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Demethylation of trimethylphosphite promoted by dichlorodiphosphineplatinum and palladium complexes. Structures of the metallophosphonate complexes $[Pt(P^P){P(O)(OMe)_2}_2]$ (P^P=dppe, dppp)

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Abstract

Platinum and palladium complexes of the type $[MCl_2(P^P)]$ ($P^P=dppm$, dppe, dppp) react with $P(OMe)_3$ at low temperatures to generate the bis(phosphite) species $[M(P^P)]P(OMe)_3]_2]^{2^+}$, which have been characterized by ³¹P NMR spectroscopy at low temperatures. On warming, the $[M(P^P)]P(OMe)_3]_2]Cl_2$ complexes undergo an Arbuzov-like reaction to generate the bis(phosphonate) derivatives $[M(P^P)]P(O)(OMe)_2]_2]$, which have been characterized by elemental analysis and NMR spectroscopy. The platinum complexes with $P^P=dppe$ and dpp have been characterized in the solid state by single crystal X-ray diffraction; each complex exhibits square planar geometry about the metal center. $[Pt(dppe)\{P(OMe)_3\}_2][PF_6]_2$ was isolated by performing the reaction of $[PtCl_2(dppe)]$ with $P(OMe)_3$ in the presence of 2 mol equiv. of $TlPF_6$, whereas the mixed phosphite–phosphonate complex $[Pt(dppe)\{P(OMe)_3\}\{P(O)(OMe)_2\}]PF_6$ was prepared by carrying out the reaction in the presence of only 1 mol equiv. of $TlPF_6$. Formation of the phosphite complexes is rapid and quantitative for both metals, as observed by low temperature ³¹P NMR spectroscopy. At ambient temperature, an equilibrium exists between free and coordinated phosphite, the latter being favored for platinum but apparently not for palladium. This results in formation of the phosphonate complexes being much faster for Pt than for Pd, unless a considerable excess of $P(OMe)_3$ is added. The demethylation reactions could be reversed by treating $[Pt(dppe)\{P(O)(OMe)_2\}_2]$ or $[Pt(dppe)\{P(O)(OMe)_2\}_2]PF_6$ with $Me_3O^+BF_4^-$, although the reactions were not quantitative. Protonation of $[Pt(dppe)\{P(OH)_2\}_2]^{2^+}$. (© 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Metallophosphonate complexes have been known for a number of years. Platinum complexes of the type $[Pt{P(O)(OR)_2}_4H_2]$ have been prepared by reaction of K_2PtCl_4 with HP(O)(OR)_2 [1] and subsequent displacement with dppe gave $[Pt(dppe){P(O)(OR)_2}_2]$ [2]. The latter could be prepared alternatively by reaction of $[PtCl_2(dppe)]$ with AgOP(OR)_2. The palladium dimer $[Pd_2(\mu-Cl)_2{P(O)(OR)_2}_4H_2]$ was produced from $[Pd_2(\mu-Cl)_2(\eta^3-C_3H_4Me)_2]$ and HP(O)(OR)_2 [3]. A recurring feature in complexes prepared from HP(O)(OR)_2 is the presence of a hydrogen bridging between two P–O moi-

eties in order to maintain electroneutrality [2–8]. Neutral complexes, in contrast, do not typically contain such H^+ ions. The protons may be abstracted by base, and the free metallophosphonates may serve as ligands to another transition metal center, including cobalt, nickel, copper and zinc.

There have been several reports of an alternative approach to metallophosphonates, namely reactions of transition metal halide complexes with tertiary phosphites [9,10]. These reactions, metal-substituted versions of the well-known Arbuzov reaction, have been observed for complexes of metals including iron [11–14], cobalt [15,16], ruthenium [17,18], rhenium [19] and platinum [20], and an intramolecular example involving a cobalt system has been reported recently [21]. The metal-mediated Arbuzov reaction has been shown to occur either by

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an ionic or a radical mechanism [10]. In the ionic mechanism, a halide is displaced from the metal center to generate a phosphite complex. Subsequent attack of halide on the coordinated phosphite leads to expulsion of an alkyl halide and generation of the metallophosphonate. There is considerable evidence for the operation of this mechanism in some cases, and the intermediate metal phosphite complex may be detected or even isolated.

Trimethylphosphite complexes of platinum have been shown to undergo single, double and even quadruple demethylation reactions to give metallophosphonate complexes [20]. Diphosphinepalladium and platinum phosphonate complexes have been prepared, but not by the demethylation route. The chloride-bridged palladium complex $[Pd_2(\mu-Cl)_2\{P(O)(OMe)_2\}_4H_2]$ reacts with dppe, for example, in the presence of AgPF₆ to produce the cationic complex $[Pd(dppe)\{P(O)(OMe)_2\}_2H]PF_6$, in which the bridging hydrogen is retained [22]. The platinum complex $[Pt(dppm)\{P(O)(OMe)_2\}_2]$ has been generated by reaction of $[Pt\{P(O)(OMe)_2\}_4H_2]$ with dppm, and has been employed as an O,O-donor towards a number of organometallic fragments [23].

In this paper, we report the reactions of diphosphinepalladium and platinum complexes of the type $[MCl_2(P^P)]$ with $P(OMe)_3$, which result in demethylation of two phosphite ligands to generate the neutral metallophosphonate species $[M(P^P){P(O)(OMe)_2}_2]$ (M=Pd, Pt; P^P= dppm, dppe, dppp). The intermediate phosphite complexes $[M(P^P){P(OMe)_3}_2]^{2+}$ have been characterized by ³¹P NMR spectroscopy at low temperatures, and have been isolated in one case. We also report the crystal structures of the platinum phosphonate derivatives $[Pt(P^P)-{P(O)(OMe)_2}_2]$ (P^P=dppe, dppp).

2. Results and discussion

Treatment of CH_2Cl_2 solutions of $[PtCl_2(P^P)]$ with 1 mol equiv. of $P(OMe)_3$ resulted in mixtures of the mono-

 $[PtCl(P^P)-$ (phosphonate)platinum complexes $\{P(O)(OMe)_2\}$, bis(phosphonate) complexes $[Pt(P^P) \{P(O)(OMe)_2\}_2$ and unreacted starting material. ³¹P NMR data for the mono(phosphonate) complexes are given in Table 1. In each case, three resonances, with ¹⁹⁵Pt satellites, were observed. A large ${}^{2}J(P,P)$ coupling constant (over 600 Hz) was found between the *trans* P atoms P^1 and P^3 , and two smaller couplings were seen between the pairs of P atoms *cis* to one another. The signal due to P^2 exhibits a coupling to ¹⁹⁵Pt of around 3500 Hz, as expected for a P atom lying opposite a relatively low trans-influence ligand such as chloride. Of the two mutually trans P atoms, the phosphonate displays a much larger coupling than the tertiary phosphine, as observed previously [22].



With two or more equiv. of P(OMe)₃, further reaction occurs to generate the bis(phosphonate) complexes quantitatively. Each complex of the type $[Pt(P^P) \{P(O)(OMe)_2\}_2$ gave rise to two sets of signals in its ³¹P NMR spectrum, each of which exhibited coupling to platinum (Table 2). Excluding the ¹⁹⁵Pt satellites, the four P atoms constituted an AA'XX' spin system, giving rise to two ten-line patterns [24], and the spectra have been simulated as such in each case. Each ten-line pattern was dominated by the large coupling, in excess of 500 Hz, between mutually trans P atoms. Assuming this coupling to be of positive sign [25], the *cis* coupling between the diphosphine and phosphonate P atoms must be negative (approx. -30 Hz) in all cases. The *cis* couplings between the two P atoms of the diphosphine and between the two phosphonate P atoms must be of the same sign (although their absolute signs cannot be determined).

The analogous reactions of $[PdCl_2(P^P)]$ with 1 mol equiv. of P(OMe)₃ also produced mixtures of $[PdCl(P^P)-$

Table 1

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umeters for the complexes $[MCl(P^{P}){P(O)(OMe)}]^{Pl}$ $(P1 \ P2 \ P3(O)(OMe)_2)$

1 Nink parameters for the complexes $[MCl(1,1)]_1(0)(OMC)_{2f1}$ 12 $10(0)(OMC)_{2}$						
M, P [^] P	δP_1^{b}	δP_2^{b}	δP_3^{b}	$^{2}J(\mathbf{P}_{1},\mathbf{P}_{2})$	$^{2}J(\mathbf{P}_{1},\mathbf{P}_{3})$	$^{2}J(P_{2},P_{3})$
Pd, dppm	-59.6 dd	-35.9 dd	66.3 dd	99	766	21
Pd, dppe	39.2 dd	57.3 t	67.7 dd	25	678	25
Pd, dppp	-5.1 dd	16.7 dd	64.8 dd	54	679	40
Pt, dppm	-46.8 dd	-44.7 d	58.3 d	50	650	15
	(1364)	(3467)	(4122)			
Pt, dppe	43.3 dd	41.3 dd	68.2 dd	7	600	22
	(1772)	(3803)	(3924)			
Pt, dppp	0.7 dd	-1.9 dd	61.4 dd	28	598	21
	(1613)	(3722)	(3856)			

^a Spectra were recorded for CDCl₃ solutions at ambient temperature.

 $^{b \ 1}$ J(Pt,P) values are given in parentheses.

³¹ P NMR parameters for the complexes $[M(P \land P){P(O)(OMe)_2}]^4 P2 \longrightarrow P^3(O)(OMe)_2$						
M, P∧P	$\delta P_1, P_2^{b}$	$\delta P_3, P_4^{b}$	${}^{2}J(\mathbf{P}_{1},\mathbf{P}_{2})$	${}^{2}J(\mathbf{P}_{1},\mathbf{P}_{3}) =$ ${}^{2}J(\mathbf{P}_{2},\mathbf{P}_{4})$	${}^{2}J(\mathbf{P}_{1},\mathbf{P}_{4}) =$ ${}^{2}J(\mathbf{P}_{2},\mathbf{P}_{3})$	${}^{2}J(\mathbf{P}_{3},\mathbf{P}_{4})$
Pd, dppm	-29.7	75.0	±47	593	4	∓ 48
Pd, dppe	43.1	73.9	±26	545	-27	
Pd, dppp	0.5	70.5	± 70	543	-25	 + 5 1
Pt, dppm	-39.6 (1612)	70.7 (4358)	± 28	546	-12	∓37
Pt, dppe	47.6 (1866)	68.6 (4194)	± 9	507	-31	± 28
Pt, dppp	4.3 (1840)	67.9 (4172)	± 20	510	-32	±30

Table 2 _P4(O)(OMe)₂

^a Spectra were recorded for CDCl₃ solutions at ambient temperature.

 $^{b-1}J(Pt,P)$ values are given in parentheses.

 $\{P(O)(OMe)_2\}$, $[Pd(P^P)\{P(O)(OMe)_2\}_2]$ and unreacted $[PdCl_2(P^P)]$ and, again, with two or more equiv. of P(OMe)₃, the bis(phosphonate) complexes were the exclusive products. The ³¹P NMR spectra of the palladium complexes were qualitatively similar to those of their platinum analogues (except for the absence of satellites). In contrast to their platinum analogues, in the bis(phosphonate) palladium complexes, the two *cis* couplings between the two P atoms of the diphosphine and between the two phosphonate P atoms must be of opposite sign in order to simulate the spectrum correctly (Table 2).

Curiously, the reactions of the platinum complexes to generate the bis(phosphonate) derivatives were over within a few minutes, whereas the reactions involving palladium took several days to go to completion. This was unexpected in view of the usually much greater reactivity of palladium compounds. When a solution of [PtCl₂(dppe)] was treated with 25 mol equiv. of P(OMe)₃, the rate of reaction was unchanged, but when [PdCl₂(dppe)] was treated similarly, the bis(phosphonate)palladium complex was formed as rapidly as its platinum analogue. These results suggest the existence of an equilibrium involving coordinated and free phosphite at ambient temperature (Eq. 1), with coordinated P(OMe)₃ being favored in the platinum case. For palladium, the equilibrium position would favor the free phosphite in the presence of only 2 equiv. of $P(OMe)_3$, but the addition of a large excess of phosphite would drive the reaction to the right.

$$Ph_{2} \xrightarrow{Ph_{2}} Cl + 2 P(OMe)_{3} \xrightarrow{Ph_{2}} \left[\underbrace{P}_{Ph_{2}} \xrightarrow{P(OMe)_{3}} P(OMe)_{3} \right]^{2+} + 2Cl^{-}$$

$$Ph_{2} \xrightarrow{Ph_{2}} P(OMe)_{3} \xrightarrow{Ph_{2}} P(OMe)_{3$$

When CD_2Cl_2 or $CDCl_3$ solutions of $[PtCl_2(P^P)]$ were treated with 4 mol equiv. of P(OMe)₃ at low temperatures, the bis(phosphite) complexes $[Pt(P^P){P(OMe)_3}_2]^{2+}$ were formed rapidly, but warming to ambient temperature caused conversion to the bis(phosphonate) derivatives and MeCl (δ H 3.0) (Eq. 2). The bis(phosphite)platinum cations also exhibited AA'XX' patterns in their ³¹P{¹H} NMR spectra, and the appropriate parameters are given in Table 3.

$$\begin{pmatrix} P \\ P \end{pmatrix} Pt \begin{pmatrix} Cl \\ -78^{\circ}C \end{pmatrix} = \begin{pmatrix} P \\ P \end{pmatrix} Pt \begin{pmatrix} P(OMe)_{3} \\ P \end{pmatrix} \begin{pmatrix} P \\ P(OMe)_{3} \end{pmatrix} \begin{pmatrix} P \\ 2 Cl \end{pmatrix} \\ \frac{-MeCl}{25^{\circ}C} \end{pmatrix} \begin{pmatrix} P \\ P \end{pmatrix} Pt \begin{pmatrix} P(O)(OMe)_{2} \\ P(O)(OMe)_{2} \end{pmatrix} (2)$$

The dppe complex $[Pt(dppe){P(OMe)_3}_2]Cl_2$, in particular,

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	(Pl	P4(OMe) ₃	2+
1P NMR parameters for the complexes $[M(P \land P) \{P(OMe)_3\}_2]Cl_2$		$P^3(OMe)_3$	

M, P∧P	$\delta P_1, P_2^{b}$	$\delta P_{3}, P_{4}^{b}$	${}^{2}J(\mathbf{P}_{1},\mathbf{P}_{2})$	${}^{2}J(\mathbf{P}_{1},\mathbf{P}_{3}) =$ ${}^{2}J(\mathbf{P}_{1},\mathbf{P}_{3})$	${}^{2}J(\mathbf{P}_{1},\mathbf{P}_{4}) =$ ${}^{2}I(\mathbf{P},\mathbf{P}_{4})$	$^{2}J(\mathrm{P}_{3},\mathrm{P}_{4})$
	22.4	104.5	1.21	505	10	1.50
Pa, appm	-32.4	104.5	±21	585	19	±59
Pd, dppe ^c	54.9	103.0	± 4	523	-12	±33
Pd, dppp	4.2	100.3	± 20	536	-4	∓35
Pt, dppm	-46.1 (2022)	87.8 (4699)	± 42	536	-13	± 56
Pt, dppe	39.7 (2327)	85.0 (4551)	± 10	500	-31	± 48
Pt, dppp	-19.8 (2247)	82.4 (4438)	±39	492	-29	±45

^a Spectra were recorded for $CDCl_3$ solutions at $-53^{\circ}C$.

^b $^{1}J(Pt,P)$ values are given in parentheses.

^c Recorded for a CD_2Cl_2 solution at $-93^{\circ}C$.

exhibited one set of resonances at 39.7 ppm $[{}^{1}J(Pt,P) = 2327 \text{ Hz}]$ due to the dppe P atoms and another at 85.0 ppm $[{}^{1}J(Pt,P) = 4551 \text{ Hz}]$ due to the coordinated P(OMe)₃. The corresponding reactions of $[PdCl_2(P^{P})]$ with P(OMe)₃ at -78° C also generated the bis(phosphite)palladium cations quantitatively in situ. Their 31 P NMR parameters are also collected in Table 3.

Treatment of [PtCl₂(dppe)] with 2 mol equiv. of $P(OMe)_3$ at $-78^{\circ}C$, followed by 2 mol equiv. of TlPF₆, allowed isolation of the bis(phosphite)platinum cation as its PF_6^- salt. Interestingly, the ³¹P NMR parameters for $[Pt(dppe){P(OMe)_3}_2][PF_6]_2$ [δP 51.6, ${}^1J(Pt,P) = 2138$ Hz; δP 96.8, ¹J(Pt,P)=4056 Hz] are significantly different from those of its chloride salt. This suggested to us that there might be some association of the chloride ions with the metal complex at low temperature in that case. To test this, we treated $[PtI_2(dppe)]$ with 2 mol equiv. of $P(OMe)_3$ at -78° C to generate the bis(phosphite) complex as its iodide salt, which exhibited a further different set of ³¹P NMR parameters [δP 29.8, ${}^{1}J(Pt,P) = 2290$ Hz; δP 77.4, $^{1}J(Pt,P) = 4592$ Hz]. We have previously observed similar variations in δP and ${}^{1}J(Pt,P)$ that we attributed to ionpairing, iodide interacting more strongly than chloride with the complex [26]. A stronger interaction with iodide is apparent here also, based on the magnitudes of the chemical shift changes.

When a CDCl₃ solution of $[PtCl_2(dppe)]$ and 4 mol equiv. of $P(OMe)_3$ was allowed to warm gradually, the signals due to $[Pt(dppe){P(OMe)_3}_2]^{2+}$ and free $P(OMe)_3$ became broad and, at 25°C, the signals due to the complex were so broad that they disappeared into the baseline. This suggests that there is rapid exchange of free and coordinated phosphite at this temperature. On standing at ambient temperature, the resonances due to the bis(phosphonate) complex gradually grew in and increased in intensity. The palladium system behaved similarly, except that the signals due to $[Pd(dppe){P(O)(OMe)_2}_2]$ grew in much more slowly.

Conversion of the bis(phosphite) complex to its bis-(phosphonate) counterpart should occur by stepwise demethylation of the two phosphite ligands. Thus, a species of the form $[Pt(dppe){P(OMe)_3}{P(O)(OMe)_2}]^+$ should be an intermediate in this process. We generated this complex by reacting $[PtCl_2(dppe)]$ with 2 equiv. of $P(OMe)_3$ in CH_2Cl_2 solution at $-78^{\circ}C$ in the presence of 1 equiv. of $TIPF_6$, followed by warming to ambient temperature, as shown in Eq. 3. This resulted in precipitation of TlCl, thereby leaving only one chloride ion to react with the bis(phosphite) complex so that only one demethylation step could occur.

$$\begin{bmatrix} P \\ P \\ Cl \end{bmatrix} + 2 P(OMe)_3 + TIPF_6 \xrightarrow{-78^\circ - 25^\circ C}_{-TICl, -MeCl}$$

$$\begin{bmatrix} P \\ P \\ P \\ P(O)(OMe)_2 \end{bmatrix}^+ PF_6^-$$
(3)

The resulting platinum complex exhibited a first order ${}^{31}P{}^{1}H$ NMR spectrum, each of the four resonances appearing as a doublet of doublets of doublets (δP_1 103.5, $^{2}J(P,P)$ 509, 41, 33 Hz, $^{1}J(Pt,P)$ 4480 Hz, P(OMe)₃; δP_{2} 61.4, ²*J*(P,P) 470, 41, 23 Hz, ¹*J*(Pt,P) 3685 Hz, P(O)(OMe)₂; δ P₃ 50.3, ²*J*(P,P) 470, 33, 10 Hz, ¹*J*(Pt,P) 1762 Hz, dppe P cis to P(OMe)₃; δP_4 49.6, ²J(P,P) 509, 23, 10 Hz, ${}^{1}J(Pt,P)$ 2413 Hz, dppe P trans to P(OMe)₃), as expected for the $[Pt(dppe){P(OMe)_3}{P(O)(OMe)_2}]^+$ cation. The spectrum remained essentially unchanged between -50 and $+50^{\circ}$ C, indicating that this species is static between these temperatures. In the presence of excess P(OMe)₃, the signals due to the complex and free phosphite were sharp at -50° C, but as the temperature was raised, the resonances at 143.7 and 103.5 ppm, due to free and coordinated P(OMe)₂, respectively became broad, indicating that phosphite exchange was occurring. A ³¹P-³¹P 2D-EXSY experiment performed at 0°C exhibited cross peaks for the free and coordinated P(OMe)₃, but not for the phosphonate P atom, indicating that exchange occurs between free and coordinated phosphite, but that methyl transfer does not occur between the phosphite and phosphonate moieties.

We investigated whether the demethylation reactions might be reversible. As indicated above, when a solution of $[M(P^P){P(OMe)_3}_2]Cl_2$ is allowed to stand at 25°C, demethylation occurs quantitatively to yield $[M(P^{P})-$ MeCl. ${P(O)(OMe)_{2}}_{2}$ When we treated and $[Pt(dppe){P(O)(OMe)_2}_2]$ with 2-3 mol equiv. of MeI or $C_5H_{11}Cl$, no reaction occurred, although MeP(O)(OMe)₂ $(\delta P 32.0)$ was formed after prolonged reaction with excess MeI. Reaction did occur with the more potent methylating $Me_3O^+BF_4^-$, agent however. When [Pt(dppe)- $\{P(O)(OMe)_2\}_2$ was treated with 1 mol equiv. of Me₃O⁺BF₄ in CDCl₃/acetone solution at 25°C (the complex is insoluble in acetone, and $Me_3O^+BF_4^-$ is insoluble in $CDCl_3$), the major product was $[Pt(dppe){P(OMe)_3} {P(O)(OMe)_2}^+$, identified by its ³¹P NMR spectrum, although other minor products were formed also. The reaction was also slow, taking approximately 24 h to go to completion. With excess $Me_3O^+BF_4^-$, the major product was the bis(phosphite)platinum cation, but again the reaction was slow and a number of other species were formed. Treatment of the mixed phosphite-phosphonate complex $[Pt(dppe){P(OMe)_3}{P(O)(OMe)_2}]PF_6$ with 1 mol equiv. of $Me_3O^+BF_4^-$ for 12 h at 25°C gave $[Pt(dppe){P(OMe)_3}_2]^{2+}$ as the major product. Thus, it is possible to reverse the demethylation reactions, although a fairly strong methylating agent is required, and this does not represent an efficient way to prepare bis(tertiary phosphite)platinum complexes.

In contrast to the above, treatment of $[Pt(dppe){P(O)(OMe)_2}_2]$ with 1 mol equiv. of HBF_4 resulted in quantitative conversion to a new species that exhibited the familiar AA'XX' pattern in its ³¹P NMR spectrum (δP 83.3, ¹J(Pt,P)= 3880 Hz; δP 48.9, ¹J(Pt,P)=

2000 Hz). Treatment with excess HBF_4 produced yet another AA'XX' pattern (δP 92.6, ¹J(Pt,P)=4046 Hz; δP 51.8, ${}^{1}J(Pt,P) = 2103$ Hz), the couplings being very reminiscent of those observed for $[Pt(dppe){P(OMe)_3}_2][PF_6]_2$. In contrast to the methylations described above, these reactions were complete within a few minutes at ambient temperature. We propose that the latter is the bis-(dimethylphosphite)platinum complex [Pt(dppe){P(OH)- $(OMe)_2_2$ [BF₄]₂, in which the phosphite is stabilized in its phosphorus(III) form by coordination to the metal. The intermediate complex exhibits a resonance at 7.9 ppm in its ¹H NMR spectrum, which is at a chemical shift similar to that found in other bis(phosphonate) complexes in which a hydrogen bridges between the two P=O moieties [2–8]. Thus, we propose the reaction sequence shown in Eq. 4 to account for these observations.



2.1. Molecular structures of $[Pt(P^P){P(O)(OMe)_2}_2]$ $(P^P = dppe, dppp)$

The dppe complex $[Pt(dppe){P(O)(OMe)_2}_2]$ crystallizes in the space group P1 with two molecules per unit cell. The molecular structure is shown in Fig. 1, and selected bond distances and angles are given in Table 4. The sum of the four cis P-Pt-P angles is 360.04°, indicating that the PtP4 unit is almost exactly planar. The smallest angle of 85.05° is that between the two P atoms of the dppe ligand, and the largest (93.99°) is between the two phosphonate groups. The Pt-P2 distance is very slightly longer than the other three Pt-P distances, which are all identical within experimental error. The P=O bonds of 1.486 Å are considerably shorter than the four P-O single bonds (average 1.595 Å), as expected. Each phosphorus atom shows some distortion from tetrahedral geometry, but probably for different reasons. The dppe P atoms exhibit smaller angles where the ligand backbone carbons are involved, presumably due to the conformational inflexibility of the five-membered chelate ring. In contrast, the Pt-P-Ph angles are in the range 115.5-117.6°, and the Ph-P-Ph is close to the perfect tetrahedral angle. In the case of the phosphonate ligands, the phosphorus(V) cen-



Fig. 1. Molecular structure of $[Pt(dppe){P(O)(OMe)_2}_2]$ showing the atom labeling scheme.

ters exhibit the largest angles between platinum and the P=O bond (117.3 and 117.4°) and the smallest between the two methoxy groups (101.1 and 102.2°). This is to be expected if the P=O double bond is considered to occupy more space than a P-O single bond.

The dppp analogue crystallizes in the space group $P2_1/n$, with two molecules per unit cell. Its molecular structure is shown in Fig. 2, with selected bond distances and angles being presented in Table 5. The sum of the four *cis* P–Pt–P angles in this case is 360.42°, again indicating that the PtP₄ unit is nearly planar. Here, the angles are all

Table 4

Selected bond distances (Å) and angles (°) for [Pt(dppe){P(O)(OMe)₂}₂]

Bond distances			
Pt-P1	2.3136(8)	Pt-P2	2.3251(8)
Pt-P3	2.3114(8)	Pt-P4	2.3111(8)
P3-O1	1.486(2)	P3-O2	1.602(2)
P3-O3	1.595(2)	P4-O4	1.486(2)
P4-O5	1.597(2)	P4-O6	1.587(2)
Bond angles			
P1-Pt-P2	85.05(3)	P1-Pt-P3	176.55(2)
P1-Pt-P4	89.18(3)	P2-Pt-P3	91.82(3)
P2-Pt-P4	174.01(2)	P3-Pt-P4	93.99(3)
Pt-P1-C1	107.08(10)	Pt-P1-C3	115.96(9)
Pt-P1-C9	116.42(10)	C1-P1-C3	104.12(14)
C1-P1-C9	102.14(13)	C3-P1-C9	109.39(13)
Pt-P2-C2	105.13(9)	Pt-P2-C15	115.51(9)
Pt-P2-C21	117.63(9)	C2-P2-C15	103.35(14)
C2-P2-C21	103.45(13)	C15-P2-C21	109.82(12)
Pt-P3-O1	117.38(10)	Pt-P3-O2	109.74(10)
Pt-P3-O3	107.40(9)	O1-P3-O2	109.78(13)
O1-P3-O3	110.16(13)	O2-P3-O3	101.13(14)
Pt-P4-O4	117.29(9)	Pt-P4-O5	108.55(9)
Pt-P4-O6	106.94(9)	O4-P4-O5	110.06(12)
O4-P4-O6	110.66(13)	O5-P4-O6	102.23(13)



Fig. 2. Molecular structure of $[Pt(dppp){P(O)(OMe)_2}_2]$ showing the atom labeling scheme.

closer to 90°, suggesting that there is less strain in the six-membered chelate ring. There is a significant difference between the Pt–P bond lengths in this complex, those to the phosphonate ligands being approximately 0.03 Å shorter. The angles around the phosphonate P atoms range from 97.5 to 120.2°, the largest value corresponding to one of the angles between platinum and a P=O bond. The smallest angles are again between the pairs of methoxy

Table 5 Selected bond distances (Å) and angles (°) for [Pt(dppp){P(O)(OMe)_2},]

Bond distances			
Pt-P1	2.3392(9)	Pt-P2	2.3459(8)
Pt-P3	2.3181(9)	Pt-P4	2.3039(8)
P3-O1	1.484(3)	P3-O2	1.604(3)
P3-O3	1.606(3)	P4-O4	1.479(2)
P4-O5	1.614(3)	P4-O6	1.609(3)
Bond angles			
P1-Pt-P2	88.59(3)	P1-Pt-P3	174.08(3)
P1-Pt-P4	92.75(3)	P2-Pt-P3	88.38(3)
P2-Pt-P4	175.01(3)	P3-Pt-P4	90.70(3)
Pt-P1-C1	111.77(12)	Pt-P1-C4	118.46(11)
Pt-P1-C10	114.22(12)	C1-P1-C4	98.8(2)
C1-P1-C10	104.9(2)	C4-P1-C10	106.8(2)
Pt-P2-C3	111.55(12)	Pt-P2-C16	114.83(11)
Pt-P2-C22	117.12(10)	C3-P2-C16	104.3(2)
C2-P2-C22	99.7(2)	C16-P2-C22	107.6(2)
Pt-P3-O1	114.76(12)	Pt-P3-O2	104.11(10)
Pt-P3-O3	116.75(12)	O1-P3-O2	113.1(2)
O1-P3-O3	109.2(2)	O2-P3-O3	97.54(14)
Pt-P4-O4	120.20(11)	Pt-P4-O5	106.48(10)
Pt-P4-O6	106.03(11)	O4-P4-O5	110.7(2)
O4-P4-O6	111.6(2)	O5-P4-O6	99.8(2)

groups. The angles around the dppp P atoms also show some variation, ranging from 98.8 to 118.5°.

The platinum-phosphonate Pt-P distances in the two complexes described here (2.304–2.318 Å) were almost identical to those reported for $[Pt{P(O)(OMe)_2}-{P(OMe)_3}_3]^+$ [2.322(3) Å] and *cis*- $[Pt{P(O)(OMe)_2}_2-{P(OMe)_3}_2]$ [2.329(10) Å] [20]. These complexes are also almost planar, the sums of the P-Pt-P angles being 362.0 and 361.9°, respectively. In these complexes, all of the P-Pt-P angles lie within the range 88–92°. The large ¹ *J*(Pt,P) values found for the phosphonate P atoms, along with the insensitivity of the Pt-P distances to the nature of the *trans* ligands, suggests that these bonds are strong and that the Pt-P distances are close to optimal.

3. Summary

Platinum and palladium complexes of the type $[MCl_2(P^P)]$ (P^P=dppm, dppe, dppp) react with P(OMe)₃ at low temperatures to give first the bis(phosphite) species $[M(P^P){P(OMe)_3}_2]^{2+}$, which, on warming, undergo an Arbuzov-like reaction with the liberated chloride to generate the bis(phosphonate) derivatives $[M(P^P){P(O)(OMe)_2}_2]$. The products have been characterized by NMR spectroscopy, and the platinum complexes with P^{P} = dppe and dppp have been subjected to single crystal X-ray diffraction studies. Formation of the phosphite complexes is rapid and quantitative for both metals at low temperatures. At ambient temperature, an equilibrium exists between free and coordinated phosphite, the latter being favored for platinum but apparently not for palladium. This results in the formation of the phosphonate complexes being much faster for Pt than for Pd, unless a considerable excess of P(OMe)₃ is added. The demethylation reactions could be reversed by treating the phosphonate complexes with $Me_3O^+BF_4^-$. Studies of the reactions of the metallophosphonate complexes are continuing.

4. Experimental

All reactions were carried out under an atmosphere of argon. Solvents were dried and distilled immediately prior to use. The diphosphines were purchased from Strem and were used as received. The complexes $[MCl_2(P^P)]$ (M= Pd, Pt; P^P=dppm, dppe, dppp) were prepared by displacement of cyclooctadiene from $[MCl_2(cod)]$ by the appropriate diphosphine [27,28]. NMR spectra were recorded on a Bruker ARX-500 spectrometer. ¹H and ³¹P chemical shifts were measured relative to the residual solvent signal and external H_3PO_4 , respectively, with positive shifts representing deshielding; coupling constants are given in Hertz. Microanalyses were performed by Atlantic Microlab Inc. (Norcross, GA, USA).

4.1. Preparation of $[Pt(dppm){P(O)(OMe)_2}]$

To a CH₂Cl₂ solution (27 ml) of [PtCl₂(dppm)] (0.10 g, 0.15 mmol) was added P(OMe)₃ (0.07 ml, 0.60 mmol). The solution was stirred for 55 min, and it changed color from colorless to yellow. The solvent and excess phosphite were removed at ambient temperature. The resulting solid was allowed to dry in vacuo overnight, leaving the product as a white solid (0.11 g, 87%). Anal. Calc. for C₂₉H₃₄O₆P₄Pt: C, 43.67; H, 4.30. Found: C, 42.92; H, 4.31. ¹H NMR (CDCl₃): δH 3.50 d, ³*J*(P,H)=11.8 Hz, 12H, OCH₃; 4.53 t, ²*J*(P,H)=9.4 Hz, 2H, CH₂; 7.5 m, 7.8 m, 20H, C₆H₅.

4.2. Preparation of $[Pt(dppe){P(O)(OMe)_2}_2]$

To a CH₂Cl₂ solution (25 mL) of [PtCl₂(dppe)] (0.10 g, 0.15 mmol) was added P(OMe)₃ (0.07 mL, 0.60 mmol). The solution was stirred for 15 min. The solvent and unreacted phosphite were removed at 0°C. The resulting solid was allowed to dry in vacuo overnight, leaving the product as a white solid (0.10 g, 84%). Anal. Calc. for $C_{30}H_{36}O_6P_4Pt$: C, 44.40; H, 4.47. Found: C, 44.28; H, 4.56. ¹H NMR (CDCl₃): δH 2.28 m, 4H PCH₂; 3.18 d, ³*J*(P,H)=11.5 Hz, 12H, OCH₃; 7.46–7.80 m, 20H, C₆H₅. Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of a CH₂Cl₂–hexane–ether solution.

4.3. Preparation of $[Pt(dppp){P(O)(OMe)_2}_2]$

Trimethylphosphite (0.035 mL, 0.30 mmol) was added to a solution of $[PtCl_2(dppp)]$ (0.10 g, mmol) in CH_2Cl_2 (25 mL). The solution was stirred for 30 min, then the solvent was removed at 0°C. The resulting solid was allowed to dry in vacuo overnight, leaving the product as a white solid (0.095 g, 78%). Anal. Calc. for $C_{31}H_{38}O_6P_4Pt$: C, 45.10; H, 4.64. Found: C, 45.04; H, 4.62. ¹H NMR (CDCl₃): δH 1.80 m, 2H, PCH₂CH₂; 2.25 m, 4H, PCH₂; 3.17 d, ³J(P,H)=11.8 Hz, 12H, OCH₃; 7.43–7.73 m, 20H, C₆H₅. Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of a CH₂Cl₂–hexane solution.

4.4. Preparation of $[Pd(dppm){P(O)(OMe)_2}_2]$

[PdCl₂(dppm)] (0.10 g, 0.18 mmol) was dissolved in CH_2Cl_2 (5 mL) and P(OMe)₃ (0.084 mL, 0.71 mmol) was added by syringe. The solution changed from pale yellow to bright yellow upon addition of the phosphite, and it was stirred for 96 h at 25°C. The solution was then passed down a Florosil column that was eluted with CH_2Cl_2 –MeOH (1:1, v/v; 50 mL). The solvents were removed and the remaining colorless powder was washed with ether (50 mL), then dried in vacuo to leave the desired product as a

colorless solid (0.102 g, 81%). Anal. Calc. for $C_{29}H_{34}O_6P_4Pd$: C, 49.12; H, 4.80. Found: C: 49.03, H: 4.79. ¹H NMR (CDCl₃): δH 3.45 d, ³*J*(P,H)=11.8 Hz, 12H, OCH₃; 4.06 t, ²*J*(P,H)=7.7 Hz, 2H CH₂; 7.30–7.66 m, 20H, C_6H_5 .

4.5. Preparation of $[Pd(dppe){P(O)(OMe)_2}_2]$

To a CH₂Cl₂ solution (5 mL) of $[PdCl_2(dppe)]$ (0.10 g, 0.17 mmol) was added P(OMe)₃ (0.082 mL, 0.695 mmol) by syringe. The solution was stirred for 96 h at ambient temperature, then passed down a Florosil column and eluted with CH₂Cl₂–MeOH (1:1, v/v; 50 mL). The solvents were removed and the resulting colorless powder was washed with ether (50 mL). The solid was dried in vacuo, leaving the desired product as a colorless solid (0.116 g, 93%). Anal. Calc. for C₃₀H₃₆O₆P₄Pd: C, 49.83; H, 4.98. Found: C, 50.03; H, 5.04. ¹H NMR (CDCl₃): δH 2.17 m, 4H, PCH₂; 3.27 d, ³J(P,H)=11.8 Hz, 12H OCH₃; 7.43–7.73 m, 20H, C₆H₅.

The dppp complex was prepared similarly and isolated as a colorless solid at a yield of 87%. Anal. Calc. for $C_{31}H_{38}O_6P_4Pd$: C, 50.52; H, 5.20. Found: C, 50.32; H, 5.17. ¹H NMR (CDCl₃): δH 1.83 m, 2H, PCH₂CH₂; 2.18 m, 4H, PCH₂; 3.18 d, ³J(P,H)=11.2 Hz, 12H, OCH₃; 7.36–7.67 m, 20H, C₆H₅.

4.6. Preparation of [$Pt(dppe){P(O)(OMe)_2}{P(OMe)_3}$] PF_6

A CH₂Cl₂ solution of [PtCl₂(dppe)] (0.10 g, 0.15 mmol) was cooled to -78°C in an acetone-dry ice bath and P(OMe)₃ (0.039 mL, 0.33 mmol) was added by syringe. TIPF₆ (0.053 g, 0.15 mmol) was added, followed by distilled methanol (2.0 mL). The acetone-dry ice bath was removed and the flask was allowed to warm gradually to ambient temperature and stirred for a further 6 h. The solvents were removed and the remaining solid was washed with benzene and ether, and dried in vacuo to leave the product as a colorless powder (0.14 g, 93%). Even after pumping under high vacuum for several days, the ¹H NMR spectrum revealed the presence of 0.2 equiv. of C₆H₆. Anal. Calc. for C_{32.2}H_{40.2}F₆O₆P₅Pt: C, 39.12; H, 4.02. Found: C, 39.10; H, 3.95. ¹H NMR (CDCl₃): δH 2.39 m, 4H, PCH₂; 3.16 d, ${}^{3}J(P,H) = 11.6$ Hz, 6H, $P(O)(OCH_3)_2$; 3.57 d, ³J(P,H) = 12.4 Hz, 9H, $P(OCH_3)_3$; 7.55–7.72 m, 20H, C₆H₅.

4.7. Preparation of $[Pt(dppe){P(OMe)_3}_2][PF_6]_2$

[PtCl₂(dppe)] (0.10 g, 0.15 mmol) was dissolved in CH₂Cl₂ (50 mL) and the solution was cooled to -78° C. Trimethylphosphite (35.4 μ L, 0.30 mmol) was added by syringe, followed by TIPF₆ (0.12 g, 0.33 mmol). The reaction mixture was allowed to warm gradually to am-

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Data collection, structure solution and refinement parameters for $[Pt(dppe){P(O)(OMe)_2}_2]$ and $[Pt(dppp){P(O)(OMe)_2}_2]$

	$[Pt(dppe){P(O)(OMe)_2}_2]$	$[Pt(dppp){P(O)(OMe)_2}_2]$
Crystal system	Triclinic	Monoclinic
Space group, Z	P(-1), 2	$P2_{1}/n, 4$
a (Å)	9.987(2)	11.58410(1)
<i>b</i> (Å)	11.254(3)	17.7003(2)
<i>c</i> (Å)	15.475(2)	16.3389(2)
α (°)	105.771(11)	90
β (°)	101.70(2)	105.2120(1)
γ (°)	99.825(14)	90
$V(\dot{A}^3)$	1591.3(5)	3232.78(6)
Density (g/cm^{-3}) (calculated)	1.731	1.696
Temperature (K)	298(2)	223(2)
Absorption coefficient (mm^{-1})	4.655	4.580
Range (deg)	1.42-29.88	1.73-29.95
Reflections collected	29 897	37 040
Independent reflections (R_{int})	7595 (0.04)	8534 (0.041)
Least squares parameters	379	379
$R(F), R_{w}(F^{2}) (F^{2} > 2.0 \sigma(F^{2}))$	0.0235, 0.0528	0.0334, 0.0648
$R(F), R_{w}(F^{2})$ (all data)	0.0300, 0.0553	0.0450, 0.0745
$S(F^2)$	1.025	1.096

bient temperature and was stirred for 1 h. The mixture was filtered and the residue was washed with benzene and ether. The resulting solid was dried in vacuo, leaving the product as a colorless powder (0.16 g, 95%). Anal. Calc. for $C_{32}H_{42}F_{12}O_6P_6Pt$: C, 33.95; H, 3.71. Found: C, 32.98; H, 3.20. ¹H NMR (CDCl₃): δH 2.41 m, 4H, PCH₂; 3.51 d, 18H, ³J(P,H)=12.2 Hz, OCH₃; 7.58–7.78 m, 20H, C₆H₅.

4.8. Detection of other $[M(P^{P}){P(OMe)_{3}}_{2}]^{2+}$ complexes

In a typical experiment, $[MCl_2(P^P)]$ (0.010 g) was dissolved in CDCl₃ (0.5 mL) at 25°C. The sample was frozen in an acetone–dry ice bath, then, P(OMe)₃ (4 equiv.) was added to the NMR tube by syringe. The tube was transferred to the probe of the NMR spectrometer, which had previously been cooled to -50° C. The ³¹P{¹H} NMR spectrum was recorded at this temperature. Resonances due to the AA'XX' system of the expected product (Table 3) and free P(OMe)₃ were observed.

4.9. X-ray structure determinations

In each case, a crystal was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed using a Siemens SMART CCD detector system single crystal X-ray diffractometer, using graphite monochromated MoK α radiation (λ =0.71073 Å), equipped with a sealed tube X-ray source (50 kV×40 mA), as described elsewhere [29]. The SMART software package was used for data collection and sAINT was used for frame integration. Structure solution and refinement were carried out using the SHELXTL-PLUS (5.03) software package [30]. Data collection, structure solution and refinement parameters are given in Table 6.

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