SOME TRANSITION METAL COMPLEXES OF SECONDARY PHOSPHINE CHALCOGENIDES

by

DAVID M. ANDERSON

Thesis presented for the Degree of
Doctor of Philosophy
University of Edinburgh
1982

DEDICATED TO

MY

MOTHER AND FATHER

Acknowledgements

My sincere thanks go to my two supervisors, Professor E.A.V. Ebsworth and Dr. T.A. Stephenson. In particular, I am grateful to Dr. Stephenson for his boundless enthusiasm and encouragement. I am also indebted to the Science and Engineering Research Council for financial assistance for the duration of this work. I would also like to thank all the members of the Chemistry Department who have assisted me by obtaining spectral and analytical data. I would especially like to thank Dr. Malcolm Walkinshaw for solving the X-ray crystal structures reported in this thesis.

Finally, I am deeply indebted to Mrs. M. Manson for typing this thesis.

Declaration

I declare that, except where otherwise stated, this thesis was composed by myself and that the work was conducted by myself from October 1979 until September 1982.

Certain of the results reported in Chapter 2 have already been published.

ABSTRACT

Chapter 1 Transition metal chemistry of secondary phosphine chalcogenides is discussed.

Chapter 2 The reactions of $Ph_2P(E)H$ (E = O, S, Se) with palladium(II) and platinum(II) dithio-acid compounds ($S_2CNR_2^-$, $S_2PR_2^-$; S_2CPh^-) are described and the products are characterised. The X-ray crystal structures of $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ and $[Pt(S_2CN^iPr_2)(Ph_2PS)]_2$ are presented. A scheme linking the various products is presented.

Chapter 3 The reactions of $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ with a variety of transition metal compounds are discussed. The compounds of the type $[Pt(S_2CNR_2)(Ph_2PS)_2]Pt(S_2CNR_2)$ have been isolated and the crystal structure of $[Pt(S_2CN^iPr_2)(Ph_2PS)_2]Pt(S_2CNEt_2)$ has been solved. Further complexes have been formed by the reaction of $[Pt(S_2CNR_2)(Ph_2PS)_2]^-$ with $M\text{-}Cl_2(L\text{-}L)$complexes, M = Pt, Pd. The novel complex Ru([illegible]η-$Ph_2PS)_2(PMe_2Ph)_2$ is described.

Chapter 4 A series of 1st row transition metal complexes, $M[Pt(S_2CNR_2)(Ph_2PS)_2]$ has been formed, and a variety of techniques, for example e.s.r. magnetic studies and visible spectroscopy, has been used to obtain structural information. The complexes $Pd[Pt(S_2CNR_2)(Ph_2PS)_2]$ are also discussed. A two stage reaction resulting in the eventual formation of $In[Pt(S_2CNEt_2)(Ph_2PS)_2]_3$ is reported.

Chapter 5 A variety of reactions are discussed. The reactions of $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ with HX (X = BF_4, Cl, Br, I) and with MeI have been investigated. $Pt(S_2CN^iPr_2)(Ph_2POMe)(Ph_2PS)$ reacts with MeI to form a mixture of products in solution. Some reactions of $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ with $F_2P(Se)H$ and H_2Se are also discussed.

Chapter 6 The reactions of $F_2P(E)H$ (E = O, S, Se) with $M(S\frown S)_2$ are briefly examined.

CONTENTS

Chapter 3 Some Reactions with Metal Complexes (1)

Chapter 4 Reactions with Metal Complexes (2)

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

Some Earlier Studies on the Coordination of Secondary Phosphine Chalcogenides

1.1 Introduction

Over the past ten to fifteen years the reactions of disubstituted phosphinous acids ($R_2P(O)H$) and esters (R_2POR') (and the analogous secondary phosphites ($(RO)_2P(O)H$; $(RO)_2POR'$)) with transition metal ions have been investigated and a recent review of some of the complexes formed has been published by Roundhill *et al*[1]. It is of some relevance to discuss a number of these reactions here, since it is of considerable interest to compare the reactions of the three diphenylphosphine chalcogenides, $Ph_2P(E)H$ (E = O, S, Se). All three compounds have been known for some years and their synthesis is comparatively straightforward[2,3,4] but reactions of the sulphide and selenide with transition metal ions have been little studied until the last few years.

Therefore this work was carried out, in part, to remedy this deficiency and, in part, to compare their chemistry with that of $Ph_2P(O)H$. The aim of this chapter is to describe some of the phosphine oxide reactions and to review the relatively small amount of work, to date, on transition metal phosphine sulphides and selenides.

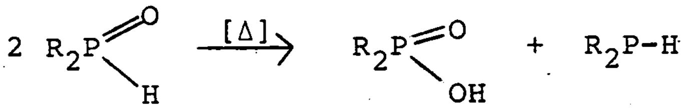
1.2 Diphenylphosphine Chalcogenides

The compounds $Ph_2P(E)H$ are all white solids of varying stability in air. A number of synthetic routes are now available, and their organic chemistry has been reviewed by Hamilton and Landis[2].

1.2.1 Diphenylphosphine Oxide

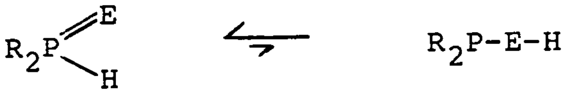
The hydrolysis of diphenylphosphinous chloride in inert solvents (diethylether or carbon tetrachloride) can be used as a route towards the isolation of $Ph_2P(O)H$ but in situ hydrolysis, in an alcohol solution, is frequently used to generate typical diphenylphosphinito complexes[5]. Passing dry air through a solution of diphenylphosphine will also yield the oxide, in high purity[6]. Our experimentally observed physical data are tabulated (Table 1.1) and these show good agreement with literature values[2].

The i.r. spectrum of diphenylphosphine oxide has been studied and interpreted as indicating a phosphorus(V) [illegible] species[2]. Thus, characteristic ν_{PH} and ν_{PO} stretching vibrations are observed. Nuclear magnetic resonance studies, in a variety of solvents, confirm this, since at ambient and low temperatures, the $^{31}P-\{^1H\}$ n.m.r. spectra consist of a singlet which splits into a large doublet ($^1J_{PH}$ 481.0 Hz) when the proton coupling is retained, indicating a directly bound proton. The ^{31}P n.m.r. chemical shift, at 21.5 p.p.m. (to high frequency, with respect to 85% H_3PO_4) is also indicative of phosphorus(V), since trivalent phosphorus acid esters resonate at higher frequencies (cf. Ph_2POMe, $\delta P = 115.6$ p.p.m.). On strong heating, most phosphine oxides will usually disproportionate to give a phosphinic acid and a secondary phosphine (Eqn. (1)):-



...(1)

Further reactions can be postulated which involve the intermediacy of an enolic phosphinous (P(III)) acid (Eqn. (2)):-



$$R_2P(=E)H \leftrightharpoons R_2P\text{-}E\text{-}H$$

...(2)

For example the slow formation of $R_2P\text{-}O\text{-}Ag$, by direct reaction of $AgNO_3$ with $R_2P(O)H$,[7] and the rapid hydrogen-deuterium exchange observed in CH_3OD solution[8] are cited as good evidence for P(III) intermediates. Spectroscopically however, the tautomer is unobservable but it can be stabilised on coordination (see later).

1.2.2 Diphenylphosphine Sulphide and Selenide

Convenient high yield synthesis of these two compounds is achieved by the careful addition of stoichiometric amounts of elemental sulphur or selenium to degassed diethylether or carbon tetrachloride solutions of diphenylphosphine under an inert atmosphere[4]. As with the oxide, both compounds exist in the P(V) form rather than the enolic P(III) form. They are less well characterised than the oxides and much less is known about their chemistry, although their physical properties have been investigated[2] (Table 1.1). Although ν_{PS} and ν_{PSe} stretching vibrations are readily assigned in the i.r. spectra of the free ligands, on complexation these bands occur below 600 cm^{-1} in regions where a number of other vibrations, such as ν_{MS}, ν_{MP} or $\nu_{M\ Halogen}$, are generally observed. Hence assignment of ν_{PE} is often difficult because of the number and the extensive coupling of vibration modes. Nuclear magnetic resonance evidence again supports the P(V) thiono and seleno forms, both in chemical shift (e.g. from ^{31}P n.m.r. studies, E = S δ = 22.8 p.p.m. and E = Se δ = 6.2 p.p.m.), and in the observation of large $^{1}J_{PH}$ (see Table 1.1). In addition, the size of $^{1}J_{PSe}$, an empirical indication of the bond order between the coupling nuclei, suggests a double bond is present.

Diphenylphosphine selenide is the least stable of the three chalcogenides and over a period of weeks in air will decompose with the liberation of elemental selenium.

The stability of $Ph_2P(S)H$, under reflux in alcohols, has also been investigated. In the absence of any metal complex, refluxing the pure sulphide in degassed dry methanol will produce no significant decomposition until a trace of H_2O is added upon which the presence of $Ph_2P(O)H$ and other, as yet unidentified species, can be inferred from ^{31}P n.m.r. studies. It is of particular interest to this work to note that diphenyldithiophosphinic acid ($Ph_2P(S)SH$; δP 55.7 p.p.m.), diphenylphosphine (Ph_2PH, δP -41.0 p.p.m.) or methyldiphenylphosphinite (Ph_2POMe, δP 115.6 p.p.m.) are <u>not</u> observed. However, when a metal compound is present, new complexes containing such ligands have been generated from $Ph_2P(S)H$ (see Chapter 2).

1.3 Coordination of Secondary Phosphine Chalcogenides

1.3.1 The Coordination of Diorganophosphinite and Diorganophosphinous Acid Ligands

A number of modes of coordination have been observed for diorganophosphine oxides (See Fig. 1.1). Two main factors contribute to this:- i) the presence of a tautomeric (enolic) phosphinous acid form which can coordinate *via* the phosphorus lone pair (A), similar to the bonding in a tertiary phosphine, or *via* the oxygen (B) on proton loss; ii) in the presence of a base, the anionic R_2PO^- moiety has been observed to coordinate *via* oxygen (B) or phosphorus (C). This ambidentate behaviour is further illustrated by the occurrence of a number of bridging R_2PO^- complexes, that is; bonding through phosphorus and oxygen to two different metals (D). The $R_2P(O)H$ ligand can also oxidatively add to metal centres (E). Finally, coordination of $R_2P(O)H$ *via* oxygen has also been observed

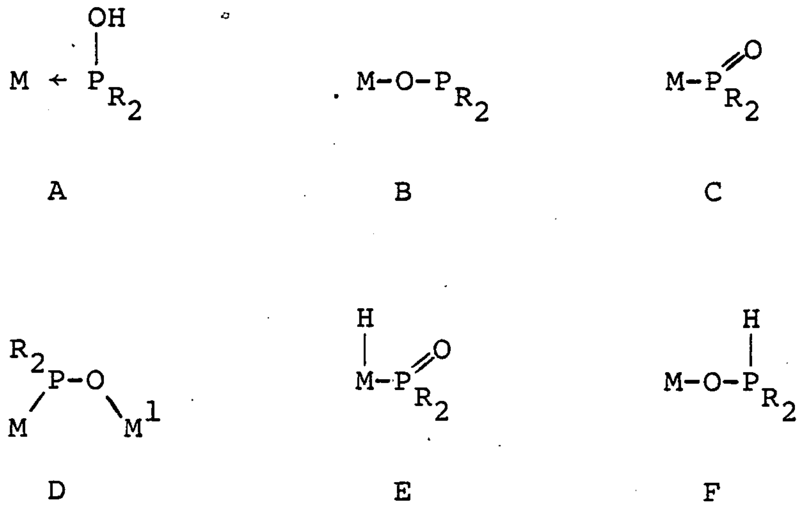


Fig. 1.1 Coordination Modes of Secondary Phosphine Oxides, $R_2P(O)H$ (R = akyl, aryl)

(F) but the resulting unstable complexes will rearrange to a coordinated phosphinous acid, P bonded (i.e. A), under mild conditions. The formation of a coordinated phosphinito ligand has also been observed by nucleophilic attack on a coordinated phosphinite[9] or halophosphine[10] ligand. It is a general observation that coordination of organophosphinites will increase the rate of hydrolysis of such ligands.

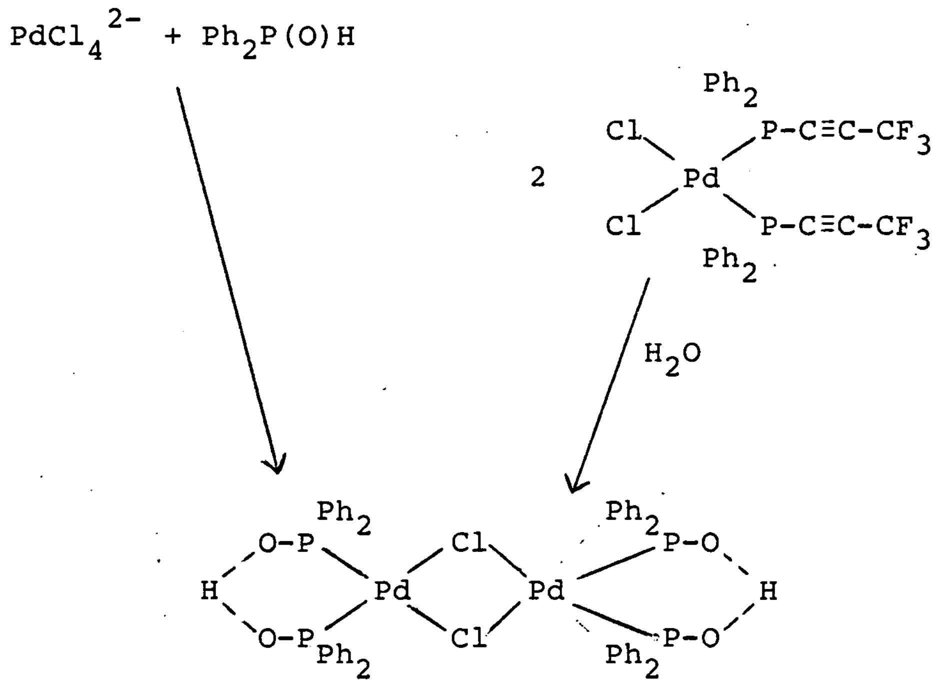
Complexes containing specifically Ph_2PO^- or $Ph_2P(OH)$ ligands are quite diverse and encompass a number of transition and main group elements. The coordination of $Ph_2P(OH)$ is characterised in the i.r. spectra by the presence of a terminal ν_{P-OH} stretching vibration at *ca*. 880 cm^{-1} and a ν_{PO-H} band at *ca*. 3100-3300 cm^{-1}. The n.m.r. evidence is less clear but often shows δH at 5-10 p.p.m. The signal is often broad with little resolved phosphorus coupling and the position of the resonance is both concentration and temperature dependent, due to intermolecular hydrogen bonding or solvent interaction.

A coordinated terminal phosphinito group is characterised by a strong i.r. band at *ca*. 1100 cm^{-1}, assigned to ν_{PO}. In the ^{31}P n.m.r. spectra of complexes containing this anion the phosphorus of the anion resonates at higher frequency than $Ph_2\underline{P}(O)H$ but at a much lower frequency than a coordinated phosphinite or $Ph_2\underline{P}(OH)$ resonance. Note however that the chemical shift is very dependent on both the other ligands present and the metal examined. Another useful guide, where appropriate, to the mode of coordination is the size of J_{MP}. For bridging

R_2PO^- groups an i.r. band is found at ca. 1010 cm^{-1} but data on phosphorus chemical shifts is lacking.

1.3.2 Transition Metal Complexes of the Heteronuclear Chelate $R_2P\text{-}O\text{--}H\text{--}O\text{-}PR_2$

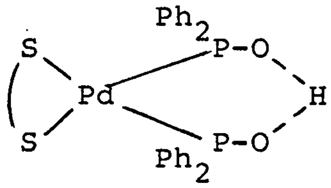
Complexes containing this basic ring form have been isolated in the case of most of the platinum group metals and for a number of first row and other second row transition metals. Several X-ray crystal structures now exist to confirm the assignments made initially on the basis of spectroscopic data and various synthetic routes to these compounds have been developed. For example, hydrolysis of coordinated ligands such as halophosphines or phosphinites produce this arrangement when a cis orientation of these ligands is present. Direct reaction of a transition metal complex with diphenylphosphine oxide will also produce the same structure. Further, ligand displacement or reaction of complexes already containing the ring has been demonstrated. For example, the $PdCl_4^{2-}$ ion will react with diphenylphosphine oxide to give $[PdCl\{(Ph_2PO)_2H\}]_2$ (1) which has been formulated as a chloride bridged dimer[11]. The i.r. stretching frequency assigned to ν_{PO} is 1040 cm^{-1} and to ν_{PdCl} is 265 cm^{-1}. The same complex(1) is produced when $PdCl_2(Ph_2PC{\equiv}CCF_3)_2$ is hydrolysed in alcoholic solvents[12] (Eqn. (3)):-



...(3)

(1)

The crystal structure of the thiocyanate derivative of (1) shows a very short O---O distance (2.42 Å) similar to that observed by Stephenson <u>et al</u>[9] in $Pd(S_2PMe_2)\{(Ph_2PO)_2H\}$(2) (2.41 Å). A wide range of compounds of this type

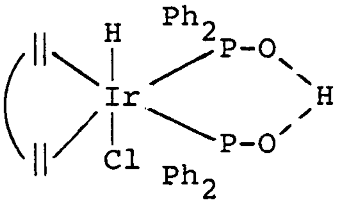


(2)

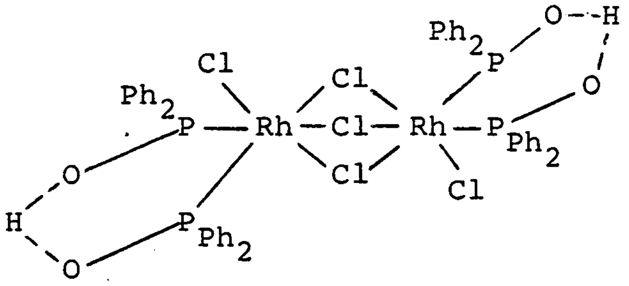
can be made by direct reaction of $M(S\frown S)_2$ (M = Pt, Pd; $(S\frown S)^-$ = $S_2CNR_2^-$, $S_2PR_2^-$, S_2COR^-) with Ph_2POMe in wet solvents or by direct treatment of compound (1) with the anions $(S\frown S)^-$. Monomeric complexes (e.g. $PdCl(PEt_3)\{(Ph_2PO)_2H\}$) containing this ring could also be generated by treating compound (1) with tertiary phosphines. In contrast, reaction of the $\text{PtCl}_4{}^{2-}$ ion gives only the monomer $\text{PtCl}\{(\text{Ph}_2\text{PO})_2\text{H}\}(\text{Ph}_2\text{POH})$[11] although treatment of this with base yields the binuclear $[\text{Pt}\{(\text{Ph}_2\text{PO})_2\text{H}\}(\text{Ph}_2\text{PO})]_2$, which contains bridging Ph_2PO^- groups. Treatment of the palladium complex (1) with base gives the polynuclear complex $[\text{Pd}(\text{Ph}_2\text{PO})_2]_n$.

Troitskoya[13] and Pidcock and Waterhouse[14] have investigated the synthesis and reactions of similar complexes with phosphinato ($(\text{RO})_2\text{PO}^-$) ligands and in the light of the above results their data are consistent with the presence of a ring structure rather than the discrete <u>cis</u>-$(\text{Ph}_2\text{PO}^-)|(\text{Ph}_2\text{POH})$ arrangement they initially described.

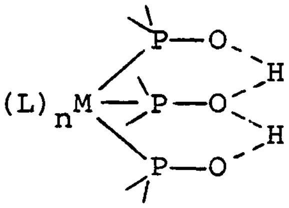
Kraihanzel[10a] has also shown that in the presence of a base, hydrolysis of <u>cis</u>-$\text{Mo(CO)}_4(\text{Ph}_2\text{PCl})_2$ will yield Et_3NH[<u>cis</u>-$\text{Mo(CO)}_4\{(\text{Ph}_2\text{PO})_2\text{H}\}$] whereas direct reaction of nickelocene and dimethylphosphinate yields $\text{Ni}(\eta\text{-C}_5\text{H}_5)\{((\text{MeO})_2\text{PO})_2\text{H}\}$[15]. Very recently the compounds (3) and (4) have been isolated by treating $[\text{IrCl(COD)}]_2$ and $[\text{RhCl(COD)}]_2$ (COD = cycloocta-1,5-diene) with prehydrolysed Ph_2PCl solutions[16]. The cyclooctadiene ligand in the iridium species (3) can then be readily substituted by a variety of bidentate donor ligands such as $\text{Ph}_2\text{E}(\text{CH}_2)_2\text{EPh}_2$ (E = P, As).



(3)



(4)



(5)

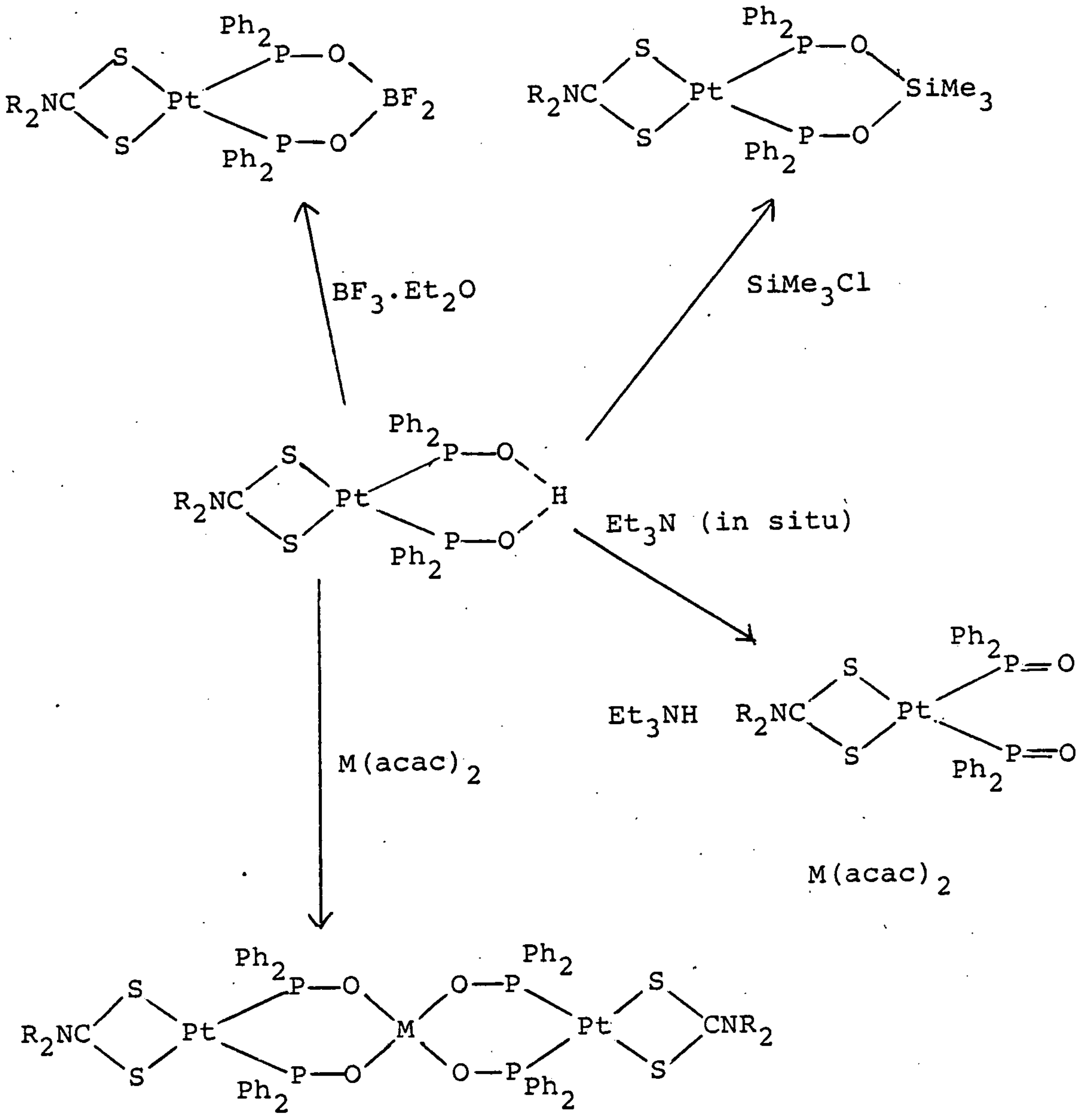
Finally, the unusual tridentate chelating arrangement (5) has been produced in a number of ruthenium complexes such as $(Ph_2POMe)_2(Ph_2POH)RuCl_3Ru\{(Ph_2PO)_3H_2\}$[17] and $Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}$[18] and in the cobalt complex $Co(\eta\text{-}C_5H_5)\{(Ph_2PO)_3H_2\}$.[21]

Assignment of the ν_{PO-H} stretching vibrations in the infrared spectra of these complexes has proved very difficult since frequencies for symmetrical hydrogen bonds are observed below 2000 cm^{-1},[20] a region frequently obscured by other bands. This has led to the tentative assignments of broad resonances in the range 1200-1600 cm^{-1} to the $\nu_{(POHOP)}$ band and further broad absorptions at 700-800 cm^{-1} to ring deformation modes[11]. The observation that deprotonation, or ring capping by ions other than protons, leads to the disappearance of these bands supports these proposals. Bands within the range 970-1040 cm^{-1} can be assigned to ν_{PO} stretching vibrations. The $^{31}P-\{^{1}H\}$ n.m.r. of many of these complexes, such as (2) and (3), shows a single phosphorus resonance at all temperatures. In the ^{1}H n.m.r. a broad resonance at high frequency has been assigned to the acidic proton (see chapter 2).

Compounds containing these chelate rings show a number of characteristic reactions. These are best illustrated by considering the reactions of the complex $Pt(S_2CNR_2)\{(Ph_2PO)_2H\}$ as shown in Fig. 1.2 . Of particular interest are the syntheses of the bridging R_2PO^-, mixed metal complexes (6). The possibility of the preparation of such complexes and the recognition that the open ring structure might act as a bidentate chelating ligand (a psuedo acetylacetonate) was realised at the outset of the investigation of these compounds[21,19,15]. These studies have now been extended to related complexes containing sulphur and/or oxygen and are fully reported in subsequent chapters.

1.3.3 Coordination Chemistry of Secondary Phosphine Sulphides and Selenides

Despite the interest shown in the coordination chemistry of phosphinite and phosphinous acid ligands, and the availability of a wide variety of stable secondary phosphine sulphides and selenides, the first report of a transition metal complex involving such ligands did not appear until the early seventies. Since then a number of areas have been investigated.



(6)

(M = VO, Ni, Co, Pd, etc.)

Fig. 1.2 Some Reactions of the Compound $Pt(S_2CNR_2)\{(Ph_2PO)_2H\}$

Unlike disubstituted phosphinites, studies[9] involving the coordination of $R_2P(SR')$, $R' = $ n-Bu, towards group VIII dithio-acid complexes have proven ambiguous[22]. The principle stumbling block was believed to be a facile Michaelis-Arbuznov rearrangement to the corresponding tertiary phosphine sulphides which are inert towards $M(S\frown S)_2$ compounds.

Lindner et al have however systematically studied the reactions of secondary phosphine sulphides with carbonyl complexes of zerovalent group VIa metals and with monovalent group VIIa halide carbonyl compounds[12,23] and have successfully produced coordinated thiophosphinite complexes. Those dialkyl- and diarylphosphine sulphides were observed to coordinate in two ways. At low or ambient temperature the displacement of a weakly coordinated solvent molecule from the group VIa $M(CO)_5L$ complexes to give an S-bonded adduct is observed (Eqn. (4)):-

$$M(CO)_5L + R_2P(S)H \rightarrow \underset{(7)}{M(CO)_5(SP(H)R_2)} + L$$

$$\left(\begin{array}{l} M = Cr;\ L = CH_3CN; \quad R = CH_3,\ C_2H_5 \\ M = Mo;\ L = THF \end{array}\right) \qquad \ldots(4)$$

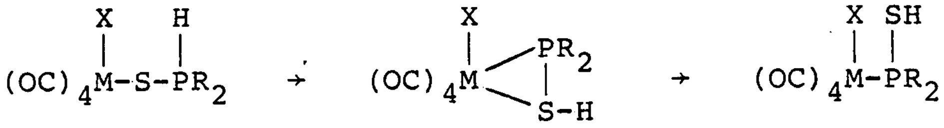
M-S and P-H bonds were clearly indicated by spectroscopic studies since the i.r. spectra showed that ν_{MS} (ca. 330 cm^{-1}), ν_{PS} (ca. 490 cm^{-1}) and ν_{PH} (ca. 2370 cm^{-1}) were present and the ^1H n.m.r. revealed a large $^1J_{PH}$ of around 400-500 Hz. Analogous complexes were formed by the group VIIa $MX(CO)_5$ compounds at higher temperatures (Eqn. (5)):-

$$MnX(CO)_5 + Me_2P(S)H \xrightarrow[\Delta(T^oC)]{} MX(CO)_4(SP(H)Me_2) + CO$$

(X = Cl; T = 40°C)

(X = Br; T = 50°C) ...(5)

On raising the temperature both types of complex were observed to isomerise to the corresponding P-bonded thiophosphinous acid complexes (8) (Eqn. (6)) which also contain a terminal SH group.



(8)

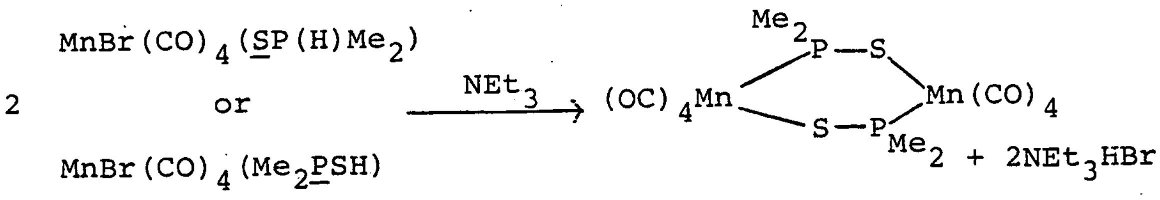
(R = Me M = Mn; X = Cl,Br

M = Cr, Mo; X = CO). ...(6)

This has been confirmed by spectroscopic studies since ν_{SH} (ca. 2500 cm^{-1}) was observed in the i.r. spectra and in the ^1H n.m.r. spectra the loss of the $^1J_{PH}$ doublet, the change in the chemical shift of the proton (from δ7.0 p.p.m. to δ3.7 p.p.m.) and the appearance of a small (ca. 4.5 Hz) $^2J_{PSH}$ coupling are consistent with the proposed intramolecular rearrangement. It is also of interest to note that sideways bonded $R_2P(S)H$ intermediates were postulated.

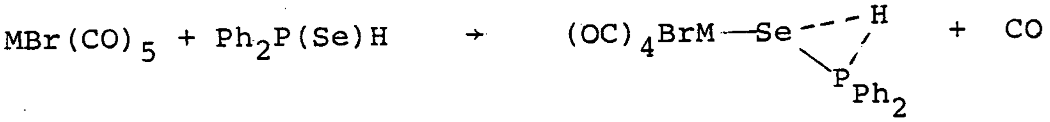
The X-ray crystal structure of the complex $Cr(CO)_5(Me_2PSH)$ has been determined. This showed a psuedo-octahedrally coordinated chromium ion with a P-Cr bond of 2.34 Å, a P-S bond 2.02 Å and a <SPCr angle

of 114°. In addition to S-methylation by CH_2N_2, to give a R_2PSMe complex, compounds (7) and (8) were deprotonated on treatment with a base such as triethylamine, or by sodium metal. The resulting anionic group VIa complexes remained stable, but those containing manganese underwent facile dimerisation to form a complex containing a heteronuclear six membered ring (Eqn. (7):-



...(7)

Further papers have been published in relation to rhenium and tungsten compounds and it has been shown that $R_2P(O)H$ undergoes a similar series of reactions. The same authors have also examined the reactions of $Ph_2P(Se)H$ with $MBr(CO)_5$, (M = Mn, Re) and suggested that the product was the Se bonded species (9) in which the proton is tautomerically linked between the Se and P atoms (Eqn. (8)):-



...(8)

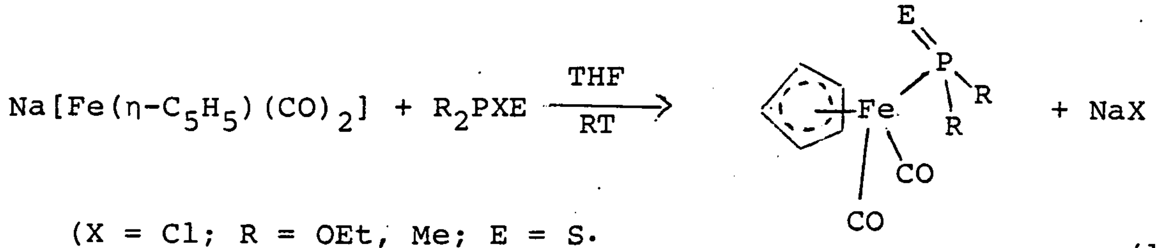
In comparison with the case where oxygen and sulphur were directly coordinated (compound (7)) rearrangement to the P-coordinated form, on heating in heptane solution, now occurs with the loss of Se, as H_2Se (Eqn. (9)):-

$$MBr(CO)_4(Se(H)PPh_2) \xrightarrow[\Delta]{} MBr(CO)_4(Ph_2PH) \quad ...(9)$$

This secondary phosphine complex has also been generated by direct reaction of Ph_2PH with $MBr(CO)_5$.[24] The absence of ν_{MSe} and ν_{PSe} vibrations is confirmed by examination of the i.r. spectra and in the ^{31}P n.m.r. spectra the change in chemical shift, the loss of $^1J_{PSe}$ and the observation of a large $^1J_{PH}$ value on thermolysis of compound (9) confirm the assignment.

Other work[25] has shown that R_2PS^- and R_2PSe^- complexes can be generated by the action of elemental chalcogenides on the iron complex $Fe(\eta-C_5H_5)(CO)_2((CF_3)_2P)$. The sulphuration and selenation occurs under milder conditions than those required for addition to main group phosphides, probably as a result of the polarisation of the M-P σ bond towards phosphorus, and additional build up of charge on the phosphorus through π-bonding. Irradiation of these $(CF_3)_2PE^-$ complexes gave complex mixtures from which could be isolated and characterised, in the case of S and Se, the isomeric E-bonded analogues. Spectroscopically, this process can be monitored by the loss of $^3J_{\underline{P}MC\underline{H}}$ in the ^1H n.m.r. spectrum and by the changes in i.r. band positions.

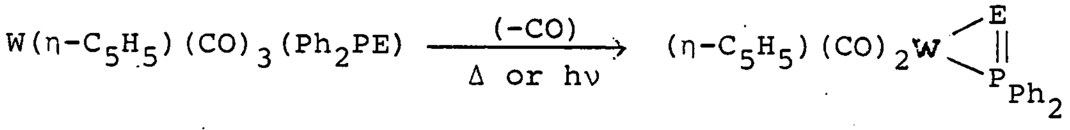
A wider range of such complexes has been synthesised by Piraino and Faraone[26] by direct reaction of $Na[Fe(\eta-C_5H_5)(CO)_2]$ with various R_2PXE compounds (Eqn. (10)):-



(X = Cl; R = OEt, Me; E = S.
X = Br; R = Ph; E = Se)

...(10)

Spectroscopic analysis again suggested P-bonded structures are initially generated. Further complexes can be prepared by CO-substitution with tertiary phosphines, such as PPh_3 and PMe_2Ph, and the sulphur or selenium atom can be readily methylated to form the cationic $Fe(\eta-C_5H_5)(CO)_2(R_2PEMe)^+$ complexes. Similar molybdenum and tungsten complexes $(M(\eta-C_5H_5)(CO)_3(Ph_2PE))$ have been prepared by Malisch et al[27], by treatment of $M(\eta C_5H_5)(OC)_3(Ph_2P)$ with sulphur or selenium. In this instance $^{183}W-^{31}P$ coupling is observed, in the range expected for a one-bond coupling, and the ^{31}P n.m.r. chemical shifts correlate with those found in other samples. On heating or photolysing the tungsten compounds, the ligand coordination can be changed to η^2-Ph_2PS or η^2-Ph_2PSe, i.e. producing stable examples of "side-on" coordinated P = E moieties (Eqn. (11):-



$$W(\eta-C_5H_5)(CO)_3(Ph_2PE) \xrightarrow[\Delta \text{ or } h\nu]{(-CO)} (\eta-C_5H_5)(CO)_2W\overset{E}{\underset{PPh_2}{\|}}$$

...(11)

Another synthetic route to η^2-R_2PS complexes is shown in Eqns.(12) and (13)[28]:-

$$MCl(\eta\text{-}C_5H_5)(CO)_3 + Ph_2P(S)H \xrightarrow[C_6H_6|\Delta]{Et_3N} M(\eta C_5H_5)(CO)_2(\eta^2\text{-}Ph_2PS)$$

...(12)

$$MCl_2(CO)_3(PPh_3)_2 + Ph_2P(S)H \xrightarrow[C_6H_6]{Et_3N} M(CO)_2PPh_3(\eta^2\text{-}Ph_2PS)_2$$

...(13)

Phosphorus-31 n.m.r., molecular weight and infrared studies agree with these assignments and the X-ray crystal structure analysis of the complex $M(CO)_2PPh_3(\eta^2\text{-}Ph_2PS)_2$ has been determined. The complex is a seven-coordinate, psuedo-pentagonal bi-pyramid with an almost planar arrangement of phosphorus and sulphur atoms. The PS bond distances (2.015 Å) are closer to those found in known PS double bond systems (ca. 1.95 Å) than in PS single bonds (*ca*. 2.20 Å). The carbonyl groups occupy the axial positions and the triphenylphosphine is *cis* to both sulphur atoms.

During investigations of the reactions of coordinated halophosphine ligands, Kraihanzel *et al*[29,10a] have also prepared a number of thio- and seleno-phosphinito complexes. For example, $Mo(CO)_5(R_2PCl)$ and *cis*-$Mo(CO)_4(Ph_2PCl)_2$ readily react with a variety of nucleophiles to yield $Mo(CO)_5(R_2PX)$ and *cis*-$Mo(CO)_4(R_2PX)_2$ complexes. Thus when the complexes are treated with H_2S or ethane thiol, in the presence of triethylamine, the expected products are obtained (Eqns. (14) and (15)):-

$$Mo(CO)_5(R_2PCl) + R'SH + Et_3N \longrightarrow Mo(CO)_5(R_2PSR') + Et_3NHCl$$

(R = Me, Ph   R´ = Et)

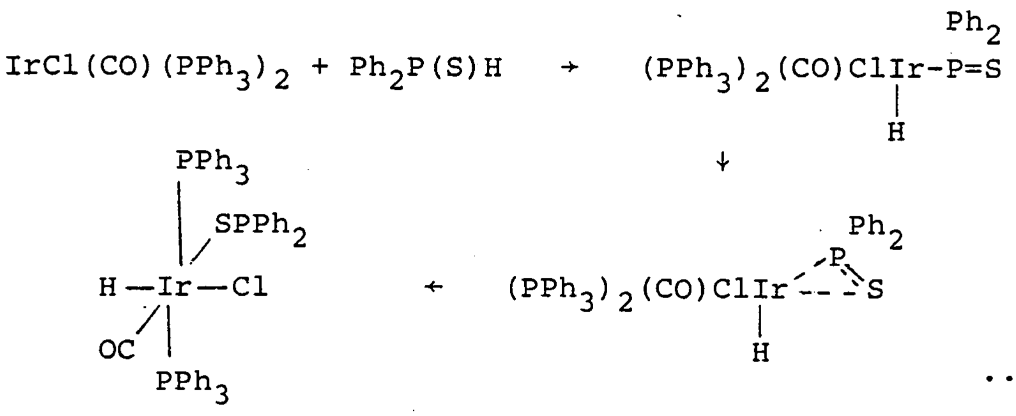
(R = Ph   R´ = H) ...(14)

$$\underline{cis}\text{-}Mo(CO)_4(Ph_2PCl)_2 + 2HSEt \xrightarrow{NEt_3} \underset{(10)}{Mo(CO)_4(Ph_2PSEt)_2} + 2Et_3NHCl$$

...(15)

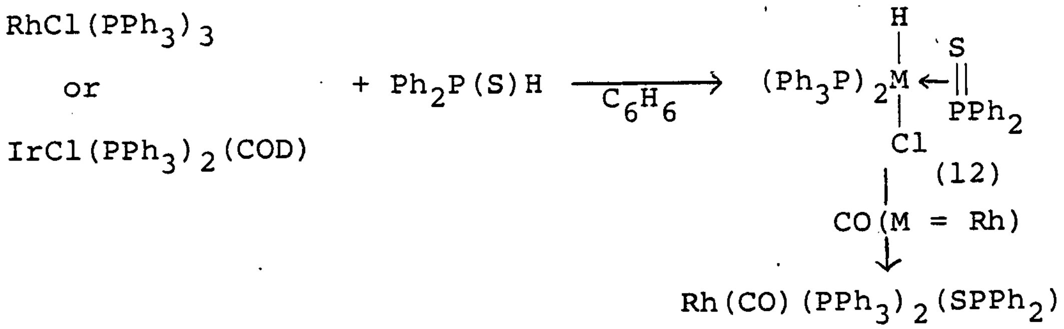
The latter compound (10) appears to be the only complex with two cis-R_2PSR ligands and although the authors prepared >P-OHO-P< systems and examined their reactions no mention is made in their papers of related >P-SHS-P< moieties which in principle could be prepared by reaction of H_2S with the cis-halophosphine molybdenum complex.

Diphenylphosphinesulphide will react in a single step with $IrCl(CO)(PPh_3)_2$ in benzene at room temperature to produce the S-bonded Ir(III) oxidative addition product, $IrClH(CO)(PPh_3)_2(SPPh_2)$[30]. Infra-red and ^{31}P n.m.r. studies were used to determine the configuration of the ligands and to show that the hydride and sulphur atoms were cis-orientated. An intramolecular rearrangement of an initially P-bonded adduct is proposed to explain the configuration of the final product (Eqn. (16)):-



...(16)

A similar reaction with $RhCl(CO)(PPh_3)_2$ gave a mixture of starting material and a species believed to be the S-bonded complex $Rh(CO)(PPh_3)_2(SPPh_2)$. This complex has also been isolated via another route by Thewissen[31], who confirms the end-on coordination although in most other thiophosphinito complexes prepared by the same author the coordination is almost exclusively η^2-R_2PS^-. Thus when $RhCl(PPh_3)_3$ is treated with $Ph_2P(S)R$ [R = (C(Np-tol)NH(p-tol)),(C(O)NHPh)] in the presence of a base, $Rh(PPh_3)_2(\eta^2$-$Ph_2PS)$ (11) is obtained. This complex was in fact the first reported η^2-Ph_2PS^- complex. Direct reaction of $RhCl(PPh_3)_3$ and $IrCl(PPh_3)_2(COD)$ (COD = cycloocta-1,5-diene) with $Ph_2P(S)H$ yields Rh(III) and Ir(III) monomers with trans H and Cl groups (Eqn. (17)):-

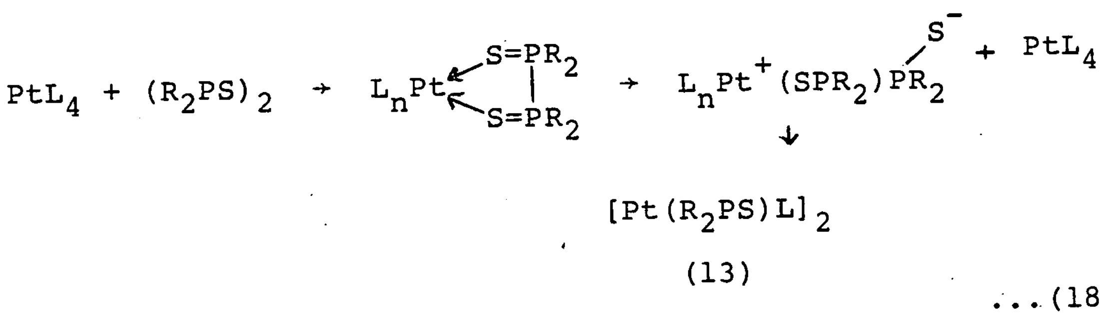


...(17)

The ^{31}P-$\{^1H\}$ n.m.r. spectra show three magnetically inequivalent phosphorus nuclei of which the S$\underline{P}$Ph$_2$ resonance occurs at highest frequency. In the Rh complexes this signal is characterised by a low value of $^1J_{(^{103}Rh-^{31}P)}$ (119 Hz (11); 82 Hz (12)) which is taken to be an effect due to the three membered ring. Both the Rh(I) complex(11) and the Rh(III) complex(12) will react with CO to give the complex Rh(CO)$(PPh_3)_2(SPPh_2)$ which was spectroscopically observed by Marsala[30].

Some reactions involving the coordination of thiophosphinito groups to group VIII metals have been examined. Whilst exploring the coordination of tetraalkylbiphosphinebisulphides $(R_2P(S)-P(S)R_2)$, which normally coordinate in a bidentate manner[32] to low valent metal complexes, Treichel _et al_[33] isolated the dinuclear platinum(I) species $[Pt(R_2PS)L]_2$(13) $(R_2 = Me_2, Et_2,$ PhMe; $L = P(OPh)_3, PPh_3, PPh_2Me)$. The X-ray crystal structure of (13), $L = P(OPh)_3$; R = Et, has been solved and shows the molecule is a dimer, the platinum atoms being linked by two bridging $(C_2H_5)_2PS^-$ ligands and a single metal-metal bond (Pt-Pt; 2.63 Å). The $(C_2H_5)_2PS^-$ groups are mutually twisted resulting in small distortions to the, essentially planar, central framework.

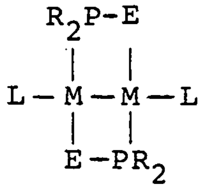
None of the expected tetraalkylbiphosphinebisulphide complexes were observed, good yields of the compounds(13) being obtained. The reaction was presumed to proceed by oxidative addition to the platinum(O) starting material, followed by ligand rearrangement and further reaction with a second molecule of starting material (Eqn. (18)):-



$$PtL_4 + (R_2PS)_2 \rightarrow L_nPt\begin{matrix} \leftarrow S{=}PR_2 \\ | \\ \leftarrow S{=}PR_2 \end{matrix} \rightarrow L_nPt^+(SPR_2)PR_2S^- + PtL_4 \rightarrow [Pt(R_2PS)L]_2\ (13)$$

...(18)

Another high yield synthesis of the same class of compounds has been recently reported by Walther et al. Treatment of benzene solutions of $M(PR_3)_4$ with secondary phosphine sulphides (or selenides) at room temperature results in the isolation of a range of products (13).

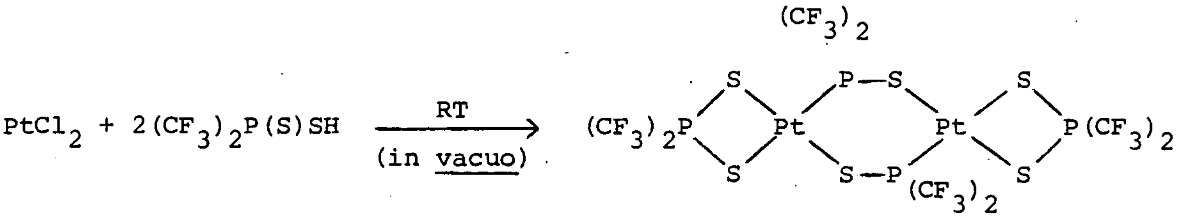


$$\begin{array}{ccc} & R_2P-E & \\ & | \quad\ | & \\ L- & M-M & -L \\ & | \quad\ | & \\ & E-PR_2 & \end{array}$$

(L = $PMePh_2$; M = Pt,Pd; R = Et,Ph; E = S)
(L = Ph_3P; M = Pt,Pd; R = MePh; E = S)
(L = Ph_3P; M = Pt,Pd; R = Ph; E = Se)

The reaction is again proposed to proceed via oxidative addition with the subsequent reductive elimination of hydrogen and concomitant dimerisation. At least one unisolated intermediate is inferred from the colour changes which accompany the reactions. The diamagnetic products are reported to be air unstable, but the usual spectroscopic measurements have been made. An ESCA study has confirmed the formal oxidation of the metal ions as (I)[35]. Infrared studies of the ν_{PS} stretching vibrations show a consistent 60 cm^{-1} (R = Ph) or 40 cm^{-1} (R = Me, Et) shift to lower wavenumber, relatively independent of M and L, which reflects their very small influence on the PS bonding. The $^{1}J\ ^{195}Pt-^{195}Pt$ coupling constants have been calculated from the second order part of the $^{31}P-\{^{1}H\}$ n.m.r. spectra (see also section 2.2.5). This parameter is known[36] to be sensitive to the ligand trans to the metal-metal bond and the values observed, from 100-465 Hz, are indeed small for directly bound platinum couplings although the remaining n.m.r. parameters are consistent with the proposed formulation.

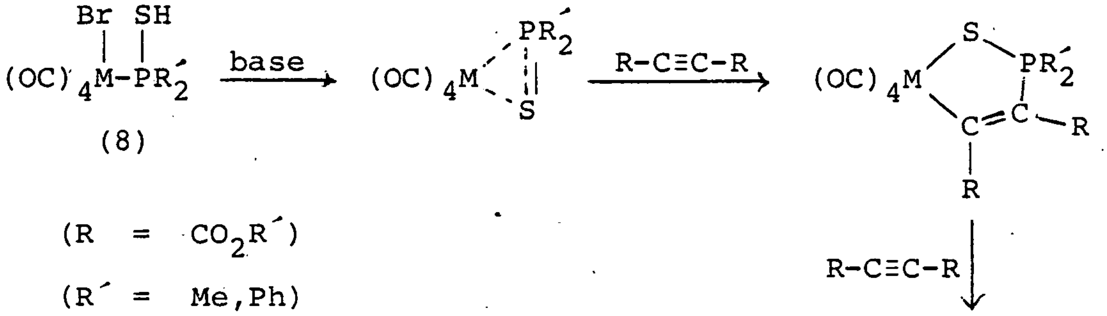
Another thiophosphinito bridged platinum dimer has been proposed by Cavell et al[37] to explain an anomolous product obtained when $PtCl_2$ was reacted with bis(trifluoromethyl)dithiophosphinic acid ($(CF_3)_2P(S)SH$). The monomeric $Pt(S_2P(CF_3)_2)_2$ complex was not obtained; instead elemental analyses, molecular weight, i.r. and ^{19}F n.m.r. evidence indicated that a platinum(II) dimer (14), with two thiophosphinito bridges, had been formed (Eqn. (19)):-



(14)

...(19)

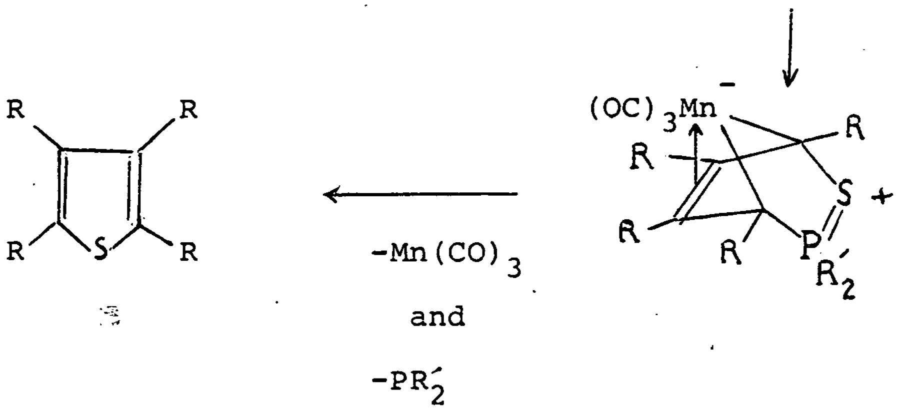
Very recently Lindner et al have significantly extended the type of reaction undergone by the ($R_2P = S$) complexes(8) originally synthesised by them. A new synthesis of organic thiophenes has been discovered via the insertion of activated acetylenes into the (P-M) bond. The same reaction is also cited as evidence for the intermediacy of "side on" bonding $R_2P = S^-$ groups in the dimerisation of $[MBr(CO)_4\ (PR'_2(SH))]$ (M = Mn, Re)[39] (Eqn. (20)):-



(8)

($R = CO_2R'$)

($R' =$ Me,Ph)

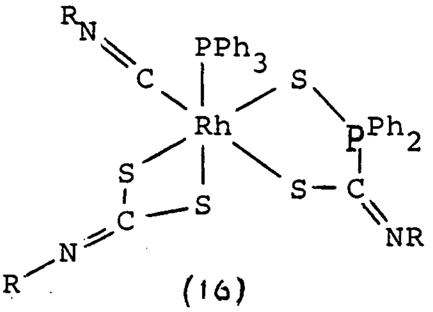


...(20)

The complex(15) (R = CO_2CH_3, R$'$ = Me) has been fully characterised by X-ray structural analysis.

The PS distance (2.04 Å) is between that expected for a single and for a double bond, and this is mirrored by the low (530 cm^{-1}) ν_{PS} stretch in the i.r. spectra and the high (δ = 74.0 p.p.m.) $^{31}P-\{^1H\}$ n.m.r. chemical shift. These values are also influenced by the positive charge on the R_2PS part of the complex. The nickel dimer, $[Ni(\eta-C_5H_5)(R_2PS)]_2$, will react in a similar fashion[39b].

Finally, the complex $Rh(PPh_3)_2(\eta-Ph_2PS)$ will react with organic derivatives to produce novel metallocycles[31]. In this case, under elevated temperatures, three molecules of phenylisothiocyanate (PhN=C=S) will react with $Rh(PPh_3)_2(\eta-Ph_2PS)$, with the elimination of triphenylphosphine, to yield complex(16). This species can also be synthesised from $Rh(PPh_3)_2[Ph_2P(S)C(S)NPh]$



(16)

The generation of organic heterocycles through the intermediacy of a transition metal complex may have considerable relevance in synthetic organic chemistry.

Table 1.1 Some Physical Characteristics (Literature values in parentheses) of Diphenylphosphine Chalcogenides

			principle i.r. bands		n.m.r. data[a]			
	mp	Mw	νP-H/ cm^{-1}	νP=E / cm^{-1}	δP/ ppm	δPH/ ppm	${}^{1}J$ PH/Hz	
$Ph_2P(O)H$	–[b] (53-55°C)	(202)	2240 (–)	1090 (–)	21.5 (25.9)	–	481 (513)	
$Ph_2P(S)H$	92-95°C (95-97°C)	(218)	2300[d] (2320)	630 (635)	22.8 (19.55)	8.12	467 (444)	
$Ph_2P(Se)H$	105-106°C (111-112°C)	(265)	2300 (2335)	540 (–)	6.2 (5.8)	–	469 (450)	${}^{1}J_{PSe}$ 757 Hz

[a] All $^{31}P-\{^{1}H\}$ and ^{1}H n.m.r. data was obtained in $CDCl_3$ at 298 K. Literature values were taken from reference 2.

[b] Reference 40.

[c] References 3 and 4.

[d] Reference 41.

CHAPTER 2

Synthesis of Platinum(II) and Palladium(II) dithio compounds with secondary phosphine chalcogenide ligands

2.1 Introduction

In Chapter One the known coordination chemistry of secondary phosphine sulphides and selenides has been extensively reviewed. It can be seen that no transition metal complexes containing the thio or seleno analogues of the chelating $R_2PO{-}{-}H{-}{-}OPR_2$ group have been obtained to date.

A major aim of the work described in this thesis has been to examine the reactions of the $Ph_2P(E)H$ ligands with square planar platinum(II) and palladium(II) complexes of mono-anionic bidentate ligands, $M(S\frown S)_2$ ($S\frown S^- = S_2CNR_2^-$, $S_2PR_2^-$, S_2CPh^-). Displacement of a single ligand should produce two free coordination sites which are mutually <u>cis</u> and hopefully should result in the formation of complexes containing $R_2PE{-}{-}H{-}{-}EPR_2$ ($E = S$, Se) and related ligands.

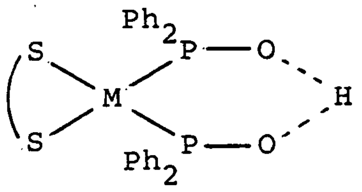
Diphenylphosphine oxide will react with various $M(S\frown S)_2$ to yield a single type of product (2). This observation follows the earlier work of Cornock and Stephenson[9] and is fully discussed in the following section. In contrast diphenylphosphine sulphide will react with palladium(II) and platinum(II) dialkyldithiocarbamates to form five distinct compounds whereas with the corresponding dithiophosphinates only one product has been observed. Similarly reaction of diphenylphosphine selenide with $M(S\frown S)_2$ gives only one metal-containing product. In general, the reactions of the palladium(II) substrates mirror those of their platinum analogues although reaction times are much shorter.

All the compounds that are described in this chapter are air stable solids. In a number of cases crystals have been obtained and their structures solved by X-ray crystallography although, despite strenuous attempts, some compounds have not been obtained in a crystalline state. In these cases elemental analyses, osmometric molecular weight determinations, i.r., multinuclear n.m.r. and mass spectroscopic studies have been used to identify and characterise the products.

Furthermore, a number of compounds either do not react or give anomalous results. For example, no reaction was observed between $Ph_2P(E)H$ and $Ni(S_2CNR_2)_2$ (R = Et, ^iPr), $Pd(S_2CN^iPr_2)_2$ and $Pt(S_2CNMe_2)_2$ (the latter is probably because of the extreme insolubility of the platinum complex). The product of reaction of $Ph_2P(S)H$ with $Pt(S_2PPh_2)_2$ differs from that obtained with other dithiophosphinates and dithiophosphates and the products which are observed in the high temperature (150-180°C) reaction of $M(S_2CNR_2)_2$ and $Pd(S_2CPh)_2$ in benzonitrile with $Ph_2P(S)H$ also differ from the more conventional products described in this chapter.

2.1.2 The Reaction of Diphenylphosphine Oxide with $M(S\frown S)_2$

Stephenson et al have examined the reaction of tertiary phosphines (PR_3)[42] and phosphinites (R_2POR')[9] with the square planar $M(S\frown S)_2$ complexes (M = Pt, Pd; $S\frown S^- = S_2CNR_2^-$, $S_2PR_2^-$, S_2COR^-, etc.). The stepwise cleavage of M-S bonds was observed finally resulting in the isolation of ionic, bisubstituted $[M(S\frown S)L_2]$ $(S\frown S)^-$ compounds. If, with L = R_2POR', the reaction solution was left for twentyfour hours a further reaction occurred. The conductivity of the methylene chloride solution decreased and the colour changed. Monomeric non-conducting products could be precipitated by adding diethylether and elemental analyses, i.r. and n.m.r. spectroscopic measurements suggested structure (2), with a hydrogen bridged heteronuclear six membered ring.



(2)

(M = Pt; S⌢S$^-$ = $S_2CNEt_2^-$, $S_2PMe_2^-$.
M = Pd; S⌢S$^-$ = $S_2CNEt_2^-$, $S_2PMe_2^-$,
$S_2PPh_2^-$).

This structure (2) is similar to that postulated by other workers[1] (see Chapter 1) and has been confirmed for [Pd(S_2PMe_2){($PPh_2O)_2H$}] by a single crystal X-ray analysis[9]. A short P-O distance is observed (1.54 Å) and a very short O----O distance (2.41 Å) which is compatible with a symmetrical hydrogen bond. Furthermore, the two Ph_2PO^- groups are symmetry related, and the plane defined by P-O-O-P is tilted with respect to the coordination plane by 26.1°. Recently the same complexes have been obtained by the direct reaction of diphenylphosphine oxide with M(S⌢S)$_2$ or by in situ hydrolysis of diphenylphosphinous chloride (PPh_2Cl) in the presence of M(S⌢S)$_2$. Thus when an excess of $Ph_2P(O)H$ is dissolved in methanol and shaken overnight with M(S⌢S)$_2$ the colour changes (e.g. for Pt complexes the solution goes from yellow to colourless) and the product, when filtered and dried, is identical to that obtained earlier. The other method, starting with an excess of PPh_2Cl in either technical methanol or methylene chloride to which a small amount of water has been added, yields the same products. Both platinum(II) dialkyldithiocarbamate and palladium(II) dithiophosphinate complexes can be synthesised by either method. It is not clear, however, whether the mechanism by which these products arise is the same as the stepwise displacement process observed by Cornock, or whether an oxidative addition-reductive elimination cycle is valid. Phosphorus-31 n.m.r. studies have shown that no intermediates in significant concentration are present during the reaction but it is known that $Ph_2P(O)H$ will slowly react through an enolic P(III) form, analogous to $R_2P(OR')$. However, the ^{31}P n.m.r. chemical shift (ca. 60 p.p.m.) of these ligands is to much lower frequency than coordinated $R_2P(OR')$ (ca. 115 p.p.m.) and only a singlet is observed in the proton decoupled spectra at all temperatures (from 183 - 301 K).

In addition to these synthetic studies, the ^1H n.m.r. spectra (obtained at 360 MHz) of these compounds(2) have been closely investigated. Previous spectroscopic detection of the acidic proton, at 100 MHz on a Varian HA 100 n.m.r. spectrometer, was unsuccessful[43] but in the Fourier Transform spectra, obtained at 360 MHz and ambient temperature for $[Pt(S_2CNR_2)\{(PPh_2O)_2H\}]$ (R = Et, ^iPr), broad, high frequency resonances are observed. Thus for R = Et δH is 10.44 p.p.m. (width at half height = 250 Hz) and for R = ^iPr δH is 10.2 p.p.m. ($w_{1/2}$ = 400 Hz).

Previous observation of similar acidic protons have placed the chemical shifts at δ13.43 p.p.m. for

$PtH(PMePh_2)\{(PPh_2O)_2H\}$[44] and other workers in this department have investigated a number of iridium and rhodium complexes containing the R_2PO--H--OPR_2 unit and δH values are comparable[45]. Thus for $AsPh_4[Rh_2Cl_5\{(PPh_2O)_2H\}_2]$ δH = 9.4 p.p.m. and this signal can be observed on a 100 MHz spectrometer. In a series of $IrHCl(L-L)\{(PPh_2O)_2H\}$ compounds (L L = $(PhSCH_2)_2(Ph_2AsCH_2)_2$, cycloocta-1,5-diene) δH varies from ca. 11.3 to 7.5 p.p.m. and has been shown (for L-L = cycloocta-1,5-diene) to vary in position with concentration and temperature. In going from high (0.66 M) to low (0.16 M) concentration in $CDCl_3$ δH shifts to low frequency by 0.8 p.p.m. and this is the expected behaviour for a hydrogen-bonded system. Finally, shaking the compounds with D_2O led to facile H-D exchange and loss of these broad signals in the ^1H n.m.r. spectra.

2.2 The Reaction of Diphenylphosphine Sulphide with Platinum Bisdialkyldithiocarbamates

In contrast to the rapid reaction of $Ph_2P(O)H$ with $Pt(S_2CNR_2)_2$ (R = Me, Et, ^iPr) under mild conditions, a reaction between $Ph_2P(S)H$ and the same metal complexes will only occur under reflux in polar organic solvents such as alcohols and nitriles. No reaction was observed when the solvent was chloroform, benzene or toluene, in all of which both reactants are soluble, and extensive side reactions are observed in acetone[‡]. Thus despite the low solubility of

---

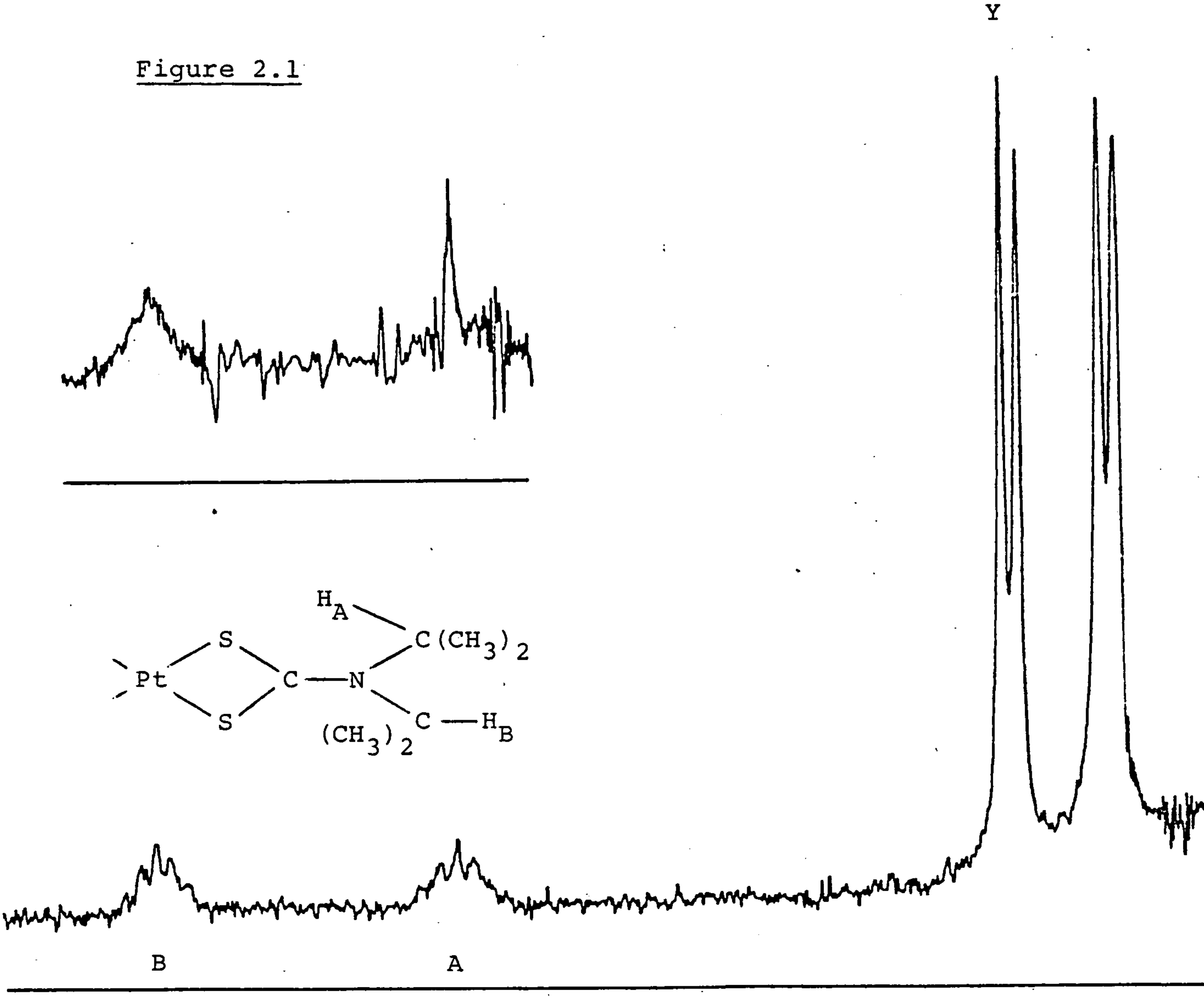
[‡] When the phosphine oxide reaction is attempted in acetone, a high proportion of a phosphine oxide acetone adduct, $[Ph_2P(O)C(OH)(CH_3)_2]$ is obtained[46]. A similar reaction occurs with $Ph_2P(S)H$ and the adduct has been isolated as a microcrystalline solid from acetone solution.

$Pt(S_2CNR_2)_2$ in ethanol, this remains the chosen solvent. Indeed the low solubility is probably advantageous in that at any one point in the reaction a proportionately high ratio of $Ph_2P(S)H$ to metal ion is present in solution.

2.2.1 The Preparation of $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ Complexes

When the compounds $Pt(S_2CNR_2)_2$ (R = Et, ^{i}Pr) are refluxed with a threefold excess of $Ph_2P(S)H$ in degassed, dry analar methanol for 8-12 h small amounts of the white crystalline solids $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ (R = Et(17a), ^{i}Pr(17b) are precipitated. Concentration of the filtrate and addition of an excess of diethylether gives more of the products to a total yield of 50-60%. The $^{31}P-\{^{1}H\}$n.m.r. (Table 2.1) and ^{1}H n.m.r. (Table 2.2) spectra support the above formulation. The ^{31}P n.m.r. chemical shifts are indicative of P(V), occurring to low frequency of ionic PPh_2S^- (δP 54.6 p.p.m.) but to high frequency of free $Ph_2P(S)H$. The observed shifts, ca. 27 p.p.m., are comparable to the shifts of Ph_2PS^- coordinated to other third row transition metals[31,34] and the size of the $^{195}Pt-^{31}P$ coupling constants indicate that the phosphorus atoms are directly bound to platinum. At low temperature the $^{31}P-\{^{1}H\}$n.m.r. of (17b) becomes a narrow AB pattern ($^{2}J_{PP}$ 2.4 Hz). Compound (17a) does not exhibit this behaviour which is attributed to a temperature effect on the confirmation of the trans ligand, $((CH_3)_2CH)_2NCS_2^-$. It is a common observation that rotation about the isopropyl C-N bond in coordinated dithiocarbamates is hindered at low temperatures leading to the freezing out of an asymmetric conformer[47] (Fig. 2.1). This is borne out

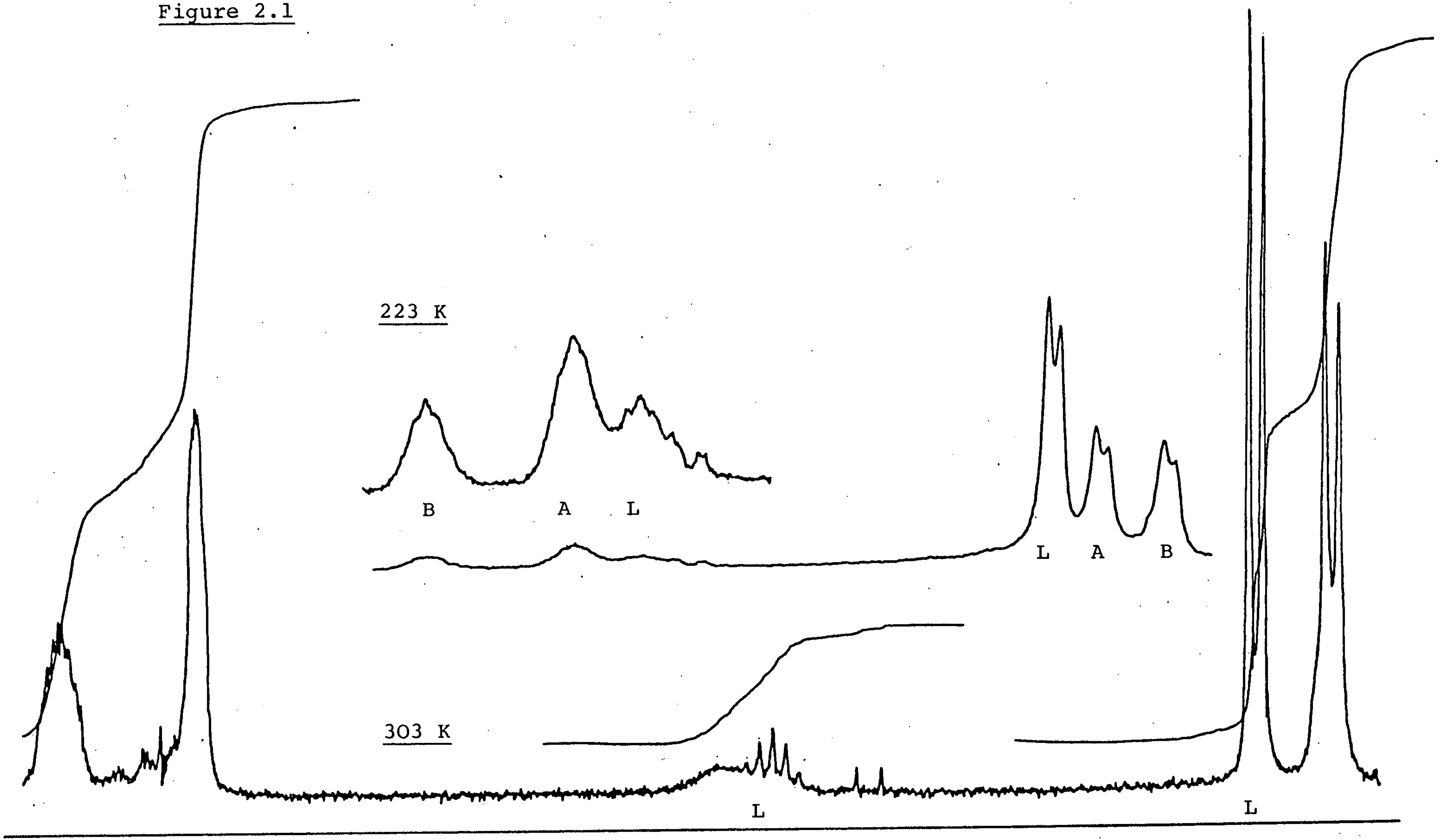
Figure 2.1



Variation in the ^{1}H n.m.r. spectra of coordinated $(S_2CN^iPr_2)^-$ groups, with temperature

a) $Pt(S_2CN^iPr_2)_2$ at 223 K (inset: result of selective decoupling at Y).

Figure 2.1



b. Hydrogen-1 n.m.r. of $N^{i}Pr_2H_2[Pt(S_2CN^{i}Pr_2)(Ph_2PS)_2]$ (17b) by examining the ^1H n.m.r. spectrum of the starting material $Pt(S_2CN^iPr_2)_2$(18) and comparing it with that of the product (17b). At room temperature the ^1H n.m.r. spectrum of (18) consists of a single methine septet and a single methyl doublet. On cooling both signals split into two. The retention of coupling means that the splitting is due to the nonequivalence of adjacent isopropyl groups in the same dithiocarbamate ligands. Decoupling experiments show the high frequency septet corresponds to the methine proton of the same isopropyl group which gives rise to the low frequency methyl doublet. The room temperature ^1H n.m.r. spectrum of (17b) shows in addition to the phenyl proton resonances, two broad resonances in the methine region (δH 4.38; 4.12 p.p.m. ($N^iPr_2H_2^+$)) and two doublets in the methyl region (δH 1.26; 1.62 p.p.m. ($N^iPr_2H_2^+$)). On cooling the low frequency doublet becomes two, centred on the original position, and the high frequency methine resonance splits also. The resonances due to the ammonium isopropyl groups remain invariant. The further assignment of the methyl and methine protons can be attempted. The ammonium ^{i}Pr-methyl protons are the least shielded. In the frozen out conformer, which can be attributed to the interference of methyl groups on adjacent substituents and to a strong hydrogen-sulphur interaction[47], the methyl groups pointing away from the ligand sulphur will be correspondingly shielded with respect to those which are orientated towards, and interact with, the sulphur atom. The methine resonances can be similarly assigned, as shown in Fig. 2.1.

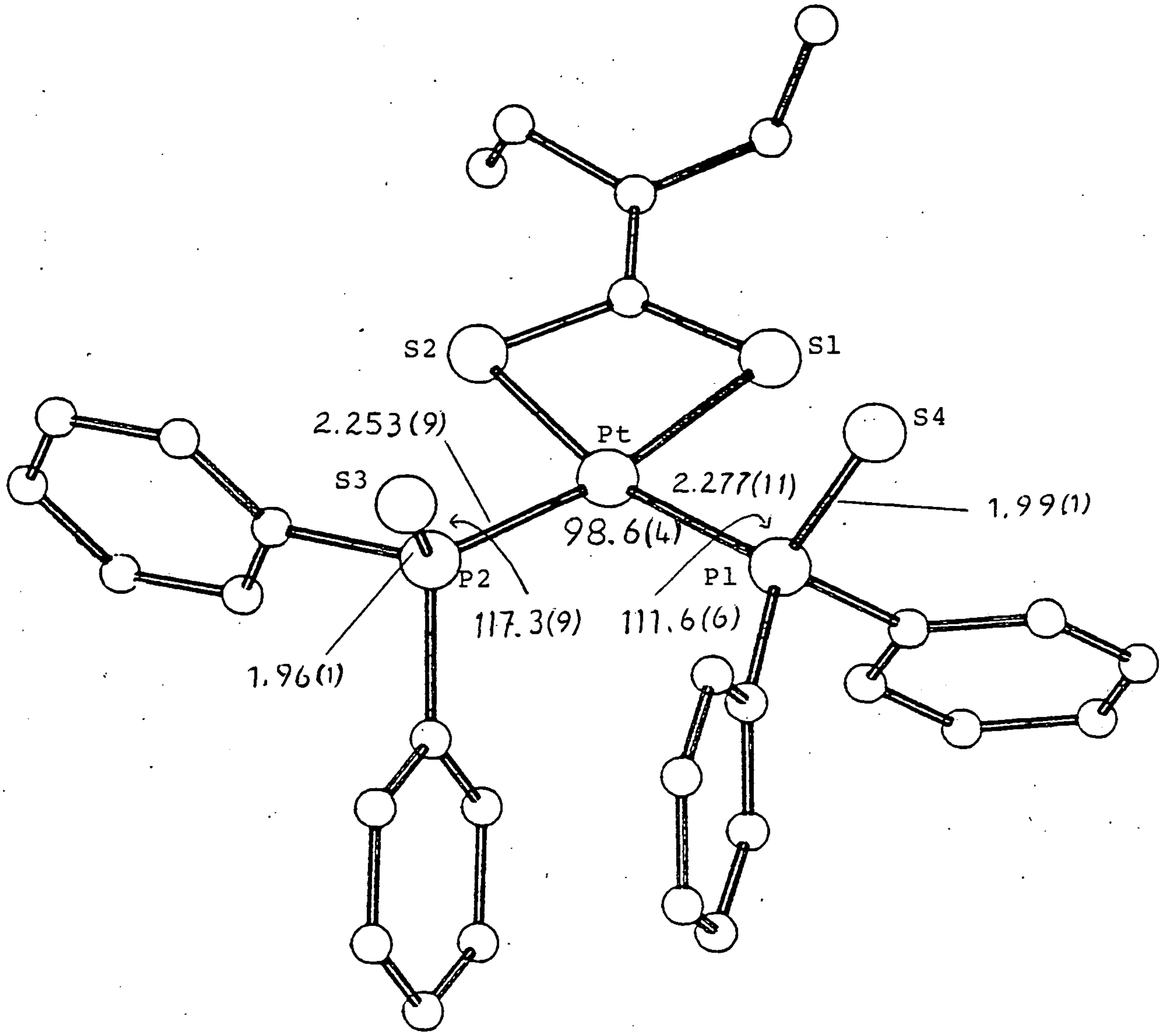
The major difference between the $Ph_2P(S)H$ and the $Ph_2P(O)H$ reaction is in the isolation of the product of the thiophosphine reaction as an ammonium salt. It is proposed that the amine NR_2H is formed in situ in both reactions by breakdown of HS_2CNR_2.[48] Other authors have found that the oxyring compounds can be deprotonated with base,[14,49] and experiments have shown the presence of $[Pt(S_2CNR_2)(Ph_2PO)_2]^-$ in solution, but this particular ion has not been isolated. The most important factor is probably the dominant effect of the hydrogen bond which determines the acidity of the proton. Thus the conjugate base is formed for the thio system but the neutral oxyring compound is more stable. Furthermore, protonation of the thio complex leads to rearrangement (see later), whereas, the cation $[Pt(S_2CNR_2)(PPh_2OH)_2]^+$ can be generated in solution.

The $NH_2R_2{}^+$ cation can be readily exchanged by reaction of compounds (17) with the appropriate reagents. Thus the Cs^+ (17c) and $Ph_3(PhCH_2)P^+$(17d) salts have been obtained by reaction of (17a) with CsCl and $Ph_3(PhCH_2)PCl$ respectively. The phosphonium salts are 1:1 electrolytes in alcohols, whereas the $NR_2H_2{}^+$ salts have a very low Λ value, indicative of a strong ion-pair interaction. This has been shown on the basis of an X-ray structural analysis (see later), to persist in the solid state. The caesium salt was too insoluble for conductimetric measurements.

The i.r. spectra of the products have been obtained in a number of different media. Those of the ammonium salts contain two broad absorptions at 2660 and 2460 cm^{-1} in both $CHCl_3$ and C_6H_6 and in KBr disc spectra. Similar bands are also present in $NEt_2H_2[Ph_2PS]$, but not in the $Ph_3(PhCH_2)P^+$ or Cs^+ salts of the $[Pt(S_2CNR_2)(Ph_2PS)_2]^-$ anions. Hence they can be assigned to NH_2^+ stretching vibrations. A number of bands are found in the ν_{PS} stretching region at 620, 600, 580, 530, 520 cm^{-1}. The positions of the lines and the relative intensities are similar in both (17a) and (17b). Changing the cation causes a general broadening and superposition of the two pairs of lines at 600, 580 and 530, 520 cm^{-1}. In the free $Ph_2P(S)H$ ligand and in the ionic species $NH_2Et_2[Ph_2PS]$ ν_{PS} can be assigned to bands at 630 and 620 cm^{-1} respectively. It is known from other studies that complexation of $Ph_2P(S)H$ will shift ν_{PS} to a lower frequency. This fact and a comparison with the bands in the starting dialkyldithiocarbamate compounds eliminate some possibilities and thus the band at 600 cm^{-1} is possibly the best assignment for ν_{PS} in these anions.

The X-ray crystal structure of $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ has been obtained. Crystals were grown from $CHCl_3|Et_2O$ solution. Details of the solution of the structure are given in the experimental section, and the anion is illustrated in Fig. 2.2. The platinum is coordinated in the expected square planar fashion by two S and two P atoms, with typical bond lengths (P-Pt 2.27 Å; S-Pt 2.37 Å). Each $NEt_2H_2^+$ ion lies close to one $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$ ion making contacts N(2)---Pt 3.65 Å, N(2)---S(4) 3.18 Å and N(2)---S(3) 3.27 Å. All atoms on other neighbouring anions are more than 4 Å from N(2). The P(1)P(2)S(3)S(4) plane is tilted 70° from the coordination plane and the sulphur atoms S(3) and S(4) are 4.7 Å apart. This is to be contrasted with

Figure 2.2



Molecular Structure of the $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$ anion (17a)

(some angles (°) and distances (Å) are given)

$Pd(S_2PMe_2)\{(Ph_2PO)_2H\}$ (Section 2.1.2) where the hydrogen bond has constrained the O--O distance and the interplane angle is very much less.

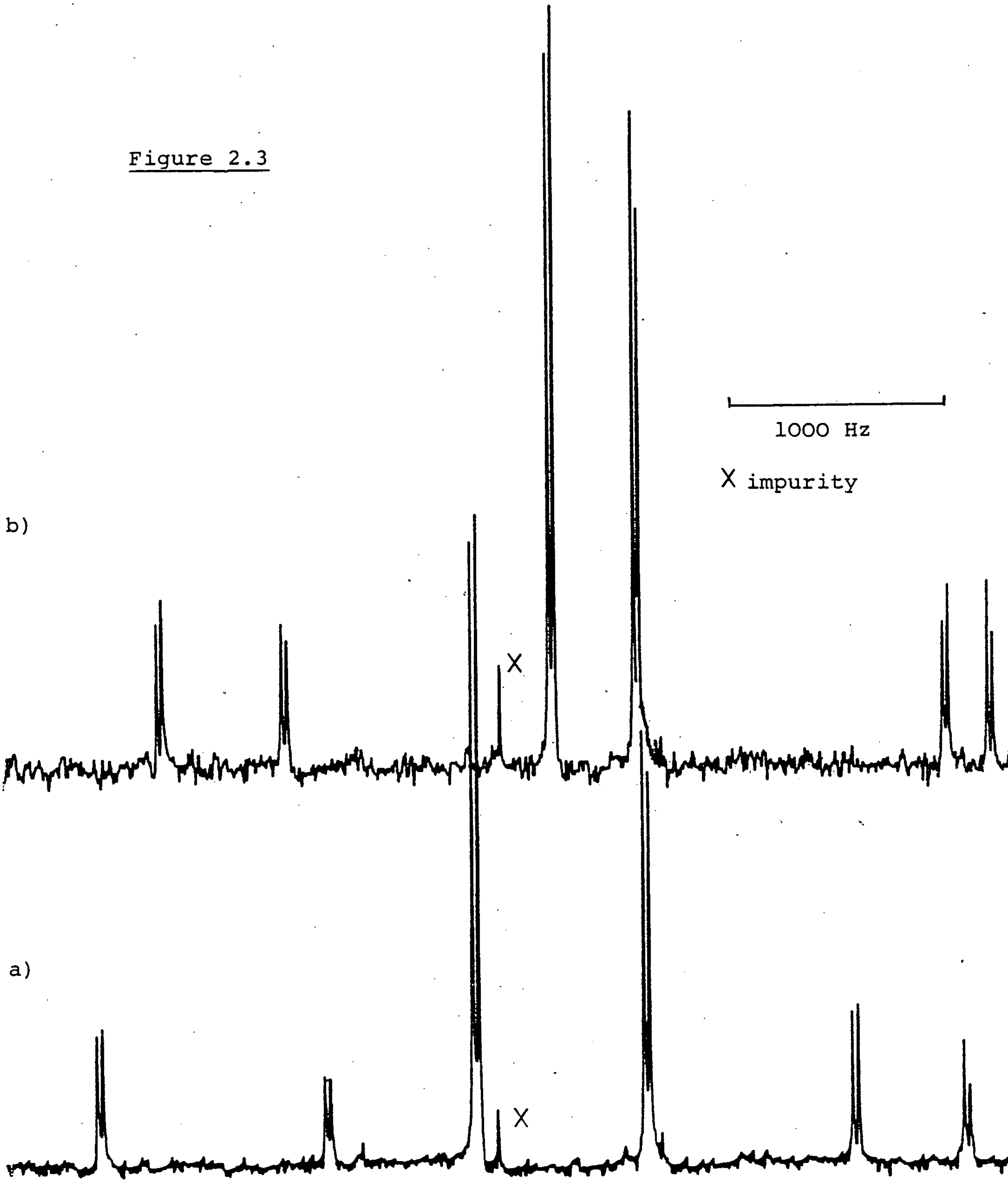
2.2.2 The Preparation of $Pt(S_2CNR_2)(Ph_2POHSPPh_2)$ Complexes

When the compounds $Pt(S_2CNR_2)_2$ (R = Et, ^iPr) and an excess of $Ph_2P(S)H$ are refluxed in degassed technical grade methanol for 8-12 h removal of the precipitates ($NR_2H_2[Pt(S_2CNR_2)(PPh_2S)_2]$) and concentration of the yellow filtrates gives small yields (ca. 20%) of the amorphous pale yellow solids, $Pt(S_2CNR_2)(Ph_2POHSPPh_2)$ (R = Et(19a), ^iPr(19b)). These complexes have been characterised as far as possible by spectroscopic techniques. The solids are soluble in most chlorinated solvents and are sufficiently soluble in methanol to be shown to be nonconducting. The mass spectrum of (19b) shows a weak molecular ion at m/e 791 indicative of a monomeric formulation, at least in the gas phase. The subsequent breakdown pattern is very complicated. Room temperature $^{31}P-\{^1H\}$ n.m.r. spectra (see Fig. 2.3a) clearly show that the compounds contain two directly bonded, magnetically inequivalent, phosphorus ligands. The size of $^2J_{PP}$ (ca. 28 Hz) suggests the ligands are cis to one another[50]. By comparing the ^{31}P chemical shifts found in complexes (19) with those in (2) and (17), the high frequency resonances (ca. 65 p.p.m.) can be assigned to the oxy-phosphorus group and the low frequency resonances (ca. 30 p.p.m.) to the thiophosphorus groups. The $^1J_{PtP}$ values are within the range found for Pt(II) phosphine compounds with trans-S ligand donors[51]. Furthermore like the complexes of type (2), the F.T. ^1H n.m.r. spectrum of (19b), obtained at 360 MHz, shows a broad resonance at high frequency (12.06 p.p.m.).No ^{31}P coupling could be resolved but the intensity of the peak is greatly reduced after a brief shake with D_2O and is therefore assigned to the presence of an acidic proton. The asymmetry of the molecules is mirrored in the signals observed for the dithiocarbamate ligand which are broadened due to the overlap of the resonances from the two magnetically inequivalent organic parts of the ligand (see Fig. 2.4). On cooling the $CDCl_3$ solution and re-examining the $^{31}P-\{^1H\}$ n.m.r. spectrum of (19b) it is found that the R.T. spectrum has been doubled up. This is believed to be due to hindered rotation about the isopropyl C-N bond resulting in the observation of equivalent amounts of the two possible conformers (Fig. 2.4).

Unfortunately, despite strenuous attempts, no crystalline samples of (19a) or (19b) have been obtained, one of the difficulties being the preparation of analytically pure samples. In the absence of any X-ray structural data, it is therefore difficult to establish unequivocally the position of the hydrogen atom; i.e. whether it is coordinated to the oxygen or to the sulphur atoms or to both via a hydrogen bridge. Support for the premise that the coordination is principally to oxygen comes from a number of observations.

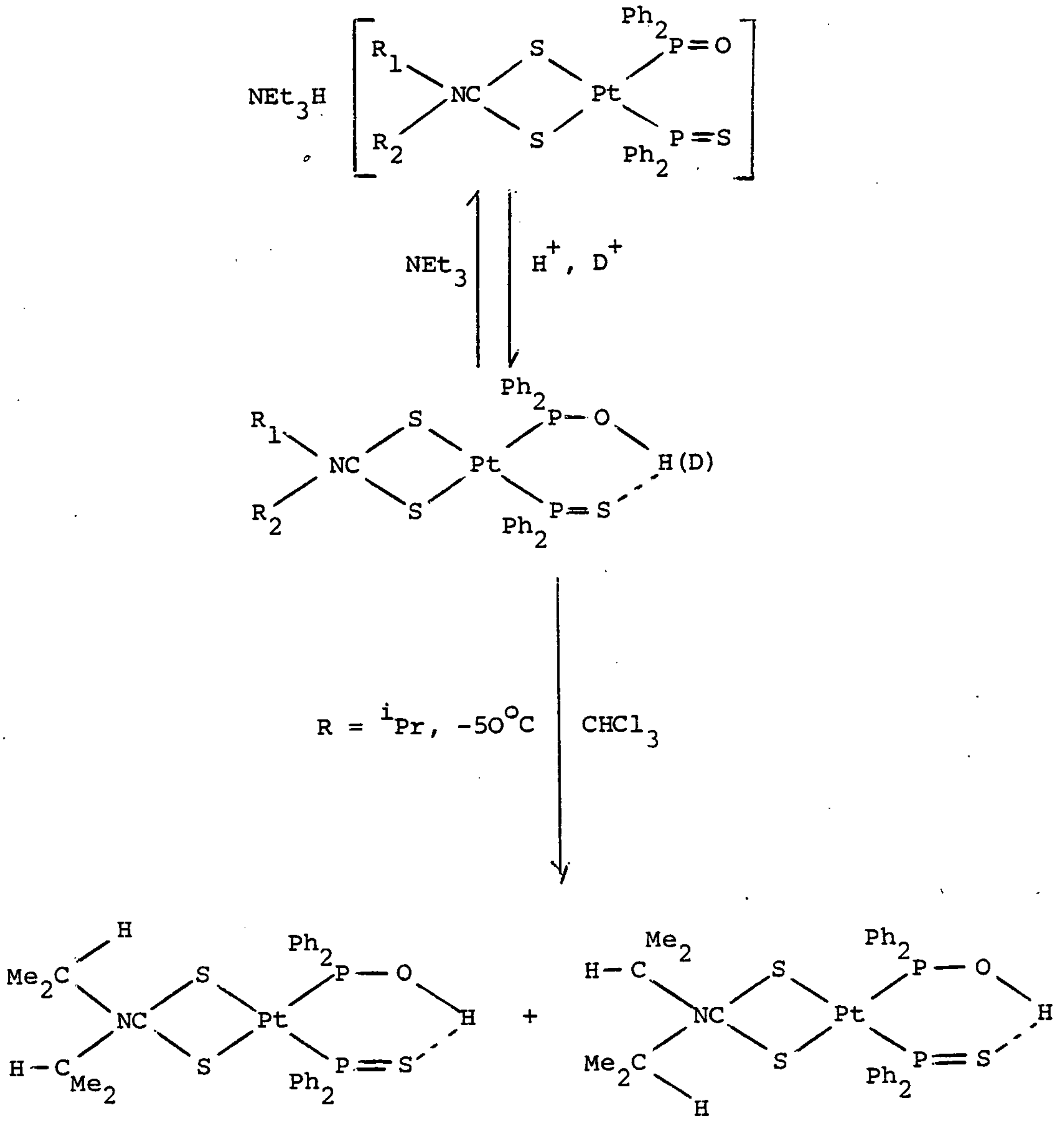
The complexes are isolated as neutral monomers and not as the $NR_2H_2^+$ salts but the addition of a base, such as NEt_3, to a $CDCl_3$ solution of (19b) leads to in situ generation of $NEt_3H[Pt(S_2CN^iPr_2)(Ph_2PO)(Ph_2PS)]$ (19c). Generation of this anion is supported by the observation that

Figure 2.3



Phosphorus-31-{^{1}H} n.m.r. spectra ($CDCl_3$, 298 K) of a) $Pt(S_2CN^iPr_2)(Ph_2POHSPPh_2)$ (19b) and b) $[Pt(S_2CN^iPr_2)(Ph_2PS)(Ph_2PO)]^-$ in $CDCl_3$ at 300 K.

Figure 2.4



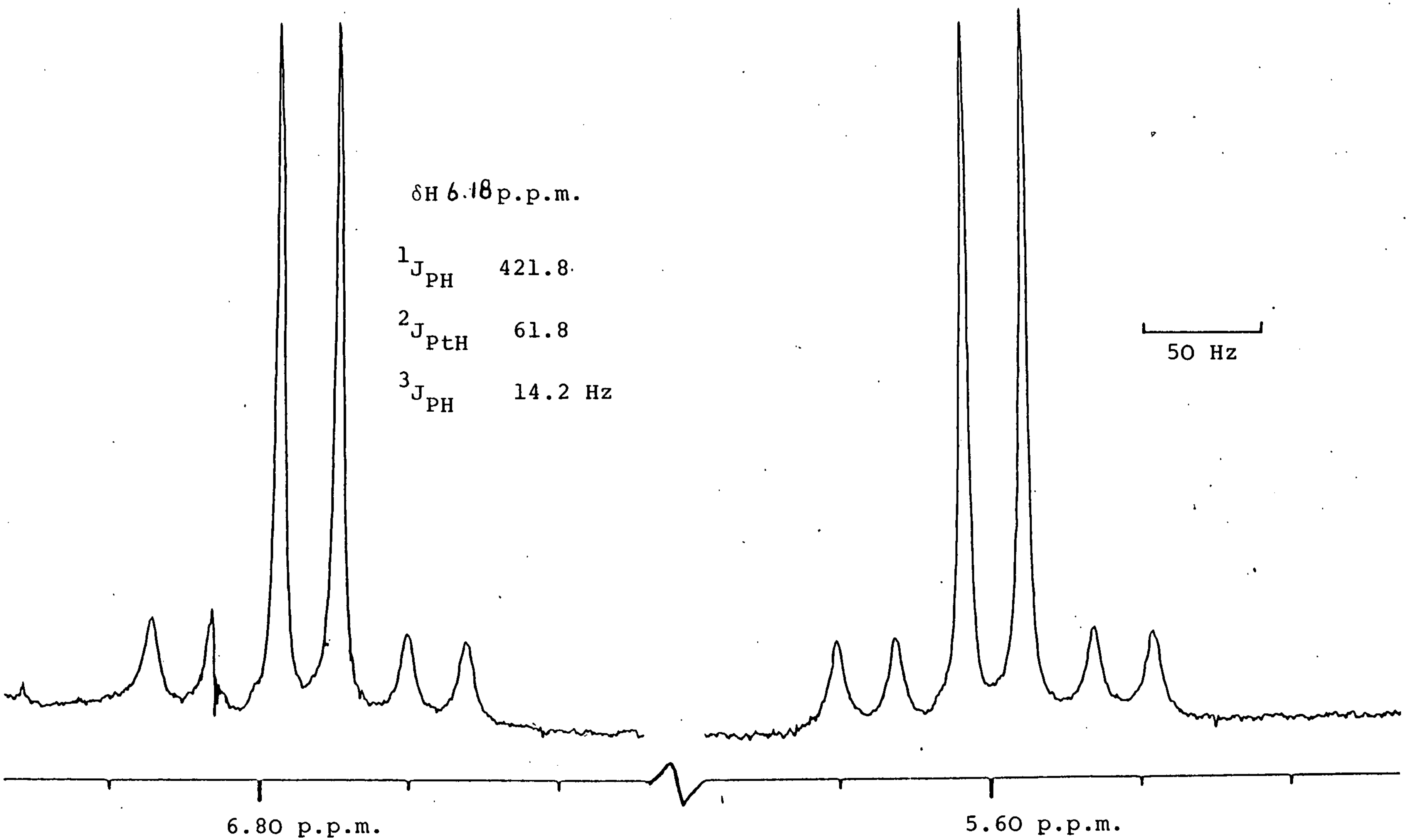
Some Properties of $Pt(S_2CNR_2)(Ph_2POHPSPh_2)$ (19)

the same reaction in methanol is accompanied by dissolution of the insoluble starting complex (19b) and a sharp rise in conductivity. The $^{31}P-\{^{1}H\}$ n.m.r. spectrum shows the following changes on deprotonation (Fig. 2.3b). The thiophosphorus shift (δ31.6 to 33.5 p.p.m.) shows little change compared with the oxyphosphorus shift (δ66.4 to 50.8 p.p.m. a shift of 15 p.p.m.) which moves to a position which is within the range expected for a P(V) four coordinate moiety[52]. However, it should be noted that these changes are accompanied by changes in $^{1}J_{PtP}$, which suggest some association of the proton with sulphur, i.e. the oxyphosphorus coupling increases by 131.9 Hz whereas the thiophosphorus coupling increases by 319.9 Hz to 3449.7 Hz, a value similar to that recorded for compound (17b). Deuteration does not affect the ^{31}P chemical shifts, although, in the presence of excess DCl, the oxyphosphorus resonance is broadened compared with that of the thiophosphorus.

The addition of an aqueous methanol solution of CsCl to the above basic solutions of the anion (19c) precipitates the insoluble $Cs[Pt(S_2CN^{i}Pr_2)(Ph_2PO)(PPh_2S)].2H_2O$ (19d) from which the parent complex can be regenerated by treatment with H^+. If DCl is used the complex $[Pt(S_2CN^{i}Pr_2)(Ph_2PODSPPh_2)]$ is generated <u>in situ</u> and its ^{2}H n.m.r. spectrum shows δD at 7.42 p.p.m.

Detailed examinations of the i.r. spectra have been carried out to try and assign the $\nu(Ph_2POH{-}{-}{-}SPPh_2)$ vibration. The i.r. spectrum of (19b) contains a broad band at 2190 cm^{-1} which is not present in the Cs salt (19d). The literature[11]

Figure 2.5



High Resolution ^{1}H-n.m.r. Spectrum (CDCl$_3$ 300 K) of the Ph$_2$P<u>H</u> resonance of Pt(S$_2$CN^{i}Pr$_2$)(Ph$_2$PS)(Ph$_2$PH) (20b) suggests that a terminal ν_{PO-H} occurs at ca. 3200 cm^{-1}. A completely symmetrical hydrogen bond, such as that occurring in complexes of type (2), is characterised by a broad absorption between 1200 and 1600 cm^{-1}. Therefore the observed band can be tentatively assigned to a $\nu_{(Ph_2P\underline{O-H---S}PPh_2)}$ stretching vibration, where significant interaction with the cis sulphur atom has lowered the frequency. The products from the deuteration studies support this conclusion. Careful examination reveals that the above i.r. band is much reduced in intensity and a new absorption band, which can be assigned to $\nu_{(Ph_2P\underline{O-D---S}PPh_2)}$, occurs as a broad shoulder on the ν_{CN} (1500 cm^{-1}) absorption at 1530 cm^{-1}. Possibly the most convincing evidence for a strong O-H interaction is the effect on the ν_{PO} vibration on going from the original complex (19b) to the caesium salt (19d). In (19b) ν_{PO} occurs at 910 cm^{-1} whereas a lower frequency band at ca. 880 cm^{-1} would be typical of a pure $\nu_{(P-OH)}$ vibration. In the Cs salt (19d) this band is absent and a strong new band at 1050 cm^{-1} is assigned to ν_{PO}. In contrast, the positions of the five strong bands in the PS stretching region do not alter. The results of this analysis suggest structure (19) (This is shown in Fig. 2.4) containing a coordinated phosphinous acid, the proton of which interacts significantly with the cis sulphur atom of a coordinated Ph_2PS group.

2.2.3 The Preparation of $Pt(S_2CNR_2)(Ph_2PH)(Ph_2PS)$ Complexes

In a more direct attempt to synthesise $Pt(S_2CN^iPr_2)(Ph_2PODSPPh_2)$, $Pt(S_2CN^iPr_2)_2$ was treated with an excess of $Ph_2P(S)H$ in degassed, dry methanol to which some D_2O was added. However, after refluxing for 24 hours the small amount (20%) of white precipitate produced is not $[Pt(S_2CN^iPr_2)(Ph_2PODSPPh_2)]$ but the unusual secondary phosphine complex $[Pt(S_2CN^iPr_2)(Ph_2PS)(Ph_2PH)]$ (20b). It should be noted that <u>in situ</u> n.m.r. studies reveal that products such as (17b) and (19b) are still present in solution. Evidence for this formulation is based on $^{31}P-\{^1H\}$ and high resolution ^1H n.m.r. studies (Tables 2.1 and 2.2), elemental analyses, molecular weight determinations (monomer in C_6H_6), conductance data (non-conducting in methanol) and the observation that reaction of $N^iPr_2H_2[Pt(S_2CN^iPr_2)(Ph_2PS)_2]$ (17b) with an excess of Ph_2PH in chloroform gives an almost quantitative yield of the same product.

The $^{31}P-\{^1H\}$ n.m.r. of (20b) is again a characteristic 1st order AXM (AX:P_AP_X; M:Pt) pattern. The $Ph_2\underline{P}S^-$ chemical shift is observed at a typical position, <u>ca</u>. 30 p.p.m., and the $Ph_2\underline{P}H$ resonance is observed at 5.6 p.p.m., which represents a shift up frequency of 47 p.p.m. compared with the free ligand. Retention of proton coupling splits this doublet into two doublets, $^1J_{PH}$ being 422 Hz. The high resolution ^1H n.m.r. spectrum is also helpful in confirming this structure. $\delta Ph_2P\underline{H}$ is 6.18 p.p.m. and $^1J_{PH}$, $^2J_{PtH}$ and $^3J_{PH}$ are all observed (see Table 2.2 and Fig. 2.5) and are compatible with the proposed structure. In the i.r. spectrum ν_{PH}, a broad weak absorption at 2340 cm^{-1}, and ν_{PS}, at 600 cm^{-1}, are the salient features. The complex $[Pt(S_2CNEt_2)(Ph_2PH)(Ph_2PS]$ (20a) was also synthesised, by direct reaction of (17a) with diphenylphosphine, and characterised. A collation of a number of experimental results yielded via in situ n.m.r. studies, the information that small proportions of the compounds (20) are present in the reaction solutions under all conditions. Significantly, the presence of H_2O, as well as increasing the proportion of compound (19), also increases the proportion of compound (20). Also, the most intense peak in a mass spectrum of (19b), which occurs at m/e 775, can be assigned to $[Pt(S_2CN^iPr_2)(Ph_2PS)(Ph_2PH)]^+$. The role of D_2O in the above reaction is not really understood. One possibility is that the D_2O/MeOH medium helps to precipitate out compound (20).

2.2.4 The Preparation of $[Pt(S_2CNR_2)(Ph_2POMe)(Ph_2PS)]$ Complexes

If $[Pt(S_2CN^iPr_2)_2]$ is refluxed with an excess of $Ph_2P(S)H$ in degassed, dry analar methanol for a prolonged period (36 hours), work-up gives a monomeric, neutral, pale yellow solid (45% yield) which on the basis of analytical data, together with $^{31}P-\{^1H\}$ and ^1H n.m.r. studies (Tables 2.1 and 2.2) is formulated as $[Pt(S_2CN^iPr_2)(Ph_2PS)(Ph_2POMe)]$ (21). The $^{31}P-\{^1H\}$ n.m.r. spectrum is an AXM pattern with resonances at δ92.7 ($Ph_2\underline{P}OMe$) (cf. $Pt(S_2CNEt_2)(Ph_2PO)(Ph_2POMe)$ $\delta\underline{P}OMe$ 94.1 p.p.m.[9]) and δ28.2 p.p.m. (Ph_2PS^-). The ^1H n.m.r. spectrum contains a doublet at δ3.56 p.p.m. ($^3J_{PH}$ 13.0 Hz) which is assigned to the methoxy resonance, and the remaining resonances are compatible with the proposed structure. The i.r. spectrum shows ν_{POC} at 1040 cm^{-1} and ν_{PS} at 600 cm^{-1}, in addition to the normal dithiocarbamate and ligand bands. The diethyldithiocarbamate analogue has also been observed and characterised spectroscopically.

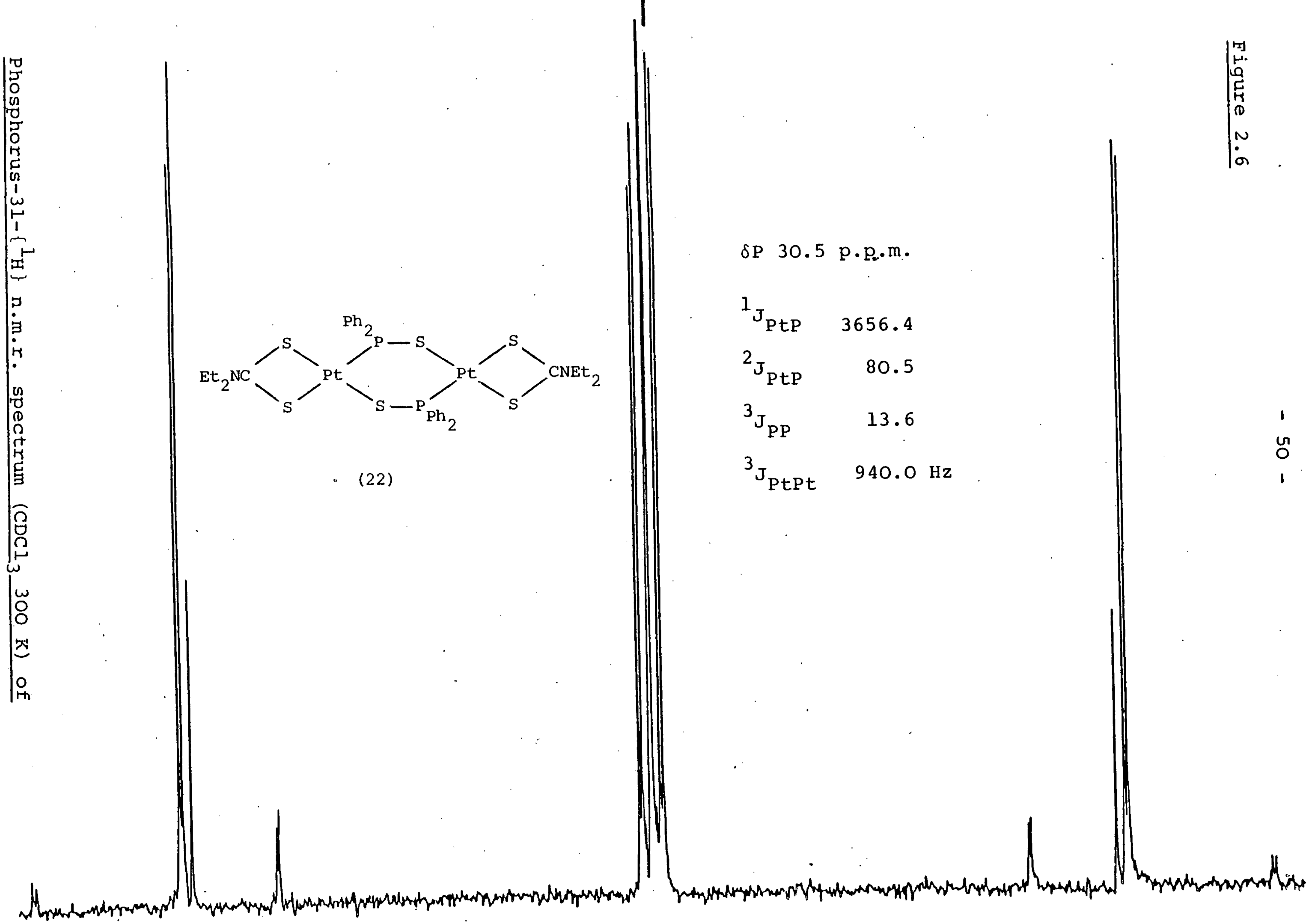
2.2.5 The Preparation of $[Pt(S_2CNR_2)(Ph_2PS)]_2$ Complexes

Finally, in this versatile $Pt(S_2CNR_2)_2/Ph_2P(S)H$ reaction, if $Pt(S_2CNEt_2)_3$ is refluxed in dry degassed ethanol with an equimolar amount of $Ph_2P(S)H$ for six hours, work up of the yellow solution gives a very small yield (ca. 10%) of the binuclear complex $[Pt(S_2CNEt_2)(Ph_2PS)]_2$(22a). The same compound and the corresponding isopropyl complex (22b) can be synthesised in almost quantitative yield by treatment of $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ (17) with HCl gas in degassed dry $CHCl_3$ (either directly or by using a few drops of a concentrated anhydrous ethanolic solution). Further experiments (see Chapter 5) indicate that addition of HCl to compound (17) leads to loss of $Ph_2P(S)H$ and subsequent facile self-dimerisation of the reactive intermediates thus formed to give compound (22). The characterisation of these complexes was achieved by a number of methods. Thus, elemental analyses are consistent with the empirical unit $[Pt(S_2CNR_2)(Ph_2PS)]_n$ and osmometric molecular weight determinations in benzene show n=2. Detailed n.m.r. studies and an X-ray structural analysis (for R = ^{i}Pr) confirm the retention of the binuclear unit in solution and in the solid phase. Considerable structural information can be obtained from the $^{31}P-\{^{1}H\}$ n.m.r. spectra (see Table 2.1b and Fig. 2.6). The spectra consist of the superimposed signals from three separate isotopomers which are caused by the presence of two Pt nuclei in the dimer (as the isotope ^{195}Pt (spin ½) is only 33.8% of the total). Thus the signal obtained for the isotopomer with no ^{195}Pt nuclei (approximately 4/9 total spectral intensity) is a singlet at δP, ca. 31 p.p.m.. The spectrum from the next isotopomer, that with a single ^{195}Pt nucleus (again approximately 4/9 of the total intensity), consists of eight lines, two doublets of doublets centred on δP. The parameters $^{1}J_{PtP}$, $^{2}J_{PtP}$ and $^{3}J_{PP}$ can be obtained and assigned directly from the spectrum as the spin system is a first order AXM pattern. The final isotopomer with two ^{195}Pt nuclei (1/9 total intensity) gives rise to a second order AA´XX´ pattern due to the magnetic inequivalence of each individual phosphorus and platinum atom with respect to the other. From the ten line spectrum, which is symmetrical about δP, the remaining unassigned coupling constants, $^{3}J_{PtPt}$, can be calculated[53] and these are found to be 940 Hz (22a) and 1000 Hz (22b). The two most intense lines in these subspectra indicate also that the two PtP coupling constants are of opposite sign‡. Thus, the only possible structure consistent with this information is that given in Fig. 2.6, in which the salient feature is the six membered Pt-P-S-Pt-P-S ring similar to that proposed by Cavell in 1972[37]. In the i.r. spectra the PS stretch is observed at 578 (22a) and 575 cm^{-1} (22b) reflecting the change in the P-S bond order[34].

Details of the solution of the crystal structure of $[\{Pt(S_2CN^iPr_2)(Ph_2PS)\}_2]2CDCl_3$ (22b) are given in the

‡ The platinum-195 n.m.r. spectra of both species (22a and 22b) were also recorded. These are simpler than the corresponding $^{31}P-\{^{1}H\}$ n.m.r. spectra, consisting of a doublet of doublets (the M part of the AXM spectra) and an XX´ spectrum, identical (in line position and intensity) to the AA´ part observed in the ^{31}P n.m.r. spectra. The only new information recorded is the ^{195}Pt chemical shifts which are given in the experimental section.

Figure 2.6



(22)

δP 30.5 p.p.m.

$^{1}J_{PtP}$ 3656.4

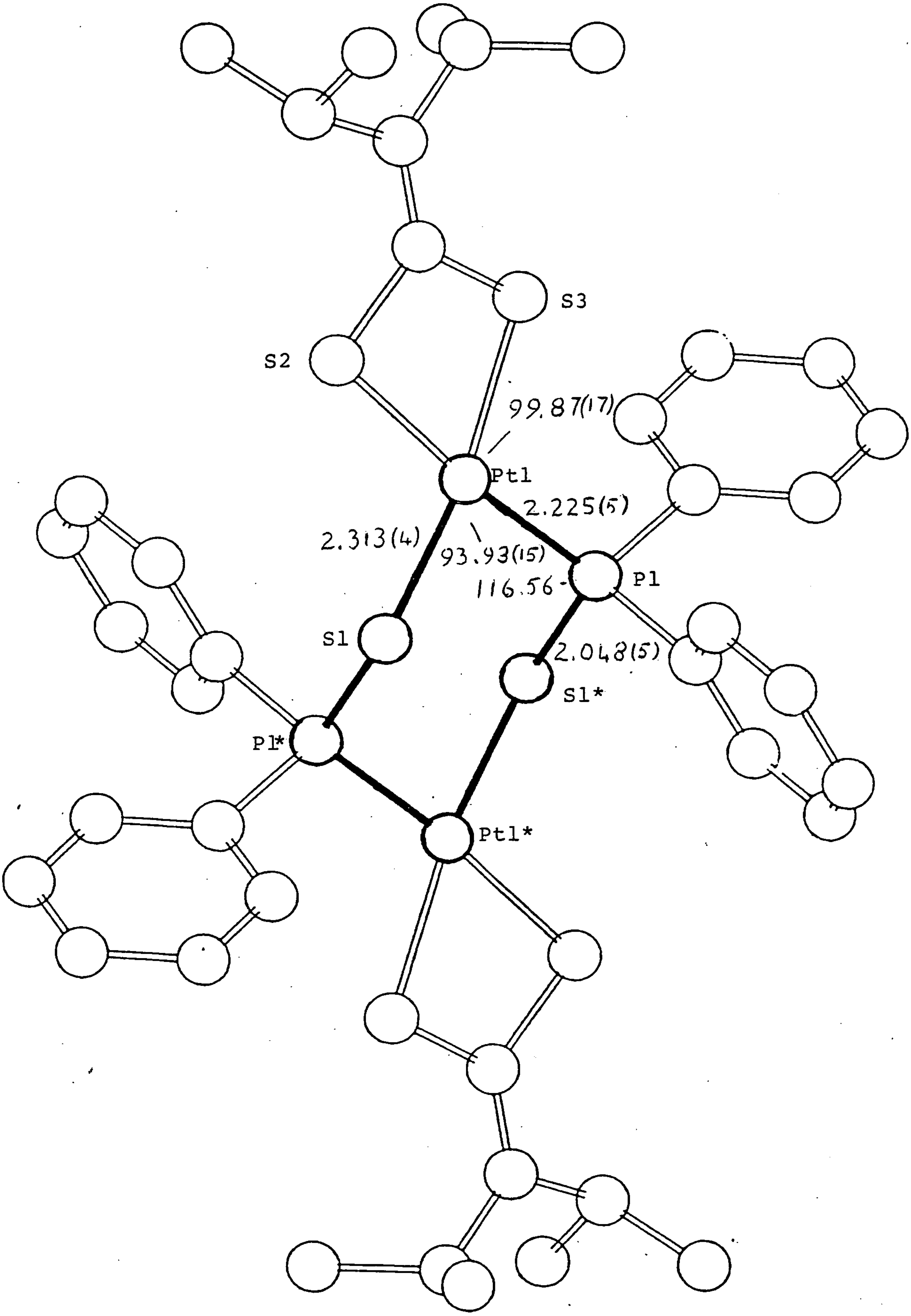
$^{2}J_{PtP}$ 80.5

$^{3}J_{PP}$ 13.6

$^{3}J_{PtPt}$ 940.0 Hz

Phosphorus-31-{^{1}H} n.m.r. spectrum ($CDCl_3$ 300 K) of $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ (22)

Figure 2.7



Molecular Structure of $[Pt(S_2CN^iPr_2)(Ph_2PS)]_2$ (22b)

(some angles (°) and distances (Å) are given).

experimental section, final atomic parameters in Table 2.5 selected bond lengths and angles in Table 2.6 and a view of the molecule in Figure 2.7. The molecule is a dimer lying on a crystallographic inversion centre with a chair shaped six membered Pt(1)-P(1)-S*(1)-Pt*(1)-P*(1)-S(1) ring. The platinum atom is coordinated in a square planar arrangement by two sulphur atoms of the dithiocarbamate group and one phosphorus atom and one sulphur atom in the six membered ring. The maximum deviation from the best plane of Pt and these four atoms is 0.04 Å. This plane is inclined by 54° from the plane defined by P(1)S(1)*P(1)*S(1) (cf. the chair shaped $[(\eta C_5H_5)Ni(Me_2PS)_2]$ molecule where the corresponding interplane angle is 56.1°)[39b]. All bond lengths and angles are within the expected ranges and the Pt-Pt through space distance is 4.57 Å (see Table 2.6). The shortest intermolecular contacts are between Cl(1)...C(15) and S(2)...C(8) (both 3.6 Å).

2.3 The Reaction of Diphenylphosphine Sulphide with Palladium Dialkyldithiocarbamates

The compound $Pd(S_2CNEt_2)_2$ can be shown to react in a similar fashion to the platinum dialkyldithiocarbamates already described. The reactions occur much more readily to yield the same type of product mixture (from $^{31}P-\{^1H\}$ n.m.r. evidence) albeit in different ratios. Isolation of the individual products proved difficult. Some success was achieved by conventional column chromatography but careful monitoring of the reaction mixture and selective precipitation was found to be of equal use. Hence when

$Pd(S_2CNEt_2)_2$ is refluxed in degassed, dry, analar methanol with an excess of $Ph_2P(S)H$ for two hours, an orange precipitate of $[Pd(S_2CNEt_2)(Ph_2PS)]_2$ (23) is formed in high yield (60%). Work up of the yellow filtrate by concentration and then tituration with diethylether gives a small amount of $NEt_2H_2[Pd(S_2CNEt_2)(Ph_2PS)_2]$ (24). If, however, the reaction is continued, or if technical methanol is used, an inseparable mixture of (23) and a complex believed to be $Pd(S_2CNEt_2)(Ph_2POHSPPh_2)$ (25) results. Chromatography can be used to purify (23) but (25) has not been purified to a satisfactory standard. Complexes analogous to (20) and (21) have not been observed. The n.m.r. data for all three products is tabulated in Tables 2.1 and 2.2. The $^{31}P-\{^1H\}$ n.m.r. spectra are much simpler than these of the platinum species since Pd has no nuclei with $I=\frac{1}{2}$. The chemical shifts of the coordinated Ph_2PS^- ligands occur at a higher frequency than in the platinum analogues but they are comparable with those in other second row transition metal complexes of this ligand[31]. The ^1H n.m.r. spectrum of (24) consists of two distinct quartets and two triplets in addition to the phenyl resonances. The low frequency triplet and the high frequency quartet are assigned to the ethyl resonances of the coordinated dialkyldithiocarbamate ligand. Infra-red studies show that the spectra of (24) and (17a) are virtually identical apart from some weak bands below 500 cm^{-1}. Direct comparison of the spectra of (23) and (22a) shows that the strong band at 580 cm^{-1} is common to both and it is assigned to ν_{PS}. Other points to note are that confirmation of the dimeric nature of (23) is obtained by osmometric molecular weight determinations in C_6H_6 and that (24) behaves as a normal 1:1 electrolyte in methanol.

2.4 The Reaction of Diphenylphosphine Selenide with Platinum Dialkyldithiocarbamates

In contrast to the variety of products found in reaction of $Pt(S_2CNR_2)_2$ with $Ph_2P(S)H$, only one type of compound has been isolated, to date, in the reaction of $Pt(S_2CNR_2)_2$ with $Ph_2P(Se)H$, namely $Pt(S_2CNR_2)(Ph_2PSe)(Ph_2PH)$ (R = Et (26a); ^iPr (26b). These compounds which are isolated in high yield (>80%) by heating $Pt(S_2CNR_2)_2$ in degassed, dry, analar methanol with an excess of $Ph_2P(Se)H$ for five to eight hours have been characterised, as for the analogous $Pt(S_2CNR_2)(Ph_2PS)(Ph_2PH)$ (20), on the basis of elemental analyses, osmometric molecular weight determinations in C_6H_6, $^{31}P-\{^1H\}$ (Table 2.1) and ^1H (Table 2.2) n.m.r. spectroscopy. The compound $Pt(Se_2CNEt_2)(Ph_2PSe)(Ph_2PH)$ (26c) is prepared under the same conditions by reaction of $[Pt(Se_2CNEt_2)_2]$ with $Ph_2P(Se)H$.

The $^{31}P-\{^1H\}$ n.m.r. spectra of these compounds exhibit the customary AXM spectrum. $\delta Ph_2\underline{P}H$ is comparable to that observed in the compounds (20) and $\delta Ph_2\underline{P}Se$ occurs at $\delta 13$ p.p.m. On long accumulations $^1J_{PSe}$ can be observed (^{77}Se, spin ½, 7.6% abundance). The magnitude of J_{PSe} is generally considered as an empirical indication of bond order[54]. Thus, for double bonds, J_{PSe} is much larger (up to 1000 Hz) than for single bonds. The observed values (ca. 600 Hz) fit well for the proposed formulation. In (26c) the cis ^{77}Se diselenocarbamate coupling could not be resolved. Fackler et al report values of ca. 100 Hz for the trans coupling, ^{77}Se - ^{31}P, in the

$^{31}P-\{^1H\}$ n.m.r. spectra of the complexes $Pt(Se_2CNR_2)(PR_3)X$ and analysis of the $^{31}P-\{^1H\}$ n.m.r. spectrum of (26c) gives two values, 60.0 Hz assigned to $^2J_{^{77}Se-Ph_2\underline{P}Se}$ and 78.0 Hz for $^2J_{^{77}Se-Ph_2\underline{P}H}$. The accumulation of ^{77}Se n.m.r. spectra on the 360 MHz spectrometer was attempted for some, (26a) and (26c), of these compounds, but no results were obtained. Hydrogen-1 n.m.r. high resolution studies have characterised the secondary phosphine protons, the parameters being comparable to these observed for compounds of type (20) (Table 2.2). Infra-red studies reveal that the only significant differences between these complexes and the corresponding phosphine sulphide complexes (20) (section 2.2.3) is in the PS and PSe stretching region below 600 cm^{-1}. The strong band at 600 cm^{-1} in the Ph_2PS^- complexes, assigned to ν_{PS}, is absent. Instead a strong new band at 520 cm^{-1} (26b) and 515 cm^{-1} (26a, 26c) is present and is therefore assigned to ν_{PSe}. This comparison of otherwise identical compounds provides the best evidence for the assignment of ν_{PS} and ν_{PSe}.

2.5 Reaction of Platinum and Palladium Dialkyldithiophosphate and Phosphinate Complexes with $Ph_2P(S)H$ and $Ph_2P(Se)H$

In refluxing degassed anhydrous methanol $M(S_2P(OEt)_2)_2$ (M = Pt, Pd) and $Pd(S_2PPh_2)_2$ react rapidly (ca. 1 h) with an excess of $Ph_2P(S)H$, to give light orange or yellow precipitates. These products have been characterised, on the basis of elemental analyses, i.r., $^{31}P-\{^1H\}$ and ^1H n.m.r. spectroscopy, as neutral binuclear phosphinesulphide bridged species, analogous to compounds (22) and similar to the product discussed by Cavell[37] (see Chapter 1). Under identical conditions, $Pt(S_2PPh_2)_2$ gives high yields of a different, mononuclear, product which is described later.

2.5.1 The Characterisation of $[Pt(S_2P(OEt)_2)(Ph_2PS)]_2$ (27)

The second order spectra of compounds (22) have already been discussed in detail (section 2.2.5). That of (27) is more complex in that two more phosphorus atoms are present in the molecule and these are chemically, as well as magnetically, different from those present in the bridges. The two chemical shifts are readily apparent (δ95.0 p.p.m. ($S_2\underline{P}(OEt)_2^-$); δ30.3 p.p.m. ($Ph_2\underline{P}S^-$)) but a number of new details are also observed. The spectrum of the isotopomer with no ^{195}Pt nuclei is no longer first order, and can be interpreted as an AA′BB′ pattern[53], although a number of the lines are not observed. Furthermore, the isotopomer containing one ^{195}Pt nucleus can be solved directly from the spectrum to give essentially all the observed, assignable parameters (Table 2.1b). The observed coupling constants are similar to those found for compounds (22a) and (22b). Finally, only two lines of the final isotopomer, in which both platinum atoms have spin ½, are distinctly observed. The position of these confirm that $^1J_{Pt\underline{P}S}$ and $^2J_{Pt\underline{P}S}$ (PS : Ph_2PS^-) are of opposite signs. The low solubility of the complex made any further studies impractical, so the magnitude of $J_{^{195}Pt-^{195}Pt}$ remains unknown. Hydrogen-1 n.m.r. studies (Table 2.2) reveal only the integral ratios of the ligands and i.r. studies again prove difficult to interpret especially with respect to the assignment of ν_{PS}. The PS stretching region is further complicated in this case by the dithio-phosphinato ligand, the ν_{PS_2} stretches of which also absorb in the same region. Literature data suggest that ν_{PS_2} occurs in the i.r. spectra at ca. 630 and 585 cm^{-1} and these bands are sharp and strong; of the other bands observed, a strong absorption at 570 cm^{-1} can be tentatively assigned to ν_{PS} by analogy with the other bridged binuclear compounds (22).

2.5.2 The Characterisation of $\{[Pd(S_2PR_2)(Ph_2PS)]_2\}$ (R = Ph (28); OEt (29))

Compound (28) was too insoluble to give any $^{31}P-\{^1H\}$ and ^1H n.m.r. spectra. The characterisation therefore rests on a consideration of analytical data and the i.r. spectrum. The i.r. spectrum of (28) exhibits the typical ν_{PS_2} bands 620, 570 cm^{-1}, and the weaker bands 600, 580, 518 cm^{-1} agree broadly with (27) and (29) below.

The finger-print region of the i.r. spectrum of (29), is virtually identical to that of (27). Between 1600 and 500 cm^{-1}, slight differences in position are apparent i.e. ν_{PS_2} at 580 cm^{-1}, but nothing to suggest a radically different structure. The $^{31}P-\{^1H\}$ n.m.r. spectrum approaches the A_2B_2 case, where two virtual triplets are observed (i.e. the spin system is strictly $AA'BB'$, but $J_{AB} \simeq J_{AB'}$ so the spectrum appears much simpler); J_{AB} is therefore ca. 2.2 Hz. That the spectrum is not simply an A_2X_2 pattern can be demonstrated using a narrow spectral width. The 1:2:1 peak height ratio decreases and the central peak is significantly broader than the outer two. Unfortunately, on the narrowest setting of the 60 MHz instrument no actual resolution of the central peak into its constituent lines was achieved.

2.5.3 The Reaction of $Pt(S_2PPh_2)_2$ with $Ph_2P(S)H$

The product from this reaction is probably the monomeric complex $Pt(S_2PPh_2)(Ph_2POHSPPh_2)$ (30). This assignment rests principally on the analysis of the $^{31}P-\{^1H\}$ n.m.r. spectra. Analytical data is several percentage points out due to a contaminant which can be partially, but not completely, separated from the reaction product. However, the $^{31}P-\{^1H\}$ n.m.r. spectrum of the principal product is an AMX pattern and all the expected parameters for a dithiophosphinate group trans to two cis phosphinic ligands are observed. Taking account of this trans-dithiophosphinate, the shifts and coupling constants observed for the Ph_2PS (δ34.2 p.p.m.; $^1J_{PtP}$ = 3309 Hz) and Ph_2POH (δ62.3 p.p.m.; $^1J_{PtP}$ = 3982 Hz) ligands are in accord with the proposed structure. A high resolution ^1H n.m.r. study shows, in addition to the phenyl resonances, a typical broad absorption at δ12.3 p.p.m. Finally, a strong band at 910 cm^{-1} in the nujol i.r. spectrum of compound (30) is assigned to ν_{PO}. A very weak broad band at 2210 cm^{-1} can therefore be tentatively assigned to ν(PO-H---S). It is worth noting that this reaction was repeated several times under very rigorous conditions as well as in technical methanol and high yields of this single product were obtained every time.

2.5.4 The Reaction of $Ph_2P(Se)H$ with $Pt(S_2PPh_2)_2$

When the complex $Pt(S_2PPh_2)_2$ is treated with an excess of $Ph_2P(Se)H$ under the normal reaction conditions of refluxing degassed dry methanol, a high yield of $Pt(S_2PPh_2)(Ph_2PH)(Ph_2PSe)$ (31) is obtained. The $^{31}P-\{^1H\}$ n.m.r. spectrum shows that the dithiophosphinate ligand has an exceptionally low chemical shift (δ33.3 p.p.m.), but the other shifts and couplings are comparable to those of compounds (21 a-c), the dithio and diselenocarbamate analogues. The one bond phosphorus-selenium coupling constant is 594.7 Hz and a high resolution ^1H n.m.r. study (Table 2.2) showed the expected doublet of doublets with platinum satellites observed for all these coordinated secondary phosphine complexes. δH is 6.03 p.p.m. and once again the coupling constants are comparable to the previous species. The nujol i.r. spectrum is consistent with this formulation.

2.6 Miscellaneous Reactions

A number of other reactions have been carried out which have produced some results. A common denominator in the processes described here is the reaction conditions utilised, principally the solvent, PhCN, and the temperature (150-180°C). Neither $Pd(S_2CPh)_2$ or $Pd(S_2CN^iPr_2)_2$ react under the normal conditions described in the preceding sections. Only by taking the reaction to extremes of temperature was a reaction observed. Therefore, using dry degassed PhCN as the reaction medium, $Pd(S_2CPh)_2$ was heated to 150-180°C for 4 h in the presence of an excess of $Ph_2P(S)H$. After this time, slow cooling of the solution precipitated a quantity of dark red crystals (yield 30%) characterised by analytical and spectroscopic techniques as $Pd(S_2PPh_2)_2$ (32) and this was confirmed by comparison with a conventionally prepared sample[9]. In the course of this study the ^{31}P n.m.r. chemical shift of compound (32), previously unrecorded, was observed to be δ95.1 p.p.m. Under the same conditions, $Pd(S_2CN^iPr_2)_2$ yields a microcrystalline yellow precipitate. Elemental analyses, i.r. and n.m.r. studies indicate that $\{[Pd(S_2PPh_2)_2]\ 0.5\ PhCN\}_n$ (33) is the empirical formula. Thus the temperature invariant $^{31}P-\{^1H\}$ n.m.r. (singlet δ80.0 p.p.m.) and ^1H n.m.r. spectra (phenyl resonances only) show the absence of any dialkyldithiocarbamate. In the i.r. spectrum the CN stretch of PhCN in the original sample is observed and bands characteristic of coordinated dithiophosphinates, such as ν_{PS_2}, can be distinguished.

Both these reactions involve a sulphur abstraction process. This may occur in at least two ways: either by ligand disproportionation (i.e. $2Ph_2P(S)H \rightarrow Ph_2Ph + Ph_2P(S)SH$) or by rearrangement of coordinated ligands. The first suggestion can be ruled out because model reactions show no short term rearrangement of $Ph_2P(S)H$ under the reaction conditions and in none of these reactions can products attributed to Ph_2PH, or its derivatives, be observed. Given the rearrangements already observed for diphenylphosphine sulphide and the more extreme conditions utilised, the isolation of dithiophosphinate complexes may be explained perhaps by considering initial S-coordination of the diphenylphosphine sulphide and subsequent nucleophilic P-attack on the coordinated sulphur of the partially displaced dithiobenzonate. It should be possible to model experiments in which any products of the decomposition of dithiobenzonate may be determined, but as those observations are very much a side line to the main topic, no further work has been undertaken.

2.7 Conclusion

It has been demonstrated that all three diphenylphosphine chalcogenides will react with platinum and palladium dithio compounds to produce isolatable air stable products under (relatively) mild conditions. More forcing conditions produce different products. The X-ray structural data give unambiguous information on the characterisation of two of these complexes and the remainder have been characterised by the standard techniques of elemental analysis, infra-red spectroscopy and multinuclear n.m.r. spectroscopy. A number of alternative synthetic routes have been found for the species (19)-(22) which act as a further check on the characterisation of these products. A number of supplementary studies such as ion exchange and deuteration have helped to tie up some of the outstanding problems, as have variable temperature n.m.r. studies.

2.7.1 A Possible Rationalisation of the Reaction of $M(S-S)_2$ with $Ph_2P(S)H$

In describing these reactions, certain patterns have become evident. In general palladium complexes and platinum dithiophosphinate complexes, in which oxidation to and the stabilisation of, the high valency (IV) state is unfavourable[56], yield binuclear products of the general type A (Scheme 2.1). This type of product is also formed when dilute solutions and equimolar reaction ratios are used.

It is probable therefore that, in these cases, the displacement of a coordinated dithio-acid ligand will take place to form an intermediate complex (I, II or III) or with concomitant dimerisation to form A. The process occurring *via* displacement (pathway *one*) may be superseded, or supplemented, by an oxidative addition pathway (*two*), in the platinum dithiocarbamate case, leading ultimately to similar intermediates. Such intermediates can dimerise as before, or react with a second phosphorus ligand to form (17). Also, in the dithiocarbamate case, HS_2CNR_2 breaks down to form CS_2 and NR_2H and hence probably $NR_2H_2[Ph_2PS]$ *in situ* which may then react. As A (22 a,b) has been shown to react further with, for example, $Ph_2P(O)H$, it is probable that in the platinum dithiocarbamate case, any A generated *in situ* will react further with excess ligand to form (17).

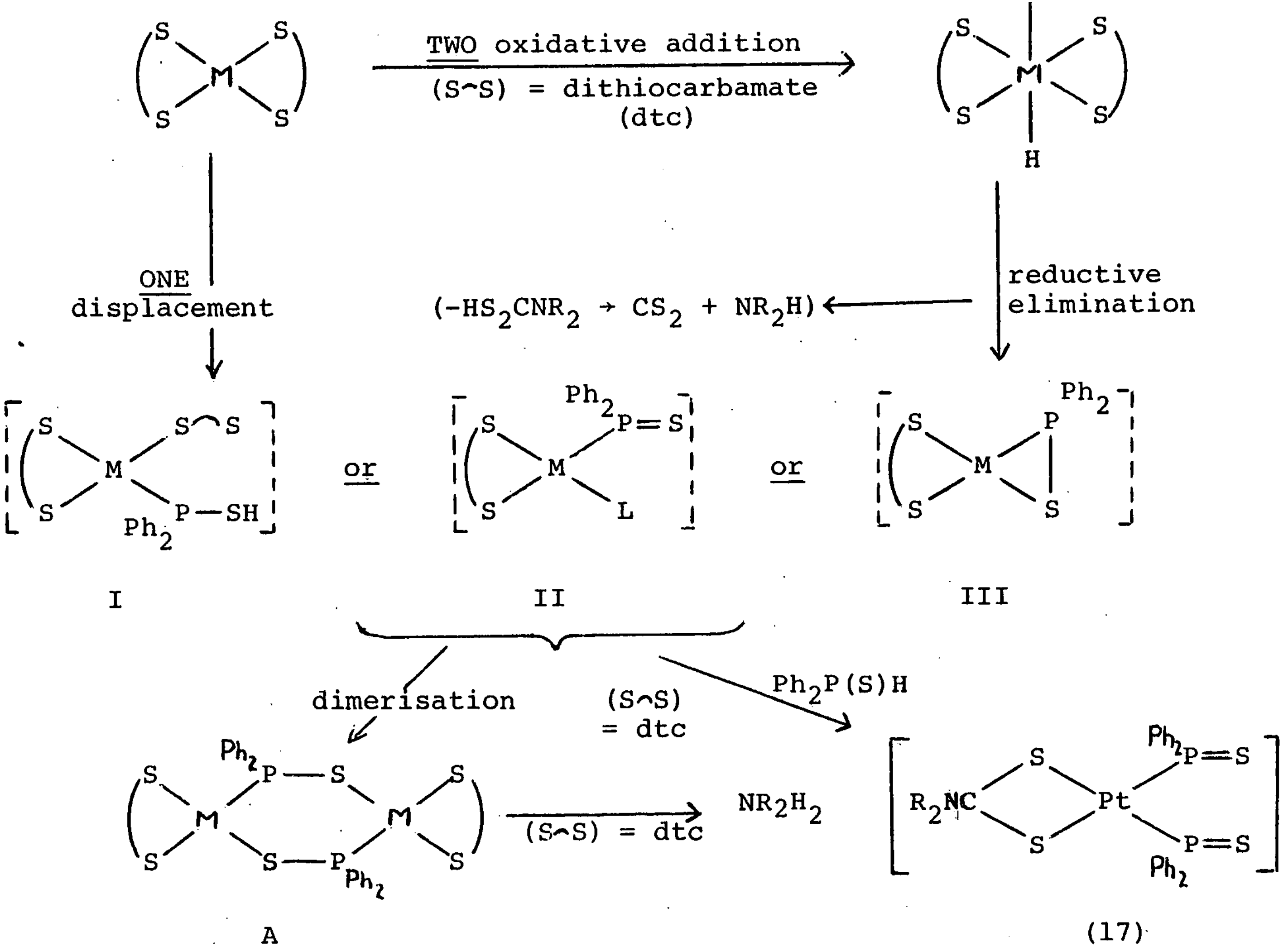
Altering the reaction conditions has been shown to produce different product ratios and significant quantities of complexes containing ligands which must be generated *in situ* (*e.g.* Ph_2POMe, $Ph_2P(O)H$ and Ph_2PH). Therefore, to determine the stability of $Ph_2P(S)H$, under the normal reaction conditions, and to examine the possibility of $Ph_2P(O)H$ formation two experiments were carried out. Thus, under stringently anhydrous conditions very little decomposition is observed when $Ph_2P(S)H$ is refluxed in methanol. (The reaction can be monitored by ^{31}P n.m.r.). The addition of H_2O to the solution produces observable amounts of $Ph_2P(O)H$ in short order, as does heating $Ph_2P(S)H$ for a short period in technical methanol. In both cases (anhydrous and "wet") Ph_2PH, Ph_2POMe or $Ph_2P(S)H$ are not observed <u>in situ</u>. It can be concluded therefore, that the presence of H_2O directly affects the amount of $Ph_2P(O)H$ formed (and thus the formation of complexes (19 a,b)).

In a second experiment $Ph_2P(S)H$ was deprotonated by NR_2H and the ammonium salt was isolated. However, it was not possible to show that this species may take part in the reaction pathway.

Although conversion of $[Pt(S_2CNR_2)(Ph_2PS)_2]^-$ (17) to $[Pt(S_2CNR_2)(Ph_2PS)]_2$ (22) has been achieved the reaction occurs in acidic media, conditions which do not hold in the main reaction. Therefore, it is unlikely that <u>A</u> are derived from compounds like (17) but possible that the reverse holds.

Under prolonged reaction times the methyl phosphinite product (21) has been isolated. The model experiment suggests that the methanolysis of a coordinated ligand must occur as no Ph_2POMe is formed when a metal complex is not present. The formation of small amounts of the secondary phosphine complexes (20) is more speculative. Attempts to generate these species by the direct removal of sulphur by treatment of (17) with Hg or PPh_3 lead to uncontrolled decomposition or substitution. It has been demonstrated that reaction of (17) and (22) with Ph_2PH under very mild conditions will give high yields of (20). It is also known that $Ph_2P(O)H$ will disproportionate to give Ph_2PH and $Ph_2P(O)OH$ under forcing conditions. It may be that $Ph_2P(S)H$ will behave similarly but Ph_2PH reacts rapidly with methanol. Therefore it is probable that abstraction of sulphur from a coordinated ligand does occur. Similar reactions (loss of S and Se to form coordinated Ph_2PH) have been observed previously[23b], but no mechanisms have been suggested. Certainly, after prolonged refluxing, decomposition does take place as unidentified peaks are observed in the $^{31}P-\{^1H\}$ n.m.r.

The observation of high yields of $Pt(S_2CNR_2)(Ph_2PSe)(Ph_2PH)$ from reaction of $Pt(S_2SNR_2)_2$ with $Ph_2P(Se)H$ could also be explained by postulating the transient formation of a species $[Pt(S_2CNR_2)(Ph_2PSe)_2]^-$



SCHEME 2.1 Possible route of formation of Pd(II) & Pt(II) diphenylphosphine sulphide complexes

followed by rapid Se loss and protonation by interaction with further $Ph_2P(Se)H$ or with NHR_2, H_2O or MeOH. The observation that this reaction and the foregoing proceed as well or better in the presence of trace amounts of H_2O suggests that this is an area where further investigation may yield more information on the processes occurring during the reaction.

Finally, it was noted in section 2.1.1 that the reaction with diphenylphosphine oxide yields only a single product under all conditions. A similar scheme can be proposed, involving reactive intermediates of the type noted, except that reaction of "$Pt(S\frown S)(Ph_2PO)$" with $Ph_2P(O)H$ produces only the very stable and methanol insoluble $Pt(S\cdot S)\{(Ph_2PO)_2H\}$.

2.8 Experimental

2.8.1 Techniques and Materials

Microanalyses were by the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the 250-4000 cm^{-1} region on Perkin-Elmer 457 and 557 grating spectrometers using nujol mulls on caesium iodide plates or 13 mm KBr pressed discs. Molecular weights were recorded in benzene on a Perkin-Elmer-Hitachi model 115 osmometer calibrated with benzil. Hydrogen-1-n.m.r. spectra were recorded on a Varian Associates HA-100 spectrometer equipped with a variable temperature probe and on a Bruker WH-360 spectrometer; proton noise decoupled phosphorus-31-n.m.r. spectra on a Jeol FX-60Q spectrometer operating in the pulse and Fourier Transform mode at 24.24 MHz (chemical shifts are reported in p.p.m. to high frequency of 85% H_3PO_4). Carbon-13-n.m.r. spectra (proton noise decoupled) on a Varian Associates CFT 20 spectrometer (^{13}C chemical shifts are quoted in p.p.m. to high frequency of $SiMe_4$) and platinum-195-n.m.r. Spectra on the Bruker WH 360 spectrometer (^{195}Pt chemical shifts are referenced to 77.068725 MHz, equivalent to 21.4 MHz when external $SiMe_4$ resonates at 100 MHz). Conductivity measurements were obtained on a Portland Electronics 310 conductivity bridge at 298 K. Melting points were determined with a Kofler hot-stage microscope and are uncorrected.

Palladium(II) chloride, potassium tetrachloroplatinate(II) (Johnson Matthey PLC), sodium diethyldithiocarbamate (BDH Chem.), diphenylphosphinous chloride (Aldrich) and diphenylphosphine (Maybridge Chem.) were obtained as indicated. All other materials were prepared by standard methods. These include $Na[S_2CN^iPr_2]_2.2H_2O$,[57] $Na[S_2CNEt_2].2H_2O$,[57] HS_2PPh_2[57] and all $M(S^\frown S)_2$ complexes. CSe_2, $NEt_2H_2[SeCNEt_2]$ and hence $Pt(SeCNEt_2)_2$ were all prepared by the method of Fackler _et al_[55]. Modified syntheses are noted in full subsequently. Phosphorus-31-{^{1}H} and ^{1}H n.m.r. data for these complexes are collected in Tables 2.1 and 2.2. Reactions were carried out under nitrogen in degassed analar methanol (freshly distilled from magnesium turnings), dry degassed chloroform, ethanol or degassed technical grade methanol using standard Schlenk techniques for work-up and isolation. Volatile gases were handled on a pyrex vacuum line using standard techniques further described in Chapter 5.

2.8.2 Crystal Structure Determination of $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (17a)

Crystal data $C_{33}H_{42}N_2P_2PtS_4$, M = 850, clear yellow orthorhombic plates; $a = 21.098(18)$, $b = 11.679(8)$, $c = 14.816(18)$ Å, $U = 3650.7$ Å^3, $Z = 4$, $D_c = 1.546$ g cm^{-3}, space group $P2_12_12_1$ (No. 19) MoK$_\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 43.74$ cm^{-1}. Intensity data were measured using a Stoe Stadi-2 diffractometer. A crystal of dimensions 0.08 x 0.2 x 0.28 mm (rotation axis) was used to record layers hk0 through hk15 with $2\theta_{max} = 50^o$ in the w. scan mode. 1480 unique reflections had $I > 3\sigma(I)$ and an empirical absorption correction was applied[58].

The MULTAN-77 system[59] was used to locate the Pt atom and its four square planar coordinated atoms. Subsequent full matrix least squares refinement and interpretation of difference Fourier maps using SHELX[60] enabled all non-hydrogen atoms in the structure to be located. Positional and anisotropic vibrational parameters for the Pt, S and P atoms were refined. For all other non-hydrogen atoms only the positional and isotropic vibrational parameters were varied. The phenyl rings were constrained to be planar with all C-C distances 1.395 Å. In the final cycles of full matrix least squares refinement a number of bond lengths between carbon and nitrogen atoms were restrained with a low weight to their expected values (Table2.4). A unit weighting scheme was found to give satisfactory variances of $|F|$ analysed in ranges of $|F|$. In the last cycle of refinement no shifts were greater than 0.1 times the estimated standard deviation, and the final R was 0.064. Fractional coordinates of atoms and observed bond distances and angles are given in Tables 2.3 and 2.4.

2.8.3. Crystal Structure Determination of $[\{Pt(S_2CN^iPr_2)(Ph_2PS)\}_2]2CDCl_3$ (6b)

Crystal data. $C_{40}H_{48}N_2P_2Pt_2S_6.2CDCl_3$, M = 1378, clear yellow monoclinic plates; a = 12.192(7), b = 9.272(6), c = 24.958(15) Å, β = 116.232(28)°, U = 2531 Å^3, Z = 2, D_c = 1.81 g cm^{-3}, space group $P2_{1/c}$ (No. 14), MoK_α radiation, λ = 0.71069 Å, μ = 63.9 cm^{-1}. After preliminary photography, intensity data were measured on a Stoe Stadi-2 diffractometer. A crystal of dimensions 0.28 x 0.28 x 0.15 mm was used to record layers h0l through h10ℓ with $2\theta_{max}$ = 50°. Of 4453 unique reflections, 3126 had I > 2σ(I) based on counting statistics. An empirical absorption correction was applied[58].

The position of the Pt atom was determined from a Patterson map. Subsequent difference Fourier syntheses revealed all non-hydrogen atoms in the molecule. Structure refinement was carried out using SHELX[60]. The phenyl rings were constrained to be planar with all C-C distances 1.395 Å. In the final cycles of least squares refinement Pt, P, S and Cl were given anisotropic vibration parameters. No hydrogen atoms were included. A unit weighting scheme was found to give satisfactory variances of |F| analysed in ranges of sinθ and |F|. The final R factor was 0.064 based on 3126 reflections. Fractional coordinates of atoms and of observed bond distances and angles are given in Tables 2.5 and 2.6.

2.8.4. Complexes

Diphenylphosphine oxide

Method A Diphenylphosphine (2.0 g) was dissolved in diethylether (20 cm^3) and air was passed through the solution for 4 h. Diphenylphosphine oxide separated as an oil, which was crystallised by shaking with a 50:50 diethylether petroleum ether (bp 40-60^{o}C) solution (100 cm^3). The product was collected, dried in vacuo and stored under N_2 (Yield 1.41 g; 65%) see Table 1.1 (Chapter 1) for spectral data.

Method B Diphenylphosphinous chloride was shaken in a technical methanol-H_2O mixture (20:1 ratio). A $^{31}P-\{^{1}H\}$ n.m.r. spectrum confirmed the formation of diphenylphosphine oxide. The solution was pumped down and the resultant oil was extracted with chloroform, dried over $MgSO_4$ and titrated with petroleum ether (bp 40-60^{o}C) to give the product.

Diphenylphosphine sulphide

Diphenylphosphine (11.5 g) was dissolved in degassed carbon tetrachloride (20 cm^3). Sulphur (1.98 g) was added carefully and the suspension was stirred until a clear solution was obtained. On cooling, diphenylphosphine sulphide precipitates out, and complete precipitation is achieved by adding petroleum ether (bp 40-60^{o}C) (100 cm^3) and cooling the solution in an ice-salt bath. The product is filtered under nitrogen, dried in vacuo and stored under nitrogen (Yield 11.0 g; 82%).

Diphenylphosphine selenide

The method is identical to that described above using Ph_2PH and selenium. Typical yields of 50-65% are achieved.

Diethylammonium diphenylphosphine sulphide

The compound $Ph_2P(S)H$ (0.42 g 2.0 mmol) was suspended in degassed dry methanol (20 cm^3) and diethylamine (1 cm^3). The solution was stirred for 5 h until the phosphine sulphide had completely dissolved. Removal of most of the solvent and addition of 50 cm^3 of a cooled solution of 50:50 diethylether/petrol ether precipitated the microcrystalline white product (0.47 g 80%).
Soln. ($CHCl_3$) I.r. spectrum:- $\nu_{NH_2^+}$ 2260, 2460 cm^{-1}; ν_{PS} 620 cm^{-1}.

Diphenylphosphine oxide (diphenylphosphinous acid)(N,N'-diethyldithiocarbamato)platinum(II)

Method A The compound $Pt(S_2CNEt_2)_2$ (0.14 g; 0.30 mmol) was suspended in technical methanol (30 cm^3) and shaken for 6 h with a threefold excess of $Ph_2P(O)H$ (0.20 g, 1.0 mmol). The product was precipitated as a white solid which was filtered, washed with ethanol and diethylether and dried *in vacuo*. The product can readily be crystallised from chloroform/diethylether. mp 242-244°C (Yield 0.13 g; 60%).
Found:-C, 46.7; H, 4.2; N, 1.8 Calc for $C_{29}H_{31}NO_2P_2PtS_2$:- C, 46.7; H, 4.2; N, 1.9%.
Mull i.r. spectrum:- ν_{CN} 1530 cm^{-1}; ν_{PO} 1020 cm^{-1}

Method B The compound $Pt(S_2CNEt_2)_2$ (0.31 g; 0.64 mmol) was shaken with excess Ph_2PCl (0.50 cm^3) in technical grade methanol (50 cm^3) until all the yellow starting material had been replaced by the white microcrystalline product. Work-up is as above (Yield 0.18 g; 85%).

Diphenylphosphine oxide (diphenylphosphinous acid)(N,N'-diethyldithiocarbamato)platinum(II)

$Pt(S_2CN^iPr_2)\{(Ph_2PO)_2H\}$ was similarly prepared by either method mp 289-292°C. Found:-C, 46.5; H, 4.4; N, 1.6 Calc for $C_{31}H_{35}NO_2P_2PtS_2$:- C, 48.1; H, 4.5; N, 1.8%.
Mull i.r. spectrum:- ν_{CN} 1510 cm^{-1}; ν_{PO} 1020 cm^{-1}.

Diphenylphosphine oxide (diphenylphosphinous acid)(diphenyldithiophosphinato)palladium(II)

Method B was used to prepare $Pd(S_2PPh_2)(\{Ph_2PO\}_2H)$, by either method, to confirm that the method would apply to both dittiophosphinates and to palladium complexes. Both methods give high (63 and 74% respectively) yields of the orange product. mp 175-177°C. Found C, 55.8; H, 3.9 Calc for $C_{36}H_{31}O_2P_3PdS_2$:- C, 57.0; H, 4.1%.
Mull i.r. spectrum:- ν_{PS_2} 620, 580 cm^{-1}; ν_{PO} 1010 cm^{-1}.

Di-isopropylammonium[(bisdiphenylphosphinesulphido)(N,N'-diisopropyldithiocarbamato)platinate(II)]

The complex $Pt(S_2CN^iPr_2)_2$ (0.95 g; 1.70 mmol) was refluxed in degassed, dried, analar methanol (50 cm^3) with an excess of diphenylphosphinesulphide (1.40 g; 6.40 mmol). After 12 h, the white product was filtered off, the yellow filtrate concentrated to ca. one quarter of its original volume and diethylether (20 cm^3) added to precipitate the bulk of the product as a white microcrystalline solid. The products were combined, recrystallised from chloroform/diethylether, washed with more diethylether and dried *in vacuo* mp 156-159°C (yield 0.82 g; 51%) Found C, 49.3; H, 5.5; N, 3.0 Calc for $C_{37}H_{50}N_2P_2PtS_4$:- C, 49.0; H, 5.5;

N, 3.1%.

Mull i.r. spectrum:- ν_{NH} 2670; δ_{NH} 1586; ν_{CN}(dtc) 1495; ν_{PS} 600 cm^{-1}. $\Lambda(2.2 \times 10^{-3}$ mol dm^{-3} in MeOH) 36.2 Scm^2 mol^{-1} $\Lambda(1 \times 10^{-2}$ mol dm^{-3} in $(CH_3)_2CO)$ 7.6 Scm^2 mol^{-1}.

$^{13}C-\{^1H\}$n.m.r. in $CDCl_3$ at 301 K:- δ19.5(s) $[^-S_2CN(CH\underline{Me}_2)_2]$, 20.0(s) $[NH_2(CH\underline{Me}_2)_2^+]$; 47.5(s) $[NH_2(C\underline{H}Me_2)_2^+]$; 50.5(s) $[^-S_2CN(C\underline{H}Me_2)_2]$ 126.3-139.7(m) $(P\underline{h}_2PS^-)$, 205.2(br) ppm $[^-S_2\underline{CN}(CHMe_2)_2]$ (no PtC coupling observed).

$^{13}C-\{^1H\}$n.m.r. in $CDCl_3$ at 214 K:- δ18.7(s), 19.5(s) [ca. 1:3 intensity, suggesting two $^-S_2CN(CH\underline{Me}_2)_2$ with $^+NH_2(CH\underline{Me}_2)_2$ superimposed on higher frequency resonance], 46.9(s) $[NH_2(C\underline{H}Me_2)_2^+]$, 49.7(s), 50.9(s) [equal intensity, $^-S_2CN(C\underline{H}Me_2)_2]$, 125.0-138.0(m) (Ph_2PS^-), 203.0 ppm (1,4,1 triplet, $^2J_{PtC}$ ca. 73 Hz) $[^-S_2\underline{CN}(CHMe_2)_2]$.

Diethylammonium[(bisdiphenylphosphinesulphido)(N,N'-diethyldithiocarbamato)platinate(II)] (17a) was similarly prepared from $Pt(S_2CNEt_2)_2$ and $Ph_2P(S)H$ mp 164-166°C (yield 30-40%) Found:-C, 46.7; H, 4.9; N, 3.1, Calc. for $C_{33}H_{42}N_2P_2PtS_4$:- C, 46.6; H, 4.9; N, 3.3%.

Mull i.r. spectrum:- ν_{NH} 2660; δ_{NH} 1588; ν_{CN}(dtc) 1510; ν_{PS} 600 cm^{-1}, $\Lambda(2.4 \times 10^{-3}$ mol dm^{-3} in MeOH) 50.0 Scm^2 mol^{-1}.

$^{13}C-\{^1H\}$n.m.r. in $CDCl_3$ at 301 K:- δ10.5(s) $[^-S_2CN(CH_2\underline{CH}_3)_2]$, 12.1(s) $[NH_2(CH_2C\underline{H}_3)_2^+]$; 39.5(s) $[NH_2(C\underline{H}_2CH_3)_2^+]$, 43.5(s) $[^-S_2CN(\underline{CH}_2CH_3)_2]$; 125.1-139.4(m) $(\underline{Ph}_2PS^-)$; 205.4 ppm (1,4,1 triplet; $^2J_{PtC}$ 78.5 Hz) $[^-S_2\underline{CN}(CH_2CH_3)_2]$.

$^{195}Pt-\{^1H\}$n.m.r. in $CDCl_3$ at 301 K:- δ116.7(t) ppm ($^1J_{PtP}$ 3428 Hz).

Caesium[(bisdiphenylphosphinesulphido)(N,N'-diisopropyldithiocarbamato)platinate(II)] (17c):- The compound $N^iPr_2H_2[Pt(S_2CN^iPr_2)(Ph_2PS)_2]$ (0.23 g; 0.27 mmol) was refluxed in Analar methanol (20 cm^3) with an excess of CsCl (0.20 g; 1.20 mmol) for 1 hour. Addition of degassed water (20 cm^3) to the cooled solution then precipitated the product as a sticky white solid. After washing with methanol, this was dissolved in a minimum amount of $CHCl_3$ and triturated with more methanol to give the product as a white microcrystalline solid mp 248-251°C (decomp) (0.17 g, 66%) Found:-C, 38.8; H, 3.6; N, 1.3; Calc. for $C_{31}H_{34}CsNP_2PtS_4$;- C, 39.7; H, 3.6; N, 1.5%. This compound was too insoluble for solution studies.

Mull i.r. spectrum:- ν_{CN} 1500; ν_{PS} 600 cm^{-1}.

Triphenylbenzylphosphonium[(bisdiphenylphosphinesulphido)(N,N diethyldithiocarbamato)platinate(II)] (17d):- The compound $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (0.115 g; 0.135 mmol) was refluxed in analar methanol (30 cm^3) with a three-fold excess of $[Ph_3(PhCH_2)P]Cl$ (0.16 g; 0.40 mmol) for 3 hours. The solution was filtered hot and degassed water (20 cm^3) was added to give a sticky pale yellow solid. This was washed several times with methanol, then dissolved in CH_2Cl_2 (1 cm^3) and reprecipitated by addition of methanol (20 cm^3) to give an off white solid (0.035 g; 23%) Found;-C, 57.1; H, 4.6; N, 1.2; Calc. for $C_{54}H_{52}NP_3PtS_4$:- C, 57.4; H, 4.6; N, 1.2%, Λ(3.5 x 10^{-3} mol dm^{-3} in CH_3OH) 92.5 S cm^2 mol^{-1}.

Mull i.r. spectrum:- ν_{CN} 1510; ν_{PS} 600 cm^{-1}.

Diphenylphosphinesulphido(diphenylphosphinous acid) (N,N'-diethyldithiocarbamato)platinum(II) (19a):- The complex

$Pt(S_2CNEt_2)_2$ (0.71 g; 1.50 mmol) was refluxed in degassed technical grade methanol (30 cm^3) with $Ph_2P(S)H$ (0.87 g; 4.00 mmol) for 12 h. Careful trituration of the solution with diethyl ether/petroleum ether (bp 40-60°C) (1:1 v/v), then gave a precipitate of $Et_2NH_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (0.45 g; 35%). Removal of solvent from the filtrate, dissolution in chloroform and addition of diethyl ether gave the product as an amorphous pale yellow solid.

The same compound was prepared by direct reaction of $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ with $Ph_2P(O)H$ (1:1 molar ratio) in $CDCl_3$. After heating to 60°C for 5 m and then leaving for 30 m, the ^{31}P-{^1H} n.m.r. spectrum showed that considerable amounts of (19a) had been generated together with free $Ph_2P(S)H$.

Diphenylphosphinesulphido(diphenylphosphinous acid) (N,N'-di-isopropyldithiocarbamato)platinum(II) (19b):- The complex $Pt(S_2CN^iPr_2)_2$ (0.55 g; 1.00 mmol) was refluxed in degassed technical-grade methanol (30 cm^3) with $Ph_2P(S)H$ (0.76 g; 3.00 mmol) for 12 h. After filtering off the white solid, $N^iPr_2H_2[Pt(S_2CN^iPr_2)(Ph_2PS)_2]$ (0.27 g; 30%), the yellow solution was concentrated and then triturated with diethylether to give an amorphous pale yellow solid. This was washed with more diethylether and dried in vacuo mp 175-178°C (0.16 g; 20%) Found:-C, 47.1; H, 4.5; N, 1.7; Calc. for $C_{31}H_{35}NOP_2PtS_3$:- C, 47.1; H, 4.5; N, 1.8%.
Mull i.r. spectrum:- ν(PO-H) 2190; $\nu_{(CN)}$ 1500; ν(P-OH) 905; $\nu_{(PS)}$ 600 cm^{-1}

Caesium[Diphenylphosphinesulphido(diphenylphosphineoxido)(N,N'-diisopropyldithiocarbamato)platinate(II)]diaqua solvate (19d):- The complex Pt($S_2CN^iPr_2$)($Ph_2PSHOPPh_2$) (0.25 g; 0.31 mmol) was refluxed in technical methanol (20 cm^3) and Et_3N (1 cm^3) for 1 hour. An aqueous solution of excess CsCl was then added to the cooled solution and a small amount of sticky yellow solid was filtered off. The solution was then concentrated to precipitate the white product mp 271-275°C (0.16 g; 55%) Found:- C, 39.2; H, 4.0; N, 1.5. Calc. for $C_{31}H_{38}CsNO_3P_2PtS_3$:- C, 38.8; H, 4.0; N, 1.5%.
Mull i.r. spectrum:- ν_{CN} 1500; ν_{PO} 1050; ν_{PS} 600 cm^{-1}.

Diphenylphosphinesulphido(diphenylphosphine)(N,N'-diisopropyldithiocarbamato)platinum(II) (20b)

Method A The complex $N^iPr_2H_2$[Pt($S_2CN^iPr_2$)(Ph_2PS)$_2$] (0.07 g; 0.15 mmol) was dissolved in a minimum amount of degassed chloroform (5.0 cm^3) and treated with an excess of Ph_2PH (0.10 cm^3) in degassed benzene (1.0 cm^3). After stirring for 2 h at ambient temperature, the product had precipitated as a white microcrystalline solid which was washed with diethylether and dried in vacuo mp 190-192°C (0.09 g; 80%) Found:- C, 48.1; H, 4.5; N, 2.0; M(C_6H_6, osmometrically) 730. Calc. for $C_{31}H_{35}NP_2PtS_3$:- C, 48.1; H, 4.5; N, 1.8% M 774.
Mull i.r. spectrum:- ν_{CN} 1505; ν_{PS} 600 cm^{-1} [ν_{PH}(KBr disc) 2350 cm^{-1}].

Method B The compound Pt($S_2CN^iPr_2$)$_2$ (0.52 g; 1.00 mmol) was refluxed with an excess of $Ph_2P(S)H$ (0.70 g; 3.20 mmol) in dry degassed methanol (50 cm^3) to which D_2O (1 cm^3) had been added. After 24 h, a small amount of the white product was filtered off (0.17 g; 22%). The pale yellow filtrate was examined by $^{31}P-\{^1H\}$ n.m.r. spectroscopy and shown to consist of a mixture of $Pt(S_2CN^iPr_2)(\{Ph_2PO\}_2H)$ (2), $Pt(S_2CN^iPr_2)(Ph_2POHSPPh_2)$ (19b), $Pt(S_2CN^iPr_2)(Ph_2PS)(Ph_2PH$ (20b) and unreacted $Ph_2P(S)H$.

In fact, small amounts of $Pt(S_2CN^iPr_2)(Ph_2PS)(Ph_2PH)$ have been observed (by $^{31}P-\{^1H\}$ n.m.r. spectroscopy) in virtually every reaction between $Pt(S_2CN^iPr_2)_2$ and $Ph_2P(S)H$.

Diphenylphosphinesulphido(methyldiphenylphosphinite)(N,N'-di-isopropyldithiocarbamato)platinum(II) (21):- The compound $Pt(S_2CN^iPr_2)_2$ (0.55 g; 1.00 mmol) was refluxed in degassed, dried Analar methanol (30 cm^3) with diphenylphosphinesulphide (0.76 g; 3.50 mmol) for a prolonged period (36 h). The cloudy pale yellow solution was then filtered and, on cooling, a pale yellow solid was precipitated. This was redissolved by refluxing (in methanol (20 cm^3)) for 30 m and then refiltered. After cooling and triturating with diethyl ether, the product was obtained as a creamy white microcrystalline solid which was washed with ethanol and diethyl ether and dried in vacuo mp 187-189°C (0.36 g; 45%) Found:-C, 47.8; H, 4.6; N, 1.8; M(C_6H_6, osmometrically) 795; Calc for $C_{32}H_{37}NOP_2PtS_3$:- C, 47.8; H, 4.6; N, 1.7%, M, 804. Mull i.r. spectrum:- ν_{CN} 1505; $\nu_{(P-OC)}$ 1040; ν_{PS} 600 cm^{-1}. The same compound was readily formed in high yield (n.m.r. studies) by direct reaction of $N^iPr_2H_2[Pt(S_2CN^iPr_2)(Ph_2PS)_2]$ with $Ph_2P(OMe)$ in $CDCl_3$ at ambient temperature.

Bis[(μ-diphenylphosphinesulphido)(N,N'-diethyldithiocarbamato)-platinum(II)] (22a)

Method A The complex $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (0.38 g;

0.45 mmol) was dissolved in degassed, dry chloroform (5 cm^3) and treated with an excess of concentrated dry ethanolic HCl (0.50 cm^3) and stirred at ambient temperature for 24 h. Further ethanol (5 cm^3) was then added to complete the precipitation of the pale yellow product which was washed with ethanol, cold diethylether/petroleum ether (bp 40-60°C) (1:1 v/v) and dried *in vacuo* mp 237°C (decomp) (0.21 g; 84%) Found:- C, 36.2; H, 3.7; N, 2.6; Calc. for $C_{34}H_{20}N_2Pt_2S_6$:- C, 36.4; H, 3.6; N, 2.5%.
Mull i.r. spectrum:- ν_{CN} 1516, ν_{PS} 580 cm^{-1}. The same compound could be made by reaction of $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ with an excess of gaseous HCl in $CHCl_3$. After leaving for 1 hour at ambient temperature the bright yellow solution was treated with diethylether/petroleum ether (bp 40-60°C) (1:1 v/v) to give the yellow product (quantitative yield).

Method B The complex $Pt(S_2CNEt_2)_2$ (0.29 g; 0.60 mmol) was refluxed in degassed dry ethanol (30 cm^3) for 6 hours with an equimolar amount of $Ph_2P(S)H$ (0.13 g; 0.60 mmol). The bright yellow solution was evaporated to dryness and the residue shaken with diethylether. After concentration of the diethylether solution and leaving for 24 hours, a small amount of yellow crystalline product was obtained (0.034 g; 10%).

$^{195}Pt-\{^1H\}$ n.m.r. spectrum in $CDCl_3$ at 301 K:- $\delta Pt_X\ Pt_{X'}$, 368.4 ppm; $^1J_{Pt_XP_a}$ 3652.3 Hz, $^2J_{Pt_XP_{a'}}$, 80.6 Hz, $^3J_{Pt_XPt_{X'}}$ could not be measured.

Bis[(μ-diphenylphosphinesulphido)(N,N'-di-isopropyldithiocarbamato)platinum(II)] (22b):- The compound $N^iPr_2H_2[Pt(S_2CN^iPr)_2(Ph_2PS)_2]$ (0.50 g, 0.50 mmol) was treated with an excess of concentrated dry, ethanolic HCl (0.50 cm^3) in degassed, dry $CHCl_3$ (5 cm^3) at ambient temperature for 12 hr. Addition of ethanol then precipitated the pale yellow solid which was washed with ethanol and dried in vacuo mp 283°C (decomp) (0.21 g; 68%) Found: C, 39.0; H, 4.2; N, 2.2;M(C_6H_6 osmometrically) 1305; Calc for $C_{38}H_{48}N_2P_2Pt_2S_6$:- C, 38.8; H, 4.1; N, 2.4%;M, 1176. Mull i.r. spectrum:- ν_{CN} 1500; ν_{PS} 580 cm^{-1}.

Recrystallisation from $CDCl_3$ gave crystals containing two $CDCl_3$ of solvation which were suitable for X-ray analysis.

Bis[(μ-diphenylphosphinesulphido)(N,N'-diethyldithiocarbamato)-palladium(II)] (23):- The compound $Pd(S_2CNEt_2)_2$ (0.60 g; 1.50 mmol) was refluxed in degassed dry Analar methanol (30 cm^{-1}) with an excess of $Ph_2P(S)H$ (0.98 g; 4.50 mmol) for two hours. The deep orange microcrystalline solid was filtered off and washed with diethylether and dried in vacuo mp 193-195°C (0.42 g; 60%) Found:-C, 43.3; H, 4.3; N, 2.9; M(C_6H_6 osmometrically) 932, Calc for $C_{34}H_{40}N_2P_2Pd_2S_6$:- C, 43.3; H, 4.3; N, 3.0%; M 942.
Mull i.r. spectrum:- ν_{CN} 1510; ν_{PS} 585 cm^{-1}.
Treatment of the yellow filtrate with diethylether (50 cm^3) and subsequent cooling for 6 h gave the yellow crystalline solid diethylammonium[(bis diphenylphosphinesulphido)(N,N'-diethyldithiocarbamato)palladate(II)] (24) which was washed with cold diethylether and dried in vacuo mp 130-132°C

(0.21 g; 18%) Found:- C, 51.2; H, 5.5; H, 3.4; Calc for $C_{24}H_{42}N_2P_2PdS_4$:- C, 52.7; H, 5.4; N, 3.6%.
Mull i.r. spectrum:- ν_{NH} 2645; δ_{NH} 1590; ν_{CN}(dtc) 1510; ν_{PS} 600 cm^{-1}

Diphenylphosphineselenido(diphenylphosphine)(N,N'-diethyldithiocarbamato)platinum(II) (26a):- The compound $Pt(S_2CNEt_2)_2$ (0.31 g; 0.64 mmol) was refluxed in degassed dried Analar methanol (30 cm^3) with diphenylphosphineselenide (0.50 g; 1.90 mmol) for eight hours. The microcrystalline pale yellow precipitate was filtered off, washed with methanol and diethylether and dried in vacuo mp 198-200°C (decomp) (0.44 g; 84%) Found: C, 43.2; H, 3.9; N, 1.8; M(C_6H_6, osmometrically) 632. Calc for $C_{29}H_{31}NP_2PtS_2Se$:- C, 43.0; H, 3.8; N, 1.7%; M, 791.
Mull i.r. spectrum:- ν_{PH} 2320; ν_{CN} 1500; ν_{PSe} 520 cm^{-1}.

Diphenylphosphineselenido(diphenylphosphine)(N,N'-diisopropyldithiocarbamato)platinum(II) (26b):- The compound $Pt(S_2CN^iPr_2)_2$ (0.58 g; 1.10 mmol) and $Ph_2P(Se)H$ (1.14 g; 4.30 mmol) were refluxed as above to give the microcrystalline pale yellow product mp 216-217°C (0.76 g; 86%) Found:-C, 44.6; H, 4.3; N, 1.6; M(C_6H_6 osmometrically) 796, Calc for $C_{31}H_{35}NP_2PtS_2Se$:- C, 44.4; H, 4.2; N, 1.7%; M, 820.
Mull i.r. spectrum:- ν_{PH} 2340; ν_{CN} 1500; ν_{PSe} 520 cm^{-1}.

Bis[(μ-diphenylphosphinesulphide)(diethyldithiophosphato)platinum(n)] (27):- The compound $Pt(S_2P(OEt)_2)_2$ (0.12 g; 0.20 mmol) and $Ph_2P(S)H$ (0.17 g; 0.80 mmol) were dissolved in degassed dry analar methanol (30 cm^3) and refluxed together for 1 hr. A pale yellow solid precipitated on cooling the reaction solution. The solid was filtered off washed with methanol and diethylether and dried in *vacuo* mp 211-213°C (0.11 g; 90%). Found:-C, 32.4; H, 3.3. Calc for $C_{32}H_{40}O_4P_4Pt_2S_6$:- C, 32.2; H, 3.4%.

Mull i.r. spectrum:- ν_{PS_2} 630, 587; ν_{PS} 570 cm^{-1}.

This method was also used to synthesise bis[(μ-diphenylphosphinesulphide)(diethyldithiophosphato)palladium(II)] (29) mp 288-290°C (0.25 g; 82%) Found:-C, 37.9; H, 3.9. Calc for $C_{32}H_{40}O_4P_4Pd_2S_6$:- C, 37.8; H, 3.9%.

Mull i.r. spectrum:- $_{PS_2}$ 630, 580; $_{PS}$ 570 cm^{-1}; and bis[(μ-diphenylphosphinesulphide)(diphenyldithiophosphinato)-palladium(II)] (28) mp 272-275°C (0.18 g; 48%) Found: C, 49.8; H, 3.5. Calc for $C_{48}H_{40}P_4Pd_2S_6$:- C, 50.4; H, 3.5%.

Mull i.r. spectrum:- ν_{PS_2} 605, 568; ν_{PS} 580 cm^{-1}.

Diphenylphosphinesulphido(diphenylphosphinous acid)(diphenyldithiophosphinato)platinum(II) (30):- The compound $Pt(S_2PPh_2)_2$ (0.33 g; 0.50 mmol) was refluxed for 5 h with excess $Ph_2P(S)H$ (0.62 g; 2.80 mmol) in degassed dry analar methanol (30 cm^3). A yellow solid was recovered, washed with ethanol and diethylether and dried *in vacuo* (0.28 g; 65%) Found:-C, 47.4; H, 3.5. Calc for $C_{36}H_{31}O_1P_3Pt_1S_3$:- C, 50.1; H, 3.6%.

Mull i.r. spectrum:- ν(PO-H---S) 2210; ν_{PO} 910; ν_{PS_2} 610, 580 cm^{-1}).

Diphenylphosphineselenido(diphenylphosphino)(diphenyldithiophosphinato)platinum(II) (32)

The compound $Pt(S_2PPh_2)_2$ (0.80 g; 1.2 mmol) and an excess of $Ph_2P(Se)H$ (0.90 g; 3.41 mmol) were refluxed in degassed dry analar methanol (30 cm^3) for 6 h. The dark orange precipitate was filtered off, washed with methanol and diethylether and dried <u>in vacuo</u> mp 278-281°C (0.77 g; 72%).

<u>Mull i.r. spectrum</u>:- ν_{PH} 2330; ν_{PSe} 515 cm^{-1}.

<u>Bis(diphenyldithiophosphinato)palladium(II) (33)</u>

The compound $Pd(S_2CPh)_2$ (0.21 g; 0.50 mmol) was refluxed in dry degassed PhCN (30 cm^3) with an excess of $Ph_2P(S)H$ (0.5 g; 1.4 mmol) for 4 h. Dark red crystals of the <u>product</u> precipitated from the reaction solution as it cooled. These were collected washed with ethanol and then diethylether and dried <u>in vacuo</u> mp 332-333°C Found:- C, 47.7; H, 3.3 Calc for $C_{24}H_{20}P_2PdS_4$:- C, 47.7; H, 3.3%.

<u>Mull i.r. spectrum</u>:- ν_{PS_2} 600, 570, 485 cm^{-1}.

In addition the complex $Pd(S_2CN^iPr_2)_2$ (0.28 g; 0.62 mmol) was treated as above. The bright yellow solution formed after four hours was cooled. Trituration of the solution with diethylether yielded a pale yellow powder. This was dissolved in chloroform, which was slowly evaporated to give the yellow product mp 224-6°C (decomp) (Yield 0.09 g) Found C, 50.4; H, 3.6; N, 1.1. Calc for $C_{55}H_{45}N_1P_4Pd_2S_8$:- C, 50.3; H, 3.4; N, 1.1%.

TABLE 2.1a Phosphorus-31-{^1H}-n.m.r. Data for Various Platinum(II) and Palladium(II) Complexes in $CDCl_3$ at 301 K (unles otherwise stated)

	Complex	δ_{P_a}	$^1J_{PtP_a}$ (Hz)	δ_{P_b}	$^1J_{PtP_b}$ (Hz)	$^2J_{P_aP_b}$ (
17b	$N^iPr_2H_2[Pt(S_2CN^iPr_2)(Ph_2P_aS)_2]$[a]	28.2(t)	3413.1	-	-	-
	$Ph_3(PhCH_2)P_b[Pt(S_2CN^iPr_2)(Ph_2P_aS)_2]$	29.1(t)	3486.3	22.9(s)	-	-
17a	$NEt_2H_2[Pt(S_2CNEt_2)(Ph_2P_aS)_2]$	27.3(t)	3427.3	-	-	-
	$Ph_3(PhCH_2)P_b[Pt(S_2CNEt_2)(Ph_2P_aS)_2]$	27.4(t)	3530.0	22.1(s)	-	-
19b	$[Pt(S_2CN^iPr_2)(Ph_2P_bOHSP_aPh_2)]$[b]	31.6(t.d)	3129.8	66.4(t.d)	3715.8	29.3
19a	$[Pt(S_2CNEt_2)(Ph_2P_bOHSP_aPh_2)]$	31.2(t.d)	3172.0	65.4(t.d)	3774.0	28.0
19c	$NEt_3H[Pt(S_2CN^iPr_2)(Ph_2P_bO)(Ph_2P_aS)]$[c]	33.5(t.d)	3449.7	50.8(t.d)	3847.7	27.0
21	$[Pt(S_2CN^iPr_2)(Ph_2P_bOMe)(Ph_2P_aS)]$	28.2(t.d)	3059.1	92.7(t.d)	4170.9	25.0
20b	$[Pt(S_2CN^iPr_2)(Ph_2P_bH)(Ph_2P_aS)]$	29.2(t.d)	2944.3	5.6(t.d)	3554.7	24.4
20a	$[Pt(S_2CNEt_2)(Ph_2P_bH)(Ph_2P_aS)]$					
26b	$[Pt(S_2CN^iPr_2)(Ph_2P_bH)(Ph_2P_aSe)]$	13.8(t.d)[d]	2871.6	7.5(t.d)	3540.4	22.8
26a	$[Pt(S_2CNEt_2)(Ph_2P_bH)(Ph_2P_aSe)]$	13.0(t.d)[e]	2902.8	8.1(t.d)	3601.0	21.8
26c	$[Pt(Se_2CNEt_2)(Ph_2P_bH)(Ph_2P_aSe)]$	13.1(t.d)[f]	2876.8	7.1(t.d)	3555.2	20.1
2a	$[Pt(S_2CN^iPr_2)(\{Ph_2P_aO\}_2H)]$	62.1(t)	3459.5	-	-	-
2b	$[Pt(S_2CNEt_2)(\{Ph_2P_aO\}_2H]$	61.4(t)	3570.7	-	-	-
24	$NEt_2H_2[Pd(S_2CNEt_2)(Ph_2P_aS)_2]$	50.2(s)	-	-	-	-
25	$[Pd(S_2CNEt_2)(Ph_2P_bOHSP_aPh_2)]$					
30	$[Pt(S_2P_cPh_2)(Ph_2P_bOHSP_aPh_2)]$[g]	34.2(t.dd)	3309.4	62.3(t.dd)	3982.0	22.0
31	$[Pt(S_2P_cPh_2)(Ph_2P_bH)(Ph_2P_aSe)]$[h]	18.2(t.dd)[i]	2924.8	7.3(t.dd)	3735.4	14.8
32	$Pd(S_2PPh_2)_2$	95.1	-	-	-	-
33	$[Pd(S_2PPh_2)_2 0.5PhCN]_n$	80.0	-	-	-	-

[a] At 210 K in CH_2Cl_2, central resonance at δ26.3 p.p.m. is AB pattern with δ_{AB} 21.7 Hz and J_{AB} 23.0 Hz.

[b] At 183 K in CH_2Cl_2, observe two sets of triplets of doublets

δ_{P_a}	$^1J_{PtP_a}$	δ_{P_b}	$^1J_{PtP_b}$	$^2J_{P_aP_b}$
31.4	3095.7	66.0	3665.7	29.5
30.9	3107.9	65.8	3642.3	29.5

[c] Generated *in situ* by addition of NEt_3 to $CDCl_3$ solution of $Pt(S_2CN^iPr_2)(Ph_2POHSPPh_2)$

[d] ^{77}Se satellites on major doublet; $^1J_{PSe}$ = 589.9 Hz

[e] ^{77}Se satellites on major doublet; $^1J_{PSe}$ = 590.7 Hz

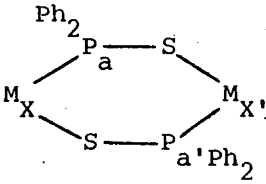
[f] ^{77}Se satellites on major doublet; $^1J_{PSe}$ = 588.2 Hz

[g] Chemical shift of $P_c(S_2P_cPh_2)$: 80.4 p.p.m. $^2J_{PtP_c}$ 201.0 $^3J_{P_{a/b}P_c}$ 8.5 Hz

[h] Chemical shift of $P_c(S_2P_cPh_2)$: 33.3 p.p.m. $^2J_{PtP_c}$ 286.1 Hz $^3J_{P_{a/b}P_c}$ 4.0 Hz

[i] ^{77}Se satellites on major doublet; $^1J_{PSe}$ = 594.7 Hz.

TABLE 2.1b Phosphorus-31{^{1}H}n.m.r. Data of [(S⌢S)M_X $M_{X'}$ (S⌢S)] Complexes in $CDCl_3$ at 301 K



M	(S⌢S)$^-$	R	$\delta P_a, P_{a'}$	$^1J_{Pt_XP_a}$	$^2J_{Pt_XP_{a'}}$	$^3J_{P_aP_{a'}}$	$^3J_{Pt_XPt_{X'}}$	$\delta P_bP_{b'}$	$^3J_{P_aP_b}$
Pt	$(S_2CNR_2)^-$	Et (22a)	30.5	3656.4	80.5	13.6	940	-	-
	"	^{1}Pr (22b)	31.3	3604.9	78.2	12.2	1000	-	-
Pd	"	Et (23)	53.9	-	-	-	-	-	-
Pt	$(S_2P_b(OEt)_2)^-$	- (27)^a	30.3	3836.9	88.5	15.1	NR	95.0	6.3
Pd	$(S_2P_b(OEt)_2)$	- (29)	57.5	-	-	-	-	98.5	2.4

[a] also recorded were $^4J_{P_aP_{b'}}$ < 1 Hz; $^2J_{P_bPt}$ 319.8 Hz.

TABLE 2.2 Hydrogen-1-n.m.r. Data for Various Platinum(II) and Palladium(II) Complexes in $CDCl_3$

	Complex	T°K	Dithio-ligand		δ ± 0.01 p.p.m.	Others
			CH_3	CH_2	CH	
17b	$N^{i}Pr_2H_2[Pt(S_2CN^{i}Pr_2)(Ph_2PS)_2]^{a}$	301	$1.26(d)^{b}$	-	4.38(br)	$1.62(d)^{c}$, 4.12
						$7.00\text{-}8.00(m)^{e}$
		220^{f}	$1.08(d)^{b}$		$4.90(st,br)^{b}$	$1.66(d)^{c}$, 4.12^{d}
			$1.42(d)^{b}$		$3.78(st,br)^{b}$	$7.00\text{-}8.00(m)^{e}$
	$Ph_3PhCH_2P[Pt(S_2CN^{i}Pr_2)(Ph_2PS)_2]$	301	$1.20(d)^{b}$	-	4.36(br)	$5.24(d)^{g}$
		200	1.20(br)		4.90(br)	$7.00\text{-}8.00(m)^{e}$
			1.46(br)		3.86(br)	
17a	$NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]^{a}$	301	$1.05(t)^{b}$	$3.43(q)^{b}$		$1.52(t)^{h}$, 3.43^{i}
						$7.00\text{-}8.00(m)^{e}$
	$Ph_3(PhCH_2)P[Pt(S_2CNEt_2)(Ph_2PS)_2]$	301	$1.02(t)^{b}$	$3.39(q)^{b}$	-	$5.22(d)^{g}$
						$6.80\text{-}8.00(m)^{e}$
19b	$[Pt(S_2CN^{i}Pr_2)(Ph_2POHSPPh_2)]$	301	$1.26(d)^{b}$	-	4.38(br)	$7.17\text{-}8.00(m)^{e}$
						$12.06(br)^{j}$
21	$[Pt(S_2CN^{i}Pr_2)(Ph_2POMe)(Ph_2PS)]$	301	$1.26(d,br)^{b}$	-	4.40(br)	$3.56(d)^{k}$
						$7.00\text{-}8.00(m)^{e}$
20b	$[Pt(S_2CN^{i}Pr_2)(Ph_2PH)(Ph_2PS)]$	301	1.34(d), $1.36(d)^{b}$	-	4.43(br)	6.18^{l}
						$7.18\text{-}7.92(m)^{e}$
26b	$[Pt(S_2CN^{i}Pr_2)(Ph_2PH)(Ph_2PSe)]$	301	$1.36(d)^{b}$	-	4.44(br)	6.16^{m}
			$1.43(d)^{b}$			$7.10\text{-}7.90(m)^{e}$
26a	$[Pt(S_2CNEt_2)(Ph_2PH)(Ph_2PSe)]$	301	$1.18(t)^{b}$	$3.53(q)^{b}$	-	6.21^{n}
			$1.20(t)^{b}$	$3.59(q)^{b}$	-	$7.00\text{-}8.10(m)^{e}$
22b	$[\{Pt(S_2CN^{i}Pr_2)(Ph_2PS)\}_2]$	301	$1.23(d)^{b}$	-	4.36(br)	$7.10\text{-}8.10(m)^{e}$
			$1.44(d)^{b}$			
22a	$[\{Pt(S_2CNEt_2)(Ph_2PS)\}_2]$	301	$1.16(t)^{b}$	$3.46(q)^{b}$	-	$7.10\text{-}8.30(m)^{e}$
			1.22(t)	$3.58(q)^{b}$	-	
2b	$[Pt(S_2CN^{i}Pr_2)(\{Ph_2PO\}_2H)]$	301	$1.34(d)^{b}$	-	4.50(br)	$10.20(br)^{p}$
		223^{o}	$1.17(d)^{b}$		5.02(br)	$7.20\text{-}7.90(m)^{e}$
			$1.53(d)^{b}$		3.87(br)	
2a	$[Pt(S_2CNEt_2)(\{Ph_2PO\}_2H)]$	301	$1.18(t)^{b}$	$3.54(q)^{b}$	-	$7.25\text{-}7.73(m)^{e}$
						$10.44(br)^{p}$
23	$[\{Pd(S_2CNEt_2)(Ph_2PS)\}_2]$	301	$1.10(t)^{b}$	$3.51(q)^{b}$		$7.20\text{-}8.00(m)^{e}$
			$1.19(t)^{b}$	$3.66(q)^{b}$		
24	$NEt_2H_2[Pd(S_2CNEt_2)(Ph_2PS)_2]$	301	$1.06(t)^{b}$	$3.56(q)^{b}$	-	$1.45(t)^{h}$, 2.23^{i}
						$7.00\text{-}7.90(m)^{e}$

TABLE 2.2 (continued)

			δ ± 0.01 p.p.m.			
	Complex	T°K	Dithio-ligand			Others
			$\underline{CH}_3$	$\underline{CH}_2$	$\underline{CH}$	
18	$Pt(S_2CN^iPr_2)_2$	301	1.43(d)^b	-	4.65^b	
		251	1.23(d)^{b}1.63(d)^b	-	3.94(m)^{b}5.19(m)^b	
27	$[Pt(S_2P(OEt)_2)(Ph_2PS)]_2$	301	1.29(t)^b	4.07(dq)^b	-	7.00–8.00^e(m
29	$[Pd(S_2P(OEt)_2)(Ph_2PS)]$	301	1.30(t)^b	4.02(dq)^b	-	7.00–8.00^e(m
30	$[Pt(S_2PPh_2)(Ph_2PO\underline{H}SPh_2)]$		-	-	-	7.00–8.00^e(m 12.03(br)^q
31	$[Pt(S_2PPh_2)(Ph_2PH)(Ph_2PSe)]$		-	-	-	7.00–8.00^e(m 6.03^r
	$NEt_2H_2[Ph_2PS]^a$	301	1.19(t)^b	2.73(q)^b		7.20–8.00^e(m 9.44(bs)

d(doublet), t(triplet), q(quartet), st(septet), m(multiplet)

a No $N R_2\underline{H}_2^+$ resonance observed due to quadrupolar broadening from ^{14}N, and phenyl overlap

b $^3J_{HH}$ 7.0 Hz

c $NH_2(CH\underline{Me}_2)_2^+$ resonance, $^3J_{HH}$ 6.0 Hz

d $NH_2(\underline{CH}Me_2)_2^+$ resonance

e Phenyl resonances

f Homonuclear decoupling studies show that resonances at δ1.08; 4.90 p.p.m. and δ1.42; 3.78 p.p.m. respectively are coupled

g $Ph_3(Ph\underline{CH}_2)P^+$ resonance ($^2J_{PCH_2}$ 14.0 Hz)

h $N(CH_2\underline{CH}_3)_2H_2^+$ resonance

i $N(\underline{CH}_2CH_3)_2H_2^+$ resonance, $^3J_{HH}$ 7.0 Hz

j $Ph_2PO\underline{H}SPPh_2$ resonance

k $Ph_2PO\underline{Me}$ resonance $^3J_{PH}$ 13.0 Hz

l $Ph_2P\underline{H}$ resonance; doublet of doublets with platinum satellites $^1J_{PH}$ 421.8 Hz, $^2J_{PtH}$ 61.8 Hz, $^3J_{PH}$ 14.2 Hz

m $Ph_2P\underline{H}$ resonance; doublet of doublets with platinum satellites $^1J_{PH}$ 421.0 Hz, $^2J_{PtH}$ 60.2 Hz, $^3J_{PH}$ 15.0 Hz

n Ph_2PH resonance; doublet of doublets with platinum satellites $^1J_{PH}$ 423.6 Hz; $^2J_{PtH}$ 79.0 Hz, $^3J_{PH}$ 14.8 Hz

o Homonuclear decoupling studies show that resonances at δ1.17; 5.02 p.p.m. and δ1.53; 3.87 p.p.m. respectively are coupled

p $Ph_2PO\underline{H}OPPh_2$ resonance (half width ca. 260 Hz)

q $Ph_2PO\underline{H}SPh_2$ resonance

r $Ph_2P\underline{H}$ resonance; doublet of doublets with platinum satellites $^1J_{PH}$ 423.0 Hz, $^2J_{PtH}$ 76.7 Hz, $^3J_{PH}$ 15.7 Hz

TABLE 2.3 Fractional Coordinates of Atoms with Standard Deviations for $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (17a)

	X	Y	Z
Pt	0.46240(10)	0.05740(10)	0.48930(10)
S(1)	0.5305(5)	-0.1040(7)	0.4931(10)
P(2)	0.4150(4)	0.2303(7)	0.4861(9)
P(1)	0.3848(5)	-0.0423(9)	0.5615(8)
S(2)	0.5587(5)	0.1191(9)	0.4231(8)
S(4)	0.4100(6)	-0.0827(9)	0.6869(8)
S(3)	0.3979(6)	0.3044(9)	0.6024(8)
C(11)	0.3762(10)	-0.1788(16)	0.5011(17)
C(12)	0.3822(10)	-0.1819(16)	0.4074(17)
C(13)	0.3770(10)	-0.2858(16)	0.3616(17)
C(14)	0.3659(10)	-0.3866(16)	0.4095(17)
C(15)	0.3599(10)	-0.3835(16)	0.5032(17)
C(16)	0.3650(10)	-0.2796(16)	0.5490(17)
C(21)	0.4614(13)	0.3305(20)	0.4169(18)
C(22)	0.4938(13)	0.4208(20)	0.4578(18)
C(23)	0.5265(13)	0.5001(20)	0.4049(18)
C(24)	0.5268(13)	0.4891(20)	0.3112(18)
C(25)	0.4943(13)	0.3988(20)	0.2703(18)
C(26)	0.4617(13)	0.3195(20)	0.3231(18)
C(31)	0.3418(11)	0.2237(24)	0.4188(18)
C(32)	0.3349(11)	0.1502(24)	0.3453(18)
C(33)	0.2790(11)	0.1512(24)	0.2951(18)
C(34)	0.2299(11)	0.2257(24)	0.3184(18)
C(35)	0.2368(11)	0.2992(24)	0.3920(18)
C(36)	0.2928(11)	0.2982(24)	0.4422(18)
C(41)	0.3035(11)	0.0143(24)	0.5720(23)
C(42)	0.2591(11)	-0.0055(24)	0.5039(23)
C(43)	0.1986(11)	0.0420(24)	0.5102(23)
C(44)	0.1825(11)	0.1093(24)	0.5845(23)
C(45)	0.2269(11)	0.1290(24)	0.6526(23)
C(46)	0.2874(11)	0.0816(24)	0.6463(23)
C(1)	0.5849(19)	-0.0157(21)	0.4416(26)
N(1)	0.6475(15)	-0.0442(30)	0.4292(22)
C(2)	0.6980(26)	0.0370(50)	0.3990(40)
N(2)	0.4915(15)	0.1416(28)	0.7226(22)
C(7)	0.5595(17)	0.1461(38)	0.6900(29)
C(8)	0.4858(30)	0.1440(53)	0.8232(29)
C(6)	0.5928(23)	0.0360(44)	0.7189(33)
C(9)	0.4201(31)	0.1567(56)	0.8480(44)
C(4)	0.6718(26)	-0.1629(37)	0.4483(37)
C(5)	0.7110(32)	0.0157(61)	0.2985(42)
C(3)	0.6962(34)	-0.1715(65)	0.5452(42)

TABLE 2.4 Interatomic Distances and Angles for Compound (17a) with Estimated Standard Deviations in Parentheses

(a) Distances (Å)

Pt-S(1)	2.372(9)
Pt-S(2)	2.368(11)
Pt-P(1)	2.277(11)
Pt-P(2)	2.253(9)
S(1)-C(1)	1.72(3)
S(2)-C(1)	1.69(2)
P(1)-S(4)	1.99(1)
P(2)-S(3)	1.96(1)
P(1)-C(11)	1.83(2)
P(1)-C(41)	1.84(2)
P(2)-C(31)	1.84(2)
P(2)-C(21)	1.83(2)
C(1)-N(1)	1.37(5)
N(1)-C(2)	1.49(6)*
N(1)-C(4)	1.50(5)*
C(3)-C(4)	1.53(8)*
C(2)-C(5)	1.52(8)*
N(2)-C(8)	1.49(5)*
N(2)-C(7)	1.51(4)*
C(8)-C(9)	1.44(8)
C(7)-C(6)	1.52(6)

* Bonds restrained to be near their expected values using the DFIX facility in SHELX which for example allows a C-C bond to be restrained to 1.54 Å with a standard deviation of 0.04.

(b) Angles (°)

S(1)-Pt-S(2)	74.4(4)
S(1)-Pt-P(1)	91.0(4)
S(2)-Pt-P(2)	95.7(4)
P(1)-Pt-P(2)	98.6(4)

Pt-S(1)-C(1)	85.2(1.1)
Pt-S(2)-C(1)	86.1(1.4)
S(1)-C(1)-S(2)	114.3(2.2)
C(1)-N(1)-C(2)	124.8(3.2)
C(1)-N(1)-C(3)	121.7(3.3)
N(1)-C(2)-C(5)	108.4(4.6)
N(1)-C(4)-C(3)	110.6(4.3)

Pt-P(1)-S(4)	111.6(6)
Pt-P(2)-S(3)	117.3(9)
Pt-P(1)-C(11)	106.6(9)
Pt-P(1)-C(41)	121.7(1.1)
Pt-P(2)-C(21)	110.3(9)
Pt-P(2)-C(31)	110.3(1.0)

TABLE 2.5 Fractional Coordinates of Atoms with Standard Deviations for $[\{Pt(S_2CN^iPr_2)(Ph_2PS)\}_2]2CDCl_3$ (22b)

	X	Y	Z
Pt(1)	0.20622(5)	-0.01141(6)	0.05880(3)
P(1)	0.0528(3)	0.0277(4)	0.0824(2)
S(1)	-0.1042(3)	-0.0876(4)	0.0356(2)
S(2)	0.3798(4)	-0.0575(5)	0.0437(2)
S(3)	0.3497(4)	-0.1019(5)	0.1481(2)
C(1)	0.5475(14)	0.1081(17)	0.8807(7)
N(1)	0.4300(12)	0.1398(14)	0.8534(6)
C(2)	0.6303(17)	-0.1873(20)	0.2098(8)
C(3)	0.6361(20)	-0.0647(24)	0.2519(10)
C(4)	0.5807(22)	-0.3278(26)	0.2210(11)
C(5)	0.6460(16)	-0.1339(19)	0.1136(8)
C(6)	0.6870(22)	-0.2831(27)	0.1061(11)
C(7)	0.7532(19)	-0.0262(24)	0.1456(10)
C(11)	0.0126(10)	0.2158(9)	0.0796(5)
C(12)	0.1004(10)	0.3189(9)	0.0852(5)
C(13)	0.0730(10)	0.4654(9)	0.0838(5)
C(14)	-0.0422(10)	0.5087(9)	0.0767(5)
C(15)	-0.1300(10)	0.4056(9)	0.0710(5)
C(16)	-0.1026(10)	0.2592(9)	0.0724(5)
C(21)	0.0837(10)	-0.0243(11)	0.1578(4)
C(22)	0.0720(10)	0.0685(11)	0.1990(4)
C(23)	0.0889(10)	0.0163(11)	0.2546(4)
C(24)	0.1174(10)	-0.1287(11)	0.2689(4)
C(25)	0.1290(10)	-0.2214(11)	0.2277(4)
C(26)	0.1122(10)	0.1693(11)	0.1722(4)
Cl(1)	0.3739(7)	0.0250(11)	0.5684(4)
Cl(2)	0.5239(10)	0.2150(10)	0.6596(4)
Cl(3)	0.5554(9)	0.1887(11)	0.5552(4)
C(8)	0.4497(22)	0.1863(27)	0.5834(11)

TABLE 2.6 Interatomic Distances and Angles for Compound (22b) with Estimated Standard Deviations in Parentheses

a) Distances (Å)

Pt(1) - P(1)	2.225(5)	N(1) - C(5)	1.488(30)
Pt(1) - S(1)	2.313(4)	C(5) - C(7)	1.556(27)
Pt(1) - S(2)	2.347(5)	C(5) - C(6)	1.510(33)
Pt(1) - S(3)	2.299(4)	C(2) - C(3)	1.528(32)
P(1) - S(1)*	2.048(5)	C(2) - C(4)	1.513(34)
P(1) - C(11)	1.804(10)	Pt(1)...Pt(1)*	4.571(7)
P(1) - C(21)	1.814(11)	S(1) ...S(1)*	4.030(7)
S(2) - C(1)	1.757(16)	P(1) ...P(1)*	3.763(5)
S(3) - C(1)	1.699(21)	C(8) - Cl(1)	1.710(26)
C(1) - N(1)	1.319(20)	C(8) - Cl(2)	1.728(25)
N(1) - C(2)	1.482(23)	C(8) - Cl(3)	1.720(34)

b) Angles (°)

P(1) -Pt(1)-S(1)	93.93(15)	S(2)-C(1)-S(3)	109.2(8)
P(1) -Pt(1)-S(3)	99.87(17)	S(3)-C(1)-N(1)	128.7(13)
S(2) -Pt(1)-S(1)	91.47(16)	S(2)-C(1)-N(1)	122.1(16)
S(2) -Pt(1)-S(3)	74.65(18)	C(2)-N(1)-C(1)	122.0(17)
Pt(1)-P(1) -S(1)*	116.56(23)	C(5)-N(1)-C(1)	120.4(14)
Pt(1)-S(1) -P(1)*	108.66(22)	C(3)-C(2)-C(4)	114.5(22)
C(11)-P(1) -C(21)	103.11(60)	C(6)-C(5)-C(7)	113.7(17)
Pt(1)-S(3) -C(1)	89.4 (5)		
Pt(1)-S(2) -C(1)	86.5 (7)		

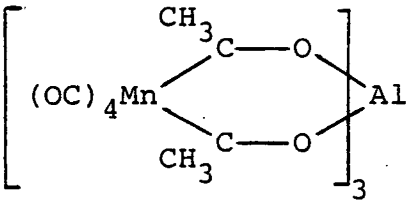
* Denotes atom related by a centre of inversion

CHAPTER 3

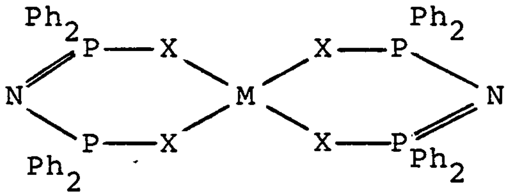
Some Reactions with Metal Complexes (1)

3.1 Introduction

In Chapter 1 it was briefly noted that the acidic proton in compounds containing the fragment $M\{(R_2PO)_2H\}$ could be replaced by a metal ion; i.e. that the compounds will act as bidentate O,O´-donor ligands. The mixed metal oligomers thus formed have been structurally compared to metallo-acetylacetonate[61] (34), imidodiphenylphosphinate[62] (35) and the parent acetylacetonate complexes, $M(acac)_n$($n = 2,3$).



(34)



(35)

($X = O$; $M = Zn$(a)

$X = S$; $M = Ni$(b), Cd(c))

A range of first row transition metal and main group metal complexes has been characterised. These include, for example, the neutral complexes, $M[PtCl(PR_3)\{(CH_3CO)_2PO\}_2]_n$[19,63] ($n = 2$; M = Co. $n = 4$; M = Th), $VO[PtCl(PEt_3)(Ph_2PO)_2]_2$[64] or $M[Ni(\eta C_5H_5)\{(CH_3O)_2PO\}_2]_2$[65] (M = Co, Zn); the cationic complexes, $[M\{Pt(L\frown L)((CH_3O)_2PO)_2\}_2](ClO_4)_2$[63] (M = Cu, Co; L⌒L = diphos, diars‡) and also compounds, such as $Ni(NH_3)_2[Ni(\eta C_5H_5)\{(CH_3O)_2PO\}_2]_2$[65], in which the original ligands of the substrate metal ions are not entirely substituted.

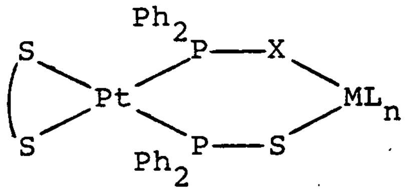
Further examples, originally synthesised in this

---

‡ A number of abbreviations for common organic ligands are used throughout this and subsequent chapters. An explanation of these is given in the Experimental Section, 3.5.

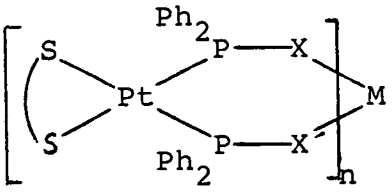
laboratory are of particular relevance: i.e. the complexes $M[Pt(S_2CNR_2)(Ph_2PO)_2]_{2\text{ or }3}$ [5a,6b] (6), where M is a first row transition metal. Such complexes are readily prepared in high yield by mixing stoichiometric amounts of the phosphinite complex (2) dissolved in toluene, methanol or a chlorinated solvent at room temperature with a metal substrate which can be an acetylacetonate, acetate or halide salt. No scrambling of the phosphinite ligand, $(Ph_2PO)^-$, is observed: i.e. the Pt-P bond remains intact and exclusive O-coordinate of the substrate metal is achieved. In this way a number of complexes containing both soft (platinum(II)) and hard (first row transition metal ions) metals linked by the ambidentate phosphinite ligand have been isolated. No X-ray structural determinations of these oligomers have yet been obtained, although a study of the complex $Co[Pt(S_2CNEt_2)(Ph_2PO)_2]_2$ is in progress,[67] but the stereochemistry around the central metal ion can be investigated by a number of other techniques. These include e.s.r. and electronic spectroscopy and magnetic measurements over a range of temperatures[63,66b].

It has now been demonstrated that complexes similar to $Pt(S_2CNR_2)\{(Ph_2PO)_2H\}$ (2) but containing thiophosphinite ligands can be synthesised (see Chapter 2). The preparation and characterisation of some mixed metal complexes, containing the new "ligands" (17a,b) and (19b) will be described in two chapters. In this chapter various compounds with, generally, a single bidentate psuedothioacac ligand are described (Type A). In Chapter 4 transition metal complexes which contain only the new ligands (Type B) are discussed and a comparison with the oxo-equivalents, which are already well known, is made.



type A

(X = O,S)



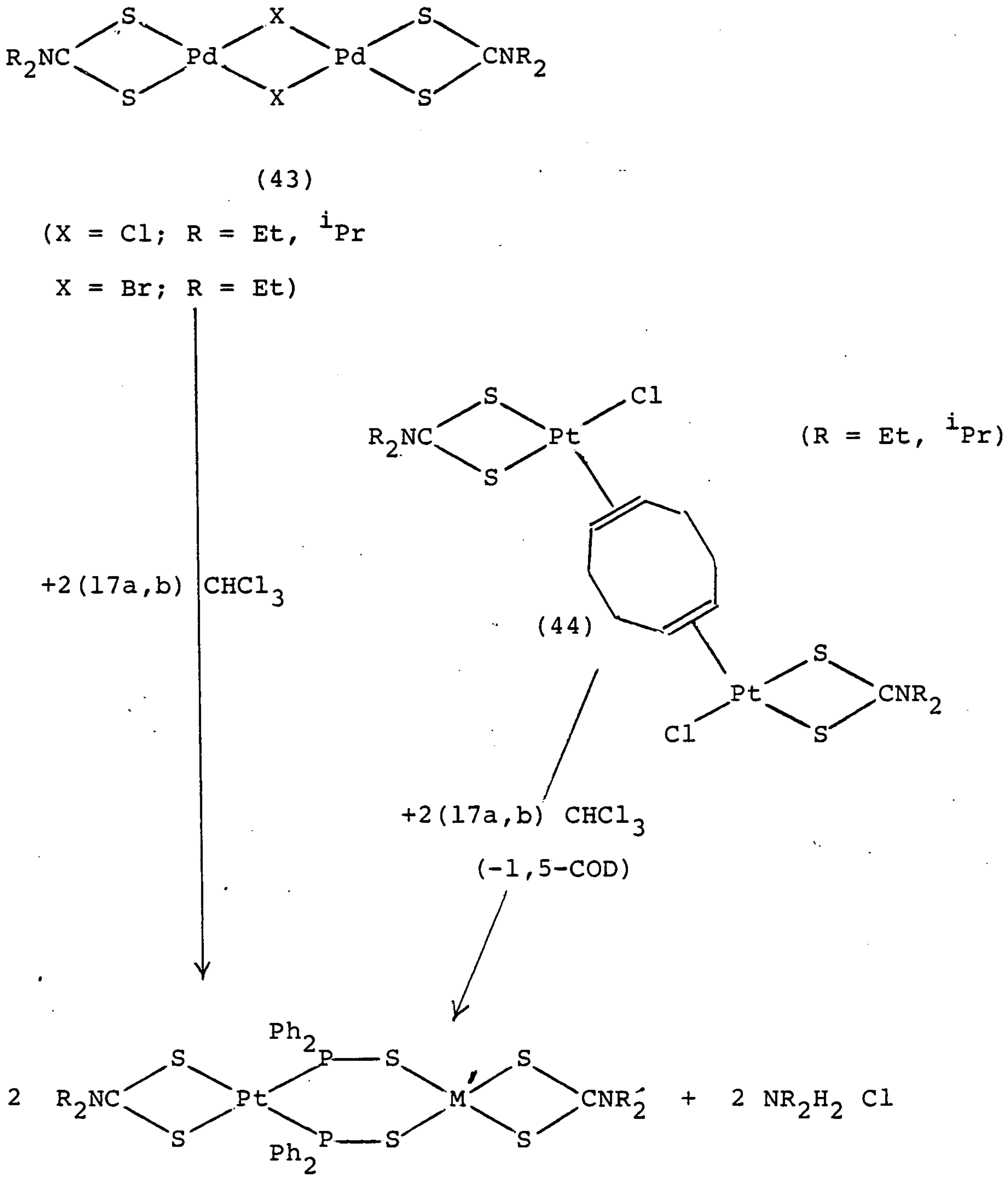
type B

(X,X´ = O,O; S,S; O,S)

3.2 Mixed Dialkyldithiocarbamate Compounds

The salts (17a,b) described in Chapter 2 have been used to synthesise a series of binuclear palladium(II) and platinum(II) complexes (36-42) which are essentially isomeric to the binuclear compounds (22) found in the original reaction. The anions of (17 a and b) act, as before, as bidentate ligands, to cleave the halide or diene bridges in the second reactant (43, 44) (Eqn. 21). The reaction takes place under mild conditions, occurring readily in chloroform solution at room temperature. Precipitation of the product by adding an excess of methanol avoids any problems with the displaced ammonium chlorides, as they remain in solution. The compounds have been characterised by analytical data and i.r., $^{31}P-\{^{1}H\}$ n.m.r. and ^{1}H n.m.r. spectral measurements and, for compound (41), by an X-ray crystal structure determination.

The yellow Pt-Pt or orange Pt-Pd compounds are indefinitely stable in air, in the solid phase, or in degassed organic solvents. They are, however, rather insoluble (generally <1 x 10^{-3} moles ℓ^{-1}) and this has made solution data difficult to accumulate.



(43)

(X = Cl; R = Et, ^{i}Pr
X = Br; R = Et)

(44)

(R = Et, ^{i}Pr)

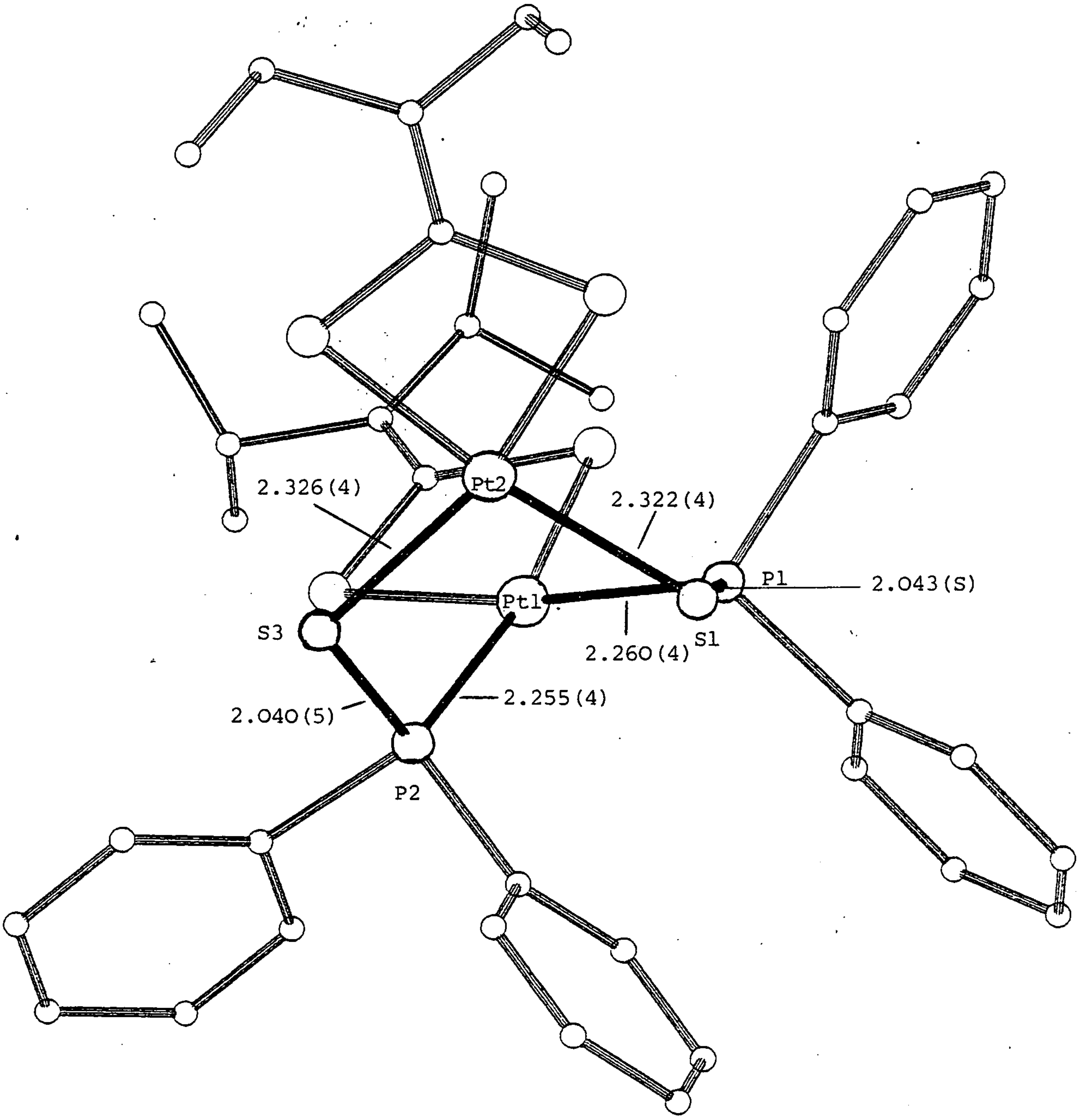
(R = Et; M′ = Pd; R′ = Et(36), ^{i}Pr(37)
R = Et; M′ = Pt; R′ = Et(38), ^{i}Pr(39) ... (21)
R = ^{i}Pr; M′ = Pd; R′ = Et(40)
R = ^{i}Pr; M′ = Pt; R′ = Et(41), ^{i}Pr(42))

By examination of their $^{31}P-\{^{1}H\}$ n.m.r. spectra, the compounds can be grouped into two distinct classes, even without considering the presence of a second platinum atom in some cases. Thus, the Pt-Pd compounds consistently have a higher phosphorus-31 chemical shift, by _ca_. 4 p.p.m., than the Pt-Pt compounds. The chemical shifts of both types are still consistent with a thiophosphorus group P-bonded to platinum(II) rather than palladium(II) and the magnitude of the $^{195}Pt-^{31}P$ coupling constants (_ca_. 3500 Hz) confirms this fact. The complexes which contain two Pt atoms yield proton decoupled spectra due to the superposition of the spectra of four isotopomers. The phosphorus atoms are magnetically equivalent in all of these which means that they are related by a mirror plane in the molecule. The two bond $^{195}Pt-^{31}P$ coupling constant is approximately 20 Hz smaller than for the isomeric complexes (22). In the case where the molecule contains two ^{195}Pt atoms, the phosphorus spectrum is second order, the X part of an ABX_2 spin system (A, B = ^{195}Pt). As no ^{195}Pt n.m.r. spectra have been recorded (despite some attempts), no measurements of $J(^{195}Pt-^{195}Pt)$ have been obtained. This is disappointing as this parameter would be useful for comparative purposes with J_{PtPt} in (22). The ^{1}H n.m.r. spectra, where these have been obtained, confirm the stoichiometry of the products.

The i.r. spectra generally exhibit two strong C=N stretches at 1490-1530 cm^{-1} and a strong band at 580-600 cm^{-1} is assigned to ν_{PS}. This position is typical of that found in bridging diphenylphosphine sulphide - metal complexes.

Figure 3.1

P(1)-Pt(1)-P(2)	93.2(1)
S(1)-Pt(2)-S(3)	99.5(2)
Pt(1)-P(2)-S(3)	110.7(2)
Pt(1)-P(1)-S(1)	116.7(2)
P(1)-S(1)-Pt(2)	106.2(2)



Molecular Structure of $[Pt(S_2CN^iPr_2)(Ph_2PS)_2]Pt(S_2CNEt_2)$ (41)

(some angles ($^\circ$) and distances (Å) are given).

The X-ray crystal structure of $[Pt(S_2CN^iPr_2)(Ph_2PS)_2]Pt(S_2CNEt_2)$ (41) has been solved. Details of the solution are given in the experimental section as are tables of selected bond lengths and angles (3.4 a,b) and atomic parameters (3.5). A view of the molecule is given in Figure 3.1. The molecule contains a six membered Pt(1)-P(1)-S(1)-Pt(2)-S(3)-P(2) ring. Pt(1) is coordinated in a square planar fashion by two sulphur atoms of the dithiocarbamate group and two phosphorus atoms of the six membered ring. Pt(1) is coordinated by four sulphur atoms, two from the dithiocarbamate group and two from the ring. The ring can be considered to have a boat configuration which contrasts with the isomeric ring in compound (22) which has a chair configuration . All the bond lengths and angles are within the expected ranges. In particular the P-S bond length, 2.040(5) Å is considerably lower than a P-S single bond value but is comparable to the value found in other six membered P-S-metal chelates, $M[N(R_2PS)]_2$ [M = Fe (2.020(8)), Ni (2.023(6))] [68], and is thus consistent with the delocalisation of the negative charge over the $S-P-Pt-P-S^-$ chelate. The Pt-Pt through space distance also reflects the change in conformation and is now 4.0 Å compared with 4.57 Å in (22b).

3.3 Some Reactions with Palladium(II) and Platinum(II) Dichloro Complexes

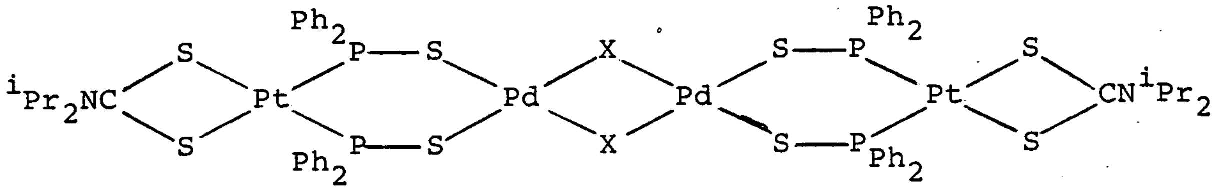
The reactions between the anionic ligands (17) and a variety of palladium and platinum halide complexes have been examined. All the reactions described occur at room temperature in chloroform or methanol. The products have been characterised, if possible, by multinuclear n.m.r. spectroscopy, i.r. spectroscopy and analytical measurements. They are all air stable solids, where they have been isolated, but a number are extremely insoluble and therefore n.m.r. and molecular weight studies, which would significantly add to the data obtained, are lacking. The low solubility appears to be inherent in the palladium complexes described and, as the platinum equivalents are soluble in solvents such as chloroform, this suggests a degree of intermolecular interaction is present in the former compounds.

3.3.1 The Reaction with PdX_2COD

When the compound $PdCl_2$(1,5-COD) was treated with a stoichiometric amount of the triphenylbenzylphosphonium salt of (17b) in $CHCl_3$ solution, an orange solid (46a) precipitated within minutes. As the product (46a) was too insoluble to obtain solution data, the reaction was monitored from the start by $^{31}P-\{^1H\}$ n.m.r. spectroscopy. Initially, a number of species containing platinum-phosphorus bonds were detected in the deep red solution that formed and as the product precipitated most of these declined in intensity with respect to the phosphonium singlet (δP 23.1 p.p.m.). The species which persisted longest was observed at δP 44.3 p.p.m. (with $^1J_{PtP}$ = 3350.0 Hz) and finally after a number of hours only the phosphonium singlet remained. When the almost colourless solution was then examined by ^1H n.m.r. spectroscopy, only strong signals due to $Ph_3(PhCH_2)P^+$ and to free (1,5-COD) were observed. This experiment was repeated using (17b) and $PdBr_2$(1,5-COD) in a 1:1 molar ratio in chloroform and a similar orange solid (47) was obtained. When this reaction is studied in situ by $^{31}P-\{^1H\}$ n.m.r. spectroscopy, the principal signal is a singlet at 41.4 p.p.m. ($^1J_{PtP}$ 3364 .3 Hz) which disappears as the product precipitates‡. Once again ^1H n.m.r. spectra show that $N^iPr_2H_2{}^+$ and (1,5-COD) remain in solution.

The only significant difference between the i.r. spectra of (46a) and (47) is the absence of a band at 295 cm^{-1} in the latter. If this is due to a Pd-Cl stretching mode in (46a) then the corresponding Pd-Br mode in (47) will occur at a lower frequency. No absorptions arising from $NH_2{}^+$ or 1,5-COD moieties are observed. In both compounds ν_{CN} (1500 cm^{-1}) and ν_{PS} (575 cm^{-1}) can be assigned. The latter value has already been shown (see Chapter 2) to be characteristic of a bridging P-S moiety.

Combining this information with the observed analytical data, the simplest structure that can be formulated is that given below:



(X = Cl (46a), Br (47))

---

‡ The ^{31}P-n.m.r. signal at ca. 40-44 p.p.m. in both reactions may possibly arise from a reaction intermediate. In most other complexes, in which P-S bridges are involved, the phosphorus chemical shift is to low frequency with respect to the shift of the starting material, (17).

The mass spectrum of (46a) was obtained but the data cannot be rationalised beyond the identification of a number of, mainly ligand, breakdown products. However, given the high molecular weight (ca. 2000 a.m.u.) of the proposed complexes and the high melting point (ca. 260°C) this is hardly surprising. Additionally the extreme insolubility of the complexes precludes any attempts to generate crystals suitable for the structural studies which might confirm the proposed assignment.

When $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (17a) is mixed with $PdCl_2$(1,5-COD), t-$PdCl_2(PhCN)_2$ or $PdCl_4^{2-}$, under a variety of conditions at room temperature, the product (46b) is the same each time.

As before, an insoluble orange solid (46b) rapidly precipitates. This occurs irrespective of the solvents (benzene, chloroform, dichloromethane or methanol) or the relative quantities of the two reactants. During the work-up of the reaction product, considerable care must be taken to extract out $NEt_2H_2^+Cl^-$ with hot methanol to avoid analytical ambiguities. High yields of (46b) are then obtained whether there is an excess or whether there is a deficiency of the palladium halide complex present at the start.

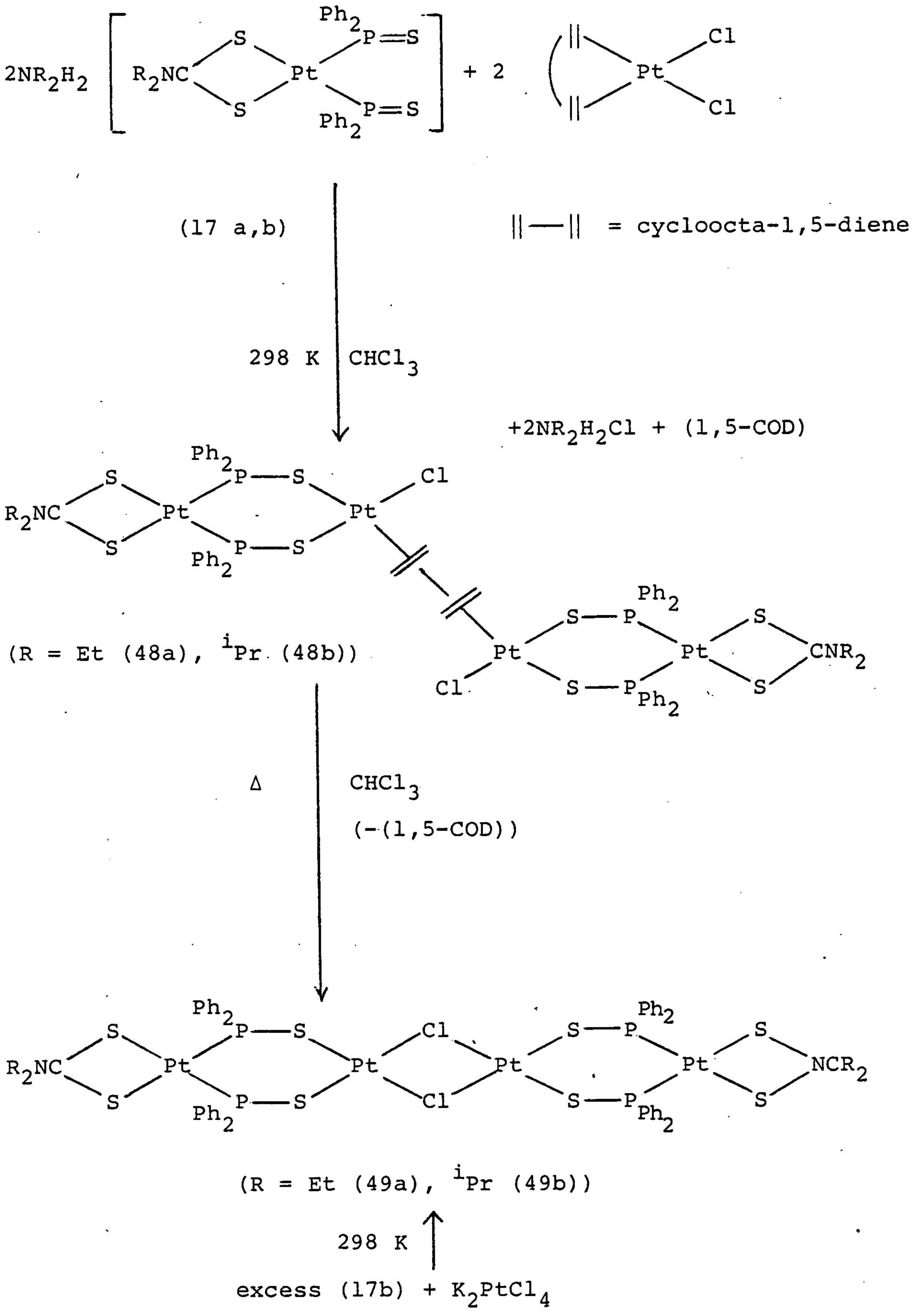
Monitoring the reaction by $^{31}P-\{^1H\}$ n.m.r. spectroscopy shows complicated line patterns which are similar in all of the reactions and which decay as the product precipitates. Infrared spectra and analytical data are consistent with the formation of a halide and phosphine sulphide bridged oligomer. Thus bands assigned to bidentate dithiocarbamate (ν_{CN}, 1530 cm^{-1}), bridging phosphine sulphide (ν_{PS}, 570 cm^{-1}) and bridging chloride (ν_{PdCl}, 290 cm^{-1}) are observed in the i.r. spectra and the fingerprint regions of the spectra do not differ from those of (46a) and (47).

The conclusion is that the three reactions proceed to form an oligomer, similar to that described already (46a), in every case. However, the data obtained for all three compounds (46-47) do not preclude the possibility of more complicated, polymeric structures (e.g. $\{PdX[Pt(S_2CNR_2)(Ph_2PS)_2]\}_n$) which are common in palladium coordination chemistry[56].

3.3.2 The Reaction with $PtCl_2$(1,5-COD)

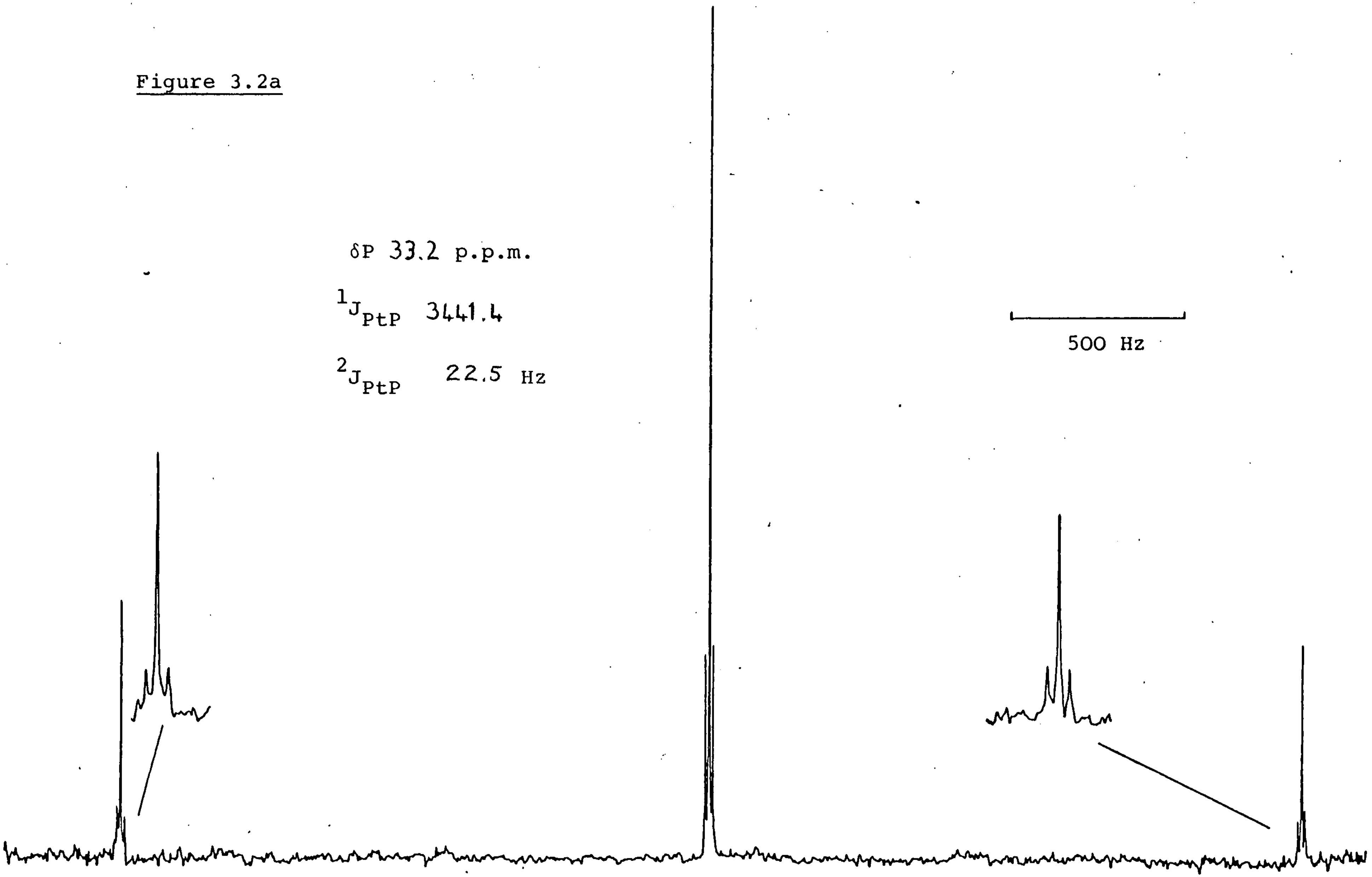
The reactions of $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ (17 a,b) with $PtCl_2$(1,5-COD) have also been examined. A single product (48 a,b) is initially formed in both reactions at room temperature and this has been shown, by analytical data and spectral measurements, to have the stoichiometry $[PtCl\{Pt(S_2CNR_2)(Ph_2PS)_2\}]_2(C_8H_{12})$. If the reaction solution is left, or if the redissolved product is heated, a rearrangement to a different species takes place, although this second compound (49 a,b) has not been isolated to date.

The complete reaction can be monitored by n.m.r. spectroscopy, and the ^{31}P n.m.r. spectra of both products (48 and 49) have been observed (Table 3.6 and fig. 3.2). Thus, when a chloroform solution of (17a) is added to a solution of $PtCl_2$(1,5-COD) a 1:1 reaction occurs until no $PtCl_2$(1,5-COD) remains. The $^{31}P-\{^1H\}$ n.m.r. of the product (48a) is a temperature invariant (300-213 K) singlet, $\delta P = 33.2$, and two platinum couplings are observed, $^1J_{PtP} = 3441.4$ Hz and $^2J_{PtP} = 22.5$ Hz. Adding an excess of



SCHEME 3.1 The Reaction of $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ (17 a,b) with $PtCl_2(1,5\text{-COD})$

Figure 3.2a



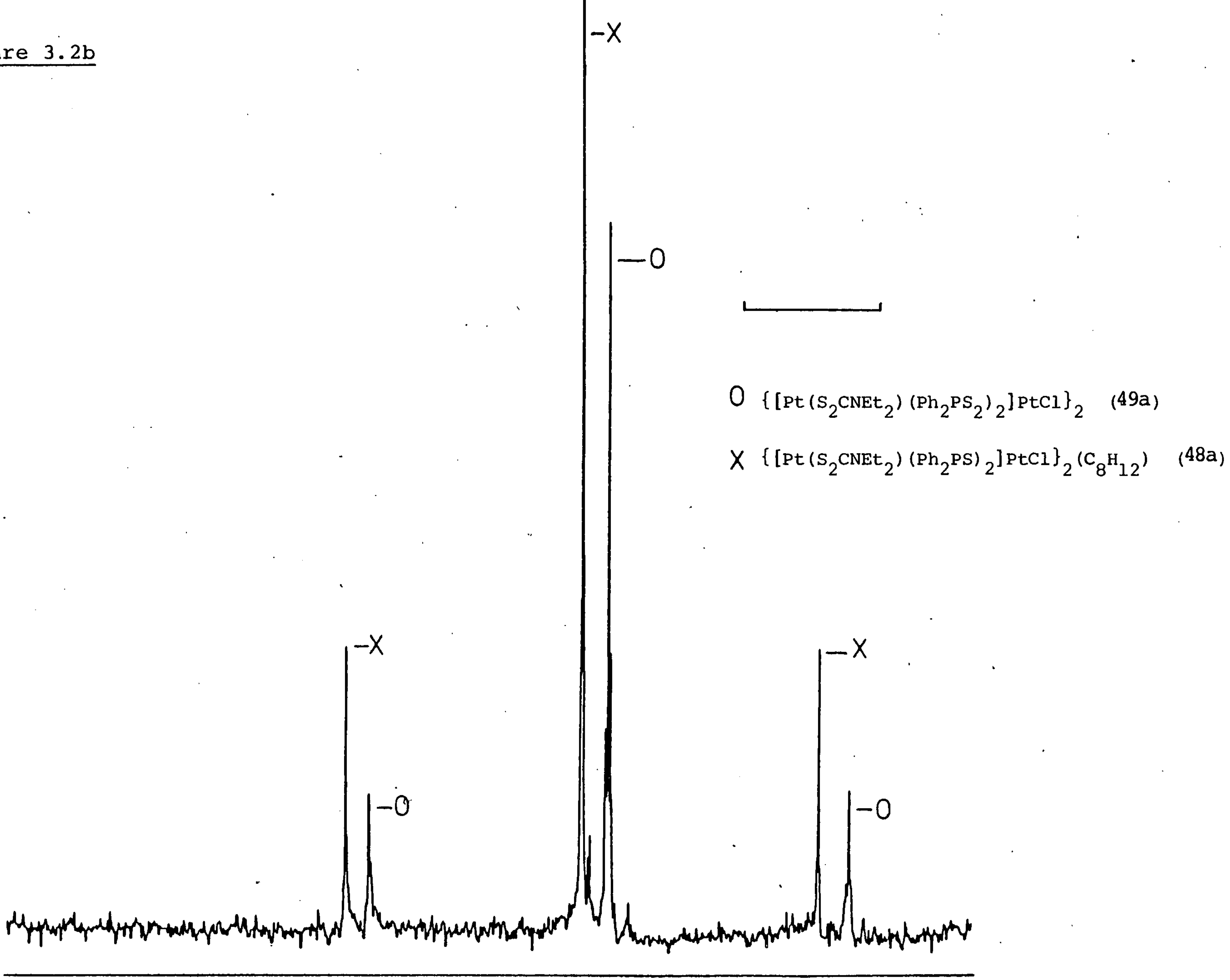
δP 33.2 p.p.m.

$^{1}J_{PtP}$ 3441.4

$^{2}J_{PtP}$ 22.5 Hz

Phosphorus-31-{^{1}H} n.m.r. spectrum of {[Pt(S_2CNEt_2)(Ph_2PS)$_2$]PtCl}$_2C_8H_{12}$ (48a) at 300 K

Figure 3.2b



Phosphorus-31-{^{1}H} n.m.r. spectrum of a solution of (48a) after heating to ca. 320 K methanol will precipitate the product and examination of the solution (by ^{1}H n.m.r.) shows $NEt_2H_2^+$ and some 1,5-COD. When the $^{31}P-\{^{1}H\}$ n.m.r. of the isolated material is examined the spectrum quoted above is reproduced. The high resolution ^{1}H n.m.r. of this product (Experimental Section) shows that there are two $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$ units per coordinated (1,5-COD) ligand (olefinic CH:- δH = 4.86 p.p.m., J_{PtH} = 54.4 Hz; cf. $PtCl_2$(1,5-COD), olefinic CH:- δH = 5.62 p.p.m., J_{PtH} = 65 Hz). The spectrum of the (1,5-COD) ligand is broad but the Pt-H coupling is distinct. The mull i.r. spectra of the compound shows bidentate dithiocarbamate (ν_{CN} = 1510 cm^{-1}), bridging diphenylphosphine sulphide (ν_{PS} = 580 cm^{-1}) and a broad band at 300 cm^{-1} which can be assigned to ν_{PtCl}. The compound is not, however, sufficiently soluble in polar solvents for conductivity data to be gathered, nor is it sufficiently soluble in benzene to give a molecular weight measurement.

When (48a) is heated in $CDCl_3$ solution a rearrangment takes place(together with some decomposition to free $Pt(S_2CNEt_2)(Ph_2POHSPPh_2)$ and $Pt(S_2CNEt_2)(Ph_2PH)(Ph_2PS))$ and a second product (48b) is observed by $^{31}P-\{^{1}H\}$ n.m.r. spectroscopy at 301 K. The chemical shift changes (δP = 25.4 p.p.m.) as do the coupling constants ($^{1}J_{PtP}$ = 3491.2; $^{2}J_{PtP}$ = 38.6 Hz). This data does however indicate that the six membered bimetallic ring is probably unaltered.

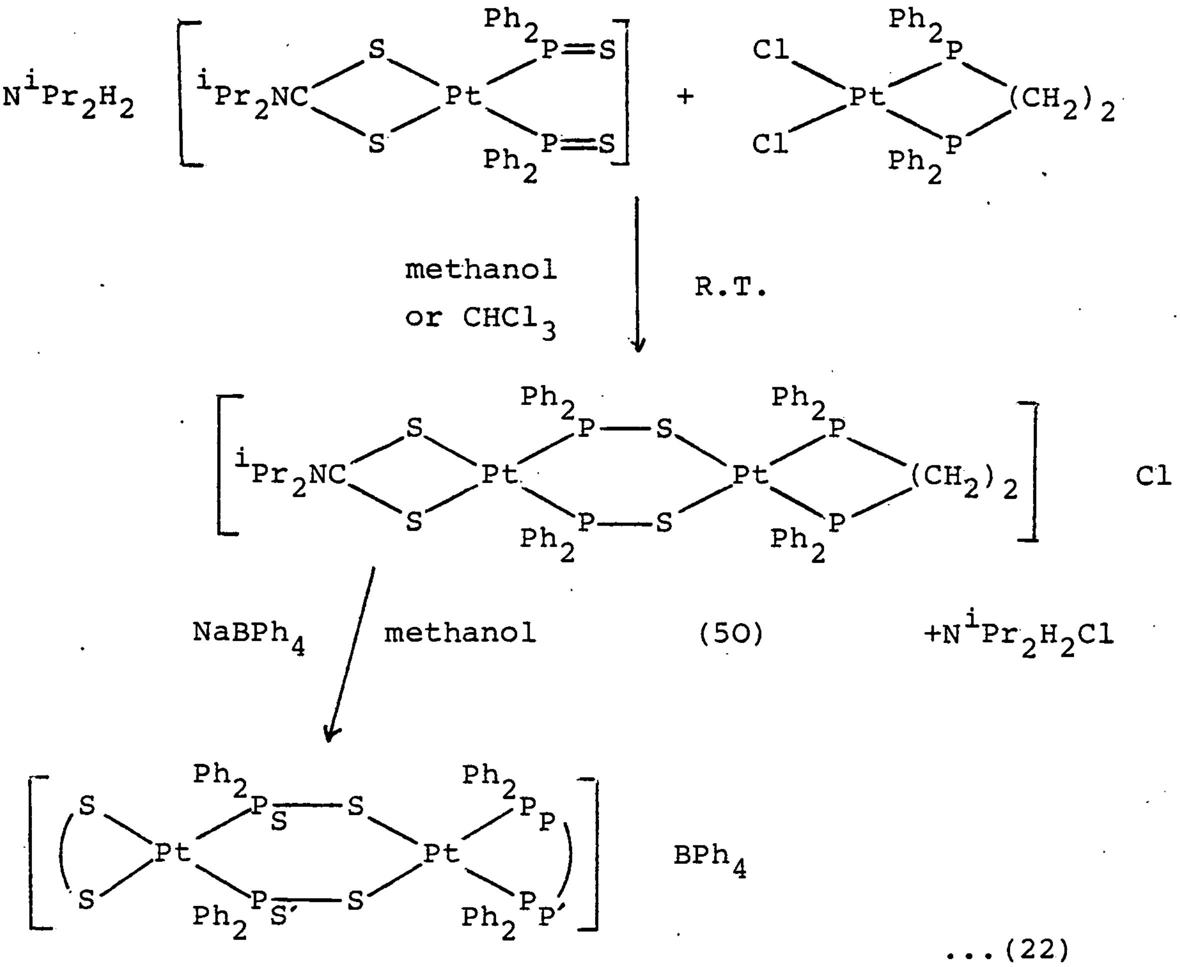
$N^{i}Pr_2H_2[Pt(S_2CN^{i}Pr_2)(Ph_2PS)_2]$ has been shown to follow the same reaction pathway with $PtCl_2$(1,5-COD). The ^{31}P n.m.r. parameters (Table 3.6) of both products (48b and 49b) are similar to those of the diethyldithiocarbamate analogue. Neither compound could be isolated in a pure form.

In addition, (49b) has been prepared by a different route and can be observed in situ by ^{31}P n.m.r. spectroscopy. Thus when an excess of (17b) suspended in a degassed water/ethanol solution of K_2PtCl_4 is shaken for 12 h a yellow solid is obtained. The principle species in this inseparable mixture has a ^{31}P n.m.r. spectrum identical to that of (49b). Free $Pt(S_2CN^iPr_2)(Ph_2POHSPPh_2)$, $Pt(S_2CN^iPr_2)(Ph_2PH)$-(Ph_2PS) and $[Pt(S_2CN^iPr_2)(Ph_2PS)]_2$ are also observed.

Therefore, on the basis of the information obtained and with due regard to the known behaviour of MCl_2(1,5-COD) with dithio acid ligands[69] the reaction scheme, shown in Scheme 3.1, is proposed. The first product (48 a,b) is tentatively formulated as a tetranuclear oligomer, with two heteronuclear six-membered rings, bridged by a single (1,5-COD) ligand (cf. $[PtCl(S_2CNEt_2)]_2$ (1,5-COD) formed by reaction of $PtCl_2$(1,5-COD) with NaS_2CNR_2 [69a]). Similarly, the assignment of (49 a,b) follows from a comparison with reactions of $PdCl_2$(1,5-COD) and dithio acid ligands, the observation by ^1H n.m.r. spectroscopy of (1,5-COD) eliminated during the reaction and the formation of a single product in which, by ^{31}P n.m.r. spectroscopy, the six membered ring has been retained. Thus (49 a,b) has been formulated as an oligomer, comparable to (46-47). Confirmation of this proposed structure must await further investigations, but the comparative behaviour of the Pd(II) and Pt(II) diene complexes with (17) is consistent with the known reactions of such compounds.

3.3.3 Some Reactions with $PtCl_2$(DIPHOS)

The compound $N^{i}Pr_2H_2[Pt(S_2CN^{i}Pr_2)(Ph_2PS)_2]$ (17b) and $PtCl_2$(DIPHOS) will react when they are dissolved in chloroform or shaken in methanol to give the complex (50) below (Eqn. 22). The product, which can be conveniently isolated as its tetraphenylborate salt (50a), has been fully characterised on the basis of analytical data, i.r. spectra (ν_{PS} at 585 cm^{-1}) and n.m.r. measurements.



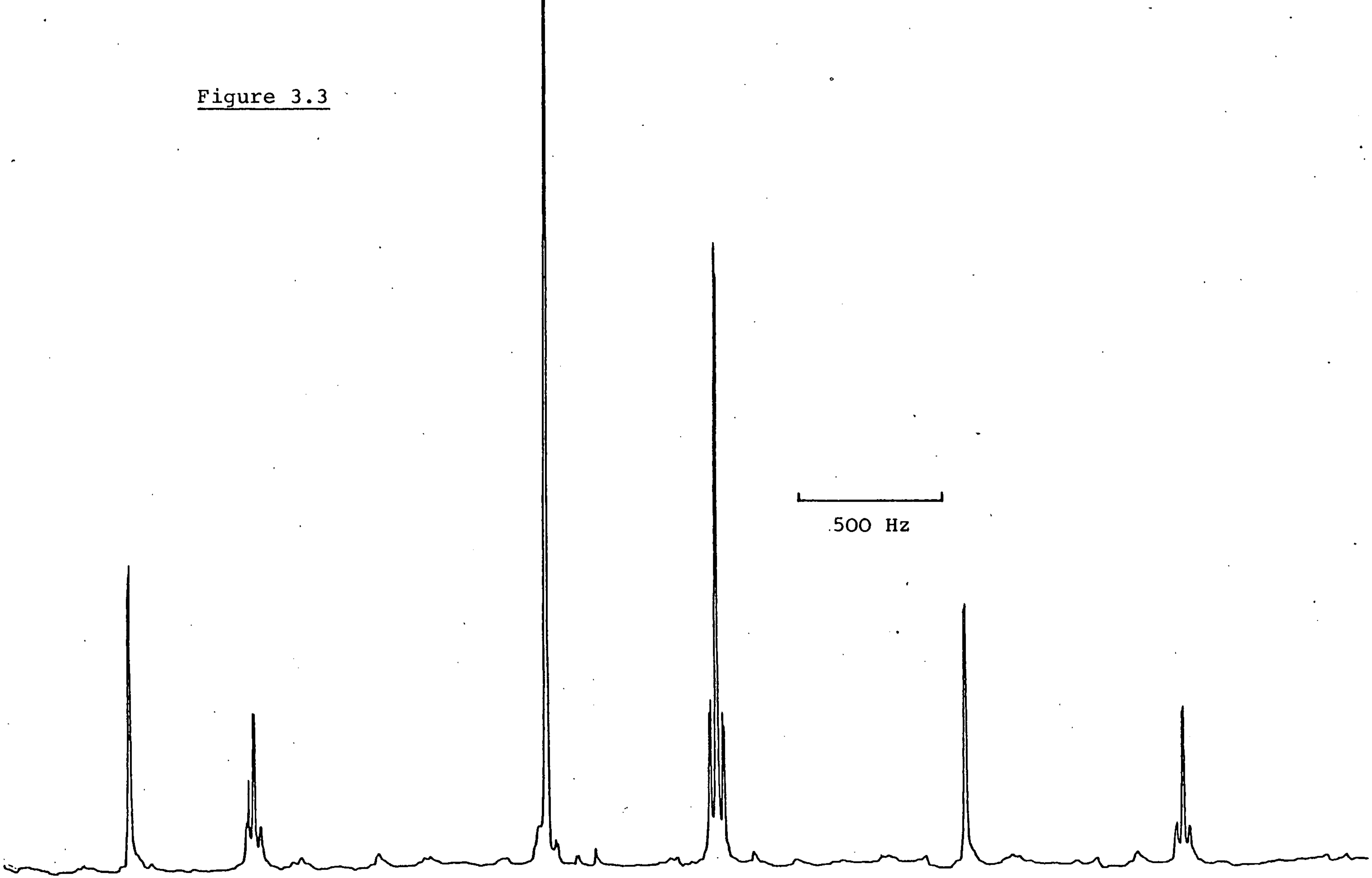
(50)

...(22)

(50a)

The $^{31}P-\{^{1}H\}$ n.m.r. spectrum of (50a) at 300 K is complex and is shown in fig. 3.3. Each pair of chemically different phosphorus atoms (S,S′ and P,P′) are formally magnetically

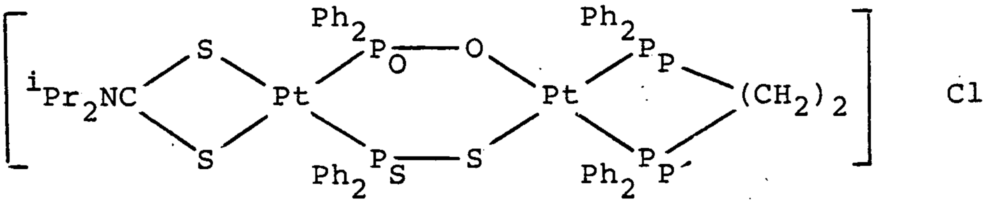
Figure 3.3



Phosphorus-31 n.m.r. spectrum ($CDCl_3$ 298 K) of $\{[Pt(S_2CN^iPr_2)(Ph_2PS)_2]Pt(DIPHOS)\}BPh_4$ (50a) inequivalent, but the spectrum consists of two single resonances, split into narrow doublets by a single ^{31}P coupling (Table 3.6). The $P_{(DIPHOS)}$' atoms couple to a single ^{195}Pt nucleus and the $P_{(Ph_2PS)}$ resonance exhibits both one and two bond platinum couplings. The single phosphorus coupling observed can be assigned to J_{SP} or $J_{SP'}$, if the other possible couplings ($J_{PP'}$, $J_{SS'}$ and $J_{SP'}$ or J_{SP}) are zero.

The ^{195}Pt n.m.r. spectrum at 301 K has also been recorded. The signals arising from the two isotopomers with only one ^{195}Pt nucleus are evident but the pattern due to the low probability isotopomer, that with two ^{195}Pt nuclei, is not observed and so $^{3}J^{195}Pt-^{195}Pt$ remains unknown.

A second reaction, between $Pt(S_2CN^iPr_2)(Ph_2POHSPPh_2)$ (19b) and $PtCl_2(DIPHOS)$, occurs rapidly at room temperature in the presence of a base to yield (51) below. This compound



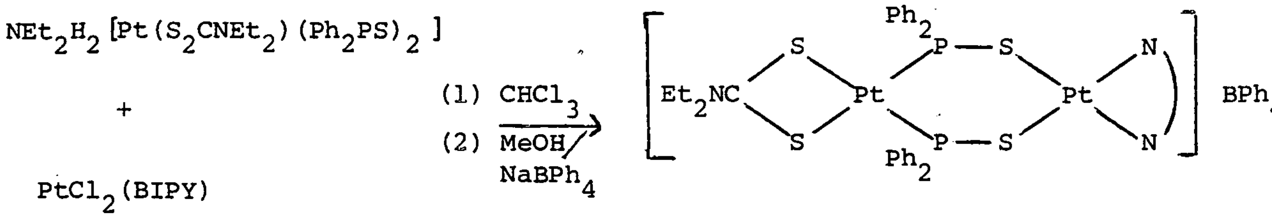
(51)

has not been isolated but the structure was deduced on the basis of ^{31}P n.m.r. spectroscopy. Four chemically different phosphorus nuclei are present in the molecule. The oxide-phosphorus (δP = 68.1 p.p.m.) and the sulphide-phosphorus (δP = 16.5 p.p.m.) can be assigned on the basis of the observed chemical shift and coupling constants. The signals observed at 46.6 p.p.m. (J_{PtP} = 3206.2 Hz) and 35.7 p.p.m. ($J_{PtP'}$ = 3740.0 Hz) are assigned to the (DIPHOS)-phosphorus atoms, *trans* to sulphur and oxygen respectively, on the basis of the different *trans*-influence of oxygen and sulphur donor ligands[70]. Thus, this latter assignment is supported by a comparison with the dithio compound (50) where $^1J_{PtP_P}$ = 3061.5 Hz. This assignment also means that the $^3J_{P_OP_{P'}}$ coupling is zero, while all other ^3J phosphorus couplings possible are observed (Table 3.6). The extra couplings observed (*i.e.* to both *trans* and *cis* (DIPHOS)-phosphorus atoms) may reflect a structural difference between compounds (51) and (50), in which only one such coupling is evident. The (^{195}Pt-^{31}P) two bond coupling through oxygen is five times smaller than the equivalent through sulphur.

The monothio complex therefore behaves like both the bisoxy(2) and bisthio(17) platinum compounds and forms mixed metal oligomers. As the molecule contains both a "hard" and a "soft" donor atom a wider range of compounds might be possible.

3.3.4 The Reaction of $PtCl_2$(BIPY)

Finally in this section, a clean, rapid reaction is observed at room temperature between $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ and $PtCl_2$(BIPY). The cationic product (52) can be trapped as the tetraphenylbor ate salt (52a) (Eqn. 23) :-



(52a)

+ NaCl + NEt_2H_2Cl

...(23)

The yellow crystalline product has been characterised by analytical data, i.r. spectra (ν_{CN} 1535; ν_{PS} 585 cm^{-1}), $^{31}P-\{^1H\}$ n.m.r. (Table 3.6) and ^1H n.m.r. (Experimental Section) at ambient temperature.

It is interesting to note that whereas $PtCl_2$(BIPY) and $PtCl_2$(DIPHOS) clearly react via displacement of both halide ions, $PtCl_2$(1,5-COD) behaves in a different manner, apparently through two stages involving first a partial loss of Cl^- and then diene displacement to yield a halide bridged compound (49). It may also be of interest to investigate the reactions of (49) with potentially halide-bridge cleaving reagents and thus extend the range of complexes observed.

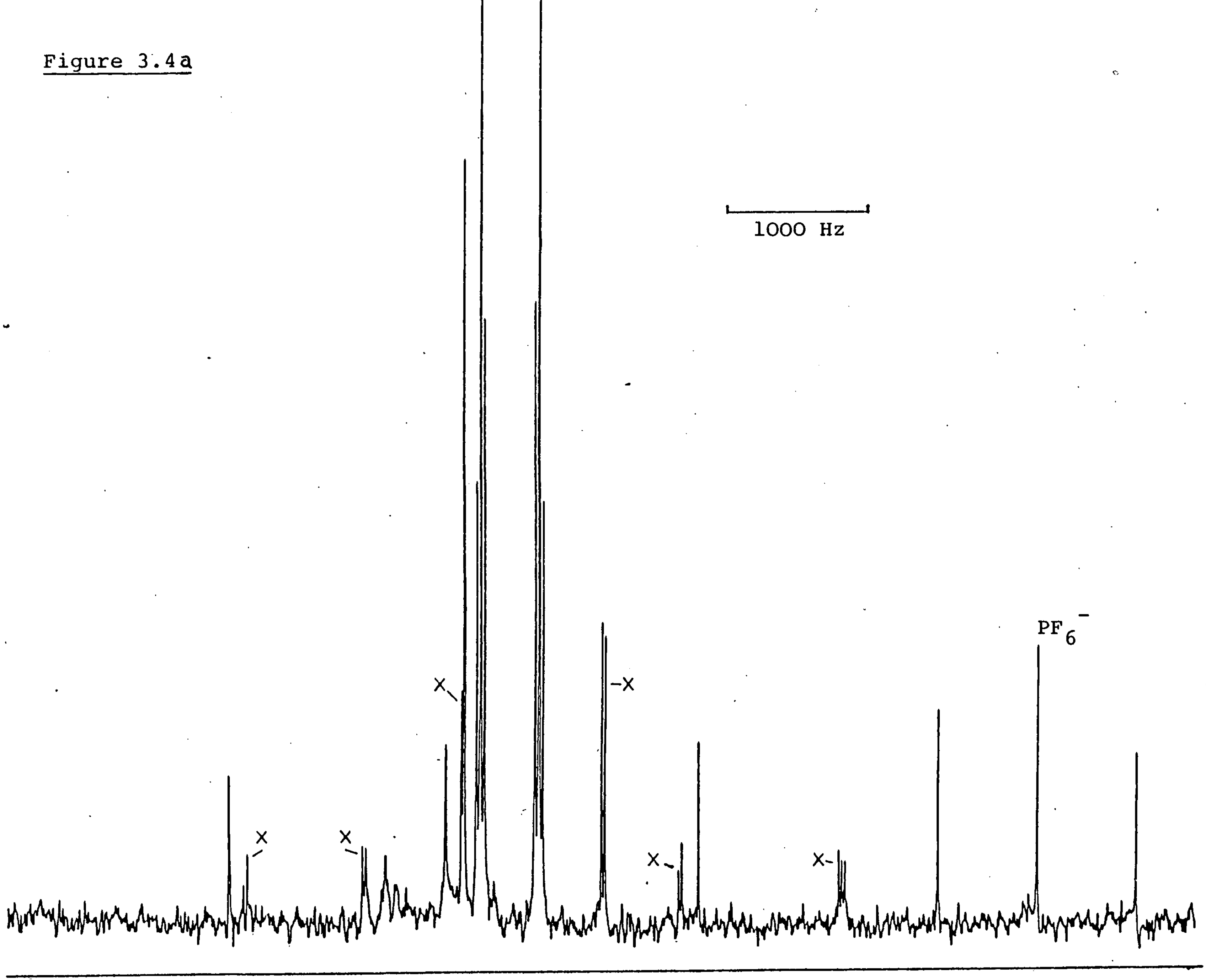
3.4 Preparation of the novel $Ru(\eta^2-Ph_2PS)_2(PMe_2Ph)_2$: a Diphenylphosphine Sulphide Transfer Reaction

The title compound was prepared in good yield by the reaction of the compound $NEt_2H_2[M(S_2CNEt_2)(Ph_2PS)_2]$ (M = Pt (17a) or Pd (24)) with the ruthenium acetate complex, $[Ru(PMe_2Ph)_4(CH_3CO_2)]PF_6$. In both cases, the room temperature reaction in chloroform does not yield the expected bimetallic, phosphine sulphide bridged compounds A (see Scheme 3.2). Instead the novel monomeric compound

$Ru(\eta^2\text{-}Ph_2PS)_2(PMe_2Ph)_2$ (53) is isolated. Elemental analysis, molecular weight determination (monomeric in benzene), i.r. spectra and multinuclear n.m.r. spectroscopic techniques were used to confirm the presence of the first ruthenium $\eta^2\text{-}Ph_2PS^-$ ligands.

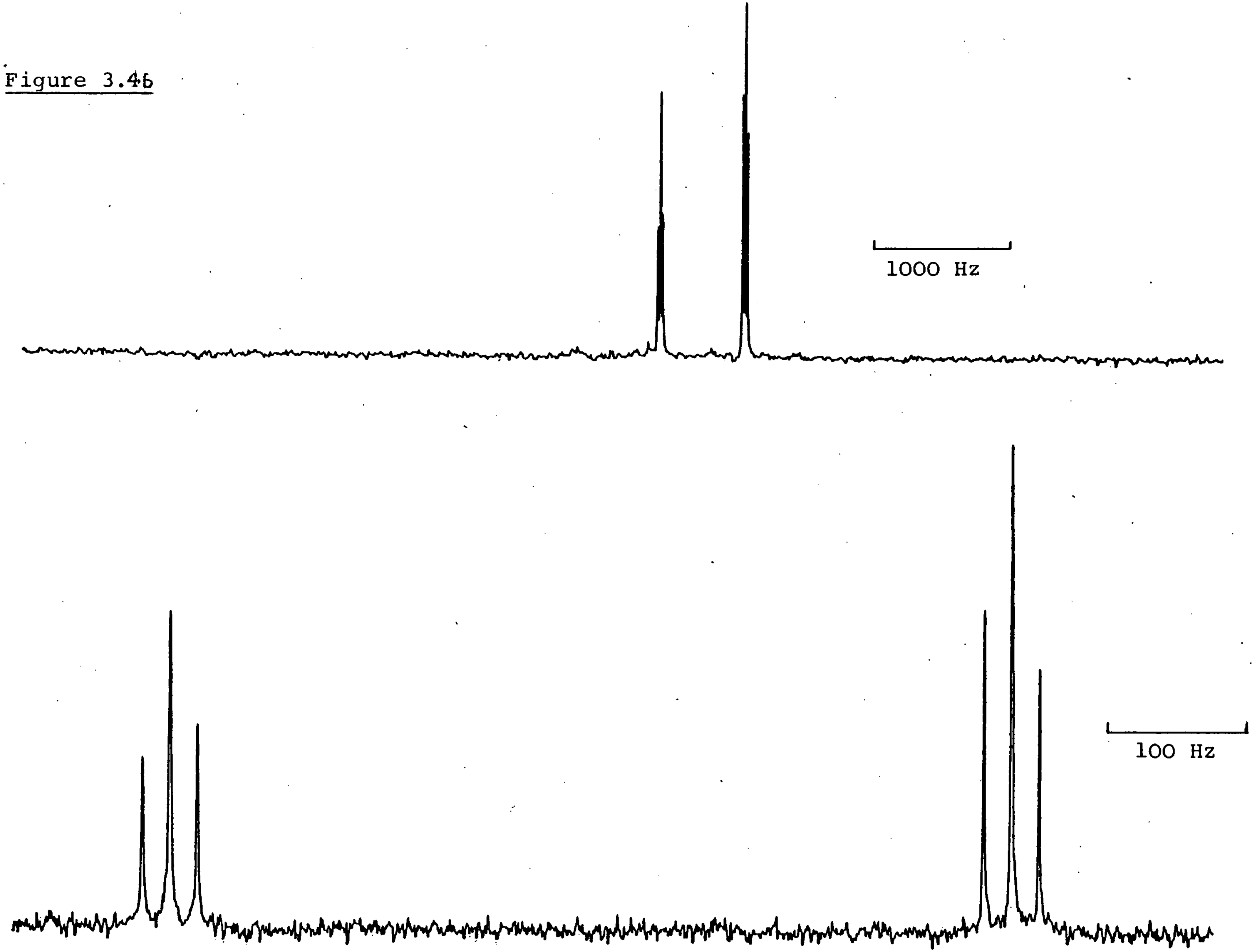
Monitoring the reaction by n.m.r. spectroscopy also proved a useful method of determining the stage the reaction had reached and the method also indicated some of the possible intermediates involved. Thus, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the ruthenium starting material is an A_2B_2 pattern (essentially two triplets; δP = 22.3, 4.7 p.p.m. $^2J_{PP}$ = 20 Hz). As the reaction proceeds, certainly for M = Pt (and possibly M = Pd), signals corresponding to the species $M(S_2CNEt_2)(PMe_2Ph)(Ph_2PS)$ (Table 3.6) are observed. A number of other broad unresolved resonances are evident but at no time is any free PMe_2Ph or $(Ph_2PS)^-$ detected. After a short time, two triplets, due to the final product (53), appear concurrently with signals consistent with the presence of the cations $[M(S_2CNEt_2)(PMe_2Ph)_2]^+$ (Table 3.6). The assignment of the ^{31}P n.m.r. spectrum of the ruthenium product may be made by comparison with other second row transition metal - $(\eta^2\text{-}Ph_2PS)^-$ complexes, such as those observed by Thewissen[31]. Thus, the high frequency resonance (44.9 p.p.m.) was assigned to $(\eta^2\text{-}Ph_2PS)^-$ and the other (19.9 p.p.m.) to PMe_2Ph. The size of $^2J_{PP}$ (19.5 Hz) indicates that the chemically different pairs of phosphorus nuclei are mutually cis.

Figure 3.4a



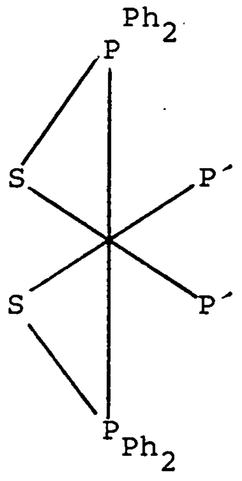
Phosphorus-31-{^{1}H} n.m.r. of the reaction between 17b and [Ru(PMe$_2$Ph)$_4$(CH$_3$CO$_2$)]PF$_6$ showing X Pt(S CNEt)(Ph PS)(PMe Ph) in situ

Figure 3.4b

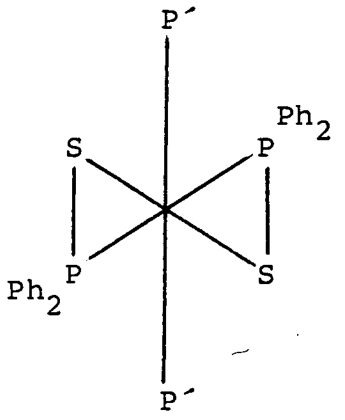


Phosphorus-31-n.m.r. spectrum ($CDCl_3$ 300 K) of $Ru(\eta\text{-}Ph_2PS)_2(PMe_2Ph)_2$ (53)

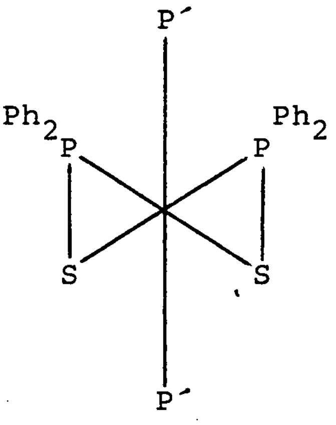
Fig. 3.5



I



II



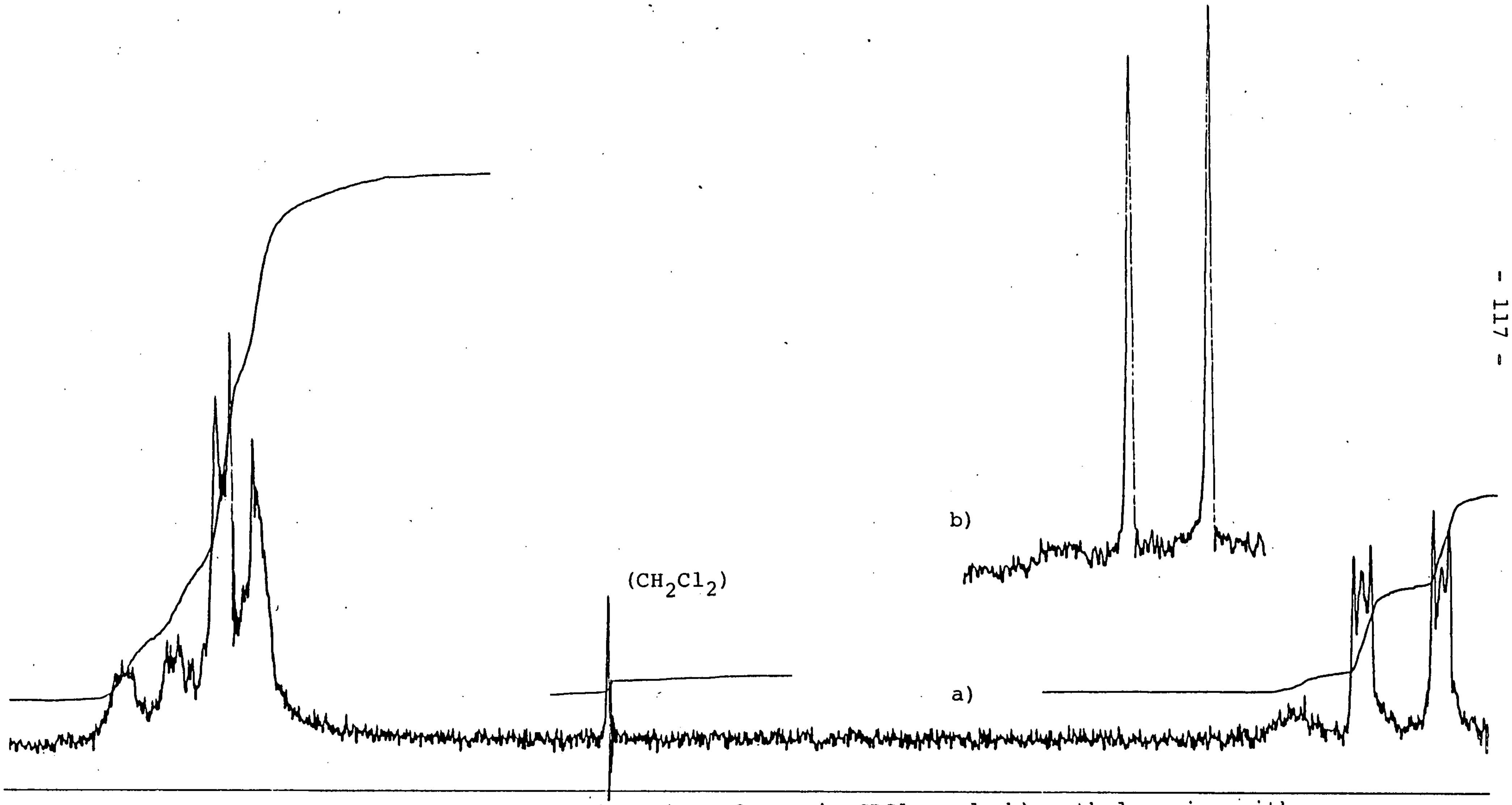
III

P´ = PMe_2Ph

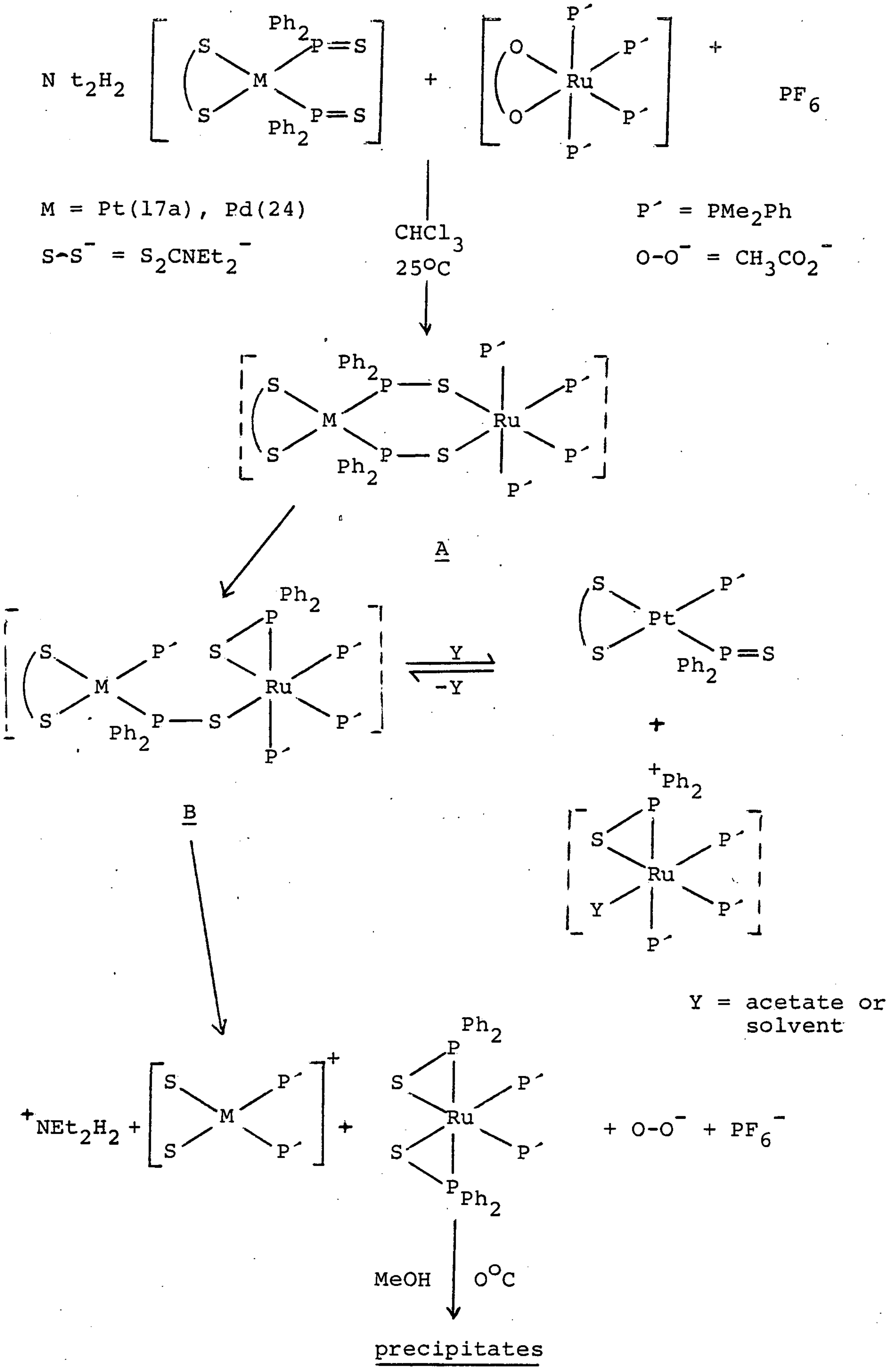
Possible molecular geometries for $Ru(\eta^2\text{-}Ph_2PS)_2(PMe_2Ph)$

There are three structures that would be consistent with the ^{31}P-n.m.r. data, but a selection between the three isomers can be made by examining the ^1H n.m.r. spectrum (fig. 3.6). In the methyl region, two identical pseudo-triplets are observed (δH = 0.98 and 1.39 p.p.m.). Phosphorus-31 irradiation at a single frequency collapses both signals to singlets. This behaviour is observed in $X_3AA'X_3'$ spin systems (X = H, A = P) and pseudo-triplets of this type are typical of cis-phosphines[71], when $J_{AA'}$ is neither very large (which results in a virtual triplet) or very small (which results in a virtual doublet) in comparison to $|J_{AX}+J_{AX'}|$. In addition, the presence of two methyl signals at room temperature means that, even if free rotation occurs about the P-Ru bond, the methyls within the

Figure 3.6



Hydrogen-1-n.m.r. of Ru(η-$Ph_2PS)_2(PMe_2Ph)_2$ a) at 300 K in $CDCl_3$ and b) methyl region with ^{31}P decoupling



SCHEME 3.2 The Reaction of $[M(S_2CNEt_2)(Ph_2PS)_2]^-$ with $[Ru(PMe_2Ph)_4(CH_3CO_2)]PF_6$: A Possible Reaction Pathway

ligand are magnetically non-equivalent and thus there is no mirror plane in the molecule, as there would be in cases II and III. Therefore, the unambiguous choice is I, in which the cis-PMe_2Ph ligands are trans to sulphur, with the ($Ph_2\underline{P}S$) atoms occupying the axial positions.

A further product is present at the end of the reaction: $[M(S_2CNEt_2)(PMe_2Ph)_2]^+$ has been identified in solution (M = Pt: $\delta P = -18.7$; $^1J_{PPt} = 3115.2$ Hz. M = Pd: $\delta P = -3.1$ p.p.m.) by ^{31}P n.m.r. spectroscopy.

Some deductions can therefore be made about the way the reaction proceeds. Displacement of the acetate to form a transient species A (Scheme 3.2) is plausible, followed by an intramolecular phosphine/phosphine sulphide exchange. Other workers have also reported phosphine transfer reactions in hetero-bimetallic complexes, which may also occur by intramolecular processes[72]. The intermediate B thus formed may then react in two ways: reversibly to form $Pt(S_2CNEt_2)(PMe_2Ph)(Ph_2PS)$ and an unidentified ruthenium compound, or with a second exchange to form the final products. A number of broad signals in the ^{31}P n.m.r. spectra, which may be due to the intermediates A or B, are observed during both reactions (M = Pt, Pd). In the platinum case, these do not change appreciably on cooling to -60°C, although they are absent when the reaction is complete.

As a comparison, the reaction of $Pt(S_2CNEt_2)\{(Ph_2PO)_2H\}$ with the same ruthenium complex was also briefly examined. Thus in the presence of a base, a slow reaction commenced. The compound $Pt(S_2CNEt_2)(Ph_2P_AO)(P_BMe_2Ph)$ ($\delta P_A = 46.7$ p.p.m.,

$^{1}J_{PtP}$ = 3421.6 Hz and δP_B = -12.5 p.p.m., $^{1}J_{PtP}$ = 3598.6 Hz; $^{2}J_{PP}$ = 29.3 Hz) could be identified by ^{31}P n.m.r. spectroscopy, indicating that a phosphine transfer does take place, but $[Pt(S_2CNEt_2)(PMe_2Ph)_2]^+$ was not observed: it may be that a second ligand transfer is no longer possible and the reaction stops at this stage. No ruthenium compound could be identified or isolated in a pure state. Another phosphine transfer reaction was observed when $Ni(PEt_3)_2Cl_2$ was mixed with $N^iPr_2H_2[Pt(S_2CN^iPr_2)(Ph_2PS)_2]$ in a similar n.m.r. experiment. After two hours at room temperature, $[Pt(S_2CN^iPr_2)(PEt_3)_2]^+$ was observed (δP = 6.5 p.p.m., $^{1}J_{PtP}$ = 3056.6 Hz) and a singlet at 27.0 p.p.m. may arise from a Ni-phosphinesulphide adduct but neither compound could be isolated. Again evidence for the formation of $Pt(S_2CN^iPr_2)(PEt_3)(Ph_2PS)$ during the reaction was obtained by ^{31}P n.m.r. spectroscopy.

It is interesting to note that hitherto, the Pt-P bond in bridging phosphinite complexes is <u>not</u> broken during coordination reactions and no rearrangements have been observed. The lability of coordinated $(Ph_2\underline{P}S)^-$ and especially $Ph_2\underline{P}$-SR (R = Alkyl) will be discussed more fully in a subsequent chapter, but it is apparent, given a strong M-S bond, that the possibility of breaking the Pt-P bond is large and a careful selection of the "capping" complexes must be made to minimise this. On the other hand, it is possible that this route may be utilised as a relatively clean way of synthesising novel $(Ph_2PS)^-$ complexes.

3.5 Experimental

Physical methods were as for those described in Chapter 2. Phosphorus-31 n.m.r. data are collected in Tables 3.2 and 3.6. Hydrogen-1 n.m.r. data are collected in Table 3.3 or are given with the relevant experimental details.

The following abbreviations are used throughout this and the subsequent chapter: (acac), acetylacetonate; (BIPY), 2,2'-bipyridyl; (DIPHOS), 1,2-diphenylphosphinoethane; (1,5-COD), cyclo-octa-1,5-diene; (DIARS), 1,2 diphenylarsinoethane.

3.5.1 Materials

The compounds $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ (17 a,b) and $Pt(S_2CN^iPr_2)(Ph_2POHSPPh_2)$ (19b) were synthesised as described in Chapter 2. Standard literature methods were used to prepare the following complexes: $[PdCl(S_2CNR_2)]_2$ (R = Et, ^iPr); $[PdBr(S_2CNEt_2)]_2$; $[\{PtCl(S_2CNR_2)\}_2(1,5\text{-COD})]$; t-$PdCl_2(PhCN)_2$; PdX_2(1.5-COD) (X = Cl, Br); $PtCl_2$(1,5-COD); $PtCl_2$(DIPHOS); $PtCl_2$(BIPY) and $[Ru(PMe_2Ph)_4(CH_3CO_2)]PF_6$. K_2PtCl_4 (Johnson Matthey) and $NaBPh_4$ (B.D.H.) were used as received. $PdCl_2$ (Johnson Matthey) was utilised as the more soluble Na_2PdCl_4 salt formed by refluxing in methanol with a stoichiometric amount of NaCl.

3.5.2 Crystal Structure Determination of $[Pt(II)(S_2CN^iPr_2)(Ph_2PS)_2]\ Pt(II)\ (S_2CNEt_2)$ (41)

Crystal data $C_{36}H_{44}N_2P_2Pt_2S_6$, M = 1148, yellow monoclinic needles; a = 10.888(3), b = 12.281(15), c = 18.368(8) Å; α = 76.34(5), β = 76.94(3), γ = 74.97(6) °;

u = 2257.5 Å^3, z = 2, D_c = 1.69 g cm^3, space group P$\bar{1}$ (No. 2) MoK$_\alpha$ radiation, λ = 0.71069 Å, μ = cm^{-1}. Intensity data were measured using a CAD4 diffractometer. A crystal of dimensions 0.25 x 0.25 x 0.20 mm was used to measure 4200 unique reflections out to $\theta = 20^\circ$. 3635 were classed as observed with $I > 2.5\,\sigma(I)$. An empirical absorption correction was applied^{58}.

The position of the platinum atoms was determined from a Patterson map. Subsequent difference Fourier syntheses revealed all non-hydrogen atoms in the molecule. Structure refinement was carried out using SHELX. The phenyl rings were constrained to be planar with all C-C distances 1.395 Å. In the final cycles of least squares refinement positional and anisotropic vibrational parameters for the Pt, P and S atoms were refined. A unit weighting scheme was found to give satisfactory variances of $|F|$ analysed in ranges of sinθ and $|F|$. The final R factor was 0.049 based on 3635 reflections. Final atomic parameters are given in Table 3.5, selected bond lengths in Table 3.4a and angles in Table 3.4b.

3.5.3 Complexes

[M´(II)(S$_2$CNR´$_2$)(Ph$_2$PS)$_2$]M(II)(S$_2$CNR$_2$) complexes (36-42)

General Method Stoichiometric quantities of the salts NR$_2$H$_2$[Pt(S$_2$CNR$_2$)(Ph$_2$PS)$_2$] (17 a,b) and the dimers [PdX(S$_2$CNR$_2$)]$_2$ (X = Cl; R = Et, ^{i}Pr. X = Br; R = Et) or [PtCl(S$_2$CNR$_2$)]$_2$ (1,5-COD)(R = Et, ^{i}Pr) were mixed together in the minimum amount of chloroform (1-10 cm^3) and the solution was shaken for up to six hours to ensure complete reaction. When an excess of methanol was added, high yields of the non-conducting micro-crystalline *products* were obtained. Some physical data are given in Table 3.1. The $^{31}P-\{^{1}H\}$ n.m.r. (Table 3.2) and ^{1}H n.m.r. (Table 3.3) data are also given where these were obtained: some compounds were too insoluble to give satisfactory ^{1}H n.m.r. spectra.

$\{[Pt(II)(S_2CN^iPr_2)(Ph_2PS)_2]Pd(II)(\mu\text{-}Cl)\}_2$ (46a)

The compound $[Ph_3(PhCH_2)P][Pt(S_2CN^iPr_2)(Ph_2PS)_2]$ (0.04 g, 0.04 mmol) and $PhCl_2$ (1,5-COD) (0.01 g, 0.04 mmol) were dissolved in chloroform (1 cm^3). The orange *solid* which precipitated was washed with methanol and diethyl-ether and dried *in vacuo*. mp 245-7°C (0.03 g; 80%).
Found:- C, 40.5; H, 3.7; N, 1.4. Calc for $C_{62}H_{68}Cl_2N_2P_4Pd_2Pt_2S_8$:- C, 39.3; H, 3.6; N, 1.5%.
Mull i.r. spectrum:- ν_{CN} 1500, ν_{PS} 575, ν_{PdCl} 295 cm^{-1}.

The bromide analogue, $\{[Pt(II)(S_2CN^iPr_2)(Ph_2PS)_2]\text{-}Pd(II)(\mu\text{-}Br)\}_2$ (47), a similar orange *solid*, was prepared by a similar method. mp 266°C decomposes (0.01 g; 65%).
Found:- C, 34.7; H, 3.2; N, 1.4. Calc for $C_{62}H_{68}Br_2N_2P_4Pd_2Pt_2S_8$:- C, 37.5; H, 3.4; N, 1.4%.
Mull i.r. spectrum:- ν_{CN} 1500, ν_{PS} 575 cm^{-1}.

$\{[Pt(II)(S_2CNEt_2)(Ph_2PS)_2]Pd(II)(\mu\text{-}Cl)\}_2$ (46b)

When the compound $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (17a) (0.17 g, 0.20 mmol) and $PdCl_2$ (1,5-COD) (0.06 g, 0.20 mmol) were mixed at room temperature in chloroform (5 cm^3) a deep red solution formed, from which an orange micro-crystalline solid precipitated on standing. This solid was refluxed in degassed anhydrous methanol to remove the co-precipitate of NEt_2H_2Cl, then washed with diethylether and dried in vacuo. mp 208-211°C. Found:- C, 37.1; H, 3.2; N, 1.4. Calc for $C_{58}H_{60}Cl_2N_2P_4Pd_2Pt_2S_8$:- C, 37.9; H, 3.3; N, 1.5%.

Mull i.r. spectrum:- ν_{CN} 1530, ν_{PS} 570, ν_{PdCl} 290 cm^{-1}.

The same compound could be prepared from (17a) and t-$PdCl_2(PhCN)_2$ or Na_2PdCl_4, in high yields in a variety of solvents ($CHCl_3$, CH_2Cl_2, MeOH or benzene). In each case the initial product must be purified, by refluxing in methanol, to remove NEt_2H_2Cl.

$\{[Pt(II)(S_2CNEt_2)(Ph_2PS)_2]Pt(II)Cl\}_2C_8H_{12}$ (48a)

The compound NEt_2H_2 $[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (0.09 g, 0.1 mmol) and $PtCl_2$(1,5-COD) (0.04 g, 0.11 mmol) were dissolved in $CHCl_3$ (5 cm^3). A yellow-green solution formed, from which, after filtering into methanol (20 cm^3), a pale yellow solid was obtained. mp 185-87°C; (0.07 g; 70%). Found:- C, 37.1; H, 3.4; N, 1.3. Calc for $C_{66}H_{72}Cl_2N_2P_4Pt_4S_8$:- C, 37.3; H, 3.4; N, 1.3%.

Mull i.r. spectrum:- ν_{CN} 1510, ν_{PS} 580 ν_{PtCl} 300 cm^{-1}.

Hydrogen-1 n.m.r.:- t, 1.12; bs, 1.95; q, 3.42; bs, 4.86 ($^2J(^{195}Pt-^1H)$ 54.4 Hz); m, 7.0-8.0 p.p.m. When heated in a chloroform solution the above compound was spectroscopically observed to rearrange, with the liberation of (1,5-COD). This compound (49) was not isolated. The diisopropyldithiocarbamate analogues (48b, 49b) were also observed by $^{31}P-\{^1H\}$ n.m.r. spectroscopy (Table 3.6).

$\underline{\{[Pt(II)(S_2CN^iPr_2)(Ph_2PS)_2]Pt(II)(DIPHOS)\}BPh_4}$ (50a)

Equimolar quantities of the compound $N^iPr_2H_2[Pt(S_2CN^iPr)(Ph_2PS)_2]$ (17b) (0.25 g, 0.27 mmol) and $PtCl_2$(DIPHOS) (0.18 g, 0.27 mmol) were stirred in methanol (20 cm^3) for 12 h. The yellow solution was filtered into an excess of $NaBPh_4$ dissolved in methanol (10 cm^3) to give an immediate white precipitate. This was washed and dried in the usual manner. mp 273-5°C; (0.34 g; 74%). Found:- C, 56.9; H, 4.7; N, 1.5. Calc for $C_{81}H_{78}BNP_4Pt_2S_4$:- C, 56.6; H, 4.5; N, 0.8%.

Mull i.r. spectrum:- ν_{CN} 1500; ν_{PS} 585 cm^{-1}. Phosphorus-31 data are given in Table 4.6. Hydrogen-1 n.m.r.:- d, 1.23; bs, 4.31; bs, 6.92; ms, 7.0-8.0 p.p.m. Platinum-195-n.m.r.:- tt, 167.9 p.p.m. ($^1J_{PtP}$ 3068.2, $^2J_{PtP}$ 50 Hz); t, 437.9 p.p.m. ($^1J_{PtP}$ 3404.6 Hz).

The compound, $\underline{\{[Pt(II)(S_2CN^iPr_2)(Ph_2PS)_2]Pt(II)(DIPHOS)\}BPh_4}$ (51) was observed in situ, by ^{31}P n.m.r. spectroscopy (Table 4.6) when $Pt(S_2CN^iPr_2)(Ph_2POHSPPh_2)$ (19b) (0.04 g, 0.05 mmol) and $PtCl_2$(DIPHOS) (0.03 g, 0.05 mmol) were mixed in $CDCl_3$ (0.5 cm^3) in the presence of NEt_3. This compound could not be isolated. Thus, when added to a solution of $NaBPh_4$ in methanol, a sticky white gum precipitated, but this could not be crystallised.

$\underline{\{[Pt(II)(S_2CNEt_2)(Ph_2PS)_2]Pt(II)(BIPY)\}BPh_4}$ (52a)

The compound $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (17a) (0.07 g, 0.09 mmol) and $PtCl_2$(BIPY) (0.04 g, 0.09 mmol) were stirred in chloroform (5 cm^3) for six hours. The bright yellow solution was filtered into an excess of $NaBPh_4$ in methanol (10 cm^3) to give a yellow <u>precipitate</u> which was worked up in the normal fashion. mp 249-251°C (decomp). Found:- C, 51.9; H, 4.0; N, 2.7. Calc for $C_{63}H_{58}BN_3P_2Pt_2S_4$:- C, 52.3; H, 4.0; N, 2.9%.

<u>Mull i.r. spectrum</u>:- ν_{CN} 1535; ν_{PS} 585 cm^{-1}.

<u>Hydrogen-1 n.m.r. spectrum</u>:- t, 1.12; q, 3.41; m, 6.85-7.65; dd, 8.88 p.p.m.

<u>bis-η^2-(diphenylphosphinesulphide)bis(dimethylphenylphosphine) ruthenium(II):- $Ru(\eta^2-Ph_2PS)_2(PMe_2Ph)_2$ (53)</u>

<u>Method 1</u> Equimolar amounts of the compound $NEt_2H_2[Pt(S_2CNEt_2)-(Ph_2PS)_2]$ (0.08 g, 0.09 mmol) and $[Ru(PMe_2Ph)_4(CH_3CO_2)]PF_6$ (0.08 g, 0.09 mmol) were dissolved in degassed chloroform and the solution was stirred for six hours. Methanol (10.0 cm^3) was added and the solution was cooled overnight to precipitate pale yellow <u>needles</u>. These were collected, washed and dried in the usual manner. mp. 278-28°C; (0.04 g; 56%). Found:- C, 57.8; H, 5.3. Calc for $C_{40}H_{42}P_4RuS_2$:- C, 59.2; H, 5.2%. <u>Mol. wt. Found</u>:- 842 (811).

<u>Mull i.r. spectrum</u>:- ν_{PS} 585 cm^{-1}.

<u>Hydrogen-1 n.m.r. spectrum</u>:- pt, 0.98, 1.39 (pt : psuedo triplet); m, 7.0-8.0.

<u>Method 2</u> Alternatively $NEt_2H_2[Pd(S_2CNEt_2)(Ph_2PS)_2]$ (0.04 g, 0.05 mmol) and $[Ru(PMe_2Ph)(CH_3CO_2)]PF_6$ (0.04 g, 0.05 mmol) were mixed in $CDCl_3$ (0.5 cm^3) and the product was obtained as above (0.02 g; 47%).

TABLE 3.1 Some Physical Data for $Pt(II)(S_2CNR_2)(Ph_2PS)_2M(II)(S_2CNR'_2)$ Compounds

Cmpd.	Microanalyses[a]			mw[b]	yield	mp/°C	ir[c] ν_{CN}/cm^{-1}		ν_{PS}/cm^{-1}	Comments
	C%	H%	N%							
(36)	38.4 (39.6)	3.8 (3.9)	1.9 (2.7)	NR[d]	41%	233-235	1525		590	orange
(37)	41.3 (41.5)	4.2 (4.1)	2.7 (2.6)	1045 (1057)	65%	195-198	1500	1520	595	orange
(38)	36.2 (36.4)	3.6 (3.6)	2.2 (2.5)	NR	62%	179-181	1515		590	lemon yellow
(39)	37.4 (37.6)	3.8 (3.8)	2.7 (2.4)	1110 (1148)	45%	165-167	1500	1520	585	yellow
(40)	38.0 (41.5)	3.8 (4.1)	2.5 (2.6)	NR	70%	254-256	1500	1525	585	light orange
(41)	36.0 (37.6)	3.6 (3.8)	2.3 (2.4)	NR	87%	NR	1495	1530	580	bright yellow
(42)	NR (38.8)	NR (4.1)	NR (2.4)	NR	90%	230-232	1500		580	bright yellow

[a] Calculated values in parentheses

[b] Most compounds were too insoluble in benzene to record this data

[c] Mull i.r. spectra

[d] N.R. : not recorded.

TABLE 3.2 Phosphorus-31-{^1H} n.m.r. (300 K) Data[a] for $[Pt(S_2CNR_2)(Ph_2PS)_2]M(S_2CNR'_2)$ Compounds

Compound	δP/p.p.m.	$^1J_{PtP}$/Hz	$^2J_{PtP}$/Hz
(36)	29.9	3519.3	-
(37)	30.2	3520.5	-
(38)	24.3	3409.4	62.2
(39)	24.5	3413.2	63.4
(40)[b]	29.5	3459.5	-
(41)	25.3	3452.2	58.6
(42)	25.5	3459.5	61.0

[a] Recorded in $CDCl_3$, unless stated.

[b] Recorded in CH_2Cl_2 (d^6-acetone capilliary lock).

TABLE 3.3 Hydrogen-1 n.m.r. Spectra[a] of $[Pt(S_2CNR_2)(Ph_2PS)_2]M(S_2CNR'_2)$ Compounds

Compound	CH_3–[b]	CH_2–[b]	CH[b]	other[c]
(36)	t,1.14; t,1.17	q,3.45; q,3.57	-	m,7.15-8.0
(37)	t,1.11; d,1.23	q,3.46	m,4.49	m,7.1 -8.0
(38)	-[d]	-	-	-
(39)	t,1.15; d,1.39	q,3.49	m,4.38	m,7.05-8.0
(40)	-[d]	-	-	-
(41)	t,1.21; bd,1.30	q,3.50	bm,4.34	m,7.2 -7.8
(42)	d,1.45; d,1.62	-	bm,4.44	m,7.0 -8.0

[a] Recorded in $CDCl_3$ at 300 K; shifts in p.p.m. from T.M.S.

[b] $^3J_{HH} = 7.0$ Hz

[c] Ar-H resonances

[d] Insufficiently soluble

TABLE 3.4 Interatomic Distances and Angles for Compound (41) with Estimated Standard Deviations in Parentheses

(a) Distances (A$^{\circ}$)

Pt(1)-S(2)	2.344(4)
Pt(1)-S(5)	2.342(4)
Pt(1)-P(1)	2.260(4)
Pt(1)-P(2)	2.255(4)
Pt(2)-S(1)	2.326(4)
Pt(2)-S(3)	2.322(4)
Pt(2)-S(4)	2.320(4)
Pt(2)-S(6)	2.306(4)
P(1)-S(1)	2.043(5)
P(2)-S(3)	2.040(5)
S(2)-C(25)	1.752(15)
S(5)-C(25)	1.706(15)
S(4)-C(26)	1.695(18)
S(6)-C(26)	1.721(19)
P(1)-C(1)	1.827(9)
P(1)-C(19)	1.842(9)
P(2)-C(7)	1.854(9)
P(2)-C(13)	1.811(8)

N(1)-C(25)	1.319(18)
N(2)-C(26)	1.352(20)
N(1)-C(31)	1.499(23)
N(1)-C(34)	1.510(21)
C(31)-C(32)	1.568(27)
C(31)-C(33)	1.521(28)
C(34)-C(35)	1.445(28)
C(34)-C(36)	1.493(28)
N(2)-C(27)	1.469(26)
N(2)-C(29)	1.470(23)
C(27)-C(28)	1.558(32)
C(29)-C(30)	1.571(27)
Pt(1)---Pt(2)	4.002

(b) Selected Bond Angles ($^{\circ}$)

P(1)-Pt(1)-P(2)	93.2(1)
P(1)-Pt(1)-S(2)	96.9(1)
P(2)-Pt(1)-S(5)	95.2(1)
S(5)-Pt(1)-S(2)	74.6(1)
Pt(1)-S(2)-C(25)	87.0(5)
Pt(1)-S(5)-C(25)	88.1(5)
S(2)-C(25)-S(5)	110.4(8)

S(1)-Pt(2)-S(3)	99.5(2)
S(1)-Pt(2)-S(4)	95.3(2)
S(3)-Pt(2)-S(6)	90.1(2)
S(4)-Pt(2)-S(6)	74.9(2)
Pt(2)-S(4)-C(26)	87.2(6)
Pt(2)-S(6)-C(26)	87.0(6)
S(4)-C(26)-S(6)	110.9(10)

Pt(1)-P(1)-S(1)	116.7(2)
Pt(1)-P(2)-S(3)	110.7(2)
Pt(2)-S(1)-P(1)	106.2(2)
Pt(2)-S(3)-P(2)	107.8(2)
Pt(1)-P(1)-C(1)	113.7(4)
Pt(1)-P(1)-C(19)	111.5(4)
Pt(1)-P(2)-C(7)	113.4(4)
Pt(1)-P(2)-C(13)	117.7(4)

TABLE 3.5 Fractional Coordinates of Atoms with Standard Deviations for Compound (41)

	X	Y	Z
Pt(1)	0.14046(5)	0.15654(5)	0.28062(3)
Pt(2)	0.10954(6)	0.48321(5)	0.16845(3)
S(1)	0.2966(4)	0.4032(3)	0.2202(3)
S(2)	0.2054(4)	0.0006(4)	0.2166(3)
S(3)	-0.0436(4)	0.4420(4)	0.2756(3)
S(4)	0.2151(5)	0.5546(4)	0.0488(3)
S(5)	-0.0336(4)	0.0645(4)	0.3137(3)
S(6)	-0.0530(5)	0.5851(4)	0.1013(3)
P(1)	0.3204(4)	0.2284(3)	0.2354(3)
P(2)	0.0415(4)	0.3002(3)	0.3454(2)
N(1)	0.0114(12)	-0.1169(11)	0.2460(7)
N(2)	0.0391(13)	0.6788(12)	-0.0419(8)
C(1)	0.4126(10)	0.1842(9)	0.1469(5)
C(2)	0.4790(10)	0.0698(9)	0.1477(5)
C(3)	0.5548(10)	0.0368(9)	0.0811(5)
C(4)	0.5644(10)	0.1181(9)	0.0137(5)
C(5)	0.4981(10)	0.2325(9)	0.0129(5)
C(6)	0.4222(10)	0.2655(9)	0.0795(5)
C(7)	-0.0958(8)	0.2655(9)	0.4205(5)
C(8)	-0.2202(8)	0.3348(9)	0.4248(5)
C(9)	-0.3167(8)	0.3077(9)	0.4859(5)
C(10)	-0.2888(8)	0.2114(9)	0.5478(5)
C(11)	-0.1644(8)	0.1421(9)	0.5386(5)
C(12)	-0.6789(8)	0.1691(9)	0.4774(5)
C(13)	0.1354(9)	0.3419(8)	0.3999(6)
C(14)	0.2300(9)	0.2589(8)	0.4347(6)
C(15)	0.3024(9)	0.2908(8)	0.4767(6)
C(16)	0.2802(9)	0.4057(8)	0.4840(6)
C(17)	0.1856(9)	0.4887(8)	0.4492(6)
C(18)	0.1132(9)	0.4568(8)	0.4072(6)
C(19)	0.4431(9)	0.1634(9)	0.2967(6)
C(20)	0.5363(9)	0.2218(9)	0.2988(6)
C(21)	0.6253(9)	0.1726(9)	0.3478(6)
C(22)	0.6212(9)	0.0652(9)	0.3946(6)
C(23)	0.5280(9)	0.0068(9)	0.3925(6)
C(24)	0.4390(9)	0.0560(9)	0.3435(6)
C(25)	0.0543(13)	-0.0320(12)	0.2575(8)
C(26)	0.0670(17)	0.6170(15)	0.0260(10)
C(27)	0.1430(22)	0.6936(20)	-0.1078(13)
C(28)	0.1712(24)	0.8155(22)	-0.1179(14)
C(29)	-0,0936(19)	0,7307(17)	-0,0551(12)
C(30)	-0.1571(20)	0.8424(18)	-0.0205(12)
C(31)	0.0922(19)	0,2052(17)	0.2001(12)
C(32)	0.1129(20)	-0.1442(18)	0.1144(12)
C(33)	0,2127(21)	-0,2717(19)	0.2329(13)
C(34)	-0.1250(17)	-0.1304(16)	0.2797(10)
C(35)	-0.1925(24)	-0.1267(22)	0.2196(14)
C(36)	-0.1190(23)	-0.2418(21)	0.3355(13)

TABLE 3.6 Miscellaneous Phosphorus-31-{^1H} n.m.r. Data

Compound	δP/p.p.m.	$^1J_{PtP}$/Hz	$^2J_{PtP}$/Hz	Other/Hz
(48a)	33.2	3441.4	22.5	
(48b)	33.2[b]	3399.7	20.8	
(49a)	25.4[b]	3491.2	38.6	
(49b)	25.7[b]	3452.2	40.3	
(50a)[c]	23.8	3399.6	48.8	$^3J_{PP}$ 6.1
(51) P_S[d]	16.5[b]	3438.5	52.7	
P_O[e]	68.1[b]	3548.8	9.8	$J_{P_OP_S}$ 39.1
(52a)	31.7	3472.7	33.2	
$Pt(S_2CNEt_2)(Ph_2P_AS)(P_BMe_2Ph)$ P_A	27.5[b]	3166.5		$J_{P_AP_B}$ 24.5
P_B	-14.7[b]	3483.9		
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]^+$	-18.7[b]	3115.2	-	
$[Pd(S_2CNEt_2)(PMe_2Ph)_2]^+$	-3.1[b]	-	-	
$Ru(Ph_2P_AS)(P_BMe_2Ph)_2$ P_A	44.9	-	-	$^2J_{P_AP_B}$ 19.6
P_B	19.9	-	-	

[a] recorded in $CDCl_3$ at 300 K.

[b] observed *in situ* only.

[c] δP_{DIPHOS}: 49.5 p.p.m.; $^1J_{PtP}$ 3061.5 Hz

[d] δP_{DIPHOS} (*trans* to S): 46.6 p.p.m.; ^1J 3206.2, $^3J_{PP_S}$ 5.8, $^3J_{PP}$ 5.9, $^3J_{PP_O}$ 3.0 Hz

[e] δP_{DIPHOS} (*trans* to O): 35.7 p.p.m.; ^1J 3740.0, $^3J_{PP_S}$ 5.9 Hz.

Chapter 4

Reactions with Metal Complexes (2)

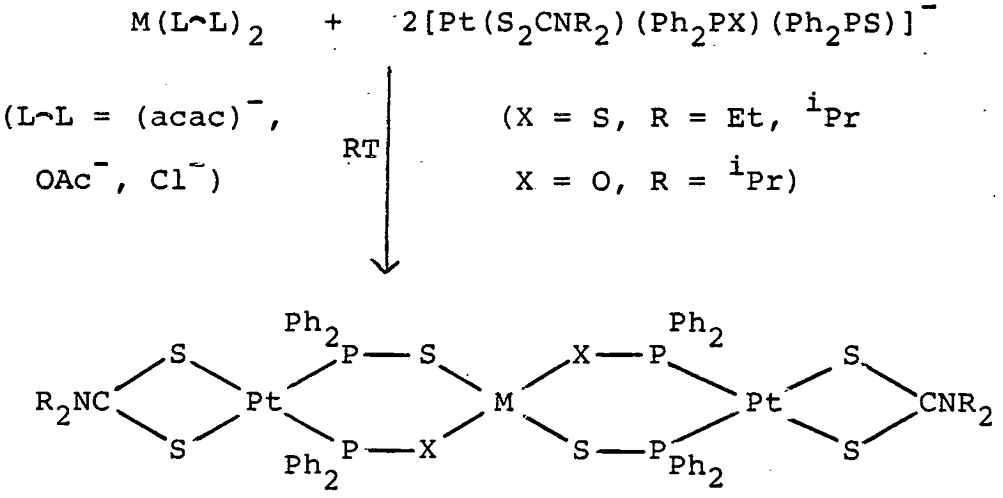
4.1 The Reactions of $[Pt(S_2CNR_2)(Ph_2PS)_2]^-$ and $Pt(S_2CN^iPr_2)(Ph_2POHSPPh_2)$ with First Row Transition Metal Ions

4.1.1 Introduction

The compounds $Pt(L)_2\{(R_2PO)_2H\}$ have principally been used as ligands with first row transition metal complexes[1,19,64]. It was therefore an obvious extension to examine the reactions of the corresponding dithio and monothio anions, (17) and (19), with the same metal salts. A number of such reactions have been attempted and are discussed below and a number of comparisons have been drawn in the course of this discussion.

Some experimental difficulties which do not occur in the original phosphinite reactions have been observed. For example, considerable care must be taken to exclude oxygen from reaction solutions to prevent decomposition. In the phosphinite case oxygen, a class a ligand, forms many stable complexes with the class a metals of the first transition series. In the thiophosphinite case, sulphur being a class b ligand, M-S bonds are less likely to form and the analogues of a number of the more readily prepared phosphinite complexes (e.g. with VO^{2+}) could not, therefore, be prepared.

These problems notwithstanding, when $CHCl_3$, C_6H_6 or MeOH solutions of a divalent metal $(acac)^-$, $(OAc)^-$ or halide salt are treated with solutions of the chelating metal complex, the preliminary results indicate that a single type of reaction takes place (Eqn. 23).



$X = S$; $R = Et$; $M = Fe$(54), Co(55), Ni(56), Cu(57), Zn(58)
$X = S$; $R = {}^{i}Pr$; $M = Co$(59), Ni(60), Cu(61)
$X = O$; $R = {}^{i}Pr$; $M = Co$(62), Ni(63)

...(23)

The products listed in the equation have all been isolated and characterised and a number of techniques hitherto not used in this study have been utilised. In addition to the electronic spectra of the complexes some e.s.r. spectra have been recorded and some magnetic moments have been calculated in solution over a range of temperatures. The data are given in Table 4.2 and a series of Curie-Weiss plots thus obtained are shown in Fig. 4.1.

4.1.2 The Reaction of (17 a,b) with the Early Transition Metal Ions

The reactions of (17a) with $VO(acac)_2$, $VO(OAc)_2$-$[Cr(OAc)_2]_2$ and $Mn(OAc)_2$ were examined. $[Cr(OAc)_2]_2$ was inert under all the conditions tried. A white solid was obtained by workup of the manganese reaction solution, but subsequent analysis of infrared and n.m.r. spectra showed this sample to be a mixture of the original platinum species (17a) and an unidentified product which might be the required adduct. The mixture could not be separated, however, and no firm characterisation was made.

When $VO(acac)_2$ and the $[Pt(S_2CNR_2)(Ph_2PS)_2]^-$ anion were mixed at room temperature a dark green solution slowly formed. When the solution was refluxed a similar solution was rapidly formed, but trituration with methanol yielded only small quantities of $Pt(S_2CNR_2)_2$, which was identified by its i.r. and ^1H n.m.r. spectra. A pale green solid could be obtained from the room temperature reaction solution. However, $^{31}P-\{^1H\}$ n.m.r. and i.r. studies clearly showed that this contained the platinum starting material. An e.s.r. spectrum of this product in CH_2Cl_2 at 153 K showed that $VO(acac)_2$ was the only paramagnetic species present. Thus, the experimental $g_{\parallel}$ (1.945, $A_{\parallel}$ = 185 G) and $g_{\perp}$(2.010, $A_{\perp}$ = 65 G) compare well with literature data[73]. On repeating the experiment, careful trituration of the green solution with methanol and diethylether yielded, successively, small quantities of pure $VO(acac)_2$ and (17a). An intractable green oil was left but attempts to characterise this by n.m.r. or i.r. studies were unsuccessful and so no further work was carried out.

This behaviour is in marked contrast to the corresponding reaction of $Pt(S_2CNEt_2)\{(Ph_2PO)_2H\}$ (2) with

$VO(acac)_2$, in which both acetylacetonate ligands are readily displaced to give a trinuclear oligomer[66b] similar to the type described already (Section 4.1.1). The data gathered for this species (by e.s.r. and electronic spectra and by magnetic measurements), are consistent with the presence of a distorted five coordinate V(IV) ion. It is of further interest to note that this and other similar VO^{2+} adducts[64] exhibit broad line e.s.r. spectra, ca. 50 G compared with 10 G in $VO(acac)_2$, due to unresolved ^{31}P-nuclear coupling. This distinguishing feature further confirms the failure of the $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$ reaction.

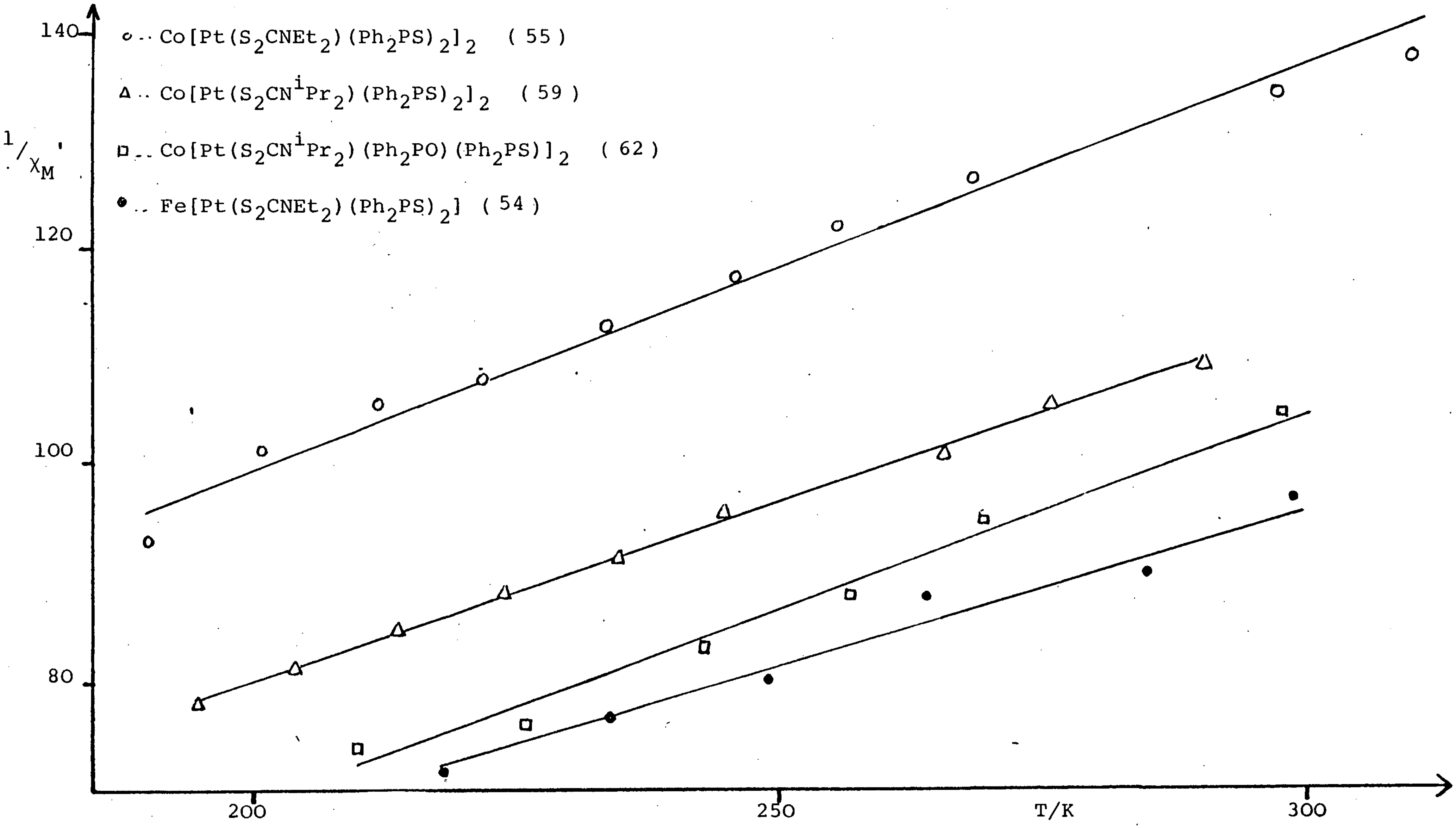
4.1.3 The Reactions with the Later Transition Metal Ions

A greater degree of success was obtained, when solutions of (17a) and $M(acac)_2$ were mixed at room temperature, when M = Fe - Zn. Analytical measurements indicate that the compounds (54-58) all have the same stoichiometry. A number of the diisopropyldithiocarbamate analogues have been synthesised (59-61) and the series has been extended to include some complexes of (19b) (62,63) (Eqn. 23).

The infrared spectra of these complexes are very similar. They contain a strong ν_{PS} band at 575-590 cm^{-1}. Compounds (62) and (63) also exhibit a P-O stretching band at 1050 cm^{-1}. These and other data are given in Table 4.1.

The orange Fe(II) complex (54) is paramagnetic and no n.m.r. spectra could be obtained. The magnetic moment in solution at ambient temperature (299 K) is 5.00 BM and the compound obeys the Curie-Weiss law over the range 218-299 K (θ = 23 K; see Table 4.4 and Fig. 4.1). Typically,

Figure 4.1



Inverse Magnetic Susceptibility vs. Temperature (Curie-Weiss Plot) observed moments for high spin four coordinate (d^6)(Fe(II) complexes, are in the range 5.1-5.5 BM. However, the tetrahedral species Fe{N(Me_2PS)$_2$}$_2$, which also has an FeS_4 core, confirmed by X-ray analysis, has a moment of 4.99 BM[74]. It is possible, therefore, that (54) is also tetrahedral, but this cannot be confirmed as yet. If it is so, however, electronic spectra in the 3000-6000 cm^{-1} (near i.r.) region should show the presence of the Δ_t transition ($^5E \rightarrow {}^5T_2$) and such observations should be included in subsequent studies. No e.s.r. spectra were observed at low (153 K) or ambient temperatures. In solution, in air, the complex decomposes to give a darker brown, presumably Fe(III) species, but this process, again, has not yet been fully examined.

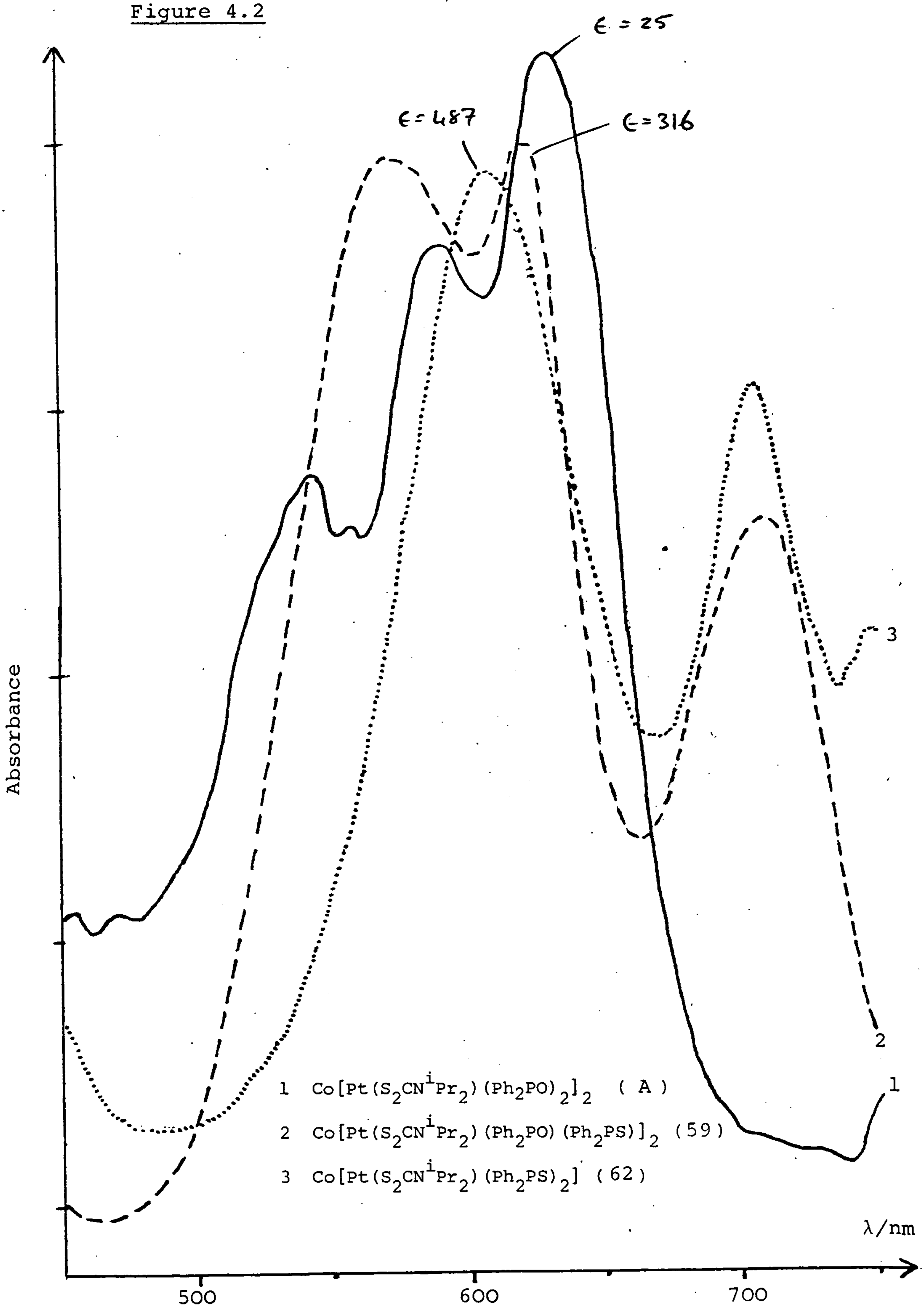
The complexes with the CoS_4 core (55,59) differ in many respects from the CoS_2O_2 (62) and CoO_4[66b] species. The former are isolated as green solids and the latter two are blue. No ^{31}P or ^1H n.m.r. spectra could be obtained for the CoS_4 species but contact shifted ^1H n.m.r. spectra of the CoS_2O_2 (62) and CoO_4 analogues have been obtained (although they are not strictly comparable). Thus, for Co[Pt($S_2CN^iPr_2$)(Ph_2PO)(Ph_2PS)]$_2$ a doublet at 0.53 p.p.m. is assigned to the CH_3 resonance and a series of multiplets at 7.92, 3.19 and 3.51 p.p.m. (intensity ratio 1:2:2) to the aromatic protons, indicating that the distant isopropyl ligand and p-aromatic protons are least affected by the paramagnetic centre. The complex Co[Pt($S_2CN^iPr_2$)(Ph_2PO)$_2$]$_2$ exhibits signals at 6.80 (ortho and meta aromatic protons) and 5.94 (para) indicative of a much reduced paramagnetic shift. As expected no ^{31}P n.m.r. spectra were obtained for these two complexes.

The trend in magnetic moments, at ambient temperature, is from high (5.02 BM, CoO_4) to low (4.64 BM, CoS_4) as the number of coordinating sulphurs increases which is possibly a reflection of changes in the spin-orbit coupling contribution to the magnetic moment, as all the values observed are still consistent with tetrahedral geometry around Co(II)[75]. The complexes obey the Curie Weiss Law over the range 190-301 K, (Table 4.2; Fig. 4.1). Further support for a tetrahedral geometry can be obtained from the visible spectra of the complexes (Fig. 4.2). In a tetrahedral ligand field, the spectra are dominated by the $^4A_2 \rightarrow {}^4T_1(P)$ transition, which is more intense (molar absorbances of several hundred $mol^{-1}\ cm^{-1}$) and occurs at lower energies than the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition observed in an octahedral environment.

The visible spectra of the Co(II) complexes exhibit the expected several bands in the 14000-16000 cm^{-1} region, with absorbances of around 400-500 $mol^{-1}\ cm^{-1}$ and are thus consistent with a tetrahedral CoL_4 core. Whereas the CoO_2S_2 chromophore (62) exhibits a 3 band spectrum which is very similar to the CoO_4 spectrum, the absorption envelope of the CoS_4 (55,59) species differs in that only two distinct peaks are observed (Fig. 4.2).

Further bands, occurring in the near infrared region ($^4A_2 \rightarrow {}^4T_1(F)$ transition), are observed for the CoO_4 species and spectra of this region should be obtained in subsequent studies of the CoS_4 and CoO_2S_2 species. No e.s.r. spectra

Figure 4.2



1 $Co[Pt(S_2CN^iPr_2)(Ph_2PO)_2]_2$ (A)

2 $Co[Pt(S_2CN^iPr_2)(Ph_2PO)(Ph_2PS)]_2$ (59)

3 $Co[Pt(S_2CN^iPr_2)(Ph_2PS)_2]$ (62)

Visible Spectra of the Cobalt complexes (59), (62) and (A).

could be obtained for any of these complexes at low or room temperature but Sperline and Roundhill[19] do report a spectrum obtained for the complex $Co[PtCl(PPh_3)((OMe)_2PO)_2]_2$ (g = 4.27; 2.07), interpreted as being due to a distorted tetrahedral CoO_4 moiety.

When a methanol suspension, or chloroform solution, of the complexes (55) or (59) is heated under reflux in chloroform, $Pt(S_2CNR_2)_2$, characterised readily by its infrared and ^1H n.m.r. spectra, can be obtained from solution. The process taking place here is unknown. No n.m.r. spectra can be obtained from the reaction solution and no Co-containing compound could be isolated.

The nickel complexes $Ni[Pt(S_2CNR_2)(Ph_2PS)_2]_2$ (R = Et(56), ^iPr(60)) are insoluble brown solids which rapidly precipitate from solution despite varying the solvent and the Ni(II) substrate. It has proven impossible to obtain any solution data (e.s.r., Evan's method and multinuclear n.m.r. studies) and solid state susceptibilities and electronic spectra have not been recorded. However, by comparison with other similar systems, some tentative conclusions can be drawn.

The complexes $Ni[Pt(S_2CN^iPr_2)(Ph_2PS)(Ph_2PO)]_2$ (63) and $Ni[Pt(S_2CN^iPr_2)(Ph_2PO)_2]_2$[66b] are both blue, relatively soluble complexes. Neither show n.m.r. signals. The electronic spectra of the latter, and the magnetic moment (2.67 BM) have been interpreted on the basis of octahedral geometry (there is evidence that a single (acacH) ligand may be weakly coordinated in some manner. The complex $Ni[N(Me_2PS)_2]_2$ is tetrahedral[68a,b], but this is exceptional for $Ni(II)S_4$ chelates. In contrast, $Ni[Pt(DIPHOS)\{(OMe)_2PO\}_2]_2(ClO_4)_2$[19] is diagmagnetic and has a square planar geometry.

It is therefore very possible that the change in colour (brown being indicative of a square planar geometry) and the different behaviour (cf. the equally insoluble square planar palladium trinuclear complex discussed subsequently) of the NiS_4 complexes are indicative of a square planar geometry. This will, of course, be resolved as more information is gained in later studies.

The dark green Cu(II) complexes (57, 61) precipitate rapidly from solution, as they are formed, irrespective of the medium used. If left as a suspension, the initial product becomes yellow, presumably due to an intramolecular redox reaction to yield a Cu(I) species (57a). This second product has not yet been identified.

The initial products, which are stable in the solid state, for considerable periods when isolated, exhibit i.r. spectra similar to those obtained for the other complexes in this series. No visible spectra could be obtained due to low solubility and the decomposition problems. The intense blue-green colour, however, may be indicative of a distorted square planar arrangement. Solid state spectra may help to resolve such problems.

The complex (57) exhibits a well resolved e.s.r. spectrum. At 153 K both the parallel ($g_{\parallel} = 2.129$; $A_{\parallel} = 119$ G) and perpendicular ($g_{\perp} = 2.034$; $A_{\perp} = 40$ G) signals are resolved and show splitting due to nuclear hyperfine coupling ($^{63}Cu/^{65}Cu$; spin 3/2). In contrast, the e.s.r. spectra of $Cu\{PtCl[(OMe)_2PO]_2(PPh_3)\}_2$, observed by Sperline and Roundhill[19], does not show an $A_{\perp}$ coupling, and the observed $A_{\parallel}$ coupling is considerably less ($g_{\parallel} = 2.365$;

$A_{\parallel}$ = 141 G; $g_{\perp}$ = 2.058). The complex prepared by Veitch[66b], $Cu[Pt(S_2CN^iPr_2)(Ph_2PO)_2]_2$ does however exhibit both couplings ($g_{\parallel}$ = 2.37; $A_{\parallel}$ = 170 G; $g_{\perp}$ = 2.044; $A_{\perp}$ = 25 G). Using the relationships $g_{\perp} = 2.00 - {}^{2\lambda}/_{\delta}$ and $g_{\parallel} = 2.00 - {}^{8\lambda}/_{\Delta}$ a value less than unity for the ratio Δ/δ is found, indicating a square planar geometry for all three complexes. (Both these CuO_4 complexes exhibit electronic spectra which can also be interpreted as being due to a square planar ligand arrangement). The e.s.r. lines are not broadened (at <u>ca</u>. 14 G) to any extent and this contrasts with the VO^{2+} species already discussed.

The green Cu(II) complex (57) also gives an e.s.r. spectrum at room temperature with an isotropic g-value of 2.066 ($A_{\perp}$ = 52.5 G). Within minutes, however, this pattern alters with a concomitant loss of intensity: a second signal ($g_{\perp}$ = 2.015; $A_{\perp}$ = 59.6 G) is observed during this change which suggests at least one intermediate is involved during the reaction to form the Cu(I) species. When the e.s.r. signal had completely decayed, subsequent examination showed only the fine yellow precipitate (57a) was present.

No significant differences are observed between the i.r. spectra of the green precursor (57) and the yellow derivative (57a), indicating that the CuS_4 core may remain intact.

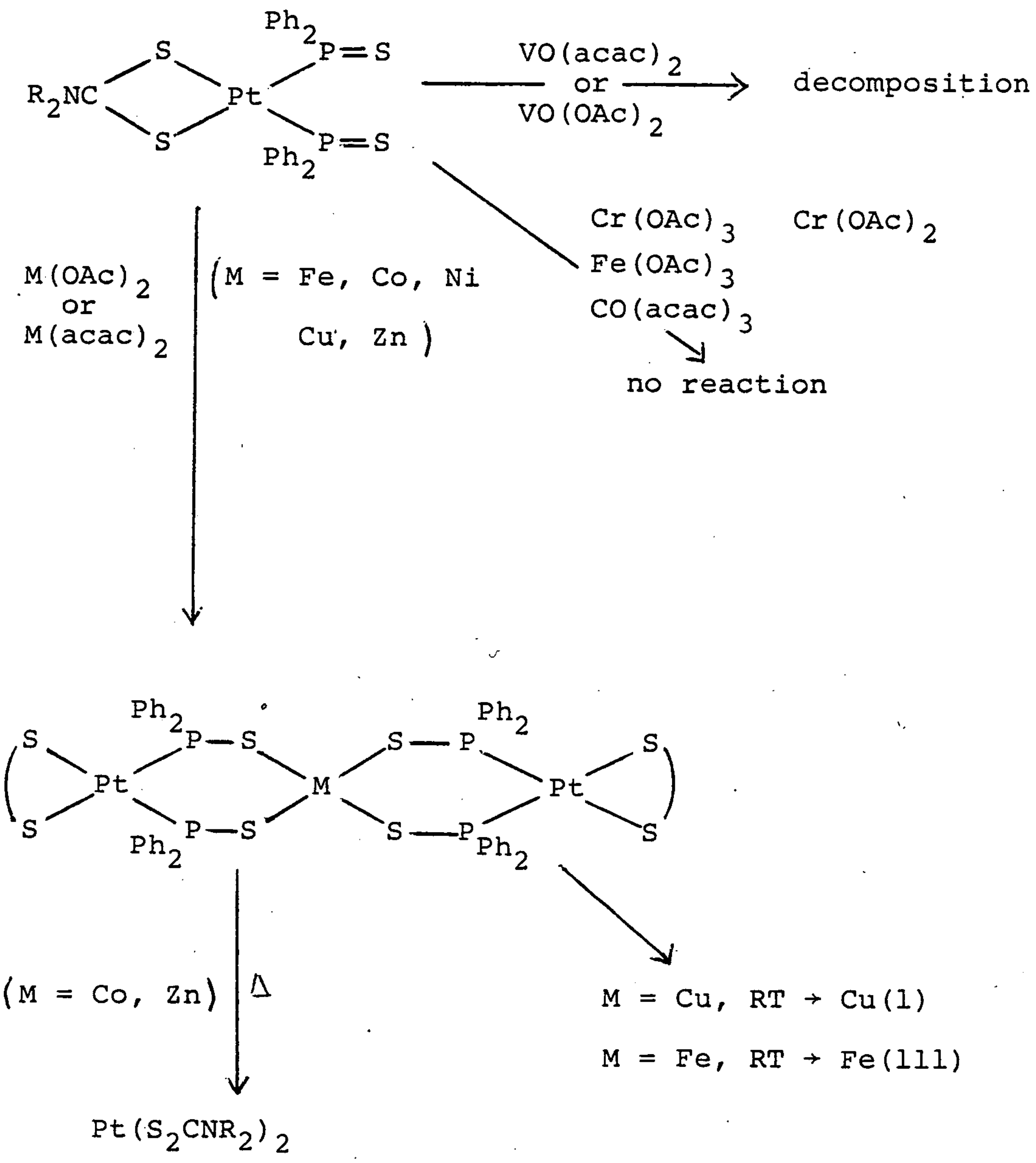
When Cu(I) chloride is mixed with $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2$ an orange yellow solid is obtained, which gives an identical i.r. spectrum (to 57 and 57a) apart from in the P-S stretching region, where a second strong band is observed (560 cm^{-1}).

No magnetic or n.m.r. measurements were obtained for these complexes for the reasons discussed earlier.

Finally, $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ will react with $Zn(OAc)_2$ to give a diagmagnetic white solid, $Zn[Pt(S_2CNEt_2)(Ph_2PS)_2]_2$ (58). This product has been characterised by conventional techniques. Thus the mull i.r. spectrum is similar to those of the other products in this series (ν_{CN} 1518 and ν_{PS} 585 cm^{-1}). The $^{31}P-\{^1H\}$ n.m.r. spectrum is a sharp singlet with Pt satellites (δP 30.3 p.p.m.; $^1J_{PtP}$ = 3482.7 Hz) and the ^1H n.m.r. spectrum is consistent with the proposed formulation. The complex is probably tetrahedral. Like the CoS_4 complexes, one of the rearrangement products obtained on heating a solution of this complex is $Pt(S_2CNEt_2)_2$.

In conclusion, a series of transition metal $M(L\frown L)_2$ complexes has been prepared where M = Fe - Zn and $L\frown L$ is the anionic platinum chelates (17 a,b) and (19b) (Fig. 4.3). The complexes show several differences from the analogous $M[Pt(S_2CNR_2)(Ph_2PO)_2]_2$ compounds, principally where M = Cu(II) and Ni(II). In the latter case a square planar geometry around Ni and intermolecular association may explain the low solubility. Further measurements, for example, bulk magnetic and solid state electronic spectra, should now be made to examine the validity of this premise. In the Cu(II) case the known character of Cu(II)-thioligand systems supports the possibility of a rapid redox reaction. Many previous attempts to generate $Cu(II)S_4$ complexes have led to Cu(I) species. For example, in the series of <u>tetrahedral</u> $M[N(Ph_2PS)_2]_2$ (M = Fe, Co, Ni, Zn) complexes prepared by Davison and Switkes[68a], the copper(II) reaction yielded copper(I) species and, also, no 2,5-dithiolene

Fig. 4.3 Synthesis of 1st row complexes (54-63)



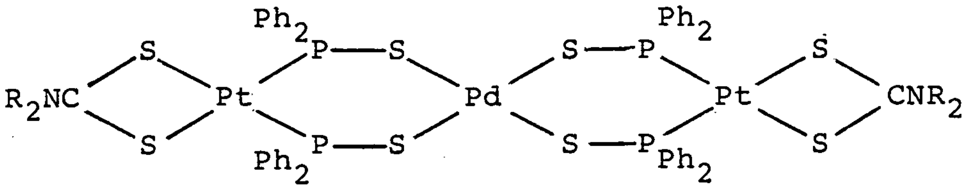
complexes (Sacsac) of Cu(II) have been isolated, oxidised dithiolium-copper(I) salts being obtained instead.

The mixed species, MO_2S_2, appear to resemble the MO_4 analogues more than the MS_4 species, but a considerable amount of further work must now be done before any real comparisons can be drawn.

In particular, the various decomposition or subsidiary reactions should be examined in depth. For example, an insight into the reactions taking place in the Vanadyl system, which could not be resolved, may be gained by examining, isolating and characterising the products resulting when the CoS_4 and ZnS_4 complexes are heated. Additionally, it would be valuable to characterise the Cu(I) or the possible Fe(III) species, as this too, would give more information on the complexes from which they are derived.

4.2 The Reaction with $Pd(L^\frown L)_2$ Compounds

The trimetallic (2 Pt, 1 Pd) complexes (64), below, have been prepared. Both the diethyl and diisopropyl dithiocarbamate complexes



(R = Et(64a), ^{i}Pr(64b))

are very insoluble and could only be characterised on the basis of analytical data and i.r. spectra.

When an excess of (17 a or b) is mixed with $[Pd(OAc)_2]_3$ or $Pd(acac)_2$ in chloroform, an orange solution is formed but the product begins to precipitate within minutes. If the phosphonium salt of the platinum(II) starting material is used, the $^{31}P-\{^1H\}$ n.m.r. and ^1H n.m.r. spectra can be used to show that stoichiometric amounts of the cation $(Ph_3(PhCH_2)P^+)$ and the displaced acetate ion (in the case examined) remain in solution once precipitation of the product is complete. If the $^{31}P-\{^1H\}$ n.m.r. spectra are obtained as soon as the products are mixed only a single platinum containing species is observed in both cases. Thus for R = Et, $\delta P = 30.4$; $^1J_{PtP} = 3502.2$ and for R = ^iPr, $\delta P = 31.0$ p.p.m.; $^1J_{PtP} = 3452.1$ Hz. The chemical shifts and coupling constants observed are compatible with sulphur coordinated to palladium (see Chapter 3). However, no firm conclusions can be drawn as the isolated solids were too insoluble to obtain ^{31}P n.m.r. data.

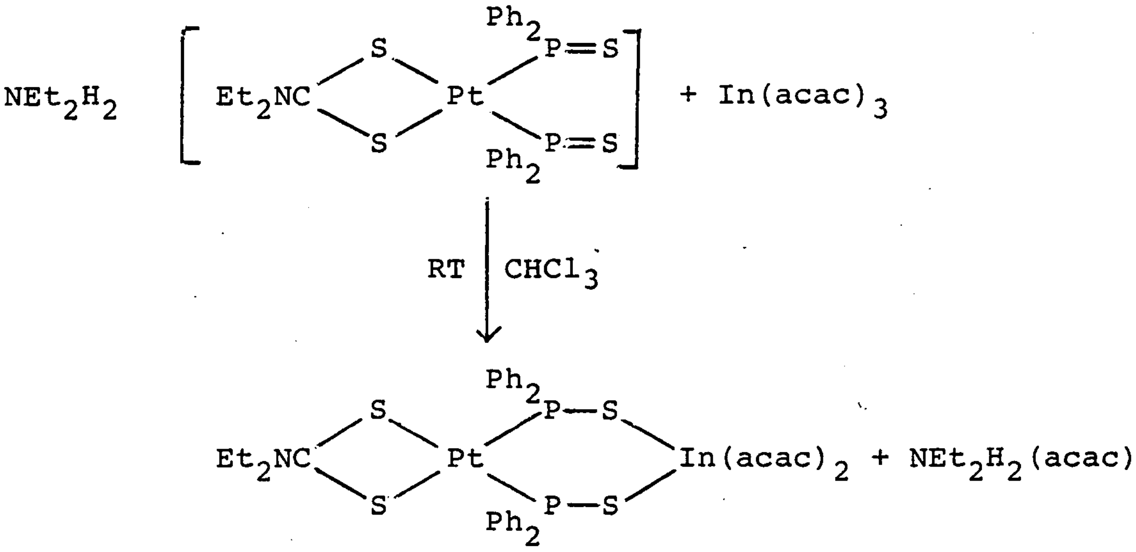
The i.r. spectra confirm that all the acetate or acetylacetonate ligands have been replaced. Bands typical of a bridging (P-S) function were observed ($\nu_{PS} = 580\ cm^{-1}$). The mass spectrum of (64a), while it gives no information about the complex, does confirm the presence of a chloroform solvate which is also reflected in the analytical data.

The behaviour of the products is similar to the $PdCl_2(L)_2$ reactions (Chapter 3). The inert and stable complex is always formed, even although the reaction conditions are varied, in terms of reactant, temperature and solvent. A comparison might be drawn between the behaviour of the Ni and Pd homologues which are both very insoluble, inert solids, and it may be that they are structurally very similar.

Finally, no reaction was obtained with $Ru(acac)_3$, under a variety of conditions.

4.3 The Reaction with $In(acac)_3$

When an excess of $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (17a) is mixed with $In(acac)_3$ in chloroform at room temperature a 1:1 reaction takes place (Eqn. 24) to yield a "mono-adduct" (65). A suitable alteration in the reaction ratios



(65)

...(24)

is sufficient to allow the isolation of the pure product, which has been fully characterised by the usual techniques. For example, strong bands due to coordinated acetylacetonate are evident in the i.r. spectrum (at 1390 and 1580 cm^{-1}) in addition to dithiocarbamate (ν_{CN} 1520 cm^{-1}) and bridging phosphine sulphide (ν_{PS} 595 cm^{-1}) bands. The $^{31}P-\{^1H\}$ n.m.r. spectrum (δP = 25.4 p.p.m.; $^1J_{PtP}$ = 3476.6 Hz) is consistent with bidentate coordination of the sulphur atoms to a metal ion.

The ^1H n.m.r. spectrum at 301 K shows only two singlets for the acetylacetonate resonances, at δ1.98 and 5.40 p.p.m. When a chloroform solution of this product (65) or $In(acac)_3$ is heated in the presence of excess of compound (17a), a pale yellow solid precipitates. This has been characterised as the tris-substituted complex, $In[Pt(S_2CNEt_2)(Ph_2PS)_2]_3$ (66), in which all three acetylacetonate ligands have been replaced. The i.r. spectrum now contains no (acac)-bands and ν_{PS} is now at 595 cm^{-1}. The compound is too insoluble for ^{31}P n.m.r. studies on the FX60 but the absence of acetylacetonate has been, however, confirmed by a high resolution ^1H n.m.r. spectrum at 301 K.

No evidence has been obtained for the intermediate $In(acac)[Pt(S_2CNEt_2)(Ph_2PS)_2]_2$ complex.

This "two-stage" reaction is as yet unique in the reactions with bis-thiophosphinite complexes with other metal ions. The compound $IrHCl\{(Ph_2As)CH_2-CH_2(Ph_2As)\}\{(Ph_2PO)_2H\}$ will react with $In(acac)_3$ to form the bis-adduct at room temperature. Thus, these products may be utilised to prepare mixed complexes, e.g. $In[Pt(S_2CNR_2)(Ph_2PO)_2]_2[Pt(S_2CNR_2)(Ph_2PS)_2]$, if (65) is treated with $Pt(S_2CNEt_2)\{(Ph_2PO)_2H\}$ or even the Ir or Rh complexes discussed previously (Chapter 2). This possibility, i.e. that of making mixed ligand, multi-metal systems by selective substitution of acetylacetonate ligands, may be worthy of further study.

Another group IIIb acetylacetonate complex, $Ga(acac)_3$ is inert towards the thiophosphinite compounds but does give a phosphinite adduct, $Ga[Pt(S_2CNR_2)(Ph_2PO)_2]_3$ [66b].

4.4 Conclusion

It has been conclusively demonstrated that the thiophosphinite complexes, $[Pt(S_2CNR_2)(Ph_2PS)_2]^-$ and $Pt(S_2CNR_2)(Ph_2POHSPPh_2)$, act as bidentate ligands towards a variety of transition and main group metal ions. The reactions, in general, proceed cleanly with little decomposition unless first row (class a) metal ions are involved. Care must also be taken in the selection of the starting materials used when the objective is to substitute only one bidentate unit. Thus, a novel phosphine sulphide transfer reaction was discussed in Chapter 3. Preliminary investigations with complexes such as $Rh(1,5\text{-}COD)(S_2CNEt_2)$, $Rh(1,5\text{-}COD)(DIPHOS)ClO_4$ or $Mo(NBD)(CO)_4$ (NBD = norbornadiene) have also shown that complicated reactions take place which do not necessarily lead to the required product (with the chelate ring $Pt(Ph_2PS)_2M$). These reactions have not been described in depth because of the lack of information as yet.

However, the basic premise, that the six membered bimetallic heteronuclear rings could be formed has been proven.

Some other areas for further study have been mentioned: for example, closer examination of the reactions of the mixed complexes $Pt(S_2CNR_2)(Ph_2POHSPPh_2)$ (19), and also no effort has been made, as yet, to examine the chelating properties of the palladium complexes, $NEt_2H_2[Pd(S_2CNEt_2)(Ph_2PS)_2]$ or $Pd(S_2CNEt_2)(Ph_2POHSPPh_2)$ or the mono-thiophosphinite complexes $Pt(S_2CNR_2)(Ph_2PE)X$ (E = S, X = Ph, POMe, Ph_2PH, Ph_3P; E = Se, X = Ph_2PH), which may form monodentate ligands with suitable complexes, and therefore, these possibilities remain available for future investigations.

4.5 Experimental

Physical measurements were obtained as described in Chapter 2 and in addition electron spin resonance spectra were obtained in the Department of Biochemistry, Edinburgh University, on a Varian E4 Spectrometer employing 100 KHz magnetic field modulation. Electronic spectra were recorded on a Beckmann 20/24 photospectrophotometer using silica cells.

Magnetic measurements were obtained using the Evans' method[76]. The HA-100 spectrometer was used over a temperature range of 190 to 311 K. The reference compound was tetramethylsilane, 2% in dichloromethane (a bulk susceptibility correction of 0.530×10^{-6} was applied). Diagmagnetic corrections were compiled from tabulated literature data[77].

The abbreviations (OAc), acetate, and (acac), acetylacetonate, are used throughout the chapter.

First Row Transition Metal Complexes: $M[Pt(S_2CNR_2)(Ph_2PS)_2]_2$ and $M[Pt(S_2CN^iPr_2)(Ph_2PO)(Ph_2PS)]_2$

A standard method is applicable to the preparation of these compounds. Thus when a chloroform or methanol solution of a metal acetate, acetylacetonate or halide salt is treated with a stoichiometric amount of $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ (17 a,b) or $Pt(S_2CN^iPr_2)(Ph_2POHSPPh_2)$ (19b) a rapid reaction takes place at room temperature for the metals of atomic number 26 (Fe) or greater. For example, when $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (0.09 g, 0.1 mmol) was added to $[Co(acac)_2]_4$ (0.013 g, 0.002 mmol) dissolved in dichloromethane (5 cm^3) a bright green solution was formed. When excess methanol (20 cm^3) was added a light green solid,

$Co[Pt(S_2CNEt_2)(Ph_2PS)_2]_2.CH_2Cl_2$ (55), precipitated. This was collected, washed with methanol and diethylether and dried in vacuo. mp 219-222^{o}C, (yield 0.06 g, 70%). Found:- C, 41.1; H, 3.5; N, 1.5. Calc for $C_{59}H_{62}Cl_2CoN_2P_4Pt_2S_8$:- C, 41.7; H, 3.7; N, 1.7%.

Mull i.r. spectrum: ν_{CN} 1520, ν_{PS} 580 cm^{-1}. Some physical data for the ten complexes (54-63) isolated are collected in Table 4.1.

Palladium Complexes

a) $Pd[Pt(S_2CNEt_2)(Ph_2PS)_2]_2$ (64a)

The compound $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (17a) (0.17 g, 0.20 mmol) and $[Pd(OAc)_2]_3$ (0.03 g, 0.07 mmol) were dissolved in chloroform (5 cm^3). An orange microcrystalline solid precipitated from the solution within minutes. An essentially quantitative yield was obtained after the solution was shaken overnight. The product was then washed with methanol and diethylether and dried in vacuo mp 258-260^{o}C. Found:- C, 38.7; H, 3.4; N, 1.5. Calc for $C_{59}H_{61}Cl_3N_2P_4PdPt_2S_8$:- C, 39.7; H, 3.4; N, 1.6%.

Mull i.r. spectrum:- ν_{CN} 1500, ν_{PS} 580 cm^{-1}. The same compound was prepared in 85% yield from a chloroform solution of (17a) and $Pd(acac)_2$ by a similar method.

b) $Pd[Pt(S_2CN^{i}Pr_2)(Ph_2PS)_2]_2$ (64b)

The compound $[Ph_3(PhCH_2)P][Pt(S_2CN^{i}Pr_2)(Ph_2PS)_2]$ (0.06 g, 0.05 mmol) and $[Pd(OAc)_2]_3$ (0.01 g, 0.01 mmol) gave a quantitative yield of the orange product when mixed in chloroform as above. Found:- C, 43.1; H, 4.1; N, 1.7. Calc for $C_{62}H_{68}N_2P_4PdPt_2S_8$:- C, 43.4; H, 4.0; N, 1.6%.

Mull i.r. spectrum:- ν_{CN} 1500, ν_{PS} 580 cm^{-1}.

$[Pt(S_2CNEt_2)(Ph_2PS)_2]In(C_5H_7O_2)_2$ (65)

The compound $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (0.04 g, 0.05 mmol) and $In(acac)_3$ (0.02 g, 0.05 mmol) were mixed in benzene (2 cm^3). After stirring for 1h, a 50:50 mixture of diethylether:petrol ether (bp 40-60°C) (5 cm^3) was added to precipitate the product as a white microcrystalline powder, which was washed with methanol and diethylether and dried in vacuo. mp 222-224°C (0.03 g; 50%). Found:- C, 43.1; H, 4.1; N, 1.3%. Calc for $C_{39}H_{44}NO_4P_2PtS_4$:- C, 48.0; H, 4.5; N, 1.4%. Molecular weight found:- 1085 (1090).

Mull i.r. spectrum:- ν_{CO} (acac) 1390, 1580; ν_{CN} 1520; ν_{PS} 595 cm^{-1}. Phosphorus-31-$\{^1H\}$ n.m.r. spectrum ($CDCl_3$ 301 K) δP, 25.4 p.p.m.; $^1J_{PtP}$ 3476.6 Hz. Hydrogen-1 n.m.r. spectrum: t, 1.10; s, 1.98; q, 3.47; s, 5.40; m, 6.9-7.9 p.p.m.

$[Pt(S_2CNEt_2)(Ph_2PS)_2]_3In$ (66)

The compound $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (0.20 g; 0.24 mmol) and $In(acac)_3$ (0.03 g; 0.08 mmol) were refluxed for 6 h in degassed chloroform (10 cm^3). A pale yellow solid precipitated from the reaction solution. This was collected, washed with methanol and diethylether and dried in vacuo (0.01 g, 51%). Found:- C, 41.7; H, 3.8; N, 1.7. Calc for $C_{87}H_{90}InN_3P_6Pt_3S_{12}$:- C, 42.7; H, 3.7; N, 1.7%.

Mull i.r. spectrum:- ν_{CN} 1520, ν_{PS} 595 cm^{-1}. Hydrogen-1 n.m.r. spectrum ($CDCl_3$, 301 K):- complex multiplet, 1.12; cm, 3.52; cm, 7.0-8.0 p.p.m.

TABLE 4.1 Some Physical Data for Transition Metal Complexes (54-63)

	Compound	Yield	Analytical data[a]/%			mp/	Principal i.r. bands/cm^{-1}		Notes
		/ %	C	H	N	°C	ν_{CN}	ν_{PS}	
(54)	$Fe[Pt(S_2CNEt_2)(Ph_2PS)_2]_2.CHCl_3$	NR[b]	41.2(40.9)	3.5(3.5)	1.8(1.6)	dec 273	1510	580	orange
(55)	$Co[Pt(S_2CNEt_2)(Ph_2PS)_2]_2.CH_2Cl_2$	70	41.1(41.7)	3.5(3.7)	1.5(1.7)	219 222	1520	590	green
(56)	$Ni[Pt(S_2CNEt_2)(Ph_2PS)_2]_2$	86	43.4(43.2)	3.9(3.7)	1.6(1.7)	223 225	1520	585	brown; insoluble
(57)	$Cu[Pt(S_2CNEt_2)(Ph_2PS)_2]_2$	82	41.4(43.0)	3.5(3.7)	1.7(1.7)				dark blue green
(58)	$Zn[Pt(S_2CNEt_2)(Ph_2PS)_2]_2$	52	42.8(43.0)	3.6(3.7)	1.9(1.7)	195- 196	1518	585	colourless
(59)	$Co[Pt(S_2CN^iPr_2)(Ph_2PS)_2]_2$	86	44.6(44.6)	3.9(4.1)	1.9(1.7)	295 296	1495	580	green
(60)	$Ni[Pt(S_2CN^iPr_2)(Ph_2PS)_2]_2$	71	44.4(44.6)	4.0(4.1)	1.6(1.7)	235- 238	1500	580	brown; insoluble
(61)	$Cu[Pt(S_2CN^iPr_2)(Ph_2PS)_2]_2$	46	NR	NR	NR	NR	1500	580	dark blue grey:decomp. within 24 h
(62)	$Co[Pt(S_2CN^iPr_2)(Ph_2PO)(Ph_2PS)]_2$	NR	45.3(45.5)	4.2(4.2)	1.9(1.7)	295- 296	1495 ν_{PO}1050	580	blue
(63)	$Ni[Pt(S_2CN^iPr_2)(Ph_2PO)(Ph_2PS)]_2$	NR	43.8(45.5)	4.1(4.2)	1.8(1.7)	dec 245	1490 ν_{PO}1050	575	pale blue

[a] Calculated values in parentheses

[b] Data not available.

TABLE 4.2 Magnetic Data for Some Trinuclear Complexes in Solution (CH_2Cl_2)

a. $Co[Pt(S_2CNEt_2)(Ph_2PS)_2]_2$ (55)

T/K	$X_M' \times 10^6$	μ_{eff}/B.M.
311	7282	4.27
298	7468	4.24
269	7926	4.15
256	8222	4.12
246	8539	4.12
234	8889	4.10
222	9293	4.08
212	9505	4.03
201	9892	4.00
190	10458	4.00

b. $Co[Pt(S_2CN^iPr_2)(Ph_2PS)_2]_2$ (59)

T/K	$X_M' \times 10^6$	μ_{eff}/B.M.
291	9192	4.64
276	9514	4.60
266	9961	4.62
256	10155	4.58
245	10483	4.55
235	10969	4.56
224	11348	4.53
214	11800	4.51
204	12313	4.50
195	12823	4.49

c. $Co[Pt(S_2CN^iPr_2)(Ph_2PO)(Ph_2PS)]_2$ (62)

T/K	$X_M' \times 10^6$	μ_{eff}/B.M.
298	9608	4.81
270	10608	4.81
257	11420	4.86
243	12045	4.86
226	13172	4.90
210	13547	4.79

d. $Fe[Pt(S_2CNEt_2)(Ph_2PS)_2]_2$ (54)

T/K	$X_M' \times 10^6$	μ_{eff}/B.M.
299	10364	5.00
285	11163	5.07
264	11437	4.93
249	12507	5.01
234	13060	4.96
218	13985	4.96

Chapter 5

Some Reactions with Small Main Group Containing Molecules

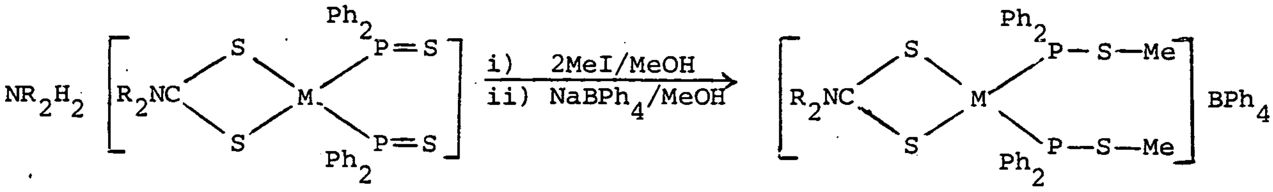
5.1 Introduction

The reactions of $Pt(S_2CNR_2)\{(Ph_2PO)_2H\}$ (2) with small main group molecules (e.g. $BF_3.Et_2O$, $SiMe_3Cl$ or HX) have been examined previously[46a,66a]. A number of comparative studies have therefore been carried out using $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ (17) and a similar range of reactants. Some investigations into the behaviour of the binuclear complexes $[Pt(S_2CNR_2)(Ph_2PS)]_2$ with those reagents are also reported.

These preliminary studies have mainly been carried out as in situ n.m.r. experiments, whereby the reaction is monitored, over a range of temperatures and time, by examining successive, mainly $^{31}P-\{^1H\}$ n.m.r. spectra. The scale of the reactions, arising from the limited availability of the reactants, and the frequently unstable nature of the products has precluded the isolation of many of the species discussed and therefore, in these cases, the conclusions drawn can only be regarded as tentative.

5.2 Some Reactions with Alkyl Halides:- S-Methylation Reactions

The bis-thiophosphinite compounds $NR_2H_2[M(S_2CNR_2)(Ph_2PS)_2]$ (M = Pt; R = Et (17a), ^iPr (17b). M = Pd; R = Et (24)) are converted to the cis, bis-methylthiophosphinite (Ph_2PSMe) complexes (Eqn. 25) when they are treated with iodomethane at room temperature and these cationic complexes can be isolated as tetraphenylborates (67 a,b,c). These complexes have been characterised by analytical data, i.r. and n.m.r. spectra ($^{31}P-\{^1H\}$ n.m.r., Table 5.1; ^1H n.m.r., Table 5.2).



$$\begin{pmatrix} M = Pt;\ R = Et\ (67a)\ {}^{i}Pr\ (67b) \\ M = Pd;\ R = Et\ (67c) \end{pmatrix}$$

... (25)

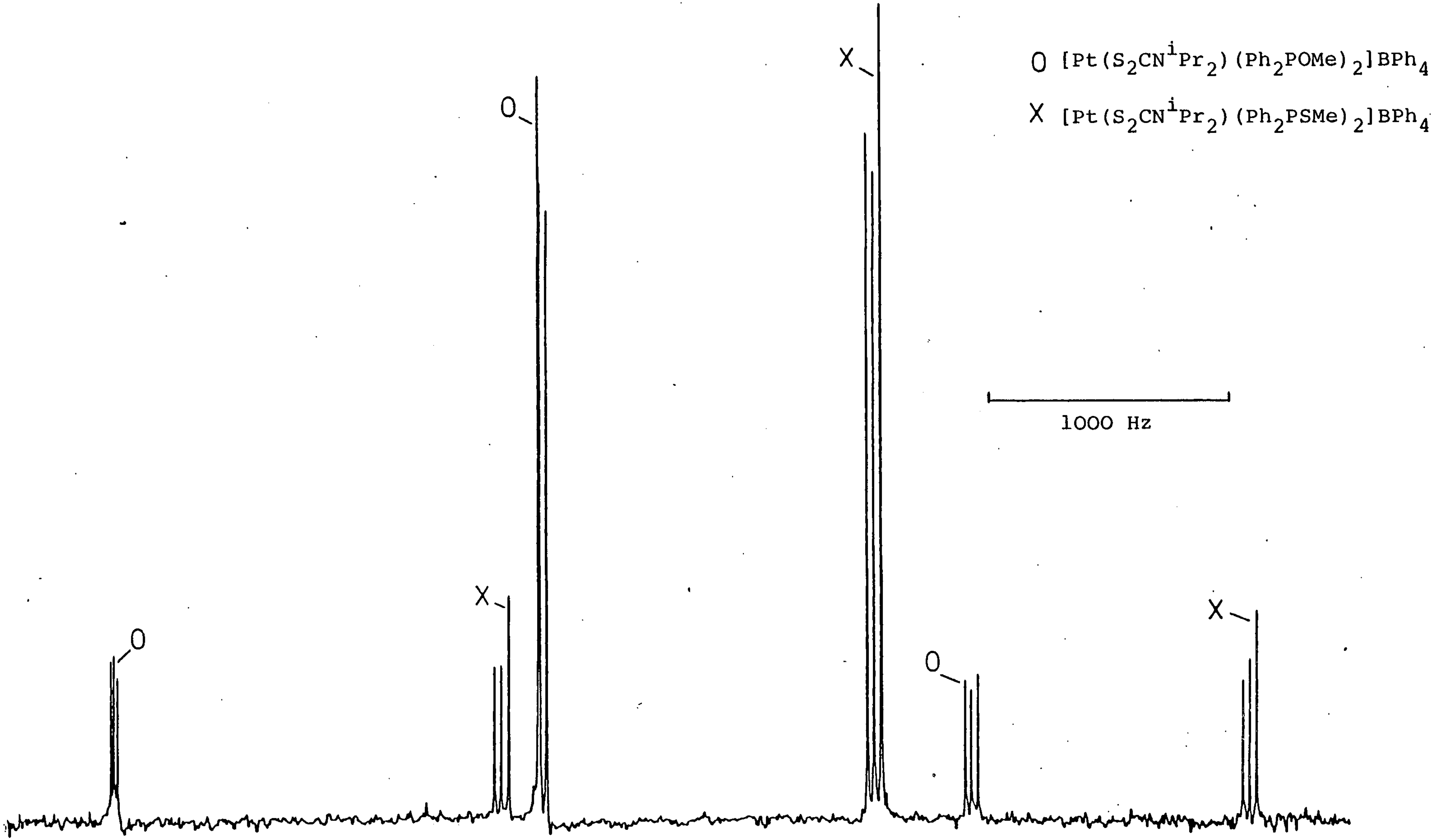
The i.r. spectra of the platinum complexes are consistent with the proposed formulation although ν_{PS} cannot be assigned with confidence as a number of bands are observed in the expected region (500-600 cm^{-1}). A strong band at 840 cm^{-1} is assigned to ν_{SC}. A single resonance with ^{195}Pt satellites is observed in the $^{31}P-\{^{1}H\}$ n.m.r. spectra obtained at 301 K. The platinum complexes (67 a,b) exhibit a chemical shift change of approximately 5 p.p.m. to high frequency and are thus consistent with the change P(V) to P(III). The PtP coupling constants (ca. 3200 Hz) confirm that the phosphorus remains directly bound to platinum(II). In the ^{1}H n.m.r. spectra, a second order "psuedo-triplet" is observed at ca. 1.7 p.p.m. $|^{3}J_{PH} + {}^{5}J_{PH}|$ is 11.0 Hz in both cases (67 a,b). (The second order signal arises for reasons similar to those discussed in Chapter 3.4). Irradiation at ^{31}P frequencies collapses the signal to a singlet.

There is no doubt that a cationic complex, analogous to the platinum species (67 a,b), is formed initially when (24) is treated with MeI because the change in conductivity of the reaction solution can be monitored as the reaction proceeds and the product (67c) can be obtained as an orange solid by adding sodium tetraphenylborate to this solution.

However, the $^{31}P-\{^{1}H\}$ n.m.r. (δP 49.2 p.p.m.) and ^{1}H n.m.r. ($\delta SC\underline{H}_3$ 1.74 p.p.m.) spectra can be used to demonstrate that the compound soon decomposes in solution at room temperature as the original signals soon disappear and a number of new, unidentified, resonances are observed.

A similar methylation is observed when $Pt(S_2CN^{i}Pr_2)-(Ph_2POMe)(Ph_2PS)$ (21) is treated with MeI in methanol. The conductivity of the solution rises to a maximum at room temperature within a few minutes, and adding $NaBPh_4$ precipitates a white solid. The analytical data and i.r. spectra are consistent with the formation of $[Pt(S_2CN^{i}Pr_2)(Ph_2POMe)(Ph_2PSMe)]BPh_4$ (68) but the $^{31}P-\{^{1}H\}$ n.m.r. (Fig. 5.1; Table 5.1) and ^{1}H n.m.r. (Table 5.2) spectra recorded in a variety of solvents ($CDCl_3$; C_6H_6/C_6D_6 and acetone/d^6-acetone) and over a range of temperatures (ca. 210-330 K), show that in solution an almost invariant mixture of three species exists. These are the three cations $[Pt(S_2CN^{i}Pr_2)(Ph_2POMe)_2]^+$ (69), $[Pt(S_2CN^{i}Pr_2)(Ph_2POMe)(Ph_2PSMe)]^+$ (68) and $[Pt(S_2CN^{i}Pr_2)(Ph_2PSMe)_2]^+$ (67b) in the approximate ratio 1:3:1 (estimated from both the ^{31}P n.m.r. and ^{1}H n.m.r. integrals). The assignment of (69) and (67b) can be confirmed by a comparison with the $^{31}P-\{^{1}H\}$ n.m.r. spectra of genuine samples and the remaining signals, assigned to (68), form the expected AXM pattern. Two doublets (δH = 1.73, 3.06 p.p.m.) observed in the ^{1}H n.m.r. are assigned to the methyl resonances of the mixed ligand species. The same ratio in solution was consistently obtained when the reaction was repeated under a

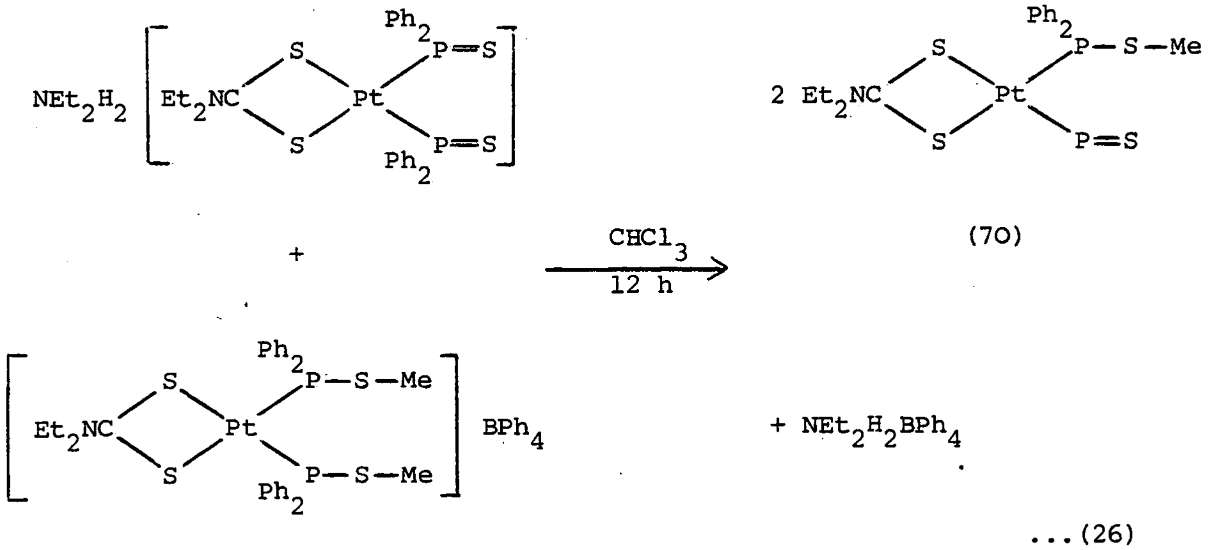
Figure 5.1



Phosphorus-31-n.m.r. spectrum ($CDCl_3$, 300 K) of the Reaction Product "[Pt($S_2CN^iPr_2$)(Ph_2POMe)(Ph_2PSMe)]BPh_4"

variety of conditions. A similar reaction with EtI gave ambiguous results and the rapid decomposition of the platinum-phosphine sulphide complex (21) could be observed by $^{31}P-\{^1H\}$ n.m.r. studies at 300 K†. The above behaviour is reminiscent of the earlier work of Cornock[43] who showed that by treating $[PdCl(S_2CNEt_2)]_2$ with NaS_2PMe_2, or by mixing $Pd(S_2CNEt_2)_2$ and $Pd(S_2PMe_2)_2$, a similar equilibrium was established at room temperature in solution between the two bis and the mixed species.

It was also found that when equimolar amounts of the bis(methylthiophosphinite complex $[Pt(S_2CNEt_2)(Ph_2PSMe)_2]BPh_4$ (67a) and $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (17a) were mixed in chloroform, the novel compound $Pt(S_2CNEt_2)(Ph_2PSMe)(Ph_2PS)$ (70) was formed (Eqn. 26). The driving force for this reaction, is presumably, the formation of the insoluble ionic



(70)

...(26)

---

† (17a) also decomposes in the presence of EtI and, to date, no ethylphosphinothioite complexes have been prepared.

product and the neutral platinum compound in a relatively non-polar solvent. Compound (70) could be observed spectroscopically by $^{31}P-\{^{1}H\}$ (Table 5.1) and ^{1}H n.m.r. (Table 5.2) spectra at 301 K. Unfortunately, normal work-up procedures gave only an intractable oil, so that other physical measurements have not been made as yet.

It is known that treating the $[Pt(S_2CNR_2)(Ph_2POMe)_2]^+$ cation or $Pt(S_2CNR_2)(Ph_2POMe)(Ph_2PO)$ complexes with $Ph_2P(O)H$ generated in situ yields $Pt(S_2CNR_2)\{(Ph_2PO)_2H\}$ (2).[9] Phosphorus-31 n.m.r. evidence indicates that this compound is also formed by treating $Pt(S_2CN^iPr_2)(Ph_2POMe)(Ph_2PS)$ with $Ph_2P(O)H$ or Ph_2POMe. No reaction was observed when $Pt(S_2CN^iPr_2)(Ph_2POMe)(Ph_2PS)$ was treated with $Ph_2P(S)H$ at room or elevated temperatures but, if the experiment could be repeated using $Pt(S_2CNR_2)(Ph_2PSMe)(Ph_2PS)$ (70) the elusive compound $Pt(S_2CNR_2)\{(Ph_2PS)_2H\}$ might at last be formed, and its comparative behaviour, to the oxyring compounds (2), examined.

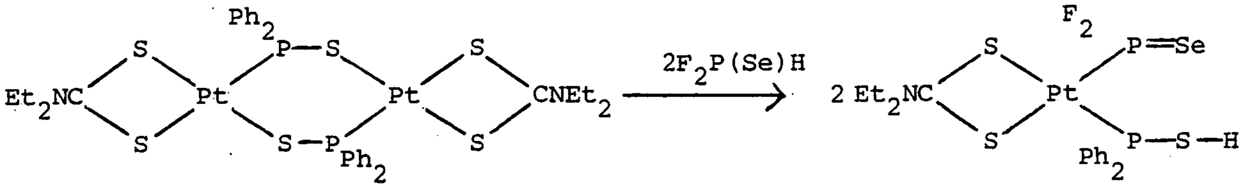
Some other reactions have also been briefly investigated. Thus $[Pt(S_2CN^iPr_2)(Ph_2PS)_2]$ $Pt(S_2CN^iPr_2)$ will react with MeI to yield the $[Pt(S_2CN^iPr_2)(Ph_2PSMe)_2]^+$ cation as the major phosphorus containing product. No evidence for oxidative addition of the alkyl-halide to the metal centres was obtained and the reaction appears to be an example of simple bridge cleavage (the counter ion in situ is probably therefore the anion $[Pt(S_2CN^iPr_2)I_2]^-$ but this could not be confirmed).

5.3 Some Reactions with Phosphorus Containing Molecules

The synthesis of $Pt(S_2CNR_2)(Ph_2PS)(Ph_2PE)$ (E = H(20), OMe (21), OH (19)) complexes by treating

$NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ (17) or $[Pt(S_2CNR_2)(Ph_2PS)]_2$ (22) with a tertiary phosphine or phosphinite was discussed in Chapter 2. The reactions all take place under mild conditions. However, care must be taken to prevent hydrolysis reactions occurring which lead, in most cases, to the formation of some $Pt(S_2CNR_2)\{(Ph_2PO)_2H\}$ in the reaction mixture.

Although no convincing evidence for the reaction of $Ph_2P(Se)H$ or $Ph_2P(S)H$ with $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ (22) was obtained even when this reaction was attempted under a variety of conditions, when the same complex (22) was treated with $F_2P(Se)H$, the novel mixed phosphine complex $Pt(S_2CNEt_2)(Ph_2PSH)$-(F_2PSe) (71) was formed (Eqn. 27).



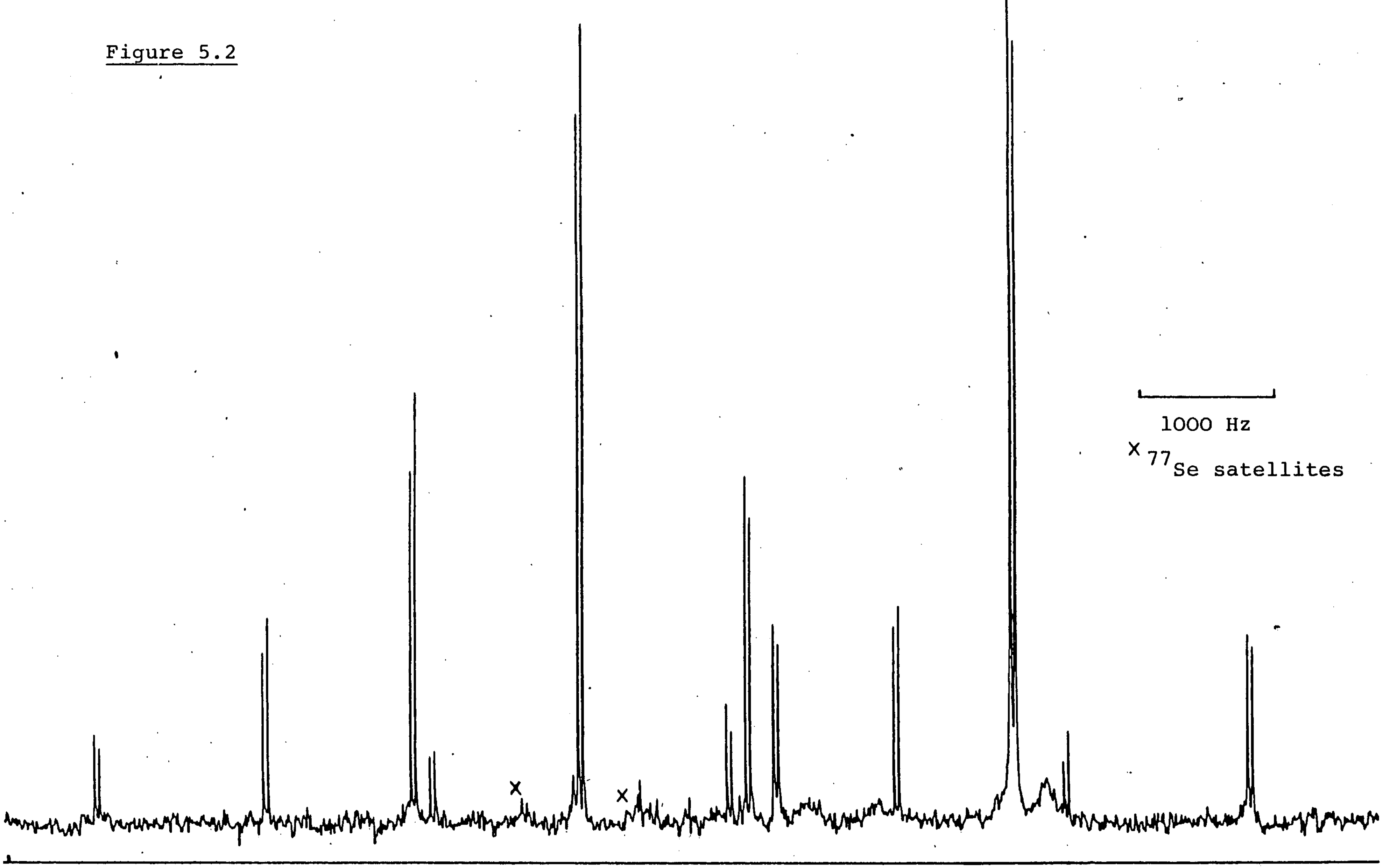
(71)

...(27)

The reaction was followed by ^{31}P n.m.r. spectroscopy from low (213 K) to ambient (300 K) temperatures but no signals arising from any intermediates could be observed.

In addition, although the product remained stable in solution, attempts at isolation gave only a red intractable oil which slowly darkened in colour. The species has been characterised, therefore, on the basis of multinuclear n.m.r. studies. Thus the ^{31}P-$\{^1H\}$ n.m.r. spectrum at 301 K (Fig. 5.2; Table 5.1) is consistent with $(F_2PSe)^-$ (δP = 156.6 p.p.m.) and $(Ph_2PS)^-$ (δP = 26.7 p.p.m.) moieties in a cis-

Figure 5.2

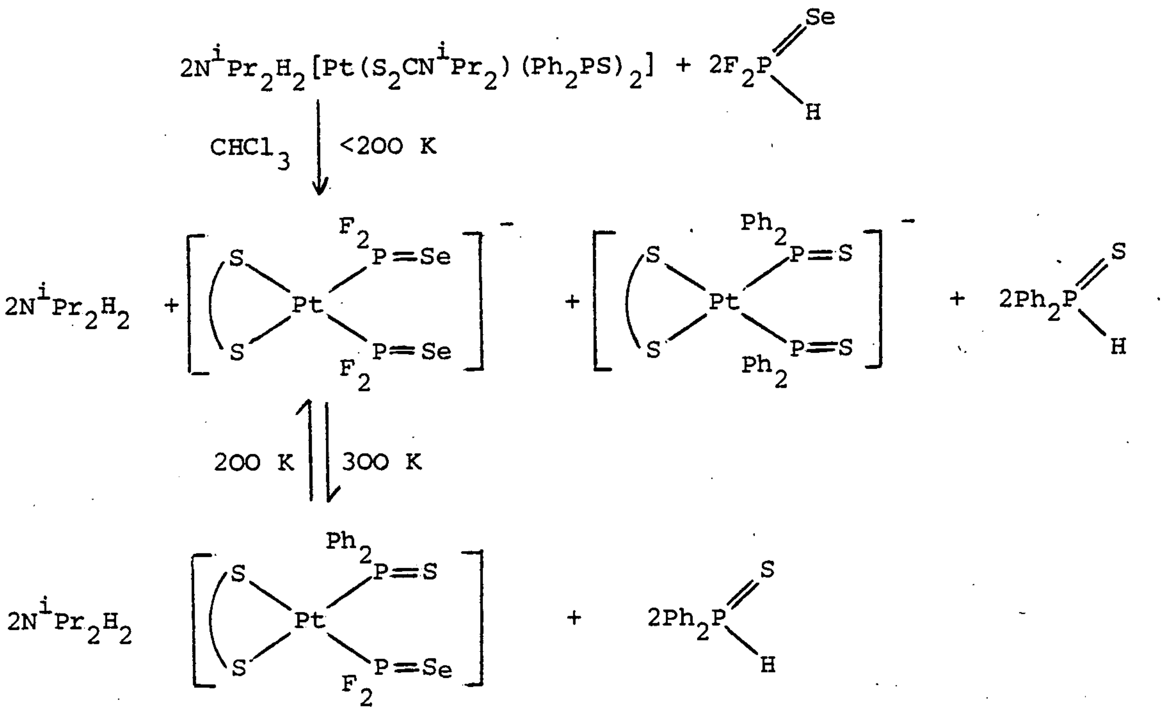


Phosphorus-31-n.m.r. spectrum ($CDCl_3$, 300 K) of $Pt(S_2CNEt_2)(Ph_2PSH)(F_2PSe)$ (71)

orientation directly bonded through phosphorus to platinum(II). The value of $^1J_{PSe}$ (824 Hz) is consistent with a PSe double bond[54] and no additional coupling is observed to the $(F_2PSe)^-$ resonance in a proton coupled spectrum. The ^{19}F n.m.r. (Table 5.3) spectrum is also consistent with the presence of a terminal P=Se group (no $^3J_{FH}$ coupling is observed). The presence of a coordinated thiophosphinous acid can be confirmed by examining the ^1H n.m.r. spectrum where a broad singlet, assigned to S$\underline{H}$, occurs at 5.91 p.p.m. ($^3J_{PtH}$ = 35.0 Hz). On the basis of this data and a comparison with other difluorophosphinite complexes (to be described in the next chapter) the complex is best described with the proton localised on the sulphur atom. Infrared studies would be invaluable in determining the degree of interaction, if any, between the proton and the selenium atom close to it.

In contrast, when equimolar amounts of the salt $N^iPr_2H_2[Pt(S_2CN^iPr_2)(Ph_2PS)_2]$ (17b) and $F_2P(Se)H$ are mixed in chloroform and when the $^{31}P-\{^1H\}$ n.m.r. spectrum of the reaction solution is examined at 200 K, three compounds are observed, namely unreacted (17b), $[Pt(S_2CN^iPr_2)(F_2PSe)_2]^-$ (see Chapter 6) and $Ph_2P(S)H$ (confirmed by the observation of $^1J_{PH}$ when proton coupling was retained). No other species were present but, as the tube was warmed, a signal corresponding to the mixed phosphine adduct (72) was observed and this was the principal species at room temperature. $Ph_2P(S)H$ was still present. The reaction stoichiometry and discrepancies in the ^{31}P n.m.r. spectral parameters (for example, $^1J_{Pt-Ph_2\underline{P}S}$ is larger in this species (72) than in the foregoing compound (71)) suggest that the product is in fact the thiophosphinite anion $[Pt(S_2CN^iPr_2)(Ph_2PS)(F_2PSe)]^-$ (Eqn. 28). The reaction can be reversed by recooling the solution at 200 K. Again, however, no conclusive characterisation (by means of analytical data, conductivity measurements and i.r. spectra) could be made as the product gave an intractable oil which decomposed when conventional isolation procedures were used.

In spite of the failure to isolate these two compounds (71,72) the method used may provide a means of synthesising a series of mixed phosphine ligand complexes.



(72) ...(28)

5.4 Some Reactions with Acids and Halogens

When some complexes containing the P-O--H--O-P fragment are treated with base, they can be deprotonated[19]. Similarly when $Pt(S_2CNR_2)\{(Ph_2PO)_2H\}$ is treated with acid the cation $[Pt(S_2CNR_2)(Ph_2POH)_2]^+$ can be observed in situ by ^{31}P n.m.r. spectroscopy. Thus in the presence of H^+, the chemical shift moves by ca. 10 p.p.m. to high frequency and the coupling constant also increases. Both these observations are consistent with the formation of a phosphinous acid complex. However, the complex readily reverts to the neutral "oxy ring" compound under conventional isolation techniques.

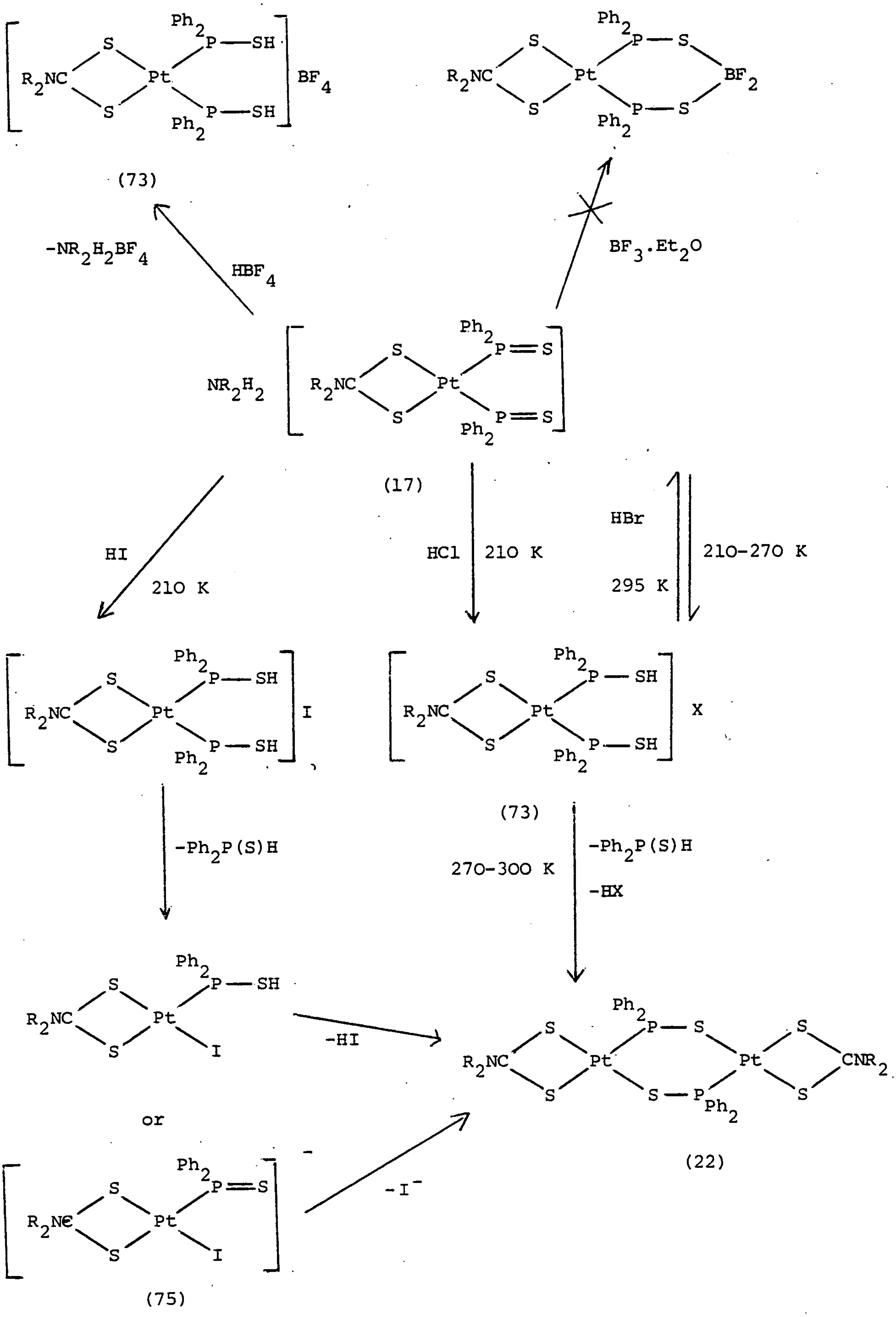
The experiments described here investigate some of the reactions that occur when the anionic complexes $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ (17 a,b) and the binuclear complex $[Pt(S_2CNR_2)(Ph_2PS)]_2$ (22) are treated with HX or X_2.

5.4.1 The Reaction of HX with $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$

The reactions of HX [X = BF_4, (F), Cl, Br, I] with (17 a,b) are complicated although the final products are always the same, $[Pt(S_2CNR_2)(Ph_2PS)]_2$ and $Ph_2P(S)H$. Thus adding 1 molar equivalent of gaseous HCl to a chloroform solution of $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (17a) gives $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ in high yield at room temperature (Chapter 2). Spectroscopic observation, by $^{31}P-\{^1H\}$ n.m.r. and ^1H n.m.r. over a range of temperatures, has been used to examine these reactions in detail. A summary of the conclusions drawn from this data is presented in Scheme 5.1.

The simplest reaction occurs when HBF_4 and (17a) are mixed. Protonation occurs at the sulphur atoms to yield $[Pt(S_2CNEt_2)(Ph_2PSH)_2]BF_4$ (73a) which can be isolated by working rapidly and under rigorous conditions at low (273-283 K) temperatures. The analytical data and i.r. spectrum are consistent with the proposed assignment. A complex of i.r. bands occurs at 1000-1200 cm^{-1} (BF stretches) and ν_{SH} is observed at 2470 cm^{-1} (KBr disc spectrum) but ν_{PS} cannot be assigned with certainty. The complex decomposes over a period of days and attempts to redissolve the product or exchange the anion induce an irreversible rearrangement to (22a) and $Ph_2P(S)H$. The $^{31}P-\{^1H\}$ n.m.r. of this thiophosphinous acid complex (δP, 31.7 p.p.m.; $^1J_{PtP}$, 3449.7 Hz) is consistent with the formulation and the spontaneous rearrangement reaction can be followed over a period of hours by examining successive n.m.r. spectra. No evidence for S<u>H</u> was observed in the ^1H n.m.r., but it is possible that it may be obscured by resonances in the phenyl region, 7.0-8.0 p.p.m.

When the reaction of (17a) with HCl is examined from low temperature (210 K) a single species is observed until <u>ca</u>. 290 K when quantities of (22a) and $Ph_2P(S)H$ are irreversibly formed. This first species is again the thiophosphinous acid complex $[Pt(S_2CNEt_2)(Ph_2PSH)_2]Cl$ (δP = 30.8 p.p.m., $^1J_{PtP}$ 3430.2 (290 K)) but in this instance it could not be isolated from the reaction mixture. No evidence for oxidative addition of HCl to platinum(II) was seen over the temperature range examined, but it is obvious that in $CDCl_3$ reaction has already commenced by 210 K. A low freezing point solvent (CD_2Cl_2 or d^8-toluene) might be utilised to re-examine this reaction by $^{31}P-\{^1H\}$ n.m.r. spectroscopy at even lower temperatures. In the presence of excess HCl appreciable quantities of a second binuclear compound are formed. This may be $[Pt(S_2CNEt_2)]_2$ (μ-Ph_2PS) (μ-Cl) (74) [δP, 22.7 p.p.m.;



SCHEME 5.1 The Reactions of $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ with HX

$^1J_{PtP'}$, 3440.7 Hz; $^2J_{PtP'}$, 52.9 Hz], but the compound could not be purified and isolated.

When equimolar amounts of gaseous HBr and $NH_2R_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ are mixed a temperature dependent equilibrium between the $[Pt(S_2CNEt_2)(Ph_2PSH)_2]^+$ cation and the original thiophosphinite complex is established (Scheme 5.1). The compound $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ forms only slowly at room temperature but remains as the final product.

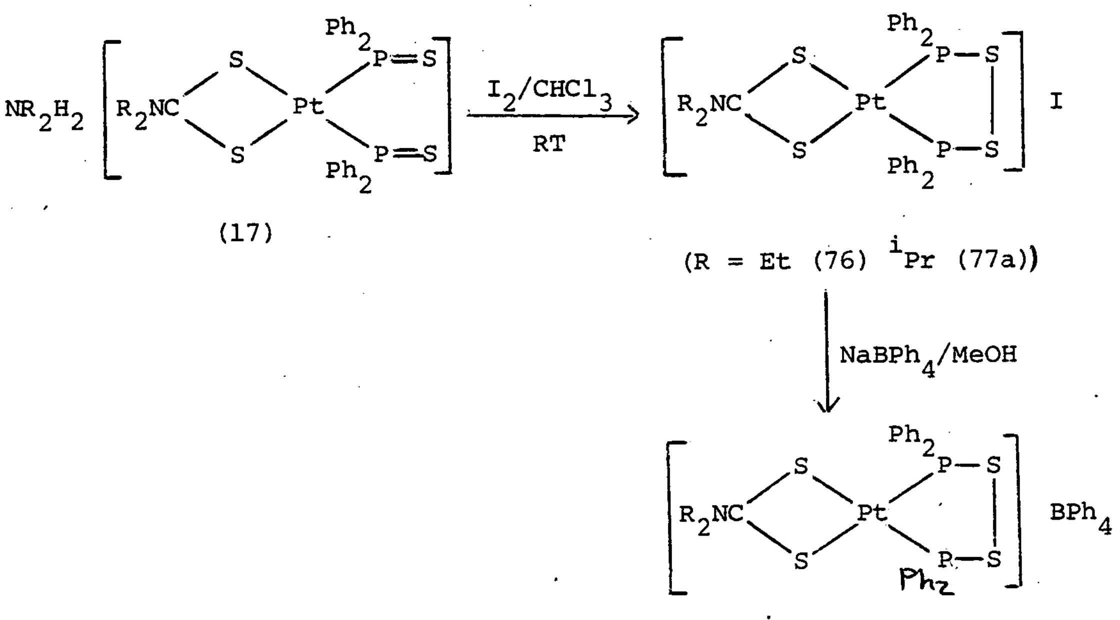
The $[Pt(S_2CN^iPr_2)(Ph_2PSH)_2]^+$ cation (73b) is also the major species formed at low temperature when (17b) is mixed with HI. On warming the solution $Ph_2P(S)H$ and a novel species (δP, 25.4 p.p.m.; $^1J_{PtP'}$, 3608.0 Hz), probably $[Pt(S_2CNEt_2)(Ph_2PS)I]^-$ (75) (although the n.m.r. evidence does not preclude $Pt(S_2CN^iPr_2)(Ph_2PSH)I$), are formed but at the same time a slow, irreversible rearrangement to (22b) occurs and the former, (75), could not be isolated.

Finally, $Pt(S_2CNEt_2)\{(Ph_2PO)_2H\}$ (2) reacts with $BF_3.Et_2O$ to form a neutral "capped" ring complex, $Pt(S_2CNEt_2)\{(Ph_2PO)_2BF_2\}$, which contains a stable BO_2F_2 moiety. In contrast $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (17a) yields only the cation (73) under the same reaction conditions, presumably by reaction with traces of HF and HBF_4 contained in the $BF_3.Et_2O$. The formation of the strong BO bonds in the first case must dominate that particular reaction, resulting in a complex inert to further substitution.

5.4.2 The Reaction of Compound (17) with I_2

A solution of I_2 will react oxidatively with $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ (17 a,b) to yield stable cationic complexes which have the stoichiometry $[Pt(S_2CNR_2)(Ph_2PS)_2]I$

(R = Et (76), ^{i}Pr (77a)). The reaction is believed to involve a two electron transfer with ring closure and the formation of an S-S bond (Eqn. 29)† which can be compared with the reaction of transition metal 2,5-dithiolene complexes, $M(C_5H_7S_2)_n$, with I_2, to form 1,2-dithiolium cations (Eqn. 30).

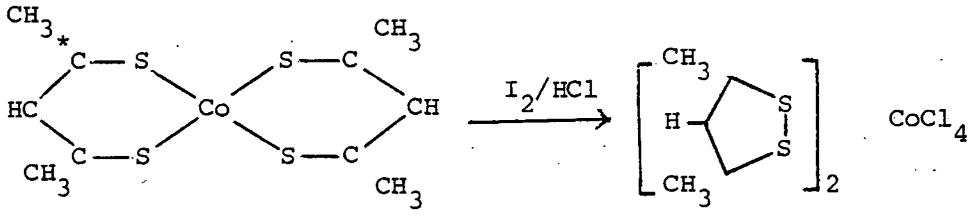


(17)

(R = Et (76) ^{i}Pr (77a))

(R = ^{i}Pr (77b))

... (29)



... (30)

†Kraihanzel has observed a similar ring closure reaction[78]. Thus when <u>cis</u>-$Mo(CO)_4(Ph_2PCl)_2$ is treated with H_2S in THF the complex <u>cis</u>-$Mo(CO)_4\{(Ph_2P)_2S\}$, containing a chelate P-S-P ligand, is isolated in good yield. The phosphorus chemical shift is given as 31.8 p.p.m. but no i.r. data is quoted for the relevant (<600 cm^{-1}) region.

The complexes were characterised by elemental analyses, i.r. spectra (two strong bands are observed at 505 and 555 cm^{-1} which may be due to PS and SS stretching vibrations) and $^{31}P-\{^{1}H\}$ n.m.r. spectroscopy (Table 5.1). The dramatic change in the structure of the ligand is confirmed by a chemical shift change of ca. 90 p.p.m. to high frequency. Thus for $[Pt(S_2CN^iPr_2)(Ph_2PS)_2]BPh_4$ δP is 117.2 p.p.m. ($^1J_{PtP}$ = 3554.7 p.p.m.). The parallel with dithiolene complexes was sustained when the reaction of $[Pt(S_2CN^iPr_2)(Ph_2PS)_2]Pt(S_2CN^iPr_2)$ with I_2 was found to yield the same cation, $[Pt(S_2CN^iPr_2)(Ph_2PSSPPh_2)]^+$.

In contrast, although the reaction with chlorine, with $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ in situ, yields a single monomeric species at room temperature, the $^{31}P-\{^{1}H\}$ n.m.r. spectrum suggests that a Pt(IV) compound is evolved ($^1J_{PtP}$ 2419.9 Hz). Unfortunately the product separated from solution as an unstable oil and remains unidentified.

5.4.3 Conclusion

These brief studies have shown that the chemistry of the thiophosphinite complexes (17,22) is considerably more extensive than that of the neutral-H capped phosphinite analogues. In particular the lability of the thiophosphinous acid (P(III)) moiety, which readily forms free (P(V))$Ph_2P(S)H$, has been demonstrated. This reactivity has complicated a number of the reactions discussed and has made the preparation of clean samples difficult.

A number of further experiments are suggested by the reactions presented here. Variable temperature ^{31}P n.m.r.

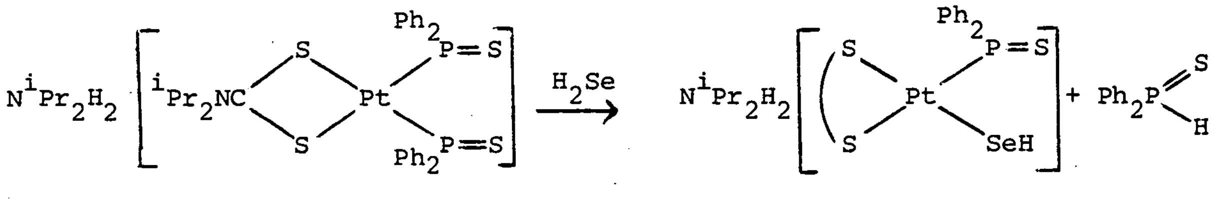
has proven a useful technique in elucidating some of the stages in the formation of (22) from (17) in the presence of HX but the initial protonation has not been spectroscopically observed and a number of further studies must be made in this area. Furthermore, a systematic study of the reactions of the halogens with the binuclear complex (22) might, from the evidence of the reaction with Cl_2 described above, provide a means of examining oxidative addition reactions to the metal centres prior to the breakdown of the bridging structure. It was also mentioned briefly that in the presence of excess HCl $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ reacts further to yield another binuclear complex (74). HI has been shown to react <u>in situ</u> with $[Pt(S_2CN^iPr_2)(Ph_2PS)]_2$ to form a monomeric species which may be $Pt(S_2CN^iPr_2)(Ph_2PSH)I$ (δP, 24.5 p.p.m.; $^1J_{PtP}$, 3608.4 Hz). These reactions can be systematically investigated in the future with a particular view to a comparison of the reactions of the halogen acids with compound (22).

5.5 Some Reactions with H_2E (E = O, S, Se)

It has been observed that in the presence of H_2O the reaction between $Ph_2P(S)H$ and $Pt(S_2CNR_2)_2$ yields considerable quantities of $Pt(S_2CNR_2)(Ph_2POHSPPh_2)$ (19) and eventually some $Pt(S_2CNR_2)\{(Ph_2PO)_2H\}$(2). Similarly if $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ (17) is refluxed in wet solvents compounds (19) and (2) are formed and can be observed by ^{31}P n.m.r. spectroscopy.

In contrast, when gaseous H_2Se is mixed with $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ in equimolar amounts a new species $NR_2H_2[Pt(S_2CNR_2)(Ph_2PS)(SeH)]$ (78) can be observed. Thus when

H_2Se and (17b) are mixed in equimolar amounts a single new compound and $Ph_2P(S)H$ are formed, (Eqn. 31) at room temperature.



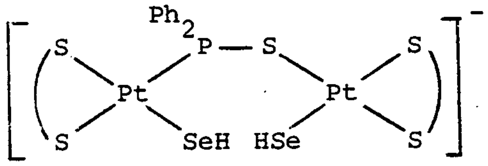
(78)

... (31)

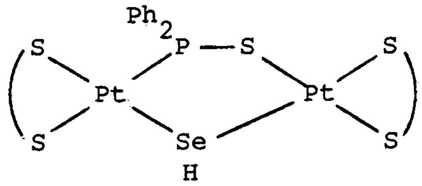
The compound was obtained only as an intractable oil but the $^{31}P-\{^1H\}$ n.m.r. spectrum (Table 5.1) is compatible with the proposed assignment. No evidence for $^2J_{^{77}Se-^{31}P}$ coupling was obtained from the $^{31}P-\{^1H\}$ n.m.r. spectrum, however, and the ^1H n.m.r. spectrum <u>in situ</u> gave no additional information beyond confirming the formation of $Ph_2P(S)H$.

The compound $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ (22a) will also react with H_2Se at room temperature, but in a 1:2 ratio. $Ph_2P(S)H$ is evolved and a second binuclear compound (79) is observed by ^{31}P n.m.r. spectroscopy, at a very different chemical shift: 78.2 p.p.m. (Table 5.1). In the ^1H n.m.r. a singlet is observed at -1.02 p.p.m. Although this position is compatible with a metal-coordinated $(SeH)^-$ moiety, other factors, such as lack of ^{31}P coupling and the intensity ratio of the observed signals (1:14.5:1; the coupling constant is 57.5 Hz and could thus be J_{PtH} <u>or</u> J_{SeH}), together with the observed ^{77}Se spectrum (singlet (sharp) at -247.9 p.p.m.) may suggest that an exchange process is occurring and that average seleno-proton and selenium signals are being observed at ambient temperature.

The reaction stoichiometry suggests that an individual $(SeH)^-$ moiety is bonded to each platinum(II) ion which are also bridged by a $(\mu\text{-}Ph_2PS)^-$ moiety (79). If this was so, then two distinct <u>SeH</u> resonances might be observed in both ^{77}Se and ^1H n.m.r. spectra. An alternative formulation (80) is not consistent with the observation that a 1:1 mixture of H_2Se and (22a) results in the presence of 50% unreacted (22a).



(79)



(80)

When a 2:1 molar ratio of H_2Se and (22a) are mixed, all the original binuclear compound reacts and the new species is formed. In the presence of a 4:1 excess of H_2Se, however, further reactions occur which lead to the formation of $[Pt(S_2CNEt_2)(Ph_2PS)(SeH)]^-$ (78) and a number of unidentified species. None of these various reactions could be worked up to study the products in isolation.

H_2S does not react with (17) or (22) at ambient or elevated (for (17b) the reaction mixture was heated to 50°C) temperatures, even when a 4:1 excess of H_2S is present. Given this observation, the premise that the first step in the H_2Se reactions with (17) is an oxidative addition to platinum(II), followed by a reductive elimination of $Ph_2P(S)H$ can be supported by the difference in bond energies between H_2S and H_2Se.

It is clear, however, that a considerable number of further studies must be made before the two selenium adducts discussed can be fully identified.

5.6 Conclusion

The diversity of the reactions undergone by the thiophosphinite platinum complexes (17) and (22), in the presence of small molecules, far exceeds the reactions of the analogous $Pt(S_2CNR_2)\{(Ph_2PO)_2H\}$ compounds. In the latter the inert open O-P-Pt-P-O structure is "capped" by small molecules with vacant sites or protonated by acids. In the former the disproportionation of $Ph_2P(S)H$ dominates the reactions, reflecting changes in the Pt-P bond strength and the stability of the P(V) form of the sulphide.

Oxidative addition reactions to the metal centre occur in a number of examples but in no cases have any Pt(IV) intermediates been observed. An objective of any future research must be to examine these reactions more closely and to investigate the reactions of the intermediate compound $Pt(S_2CNR_2)(Ph_2POHSPPh_2)$ with the same reagents.

5.7 Experimental

Physical methods were as for these described in earlier chapters. Selenium-77 n.m.r. spectra were recorded on the Brucker 360 NHz spectrometer and chemical shifts are quoted to high frequency of external Me_2Se. Phosphorus-31 data, for compounds which have been isolated, are collected in Table 5.1 and hydrogen-1 data in Table 5.2. Fluorine-19 n.m.r. spectra were obtained on a Varian Associates XL-100 spectrometer and chemical shifts are quoted to high frequency of CCl_3F (Table 5.3).

Volatile compounds were prepared by standard techniques and stored and handled on a standard pyrex glass vacuum line. Thiophosphinite complexes were prepared as described in previous chapters. MeI, EtI (Fisons), $NaBPh_4$ (B.D.H.), $BF_3.Et_2O$ (B.D.H.) and 40% HBF_4 in H_2O (Fisons) were used as obtained.

Most of the reactions described in this chapter and the subsequent one were studied by n.m.r. spectroscopy and the experiments were set up as follows: the n.m.r. tube, fitted with a B10 cone, and containing the required amount of metal complex, was attached to the vacuum line and evacuated. The solvent was then condensed into the tube and the complex dissolved. The required amount of the volatile compound was measured on the line and condensed into the tube, which was then sealed off and kept at liquid nitrogen temperatures until the spectra could be recorded. The reaction could then be studied in the n.m.r. spectrometer from low temperature without premature warming.

(N,N´-diethyldithiocarbamato)bis(methyldiphenylthiophosphinito) platinum(II) tetraphenylborate (67a)

An excess of MeI (0.5 cm^3) was added to a suspension of $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (0.21 g, 0.26 mmol) in methanol (20 cm^3) and the mixture was shaken for 12 h and then filtered into a methanolic solution of $NaBPh_4$. The white solid which precipitated was filtered off and recrystallised from

$CHCl_3$/MeOH to give the product. mp. 170-173°C, (0.22 g, 75%). Found:- C, 58.4; H, 5.0; N, 1.2. Calc for $C_{55}H_{56}BNP_2PtS_4$:- C, 58.6; H, 5.0; N, 1.2%.

Mull i.r. spectrum:- ν_{CN} 1540; ν_{SC} 1030, 845; ν_{PS} 550, 560 cm^{-1}.

The analogous compound (N,N′-diisopropyldithiocarbamato)bis (methyldiphenylthiophosphinito)platinum(II) tetraphenylborate (67b) was prepared in a similar manner (0.15 g, 65%) Found:- C, 58.7; H, 5.1; N, 1.2; Calc for $C_{57}H_{60}BNP_2PtS_4$:- C, 59.3; H, 5.2; N, 1.2%.

Mull i.r. spectrum:- ν_{CN} 1510; ν_{CS} 840; ν_{PS} 545(b) cm^{-1}.

(N,N′-diethyldithiocarbamato)bis(methyldiphenylthiophosphinito) palladium(II) tetraphenylborate (67c) was prepared in a similar manner mp. 165 dec. Found:- C, 58.1; H, 5.2; N, 1.5. Calc for $C_{55}H_{56}BNP_2PdS_4$:- C, 63.6; H, 5.4; N, 1.4%.

Mull i.r. spectrum:- ν_{CN} 1510; ν_{SC} 840; ν_{PS} 560 cm^{-1}

N,N-diisopropyldithiocarbamato(methyldiphenylphosphinito) (methyldiphenylthiophosphinito)platinum(II) tetraphenyl borate (68)

An excess of MeI (0.5 cm^3) was added to a suspension of $Pt(S_2CN^iPr_2)(Ph_2POMe)(Ph_2PS)$ (21) (0.05 g, 0.06 mmol) in methanol (10 cm^3). When the conductivity had stopped rising (30 min), an excess of $NaBPh_4$ was added to the clear, colourless solution to precipitate a sticky white solid. The supernant liquid was removed and the product was recrystallised from $CHCl_3$/MeOH as a white powder.

Found:- C, 59.3; H, 5.4; N, 1.2. Calc for $C_{57}H_{60}BNOP_2PtS_3$:- C, 60.1; H, 5.3; N, 1.2%.

Mull i.r. spectrum:- ν_{CN} 1505; ν_{PO} 1025 cm^{-1}.

N,N-diethyldithiocarbamato(diphenylthiophosphinous acid) difluorophosphine selenido) platinum(II) (71)

The above compound was formed from stoichometric amounts of $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ (0.06 g, 0.05 mmol) and $F_2P(Se)H$ (0.1 mmol) when these two reactants were mixed in chloroform in an n.m.r. tube. Reaction commenced by -60°C and was complete when the sample had reached room temperature. Titration of the solution with degassed diethylether gave an intractable orange oil which could not be crystallised. An inseparable mixture (50:50) of the product (71) and $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ (22a) was formed when the reactants were mixed in a 1:1 ratio under similar conditions.

N,N´-isopropylammonium[N,N-diisopropyldithiocarbamato(diphenylthiophosphinito)(difluoroselenophosphinito)platinate(II)] (72)

When a 1:1 molar ratio of $F_2P(Se)H$ (0.10 mmol) and $N^iPr_2H_2[Pt(S_2CN^iPr_2)(Ph_2PS)_2]$ (17b) (0.09 g, 0.10 mmol) were mixed as above, the compound (72) was the major constituent of the reaction mixture at room temperature. Once again however, an intractable oil was obtained which slowly decomposed with liberation of elemental selenium, when attempts were made to isolate the product by trituration with diethylether or methanol.

N,N´-diethyldithiocarbamatobis(diphenylthiophosphinous acid) platinum(II) tetrafluoroborate (73a)

The compound $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (17a) (0.13 g, 0.15 mmol) was dissolved in chloroform (1 cm^3) and the solution was degassed and cooled to 10°C. A degassed aqueous solution (1 cm^3) of 40% HBF_4 was added with vigorous stirring. The bright yellow chloroform layer was separated into a solution of cold methanol to precipitate the product as a yellow solid (0.05 g, 35%). Found:- C, 40.4; H, 3.7; N, 1.7. Calc for $C_{29}H_{32}BF_4NP_2PtS_4$:- C, 40.2; H, 3.7; N, 1.6%. Mull i.r. spectrum:- ν_{CN} 1510; ν_{PS} 570, 540, 510 cm^{-1}. Disc spectrum:- ν_{SH} 2470 cm^{-1}.

Reactions with HX

These reactions were carried out on an n.m.r. tube scale by the method described earlier. A scale of 0.05 mmol of the metal complex dissolved in $CDCl_3$ (0.5 cm^3) was used. When isolations were attempted, the n.m.r. tube was opened, the contents checked by ^{31}P n.m.r. for air stability, and the solution was titurated with methanol, diethylether, petroleum ethers, or a combination of these solvents. Frequently, the metal complex separated as an oil, which persisted despite subsequent attempts at crystallisation.

N,N´-diethyldithiocarbamato{1,2-bis(diphenylphosphine) disulphide}platinum(II)iodide (76)

A solution of iodine dissolved in methanol was added dropwise to a solution of $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (17a) (0.08 g, 0.09 mmol) in chloroform (1 cm^3). When the colour of the iodine just persisted in the reaction solution an excess of methanol (5 cm^3) was added and the resultant solution was cooled to precipitate the microcrystalline product (0.04 g, 52%). Found:- C, 36.7; H, 3.6; N, 1.4. Calc for $C_{29}H_{30}INP_2PtS_4$:- C, 38.5; H, 3.3; N, 1.6%. Mull i.r. spectrum:- ν_{CN} 1520, ν_{PS}/ν_{SS} 580, 515 cm^{-1}.

N,N-diisopropyldithiocarbamato{1,2-bis(diphenylphosphine) disulphide}platinum(II)iodide (77a)

This compound was prepared in a similar manner to the above (0.23 g, 63%). Found:- C, 38.1; H, 3.4; N, 1.2. Calc for $C_{31}H_{34}INP_2PtS_4$:- C, 39.1; H, 3.6; N, 1.5%. Mull i.r. spectrum:- ν_{CN} 1500; ν_{PS}/ν_{SS} 550, 500 cm^{-1}. The tetraphenylborate (77b) was prepared by adding an excess of $NaBPh_4$ dissolved in methanol to the reaction solution. The product was precipitated as an off-white solid (0.16 g, 90%) Found:- C, 58.5; H, 4.8; N, 1.4. Calc for $C_{55}H_{54}NP_2PtS_4$:- C, 58.7; H, 4.8; N, 1.3%.
Mull i.r. spectrum:- ν_{CN} 1510; ν_{SS}/ν_{PS} 560, 505 cm^{-1}.

Reactions with H_2Se and H_2S

These systems were studied in the manner described above for n.m.r. experiments. The solvent used was $CDCl_3$. The experiments and results are discussed in the text.

TABLE 5.1 Some Phosphorus-31 n.m.r. Data[a]

	Compound	δP/p.p.m.	$^1J_{PtP}$/Hz	$^2J_{PP}$/Hz
(67a)	$[Pt(S_2CNEt_2)(Ph_2PSMe)_2]BPh_4$	32.9	3276.4	-
(67b)	$[Pt(S_2CN^iPr_2)(Ph_2PSMe)_2]BPh_4$	33.6	3245.9	-
(67c)	$[Pd(S_2CNEt_2)(Ph_2PSMe)_2]BPh_4$	49.2	-	-
	$[Pt(S_2CNEt_2)(Ph_2POMe)_2]BPh_4$[b]	94.2	3749.0	-
(69)	$[Pt(S_2CN^iPr_2)(Ph_2POMe)_2]BPh_4$[c]	94.7	3706.1	-
(68)	$[Pt(S_2CN^iPr_2)\{(Ph_2POMe)]BPh_4$[c]	93.8	3742.7	29.3
	(Ph_2PSMe)	35.1	3244.6	
(70)	$Pt(S_2CNEt_2)\{(Ph_2PS)$[c]	26.6	3084.7	20.0
	(Ph_2PSMe)	34.8	3795.1	
(71)	$Pt(S_2CNEt_2)\{(Ph_2PSH)$[d]	26.7	3437.5	37.0
	(F_2PSe)	156.6	4602.0	
(72)	$N^iPr_2H_2[Pt(S_2CN^iPr_2)\{(Ph_2PS)]$[e]	27.2	4065.0	33.1
	(Ph_2PSe)	165.2	5074.0	
(73a)	$[Pt(S_2CNEt_2)(Ph_2PSH)_2]BF_4$[f]	31.7	3449.7	
(76)	$[Pt(S_2CNEt_2)(Ph_2PSSPPh_2)]I$	116.7	3568.2	
(77a)	$[Pt(S_2CN^iPr_2)(Ph_2PSSPPh_2)]I$	117.0	3551.0	
(77b)	$[Pt(S_2CN^iPr_2)(Ph_2PSSPPh_2)]BPh_4$	117.2	3554.7	

[a] Recorded in $CDCl_3$ and at ambient (300 K) temperature unless noted.

[b] reference 9

[c] recorded *in situ*

[d] $^1J_{PF}$ 1218.3; $^3J_{PF}$ 2.0; $^1J_{PSe}$ 824.0 Hz

[e] $^1J_{PF}$ 1226.5; $^3J_{PF}$ N.O.; $^1J_{PSe}$ N.O.

[f] 290 K.

TABLE 5.2 Some Hydrogen-1 n.m.r. Data

		T/K	CH_3	CH_3	CH_2|CH	Other
(67a)	$[Pt(S_2CNEt_2)(Ph_2PSMe)_2]BPh_4$	301	t,1.06[a]	pt,1.80[b]	q,3.31[a]	m,6.70-7.80[c]
(67b)	$[Pt(S_2CN^iPr_2)(Ph_2PSMe)_2]BPh_4$	"	d,1.32[a]	pt,1.72[b]	e,4.38[a]	m,6.70-7.80[c]
(67c)	$[Pd(S_2CNEt_2)(Ph_2PSMe)_2]BPh_4$	"	t,1.07[a]	bs,1.74[d]	q,3.44[a]	m,6.70-7.80[c]
	$[Pt(S_2CNEt_2)(Ph_2POMe)_2]BPh_4$[e]	"	t,1.10[a]	pt,3.27[f]	q,3.33[a]	m,6.80-7.90[c]
(68)	$\{[Pt(S_2CN^iPr_2)\{(Ph_2POMe)]\}BPh_4$[g,i] (Ph_2PSMe)	"	m,1.28	pt,1.58[b] d, 1.73[h] d, 3.06[h] pt,3.23[b]	m,4.33	m,6.70-7.80[c]
(70)	$Pt(S_2CNEt_2)\{(Ph_2PSMe)$[i] (Ph_2PS)	"	t,1.24, 1.29[a]	d, 2.01[h]	q,3.58, 3.72[a]	m,7.00-7.80[c]
(71)	$Pt(S_2CNEt_2)\{(Ph_2PSH)$ (F_2PSe)		t,1.17, 1.28[a]		q,3.51, 3.66[a]	m,7.50-7.80[c] s,5.91[j]
(77b)	$Pt(S_2CN^iPr_2)(Ph_2PSSPPh_2)BPh_4$		d,1.34[a]		m,3.86[a]	m,6.80-8.00[c]

[a] $^3J_{HH}$ 7.0 Hz. [b] $|^3J_{PH} + {}^5J_{PH}|$ = 11.0 Hz. [c] Aromatic protons. [d] Broad peak : becomes sharp singlet on ^{31}P-irradiation.

[e] reference 9. [f] $|^3J_{PH} + {}^5J_{PH}|$ = 12.0 Hz. [g] equilibrium mixture. [h] recorded in situ. [i] $^3J_{PH}$ = 11.0 Hz.

[j] $^3J_{PtH}$ 35.0 Hz ($^2J_{PH}$ N.O.)

TABLE 5.3 Some Fluorine-19 n.m.r. Data[a]

		T/K	δF/p.p.m.	$^{1}J_{PF}$/Hz	$^{2}J_{PtF}$/Hz	$^{2}J_{FSe}$/Hz	$^{3}J_{PF}$/Hz
(71)	$\mathrm{Pt(S_2CNEt_2)}\left\{\begin{array}{l}\mathrm{(Ph_2PSH)}\\ \mathrm{(F_2PSe)}\end{array}\right.$	301	-16.8	1219.9	580.0	72.9	2.0
(72)	$\mathrm{[Pt(S_2CN^{i}Pr_2)}\left\{\begin{array}{l}\mathrm{(Ph_2PS)]}\\ \mathrm{(F_2PSe)}\end{array}\right.$	301	-21.8	1225.8	606.1	66.5	5.0

[a] recorded in $CDCl_3$ and referenced to external $CFCl_3$.

Chapter 6

Some Reactions of Platinum(II) and Palladium(II) Dithio-acid Compounds with $F_2P(E)H$

6.1 Introduction

The reactions of the three difluorophosphine chalcogenides, $F_2P(E)H$ (E = O, S, Se), with a variety of platinum(II) and palladium(II) dithio acid complexes have been briefly examined. Previously, like the reactions of $Ph_2P(E)H$ with transition metal complexes, the reactions of the oxide have been investigated to a greater extent than those of the sulphide and selenide. However, no hydrogen bridged chelate ligands (i.e. of the form -P-O--H--O-P-) have been observed and this can probably be attributed to an effect of the electronegative fluorine atoms. A number of modes of coordination have been observed and these, and some relevant compounds, will be discussed below.

6.1.1 Difluorophosphine Chalcogenides

The three compounds (E = O, S, Se) have been known for a number of years and can be readily prepared by standard literature methods. The compounds are all volatile liquids which can be conveniently handled on the vacuum line and their infrared and n.m.r. (^1H, ^{19}F and ^{31}P) spectra have been recorded[79]. These studies have shown that the compounds exist in the P(V) keto form at room temperature. Thus characteristic ν_{PE} (E = O, 1377; S, 709; Se, 547 cm^{-1}) and ν_{PH} (*ca*. 2500 cm^{-1}) bands are observed in the i.r. spectra and a large one-band PH coupling is seen in ^{31}P and ^1H n.m.r. studies.

6.1.2 Transition Metal Complexes of $F_2P(E)H$

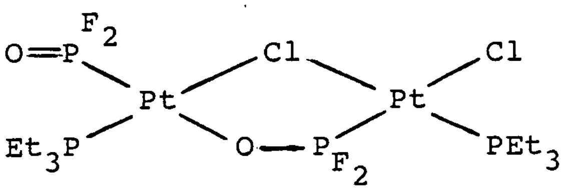
Grosse and Schmutzler were instrumental in developing a number of transition metal difluorophosphinite complexes[80]. Thus the complexes $[M(F_2PO)_4]^{2-}$ (M = Pt, Pd) were characterised and the reactions of tertiary phosphine complexes with $F_2P(OR)$ (R = C_3H_5, ${}^nPr$, ${}^nBu$ or Ph) were examined (Eqn. 32).

$$MCl_2L_2 + F_2POR \longrightarrow t - MClL_2\ (F_2PO) + RCl$$

(M = Pt, Pd
L = tertiary phosphine) ... (32)

The spectral evidence gained, and an X-ray crystal structure of $PtCl(F_2PO)(PEt_2Ph)_2$, showed that the fluorophosphine was bound through phosphorus to the metal. The observed PO bond length (1.47 Å) and the i.r. band, ν_{PO}, at ca. 1250 cm^{-1} are consistent with the presence of a terminal PO double bond.

In addition, the binuclear $(F_2PO)^-$ complexes $[MCl(PEt_3)(F_2PO)]_2$ were characterised and the X-ray structure, in the case where M = Pt (81), reveals the presence of both bridging and terminal $(F_2PO)^-$ ligands.



(81)

The complexes cis-$[MCl_2(F_2PO)_2]^{2-}$ were isolated, like the tetradifluorophosphinito complexes, as the di-anions.

The first report of a complex containing the ligand $(F_2PS)^-$ was made in 1972, when the compound $Fe(\eta\text{-}C_5H_5)(CO)_2(F_2PS)$

was prepared[81]. The authors also report that $F_2P(E)Cl$ compounds will react with $IrX(CO)(PPh_3)_2$ complexes (X = Cl, Br) by oxidative addition to form complexes of the type $IrX_2(F_2PE)(CO)(PPh_3)_2$. More recently, workers in this department have examined the oxidative addition reactions of $F_2P(E)H$ with complexes such as $IrH(CO)(PPh_3)_2$ and have observed a number of isomeric $Ir(III)-F_2P{=}E$ complexes[82]. The similar Ir(III) complexes, $IrCl_2PF_2E(CO)(PEt_3)_2$, have been isolated and characterised, for E = O, S, Se.[83]

Platinum complexes of $(F_2PE)^-$ ligands have also been examined in this department. Thus the complexes t-$PtH(F_2PE)(P(C_6H_{12})_3)_2$ (E = O, S, Se) have been isolated and a systematic study of the reactions of $F_2P(E)H$ with t$PtHX(PEt_3)_2$ (E = S, Se; X = Cl, Br, I) has been carried out.[84] The stable Pt(II) mononomers t-$PtX(F_2PE)(PEt_3)_2$ have been isolated and fully characterised by multinuclear n.m.r. measurements (δP_E occurs to high frequency, ca. 130-140 p.p.m., and $^1J_{PtPE}$ is large, ca. 5000 Hz) and by an X-ray crystal structure for $PtCl(F_2PS)(PEt_3)_2$ (82). This showed that the PS bond had considerable double bond character (1.95(1) Å; cf. 1.876(1) Å for $F_2P(S)H$ and that the Pt-P bond is short (2.213(5) Å; see also $PtCl(F_2PO)(PEt_2Ph)_2$: 2.199(6) Å)[80b] indicative of a considerable degree of π back bonding from the metal.

A number of reactions were carried out in which the above compounds were treated with bidentate ligands. One of the compounds thus prepared was $Pt(S_2CNEt_2)(F_2PS)(PEt_3)$ (83) and again the ^{31}P n.m.r. chemical shift of the $(F_2\underline{P}S)^-$ ligand is at high frequency (144.7 p.p.m.,

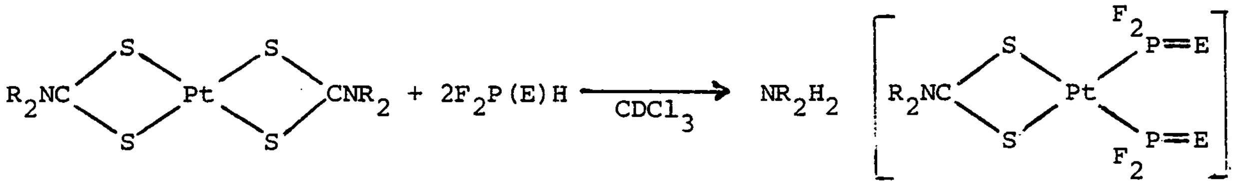
$^1J_{PtP}$ 4884 Hz). This mixed alkyl/fluorophosphine complex is similar to the compounds discussed in the previous chapter, $Pt(S_2CNEt_2)(F_2\underline{P}Se)(Ph_2PSH)$ (71) (δP 156.6 p.p.m.) and $[Pt(S_2CN^iPr_2)(F_2\underline{P}Se)(Ph_2PS)]^-$ (72) (δP 165.5 p.p.m.)

It can be seen, therefore, that the known transition metal chemistry of $F_2P(E)H$ is not extensive compared with that of the alkyl or aryl analogues, but that studies have concentrated on the oxidative addition of the parent molecule to the substrate metal ions. The compounds reported in the subsequent sections also fit in with this scheme.

6.2 The Reaction of $F_2P(E)H$ with Dithio-acid Metal Complexes

6.2.1 Platinum Dithiocarbamate Complexes

The reactions of $F_2P(E)H$ (E = O, S, Se) with the compounds $Pt(S_2CNR_2)_2$ (R = Et, ^{i}Pr) have been examined, principally by variable temperature, multinuclear n.m.r. spectroscopy. In general, the reaction commences at ca. -50°C and a 2:1 complex is formed (Eqn. 32a).



(R = Et; E = S (84)

R = ^{i}Pr; E = O (85), S (86), Se (87)).

...(32a)

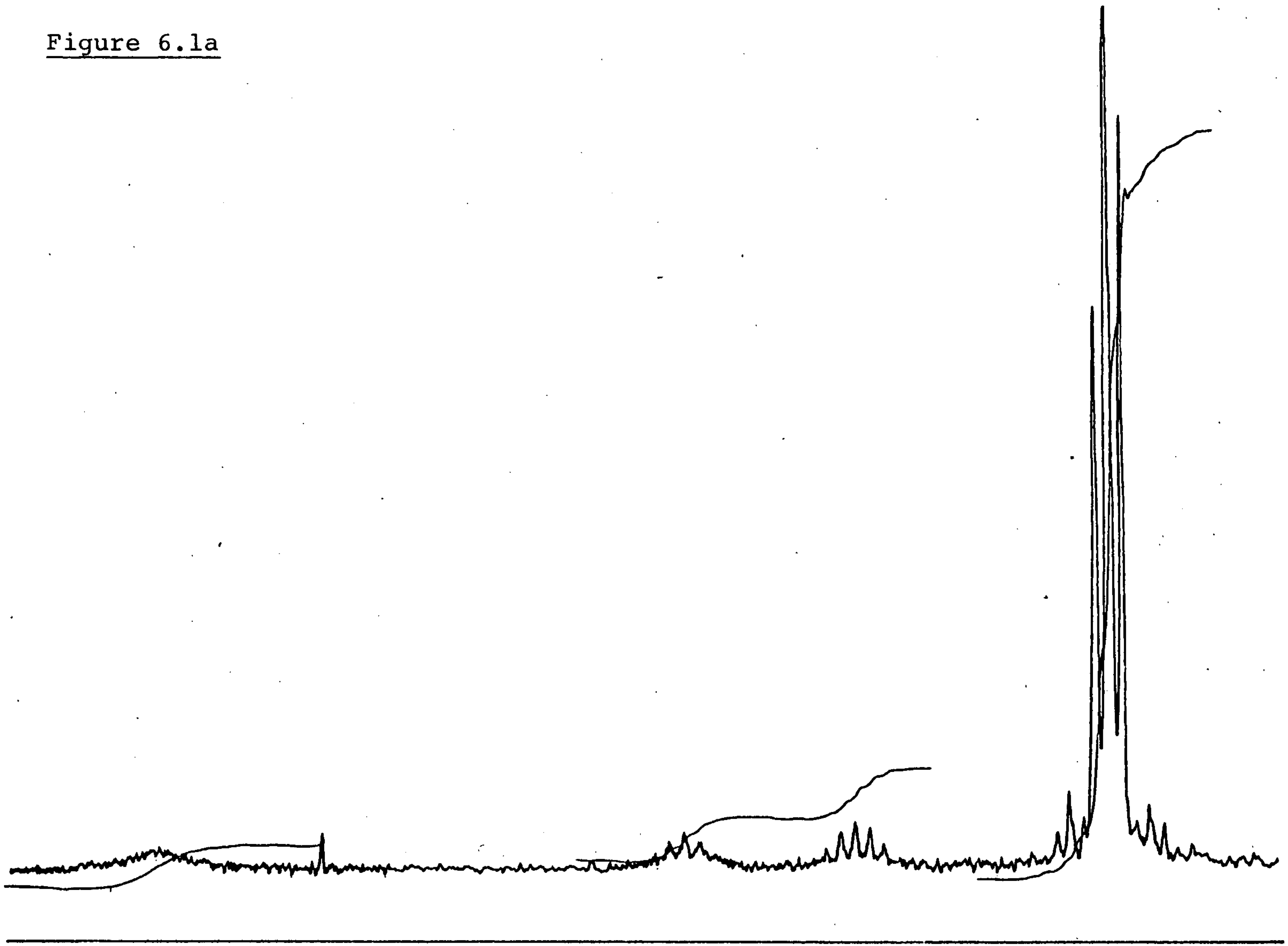
No intermediates, or any other species, are observed by $^{31}P-\{^{1}H\}$ or ^{19}F n.m.r. spectroscopy and a similar product is observed in each case, whether there is a deficiency or an excess of the fluorophosphine present initially.

Only (85) has been isolated and fully characterised as an air-stable, microcrystalline white solid. A strong band in the i.r. spectrum at 1200 cm^{-1} was assigned to ν_{PO}. The remaining compounds (84, 86-87) could only be isolated as intractable orange (S) or red (Se) oils, which resisted numerous attempts at crystallisation by tituration, solvent evaporation or cation exchange reactions. Neither the triphenylbenzylphosphonium nor the caesium salts could be made by the latter technique, which had proven successful for the diarylphosphine sulphide complexes described in Chapter 2. The characterisation rests, therefore, on a consideration of the n.m.r. spectra, which are quite unambiguous.

Thus, hydrogen-1, phosphorus-31 and fluorine-19 n.m.r. data are assembled in Tables 6.1-3 respectively. The formation of the dialkylammonium salt can be followed by ^{1}H n.m.r. Two new sets of alkyl resonances are observed as the reaction proceeds and the initial signal, due to $Pt(S_2CN\underline{R}_2)_2$, disappears. In addition, a broad resonance at ca. 8.0 ± 0.5 p.p.m. can be assigned to the $N\underline{H}_2^{+}$ resonance (Figure 6.1a).

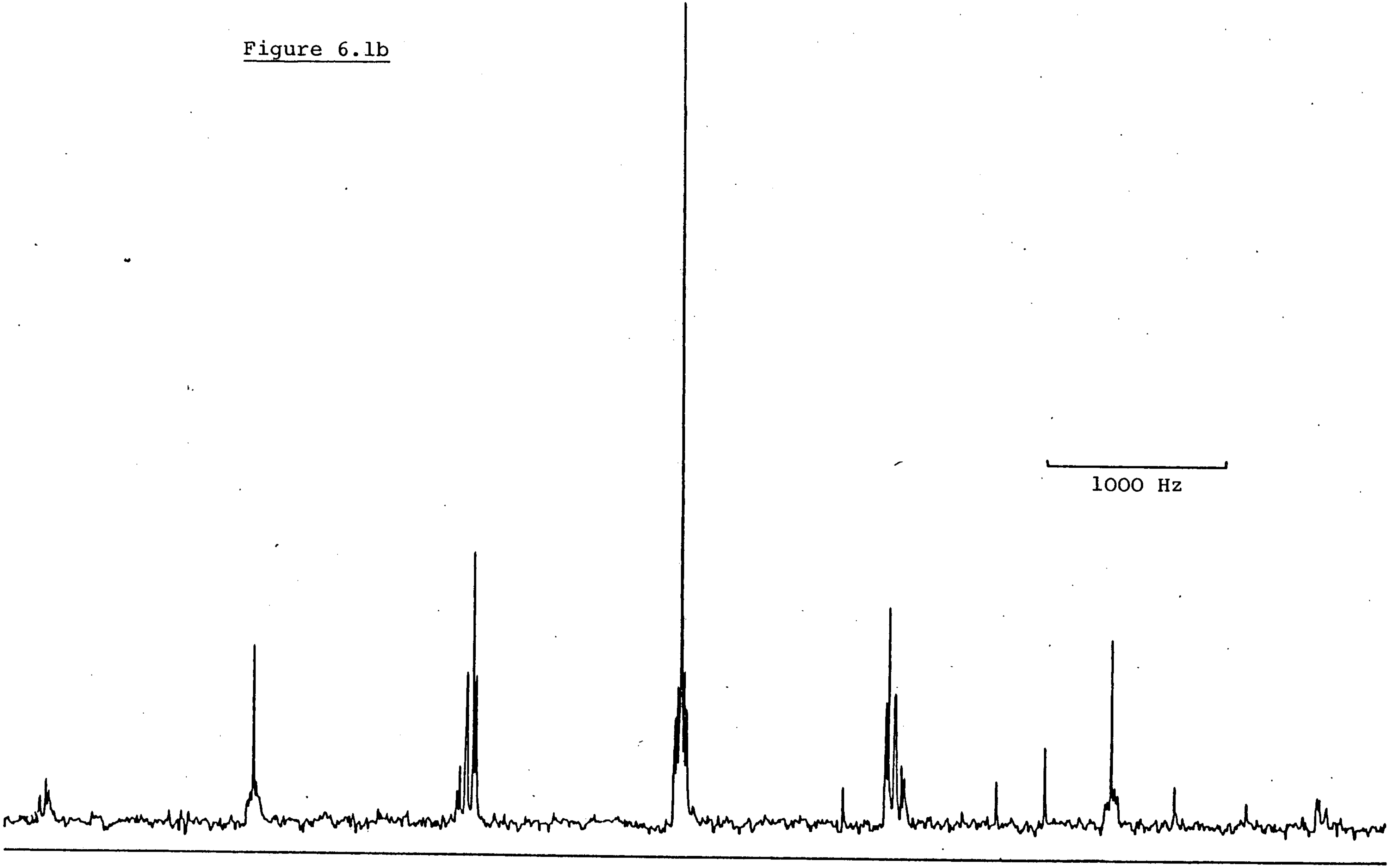
The $^{31}P-\{^{1}H\}$ and ^{19}F n.m.r. spectra are more complex. That two $(F_2PE)^-$ units are coordinated, through phosphorus, to platinum(II) is readily apparent from the spectra. The large one-bond Pt-P coupling (ca. 5000 Hz) and the high chemical shifts (ca. 150-160 p.p.m.) of the S and Se species

Figure 6.1a



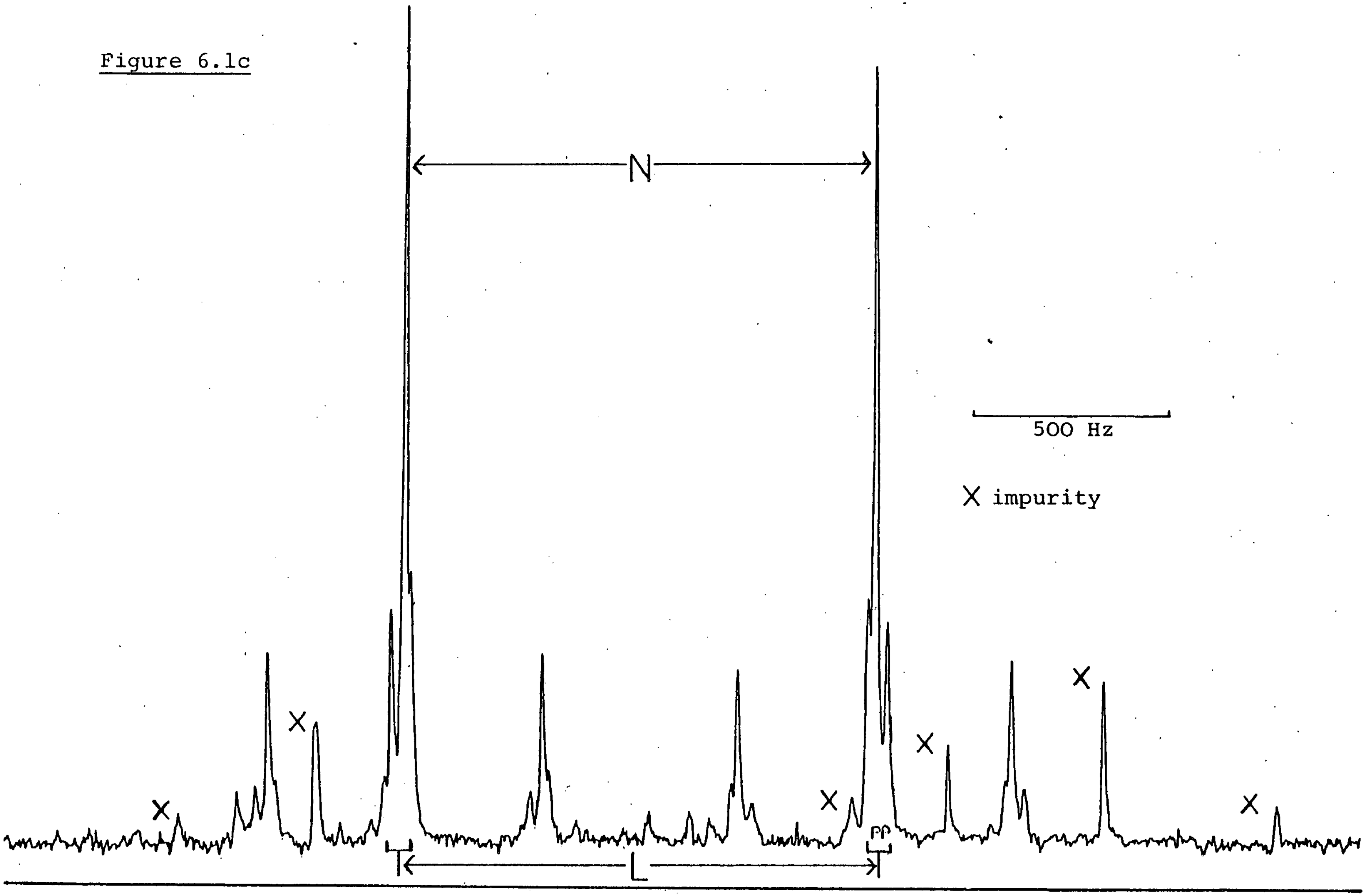
Hydrogen-1 n.m.r. spectrum (CDCl$_3$, 300 K) of $N^{i}Pr_2H_2[Pt(S_2CN^{i}Pr_2)(F_2PO)_2]$ (85)

Figure 6.1b



Phosphorus-31 n.m.r. spectrum ($CDCl_3$, 300 K) of $N^iPr_2H_2\,[Pt(S_2CN^iPr_2)(F_2PS)_2]$ (86)

Figure 6.1c



Fluorine -19 n.m.r. spectrum ($CDCl_3$, 300 K) of $NEt_2H_2[Pt(S_2CNEt_2)(F_2PS)_2]$ (84)

(84, 86-87) confirm this in the ^{31}P n.m.r., as does the appearance of the spectra. When two PF_2 units are coordinated to the same moiety, or atom, a second order spectrum often results, which can be analysed in terms of an $(AX_2)_2$ coupling pattern (where A = P, X = F).[†] In the ^{31}P n.m.r. spectrum this results, in these cases, in a complex line pattern (Fig. 6.1b) from which only the parameter $N(=|^1J_{PF} + {}^3J_{PF}|)$ can be found easily. Therefore it is usually more convenient to use the simpler ^{19}F n.m.r. pattern (Fig. 6.1c) to solve for the remaining coupling constants. N, which is directly observed (Fig. 6.1b), and $L(=|^1J_{PF} - {}^3J_{PF}|)$, which can be calculated from the next two most intense pairs of lines, give $^1J_{PF}$ and $^3J_{PF}$. It was also observed that these two parameters are of opposite sign. $^2J_{PP}$ can also be found, as shown in Fig. 6.1c.[71c]

It is interesting to note that the compounds are all observed as cation:anion pairs, and that the selenium compound (87) (with two cis fluorophosphine ligands) is also observed. Both these points may be attributed to the presence of the electro-negative fluorine which deactivate the terminal chalcogenide atoms (O, S, Se) towards protonation and must also affect the mechanism whereby a neutral $Pt(S_2CNR_2)(Ph_2PSe)(Ph_2PH)$ compound (26) was the principal product in the earlier reactions. In fact, the selenium

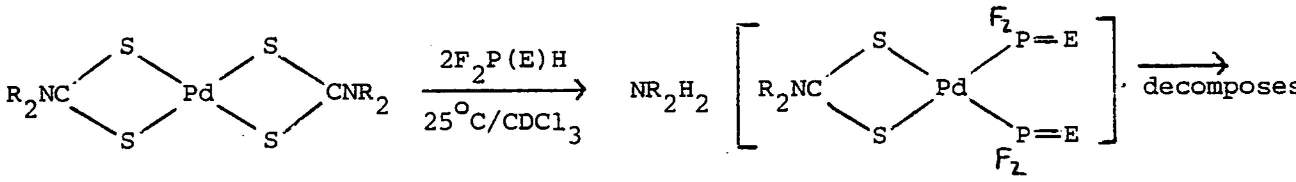
[†] Although the two moieties are usually chemically equivalent they are magnetically inequivalent. If $^3J_{PF}$ and $^2J_{PP}$ are large then the spectrum is second order and if these couplings are small or zero a simpler spectrum is observed.

compound (87) is the least stable and soon decays, <u>in vacuo</u>, with loss of Se. The decomposition products have not been identified.

As mentioned in passing, reaction commences at -50°C, and proceeds rapidly at room temperature. No other Pt-containing species have been observed by n.m.r. spectroscopy even when the reaction solution was rapidly cooled and re-examined.[†] It is presumed, however, that the initial step must be oxidative addition of $F_2P(E)H$, followed by reductive elimination of dithio-carbamic acid and subsequent substitution by F_2PE^- or a second mole of $F_2P(E)H$ and then deprotonation.

6.2.2 Palladium Dithiocarbamate Complexes

A reaction mechanism which involves oxidation to M(IV) as a first step is supported when the analogous palladium dithiocarbamate reactions are examined. Under similar reaction conditions, no reaction is observed, by ^{31}P n.m.r. spectroscopy, until <u>ca</u>. 25°C. Then, in most cases (Eqn. 33) a slow reaction commences and small quantities of the mononuclear anionic



(R = Et; E = S (88), Se (89); R = ^{i}Pr; E = S (90))

... (33)

[†] In a reaction described earlier $(F_2PSe)^-$ had completely substituted $(Ph_2PS)^-$ by the time it took to record the first low temperature ($CDCl_3$ solution) n.m.r. spectrum (Section 5.3). Unfortunately, the above reactions do not occur in toluene, which is normally utilised to examine very low temperature spectra.

products are formed. ($NR_2H_2^+$ is again observed in the ^1H n.m.r. for $NEt_2H_2[Pd(S_2CNEt_2)(F_2PSe)_2]$ (89)) The diisopropyldithiocarbamate complex was more inert than the diethyl analogue, but only the compound $NEt_2H_2[Pd(S_2CNEt_2)(F_2PSe)_2]$ (89) was formed in any appreciable quantity. The decomposition products were mainly identified by their ^{19}F n.m.r. spectra. Thus PF_3 and HPF_5^- were among those identified.

The species $[Pd(S_2CNEt_2)(F_2PO)_2]^-$ (91) was however, observed in high yield from the reaction of $F_2P(O)H$ with $[Pd(S_2CNEt_2)(Ph_2PS)]_2$. $Ph_2P(S)H$ was liberated during the reaction. Neither this compound (91) nor the other palladium species (88-90) could be isolated.

The $^{31}P-\{^1H\}$ (Table 6.2) and ^{19}F (Table 6.3) n.m.r. spectra are also $(AX_2)_2$ patterns. The phosphorus chemical shifts are consistently to higher frequency than for the platinum analogues (84-87) and the parameter N is generally greater by 30-100 Hz. $^1J_{PF}$ could only be calculated for $NEt_2H_2[Pd(S_2CNEt_2)(PF_2PSe)_2]$ (89) and was observed to be considerably higher (ca. 1300 Hz) than values observed for the platinum species (ca. 1200 Hz).

6.2.3 Miscellaneous Reactions and Conclusions

Some other observations have been made in this area. $Pt(S_2CNMe_2)_2$ does not react with $F_2P(S)H$, in $CDCl_3$, probably because of the low solubility of the complex. $Ni(S_2CNR_2)_2$ do not react with $F_2P(E)H$ (E = O, S, Se) compounds. This may again be indicative of a preliminary oxidation step, which is not favoured in the nickel systems. $Pd(S_2PR_2)_2$

(R = Me, Ph) and $Pd(S_2CPh)_2$ react only slowly with $F_2P(S)H$. However, the principal observation is the degradation of the fluorophosphine over a period of weeks at room temperature and no metal-fluorophosphine complexes were identified in any of these reactions. It is clear, however, that some reaction involving the starting complex takes place, because both $(S_2PMe_2)^-$ and $(S_2PPh_2)^-$ can be identified in their respective reaction solutions, by ^{31}P n.m.r. spectroscopy.

Finally, evidence has been obtained that a species containing a single difluorophosphine sulphide ligand is formed when $Pt(S_2PPh_2)_2$ is mixed with excess $F_2P(S)H$ in $CDCl_3$. The reaction is not clean, however, and a number of unidentified, mainly fluorophosphine species are also observed. The principal product is characterised in the ^{31}P n.m.r. by a doublet with platinum satellites, assigned to $(S_2PPh_2)^-$ (δP 74.4 p.p.m.; $^2J_{PtP}$ 152.6 Hz, $^3J_{PP}$ 19.5 Hz) and a triplet of triplets assigned to a P-coordinated (F_2P) moiety (δP 85.3 p.p.m.; $^1J_{PtP}$ 3377.7 Hz, $^1J_{PF}$ 1251.9 Hz, $^3J_{PP}$ 19.5 Hz). Due to the presence of the other fluorophosphine species the ^{19}F n.m.r. of the above mixture has not been deciphered. The probable stoichiometry is therefore $Pt(S_2PPh_2)_2(F_2P\text{-}SH)$, containing a monodentate and a bidentate dithiophosphonate ligand, which are fluxional in solution at room temperature. Further investigation, for example, variable temperature n.m.r. studies, may help to confirm this, and confirmation of the thiophosphinic acid could be obtained by high resolution ^1H n.m.r. Fluxional compounds of this type have been observed before, where a tertiary phosphine is substituted in one coordination site of bisdithio-acid platinum complexes.[42]

These reactions, in general, support the premise that an oxidation step is involved in the synthesis of the bis-difluorophosphinite complexes. Thus, palladium dithio compounds are almost inert, and reaction is only observed, to any extent, in the dithiocarbamate case, where any displaced ligand will decompose. Platinum dithiophosphinates also react, typically, by substitution and a different mechanism, involving the intermediacy of F_2P-SH, may be postulated for the observed reaction.

6.3 The Reactions of $NR_2H_2[Pt(S_2CNR_2)(F_2PE)_2]$

This potentially extensive area has only been briefly investigated. The reactions of $N^iPr_2H_2[Pt(S_2CN^iPr_2)(F_2PSe)_2]$ with the acids HX (X = Cl, Br, I) have been examined. In all cases one mole of $F_2P(Se)H$ is liberated and the solution darkens (orange→deep red) in colour. When X = Cl, Br only an intractable oil was obtained in work-up. However, when X = I a brown solid (93) was obtained. In all cases, the oil or solid separates rapidly from solution ($CDCl_3$) at low temperature. No ^{31}P or ^{19}F n.m.r. signals corresponding to any of the products were observed, but the analytical data for compound (93) and the reaction stoichiometry suggests that the products are of the form $N^iPr_2H_2[Pt(S_2CN^iPr_2)(F_2PSe)X]$ (X = halide). Conversely, no reaction was observed when $NEt_2H_2[Pt(S_2CNEt_2)(F_2PS)_2]$ (84) or $N^iPr_2H_2[Pt(S_2CN^iPr_2)(F_2PSe)_2]$ (87) were mixed with MeI, unlike the reactions $(Ph_2PS)^-$ compounds discussed earlier.

When $N^iPr_2H_2[Pt(S_2CN^iPr_2)(F_2PSe)_2]$ (87) is mixed with stoichiometric amounts of $Pd(OAc)_2$ or with $PdCl_2$(1,5-COD) brown solids precipitate from solution. However, these products have not been characterised, because, on isolation in vacuo they spontaneously blacken and irreversibly decompose. In situ monitoring of the reaction by ^{31}P n.m.r. spectroscopy shows that no fluorophosphine compounds are observed once the solid has precipitated ^1H n.m.r. spectra of the reaction solution show that $(N^iPr_2H_2)^+$ and the free ligands, $(acetate)^-$ and (1,5-COD), remain in solution.

In conclusion, therefore, it is clear that the bis-difluorophosphinite complexes will undergo a variety of reactions which differ substantially from those of the diarylphosphinite analogues. A problem is investigating these reactions, namely that of scale and handling, has made consistent results difficult to obtain. Additionally, the stability of the products is limited and most decompose readily, if warmed or exposed to air, with elimination of phosphine ligands,etc. (In some cases, for example, the reaction of compound (87) with HCl, $Pt(S_2CN^iPr_2)_2$ was recovered).

6.4 Conclusion

The studies discussed in this chapter can only be regarded as preliminary investigations into what is potentially a large field. The reaction of fluorophosphine chalcogenides with platinum and palladium dithio-acid complexes has been established and the products formed mirror those of the diarylphosphine chalcogenide analogues, to some extent.

Although no conclusive data has been obtained it has been shown that these compounds will displace coordinated ligands in other metal complexes. If a systematic method of generating such compounds could be achieved, there is no real reason why they cannot be isolated and fully characterised in the manner of the compounds discussed in Chapters 3 and 4. Similarly, the reactions with HX can be extended to the other calcogenide (O,S) complexes with a view towards isolation and characterisation of the products, to confirm the tentative assignments made so far.

As it has been noted in passing that difluorophosphine sulphide and oxide will substitute for diarylphosphine sulphide in platinum and palladium complexes a more thorough investigation may reveal the mechanism whereby this occurs and the techniques may be exploited to form a series of mixed fluoro- and aryl-phosphinite complexes.

6.5 Experimental

Physical methods were as for those described in Chapter 5. As before, most of the reactions described in this chapter were studied in situ by multinuclear n.m.r. spectroscopy using the technique also described in Chapter 5. Some hydrogen-1 data are collected in Table 6.1, phosphorus-31 data in Table 6.2 and fluorine-19 data in Table 6.3.

The difluorophosphine chalcogenides, HPF_2E (E = O, S, Se) were prepared by standard techniques and other compounds were obtained as described in earlier chapters.

N,N´-diisopropylammonium[(N,N´-diisopropyldithiocarbamato) bis(difluorophosphinito)platinate(II)] (85)

The above compound was formed when a 2:1 ratio of $F_2P(O)H$ (0.1 mmol) was condensed onto a frozen d-chloroform (0.5 cm^3) solution of $Pt(S_2CN^iPr_2)_2$ (0.03 g, 0.05 mmol) and allowed to warm. The product precipitated as a white microcrystalline solid when the reaction solution was titurated with a solution (5 cm^3) of diethylether and petroleum ether (bp 40-60°C) (50:50). mp. 178-180°C, (0.02 g, 56%). Found:- C, 24.4; H, 4.7; N, 4.1. Calc for $C_{14}H_{28}F_4N_2O_2P_2PtS_2$:- C, 24.3; H, 4.7; N, 4.4%. Mull i.r. spectrum:- ν_{CN} 1510; ν_{PO} 1200; ν_{PF} 830, 810 790 cm^{-1}.

N,N´-diisopropylammonium[(N,N´-diisopropyldithiocarbamato) bis(difluorothiophosphinito)platinate(II)] (86), N,N´-diethylammonium[N,N´-diethyldithiocarbamato)bis(difluorothiophosphinito)platinate(II)] (84) and N,N´-diisopropylammonium [(N,N´-diisopropyldithiocarbamato)bis(difluoroselenophosphinito) platinate(II)] (87) were prepared on a similar scale using $F_2P(S)H$ and $F_2P(Se)H$. In the above cases, however, tituration by a variety of methods yields only intractable oils. The compounds are, however, air stable.

Palladium Reactions

These reactions were examined by the usual techniques. $F_2P(S)H$ was mixed with $Pd(S_2CNR_2)_2$ (R = Et, ^iPr), $Pd(S_2PR_2)_2$ (R = Me, Ph) and $Pd(S_2CPh)_2$ and $F_2P(Se)H$ was mixed with $Pd(S_2CNR_2)_2$ (R = Et, ^iPr). The reactions were initially examined at low temperature and then, in some cases, over a period of weeks at room temperature before the products were observed. N.m.r. evidence for compounds of the type $NR_2H_2[Pd(S_2CNR_2)(F_2PE)_2]$ is given in the three Tables.

Reactions with HX

$N^iPr_2H_2[Pt(S_2CN^iPr_2)(F_2PSe)_2]$ was generated in situ in chloroform. The volatiles and solvents were pumped off, an n.m.r. solvent added ($CDCl_3$, 0.5 cm^3) and the solution was then tipped into an n.m.r. tube connected, via a side arm, to the reaction vessel. An equimolar amount of the halogen acid was measured on the line and condensed into the tube. The solid which precipitated at low temperature from the reaction with HI, believed to be $N^iPr_2H_2[Pr(S_2CN^iPr_2)(F_2PSe)I]$ (93), gave the following analytical data:- C, 19.3; H, 3.8; N, 3.3. Calc for $C_{13}H_{30}F_2N_2IPPtS_2Se$:- C, 20.9; H, 4.0; N, 3.7. All three compounds were observed to decompose with loss of Se. After 14 days $Pt(S_2CN^iPr_2)_2$ was isolated from the reaction with HCl and characterised by its i.r. spectrum.

Reactions with metal compounds

After generating the compound $N^iPr_2H_2[Pt(S_2CN^iPr_2)(F_2PSe)_2]$ in situ, the solution was tipped into a solution of the metal complex $Pd(OAc)_2$ or $PdCl_2$ (1,5-COD) at room temperature. An immediate reaction took place in both cases and brown solids were precipitated. These, however, decomposed on isolation in vacuo.

TABLE 6.1 Some Hydrogen-1 n.m.r. Data[a]

Compound	CH_3	CH_2	CH	Other
(84)	t,1.31[b], 1.48[bc]	q,3.20[bc], 3.68[b]	-	8.14[d]
(85)	d,1.44[b], 1.56[bc]	-	m,3.39[bc], 4.62[b]	8.53[d]
(86)	d,1.53, 1.46[c]	-	m,3.56[c], 4.54	7.68[d]
(87)	d,1.53, 1.55[c]	-	m,3.65[c], 4.60	7.64[d]
(89)	t,1.05[b], 1.28[bc]	q,3.07[bc], 3.58[b]		7.50[d]

[a] chemical shifts quoted in p.p.m. to high frequency of T.M.S.

[b] $^3J_{HH}$ 7.0 Hz

[c] dialkyl ammonium cation

[d] NH_2^+ resonance

TABLE 6.2 Some Phosphorus-31 n.m.r. Data[a]

Compound	δP	$^1J_{PtP}$	N[b]
(84)	151.1	4995.2	1196.2
(85)	57.5	5559.1	1220.7
(86)	154.6	4951.2	1201.2
(87)[c]	163.4	4687.5	1212.0
(88)	183.6	-	1241.3
(89)	197.2	-	1296.5
(90)	189.9	-	1230.4
(91)	84.1	-	1264.7

[a] Shifts quoted in p.p.m. to high frequency of external 85% H_3PO_4 and couplings are in hertz

[b] $N = |^1J_{PF} + {}^3J_{PF}|$

[c] $^1J_{PSe}$ = 442.7 Hz.

TABLE 6.3 Some Fluorine-19 n.m.r. Data[a]

Compound	δF/p.p.m.	$^{2}J_{PtF}$	N	$^{1}J_{PF}$	$^{3}J_{PF}$	$^{2}J_{PP}$
(84)	-16.5	699.8	1197.1	1206.6	9.5	49.6
(85)	-20.6	852.8	1220.6	1220.6	0.0	81.1
(86)	-17.2	682.6	1200.6	1208.0	7.5	53.3
(87)	-18.5	612.8	1212.3	-	-	
(89)	-15.5	-	1299.7	1299.7	0.0	90.0

[a] Chemical shifts are quoted to high frequency of $CFCl_3$ and all couplings are in hertz.

REFERENCES

1. D.M. Roundhill, R.P. Sperline and W.B. Beaulieu, Coord. Chem. Rev., 1978, 26, 263 and refs. therein.

2. L.A. Hamilton and P.S. Landis, Chapter 11, Organic Phosphorus Compounds (G.M. Kosolapoff and L. Maier, eds.), Wiley, 1972 and refs. therein.

3. L. Maier, Topics in Phosphorus Chemistry, 2, 43.

4. G. Peters, J. Amer. Chem. Soc., 1960, 82, 4751.

5a I.W. Robertson, Ph.D. Thesis, Edinburgh, 1981.

5b J.A.S. Duncan, Personal Communication.

6. M.M. Rauhat and H.A. Currier, J. Org. Chem., 1961, 26, 4626.

7a B.B. Hunt and B.C. Saunders, J. Chem. Soc., 1957, 2413.

7b L.D. Quin and R.E. Montgomery, J. Inorg. Nac. Chem., 1966, 28, 1750.

9. M.C. Cornock, R.O. Gould, C.L. Jones and T.A. Stephenson, J.C.S. (Dalton), 1977, 1307.

10a G.M. Gray and C.S. Kraihanzel, J. Organometallic Chem., 1978, 146, 23.

10b E.H. Wong and F.C. Bradley, Inorg. Chem., 1981, 20, 2333.

11. K.R. Dixon and A.D. Rattray, Canad. J. Chem., 1971, 49, 3997.

12. D.V. Naik, G.J. Palenik, S. Jacobson and A.J. Carty, J. Amer. Chem. Soc., 1974, 96, 2286.

13. G.A. Levshina, A.D. Troitskaya and R.R. Shagidulla, Russ. J. Inorg. Chem., 1966, 11, 985.

14. A. Pidcock and C.R. Waterhouse, J. Chem. Soc. (A), 1970, 2080; 2087.

15. H. Werner and T.N. Khac, Angew. Chem. Int. Ed. Engl., 1977, 16, 324.

16. J.A.S. Duncan, Personal Communication.

17. W.J. Sime, C.L. Jones, R.O. Gould and T.A. Stephenson, J.C.S. (Dalton), 1977, 669.

18. I.W. Robertson and T.A. Stephenson, Inorg. Chim. Acta, 1980, 45, L215.

19. R.P. Sperline and D.M. Roundhill, Inorg. Chem., 1977, 16, 2612.

20. P.J. Miller, R.A. Butler and E.R. Lippincott, J. Phys. Chem., 1972, 57, 545.

21. H. Werner, Angew. Chem. Int. Ed. Engl., 1977, 16, 1.

22. A. Bottomley, Final Year Project Report, Edinburgh University, 1978.

23a E. Lindner and W-P Meier, J. Organometallic Chem., 1973, 51, C14.

23b E. Lindner and H. Dreher, ibid, 1973, 55, 347.

23c E. Lindner and W-P Meier, ibid, 1974, 67, 277.

23d E. Lindner and H. Dreher, ibid, 1976, 105, 85.

23e E. Lindner and H. Dreher, ibid, 1976, 104, 331.

23f E. Lindner and W-P Meier, J. Strahle. Z. Anorg. Alle. Chem., 1976, 424, 154.

23g E. Lindner and W-P Meier, Chem. Ber., 1976, 109, 3323.

23h E. Lindner and B. Schilling, J. Organometallic Chem., 1976, 117, C93.

23i E. Lindner and B. Schilling, Chem. Ber., 1977, 110, 3725.

24. P.M. Treichel, W.K. Dean and W.M. Douglas, J. Organometallic Chem., 1972, 42, 145.

25. R.C. Dobbie and P.R. Mason, J.C.S. (Dalton), 1973, 1124.

26. P. Piraino and F. Faraone, ibid, 1976, 610.

27. W. Malisch, R. Maisch, I.J. Colquoun and W. McFarlane, J. Organometallic Chem., 1981, 220, C1.

28. H.P.M.M. Ambrosius, J.H. Noordik and G.J.A.A. Ariaans, J.C.S. Chem. Commun., 1980, 833.

29. C.S. Kraihanzel and C.M. Bartish, J. Organometallic Chem., 1972, 43, 343.

30. V. Marsala, F. Faraone and P. Piraino, ibid, 1977, 133, 301.

31. D.H.M.W. Thewissen, ibid, 1980, 192, 115.

32a D.W. Meek and P. Nicpon, J. Amer. Chem. Soc., 1965, 87, 4952.

32b M.A.A. Bey and K.S. Hussein, Chem. Ind. (London), 1966, 1181.

33. K.P. Wagner, R.W. Hess, P.M. Treichel and J.C. Calabrese, Inorg. Chem., 1975, 14, 1121.

34. B. Walther, B. Messbauer and H. Meyer, Inorg. Chim. Acta, 1979, 37, L525.

35. V.I. Nefedov and Y.V. Salyn, ibid, 1978, 28, L135.

36. N.M. Boag, J. Browning, C. Crocker, P.L. Goggin, R.J. Goodfellow, M. Murray and J.L. Spencer, J. Chem. Res. (S), 1978, 228; J. Chem. Res. (M), 1978, 2962.

37. R.G. Cavell, W. Byers, E.D. Day and P.M. Watkins, Inorg. Chem., 1972, 11, 1598.

38. E. Lindner and B. Schilling, Chem. Ber., 1977, 110, 3889.

39a E. Lindner, A. Rau and S. Hoehne, Angew. Chem. Int. Edn. Engl., 1979, 18, 534.

39b E. Lindner, F. Bouchir and W. Hiller, J. Organometallic Chem., 1982, 210, C37.

40. M. Grayson, C.E. Farley and C.A. Streuli, Tetrahedron, 1967, 23, 1065.

41. L. Maier, Helv. Chim. Acta, 1966, 49, 1000; 1249.

42. D.F. Steele and T.A. Stephenson, J.C.S. (Dalton), 1973, 2124.

43. M.C. Cornock, Ph.D. Thesis, Edinburgh, 1977.

44. W.B. Beaulieu, T.B. Ranchfuss and D.M. Roundhill, Inorg. Chem., 1975, 14, 1732.

45. J.A.S. Duncan, T.A. Stephenson, M.D. Walkinshaw, D. Hedden and D.M. Roundhill, Angew. Chem. Int. Edn. Engl., 1982, 21, 452.

46a I.W. Robertson, Ph.D. Thesis, Edinburgh, 1981.

46b R.C. Miller, C.D. Miller, W. Rogers, Jr. and L.A. Hamilton, J. Amer. Chem. Soc., 1957, 79, 424.

47. R.M. Golding, P.C. Healy, P.W.G. Newman, E. Sinn and A.H. White, Inorg. Chem., 1972, 11, 2435.

48. E.E. Reid, Organic Chemistry of Bivalent Sulphur, 1962, IV, 209.

49. R.P. Sperline, M.K. Dickson and D.M. Roundhill, J.C.S. Chem. Commun., 1977, 62.

50. E.G. Finer and R.K. Harris, Prog. in n.m.r. Spectroscopy, 1971, 6, 61.

51. T.G. Appleton, H.C. Clark and L.E. Manzer, Coord. Chem. Rev., 1973, 10, 335.

52. R.K. Harris and B.E. Mann, N.m.r. and the Periodic Table, Academic Press, 1978.

53. F.A. Bovey, N.m.r. Spectroscopy, Academic Press, 1969.

54. W.J. Stec, A. Okruszek, B. Uznanski and J. Michalski, Phosphorus, 1972, 2, 97.

55. W-H. Pan, J.P. Fackler and H.W. Chen, Inorg. Chem., 1981, 20, 856.

56. F.R. Hartley, The Chemistry of Platinum and Palladium, Appl. Science Publishers, 1973.

57. D. Coucouvanis, Prog. Inorg. Chem., 1970, 11, 233.

58. A.C.T. North, D.C. Phillips and F.S. Mathews, Acta Cryst., 1968, A24, 351.

59. P. Main, L. Lessinger, M.M. Woolfson, G. German and J.P. Declercq, MULTAN 1977, University of York, England and University of Louvain, Belgium.

60. G.M. Sheldrick, SHELX, 1976, Programs for Crystal Structure Determination, University of Cambridge, England.

61a C.M. Lukehart, G.P. Torrence and J.V. Zeile, J. Amer. Chem. Soc., 1975, 97, 1604.

61b C.M. Lukehart, G.P. Torrence and J.V. Zeile, Inorg. Chem., 1976, 15, 2393.

62. A. Schmidpeter, R. Bohm and H. Groeger, Angew. Chem. Int. Edn. Engl., 1964, 3, 704.

63. R.P. Sperline and D.M. Roundhill, Inorg. Syntheses, 1979, XIX, 98.

64. K.R. Dixon and A.D. Rattray, Inorg. Chem., 1977, 16, 209.

65. H. Werner and T.N. Khac, Angew Chem. Int. Edn. Engl., 1977, 16, 324.

66a N.J. Duck, Final Year Project Report, Edinburgh University, 1980.

66b P. Veitch, Unpublished work, 1982.

67. P. Veitch, Unpublished work, 1982.

68a A. Davison and E.S. Switkes, Inorg. Chem., 1971, 10, 837.

68b M.R. Churchill, J. Cooke, J.P. Fennessey and J. Wormald, ibid, 1971, 10, 1031.

68c A. Davison and D.L. Reger, ibid, 1971, 10, 1967.

69a M.C. Cornock and T.A. Stephenson, J.C.S. (Dalton), 1977, 683.

69b L.E. Manzer, ibid, 1974, 1535.

69c G. Carturan, L. Busetto, A. Palazzi and U. Belluco, J. Chem. Soc. (A), 1971, 219.

70. T.G. Appleton, M.C. Clark and L.E. Manzer, Coord. Chem. Revs., 1973, 10, 335.

71a W.J. Sime, Ph.D. Thesis, Edinburgh.

71b R.K. Harris and R.G. Hayter, Canad. J. Chem., 1964, 42, 2275.

72 J.F. Nixon and R.A. Head, J.C.S. (Dalton), 1978, 901; 909.

73a H.R. Gersmann and J.D. Swalen, J. Chem. Phys., 1962, 36, 3221.

73b C.H. Guzy, J.B. Raynor and M.C.R. Symons, J. Chem. Soc. (A) 1969, 2791.

74. M.R. Churchill and J. Wormald, Inorg. Chem., 1971, 10,1778.

75. F.A. Cotton and G. Wilkinson, Adv. Inorg. Chemistry, 3rd Edn., Interscience, 1972.

76. D.F. Evans, J. Chem. Soc., 1959, 2003.

77. A. Earnshaw, Introduction to Magnetochemistry, Academic Press, 1968.

78. G.M. Gray and C.S. Kraihanzel, J. Organometallic Chem., in press.

79a T.L. Charlton and R.G. Cavell, Inorg. Chem., 1967, 6, 2204.

79b L.F. Centofanti and R.W. Parry, ibid, 1968, 7, 1005.

79c L.F. Centofanti and R.W. Parry, ibid, 1970, 9, 744.

80a J. Grosse and R. Schmutzler, J.C.S. (Dalton), 1976, 405; 412.

80b J. Grosse, R. Schmutzler and W.S. Sheldrick, Acta Cryst. (B), 1974, 30, 1623.

80c S. Neumann, D. Schomburg and R. Schmutzler, J.C.S. Chem. Commun., 1979, 848.

81. C.B. Colburn, W.E. Hill and D.W.A. Sharp, Inorg. Nuc. Chem. Letts., 1972, 8, 625.

82. P.G. Page, Personal Communication.

83. N.T. McManus, Personal Communication.

84. J.D. Whitelock, Ph.D. Thesis, Edinburgh, 1980.

Postgraduate Courses

During the period October 1979 to October 1982 I attended the following postgraduate courses:

1. Synchrotron Radiation and its Applications
   Daresbury Group.
2. Homogeneous Catalysis
   Dr. T.A. Stephenson.
3. Inorganic Cluster Chemistry
   Dr. A.J. Welch.
4. Mass Spectroscopy
   Prof. J.H. Beynon.
5. Aspects of Industrial and Inorganic Chemistry
   ICI (Mond) Group.
6. Inorganic Research Seminars (2 years) and
   University of Strathclyde Inorganic
   Club (3 years).