

Multinuclear magnetic resonance studies on the interactions of platinum bis(dithiolates) with potentially tridentate phosphine ligands

Ray Colton*

Chemistry Department, La Trobe University, Bundoora 3083 (Australia)

and Vanda Tedesco

Inorganic Chemistry Section, School of Chemistry, University of Melbourne, Parkville 3052 (Australia)

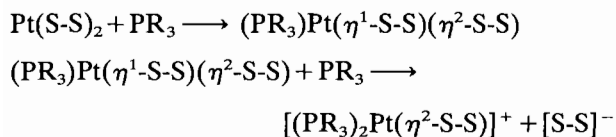
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Abstract

The reactions of platinum(II) dithiolates $\text{Pt}(\text{S-S})_2$ ($\text{S-S} = \text{S}_2\text{P}(\text{OEt})_2$, $\text{S}_2\text{CO}^n\text{Pr}$, S_2CNET_2) with two potentially tridentate phosphine ligands have been investigated by multinuclear magnetic resonance spectroscopy. The phosphines used were $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2$ ($\text{P}_2\text{P}'$) and $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ (P_3). $\text{P}_2\text{P}'$ reacts with all the dithiolates to give complexes of the type $[(\eta^3\text{-P}_2\text{P}')\text{Pt}(\text{S-S})]^+$ which are thought to be square planar. A square planar complex $(\eta^2\text{-P}_2\text{P}')\text{Pt}(\eta^2\text{-S}_2\text{P}(\text{O})\text{OEt})$ can be identified at low temperature. In contrast, P_3 acts only as a bidentate ligand in these systems to give square planar complexes of the type $[(\eta^2\text{-P}_3)\text{Pt}(\eta^2\text{-S-S})]^+$ which are fluxional at room temperature. Various reactions can be carried out with the pendant phosphine, such as reaction with sulfur and methylation, and these stop the ligand exchange reactions.

Introduction

The interactions between $\text{Pt}(\text{S-S})_2$ ($\text{S-S} = \text{S}_2\text{CNR}_2$, $\text{S}_2\text{P}(\text{OR})_2$, S_2COR etc.) and phosphine ligands have been the subject of ongoing research in recent years. Stephenson and co-workers [1–5] and Fackler and co-workers [6, 7] thoroughly investigated the reactions with monodentate Group 15 ligands and established the general reactions



In more recent papers [8–11] we have used multinuclear magnetic resonance spectroscopy to extend these studies to reactions of platinum dithiolates with potentially bidentate Group 15 and mixed Group 15/Group 16 ligands. These studies have established an order of ligand strength for both the Group 15/Group 16 ligands and for the various dithiolates. In this paper we further extend the investigations to the reactions of platinum dithiolates with the triphosphines bis(2-diphenylphosphinoethyl)phenylphosphine ($\text{Ph}_2\text{PCH}_2\text{-}$

$\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2$, $\text{P}_2\text{P}'$) and 1,1,1-tris(diphenylphosphinomethyl)ethane ($\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$, P_3) [12].

$\text{P}_2\text{P}'$ has two phosphorus atoms in the same chemical environment and a third that is different and its ^{31}P NMR spectrum consists of a doublet at $\delta -13.5$ and a triplet at $\delta -17.0$ with some second order character [13]. Molecular models indicate that when $\text{P}_2\text{P}'$ acts as a bidentate ligand it must coordinate via P' and one P atom and not through the two P atoms. When $\text{P}_2\text{P}'$ does coordinate in a bidentate mode, the chelate ring is similar to that generated by dpe ($\text{dpe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$). It has been shown that P' is more basic than P and upon coordination of $\text{P}_2\text{P}'$, the P' atom usually displays a larger coordination chemical shift than the P atoms [14].

King *et al.* investigated the reactions of K_2PtCl_4 with $\text{P}_2\text{P}'$ [15] and produced $[\text{Pt}(\eta^3\text{-P}_2\text{P}')\text{Cl}]\text{Cl}$. Levason and co-workers [16] also prepared this cation together with the corresponding bromo derivative. Meek and co-workers reacted $(\text{cod})\text{PtMe}_2$ with various di-, tri- and tetraphosphine ligands [17, 18] producing complexes of the type $[(\eta^2\text{-P}_n)\text{PtMe}_2]$ ($n = 2, 3, 4$) where the phosphine ligand is bidentate. The free arm of the phosphine ligand ($n = 3, 4$) causes some of the molecules to be fluxional with a suggested five-coordinate intermediate having the ligand bound in a tridentate mode [18]. The

*Author to whom correspondence should be addressed.

five-coordinate complex $[(P_2P')Pt(dpmSe)]^{2+}$ ($dpmSe = Ph_2PCH_2P(Se)Ph_2$) has been reported [19].

Results

All reactions were performed initially *in situ* in a NMR tube. Many of the complexes were later isolated and fully characterised by microanalysis. Subsequent dissolution in dichloromethane gave NMR spectra similar to those described here.

Reactions with P_2P'

All NMR data for compounds containing P_2P' are given in Table 1. The reaction of equimolar amounts of $Pt(S_2P\{OEt\}_2)$ ($Pt(dtp)_2$) and P_2P' at room temperature in dichloromethane solution produced a species whose ^{31}P NMR spectrum at 20 °C, shown in Fig. 1(a), consists of four singlets at δ 112.0, 93.7, 91.2 and 39.7. The two singlets at lowest frequencies, of intensity ratio 1 to 2, each display widely separated ^{195}Pt satellites indicating that all the phosphorus atoms of P_2P' are coordinated to platinum, and there is no resonance near the position of the free ligand signals. The resonance at δ 93.7 also has ^{195}Pt satellites ($^2J(Pt,P) = 50$ Hz) but they are not obvious without spectral expansion.

The remaining singlet at δ 112.0 does not have satellites and is assigned to free dithiophosphate ion [5]. The ^{195}Pt NMR spectrum, Fig. 1(b), exhibits a doublet of triplets of doublets and is entirely consistent with the ^{31}P NMR spectrum. It shows that the platinum atom is strongly coupled to two equivalent phosphorus atoms and also to another that is chemically different, as well as weaker coupling to the phosphorus atom of the dtp ligand. This data leads to the identification of the species in solution as $[(\eta^3-P_2P')Pt(dtp)]^+$ and this was confirmed by analytical data for the isolated tetraphenylborate salt (Table 2) and also by electrospray mass spectrometry [20]. However, this spectroscopic information does not distinguish between four-coordinate and five-coordinate structures and these possibilities will be discussed later.

When the solution is left to stand at room temperature for a few days the spectra change. The ^{31}P NMR spectrum at ambient temperature is broad, but at -90 °C it shows peaks due to remaining $[(\eta^3-P_2P')Pt(dtp)]^+$, and two signals with ^{195}Pt satellites at δ 85.7 and 41.8 (intensities 1:2). The positions of these resonances and their coupling constants to platinum are very similar to those reported [16] for $[(\eta^3-P_2P')PtCl]^+$. There is also a strong signal at δ 88.4 without satellites which is unidentified, although it is clearly due to some

TABLE 1. ^{31}P and ^{195}Pt NMR data for the P_2P' derivatives in dichloromethane solution

Compound	$\delta(^{31}P)$ (ppm)	$\delta(^{195}Pt)$ (ppm)	$J(Pt,P)$ (Hz)	Temperature (°C)
P_2P'	-13.5d -17.0t		$^2J(P,P) = 29$	20
$[(\eta^3-P_2P')Pt(dtp)]^+$	93.7s 91.2s 39.7s	-5005dtd	$^2J = 50$ $^1J = 2850$ $^1J = 2685$	20
$[(\eta^3-P_2P')Pt(xan)]^+$	89.6s 39.0s	-5090td	$^1J = 2730$ $^1J = 2800$	20
$[(\eta^3-P_2P')Pt(dtc)]^+$	86.3s 36.6s	-5005td	$^1J = 2790$ $^1J = 2955$	20
$(\eta^2-P_2P')Pt(\eta^2-S_2P\{O\}OEt)$	67.5s 50.5d 44.9s -16.5d	-5065ddd	$^2J = 255$ $^1J = 3230$ $^1J = 3210$	-100
$(\eta^2-PP'P\{S\})Pt(\eta^2-S_2P\{O\}OEt)$	65.5s 46.7s 45.9s 43.7s 42.8s 42.2s	-5010ddd -5015ddd	$^2J = 265$ $^1J = 3270$ $^1J = 3180$	20
$[(\eta^3-P_2P')PtCl]^+$	85.7s 41.8s	-4855dt	$^1J = 3040$ $^1J = 2470$	-90
$[(\eta^3-P_2P')PtI]^+$	92.7s 42.3s	-5255dt	$^1J = 2945$ $^1J = 2410$	20
$[(\eta^2-PP'P\{Me\})Pt(\eta^2-dtc)]^{2+}$	47.9d 42.8s 24.3d	-4840dd	$^1J = 3140$ $^1J = 3110$ $^3J(P,P) = 52$	20

s = singlet, d = doublet, t = triplet.

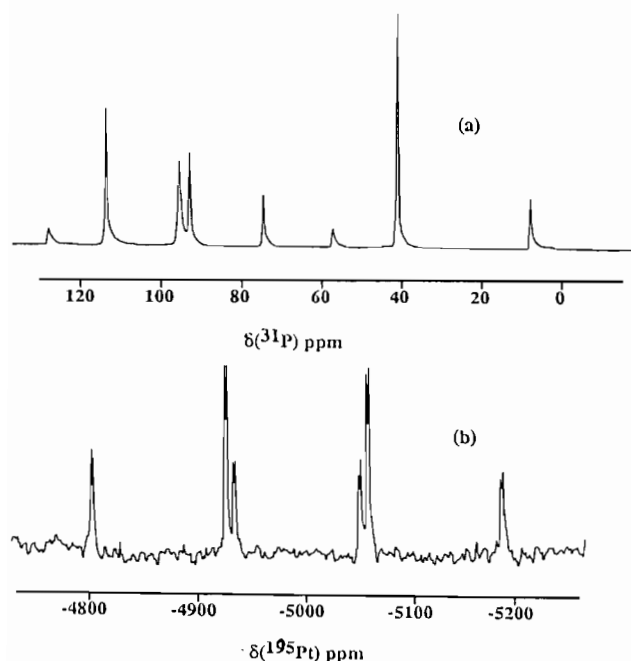


Fig. 1. NMR spectra for a dichloromethane solution of $[\eta^3-(P_2P')Pt(dtp)]^+$ at 20 °C. (a) ^{31}P , (b) ^{195}Pt .

TABLE 2. Analytical data

Compound	C (%)		H (%)		Melting point (°C)
	Found	Calc.	Found	Calc.	
$[(P_2P')Pt(dtp)]BPh_4$	60.08	60.34	5.11	5.11	313
$[(P_2P')Pt(xan)]BPh_4$	62.72	62.89	5.01	5.16	209
$[(P_2P')Pt(dtc)]BPh_4$	63.26	63.21	5.49	5.27	292
$[(P_3)Pt(dtp)]BPh_4$	60.07	62.59	5.20	5.22	166
$(P_3)Pt(S_2P\{O\}OEt)$	51.69	52.92	4.92	4.51	194
$(P_3)Pt(S_2CO)$	55.47	55.32	4.66	4.28	295

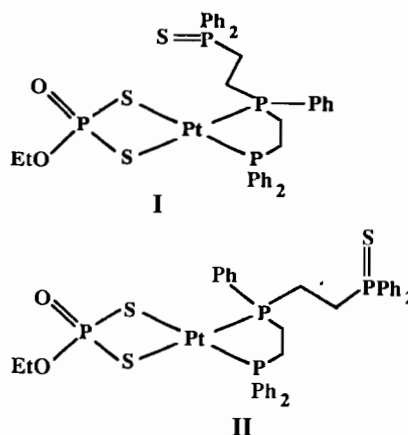
derivative of the liberated dithiophosphate ligands. The ^{195}Pt NMR spectrum contains signals assigned to remaining $[(\eta^3-P_2P')Pt(dtp)]^+$ together with a doublet of triplets, the position of which confirms the presence of $[(\eta^3-P_2P')PtCl]^+$.

A small excess of MeI was added at 20 °C to a freshly prepared solution of $[(\eta^3-P_2P')Pt(dtp)]^+$ and a rapid reaction ensued. The ^{31}P NMR spectrum showed a strong singlet at δ 94.0 assigned to the dithiophosphate ester $MeS_2P(OEt)_2$ and two other singlets with ^{195}Pt satellites at δ 92.7 and 42.3 (intensities 1:2). The ^{195}Pt NMR spectrum was a doublet of triplets. When the spectral parameters are compared with those reported [16] for $[(\eta^3-P_2P')PtCl]^+$ and $[(\eta^3-P_2P')PtBr]^+$, they indicate that the product is $[(\eta^3-P_2P')PtI]^+$.

A dichloromethane solution of $(\eta^2-dae)Pt(\eta^2-S_2P\{O\}OEt)$ [8] ($dae = Ph_2AsCH_2CH_2AsPh_2$) reacts with P_2P' at -100 °C to produce a ^{31}P NMR spectrum containing two slightly broadened singlets at δ 67.5 and

44.9 and two doublets at δ 50.5 and -16.5 , the latter doublet being close to the resonance position of the free ligand, indicating that a pendant phosphine group is present. The singlet at δ 67.5 is due to the coordinated dealkylated dithiophosphate ligand and has a coupling constant (Table 1) that is similar to those previously observed for square planar platinum(II) complexes [5, 8]. The remaining signals indicate that the three phosphorus atoms in the P_2P' ligand are in different environments. It is suggested that the square planar complex $(\eta^2-P_2P')Pt(\eta^2-S_2P\{O\}OEt)$ has been formed and the fluxional behaviour above -100 °C is similar to that reported by Meek and co-workers [17, 18] for $(P_2P')PtMe_2$ and involves exchange between the coordinated and pendant terminal PPh_2 groups.

If sulfur is added to the solution of $(\eta^2-P_2P')Pt(\eta^2-S_2P\{O\}OEt)$ the ^{31}P NMR spectrum is now sharp at 20 °C and consists of singlet peaks at δ 65.5 and 43.7 and two apparent doublets, which we believe to be two sets of singlets, at δ 46.7/45.9 and 42.8/42.2. The two resonances at highest frequencies and the pair of signals at δ 46.7/45.9 occur close to those of $(\eta^2-P_2P')Pt(\eta^2-S_2P\{O\}OEt)$ whilst the signal for the pendant phosphorus of $(\eta^2-P_2P')Pt(\eta^2-S_2P\{O\}OEt)$ has been shifted significantly from the free ligand resonance to the position for a phosphorus(V) atom coordinated to sulfur [13]. Phosphorus-sulfur bonds are not labile [21] and this sulfur coordination stops the exchange because the pendant group is no longer a free phosphine. The ^{195}Pt NMR spectrum shows two doublet of doublet of doublets at very similar chemical shifts (δ -5010 and -5015) indicating that there are two platinum containing species in solution. These are thought to be the isomers of $(\eta^2-PP'P\{S\})Pt(\eta^2-S_2P\{O\}OEt)$ shown in structures I and II.



The reaction products of $Pt(S_2CO^iPr)_2$ ($Pt(xan)_2$) and P_2P' in dichloromethane solution at 20 °C gave ^{31}P and ^{195}Pt NMR spectra similar to those observed in the dtp system (Table 1). By comparison with the

data for the $\text{Pt}(\text{dtp})_2$ and $\text{P}_2\text{P}'$ system it can be concluded that the product formed in solution is $[(\eta^3\text{-P}_2\text{P}')\text{Pt}(\text{xan})]^+$. The empirical formula was confirmed by microanalytical data (Table 2) and electrospray mass spectrometry [20]. Reaction between $[(\eta^3\text{-P}_2\text{P}')\text{Pt}(\text{xan})]^+$ and MeI gives the same product as the dithiophosphate derivative, namely $[(\eta^3\text{-P}_2\text{P}')\text{PtI}]^+$, but in this case the reaction takes about 4 h to proceed to completion.

Similarly, when equimolar quantities of $\text{Pt}(\text{S}_2\text{CNEt}_2)_2$ ($\text{Pt}(\text{dte})_2$) and $\text{P}_2\text{P}'$ are mixed in dichloromethane at ambient temperature, the NMR spectra are analogous to those observed in the dtp and xan systems suggesting that the product formed in solution is $[(\eta^3\text{-P}_2\text{P}')\text{Pt}(\text{dte})]^+$. Microanalytical data (Table 2) and electrospray mass spectrometry [20] confirm the empirical formula. $[(\eta^3\text{-P}_2\text{P}')\text{Pt}(\text{dte})]^+$ was mixed with a slight excess of MeI and the solution allowed to stand overnight. The ^{31}P and ^{195}Pt NMR spectra indicate two species are formed, one of which is $[(\eta^3\text{-P}_2\text{P}')\text{PtI}]^+$ identical to the product formed under similar conditions in the dithiophosphate and xanthate systems. The other product has three signals in the ^{31}P NMR spectrum at δ 47.9, 42.8 and 24.3. The resonance at lowest frequency does not have ^{195}Pt satellites although it is well removed from the resonance position for free ligand and it occurs in the region associated with resonances of phosphonium salts. The ^{195}Pt NMR spectrum for this species is a doublet of doublets. All of the data indicate the compound is $[(\eta^2\text{-PP}'\text{P}\{\text{Me}\})\text{Pt}(\eta^2\text{-dte})]^{2+}$ in which one of the terminal PPh_2 groups of $\text{P}_2\text{P}'$ has been methylated to give a bidentate ligand. This empirical formula has been confirmed by electrospray mass spectrometry [20].

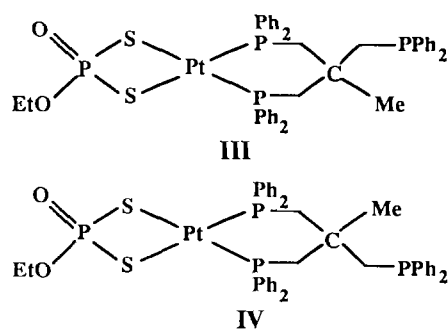
Reactions with P_3

In P_3 the phosphorus atoms are all equivalent, Table 3 contains all NMR data for derivatives containing P_3 .

When $\text{Pt}(\text{dtp})_2$ and P_3 are mixed at -30°C in dichloromethane solution the ^{31}P NMR spectrum consists of four singlets at δ 111.2, 93.3, -3.6 and -31.7 . The singlet at δ 111.2 is due to free dithiophosphate whilst the singlet at δ 93.3 with coupling to platinum, $^2J(\text{Pt},\text{P}) = 300$ Hz, is indicative of a bidentate dtp ligand in a square planar platinum(II) complex [5, 8]. The singlet at δ -3.6 also displays ^{195}Pt satellites and is shifted significantly from the free ligand resonance at δ -26.7 [13] whilst the signal at δ -31.7 is without satellites, indicating a pendant phosphine. These two singlets are in the intensity ratio 2 to 1 indicating that two of the phosphorus atoms are coordinated to platinum. The ^{195}Pt NMR spectrum at -30°C is a triplet of doublets due to two equivalent phosphorus atoms directly coordinated to platinum ($^1J(\text{Pt},\text{P}) = 3190$ Hz) and a third ($^2J(\text{Pt},\text{P}) = 300$ Hz) from the dithiophosphate

ligand. Thus, the compound formed in solution is $[(\eta^2\text{-P}_3)\text{Pt}(\eta^2\text{-dtp})]^+$. A crystal structure determination for $(\eta^2\text{-P}_3)\text{PtMe}_2$ has shown that the phosphine ligand retains its bidentate coordination in the solid state [22].

If the above solution is allowed to stand for a week, then the ^{31}P NMR spectrum at 25°C consists of three singlets at δ 94.2, 5.0 and -31.1 and an apparent doublet at δ 59.1. The singlet at δ 94.2 is due to the dithiophosphate ester, $\text{EtS}_2\text{P}(\text{OEt})_2$ [8] while the signals close to δ 59.1 are due to the coordinated dealkylated dithiophosphate ligand, $[\text{S}_2\text{P}\{\text{O}\}\text{OEt}]^{2-}$. The two singlets at δ -5.0 and -31.1 have an intensity ratio 2 to 1 with the one at lower frequency occurring near the resonance position of the parent phosphine ligand. The corresponding ^{195}Pt NMR spectrum consists of a triplet of doublets which is consistent with the ^{31}P NMR spectrum. Hence, the product formed in solution is $(\eta^2\text{-P}_3)\text{Pt}(\eta^2\text{-S}_2\text{P}\{\text{O}\}\text{OEt})$ and this has been confirmed by microanalytical data (Table 2). It is thought that the signals assigned to the coordinated dealkylated ligand are two singlets due to the presence of the isomers shown in structures III and IV.



Excess MeI was added to a sample of $[(\eta^2\text{-P}_3)\text{Pt}(\eta^2\text{-dtp})]\text{BPh}_4$ in dichloromethane. The NMR spectra (Table 3) indicate that the dithiophosphate ligand remains bidentate while the resonance position of the unbound phosphorus atom is changed significantly to the region associated with phosphonium salts, indicating that this phosphorus atom has been methylated to give the product $[(\eta^2\text{-P}_2\text{P}\{\text{Me}\})\text{Pt}(\eta^2\text{-dtp})]^{2+}$ and this formulation has been confirmed by electrospray mass spectrometry [20].

Equimolar quantities of $\text{Pt}(\text{S}_2\text{CO}^n\text{Pr})_2$ and P_3 were mixed in dichloromethane at -100°C . The ^{31}P NMR spectrum at -80°C consists of two singlets at δ -1.1 (with satellites) and δ -33.4 . The ^{195}Pt NMR spectrum is a triplet, somewhat broadened due to exchange between the bidentate and free xanthate ligands, and the product formed in solution is $[(\eta^2\text{-P}_3)\text{Pt}(\eta^2\text{-xan})]^+$.

If the solution is left to stand overnight, the ^{31}P NMR spectrum now consists of two singlets at δ -4.4 and δ -31.9 and the ^{195}Pt NMR spectrum is a new triplet at δ -4905 . As seen previously, dealkylation

TABLE 3. ^{31}P and ^{195}Pt NMR data for the P_3 derivatives in dichloromethane solution

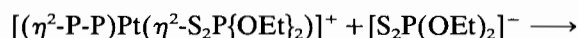
Compound	$\delta(^{31}\text{P})$ (ppm)	$\delta(^{195}\text{Pt})$ (ppm)	$J(\text{Pt},\text{P})$ (Hz)	Temperature ($^{\circ}\text{C}$)
P_3	-26.7s			20
$[(\eta^2\text{-P}_3)\text{Pt}(\text{dtp})]^+$	93.3s -3.6s -31.7s	-4985td	$^2J=300$ $^1J=3190$	-30
$[(\eta^2\text{-P}_3)\text{Pt}(\text{xan})]^+$	-1.1s -33.4s	-4840t	$^1J=2840$	-80
$[(\eta^2\text{-P}_3)\text{Pt}(\text{dte})]^+$	-5.2s -32.7s	-4825t	$^1J=2900$	-30
$(\eta^2\text{-P}_3)\text{Pt}(\text{S}_2\text{P}\{\text{O}\}\text{OEt})$	59.1d -5.0s -31.1s	-4990td	$^2J=265$ $^1J=3070$	20
$(\eta^2\text{-P}_3)\text{Pt}(\text{S}_2\text{CO})$	-4.4s -31.9s	-4905t	$^1J=2920$	-50
$[(\eta^2\text{-P}_2\text{P}(\text{Me}))\text{Pt}(\text{dtp})]^{2+}$	93.5s 15.5s -4.5s	-4955td	$^2J=300$ $^1J=3185$	20
$[(\eta^2\text{-P}_2\text{P}(\text{Me}))\text{Pt}(\text{xan})]^{2+}$	-2.4s 30.6s	-4975t	$^1J=3065$	20
$[(\eta^2\text{-P}_2\text{P}(\text{Me}))\text{Pt}(\text{dte})]^{2+}$	17.2s -5.3s	-4795t	$^1J=2990$	20

occurs to give $(\eta^2\text{-P}_3)\text{Pt}(\eta^2\text{-S}_2\text{CO})$. This dealkylation step was found to occur quite rapidly even at temperatures as low as -50°C which is somewhat surprising since most of these reactions are usually slow below -20°C . The identity of the final product was confirmed by microanalysis.

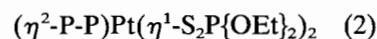
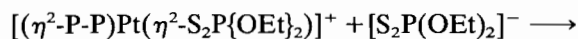
The reaction mixture of $\text{Pt}(\text{dte})_2$ and P_3 gives similar spectra. There is exchange at room temperature between the coordinated and free phosphorus atoms in the phosphine ligand. If the temperature is lowered to -30°C this exchange can be slowed to give sharp spectra which identify the product as $[(\eta^2\text{-P}_3)\text{Pt}(\eta^2\text{-dte})]^+$.

Discussion

For the $\text{P}_2\text{P}'$ derivatives, the NMR data do not unambiguously distinguish between four-coordinate structures such as $[(\eta^3\text{-P}_2\text{P}')\text{Pt}(\eta^1\text{-S-S})]^+$ and five-coordinate structures such as $[(\eta^3\text{-P}_2\text{P}')\text{Pt}(\eta^2\text{-S-S})]^+$. However, we believe the compounds are four-coordinate square planar compounds for the following reasons. In the case of the $[(\text{P}_2\text{P}')\text{Pt}(\text{dtp})]^+$ the Pt-P coupling constant (50 Hz) is low even for a monodentate dtp complex and far too low for a chelated dtp ligand [5, 8]. When the platinum dithiolates are reacted with monodentate and bidentate Group 15 ligands to give $[\text{P}_2\text{Pt}(\eta^2\text{-S-S})]^+$ and $[(\eta^2\text{-P-P})\text{Pt}(\eta^2\text{-S-S})]^+$ the dithiophosphate and xanthate complexes have to be isolated quickly to prevent further reaction with the free dithiolate ion to give a cation containing a dealkylated



dithiophosphate ligand and the dithiophosphate ester [2]. The $\text{P}_2\text{P}'$ system is the first in which this common reaction fails to occur for either the dtp or the xan complex. It has been suggested [23] that the dealkylation reaction proceeds through the step



so the absence of the reaction in the $\text{P}_2\text{P}'$ compounds can be taken as evidence that the dithiolate ligand is actually coordinated as a monodentate ligand so that reaction (2) cannot proceed. In contrast, the compounds $[(\eta^2\text{-P}_3)\text{Pt}(\eta^2\text{-S-S})]^+$ ($\text{S-S} = \text{dtp, xan}$) do readily undergo the dealkylation reaction.

Further evidence that the dithiolates are monodentate is their ready replacement by halide to give the known [17] $[(\text{P}_2\text{P}')\text{PtX}]^+$ ($\text{X} = \text{halide}$) cations. We have not previously observed this reaction in other systems where the dithiolates are unequivocally bidentate. We have established [11] an ordering of chelated dithiolate ligand strength towards platinum(II) ($\text{dtp} < \text{xan} < \text{dte} < \text{S}_2\text{P}\{\text{O}\}\text{OEt} \sim \text{S}_2\text{CO}$). Dte is a stronger ligand than dtp and xan because of delocalisation within the dte ligand when it is chelated, and as a result dte will displace both dtp and xan from compounds of the type $[(\text{P-P})\text{Pt}(\text{dtp})]^+$. However, in dichloromethane dte does not displace dtp from $[(\text{P}_2\text{P}')\text{Pt}(\text{dtp})]^+$, in fact the

product is $[(P_2P')PtCl]^+$, and this is taken as further evidence that the dithiolates are monodentate in these compounds. The $[S_2P(O)OEt]^{2-}$ ligand is the strongest chelate ligand of those we have investigated [11] at platinum(II) and the compound $(P_2P')Pt(S_2P\{O\}OEt)$ is unequivocally square planar since a pendant phosphine group is revealed by the ^{31}P NMR spectrum. The steric requirements of chelated $[S_2P(O)OEt]^{2-}$ are the same as those of the other dithiolates, so if the dtp, xan and dtc were indeed five-coordinate, there is no reason why the dealkylated dithiophosphate would not form a similar complex. The conclusion we make is that the complexes are all four-coordinate square planar derivatives. There is competition between the potentially tridentate P_2P' and the potentially bidentate S-S ligands for the four available coordination sites and in all cases except with $[S_2P(O)OEt]^{2-}$, the phosphine wins and the dithiolate remains monodentate.

Peringer and co-workers [19] have reported compounds such as $[(P_2P')Pt(dpmSe)]^{2+}$ which are undoubtedly five-coordinate since multinuclear magnetic resonance studies show that all the potential donor atoms are coordinated to platinum. The geometry of dpmSe is such that when it coordinates through phosphorus, the selenium is forced close to the metal encouraging chelation [24]. Thus, there is a fine balance between the preferences of platinum(II) for square planar geometry and the preferred coordination modes of the ligands.

The ligand P_3 can only form facial isomers in octahedral situations because of its central carbon atom and therefore it can only be bidentate, at maximum, in square planar complexes. In all its derivatives reported here it behaves as a bidentate and the chemistry of these complexes is the same as those with diphosphine ligands. For example, the dithiophosphate and xanthate complexes are readily dealkylated.

Experimental

Platinum dithiolates were prepared as described previously [10, 11] whilst P_2P' and P_3 were commercial samples (Strem). Analyses were performed by Chemical and Microanalytical Services P/L (CMAS), Geelong.

Most reactions were initially studied *in situ* in the NMR tube. Many of the products were subsequently isolated by similar reactions on a larger scale in dichloromethane solution, similar to the preparations of $[(P-P)Pt(dtc)]^+$ (P-P = diphosphine) [9]. After evaporation of the solvent the products were recrystallised from dichloromethane/n-hexane.

NMR spectra were recorded using a JEOL FX 100 spectrometer, ^{31}P at 40.32 MHz and ^{195}Pt at 21.32 MHz with external 7Li lock. External references were 85% H_3PO_4 and 1 M H_2PtCl_6 in conc. HCl; high frequency positive convention is used for chemical shifts.

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