>P resonances due to coordinated dppe appear to high frequency of those of the monodentate phosphines, and those for coordinated dppm lie to low frequency, whereas the <sup>31</sup>P shifts for coordinated dppp are similar to those found for PR<sub>3</sub>. Such observations regarding five-, four- and six-membered chelate rings, respectively, are well recognized.<sup>5</sup> Each resonance consists of a doublet of doublets, due to coupling to the remaining phosphorus atoms. The monodentate phosphine exhibits one large doublet, due to coupling to the trans phosphorus, and one smaller one. Within the bidentate ligand the phosphorus trans to  $PR_3$  is identified readily by its large coupling, whereas the phosphorus trans to chloride exhibits two smaller couplings. For [PtCl(PBu<sub>3</sub>)(dppp)]Cl the phosphorus trans to chloride is also distinguished by its larger  ${}^{1}J(Pt, P)$  value. Although

none of the chloropalladium complexes reacts with 2 equivalents of a monodentate phosphine, each reacts with its corresponding diphosphine to yield  $[Pd(dppm)_2]Cl_2$  ( $\delta P$  -25.4),  $[Pd(dppe)_2]Cl_2$  ( $\delta P$  56.4) or  $[Pd(dppp)_2]Cl_2$  ( $\delta P$  -3.2).

The reactions of  $[Pd(OTf)_2(dppe)]$  with PPh<sub>3</sub> or PBu<sub>3</sub> in CDCl<sub>3</sub> solution at ambient temperature generate species of the type  $[Pd(OTf)(PR_3)(dppe)]^+$ (Table 1), the NMR parameters of the PBu<sub>3</sub> complex being significantly different from its chloro analogue. In particular the  ${}^{2}J(P, P)$  value for coupling between the mutually trans phosphorus atoms is reduced by ca 40 Hz. [Pd(OTf)(PPh<sub>3</sub>)(dppe)]<sup>+</sup> reacts with a second PPh<sub>3</sub> to produce the  $[Pd(PPh_3)_2(dppe)]^{2+}$  cation (Table 2), whereas addition of a second PBu<sub>3</sub> to [Pd(OTf)(PBu<sub>3</sub>) (dppe)]<sup>+</sup> yields a mixture of  $[Pd(PBu_3)_2(dppe)]^{2+}$ ,  $[Pd(OTf)(PBu_3)(dppe)]^+$  and  $[PdCl(PBu_3)(dppe)]^+$ . In order for the chloropalladium cation to be formed, the displaced triflate must react with the solvent to generate chloride, which then displaces a further triflate. We have observed similar phenomena in the substitution reactions of platinum carboxylate complexes.<sup>2</sup> The <sup>31</sup>P NMR data for  $[Pd(PPh_3)_2(dppe)]^{2+}$  and  $[Pd(PBu_3)_2(dppe)]^{2+}$ will be discussed later.

When the  $[Pd(OTf)_2L_2](L_2 = dppm, dppp)$  complexes are treated with PPh<sub>3</sub> or PBu<sub>3</sub> in CDCl<sub>3</sub> solution products with NMR parameters very similar to those of  $[PdCl(PR_3)L_2]^+$  are obtained. When the reactions are carried out at  $-40^{\circ}$ C the same products are found. Initially, we thought that the products were the chloropalladium cations, formed by reaction of the triflate ion with the solvent, which would have to take place faster than in the dppe case. The reaction of [Pd(OTf)<sub>2</sub>(dppm)] with PBu<sub>3</sub> is again complicated by displacement of dppm. When the reactions are performed in acetonitrile solution, however, products with virtually identical NMR parameters are obtained. Since there is no source of chloride in this case, we conclude that the products are indeed  $[Pd(OTf)(PR_3)L_2]^+$ , whose NMR parameters are given in Table 1. We cannot rule out, however, the possibility that the chloro complexes are formed in CDCl<sub>3</sub> solution, whereas  $[Pd(OTf)(PR_3)L_2]^+$  or  $[Pd(CH_3CN)(PR_3)L_2]^{2+}$  is formed in acetonitrile (vide infra).

The reactions of  $[Pt(OTf)_2(dppm)]$  with PPh<sub>3</sub> or PBu<sub>3</sub>, and of  $[Pt(OTf)_2(dppe)]$  with PPh<sub>3</sub>, do not produce species of the type  $[PtX(PR_3)L_2]^+$ , but generate the  $[Pt(PR_3)_2L_2]^{2+}$  cations (*vide infra*) directly (Table 2). Thus, when 1 equivalent of phosphine is added an approximately 1:1 mixture of  $[Pt(OTf)_2L_2]$ and  $[Pt(PR_3)_2L_2]^{2+}$  is obtained. With a second equivalent of PR<sub>3</sub> the bis(phosphine) complex is formed quantitatively. The reaction of the dppe complex



	$\delta P_A$	$^{2}J(\mathbf{P}_{A},\mathbf{P}_{B})$	$^{1}J(\mathrm{Pt},\mathrm{P}_{\mathrm{A}})$
Complex	$\delta P_B \ \delta P_C$	$^{2}J(\mathbf{P}_{A}, \mathbf{P}_{C})$ $^{2}J(\mathbf{P}_{B}, \mathbf{P}_{C})$	$^{1}J(\text{Pt}, \text{P}_{\text{B}})$ $^{1}J(\text{Pt}, \text{P}_{\text{C}})$
[PdCl(PBu <sub>3</sub> )(dppm)] <sup>+</sup>	- 50.0 br d - 31.6 dd 14.4 dd	78 456 5	
[PdCl(PBu <sub>3</sub> )(dppe)] <sup>+</sup>	60.4 dd 63.5 dd 10.8 dd	10 406 19	
[PdCl(PBu <sub>3</sub> )(dppp)] <sup>+</sup>	0.3 dd 12.3 dd 12.3 dd	39 422 10	
[PtCl(PBu <sub>3</sub> )(dppp)] <sup>+</sup>	- 1.0 dd - 4.7 dd 7.4 dd	30 373 17	2090 3450 2280
[PtCl(PPh <sub>3</sub> )(dppp)] <sup>+</sup>	-0.3 dd -2.7 dd 24.0 dd	30 391 14	ь ь ь
[Pd(OTf)(PBu <sub>3</sub> )(dppm)] <sup>+</sup>	52.3 dd 32.6 dd 15.1 dd	85 457 5	
[Pd(OTf)(PPh <sub>3</sub> )(dppm)] <sup>+</sup>	- 51.5 dd - 38.2 d 22.2 d	81 464 c	
[Pd(OTf)(PBu <sub>3</sub> )(dppe)] <sup>+</sup>	62.5 dd 66.0 br d 14.3 dd	6 366 20	
[Pd(OTf)(PPh <sub>3</sub> )(dppe)] <sup>+</sup>	67.4 d 69.2 d 25.0 dd	ء 370 19	
[Pd(OTf)(PBu <sub>3</sub> )(dppp)] <sup>+</sup>	1.0 dd 12.8 dd 13.3 dd	40 420 11	
[Pd(OTf)(PPh <sub>3</sub> )(dppp)] <sup>+</sup>	4.8 dd 14.4 dd 27.2 dd	36 431 11	
$[Pt(CH_3CN)(PBu_3)(dppe)]^{2+d}$	38.4 dd 57.0 dd 10.1 dd	6 304 18	3691 2103 2215
$[Pt(CH_{3}CN)(PPh_{3})(dppe)]^{2+d}$	39.9 dd 57.7 dd 20.9 dd	6 319 17	3662 2263 2312
$[Pt(CH_3CN)(PBu_3)(dppp)]^{2+d}$	10.5 dd 4.6 dd 11.3 dd	32 305 17	3548 1971 2191
$[Pt(CH_{3}CN)(PPh_{3})(dppp)]^{2+d}$	-11.2 dd -4.0 dd 34.3 dd	30 322 16	3472 2117 2316

<sup>&</sup>lt;sup>*a*</sup> Chemical shifts are relative to external  $H_3PO_4$ , positive shifts representing deshielding. Coupling constants are in Hz. Spectra were recorded in CDCl<sub>3</sub> solution unless stated.

 $b^{1}J(Pt, P)$  values were not observed due to the low concentration of complex.

<sup>c</sup> Too small to be observed. <sup>d</sup> Recorded in CH<sub>3</sub>CN/CD<sub>3</sub>CN solution.

Table 2.  ${}^{31}P{}^{1}H$  NMR data for complexes of the type  $[M(PR_3)_2L_2]^{2+a}$ 



	- 6	- C	
Complex	δΡ <sub>Α,Β</sub> δΡ <sub>C,D</sub>	${}^{2}J_{AB}$ ${}^{2}J_{AC} ({}^{2}J_{BD})$ ${}^{2}J_{AD} ({}^{2}J_{BC})$ ${}^{2}J_{CD}$	$^{1}J(\text{Pt, P}_{A,B})$ $^{1}J(\text{Pt, P}_{C,D})$
[Pd(PPh <sub>3</sub> ) <sub>2</sub> (dppe)] <sup>2+</sup>	59.4 25.5		
$[Pd(PBu_3)_2(dppe)]^{2+}$	58.1 3.5	$\pm 16 + 323 - 30 \pm 28$	
[Pd(dppm)(dppe)] <sup>2+</sup>	59.4 24.6	$\pm 14 + 344 - 5 \pm 74$	
[Pd(dppm)(dppp)] <sup>2+</sup>	2.8 -29.4	$\pm 42 + 358 + 3 \pm 74$	
[Pd(dppp)(dppe)] <sup>2+</sup>	55.5 - 4.0	Ь	
[Pt(PBu <sub>3</sub> ) <sub>2</sub> (dppm)] <sup>2+</sup>	-34.7 0.3	$\pm 57 + 317 - 23 \pm 16$	1872 2356
[Pt(PPh <sub>3</sub> ) <sub>2</sub> (dppm)] <sup>2+</sup>	-33.0 13.0	$\pm 52 + 328 - 22 \pm 19$	1998 2504
[Pt(PPh <sub>3</sub> ) <sub>2</sub> (dppe)] <sup>2+</sup>	46.3 15.0		2305 2463

<sup>*a*</sup> Chemical shifts are relative to external  $H_3PO_4$ , positive shifts representing deshielding. Coupling constants are in Hz. Spectra were recorded in CDCl<sub>3</sub> solution.

 ${}^{b}{}^{2}J_{AC} + {}^{2}J_{AD} = 305$  Hz. Other couplings are unresolved.

must proceed through  $[Pt(OTf)(PPh_3)(dppe)]^+$ and, since  $[PtCl(PPh_3)(dppe)]^+$  does not react with further PPh<sub>3</sub>,<sup>1</sup> displacement of the second triflate by PPh<sub>3</sub> must occur more rapidly than the interaction of triflate with the solvent to produce chloride. The reactions of  $[Pt(OTf)_2(dppe)]$  with PBu<sub>3</sub>, and of  $[Pt(OTf)_2(dppp)]$  with PPh<sub>3</sub> or PBu<sub>3</sub>, in CDCl<sub>3</sub> solution generate species of the type [PtCl  $(PR_3)L_2]^+$ . Here the values of  ${}^1J(Pt, P)$  make it clear that the chloro rather than the triflate cations are formed. The triflate cations are not obtained in acetonitrile solution either, because in this solvent complexes of the type  $[Pt(CH_3CN)(PR_3)L_2]^{2+}$  are produced. When  $[Pt(OTf)_2(dppp)]$  is dissolved in  $CH_3CN/CD_3CN$  a single <sup>31</sup>P resonance is observed at  $\delta P - 13.6$ ,  ${}^1J(Pt, P)$  2912 Hz, which we attribute

to the  $[Pt(CH_3CN)_2(dppp)]^{2+}$  cation. Addition of 1 equivalent of PPh<sub>3</sub> or PBu<sub>3</sub> generates  $[Pt(CH_3CN)(PR_3)(dppp)]^{2+}$ . Similarly, addition of PPh<sub>3</sub> or PBu<sub>3</sub> to  $[Pt(CH_3CN)_2(dppe)]^{2+}$  produces  $[Pt(CH_3CN)(PR_3)(dppe)]^{2+}$  (Table 1). We have reported previously that the  $[Pt(CH_3CN)(PPh_3)$  $(dppe)]^{2+}$  cation is formed when PPh<sub>3</sub> is added to a CD<sub>3</sub>CN solution of  $[Pt(CD_3CN)_2(dppe)]^{2+}$ , generated from  $[Pt(cod)(dppe)][ClO_4]_2$ .<sup>4</sup> Thus, we are unable to observe complexes of the form  $[Pt(OTf)(PR_3)L_2]^+$  in either solvent.

The palladium triflate complexes react with dissimilar diphosphines to generate unsymmetrical bis(diphosphine)palladium dications. Thus, [Pd (OTf)<sub>2</sub>(dppe)] has been treated with dppm or dppp, and [Pd(OTf)<sub>2</sub>(dppp)] with dppm, to produce the three possible  $[Pd(L_2)(L'_2)]^{2+}$  species (Table 2). These, and cations of the type  $[Pd(PR_3)_2(dppe)]^{2+}$ , each gives rise to an AA'XX' pattern in its <sup>31</sup>P NMR spectrum. These have been analysed<sup>6</sup> and simulated in each case, with the exception of  $[Pd(dppp)(dppe)]^{2+}$  which is of too low solubility to be analysed fully. The <sup>31</sup>P NMR spectra of the platinum complexes  $[Pt(PPh_3)_2L_2]^{2+}$  (L<sub>2</sub> = dppm, dppe) and [Pt(PBu<sub>3</sub>)<sub>2</sub>(dppm)]<sup>2+</sup> have been treated similarly. In each case the mutually trans phosphorus atoms exhibit a two-bond coupling in excess of 300 Hz, and this is taken to be of positive sign. The signs of the couplings between chemically identical phosphorus atoms cannot be determined, but the *cis* coupling of dissimilar phosphorus atoms ranges from -29 Hz in  $[Pd(PPh_3)_2(dppe)]^{2+}$  to +3Hz in  $[Pd(dppm)(dppp)]^{2+}$ .

Finally, we found previously that attempts to prepare [Pt(cod)(dppe)][OTf]<sub>2</sub> resulted in slow, but steady, displacement of the cyclooctadiene by triflate on standing in solution.<sup>4</sup> In contrast, when  $[PtCl_2(cod)]$  is treated sequentially with dppp and AgOTf, [Pt(cod)(dppp)][OTf]<sub>2</sub> is isolated, without any contamination by [Pt(OTf)<sub>2</sub>(dppp)]. The cyclooctadiene complex reacts with PPh<sub>3</sub> or PBu<sub>3</sub> in a manner analogous to its dppe counterpart, the phosphine adding to one double bond of the cyclooctadiene, to give a species of the form  $[Pt{\sigma: \eta^2-C_8H_{12}(PR_3)}(dppp)][OTf]_2$ . Each complex is characterized by three <sup>31</sup>P resonances, each of which appears as a doublet of doublets. The  ${}^{4}J(P, P)$  values are ca 50 and 5 Hz, respectively, for coupling of the phosphonium phosphorus atom to the *trans* and *cis* phosphorus atoms of the dppp ligand. The phosphorus atom of the dppp ligand trans to the double bond has a  ${}^{1}J(Pt, P)$  value of 3850 Hz, whereas that *trans* to the  $sp^3$  carbon exhibits a coupling of ca 1600 Hz. The phosphonium phosphorus atom has a three-bond coupling to platinum of ca 200 Hz.

We have shown that only the more nucleophilic phosphine PBu<sub>3</sub> is capable of displacing chloride from palladium, and only one chloride is displaced, whereas both PPh<sub>3</sub> and PBu<sub>3</sub> can effect this substitution at platinum. In contrast, either PPh<sub>3</sub> or PBu<sub>3</sub> displaces triflate from palladium or platinum, and in some cases both triflates may be substituted. With palladium the second triflate is most readily displaced from the dppe complex, whereas substitution of both triflates from platinum occurs most easily in the dppm case. In CDCl<sub>3</sub> the reactions of the triflate complexes are complicated by reaction with the solvent to produce chloride ions. For the cyclooctadiene complex [Pt(cod)(dppp)][OTf]<sub>2</sub> attack of the phosphine on the diene occurs instead of displacement.

#### **EXPERIMENTAL**

 ${}^{31}P{}^{1}H$  NMR spectra were recorded for CDCl<sub>3</sub> solutions on a Varian XL-300 instrument, operating in the FT mode. Chemical shifts are reported relative to external H<sub>3</sub>PO<sub>4</sub>. NMR spectra were simulated using the RACCOON program.<sup>7</sup> Microanalyses were performed by Atlantic Microlab Inc., Norcross, Georgia. The complexes  $[PdCl_2(cod)], [Pd(OTf)_2(dppe)], [Pt(OTf)_2(dppm)]$ and [Pt(OTf)<sub>2</sub>(dppe)] were prepared by reported methods.<sup>4,8</sup> CH<sub>3</sub>SO<sub>3</sub>CF<sub>3</sub> (CH<sub>3</sub>OTf) and AgSO<sub>3</sub> CF<sub>3</sub> (AgOTf) were purchased from Aldrich and used without purification. Complexes of the type  $[MCl_2L_2]$  (M = Pd, Pt;  $L_2$  = dppm, dppe, dppp) were prepared by displacement of cyclooctadiene from [MCl<sub>2</sub>(cod)].<sup>9 31</sup>P{<sup>1</sup>H} NMR data for these complexes are as follows: [PdCl<sub>2</sub>(dppm)]  $\delta P$ -53.7; [PdCl<sub>2</sub>(dppe)] 64.0; [PdCl<sub>2</sub>(dppp)] 11.8;  $^{1}J(\text{Pt}, \text{P})$  $[PtCl_2(dppm)] - 64.6,$ 3074 Hz:  $[PtCl_2(dppe)]$  41.7,  ${}^{1}J(Pt, P)$  3607 Hz;  $[PtCl_2(dppp)]$ -4.9, <sup>1</sup>*J*(Pt, P) 3398 Hz.

#### Preparation of [Pd(OTf)<sub>2</sub>(dppm)]

To a CH<sub>2</sub>Cl<sub>2</sub> solution (150 cm<sup>3</sup>) of [PdCl<sub>2</sub>(dppm)] (0.36 g, 0.63 mmol) was added CH<sub>3</sub>OTf (0.29 cm<sup>3</sup>, 2.5 mmol). The initially light yellow solution darkened immediately. After 10 min the solution was concentrated, then filtered. On standing for several days the product was obtained as dark yellow crystals. Found: C, 40.7; H, 3.2. Calc. for  $C_{27}H_{22}F_6O_6P_2PdS_2$ : C, 41.1; H, 2.8%. <sup>31</sup>P{<sup>1</sup>H} NMR :  $\delta P - 52.7$ .

## Preparation of [Pd(OTf)<sub>2</sub>(dppp)]

To a  $CH_2Cl_2$  solution (50 cm<sup>3</sup>) of [PdCl<sub>2</sub>(dppp)] (0.36 g, 0.61 mmol) was added  $CH_3OTf$  (0.14 cm<sup>3</sup>, 1.2 mmol). The initially light yellow solution became dark yellow. After stirring for 10 min the solution was concentrated to 10 cm<sup>3</sup>, causing the precipitation of a yellow solid. This was filtered and washed with ether (0.21 g, 43%). Found: C, 43.3; H, 3.6. Calc. for  $C_{29}H_{26}F_6O_6P_2PdS_2$ : C, 42.6; H, 3.2%. <sup>31</sup>P{<sup>1</sup>H} NMR :  $\delta$ P 15.7.

## Preparation of [Pt(OTf)<sub>2</sub>(dppp)] · 2H<sub>2</sub>O

A colourless solution of  $[PtCl_2(dppp)]$  (0.20 g, 0.30 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 cm<sup>3</sup>) was treated with CH<sub>3</sub>OTf (0.068 cm<sup>3</sup>, 0.60 mmol). After stirring for 43 h, the solution was concentrated and ether was added to cause precipitation. The white solid was filtered and washed with ether (0.16 g, 58%). Found: C, 37.0; H, 3.2. Calc. for C<sub>29</sub>H<sub>30</sub>F<sub>6</sub>O<sub>8</sub> P<sub>2</sub>PtS<sub>2</sub>: C, 37.0; H, 3.2%. <sup>31</sup>P{<sup>1</sup>H} NMR :  $\delta$ P -4.5, <sup>1</sup>J(Pt, P) 3515 Hz.

Reactions of  $[MX_2L_2]$  (M = Pd, Pt; X = Cl, OTf; L<sub>2</sub> = dppm, dppe, dppp) with tertiary phosphines and diphosphines

In a typical reaction, the metal complex was suspended in CDCl<sub>3</sub> or CH<sub>3</sub>CN/CD<sub>3</sub>CN in an NMR tube. The ligand was added as a solid or by syringe, as appropriate, and the contents of the tube were examined immediately by  ${}^{31}P{}^{1}H{}$  NMR spectroscopy. Where necessary the reactions were monitored over a 24 h period.

## Preparation of [Pt(cod)(dppp)][OTf]<sub>2</sub>

To a  $CH_2Cl_2$  solution (20 cm<sup>3</sup>) of [PtCl<sub>2</sub>(cod)] (0.10 g, 0.27 mmol) was added dppp (0.11 g, 0.27 mmol) in portions. After 10 min, AgOTf (0.15 g, 0.56 mmol) was introduced and the mixture was stirred for 1.5 h. After filtration the solvent was removed. Crystallization from  $CH_2Cl_2/Et_2O$  gave the product as white crystals (0.13 g, 52%). Found : C, 43.7; H, 3.8. Calc. for  $C_{37}H_{38}F_6O_6P_2PtS_2$ : C, 43.8; H, 3.8%. <sup>31</sup>P{<sup>1</sup>H} NMR :  $\delta P$  – 6.3, <sup>1</sup>*J*(Pt, P) 2912 Hz.

Reactions of  $[Pt(cod)(dppp)][OTf]_2$  with tertiary phosphines

The platinum complex was suspended in CDCl<sub>3</sub> in an NMR tube and 1 mol equivalent of PPh<sub>3</sub> or PBu<sub>3</sub> was introduced. The complex dissolved and the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum was recorded. [Pt{ $\sigma: \eta^2-C_8H_{12}(PPh_3)$ }(dppp)][OTf]<sub>2</sub>:  $\delta P_A$  0.8 dd, <sup>1</sup>J(Pt, P<sub>A</sub>) 1523 Hz;  $\delta P_B$  7.5 dd, <sup>1</sup>J(Pt, P<sub>B</sub>) 3849 Hz;  $\delta P_C$  23.8 dd, <sup>3</sup>J(Pt, P<sub>C</sub>) 206 Hz; <sup>2</sup>J(P<sub>A</sub>, P<sub>B</sub>) 30 Hz, <sup>4</sup>J(P<sub>A</sub>, P<sub>C</sub>) 54 Hz, <sup>4</sup>J(P<sub>B</sub>, P<sub>C</sub>) 5 Hz. [Pt{ $\sigma: \eta^2-C_8H_{12}(PBu_3)$ }(dppp)][OTf]<sub>2</sub>:  $\delta P_A$  2.2 dd, <sup>1</sup>J(Pt, P<sub>A</sub>) 1612 Hz;  $\delta P_B$  4.6 dd, <sup>1</sup>J(Pt, P<sub>B</sub>) 3852 Hz;  $\delta P_C$  36.3 dd, <sup>3</sup>J(Pt, P<sub>C</sub>) 208 Hz; <sup>2</sup>J(P<sub>A</sub>, P<sub>B</sub>) 31 Hz, <sup>4</sup>J(P<sub>A</sub>, P<sub>C</sub>) 50 Hz, <sup>4</sup>J(P<sub>B</sub>, P<sub>C</sub>) 5 Hz.

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