Multinuclear (^{31}P, ^{77}Se, ^{195}Pt) magnetic resonance studies on the interaction of platinum bis(n-propylxanthate) with potentially bidentate ligands

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Abstract

The reactions of platinum bis(n-propylxanthate), $Pt(S_2CO^nPr)_2(Pt(xan)_2)$ with a number of potentially bidentate Group 15 and mixed Group 15/Group 16 donor ligands (L-L') have been investigated in dichloromethane solution. The products of the reactions have been identified by multinuclear (^{31}P, ^{77}Se, ^{195}Pt) magnetic resonance, infrared and analytical studies. When reactions in 1:1 molar proportions are carried out at room temperature, one xanthate ligand is often displaced to give $[(L-L')Pt(xan)]^+$ and further reaction occurs to give the dithiocarbonate complex (L-L')Pt(S_2CO) and the xanthate ester. If the reactions are carried out at low temperature this reaction is avoided and temperature dependent equilbria of the type $(\eta^1\text{-L-L'})Pt(\eta^1\text{-xan})(\eta^2\text{-xan}) \rightleftharpoons [(\eta^2\text{-L-L'})Pt(\eta^2\text{-xan})]^+ + xan^-$ occur because of the similar donor powers of the various ligands. Dithiocarbonate is a much stronger ligand to platinum than xanthate, so these reactions do not occur with this ligand.

Introduction

Stephenson [1–5] and Fackler [6, 7] and their coworkers have made extensive studies of the interactions of monodentate Group 15 ligands with platinum bis(dithiolate) complexes $Pt(S-S)_2$ $(S-S = [S_2CNR_2]^-, [S_2COR]^-, [S_2P(OR)_2]^-)$. The products of these reactions, usually $(PR_3)Pt(\eta^1\text{-S-S})(\eta^2\text{-S-S})$ and $[(PR_3)_2Pt(\eta^2\text{-S-S})]^+$, have been characterised by a variety of spectroscopic techniques and the stereochemistries have been confirmed by X-ray crystallography on isolated solid samples.

In recent papers [8, 9] we have used multinuclear magnetic resonance spectroscopy to extend these studies by interacting the platinum dithiolates with a variety of potentially bidentate Group 15 and mixed Group 15/Group 16 donor ligands. The studies with the monodentate ligands did not discriminate between the coordinating powers of either the different dithiolates or the Group 15 ligands towards platinum. In contrast, the use of bidentate ligands clearly demonstrated that diethyldithiocarbamate is a stronger ligand towards platinum(II) than O-O-diethyldithiophosphate and established a consistent order of ligand strengths for the Group 15/Group 16 donors.

In this paper, studies on the interaction of platinum bis(n-propylxanthate), $Pt(S_2CO^nPr)_2$ $(Pt(xan)_2)$, with some potentially bidentate ligands L-L' are described where $L-L' = Ph_2PCH_2CH_2PPh_2$ (dpe), $Ph_2PCH_2PPh_2$ (dpm), $Ph_2AsCH_2CH_2PPh_2$ (ape), $Ph_2P(E)CH_2PPh_2$ (E = S, Se to give dpmS, dpmSe) and $Ph_2AsCH_2CH_2P(E)Ph_2$ (apeS, apeSe). The products of the reactions were characterised principally by multinuclear magnetic resonance techniques.

Results

NMR data for all compounds are given in Table 1 while Table 2 lists analytical and infrared data.

Reactions with dpe

When equimolar proportions of Pt(xan)$_2$ and dpe are mixed in dichloromethane at room temperature, the ^{31}P NMR spectrum shows two singlets, each with ^{195}Pt satellites, indicating the presence of two species. One compound is quite rapidly converted irreversibly to the other at room temperature so the reaction was performed at −45 °C by adding dpe to a solution of Pt(xan)$_2$ precooled in the probe of the spectrometer. Under these conditions the ^{31}P NMR spectrum consists predominantly of a singlet at δ 43.9 with ^{195}Pt

TABLE 1. ^{31}P and ^{195}Pt NMR data in dichloromethane solution

Compound	$\delta(^{31}P)$ (ppm)	$\delta(^{195}Pt)$ (ppm)	$^1J(Pt-P)$ (Hz)	Temperature (°C)
$[(dpe)Pt(xan)]^+$	43.9s	−4780t	3065	−45
$(dpe)Pt(S_2CO)$	41.3s	−4905t	3030	−45
$(\eta^1-dpm)Pt(\eta^1-xan)(\eta^2-xan)^a$	4.0d, −28.0d	−4460dd	3700	−20
$[(dpm)Pt(xan)]^+$	−53.4s	−4185t	2605	−20
$(dpm)Pt(S_2CO)$	−53.6s	−4310t	2590	30
$[(\eta^1-dpm)_2Pt(xan)]^{+\,b}$	7.2t, −30.3t	−4680tt	2750	−50
$(\eta^1-dpm)_2Pt(S_2CO)^c$	3.3d, −28.2d	−4700tt	3145	−40
$[(ape)Pt(xan)]^+$	46.7s	−4890d	3000	−20
$(ape)Pt(S_2CO)$	44.6s	−5010d	3040	−20
$(\eta^1-ape)_2Pt(\eta^2-S_2CO)$	8.0s	−4780t	3100	−20
$(\eta^1-dpmSe)Pt(\eta^1-xan)(\eta^2-xan)^d$	0.1s, 22.1s	−4360dd	3890	−70
$[(\eta^2-dpmSe)Pt(xan)]^{+\,e}$	15.9d, 38.9s	−4480dd	3080	−70
$(\eta^1-dpmS)Pt(\eta^1-xan)(\eta^2-xan)^f$	−1.2s, 31.7s	−4400dd	3835	−40
$(\eta^1-apeSe)Pt(\eta^1-xan)(\eta^2-xan)^g$	35.8s	−4465s		−30
$(\eta^1-apeS)Pt(\eta^1-xan)(\eta^2-xan)$	43.2s	−4445s		−30

[a] $^2J(P,P) = 78$, $^3J(Pt,P) = 58$. [b] $^2J(P,P) = 38$. [c] $^2J(P,P) = 55$, $^3J(Pt,P) = 60$. [d] $\delta(^{77}Se) = -1585d$, $^1J(P,Se) = 747$, $^3J(Pt,P) = 30$. [e] $\delta(^{77}Se) = -1335d$, $^1J(P,Se) = 527$, $^2J(P,P) = 54$, $^3J(Pt,P) = 63$, $^1J(Pt,Se) = 195$. [f] $^3J(Pt,P) = 56$. [g] $\delta(^{77}Se) = -1670$, $^1J(P,Se) = 729$.

TABLE 2. Analytical and infrared data

Compound	Calculated (%)		Found (%)		$\nu(CO)$ (cm^{-1})
	C	H	C	H	
$(\eta^2-dpe)Pt(\eta^2-S_2CO)$	46.87	3.47	47.3	3.53	1690s, 1620vs, 1580m
$(\eta^1-dpm)_2Pt(\eta^2-S_2CO)$	57.78	4.19	58.0	4.17	1690s, 1610vs, 1580m
$(\eta^2-ape)Pt(\eta^2-S_2CO)$	44.14	3.24	44.4	3.32	1680s, 1615vs, 1580m
$(\eta^1-ape)_2Pt(\eta^2-S_2CO)$					1680s, 1610vs, 1580m

satellites and the ^{195}Pt NMR spectrum is predominantly a triplet at δ −4780 ppm. This triplet confirms that dpe is chelated to platinum. There were also weak resonances present in the spectra due to small quantities of the second species (below).

On allowing the solution to stand at room temperature for a few minutes and then recooling to prevent further reaction, the phosphorus spectrum now consists of two singlets with satellites and two triplets are observed in the platinum NMR spectrum, indicating that both species contain a chelated dpe ligand. After allowing the reaction to proceed for 1 h at room temperature only one species remained in solution which was isolated and shown to be $(dpe)Pt(S_2CO)$ by analytical and infrared ($\nu C=O$) spectroscopic techniques [2] (Table 2). The first product of the reaction between $Pt(xan)_2$ and dpe is $[(dpe)Pt(xan)]^+$ which is rapidly attacked by the free xanthate ion to give the dithiocarbonate complex. This behaviour exactly parallels that observed by Alison and Stephenson [2] in the interaction of $Pt(xan)_2$ with two moles of monodentate phosphine ligands.

When a dichloromethane solution of $Pt(xan)_2$ was cooled to −70 °C before addition of one mole of dpe (to prevent formation of the dithiocarbonate) the ^{31}P NMR spectrum again shows two singlets with satellites, one being due to the expected $[(dpe)Pt(xan)]^+$. The ^{195}Pt NMR spectrum consists of the triplet due to $[(dpe)Pt(xan)]^+$ and a quintet which identifies the second species as $[Pt(dpe)_2]^{2+}$. All NMR data for this species agree with those reported previously [8]. As the temperature is varied between −20 and −90 °C the proportion of the two species in solution varies reversibly with $[(dpe)Pt(xan)]^+$ being heavily favoured at the higher temperatures. No free dpe is observed thus demonstrating the equilibrium

$$2[(dpe)Pt(xan)]^+ \rightleftharpoons [Pt(dpe)_2]^{2+} + Pt(xan)_2 \quad (1)$$
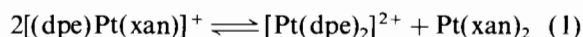
The result of the reaction between $Pt(xan)_2$ and two moles of dpe also depends upon the temperature at which the reactions are mixed. At room temperature, the ^{31}P NMR spectrum shows strong signals due to $(dpe)Pt(S_2CO)$ and free dpe and a weak signal, with satellites, assigned to $[Pt(dpe)_2]^{2+}$ on the basis of its chemical shift and

coupling constant [8]. Pre-cooling the solution of Pt(xan)$_2$ to $-20\,°C$ before the addition of dpe resulted in a solution containing $[Pt(dpe)_2]^{2+}$ as the only phosphorus containing species and its identity was confirmed by observation of the characteristic quintet in the ^{195}Pt NMR spectrum. These results suggest that at room temperature there is competition between the reactions leading from $[(dpe)Pt(xan)]^+$ to either $(dpe)Pt(S_2CO)$ or $[Pt(dpe)_2]^{2+}$ and that $(dpe)Pt(S_2CO)$ does not react with further dpe at room temperature. This was confirmed independently by addition of dpe to a solution of $(dpe)Pt(S_2CO)$ at room temperature.

Reactions with dpm

After interaction of equimolar proportions of Pt(xan)$_2$ and dpm at $-20\,°C$ the resultant solution gave the spectra shown in Fig. 1. These spectra unambiguously identify the species in solution as $[(\eta^2\text{-dpm})Pt(xan)]^+$ and $(\eta^1\text{-dpm})Pt(\eta^1\text{-xan})(\eta^2\text{-xan})$. Coupling between platinum and the pendent phosphorus in the latter compound is not discernible in the phosphorus spectrum because the combination of the small coupling constant
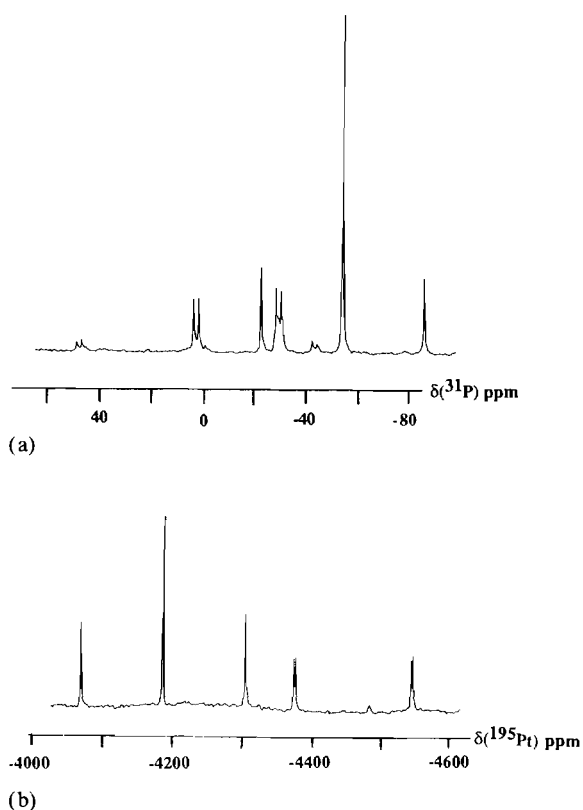

(a)

(b)

Fig. 1. NMR spectra of the solution obtained by mixing at $-20\,°C$ in dichloromethane equimolar quantities of Pt(xan)$_2$ and dpm (spectra run at $-20\,°C$): (a) ^{31}P, (b) ^{195}Pt.

and the low intensity of the satellites causes them to be lost in the foot of the signal at $\delta\ -28$ ppm. On varying the temperature over the temperature range 35 to $-50\,°C$ the relative proportions of the two species in solution vary reversibly. At $-50\,°C$ the spectrum shows very little $(\eta^1\text{-dpm})Pt(\eta^1\text{-xan})(\eta^2\text{-xan})$ to be present while at $35\,°C$ this complex accounts for about 60% of the species present (however, at this temperature some reaction with free xanthate occurs, see below). Thus the equilbrium

$$[(\eta^2\text{-dpm})Pt(\eta^2\text{-xan})]^+ + xan^- \rightleftharpoons$$

$$(\eta^1\text{-dpm})Pt(\eta^1\text{-xan})(\eta^2\text{-xan}) \quad (2)$$
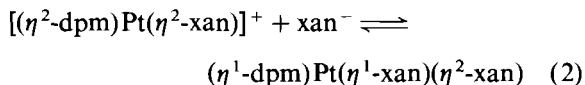
occurs in solution, but the exchange rate is slow on the NMR timescale so that separate sharp signals are observed for each complex.

On allowing the solution to stand at room temperature for several hours, a complicated reaction occurs in which unidentified intermediates are observed, but the final product is $(dpm)Pt(S_2CO)$.
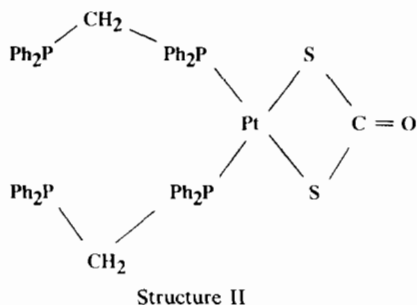
The reaction between Pt(xan)$_2$ and two moles of dpm at $-20\,°C$ gives a solution which displays two triplets in its ^{31}P NMR spectrum with the signal at higher frequency having ^{195}Pt satellites, and the position of the lower frequency signal is close to that of free dpm. This indicates the formation of $[(\eta^1\text{-dpm})_2Pt(xan)]^+$
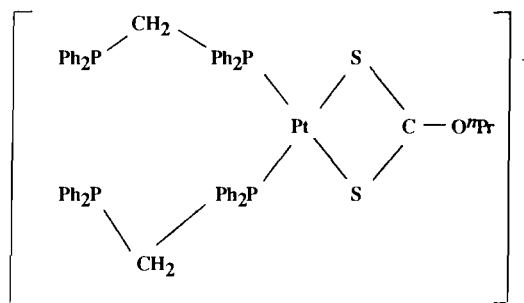
Structure I

whose phosphorus atoms constitute a AA'XX' spin system which in practice reduces to an approximate A$_2$X$_2$ system. The ^{195}Pt NMR spectrum is a broad triplet with the coupling to the pendent phosphorus atoms not being resolved. On allowing the solution to stand for 2 h at room temperature so that attack by the free xanthate ion may proceed, the ^{31}P NMR spectrum becomes two doublets (with satellites for the higher frequency signal) and the ^{195}Pt spectrum is a clearly defined triplet of triplets. These spectra are only consistent with another species containing two monodentate dpm ligands and subsequent analytical and infrared data for the isolated solid confirm

the compound to be $(\eta^1\text{-dpm})_2\text{Pt}(S_2\text{CO})$:

Structure II

Fig. 2. ^{31}P NMR spectrum of a solution of equilmolar quantities of Pt(xan)$_2$ and dpmSe mixed at -90 °C.

Reactions with ape

Mixing equimolar proportions of Pt(xan)$_2$ and ape in dichloromethane at -20 °C gives a solution whose ^{31}P NMR spectrum shows a singlet with ^{195}Pt satellites and the ^{195}Pt spectrum is a doublet with the same coupling constant. These data are consistent with the species in solution being $[(\text{ape})\text{Pt}(\text{xan})]^+$. On allowing the solution to stand at 20 °C for 1 h, similar spectra are observed with small changes in positions and coupling constant. Analytical and infrared spectral data on the isolated solid show it to be $(\text{ape})\text{Pt}(S_2\text{CO})$.

When Pt(xan)$_2$ and ape in 1:2 molar quantities are mixed together in dichloromethane solution at -70 °C extremely complicated ^{31}P and ^{195}Pt NMR spectra are observed. They indicate the presence of several species in solution but it was not possible to unequivocally identify them.

A pure sample of $(\text{ape})\text{Pt}(S_2\text{CO})$ was isolated as described in 'Experimental'. When an equimolar amount of ape was added to a solution of this compound the ^{31}P and ^{195}Pt NMR spectra obtained at 30 °C indicated that no reaction had occurred. However, upon cooling to -40 °C a new species is formed in solution which shows a singlet with satellites in its ^{31}P NMR spectrum and a triplet in the ^{195}Pt spectrum. All the evidence indicates that there is a reversible temperature dependent equilibrium

$$(\text{ape})\text{Pt}(S_2\text{CO}) + \text{ape} \rightleftharpoons (\eta^1\text{-ape})_2\text{Pt}(S_2\text{CO}) \quad (3)$$
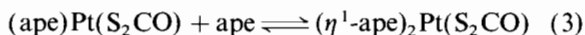
with $(\text{ape})_2\text{Pt}(S_2\text{CO})$ being favoured at low temperature. The monodentate ape ligands are bonded to platinum through phosphorus.

Reactions with dpmSe

Upon addition of one mole equivalent of dpmSe to a dichloromethane solution of Pt(xan)$_2$ precooled to -90 °C, the ^{31}P NMR spectrum shown in Fig. 2 was obtained. It consists of two singlets and two doublets. Both the singlet and doublet at lower frequency display ^{195}Pt satellites whilst the doublet at higher frequency exhibits
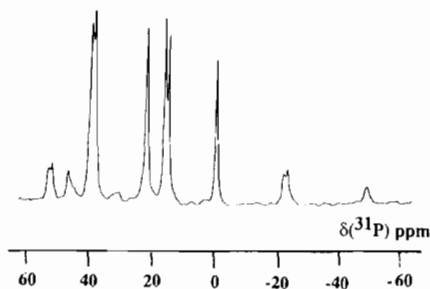
^{77}Se satellites. The singlet at higher frequency also has ^{77}Se satellites but they are obscured. This spectrum indicates the presence of two species in solution. There is no resonance near the frequency of the P(III) atom of dpmSe itself [10] confirming that phosphorus is bound to platinum in both compounds in solution.

The corresponding ^{195}Pt NMR spectrum consists of two doublets of doublets with the smaller coupling being hardly resolved (e.g. $^1J(\text{Pt,P}) = 3890$ Hz; $^3J(\text{Pt,P}) = 30$ Hz), confirming that there are two species in solution and that each contains dpmSe coordinated through phosphorus.

The ^{77}Se NMR spectrum shows two doublets (due to coupling to phosphorus). One doublet is close to the resonance position for free dpmSe and furthermore the coupling constant to phosphorus (747 Hz) is the same as that for dpmSe itself [10]. This indicates that in this species dpmSe is acting as a monodentate ligand through phosphorus only. In contrast, the second doublet is well shifted from the resonance position for dpmSe and its coupling constant is much reduced (527 Hz) from that of dpmSe. Both of these facts indicate selenium coordination [11] and this is confirmed in the most direct manner by the observation of ^{195}Pt satellites for this doublet. Thus in the second species in solution, dpmSe is chelated to platinum through phosphorus and selenium. The complexes in solution may be identified as $(\eta^1\text{-dpmSe})\text{Pt}(\eta^1\text{-xan})(\eta^2\text{-xan})$ and $[(\eta^2\text{-dpmSe})\text{Pt}(\eta^2\text{-xan})]^+$.

As the temperature is varied between -90 and -30 °C the relative proportions of the species vary in a reversible manner. At -30 °C the ratio of concentrations is about 4:1 favouring the compound containing monodentate dpmSe, at -70 °C the concentrations of the two species are about equal and at -90 °C the compound with chelated dpmSe is favoured by about 2:1. The equilibrium

$$(\eta^1\text{-dpmSe})\text{Pt}(\eta^1\text{-xan})(\eta^2\text{-xan}) \rightleftharpoons$$

$$[(\eta^2\text{-dpmSe})\text{Pt}(\eta^2\text{-xan})]^+ + \text{xan}^- \quad (4)$$
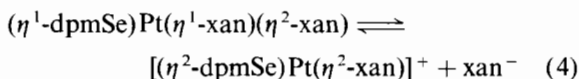
has been monitored in all three types of NMR spectra over the temperature range -90 to $-30\,°C$.

Upon allowing the solution to stand overnight at room temperature changes occur in the spectra but a dithiocarbonate is not formed, in contrast to the systems described earlier. In the ^{31}P NMR spectrum there is a resonance assigned to dpmSe$_2$ [10]. Similar results were obtained from the reaction of Pt(xan)$_2$ and two mole equivalents of dpmSe at low temperature. Signals due to dpmSe$_2$, the two dpmSe derivatives described above and dpm complexes were observed, but the spectra were complicated and rather irreproducible so that definite characterisation of all the products was not possible. However, there is no doubt that selenium transfer occurs between two molecules of dpmSe to give dpm and dpmSe$_2$ during the course of these reactions.

Reactions with dpmS

The reaction between equimolar quantities of Pt(xan)$_2$ and dpmS at $-40\,°C$ leads to the formation of only one compound, in contrast to the reaction of dpmSe. The ^{31}P NMR spectrum consists of two singlets, each with ^{195}Pt satellites (^1J(Pt,P) = 3835 Hz; ^3J(Pt,P) = 56 Hz) and the ^{195}Pt NMR spectrum is a doublet of doublets. By comparison with the data for the dpmSe system (Table 1) the species is identified as $(\eta^1\text{-dpmSe})Pt(\eta^1\text{-xan})(\eta^2\text{-xan})$.

Reactions with apeSe and apeS

After mixing equimolar quantities of Pt(xan)$_2$ and apeSe at $-30\,°C$ the ^{31}P NMR spectrum is a singlet with ^{77}Se satellites whose resonance position and coupling constant are similar to those of apeSe itself. This spectrum indicates that selenium is not coordinated to platinum and this is confirmed by the ^{77}Se NMR spectrum which is a doublet, also closely resembling that of apeSe. The ^{195}Pt NMR spectrum indicates however that reaction has actually occurred; it consists of a singlet at a quite different chemical shift to that of Pt(xan)$_2$. The chemical shift is similar to that of $(\eta^1\text{-dpmSe})Pt(\eta^1\text{-xan})(\eta^2\text{-xan})$ and is therefore assigned to $(\eta^1\text{-apeSe})Pt(\eta^1\text{-xan})(\eta^2\text{-xan})$ with apeSe being coordinated through arsenic. The results with apeS are entirely analogous.

Discussion

This work confirms the order of ligand strengths for the Group 15 and mixed Group 15/Group 16 donor ligands previously seen in studies with Pt(S$_2$P{OEt}$_2$)$_2$, Pt(dtp)$_2$ [8] and Pt(S$_2$CNEt$_2$)$_2$, Pt(dtc)$_2$ [9]. That is, dpe is the strongest ligand and is always chelated; ape, dpm, dpmSe and dpmS can coordinate in both bidentate and monodentate modes and apeSe and apeS are usually monodentate.

The behaviours of Pt(dtc)$_2$ and Pt(dtp)$_2$ with these ligands were rather different to each other, but that of Pt(xan)$_2$ has some similarities to both. Thus, except for dpe, none of the ligands can displace both xanthate ligands from platinum. In this way Pt(xan)$_2$ resembles Pt(dtc)$_2$ whereas several of these ligands can displace both dithiophosphate groups from Pt(dtp)$_2$. On the other hand, the dealkylation of xanthate to form the dithiocarbonate ligand closely resembles the dealkylation of coordinated dithiophosphate. A number of ligand combinations in this series provide examples of interesting equilibria resulting from competition for the four coordination sites at platinum by more than four potential donors of comparable ligand strengths.

Experimental

Pt(xan)$_2$ was prepared by the interaction of aqueous solutions of K$_2$PtCl$_4$ and Na[S$_2$CO^{n}Pr]. The resulting bright yellow precipitate was filtered, washed with water and dried at the pump. The ligands dpe, dpm and ape (Strem) were used as received whilst dpmE and apeE ligands were prepared as described previously [8].

Dithiocarbonate complexes were prepared by mixing Pt(xan)$_2$ and the appropriate molar quantity of the Group 15 ligand in dichloromethane and stirring the solution at room temperature for 24 h. The solution was concentrated and addition of n-hexane precipitated the product. Analytical data are given in Table 2 and analyses were performed by Chemical and Microanalytical Services P/L (CMAS), Melbourne.

Most reactions were initially studied *in situ* in the NMR tube. Many of the products were subsequently isolated and characterised by analytical and infrared techniques. In all cases the NMR spectra of the isolated products were the same as those generated directly. NMR spectra were recorded using a JEOL FX 100 spectrometer, ^{31}P at 40.32 MHz, ^{77}Se at 18.99 MHz and ^{195}Pt at 21.32 MHz. External references were 85% H$_3$PO$_4$, 1 M H$_2$PtCl$_6$ in conc. HCl and 1 M H$_2$SeO$_3$ in water, respectively; high frequency positive convention is used for chemical shifts. Infrared spectra were recorded using a JASCO A-302 instrument.

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