SYNTHETIC, STRUCTURAL AND SPECTROSCOPIC STUDIES ON MONOTHIO- AND DITHIO-ACID TRANSITION METAL COMPLEXES

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To my mother and father

DECLARATION

Except where specific reference is made to other sources, the work presented in this thesis is the original work of the author. It has not been submitted, in whole or in part, for any other degree. Certain of the results have already been published.

ACKNOWLEDGEMENT

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Finally, I am indebted to Mrs. J. Gorrie for typing this manuscript.

Abstract

Chapter 1 A brief review of some relevant chemistry of platinum (II) and palladium (II) dithio- and dioxo-acid complexes is given. The preparation of $[\{M(SOCPh)_2\}_n]$ (M = Pd,Pt) complexes and the mode of bonding of the monothiobenzoate groups is then discussed. The reaction of these $[\{M(SOCPh)_2\}_n]$ complexes with Lewis bases are described and the products compared with those obtained from analogous reactions with $M(S\text{-}S)_2$ (M = Pd,Pt) and $[\{Pd(O_2CCH_3)_2\}_3]$ complexes.

Chapter 2 A short account of the reactions of $Ni(S\text{-}S)_2$ $[S\text{-}S = {}^{-}S_2CNR_2, {}^{-}S_2CR, {}^{-}S_2COR, {}^{-}S_2P(OR)_2$ and ${}^{-}S_2PR_2]$ complexes with nitrogen and phosphorous containing Lewis bases is given. The reactions of the corresponding $[\{Ni(SOCR)_2 0.5EtOH\}_2]$ (R = Me,Ph) compounds with various nitrogen and phosphorous donor bases to form green 6 coordinate octahedral complexes with bidentate monothiobenzoate groups and red 4 coordinate square planar complexes with sulphur bonded monodentate monothiobenzoate groups respectively are discussed. Some new reactions of $Ni(S\text{-}S)_2$ $[S\text{-}S = {}^{-}S_2PMe_2, {}^{-}S_2COEt]$ with tertiary phosphines are also described.

Chapter 3 The earlier reactions of $MCl_2(diene)$ (M = Pd,Pt) complexes with dithioacid and carboxylate anions are first outlined. Then, reactions of $PdCl_2(C_8H_{12})$ with Na[SOCPh] in a 1:1 molar ratio to form $[\{Pd(SOCPh)Cl\}_n]$ and in a 1 to excess molar ratio to form

$[\{Pd(SOCPh)_2\}_n]$ are described. The corresponding reactions of $PtCl_2(C_8H_{12})$ with Na[SOCPh] in a 1:2 molar ratio forms $Pt(SOCPh)_2(C_8H_{12})$ and in a 1:1 molar ratio forms initially $Pt(SOCPh)Cl(C_8H_{12})$. Reactions of these compounds with Lewis bases are then discussed. In addition the structure of $Pd(SOCPh)Cl(PMePh_2)_2$ which was solved by X-ray analysis is given.

Chapter 4 The synthesis and bonding of binuclear molybdenum carboxylate and dithiolate complexes is reviewed. The reaction of molybdenum (II) acetate with an excess of $K[S_2COEt]$ which leads to the formation of $Mo_2(S_2COEt)_4$ and a green solution is reinvestigated, and this green compound is shown to be an anion of empirical formula $[Mo_2(S_2COEt)_5]^-$. Further reactions of $Mo_2(S_2COR)_4$ (R = Me,Et,^{i}Pr) compounds with $K[S_2COR]$ (R = Me,Et,^{i}Pr); Na[SOCPh]; $Na[S_2CNR_2]$ (R = Me,Et) in stoichiometric amounts which all lead to the formation of anions, which are suggested by conductivity measurements to be tetramers, of the general formula $[\{Mo_2(S_2COR)_4(X\text{-}Y)\}_n]^{n-}$ [X-Y = S-S or S-O]. Finally the results of some polarographic and cyclic voltammetric studies on $Mo_2(O_2CR)_4$ (R = CH_3,CF_3), $Mo_2(S_2COEt)_4$ and $[Ph_3PhCH_2P]_n$ $[\{Mo_2(S_2COEt)_5\}_n]$ complexes are presented.

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CHAPTER 1

PREPARATION AND REACTIONS OF $[\{M(SOCPh)_2\}_n]$ (M = Pd,Pt)

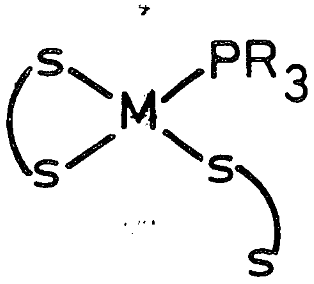
1.1 Introduction

Over the past ten to fifteen years there has been considerable interest shown in the reactions of palladium (II) and platinum (II) carboxylates and 1,1 dithiolates. During this period both of these areas have been studied extensively and the results obtained have shown that there is little similarity in either the structures or the reactions of these metal (II) dioxo and dithio compounds. In contrast very little work has been published on complexes containing the corresponding monothio ligands and therefore, this chapter is devoted to the preparation and properties of $[\{M(SOCPh)_2\}_n]$ (M = Pd,Pt) compounds and their reactions with unidentate and bidentate phosphorous and nitrogen donor Lewis bases. One important reason for these studies was to ascertain whether the mixed oxygen-sulphur systems were more like the dioxo or the dithio compounds in the structures they adopted and their overall reactivity. For this reason the first part of this chapter outlines some of the chemistry exhibited by palladium (II) and platinum (II) dithio and dioxo complexes.

1.2 Some relevant chemistry of platinum (II) and palladium (II) dithio and dioxo complexes

Although the reactions of $M(S-S)_2$ complexes have been studied extensively, very few of these unsubstituted compounds have had their structures determined fully by X-ray crystallography. However, the crystal structure of $Pd(S_2CNEt_2)_2$[1] has been reported and it is found to be isomorphous with the analogous platinum (II) compound.[2] Both of these compounds have been shown to contain a square planar MS_4 unit and the electronic spectra of these compare well with other platinum and palladium (II) 1,1 dithiolates, implying that they also contain the monomeric, square planar MS_4 chromophore. Further evidence for this comes from X-ray analysis of $Pd(S_2CO(C_6H_2Me_3))_2$ which reveals a monomeric square planar configuration.[3]

The reactions of $M(S-S)_2$ ($M = Pd,Pt$; $S-S = {}^{-}S_2PR_2$[4,5,6], ${}^{-}S_2CNR_2$[6,7], ${}^{-}S_2COR$[7], ${}^{-}S_2P(OEt)_2$[7], ${}^{-}S_2PF_2$[8]) with tertiary phosphines have been studied in considerable detail. In almost all cases the results obtained show that reaction occurs by stepwise cleavage of the M-S bonds to generate four coordinate adducts of type $M(S-S)_2PR_3$ (1) and $[M(S-S)(PR_3)_2](S-S)$ (2) respectively.



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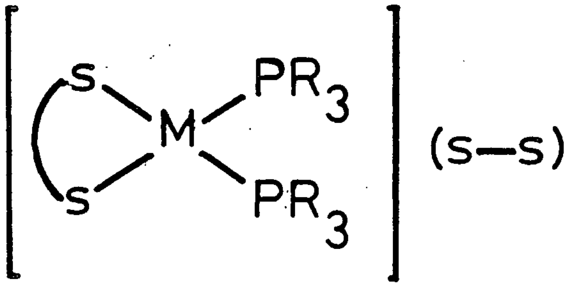
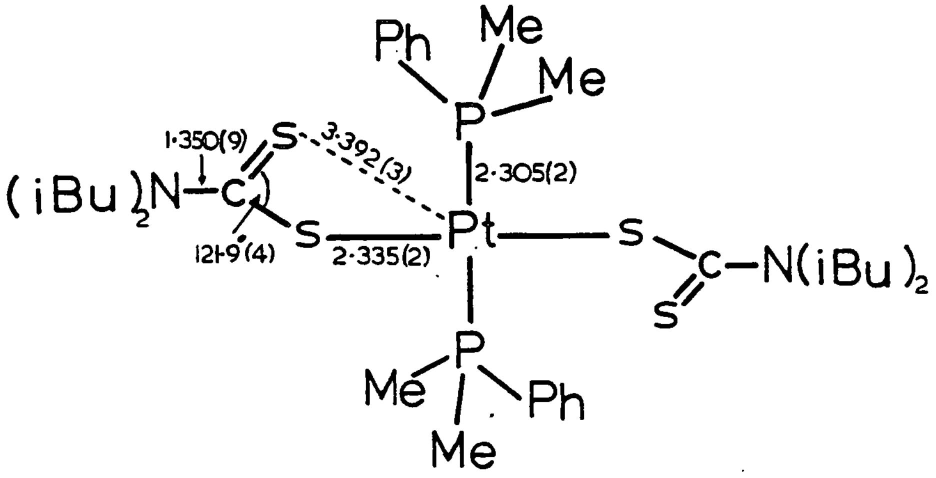


(2)

These structures were formulated on the basis of n.m.r. spectroscopy and conductivity data and in the solid state by X-ray structural analyses of $Pd(S_2PPh_2)_2PPh_3$[5], $Pd(S_2CNEt_2)_2PMePh_2$[7] and $[Pd(S_2PPh_2)(PEt_3)_2](S_2PPh_2)$[9]. In the case of the 1:2 dithiocarbamato metal (II) complexes however, there has been some recent controversy concerning the solid state structure (2) proposed. Fackler et al[10] stated that these compounds were not ionic in the solid state but were in fact neutral compounds with a trans configuration of ligands around the metal, whereas Stephenson and Alison[7] had proposed the ionic structure (2) as is found in the corresponding dithiophosphinate reactions. This latter formulation was supported by the ready synthesis of $[M(S_2CNR_2)(PR_3)_2]BPh_4$ by the addition of a methanolic solution of $NaBPh_4$ to the reaction mixture and by the positions of the C $\overline{\equiv}$ N stretching frequencies of the dithiocarbamate ligands in the i.r. spectra. Furthermore in these i.r. spectra additional bands corresponding to those found in $NaS_2CNEt_23H_2O$ but not in the spectra of compounds with only coordinated dithiocarbamate groups were observed.

However, Fackler et al[10] have reported a full X-ray structural analysis of $Pt(S_2CN(iBu)_2)_2(PMe_2Ph)_2$ (3) which shows this compound to indeed be a four coordinate neutral monomeric species with a trans configuration of unidentate ligands, (Fig. 1.1). In solution, however, even at low temperatures, complex (3) rapidly rearranged to an ionic species of structure (2).

Fig 1:1 $Pt(S_2CN(iBu)_2)_2(PMe_2Ph)_2$ showing selected bond distances and angles

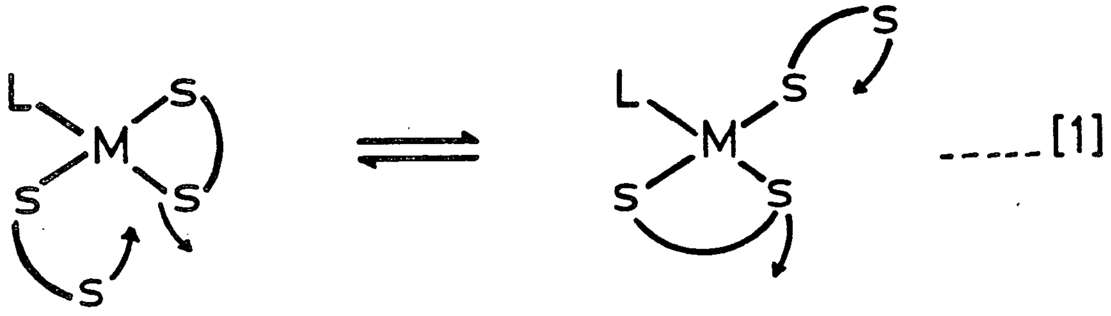


Further work in this area shows that compounds of both type (2) and (3) can be isolated depending on such variables as the solvent used, the nature and size of the tertiary phosphine, and the method of isolating the product.[11]

In the case of the 1:1 adducts (1) the ^1H n.m.r. spectra were found to be temperature dependent,[5-8] such that at ambient temperatures rapid exchange of unidentate and bidentate dithio ligands occurred to produce averaging of the protons attached to the dithio ligands. At lower temperatures however (for M=Pt) it was found that the rearrangement process was slow enough for the "frozen-out" n.m.r. spectrum to be observed in some instances.

A full n.m.r. line shape analysis was carried out on the complexes $Pt(S_2PMe_2)_2ER_3$ (ER_3=PPh_3, $PPh_2C_6F_5$, $AsPh_3$); $Pt(S_2CNEt_2)_2PPh_3$ and $Pt(S_2P(OEt)_2)_2PPh_3$ in order to obtain accurate energies, enthalpies and entropies of activation for these rearrangement processes. The close similarity found for the activation energies of the temperature-dependent reaction shown by these 1:1 adducts strongly suggested that a common mechanism to produce averaging of the protons on the dithioacid ligands existed. For $Pt(S_2PMe_2)_2PR_3$ (PR_3 = $PMePh_2$, PMe_2Ph) and all the palladium 1:1 adducts the rate of rearrangement was too rapid even at low temperatures to obtain kinetic parameters. However the rates of reaction were found to be both concentration and solvent independent indicating an intramolecular process with the absence of a solvent-assisted bound rupture step. Also the rate was found to be dependent on the tertiary phosphine present indicating that cleavage of the M-S bond <u>trans</u> to the phosphine is important in the rate determining step.

Fackler et al[12-14] had earlier interpreted this temperature dependence in terms of a metal centred rearrangement of a long lived five coordinate intermediate. However, more recent variable temperature $^{31}P-\{^1H\}$ n.m.r. studies on $Pt(S_2PPh_2)_2(PMe_2Ph)$[15] have shown unequivocally that the solid state structure (1) is maintained in solution at low temperature and that at higher temperatures, intramolecular scrambling of uni- and bidentate dithio groups occurs as shown in equation [1].



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In support of these conclusions, Fackler et al[16] have very recently examined the variable temperature $^{31}P-\{^1H\}$ n.m.r. spectra of the analogous $Pt(Se_2CN(iBu)_2)_2PEt_3$ complex and demonstrated that the lowest energy process producing n.m.r. equivalent diselenoacid ligands is also an intramolecular one. Furthermore at low temperatures, the spectrum is consistent with a structure containing bidentate and unidentant ligands, analogous to the solid state structures of the dithioacid complexes (1).[5,7]

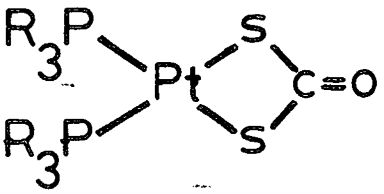
It has also been found[5-7] that all the ionic 1:2 complexes (2) readily revert to the 1:1 neutral species (1) when dissolved in non-polar solvents. Thus, the variable temperature ^1H n.m.r. spectra[7] of $[Pt(S_2CNEt_2)(PMePh_2)_2](S_2CNEt_2)$ shows that in solution the following equilibrium is established, (eqn [2])

$$[Pt(S_2CNEt_2)(PMePh_2)_2](S_2CNEt_2) \rightleftharpoons Pt(S_2CNEt_2)_2(PMePh_2) + PMePh_2 \quad ....[2]$$

At room temperature the equilibrium lies to the right hand side but on cooling, it shifts to the left and on further cooling the spectrum of the "frozen out" ionic species (2) is observed. Further support for these conclusions is obtained from the extensive variable temperature $^{13}C-\{^1H\}$ and $^{31}P-\{^1H\}$ n.m.r. studies on $Pt(S_2CN(iBu)_2)_2(PMe_2Ph)_2$[10]. As stated earlier this compound has been shown to be neutral and monomeric in the solid state but when dissolved in $CDCl_3$ or d^6-acetone, the complex converts to an ionic compound of type (2). On raising the temperature, partial conversion to the 1:1 complex (1) and free PMe_2Ph then occurs.

If however the reaction of $Pt(S_2CNEt_2)_2$ with excess PR_3 is carried out in CH_2Cl_2 rather than acetone, the complexes $[Pt(S_2CNEt_2)(PR_3)_2]Cl.H_2O$ and $CH_2(S_2CNEt_2)_2$ are isolated. The mechanism of formation of these species is shown to be <u>via</u> initial formation of $[Pt(S_2CNEt_2)(PR_3)_2](S_2CNEt_2)$ since dissolution of this compound in CH_2Cl_2 rapidly gives the same products.[7] In some of the reactions of $M(S_2PR_2)_2$ (M=Pd,Pt; R=Me,Ph) with excess PR_3 it was found that it was not possible to isolate the ionic species (2) because of facile rearrangement to the neutral complexes (1). In these cases, addition of a large anion to solutions of the ionic complexes trapped out the compounds $[M(S_2PR_2)(PR_3)_2]X$ (M=Pd,Pt; R=Me,Ph; $X=BPh_4^-, PF_6^-$).[6]

Although the reactions of $Pt(S_2COR)_2$ or $Pt(S_2P(OEt)_2)_2$ with stoichiometric amounts of PR_3 led to the formation of neutral 1:1 adducts (1), it was found that the reactions with excess PR_3 produced the unusual neutral complexes $Pt(S_2CO)(PR_3)_2$ (4) and $Pt(S_2PO\{OEt\})(PR_3)_2$ (5) respectively,[14] rather than the expected ionic products (2). The structure of (4) (for PR_3=PPh_3) has been confirmed by X-ray analysis.[10] However the reaction between $Pt(S_2COR)_2$ and excess PR_3 does



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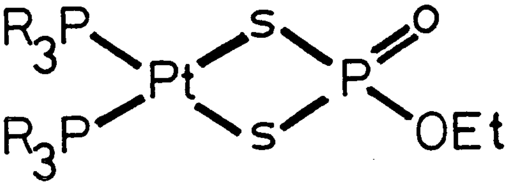
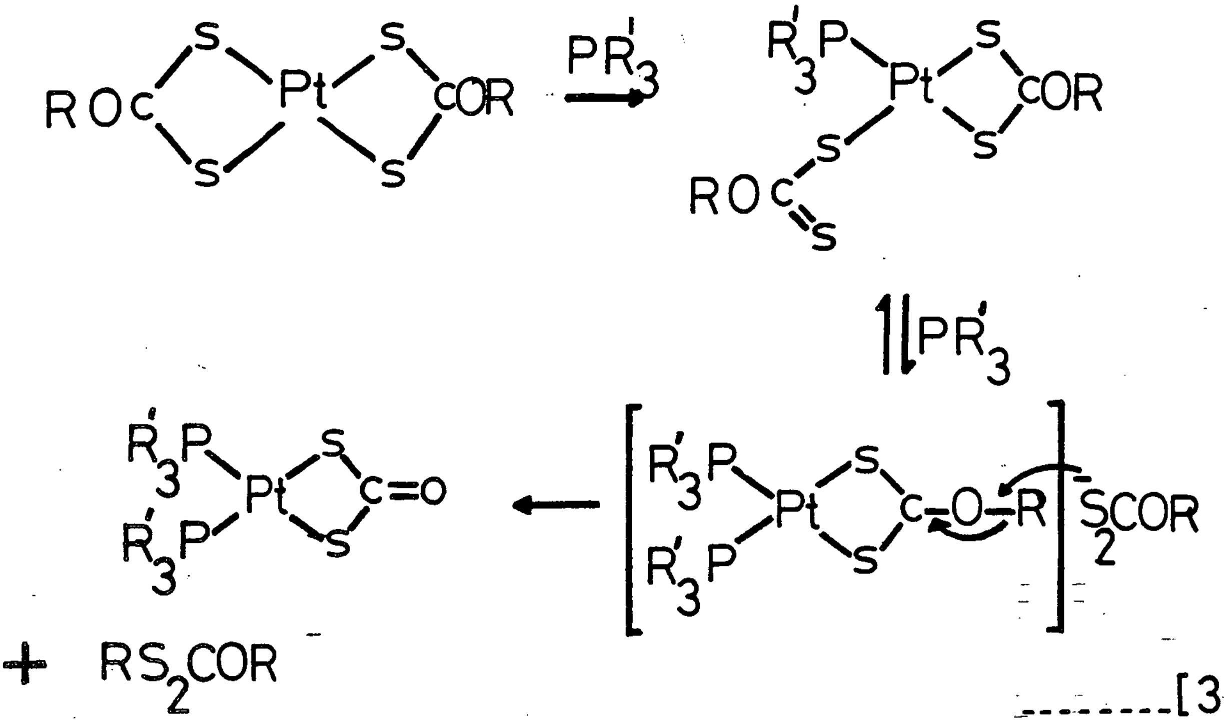


(5)

occur by stepwise cleavage of the M-S bonds to give the ionic 1:2 complex, but this is rapidly followed by nucleophilic attack of the xanthate ion on the alkoxy group of the coordinated xanthate to give the neutral dithiocarbonate complex (4) and a xanthate ester (see eqn [3]).

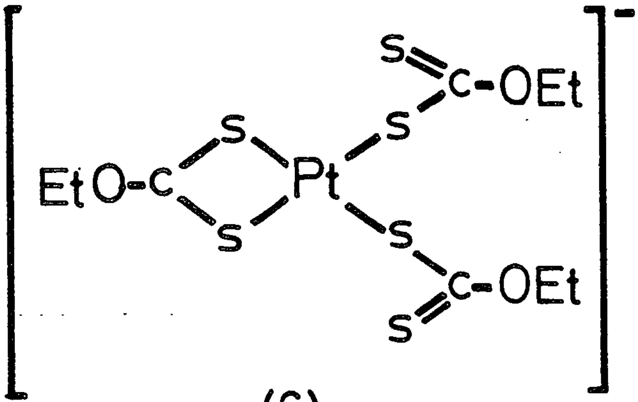
A similar mechanism for the formation of $Pt(S_2PO\{OEt\})(PR_3)_2$ can be written. Direct proof of this mechanism was obtained by trapping out the ionic intermediate by the addition of $NaBPh_4$ to an acetone/methanol solution of $Pt(S_2COR)_2$ and excess PR_3, within thirty seconds of mixing.[7]



[3]

The reaction of $Pt(S_2COEt)_2$ with an excess of $AsPh_4[S_2COEt]$ or with an excess of $K[S_2COEt]$ followed by the addition of $AsPh_4[Cl.HCl]$ was found to yield in both cases $[AsPh_4][Pt(S_2COEt)_3]$.[17,18] An X-ray analysis of this compound[18] has shown that unlike the corresponding $[NMe_3Ph][Ni(S_2COEt)_3]$ complex which was assigned a six coordinate octahedral structure,[19] the plainum remains four coordinate (6) with one bidentate and two unidentate xanthato groups. Both the mull and solution i.r. spectra and a comparison of the electronic spectrum with those of well established square planar platinum (II) complexes strongly suggest that the four coordinate structure is retained in solution. Also, the low temperature ^1H n.m.r. spectrum shows both bidentate and unidentate xanthato groups. A similar result was reported for the low temperature ^{19}F n.m.r. spectrum of $[NPr_4][Pd(S_2PF_2)_3]$[8]. At higher temperatures in both cases, the n.m.r. data showed that there was facile intramolecular unidentate/bidentate dithioacid ligand scrambling.

It was also discovered[17,18] that when $[AsPh_4][Pt(S_2COR)_3]$ ($R=Et$, ${}^{i}Pr$) were dissolved in CH_2Cl_2 or $CHCl_3$ that the compounds rearranged to $[AsPh_4][Pt(S_2CO)(S_2COR)]$ (7) <u>via</u> a similar mechanism to that shown in equation [3]. It was found that the corresponding reaction with $Pd(S_2COEt)_2$ gave $[AsPh_4][Pd(S_2CO)(S_2COEt)]$ as the major product and that only small amounts of the $[Pd(S_2COEt)_3]^-$ anion could be isolated. These observations indicated that the palladium complexes rearranged very readily to the dithiocarbonato species which is consistent with the expected lability of Pd-S compared to Pt-S bonds.



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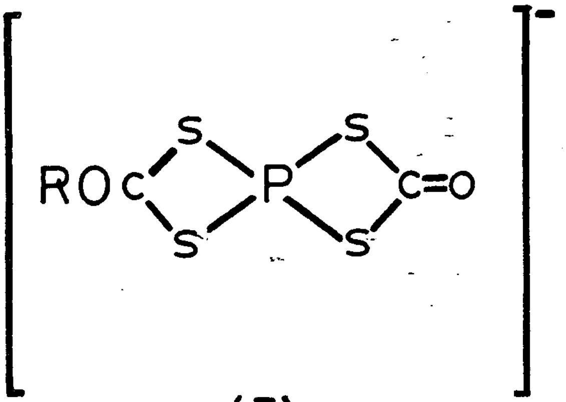
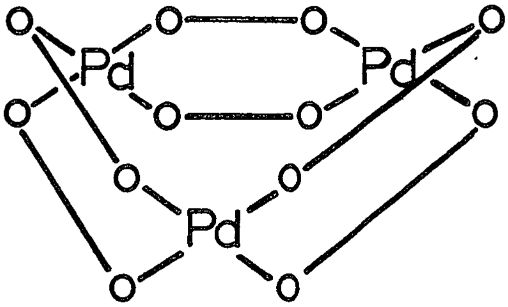


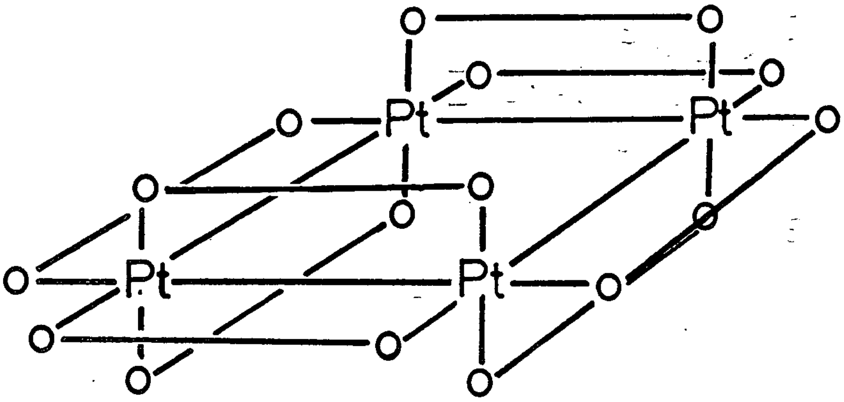
(7)

In contrast to the reactions of these 1:1 dithiolates, palladium (II) and platinum (II) carboxylates have been found to exhibit a quite different chemistry. Palladium (II) carboxylates $[\{Pd(OCOR)_2\}_n]$ ($R=Me,Et,Ph,CF_3,C_2F_5$) were first synthesised by Stephenson <u>et al</u>[20] and molecular weight measurements in benzene indicated that n=3 for R=Me,Et,Ph and n=1 for $R=CF_3,C_2F_5$.

A full structural analysis later showed $[\{Pd(O_2CMe)_2\}_3]^{21}$ (8) to indeed be a cyclic trimer of approximate D_3h symmetry in which each of the palladium atoms is joined to the other two by double acetate bridges. Recently however, $[\{Pt(O_2CMe)_2\}_n]$ has been shown to be a tetrameric square cluster complex (9) with short Pt-Pt bonds and octahedral coordination geometry, in which each side of a Pt-Pt bond is spanned by two acetate groups.



(8)

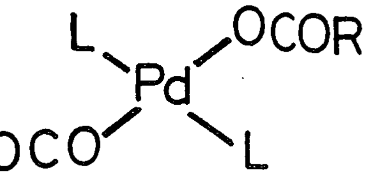


(9)

Most of the published work on the chemistry of these carboxylate compounds has been concerned with the palladium complexes, due partly to the difficulties and dangers,[23,24] in preparing pure samples of the platinum compounds (although a safe synthetic route[25] appears to have now been found) and to the uncertain composition of the adducts. For example, reaction of $[\{Pt(O_2CMe)_2\}_n]$ with Et_2NH is said to give a green material of formula $[Pt_3(O_2CMe)_6(Et_2NH)_4]$ (?).[20]

As described in the original paper,[20] the reaction of $[\{Pd(O_2CR)_2\}_n]$ with an excess of various Lewis bases L(> 1:4 molar ratio) gave products of general formulae $Pd(O_2CR)_2(L)_2$[20] (10) (L = PPh_3,$AsPh_3$,C_5H_5N, Et_3N, Et_2NH, Me_2SO <u>etc</u>.) whilst reaction with L (1:2 molar ratio for

R=Me) gave products of formulae $[\{Pd(O_2CMe)_2(L)\}_2]$[26] (11) ($L=PPh_3, AsPh_3$).



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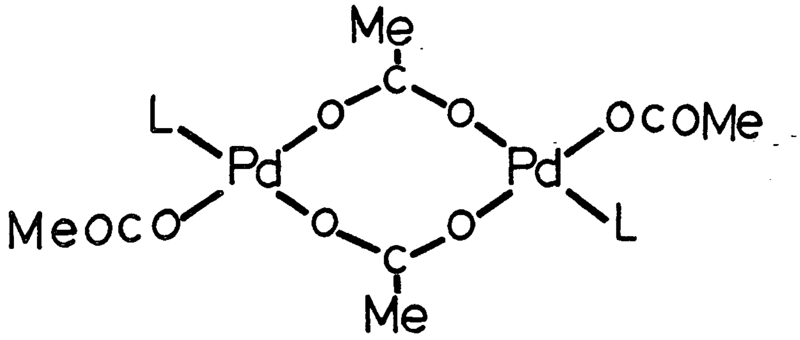

(11)

The trans configuration (10) was assigned on the basis of a dipole moment determination for the Et_2NH compound, and detailed infrared spectral studies.[20] Structure (11) was based on the observation of bands corresponding to both unidentate and bridging carboxylate stretching frequencies in the i.r. spectra of these dimeric compounds. A further study[11] of the reaction of $[\{Pd(O_2CMe)_2\}_3]$ with excess PMe_2Ph in benzene has recently been made and the product obtained was formulated on the basis of i.r., ^1H n.m.r. spectroscopy and elemental analysis as $Pd(O_2CMe)_2(PMe_2Ph)_2$. However the ^1H n.mr. spectra of this compound showed a "Pseudo-doublet"[≠] pattern for the phosphine methyl resonance indicative of the cis configuration (12). Therefore, although the dipole moment of the diethylamine complex

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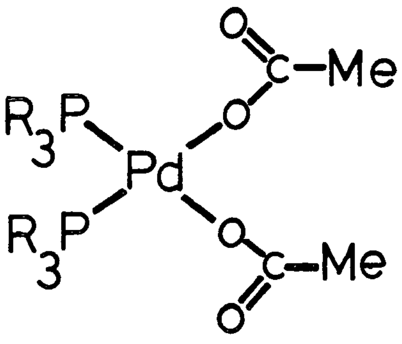
[≠] A "Pseudo-doublet" is a sharp doublet with additional signal intensity situated between the doublet. This spectral pattern is indicative of a small but non-zero J(PP) value when compared to $|J(PH) + J(PH)^1|$.



(12)

suggested a trans configuration (10) it now seems clear that the isomer formed depends critically on the nature of L. Thus with high trans effect influence ligands such as PMe_2Ph and $PMePh_2$, the cis configuration (12) is apparently favoured.* In the earlier paper[20] it was stated that molecular weight determinations of the triphenylphosphine adducts (10 or 12) were impossible due to their ready dissociation and decomposition in warm solvents. However, a more recent study[11] of $Pd(O_2CMe)_2(PPh_3)_2$ shows that it rearranges readily to $[\{Pd(O_2CMe)_2(PPh_3)\}_2]$ when left in benzene for 12 hours, whereas the $Pd(O_2CMe)_2(PR_3)_2$ (PR_3 = $PMePh_2$,PMe_2Ph) complexes were recovered unchanged from benzene solution. A mechanism for this rearrangement to the carboxylate bridged dimer (11) via facile dissociation of a triphenylphosphine ligand has been suggested (equation [4]).

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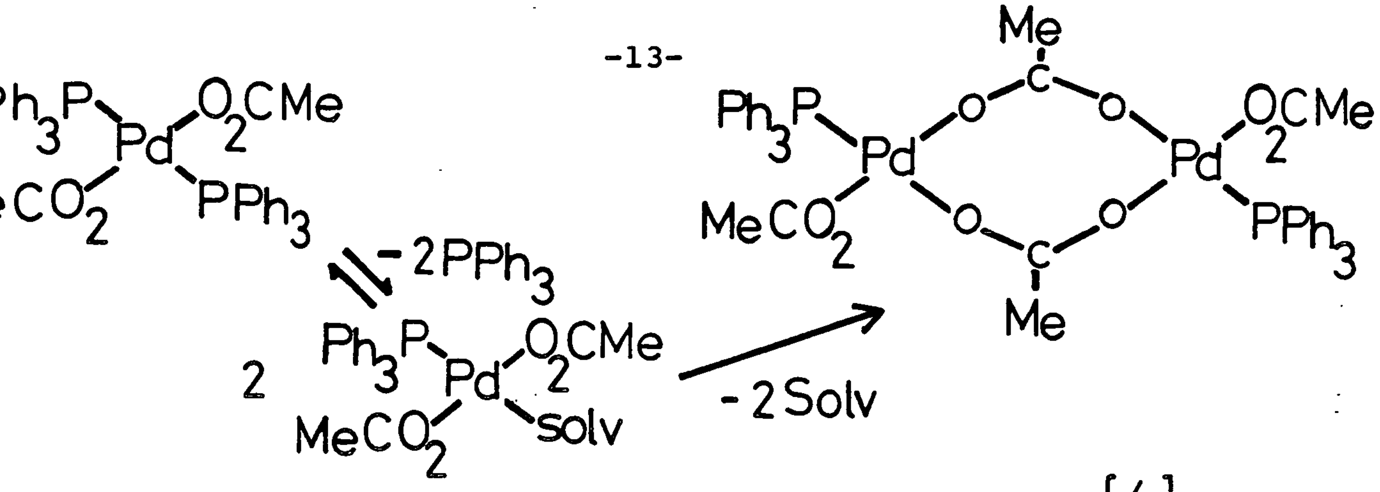
*For $Pt(O_2CCF_3)_2(PMe_2Ph)_2$, however, made by reaction of $PtCl_2(PMe_2Ph)_2$ with $Ag[O_2CCF_3]$ the ^1H n.m.r. spectrum showed a "virtually coupled" triplet pattern indicating a trans structure. Hence factors determining the preferred isomer are not so straightforward.



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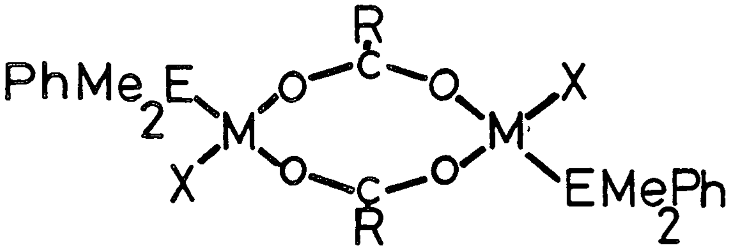
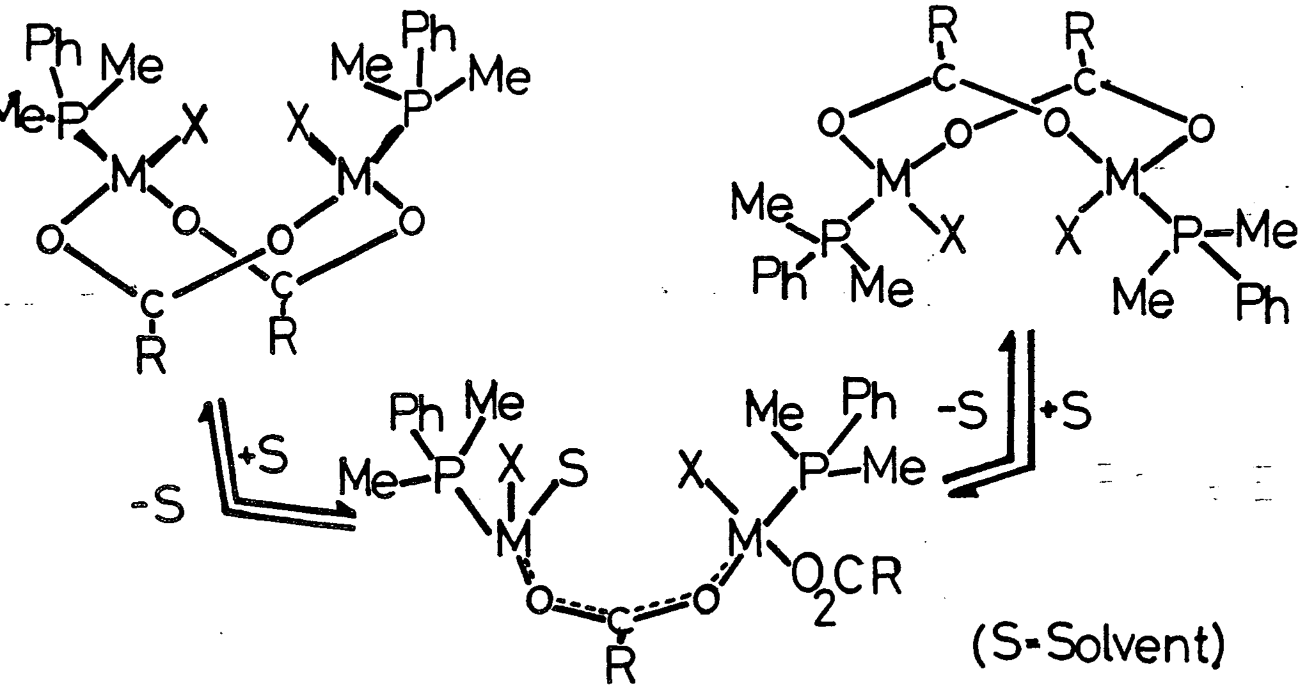


(13)

This reluctance to lose a PR_3 group in the case of the other two compounds can be correlated with the higher basicity and smaller size of these alkyl- substituted phosphines compared with PPh_3. Similar carboxylate bridged dimers (13) can also be prepared by the reaction of $[\{MX_2(EMe_2Ph)\}_2]$ with $Ag[O_2CR]$ (1:2 molar ratio)[27] ($X=Cl^-, Br^-, I^-$; $M=Pd, Pt$; $E=P, As$; $R=CH_3, CH_2Cl, CH_2Br, CF_3, CCl_3, CMe_3, CPh_3$). Interestingly the ^1H n.m.r. spectra of $[\{Pd(O_2CR)X(PMe_2Ph)\}_2]$[27] showed that the methyl groups of the teriary phosphine were magnetically equivalent at ambient temperature although the expected inequivalence was observed at lower temperatures. The same workers also studied variable temperature ^1H n.m.r. spectra of $[\{Pd(PR_3)(O_2CR)_2\}_2]$ (11) and $[\{Pd(PMe_2Ph)(O_2CR)(O_2CR')\}_2]$[28] and again found magnetic equivalence of the methyl groups on the PMe_2Ph ligands at ambient temperature. The solvent assisted ring opening process shown in Fig. 1:2 was proposed to explain these observations.

Fig. 1:2 Proposed scrambling process in $[\{M(O_2CMe)X(PMe_2Ph)\}_2]$ $(M = Pd,Pt; X = halide, {}^-O_2CR)$



Finally, since many palladium (II)acetate catalysed reactions have been carried out in acetic acid, Pandez and Henry[29] have made a detailed study of this system in the presence and absence of free acetate ion. They have confirmed that in the absence of acetate ion $[\{Pd(O_2CMe)_2\}_n]$ exists as a trimer but on addition of acetate ion, this breaks down to a dimer and at very high concentrations a monomer.

As stated in the introduction, very little work on the corresponding monothioacid complexes of palladium (II) and platinum (II) has been published and, any relevant work will be included in the next section in which my own work, on $[\{M(OSCPh)_2\}_n]$ compounds is presented. A full discussion of monothioacid complexes in general can be found in the Ph.D. thesis of Miss M.A. Thomson.[30]

1.3 Results and Discussion

1.3.1 Preparation of $[\{M(SOCPh)_2\}_n]$ complexes

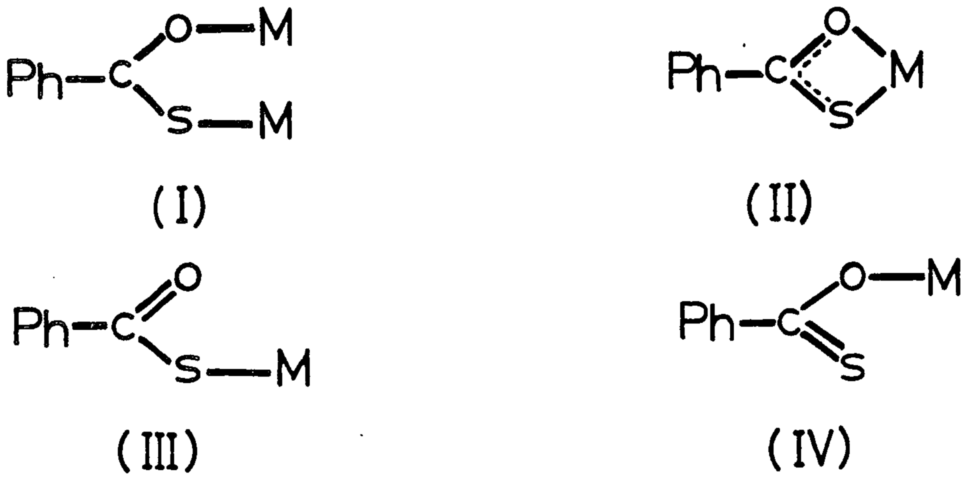
Dropwise addition of monothiobenzoic acid to a benzene solution of palladium (II) acetate gave an immediate red-brown precipitate of $[\{Pd(SOCPh)_2\}_n]$; a higher yield could be obtained by further treatment of the filtrate with light petroleum (b.p. 60-80°C). The same compound could also be readily prepared by reacting an aqueous solution of $Na_2[PdCl_4]$ with an aqueous solution of excess Na[SOCPh].

The analogous platinum complex was more difficult to make and was always obtained in low yield. However the best method of preparation was by prolonged shaking at room temperature for 3 to 5 days of a mixture of $Na_2[PtCl_4]$ and an excess of Na[SOCPh] in ethanol, and then filtering off the insoluble products.

Although the platinum species was not sufficiently soluble for molecular-weight studies, osmometric molecular-weight measurements on the palladium complex in chloroform over a range of concentrations (1.0-4.0 g dm^{-3}) produced concentration dependent molecular-weights varying from 1100 to 1700 respectively. These values suggest that at lowest concentration the palladium complex exists as a trimer (found 1125; expected 1140 for a trimer) but as the concentration is increased molecular association takes place to form at least a tetramer. Similar concentration-dependent association phenomena have been observed for various metal thiophosphinato- and selenophosphinato complexes in benzene or chloroform and this has been ascribed to differing amounts of ligand bridge formation.[31] Also, since X-ray structural analyses have shown that both $[\{Pd(O_2CMe)_2\}_3]$[21] and $[\{Pd(S_2CPh)_2\}_3]$[32] are trimeric in the solid state (although of quite different molecular structure)* and molecular-weight studies in solution of $[\{Pd(O_2CMe)_2\}_3]$ indicate a trimer,[20] it seems reasonable to expect that $[\{Pd(SOCPh)_2\}_n]$ would also possess at least a trimeric structure in the solid state. A dipole moment measurement of the palladium complex in benzene showed the molecule to have no dipole.

As previously discussed by Savant et al.[34] the best method for establishing the mode of bonding of the monothiobenzoate group is i.r. spectroscopy. They have shown that for the monothiobenzoate anion coordination to a metal can occur in four different ways (Figure 1.3).

Fig. 1.3 Different possible modes of bonding of monothiobenzoate ligands to metal ions



(I) (II)

(III) (IV)

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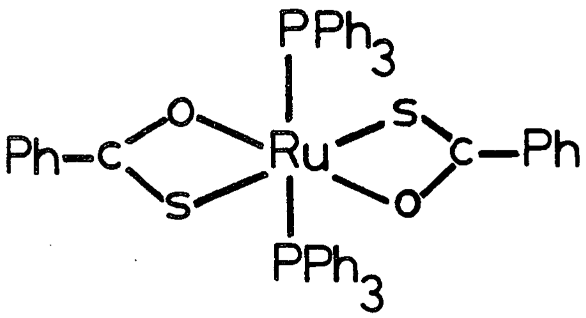
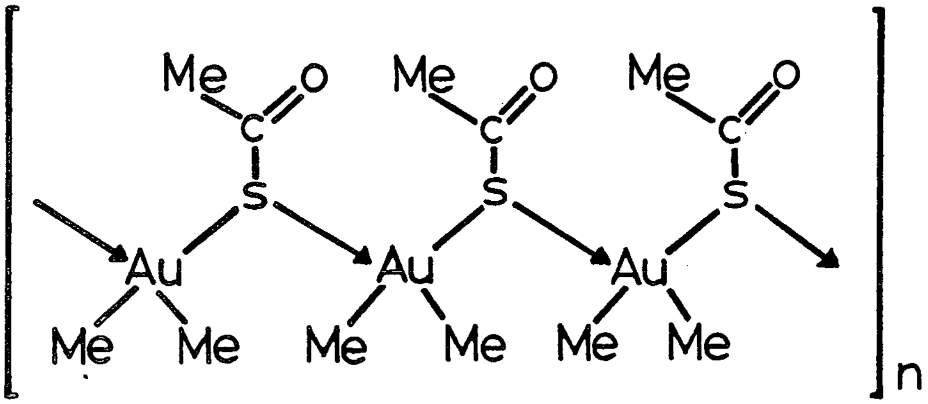
*Palladium (II) dithiobenzoate has a stacked trimeric structure in the solid state but osmometric molecular-weight measurements in benzene[33] reveal a monomeric structure in solution, whereas palladium (II) acetate has a cyclic trimeric structure which osmometric molecular-weight studies[20] in benzene at 37°C indicate

For the ionic Na[SOCPh] salt, ν(CO) occurs at 1500 cm^{-1} and ν(CS) at 960 cm^{-1}. Furthermore, when the monothiobenzoate group acts as a bidentate ligand, (Type II), and the bonding in the M-O and M-S linkages is more or less symmetrical, then ν(CO) and ν(CS) are expected to remain almost unaffected e.g. for $Ru(SOCPh)_2(PPh_3)_2$ (14), ν(CO) occurs at 1500 cm^{-1} and ν(CS) at 965 cm^{-1}.[35] However, as the interaction with the metal through sulphur increases and that through oxygen decreases (Type III) it is expected that ν(CO) will increase and ν(CS) will decrease in energy; e.g. for $Zn(SOCPh)_2$ ν(CO), 1545 cm^{-1}; ν(CS) 955 and 928 cm^{-1} and for $Cd(SOCPh)_2$, ν(CO) and ν(CS) occur at 1590 and 930 cm^{-1} respectively.

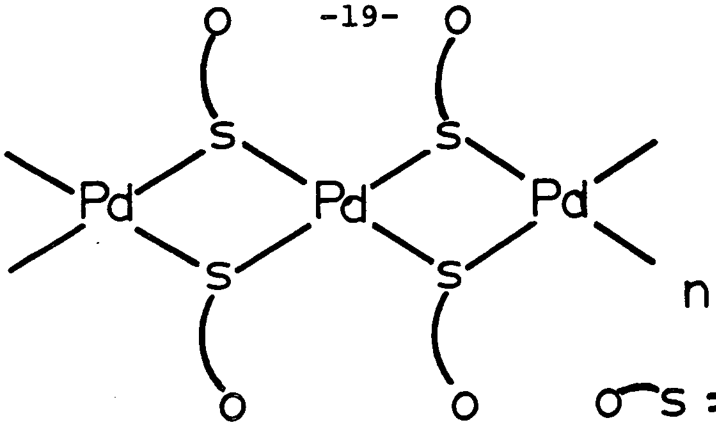


(14)

If however the asymmetry lies in the opposite direction with a stronger M-O and a weaker M-S bond (Type IV) then there is a lowering in energy of ν(CS) and a corresponding increase in energy of ν(CO). This type of bonding is found for Cr(SOCPh) where ν(CO) is lowered to 1465 cm^{-1} while ν(CS) is raised to 982 cm^{-1}. For $[\{Pd(SOCPh)_2\}_n]$ strong bands are observed at 1670 and 875 cm^{-1} suggesting a strong Pd-S bond and at best a very weak Pd-O interaction. For monothiobenzoic acid, ν(CO) occurs at 1690 cm^{-1} but the absence of a band at 2560 cm^{-1} (ν(S-H)) shows that no free monothiobenzoic acid is present here. The i.r. spectrum of $[\{Pd(SOCPh)_2\}_n]$ is very similar to that of $[\{Hg(SOCPh)_2\}_n]$ where ν(CO) is observed at 1630 cm^{-1} and ν(CS) at 912 cm^{-1} and it has been suggested that this is a sulphur bridged polymer.[34] Likewise for the complex $[\{AuMe_2(SOCMe)\}_n]$ (ν(CO) 1710, 1700 cm^{-1}) a sulphur bridged polymeric structure (15) has been proposed.[36] The highly insoluble, red brown $[\{Pd(SOCNR_2)_2\}_n]$ have also been suggested to have a sulphur bridged polymeric structure.[37] Therefore, it would seem very reasonable to suggest that in the solid state $[\{Pd(SOCPh)_2\}_n]$ had a sulphur bridged polymeric structure (16) with very little coordination to the palladium atoms from the oxygens of the monothiobenzoato ligands. This proposed structure would also be consistent with the zero dipole moment. However, without X-ray structural analyses this must remain a matter of conjecture, and unfortunately all attempts to grow single crystals have failed.



(15)



(16)

O⌒S = ⁻SOCPh

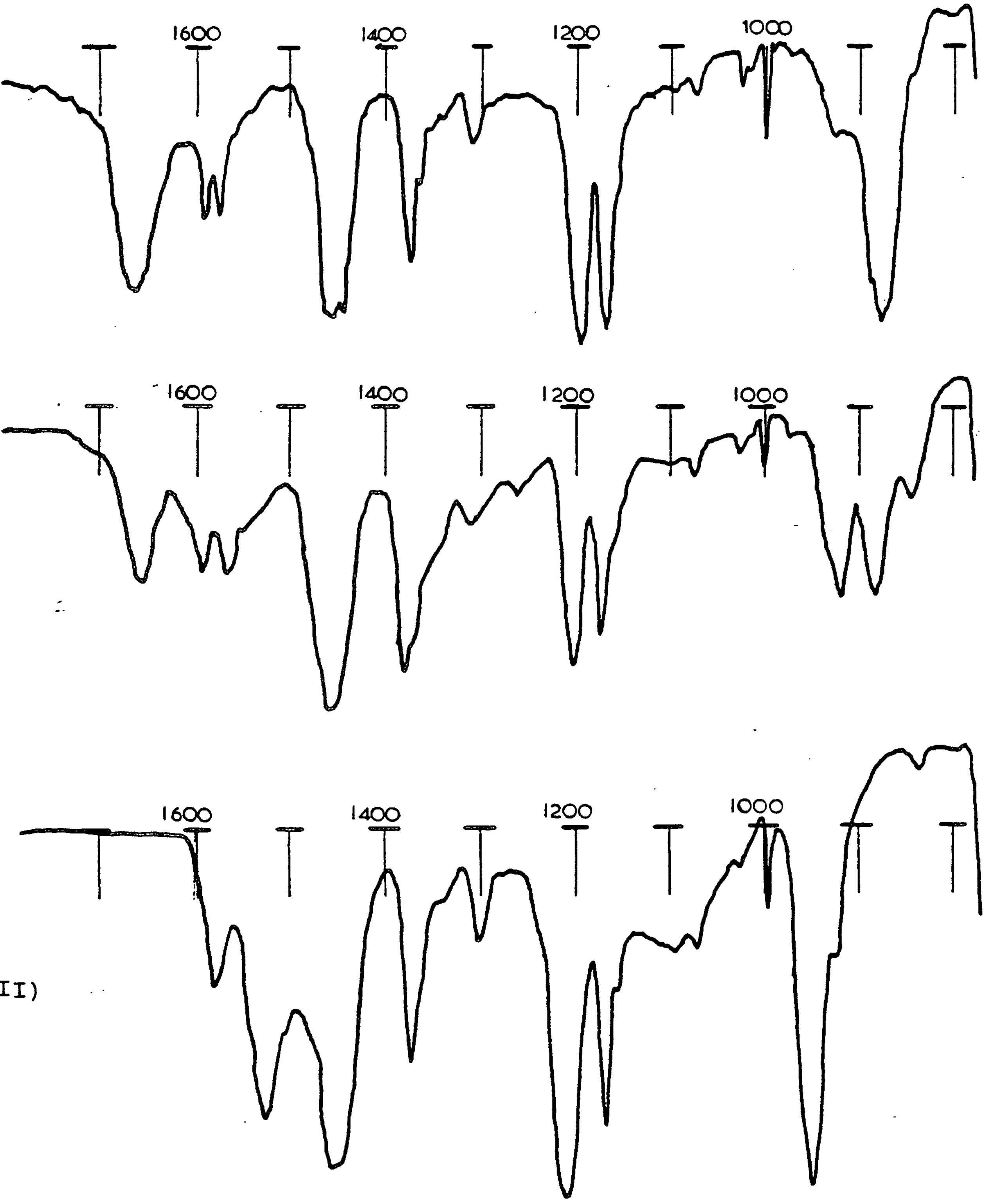
For [{Pt(SOCPh)$_2$}$_n$], prepared from Na$_2$[PtCl$_4$] and Na[SOCPh] in ethanol the i.r. spectrum showed strong bands at 1660 and 880 cm^{-1} but in addition there was a second set of strong peaks at 1595, 1575 and 920 cm^{-1} which could also be assigned to ν(CO) and ν(CS) vibrations respectively. This second set of bands again suggests strong Pt-S and weak Pt-O interactions and their presence can be explained in one of two ways. First these extra bands might signify that the overall structure of [{Pt(SOCPh)$_2$}$_n$] is different from that of [{Pd(SOCPh)$_2$}$_n$]. This is a very reasonable conclusion since both platinum (II) acetate[22] and the platinum (II) aryldithiocarboxylates[38] have been shown by X-ray analysis to have different molecular structures from the corresponding palladium complexes. Thus platinum (II) acetate has the tetrameric structure (9) whereas platinum (II) p-isopropyldithiobenzoate has a dimeric structure with strong metal-metal bonds. The i.r. spectrum of [{Pt(S$_2$CPh)$_2$}$_2$] indicates that it has a similar dimeric structure. The other possibility is that the product obtained consists of several rather insoluble complexes of stoichiometry [{Pt(SOCPh)$_2$}$_n$] one of which has the same structure as [{Pd(SOCPh)$_2$}$_n$].

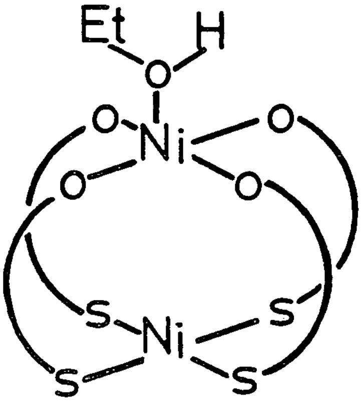
Further work has shown that the latter suggestion is more likely and that the reaction products here are very sensitive to both the reaction conditions and work-up procedure. Thus, work-up of the filtrate from the $Na_2[PtCl_4]$/Na[SOCPh] reaction in ethanol gave a yellow solid which analysed quite closely for $[\{Pt(SOCPh)_2(HOEt)\}_n]$ and whose i.r. spectrum showed strong peaks at 1590, 1570, and 920 cm^{-1} but only weak peaks at 1660 and 880 cm^{-1}. Additional peaks occurred at 1530 and 950 cm^{-1}. Reaction of $Na_2[PtCl_4]$ and Na[SOCPh] in aqueous solution also produced several products (see Experimental Section and Fig. 1:4), one of which contained strong bands in its i.r. spectrum at 1530 and 950 cm^{-1} and weak peaks at 1590, 1570, and 920 cm^{-1}. Furthermore, in a closely related study, it has recently been shown that reaction of $K_2[PdCl_4]$ with $MeCS_2H$ produced several structural variations of $[\{Pd(S_2CMe)_2\}_n]$ which exhibit different multiplicities of ligand vibrations in their i.r. spectra.[39,39a] Also, tests for chloride on all of the platinum species isolated proved negative indicating that no mixed anion complexes were being formed as is found in the reactions of niobium, tantalum and protactinium chlorides and bromides with $Na[S_2CNEt_2]$.[40]

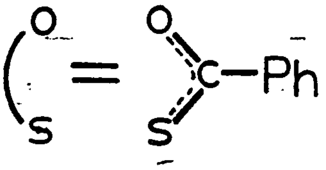
Without X-ray structural analyses further speculation on these various complexes is unwarranted, although by analogy with $[Ni(SOCPh)_2\ _2]EtOH$ (17) (ν(CO) at 1508; ν(CS) at 958 cm^{-1})[41,42] the platinum complex exhibiting i.r. bands at 1530 and 950 cm^{-1} may also have a dimeric structure with bridging $[SOCPh]^-$ groups.

Fig. 1.4

I.R. spectra of (I) $[\{Pd(SOCPh)_2\}_n]$ (II) and (III) $[\{Pt(SOCPh)_2\}_n]$







(17)

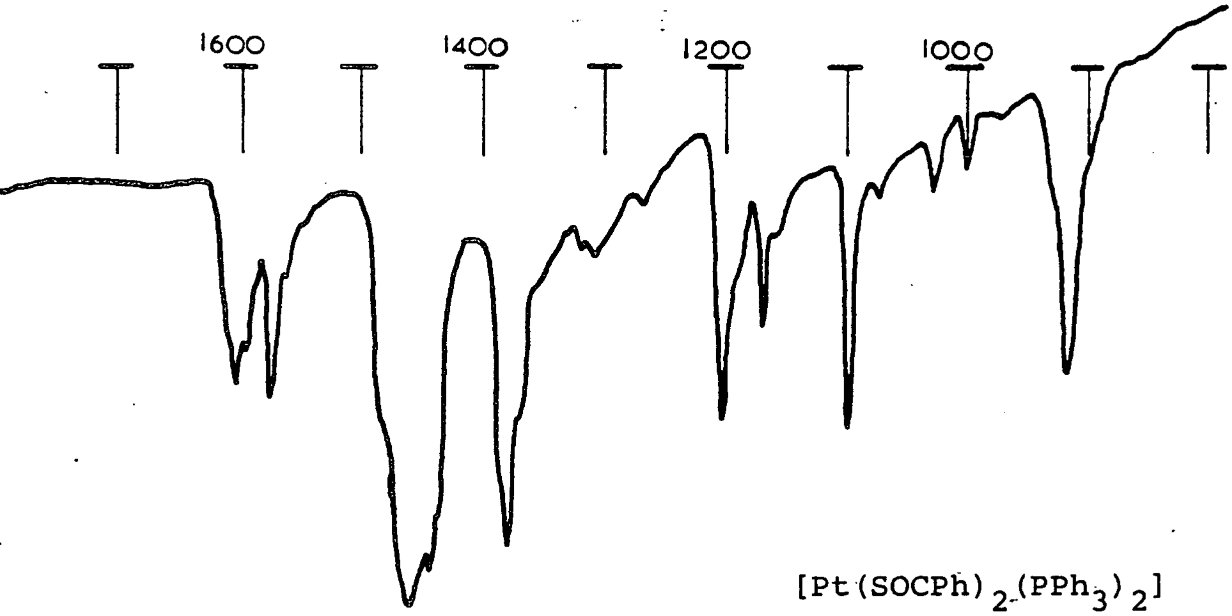
In fact Oro et al.[43] reported that reaction of $PdCl_2$ with $Na[SOCPh]$ in water gave $[\{Pd(SOCPh)_2\}_2]$ (ν(CO) = 1530 cm^{-1}) which was dimeric in benzene. In our hands, however, reaction of $Na_2[PdCl_4]$ and $Na[SOCPh]$ in water gave a material with strong peaks in its i.r. spectrum at 1660 and 880 cm^{-1} plus very weak peaks at 1590 and 920 cm^{-1}.

1.3.2 Reaction of $[\{M(SOCPh)_2\}_n]$ compounds with Lewis bases

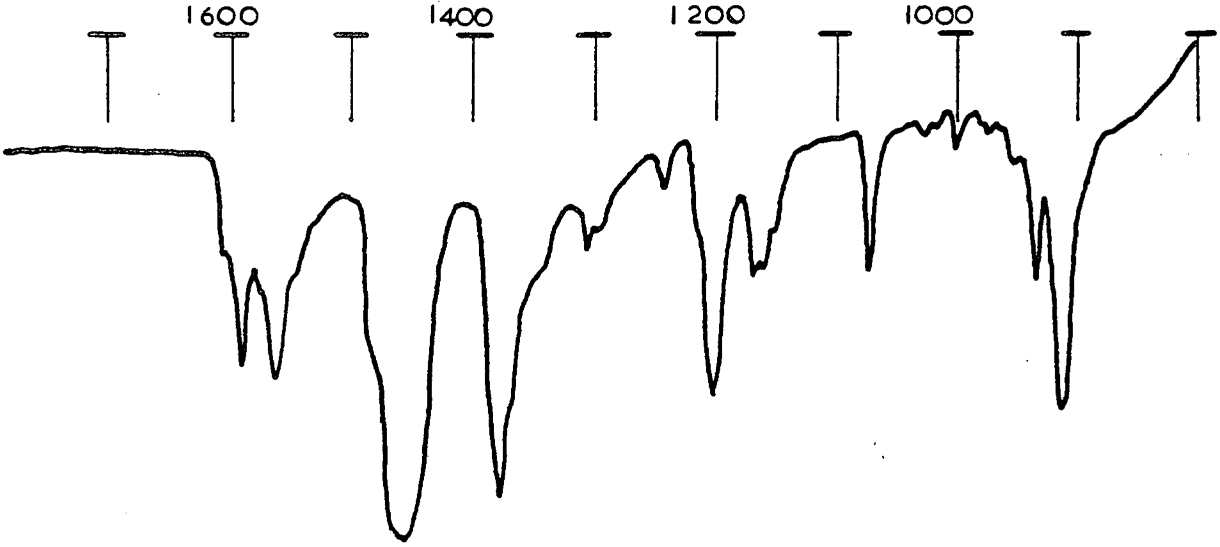
Although complete characterisation of the $[\{M(SOCPh)_2\}_n]$ (M=Pd,Pt) compounds was not possible, all these materials reacted with an excess of a variety of Lewis bases (L) to give monomeric, non-conducting compounds of stoichiometry $M(SOCPh)_2L_2$ (M=Pd,Pt; L=PPh_3,$PMePh_2$, PMe_2Ph, $AsPh_3$, $SbPh_3$ or C_5H_5N). These 1:2 adducts were all yellow to pale brown in colour and were characterised by analytical, i.r., electronic and n.m.r. spectral evidence. The i.r. spectra of all the compounds showed ν(CO) bands between 1550 and 1600 cm^{-1}, and ν(CS) bands between 900 and 940 cm^{-1} (see examples in Fig. 1.5). These band positions were again indicative of strong M-S and weak M-O interactions, e.g.

Fig. 1.5

I.R. spectra of $M(SOCPh)_2L_2$



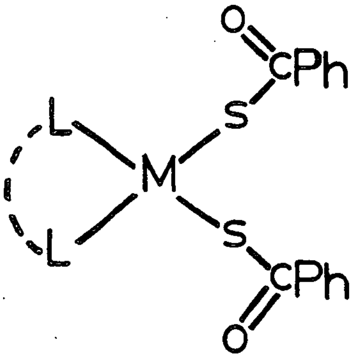
$[Pt(SOCPh)_2(PPh_3)_2]$



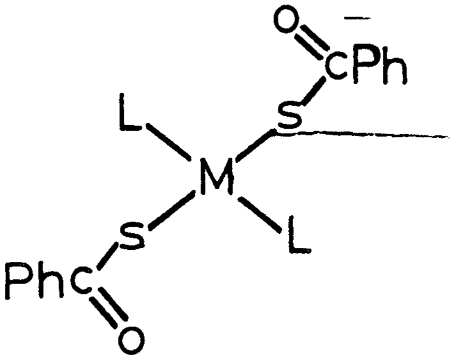
$[Pd(SOCPh)_2\ (C_5H_5N)_2]$

$Ru(CO)_2(PMe_2Ph)_2(SOCPh)_2$ has ν(CO) of the monothiobenzoato groups at 1600 and 1570 cm^{-1} and ν(CS) at 945 cm^{-1} and has been shown to have only S-bonded monothiobenzoate groups.[35] However it should be noted that Oro et al[43] have previously reported the synthesis of $Pd(SOCPh)_2(C_5H_5N)_2$ which had ν(CO) at 1700 cm^{-1} but this band was not found in the i.r. spectrum of the sample prepared in the work described here.

Molecular-weights of $Pd(SOCPh)_2L_2$ ($L=AsPh_3, SbPh_3$) were found by vapour pressure osmometry and these showed the compounds to be monomers. Furthermore, the electronic spectra of all the compounds were similar to those of other well established square-planar palladium (II) and platinum (II) complexes, and together with the i.r. evidence suggests structures (18) and/or (19).



(18)

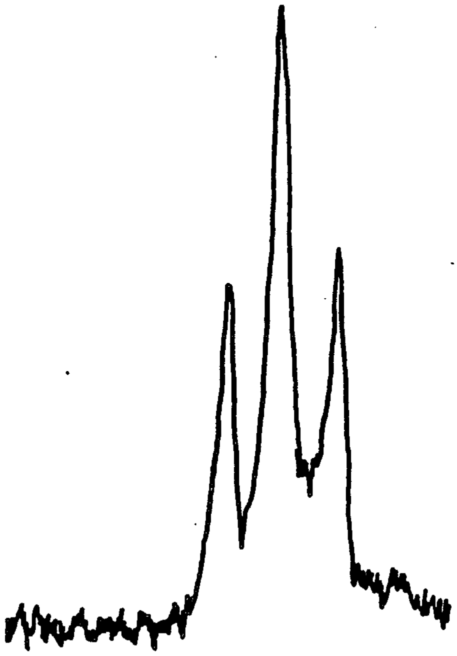


(19)

The $^{31}P-\{^1H\}$ n.m.r. spectra showed only a singlet for the palladium compounds and a 1:4:1 triplet for the platinum compounds indicating that in all cases only one isomer was present in solution. The ^1H n.m.r. spectra however showed "a virtually coupled" triplet pattern for the methyl resonances of the phosphines in the $M(SOCPh)_2(PR_3)_2$ ($M=Pd,Pt$; $PR_3=PMePh_2$,

Fig. 1.6

^{1}H n.m.r. spectra (Me region) of $[Pd(SOCPh)_2(P)_2]$



$[Pd(SOCPh)_2(PMePh_2)_2]$

$[Pd(SOCPh)_2(PMe_2Ph)_2]$

PMe_2Ph) complexes (Fig. 1.6) which is indicative of the trans[44] structure (19). The same trans configuration has been found by ^1H n.m.r. spectroscopy for the corresponding monothiocarbamato compound $Pd(pyrm)_2(PMe_2Ph)_2$ (pyrm = pyrrolidin-1-ylmonothiocarbamate).[45]

Recently a full X-ray structural analysis of $Pd(SOCPh)_2(PMe_2Ph)_2$ was completed and this confirmed the trans structure (19) (Fig. 1.7). As can be seen in Fig. 1.7 the palladium atom is in a four coordinate square planar configuration, bound to the monothiobenzoato groups through the sulphurs only, with the oxygen atoms sitting approximately above and below the palladium in effectively the fifth and sixth positions. However, the Pd-O distances of 3.313(3)Å show that these are too long for any form of bonding. This Pd-O distance is comparable with the non-bonded Pd-S distance of ca. 3.5Å[5] in $Pd(S_2PPh_2)_2(PPh_3)$ (1). In $Pd(SOCPh)_2(PMe_2Ph)_2$ the molecule is situated with the palladium on a centre of symmetry and therefore the Pd,S and P atoms are all coplanar with S-Pd-P angles of 90° (see Table 1.1).

As can be seen from the i.r. data, $\nu(CO)$ values for the 1:2 adducts are lower than those for the parent $[\{M(SOCPh)_2\}_n]$ compounds (see Table 1.2) implying there is a stronger M-O interaction in the 1:2 adducts. However any Pd-O bonding has been ruled out by the X-ray structure of $Pd(SOCPh)_2(PMe_2Ph)_2$ ($\nu(CO)$ at 1595 and 1575 cm^{-1}).

It would therefore appear that in the polymeric $[\{M(SOCPh)_2\}_n]$ compounds where there are very strong M-S bonds from the sulphur bridges adduct formation results in a general weakening of the M-S bonds and consequently some

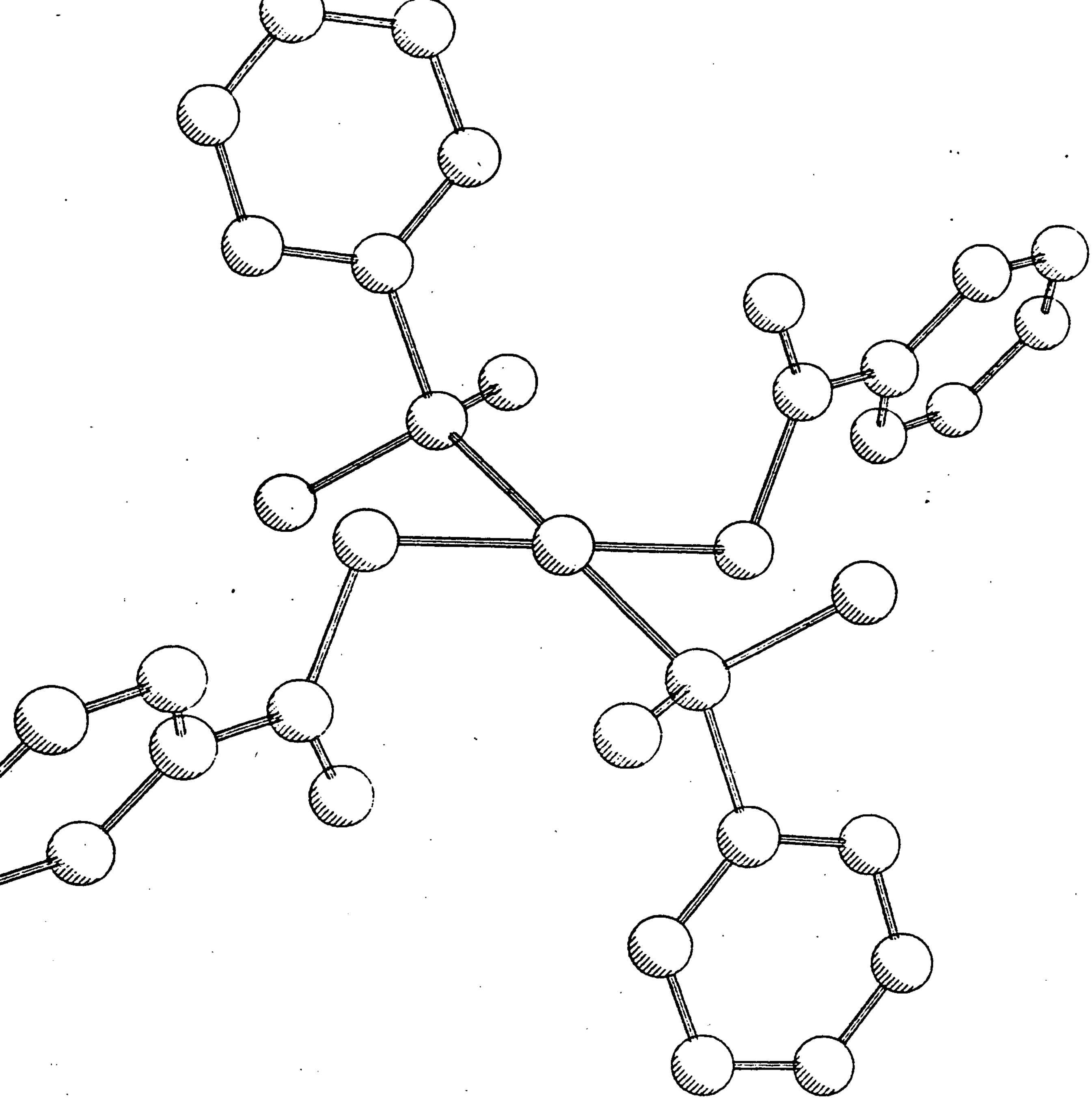


Fig. 1.7 Crystal Structure of

$[Pd(SOCPh)_2(PMe_2Ph)_2]$

electron density is delocalised into the C=O bond making it stronger and so moving it to lower frequency. Further support for this comes from the ν(CS) values which lie in the range 900-940 cm^{-1} for the 1:2 adducts but are around 875-880 cm^{-1} in the original $[\{M(SOCPh)_2\}_n]$ compounds.

The reactions of $[\{M(SOCPh)_2\}_n]$ with bidentate ligands L-L (L-L = 2,2'bipyridyl, $Ph_2PCH_2PPh_2$, $Ph_2P(CH_2)_2PPh_2$) were also studied and elemental analysis confirmed the products as $M(SOCPh)_2(L-L)$. Again i.r. spectroscopy showed that the $^{-}SOCPh$ groups were S-bonded, but in these compounds they had to be in a cis configuration (18). Further evidence for this assignment was obtained from molecular-weight measurements (Table 1.2) of two of these compounds which again showed them to be monomers.

An interesting feature of these compounds is the large difference between the positions of the ^{31}P n.m.r. resonances in M $(SOCPh)_2(Ph_2PCH_2PPh_2)$ [δ-37.3(Pd) and -49.1 p.p.m. (Pt)] and $M(SOCPh)_2(Ph_2P(CH_2)_2PPh_2)$ [δ 57.0 (Pd) and 45.8 p.p.m. (Pt)]. This difference in ^{31}P n.m.r. chemical shifts in four and five membered phosphorous ring compounds has been found before[46] but as yet an acceptable explanation has not been suggested.

Comparison of the platinum-phosphorous coupling constants in the various complexes indicates that the trans influence of the $^{-}SOCPh$ group is slightly lower than that of PMe_2Ph or $PMePh_2$, but considerably greater than chloride. Thus, trans-$Pt(SOCPh)_2(PMe_2Ph)_2$ and trans-$Pt(SOCPh)_2(PMePh_2)_2$ have ^{1}J (Pt-P) values of 2546 and 2655 Hz respectively compared to 2761 and 3018 Hz in cis-$Pt(SOCPh)_2(Ph_2PCH_2PPh_2)$ and cis-$Pt(SOCPh)_2$

$(Ph_2P(CH_2)_2PPh_2)$ respectively. The complexes cis-$PtCl_2(PMe_2Ph)_2$ and cis-$PtCl_2(PMePh_2)_2$ have ^1J (Pt-P) values of 3549 and 3616 Hz respectively.[47]

In contrast to the reactions of $[\{Pd(O_2CR)_2\}_n]$ with unidentate ligands L (1:2 molar ratio) which gave dimers of the form $[\{Pd(O_2CR)_2L\}_2]$ (11) and the reactions of $M(S-S)_2$ with stoichiometric amounts of L which gave monomers $M(S-S)_2L$ (1), all attempts to obtain the 1:1 adducts $[\{M(SOCPh)_2L\}_n]$ by the reaction of $[\{M(SOCPh)_2\}_n]$ with L failed.

Thus, although reactions of $[\{Pd(SOCPh)_2\}_n]$ with L (L = PPh_3, P $MePh_2$) (1:1 molar ratio) in benzene gave on work-up, solids which analysed for $[\{Pd(SOCPh)_2(L)\}_n]$, the i.r. spectra of these compounds showed ν(CO) (PPh_3 adduct) at 1665, 1595 and 1575 cm^{-1}; ($PMePh_2$ adduct) at 1670, 1590 and 1565 cm^{-1}, implying that the compounds were mixtures of $[\{Pd(SOCPh)_2\}_n]$ and $Pd(SOCPh)_2(L)_2$. Further support for this came from thin layer chromatographic studies which showed separate spots, although there was some streaking and decomposition. Final proof of a mixture was obtained from $^{31}P-\{^1H\}$ n.m.r. studies which showed only one signal in the case of the $[\{Pd(SOCPh)_2\}_n]$/$PMePh_2$ reaction at 12.3 p.p.m. which corresponded to $Pd(SOCPh)_2(PMePh_2)_2$. Furthermore, monitoring the reaction between $[\{Pd(SOCPh)_2\}_n]$ and small amounts of $PMePh_2$ in d^6-benzene by n.m.r. spectroscopy confirmed that only the bis phosphine complex was spectroscopically detectable.

In contrast the the reactions of $M(S-S)_2$ complexes with excess L which gave the ionic products $[M(S-S)(L)_2](S-S)$ (2) all attempts to make the analogous $[M(SOCPh)(L)_2]$ (SOCPh) compounds failed. The only product obtained from the reaction of $[\{Pd(SOCPh)_2\}_n]$ with an excess of $PMePh_2$ in acetone in the presence of a large anion was $Pd(SOCPh)_2(PMePh_2)_2$.

Similarly in monitoring the conductivity of the reactions of $[\{M(SOCPh)_2\}_n]$ with various Lewis bases L in acetone, <u>no</u> increase in conductivity was observed and only the neutral $M(SOCPh)_2(L)_2$ adducts were isolated from the reactions. In contrast to this it was found that the reactions of $[\{Pd(O_2CMe)_2\}_3$ or $Pd(O_2CCF_3)_2$ with an excess of PR_3 (PR_3 = $PMePh_2$, PMe_2Ph) did produce a highly conducting solution, although only the neutral 1:2 adducts could be isolated. In the reactions of $[\{Pd(O_2CMe)_2\}_3]$ with excess PR_3 several attempts to "trap out" a large anion or cation with $AsPh_4.[Cl.HCl]$ or $NaBPh_4$ respectively were made, but these were all unsuccessful. By analogy with the reaction of $K_2[PtCl_4]$ and PR_3 in water which gives initially $[Pt(PR_3)_4][PtCl_4]$ and then rearranges to $PtCl_2(PR_3)_2$,[48] the ionic species here are probably $[Pd(PR_3)_4][Pd(O_2CMe)_4]$.

Finally, an attempted synthesis of $[\{Pd(SOCMe)_2\}_n]$ was made for comparison with the $^{-}SOCPh$ group and to provide a better ^1H n.m.r. "handle". Treatment of a benzene solution of $[\{Pd(O_2CMe)_2\}_3]$ with an excess of monothioacetic acid dropwise under Schlenk conditions gave a very dark purple (almost black) precipitate. This solid was filtered off under dry nitrogen but on exposure to air it slowly decomposed. The product obtained was formulated as $[\{Pd(SOCMe)_2\}_n]$ from elemental analysis and its i.r. spectrum showed strong bands at 1675 and 835 cm^{-1} which were assigned to $\nu(CO)$ and $\nu(CS)$

vibrations respectively. The positions of these bands again indicated strong M-S and weak M-O interactions and ν(CO) at 1675 cm^{-1} compares well with the sulphur bridged polymer $[\{AuMe_2(SOCMe)\}_n]$[36] (ν(CO) = 1710, 1700 cm^{-1}) (15). However, the compound was totally insoluble in all common solvents and did not appear to react with either PR_3 or pyridine ligands, even under reflux conditions. On the basis of the insolubility, i.r. spectral data and lack of reactivity of $[\{Pd(SOCMe)_2\}_n]$, the compound was assigned the sulphur bridged polymeric structure (16) as suggested for the monothiobenzoato complexes.

1.4 Conclusions

Although the reaction of $[\{Pd(O_2CMe)_2\}_3]$ with various Lewis bases (L) gives both the 1:1 and 1:2 adducts $[\{Pd(O_2CMe)_2L\}_2]$ (11) and $Pd(O_2CMe)_2(L)_2$ (10)/(12), and likewise, with $M(S\text{-}S)_2$, reaction with tertiary phosphines gives $M(S\text{-}S)_2(PR_3)$ (1), $[M(S\text{-}S)(PR_3)_2](S\text{-}S)$ (2), or $M(S\text{-}S)_2(PR_3)_2$ (3), reaction of $[\{M(SOCPh)_2\}_n]$ with a variety of Lewis bases gives only the neutral $M(SOCPh)_2L_2$ or $M(SOCPh)_2(L\text{-}L)$ complexes. Furthermore ^-SOCPh cannot be considered as acting as a true bidentate ligand in bonding to platinum or palladium, as only the sulphur interacts, and it should be looked on more as a pseudo thiol ligand (see also Chapter 3).

1.5 Experimental

Microanalyses were by the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab vapour-pressure osmometer (model 301) calibrated with benzil. Infrared spectra were recorded in the 250-4000 cm^{-1} region on a Perkin-Elmer 557 grating spectrometer using Nujol and hexabutadiene mulls on caesium iodide plates. Electronic spectra were obtained on a Unicam SP800 spectrophotometer using unmatched silica cells. Hydrogen-1 n.m.r. spectra were recorded on a Varian Associates HA-100 spectrometer equipped with a variable temperature probe and proton-noise decoupled ^{31}P n.m.r. spectra on a Varian XL100 spectrometer operating in the pulse and Fourier-transform modes at 40.5 M Hz (^{31}P chemical shifts quoted in p.p.m. to high frequency of 85% H_3PO_4). Conductivity measurements were obtained on a Portland Electronics 310 conductivity bridge at 298 K. Melting points were determined with a Köfler hot-stage microscope and are uncorrected. Palladium (II) chloride, potassium tetrachloroplatinate (II) (Johnson, Matthew Ltd.), monothiobenzoic acid (Aldrich), triphenylphosphine (B.D.H.), dimethylphenylphosphine, and methyldiphenylphosphine (Maybridge Chemical Co.) were obtained as indicated. The compounds Na[SOCPh][35], $Ph_2PCH_2PPh_2$,[49] $Ph_2P(CH_2)_2PPh_2$[50] and $[\{Pd(O_2CMe)_2\}_3]$[20] were prepared as described earlier. Analytical data and characteristic i.r. bands for various monothiobenzoato-complexes are given in Table 1.2 and ^{1}H and $^{31}P-\{^{1}H\}$ n.m.r. data for selected monothiobenzoato- and acetato-complexes in Table 1.3.

Reactions involving tertiary phosphines were carried out under a nitrogen atmosphere.

Bis(monothiobenzoato)palladium (II):- Palladium (II) acetate (0.40 g) was dissolved in a minimum volume of cold benzene (30 cm^3) and monothiobenzoic acid (2.0 cm^3) added dropwise to the resulting red-brown solution to give an immediate red-brown precipitate. Complete precipitation was induced by the addition of an excess of light petroleum (b.p. 60-80°C). The product was then filtered off, washed with diethyl ether to remove any free PhCOSH, and then dried in vacuo at 40°C, m.p. 118-121°C (yield 0.30 g). [Found: C, 43.3; H, 2.7%; M in $CHCl_3$ 1125 (0.90), 1504 (2.08), 1672 (4.08 g dm^{-3}). Calc. for $C_{14}H_{10}O_2Pd\ S_2$: C, 44.2; H, 2.6%; M 380 (monomer)]. Infrared spectrum (nujol mull): 1670 vs [ν(CO)] and 875 vs cm^{-1} [ν(CS)], (see Fig. 1:4 spectrum (I)).

Bis(monothiobenzoato)platinum (II):- The compound $Na_2[PtCl_4]$ (0.50 g), prepared by passing $K_2[PtCl_4]$ down a cation exchange column, was suspended in ethanol (25 cm^3)/water (5 cm^3) and treated with Na[SOCPh] (0.40 g) dissolved in ethanol (40 cm^3). This mixture was shaken at room temperature for 5 days and then the resulting yellow brown precipitate was filtered off, washed with ethanol, and dried in vacuo at 40°C, m.p. 194°C (decomp.) (Yield .27 g) [Found: C, 35.6; H, 2.2%. Calc. for $C_{14}H_{10}O_2PtS_2$: C, 35.8; H, 2.1%]. Infrared spectrum (nujol mull) (See Fig. 1:4 spectrum (II)) 1660s, 1595s and 1575s [ν(CO)]; 920s, and 880s cm^{-1} [ν(CS)].

The remaining red filtrate was evaporated almost to dryness and then treated with an excess of light petroleum to give a yellow precipitate which was washed with more light petroleum and dried in vacuo at 40°C (yield .11 g). [Found: C, 38.3, H, 2.6%, Calc. for $[\{Pt(SOCPh)_2(HOEt)\}_n]$: C, 37.3, H, 3.1%). Infrared spectrum (nujol mull): 1660 w, 1590 vs, and 1570-1520 vs, br[ν(CO)]; 950-920 vs, br and 880 w, cm^{-1} [ν(CS)].

When $Na_2[PtCl_4]$ (1.00 g) was dissolved in hot water (15 cm^3) and treated with an aqueous solution (40 cm^3) of Na[SOCPh] (2.00 g) a brown precipitate was produced. After filtering, extracting into dichloromethane, and drying over $Mg[SO_4]$ for 12 hrs the solution was filtered, solvent partially removed, and excess of light petroleum added to give a pinkish solid. (yield .28 g) (Found: C, 40.6; H 2.6%). Infrared spectrum (nujol mull): 1580 w and 1530 vs [ν(CO]; 950 vs and 920 w cm^{-1} [ν(CS)] (see Fig. 1:4 spectrum (III)). On leaving the aqueous solution which remained after removal of the brown solid, a yellow solid precipitated out after 2 days and was filtered off and dried in vacuo (yield .31 g) (Found: C, 38.1; H, 2.4%). Infrared spectrum (nujol mull): 1660 s and 1590-1520 vs, br [ν(CO)]; 950-920 vs, br and 880 w cm^{-1} [ν(CS)]. Qualitative analysis showed that none of these platinum monothiobenzoates contained any chlorine.

<u>General Method of Preparation of $M(SOCPh)_2L_2$ and $M(SOCPh)_2(L-L)$ Complexes</u>:

The complexes $[\{M(SOCPh)_2\}_n]$ (M=Pd,Pt) were dissolved or suspended in benzene or dichloromethane and treated with an excess of Lewis base (L). After shaking for 2-3 hrs the volume was reduced and light petroleum added to precipitate out the products. These were filtered off, washed with diethyl ether, and dried <u>in vacuo</u> at 40°C. For L = $SbPh_3$ or $AsPh_3$ the dichloromethane solutions were heated for 2-3 hrs to induce complete reaction and the complexes which then crystallised out contained one molecule of dichloromethane of solvation. Several attempts to obtain the $Pt(SOCPh)_2(C_5H_5N)_2$ complex were made but the solids isolated always contained starting material even after prolonged refluxing (approx. 36 hrs) of the reactants. For the bidentate ligands (L-L) the same procedure as before was used, but an excess of ligand was avoided in order to help prevent complete displacement of the monothiobenzoate groups. Yields varied between 60-85%.

A full list of analyses, infrared bands, melting points and colours of the products is given in Table 1:2, and ^1H and $^{31}P-\{^1H\}$ n.m.r. data in Table 1.3.

<u>Attempted preparation of $M(SOCPh)_2PR_3$</u>: $[\{M(SOCPh)_2\}_n]$ was dissolved in CH_2Cl_2 and to this was added dropwise with constant stirring a very dilute solution of PR_3 (PR_3 = PPh_3, PMe_2Ph) in CH_2Cl_2. After 2-3 hrs solvent was removed (using high vacuum only, and no heat), to a minimum volume and then treated with an excess of light petroleum to give the solid precipitate.

Bis(monothioacetato)palladium (II): Palladium (II) acetate (0.21 g) was dissolved in dried benzene and to this was added slightly more than 2 moles of monothioacetic acid ($0.10\ cm^3$). On mixing the solution immediately darkened in colour and after 5 mins a very dark purple solid had precipitated out. This solid was filtered off washed with light petroleum and dried under high *vacuo* at room temperature, [Found: C, 18.3; H 2.2% Calc. for $C_4H_6O_2PdS_2$: C, 18.8; H, 2.3%]. Infrared spectrum (nujol mull): 1675 s [ν(CO)]; 835 s cm^{-1} [ν(CS)]. In this last preparation all manipulations were carried out under Schlenk conditions and dried solvents were used.

Table 1.1

Bond lengths and angles for the palladium coordinates in

$Pd(SOCPh)_2(PMe_2Ph)_2$

Pd—S	2.336 (2)	Å
Pd—P	2.318 (2)	Å
S—Pd—P angle	92.50 (6)	°
Pd --- O	3.313 (3)	A°

Molecule is situated with palladium on a centre of symmetry.

Crystal Data.

Triclinic, $P\bar{1}$

$a = 8.122$ $\quad b = 8.923$ $\quad c = 11.420$ Å

$\alpha = 100.26$ $\quad \beta = 98.44$ $\quad \gamma = 112.22$ °

$Z = 1$

Structure determined on 1951 independent data to a resolution of 0.91 Å to R = 5.0%.

Complex	Colour	M.P. (θ_o/°C)	Analysis (%) Found			Calc.			M^a	Infrared bands (cm^{-1})	
			C	H	N	C	H	N		ν(CO)	ν(CS)
$[Pd(SOCPh)_2(PPh_3)_2]$	Yellow	215-220	67.3	4.7		66.3	4.4			1595s, 1570s	910vs
$[Pd(SOCPh)_2(PMePh_2)_2]$	Yellow	190-192	61.6	4.7		61.5	4.6			1590s, 1565s	930(sh, 915vs
$[Pd(SOCPh)_2(PMe_2Ph)_2]$	Yellow	168	54.1	5.3		54.8	4.9			1595s, 1560s	910vs[b]
$[Pd(SOCPh)_2(AsPh_3)_2].CH_2Cl_2$	Pale Brown	173-174	56.5	3.9		56.8	3.9		1045 (1077)	1590s, 1560s	925(sh),910vs
$[Pd(SOCPh)_2(SbPh_3)_2].CH_2Cl_2$	Yellow	175	52.3	3.7		52.3	3.6		1160 (1171)	1600s, 1570s	910vs
$[Pd(SOCPh)_2(C_5H_5N)_2]$	Pale Brown	129	53.5	3.9	5.6	53.5	3.7	5.3		1590s, 1565s	935m, 912s
$[Pd(SOCPh)_2(bipy)]$	Yellow	280 (decomp.)	54.8	3.5	5.0	53.7	3.4	5.2		1600vs, 1570m	930s, 910vs
$[Pd(SOCPh)_2(Ph_2PCH_2PPh_2)]$	Brown	194-196	61.4	4.3		61.3	4.2			1595vs,1560s	930(sh),910vs
$[Pd(SOCPh)_2(Ph_2P(CH_2)_2PPh_2)]$	Pale Brown	231	61.9	4.4		51.7	4.1			1590s, 1560s	925(sh), 911vs
$[Pt(SOCPh)_2(PPh_3)_2]$	Yellow	263-264	59.4	4.2		59.4	4.0			1600s, 1575s	915vs
$[Pt(SOCPh)_2(PMePh_2)_2]$	Pale Yellow	160-164	55.0	4.1		55.2	4.1			1593s, 1570s	930s, 910vs
$[Pt(SOCPh)_2(PMe_2Ph)_2]$	Pale Yellow	203	48.2	4.5		48.3	4.3			1600s, 1570m	910vs[b]
$[Pt(SOCPh)_2(AsPh_3)_2].CH_2Cl_2$	Pale brown	250-252	53.0	3.7		52.5	3.6			1590s, 1570s	925(sh), 905vs
$[Pt(SOCPh)_2(bipy)]$	Pale brown	>300	45.3	2.9	4.0	46.1	2.9	4.5		1595s, 1565s	935(sh), 920vs
$[Pt(SOCPh)_2(Ph_2PCH_2PPh_2)].CH_2Cl_2$	Pale brown	148-155	50.7	3.6		49.9	3.4		929 (937)	1595s, 1570s	925(sh), 910vs
$[Pt(SOCPh)_2\{Ph_2P(CH_2)_2PPh_2\}]$	Yellow	228	55.0	4.0		55.4	3.9		895 (866)	1590s, 1565s	910vs

[a] Osmometrically at 37°C in chloroform; claculated values are given in parentheses. [b] Partially masked by strong PMe_2Ph

Hydrogen-1 and P-{ H} n.m.r. data in CDCl$_3$ for

Complex	^{1}H n.m.r. (δ)^a			^{31}P n.m.r.	
	Me (carboxylate)	Me (phosphine)	Ph	δ^b	J(PtP)/Hz
$[Pd(SOCPh)_2(PMePh_2)_2]$		2.14(t)^c	7.0-8.2(m)	12.3(s)	
$[Pd(SOCPh)_2(PMe_2Ph)_2]$		1.79(t)^c	7.0-7.8(m)	- 2.6(s)	
$[Pd(SOCPh)_2(Ph_2PCH_2PPh_2)]$		4.10(t)^d	7.0-8.0(m)	-37.3(s)	
$[Pd(SOCPh)_2\{Ph_2P(CH_2)_2PPh_2\}]$		2.33(m)^c	7.0-8.2(m)	57.0(s)	
$[Pd(O_2CMe)_2(PMe_2Ph)_2]$	2.00(s)	1.42(pd)^f	7.0-8.0(m)	5.3(s)	
$[Pd(O_2CMe)_2(PMePh_2)_2]$	1.64(s)	1.68(pd)^f	7.0-8.0(m)		
$[Pd(O_2CMe)_2(PPh_3)_2]$	0.85(s)		7.0-7.8(m)	14.8(s)	
$[\{Pd(O_2CMe)_2(AsPh_3)\}_2]$	1.44(s) 1.47(s) 1.41(s)^g		7.0-8.0(m)		
$[\{Pd(O_2CMe)_2(PPh_3)\}_2]$	1.42(s)		7.0-8.0(m)	19.7(s)	
$[Pt(SOCPh)_2(PMePh_2)_2]$		2.23(t of t)^{c,h}	7.0-7.9(m)	8.2(t)^i	2655.2
$[Pt(SOCPh)_2(PMe_2Ph)_2]$		1.86(t of t)^{c,h}	7.0-8.0(m)	- 6.2(t)^i	2546.2
$[Pt(SOCPh)_2(Ph_2PCH_2PPh_2)]$		4.43^j	7.0-8.0(m)	-49.1(t)^i	2761.7
$[Pt(SOCPh)_2\ Ph_2P(CH_2)_2PPh_2]$		2.18(m)^e	7.0-8.0(m)	45.8(t)^i	3017.8

s = Singlet, pd = pseudo-doublet, t = triplet, and m = multiplet.

[a] $\pm$0.01 p.p.m. [b] $\pm$0.05 p.p.m. [c] $|^2J(PH) + 4J(PH)|$ 7.0 Hz. [d] CH_2 resonance, $^2J(PH)$ 10.0 Hz. [c] CH_2 resonance.

[f] $|^2(PH) + ^4J(PH)|$ 11.0 Hz. [g] At 223 K. [h] $^2J(PtH)$ 28.0 Hz. [i] 1:4:1 Triplet. [j] Too insoluble to determine splitting pattern.

CHAPTER 2

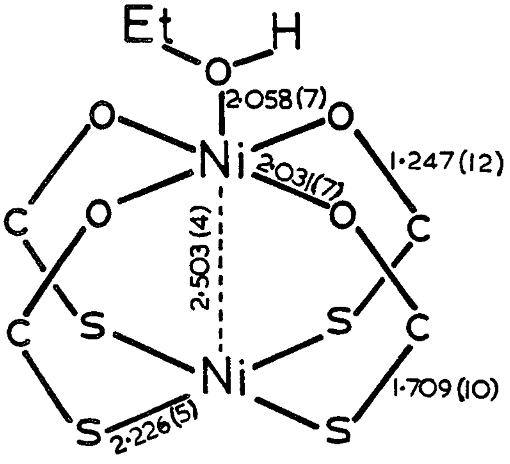
PREPARATION AND REACTIONS OF $[\{Ni(SOCR)_2 0.5\ EtOH\}_2]$ (R = Me,Ph)

2.1 Introduction

In Chapter 1 the syntheses of the sulphur-bridged polymers $[\{M(SOCPh)_2\}_n]$ (n > 3, M = Pd,Pt) and their reactions with a variety of Lewis bases L or L-L to give the neutral, square-planar, monomeric complexes $M(SOCPh)_2L_2$ or $M(SOCPh)_2(L\text{-}L)$ containing unidentate, S-bonded $^{-}$SOCPh groups was discussed.

In contrast, earlier workers[34,42,51] have reported that reaction of various nickel (II) salts with either Na[SOCPh] or HSOCR (R = Me,Et) gave the dimeric $[\{Ni(SOCR)_2\ 0.5\ EtOH\}_2]$ complexes, shown by X-ray analysis[41,52] (for R = Ph) to have structure (17). (See Fig. 2.1).

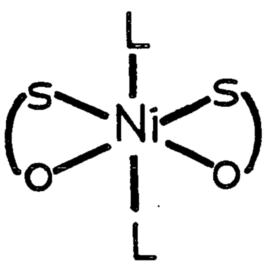
Fig 2.1 Structure of $[\{Ni(SOCPh)_2 0.5\ EtOH\}_2]$ showing bond lengths



(17)

In $[\{Ni(SOCPh)_2 0.5\ EtOH\}_2]$ the two nickel atoms are bridged by the four monothiobenzoate ligands so that one metal atom is surrounded by four sulphur atoms in a square planar fashion and the other by four oxygen atoms in a similar manner. The fifth coordination site of the second Ni atom is occupied by the oxygen atom of an ethanol group. The Ni-S distances of 2.221-2.230 (5) Å are characteristic of square planar, low spin complexes while the Ni-O distances, (2.010-2.058 (7) Å), are compatible with those found in high-spin complexes. The unusual magnetic moment of 2.4 per nickel (II) ion found for the dimer at 291 K is proposed to arise from the presence of two unpaired electrons on the nickel ion of C_{4V} symmetry, and, despite a Ni-Ni separation of only 2.503 (4) Å, it is believed that the Ni-Ni interaction is probably very weak.

Reaction of compound (17) with various unidentate, heterocyclic nitrogen donor ligands (L) results in the formation of green, monomeric, octahedral complexes $Ni(SOCR)_2L_2$(20), (21) and/or (22) (L = C_5H_5N, 2-MeC_5H_4N, 3-MeC_5H_4N, 4-MeC_5H_4N etc)[34,42,51] in which the monothiocarboxylate groups are coordinated in a bidentate fashion. Similar octahedral nickel (II) complexes $Ni(S\text{-}O)_2L_2$ containing nitrogen bases and other monothioacid ligands ($S\text{-}O^-$ = ^-SOCOEt,[53] $^-SOCNR_2$)[45,54] have also been synthesised.



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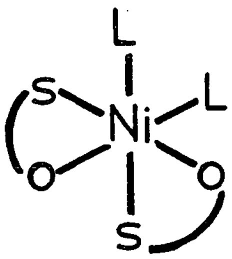

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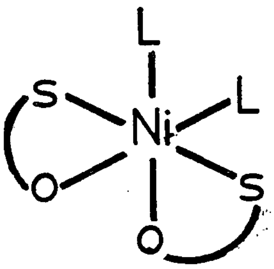

(22)

In this chapter, I now wish to describe, reactions of $[\{Ni(SOCR)_2 0.5\ EtOH\}_2]$ (R = Me,Ph) and some $Ni(S\text{-}S)_2$ (S-S = $^-S_2PMe_2$, $^-S_2COEt$) complexes with various phosphorous donor ligands and to compare the results with those found using nitrogen donor ligands. For this reason, a brief survey of the chemistry to date of nickel (II) 1,1 dithiolate complexes with nitrogen and phosphorous containing Lewis bases is given in the next section.

2.2 Some chemistry of $Ni(S\text{-}S)_2$ complexes with nitrogen and phosphorous containing Lewis bases

Numerous complexes of the type $Ni(S\text{-}S)_2$ [$S\text{-}S = {}^-S_2CNR_2$[55], ${}^-S_2CR$[33], ${}^-S_2COR$[56], ${}^-S_2P(OR)_2$[55] and ${}^-S_2PR_2$][57-59] have been prepared and with one exception* all of the compounds investigated by X-ray analyses[60] have been found to contain a square-planar MS_4 unit.

However, these nickel complexes show a variable affinity towards nitrogen donor Lewis bases[19,62] to form both five[63] and six[64] coordinate adducts, a tendency which is not exhibited by the analogous palladium (II) and platinum (II) 1,1 dithiolates (see Chapter 1). Thus $Ni(S_2CNEt_2)_2$ does not react with pyridine at room temperature,[19] whereas $Ni(S_2P\{OEt\}_2)_2$ forms adducts with pyridine, 4-methylpyridine and the much weaker base butylamine,[65] whilst $Ni(S_2COEt)_2$ is intermediate in reactivity. Generally, sterically unhindered nitrogen Lewis bases react to form 2:1 adducts with octahedral or pseudo-octahedral stereochemistry chelation,[6] whilst hindered bases such as quinoline or 2-methylpyridine form only

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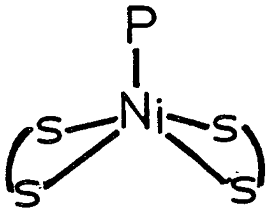
*The one exception is $[Ni(SPMe_2NPMe_2S)_2]$ which has a tetrahedral configuration.[61]

1:1 adducts.[66] Electronic spectral data show the 1:1 adducts formed with sterically hindered bases to have an essentially square-pyramidal configuration.[67]

This variable reactivity of nickel (II) 1,1 dithiolates with nitrogen donor bases has been rationalised by Fackler et al[19] in terms of the ability of the dithio ligand to mesomerically shift electron density into the metal $4p_z$ orbital through its π-orbital system. Thus a strong interaction with the 1:1 dithiolate would decrease the availability of this orbital for interaction with donor bases.

Although these reactions of nickel (II) 1,1 dithiolates with nitrogen donor bases have been extensively studied, there is very little information in the literature concerning their reactions with phosphorous donor Lewis bases. In 1972, Zink et al[68] reported briefly the formation of the paramagnetic 1:1 complex $Ni(S_2P(OEt)_2)_2PPh_3$ shown later by X-ray analysis[69] to have a square pyramidal MS_4P geometry (23). The formation of similar 1:1 adducts has also been claimed by reaction of tributyl phosphine with $Ni(S_2P\{OR\}_2)_2$ ($R = C_2H_5$, $PhCH_2CH_2$, C_8H_{11}).[70] In contrast, Zagal and Costamagna[71] have reported that an excess of tributylphosphine reacts with $Ni(S_2COR)_2$ in ethanol to give the red, diamagnetic complexes $Ni(S_2COR)_2(P^nBu_3)_2$ formulated as four coordinate, square-planar compounds containing unidentate, xanthato groups, in the cis-configuration (24).



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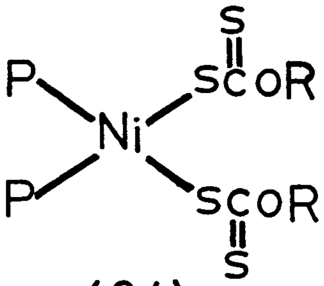
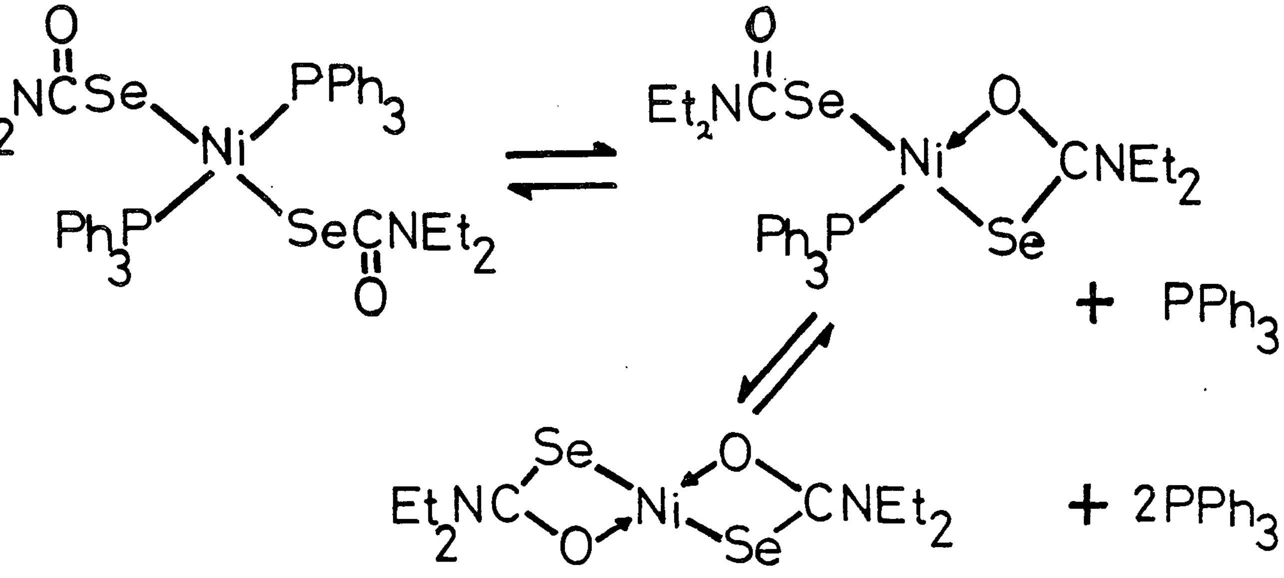


(24)

No reactions of phosphorus donor ligands with nickel (II) monothioacid complexes have previously been reported. However, there is one report in the literature of the synthesis of Ni(P)$_2$(SeCONEt$_2$)$_2$ and Ni(P-P)(SeCONet$_2$)$_2$ (P = PPh$_3$; P-P = Ph$_2$PCH = CHPPh$_2$ complexes by the reaction of NiP$_2$Cl$_2$ with [Et$_2$NH$_2$][SeCONEt$_2$] in a 1:2 molar ratio.[72] These compounds although stable in air in the solid state are reported to be somewhat unstable in solution. Magnetic measurements show them to be diamagnetic suggesting a square-planar configuration around the nickel. However, molecular-weight measurements and detailed solid and solution infrared studies indicate that dissociation of the phosphines occurs in solution, eqn [5].



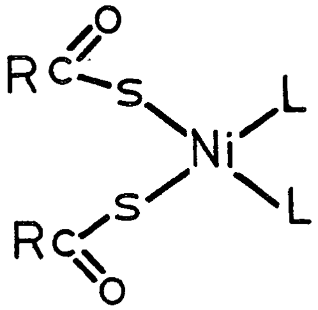
..........[5]

2.3 Results and Discussion

2.3.1 Reaction of $[\{Ni(SOCR)_2 0.5\ EtOH\}_2]$ (R = Me,Ph) with various nitrogen and phosphorous donor Lewis bases

As found by other workers,[42,51] $[\{Ni(SOCR)_2 0.5\ EtOH\}_2]$ (17) (R = Me,Ph) readily reacted with a 5 to 10 fold excess of pyridine or 4-methylpyridine (L) in ethanol to give green solutions from which green solids of stoichiometry $[Ni(SOCR)_2L_2]$ (20) or (21) were readily isolated. As reported earlier, these complexes are monomeric, paramagnetic (Table 2.1) and on the basis of electronic spectral studies contain octahedrally co-ordinated nickel (II) ions. Similarily, reaction of (17) (R = Me, Ph) with 2,2'-bipyridyl (1:2 molar ratio) gave green $[Ni(SOCR)_2bipy]$ complexes with similar spectroscopic and magnetic properties (Table 2.1).

In contrast, reaction of (17), (R = Me,Ph) with an excess of various tertiary phosphines (PR'_3) gave orange-red compounds of stoichiometry $[Ni(SOCR)_2(PR_3')_2]$ (25) or (26) (PR_3' = PPh_3, $PMePh_2$, PMe_2Ph) which were diamagnetic in the solid state. Similarly, orange, diamagnetic compounds $[Ni(SOCR)_2(Ph_2P[CH_2]_xPPh_2)]$ (x = 1 or 2) were isolated on reaction of (17) (R = Me,Ph) with $Ph_2P[CH_2]_xPPh_2$ (1:2 molar ratio).



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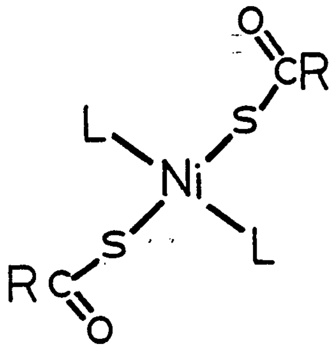


(26)

As discussed in Chapter 1, the positions of the ν_{CO} and ν_{CS} vibrations in the ir spectra of the compounds are diagnostic of the mode of bonding of the monothiocarboxylate group. Thus for $[\{Ni(SOCPh)_2 0.5\ EtOH\}_2]$, ($\nu_{CO}$ 1508; ν_{CS} 958 cm^{-1}), the values are very similar to those found in Na[SOCPh], (ν_{CO} 1500; ν_{CS} 960 cm^{-1}), indicative of more or less symmetrical bonding of the oxygen and sulphur atoms to nickel, as expected for the bridged structure (17). However, the ir spectra of compounds (25),(26) (R = Ph) all show ν_{CS} vibrations at *ca* 910 cm^{-1} and ν_{CO} vibrations between 1550-1590 cm^{-1} (Table 2.1) indicative of strong Ni-S and weak Ni-O interactions respectively [*cf* $[Pd(SOCPh)_2(PMe_2Ph)_2]$, (ν_{CO} 1595, 1560; ν_{CS} 910 cm^{-1}), shown by X-ray analysis (Chapter 1) to have a square planar structure with *trans* S-bonded $^-$SOCPh groups]. Similarly, comparing $[\ Ni(SOCMe)_2$-0.5 EtOH $_2]$ (ν_{CO} 1540; ν_{CS} 975 cm^{-1}) with compounds (25) and (26) (R = Me) ν_{CO} *ca* 1600 cm^{-1}, ν_{CS} *ca* 940 cm^{-1}) (Table 2.1) suggests strong Ni-S and weak Ni-O interactions respectively in the latter.

For the green $[Ni(SOCR)_2(4\text{-}MeC_5H_4N)_2]$ (20),(21) or (22) ν_{CS} occurs at 965 cm^{-1}, whilst ν_{CO} occurs at *ca* 1600 cm^{-1}, suggesting that some weakening of the Ni-O interaction compared to that in compound (17) has occurred. This is probably due to a substantial *trans* bond weakening effect produced by either the sulphur and/or the nitrogen donor atoms, depending on whether structure (20),(21) or (22) is present. In fact, a recent X-ray analysis on $[Ni(SOCMe)_2(C_5H_5N)_2]$ [73] shows the structure to be (22) although the structure adopted may vary with slight changes of ligand. (cf. the related $[Ni(S_2PPh_2)_2(C_5H_5N)_2]$ which has a *trans* configuration).[74] For

[Ni(SOCR)$_2$bipy], only structures (21) or (22) are of course possible.

Presumably the main reason for this difference in behaviour between N and P donor ligands towards Ni(II) monothio- and dithio- acid compounds is that the P donor ligands are high enough in the spectrochemical series to encourage the Ni(II) ion to adopt a low spin, square planar configuration (<u>cf</u> $Ni(CN)_4^{2-}$ and $Ni(H_2O)_6^{2+}$)[75]. For palladium (II) and platinum (II) however, the larger ligand field splitting values associated with these heavier elements lead to square planar configurations even for weak field ligands and, hence, no structural differences between N and P donor ligand complexes of Pd(II) and Pt(II) monothioacid compounds have been observed (see Chapter 1).

Although there is strong evidence that the [Ni(SOCR)$_2$-(PR$_3$')$_2$] compounds have a square planar configuration in the solid state, molecular weight and electronic spectral studies in acetone and dichloromethane respectively at ambient temperature reveal that substantial changes occur on dissolution. Thus, osmometric molecular weight measurements in acetone are much lower than expected for monomers (Table 2.1) indicating some dissociation of ligands has occurred. Although conductivity measurements in acetone show that no ionic species are formed in solution electronic spectral studies (see Fig. 2.2) demonstrate that addition of free tertiary phosphine produces changes in the position of the absorption bands in the visible region, suggesting the following equilibrium is set up at ambient temperature:-

$$[Ni(SOCR)_2(PR_3{}')_2] \rightleftharpoons [Ni(SOCR)_2(PR_3{}')] + PR_3{}' \ldots.[6]$$

On removal of solvent, however, only $[Ni(SOCR)_2(PR_3{}')_2]$ complexes were obtained. The degree of dissociation depended on the $PR_3{}'$ groups present, the order observed being $PPh_3 > PMePh_2 > PMe_2Ph$. For $[Ni(SOCR)_2(Ph_2P(CH_2)_xPPh_2)]$, however, normal molecular weights were found and no change in the electronic spectra occurred on addition of $PPh_2(CH_2)_x$-PPh_2, indicating that the square planar configuration (25) was retained in solution. Several possible structures can be written for the intermediate complex $[Ni(SOCR)_2PR_3{}']$, but in view of the close similarity of the electronic spectra of $[Ni(SOCR)_2(PR_3{}')_2]$ in the absence and presence of $PR_3{}'$, a square planar configuration (27) with chelating and S-bonded unidentate ^-SOCPh groups is most likely for the <u>major</u> species in solution at ambient temperature. (<u>cf</u>. the solution behaviour of $Ni(SeOCNEt_2)_2(PPh_3)_2$).[72]

For some of these tertiary phosphine compounds, solution magnetic measurements at ambient temperature by the Evans's method [76] (see experimental section) reveal the presence of a very small amount of paramagnetic material (< 5%). By analogy with earlier work on $[NiX_2(PR_3{}')_2]$ compounds (X = Cl, Br, I),[77,78] the most probable explanation for this is the formation, in solution, of small amounts of paramagnetic tetrahedral isomers although, of course, the formation of paramagnetic five or six coordinate isomers cannot be discounted.

A study of the variable temperature ^1H and ^{31}P-$\{^1H\}$ n.m.r. spectra of some of these phosphine complexes provides further information about their behaviour in solution. Thus, the

Fig. 2.2

Electronic spectra showing changes in peaks with addition of PR_3

(1) $[Ni(SOCPh)_2(PMe_2Ph)_2]$ (2) and (3) $[Ni(SOCPh)_2(PMe_2Ph)]$ plus free PMe_2Ph

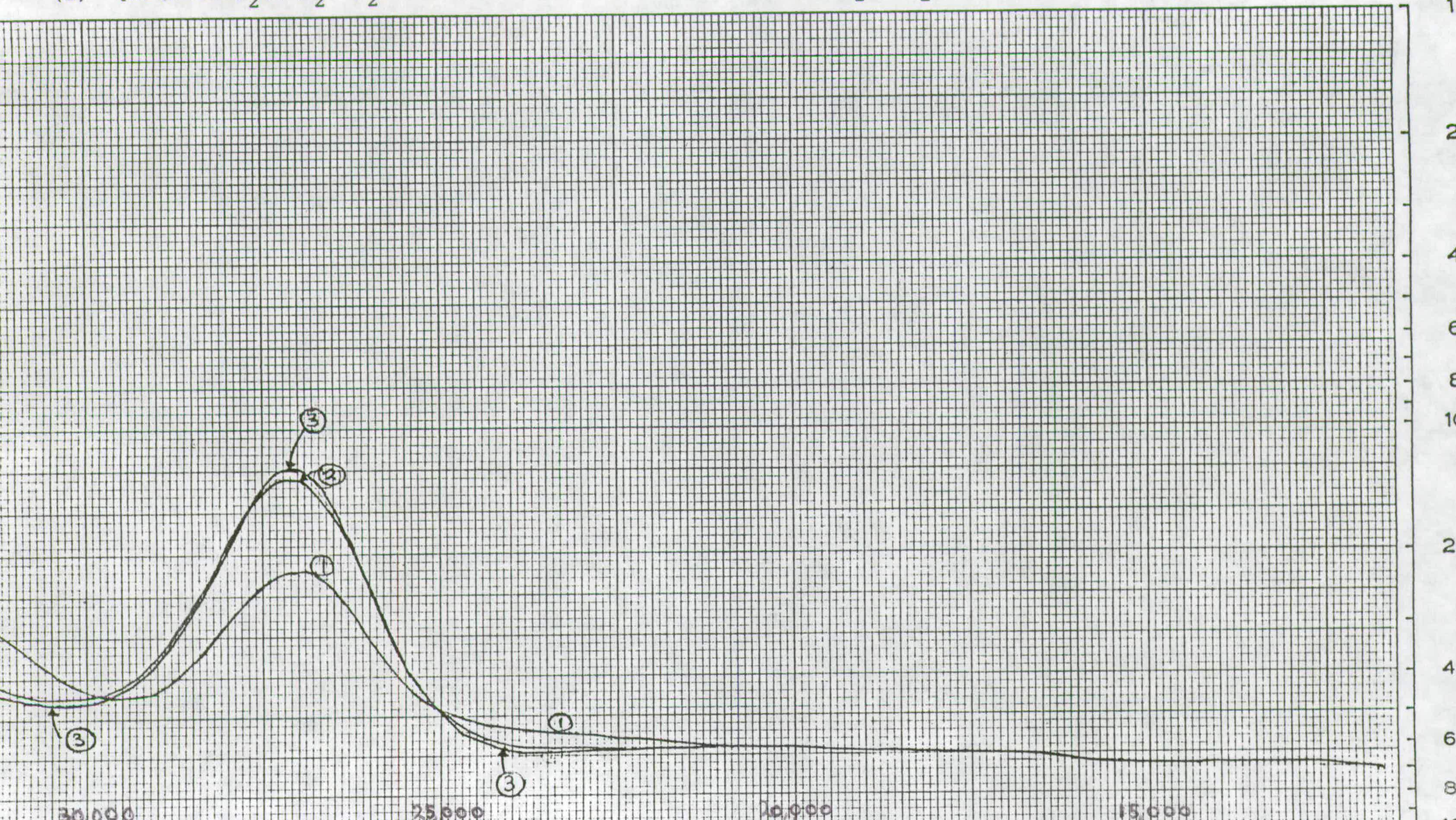
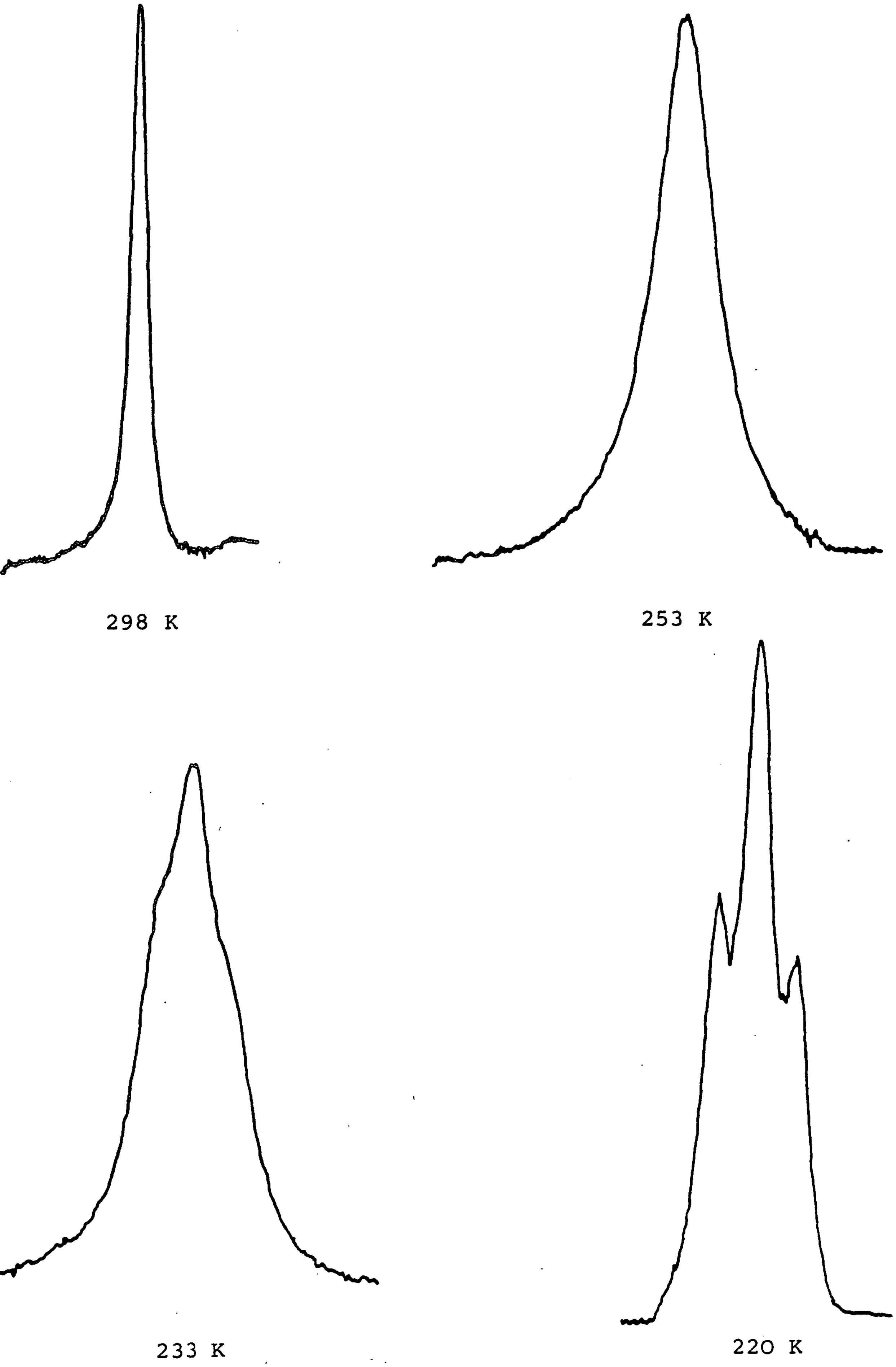


Fig. 2.3a

V.T. ^1H n.m.r. spectrum of $[Ni(SOCPh)_2(PMe_2Ph)_2]$



298 K

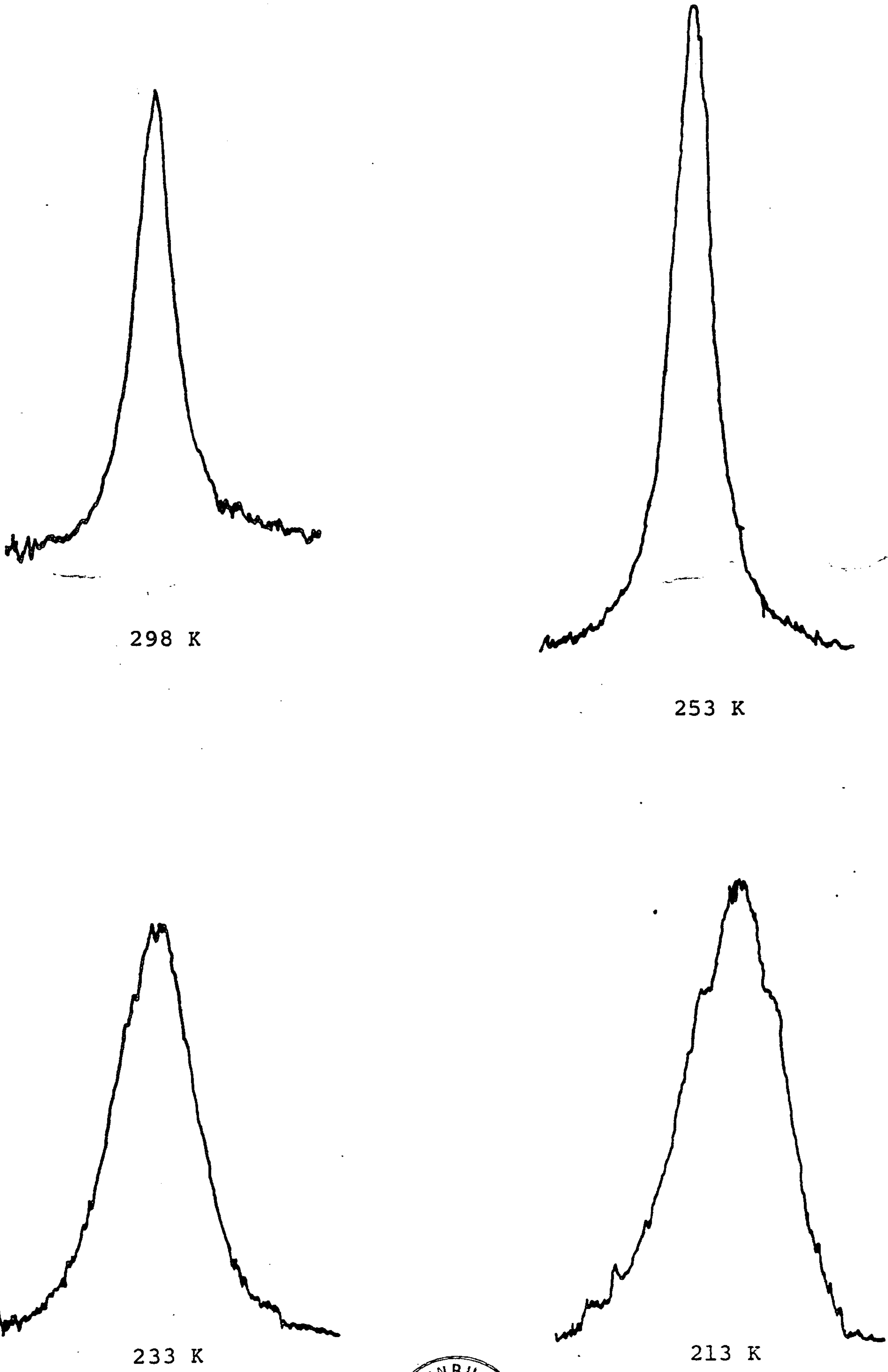
253 K

233 K

220 K

Fig. 2.3b

V.T. ^{1}H n.m.r. spectrum of $[Ni(SOCPh)_2(PMePh_2)_2]$



298 K

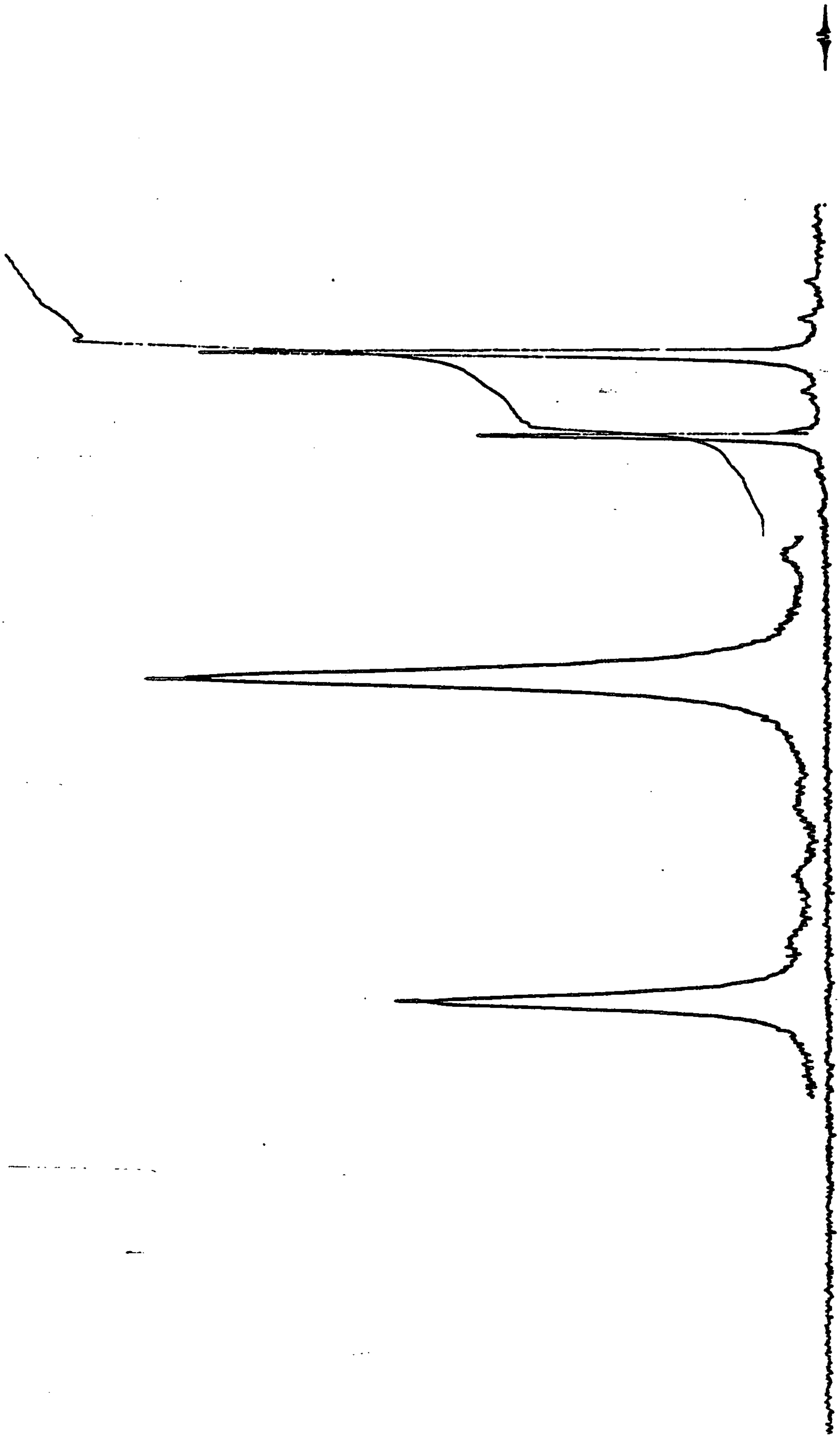
253 K

233 K

213 K

Fig. 2.4

^{1}H n.m.r. spectrum of $[Ni(SOCMe)_2(PMe_2Ph)_2]$



^1H n.m.r. spectra (methyl region) of $[Ni(SOCPh)_2(PMe_2Ph)_2]$ (see Fig. 2.3a) and of $[Ni(SOCPh)_2(PMePh_2)_2]$ (see Fig. 2.3b) below 220K in CD_2Cl_2 consist of 'virtually-coupled' triplet patterns[44] whereas at higher temperatures (up to 303K) only a sharp singlet (at almost the same chemical shift as the triplet) is observed (Table 2.2) (Figs. 2.3a, 2.3b and 2.4). This suggests that at low temperatures, equilibrium (1) lies completely to the left-hand side with the square planar, trans isomer (26) exclusively formed (cf the ^1H n.m.r. spectrum of trans-$[Pd(SOCPh)_2(PMePh_2)_2]$ (see Fig. 1.6, Chapter 1). Similar observations have been made for the related $[Pt(S_2CNR_2)(PMePh_2)_2]S_2CNR_2$ which are stable at 213K in $CDCl_3$ but extensively dissociated into $[Pt(S_2CNR_2)_2(PMePh_2)]$ and $PMePh_2$ at ambient temperature equation [7].[7]

$$[Pt(S_2CNR_2)(PMePh_2)_2]S_2CNR_2 \rightleftharpoons [Pt(S_2CNR_2)_2(PMePh_2)] + PMePh_2 \qquad ....[7]$$

The $^{31}P-\{^1H\}$ n.m.r. spectra of all the $[Ni(SOCR)_2(PR_3')_2]$ compounds at temperatures below 220K showed a singlet (Fig. 2.5) and for $PR_3' = PMe_2Ph$, selective decoupling of the phenyl protons showed $J_{\underline{P}C\underline{H}_3}$ to be present. On raising the temperature, the phosphorus-hydrogen coupling disappeared although the position of the singlet remained virtually invariant up to ca 273K. Above this temperature, however, the singlet broadened and then disappeared (Fig. 2.5). Addition of an excess of free phosphine at temperatures below 273K produced two $^{31}P-\{^1H\}$ n.m.r. signals, one corresponding to free phosphine and the other to the species present in the absence of free phosphine (Fig. 2.6). Thus, this clearly shows that loss of

V.T. $^{31}P-\{^{1}H\}$ spectrum of $[Ni(SOCMe)_2(PMePh_2)_2]$

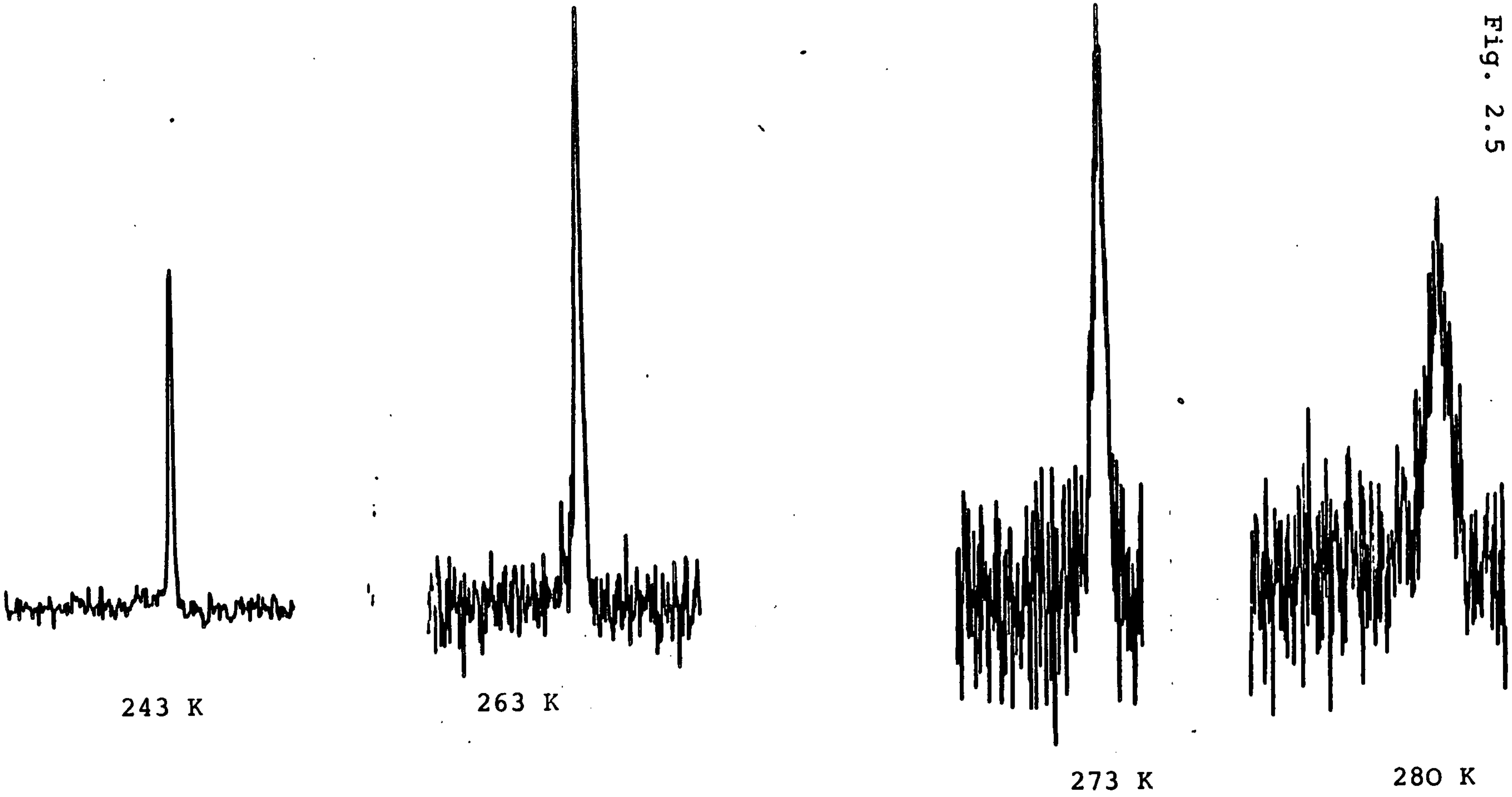
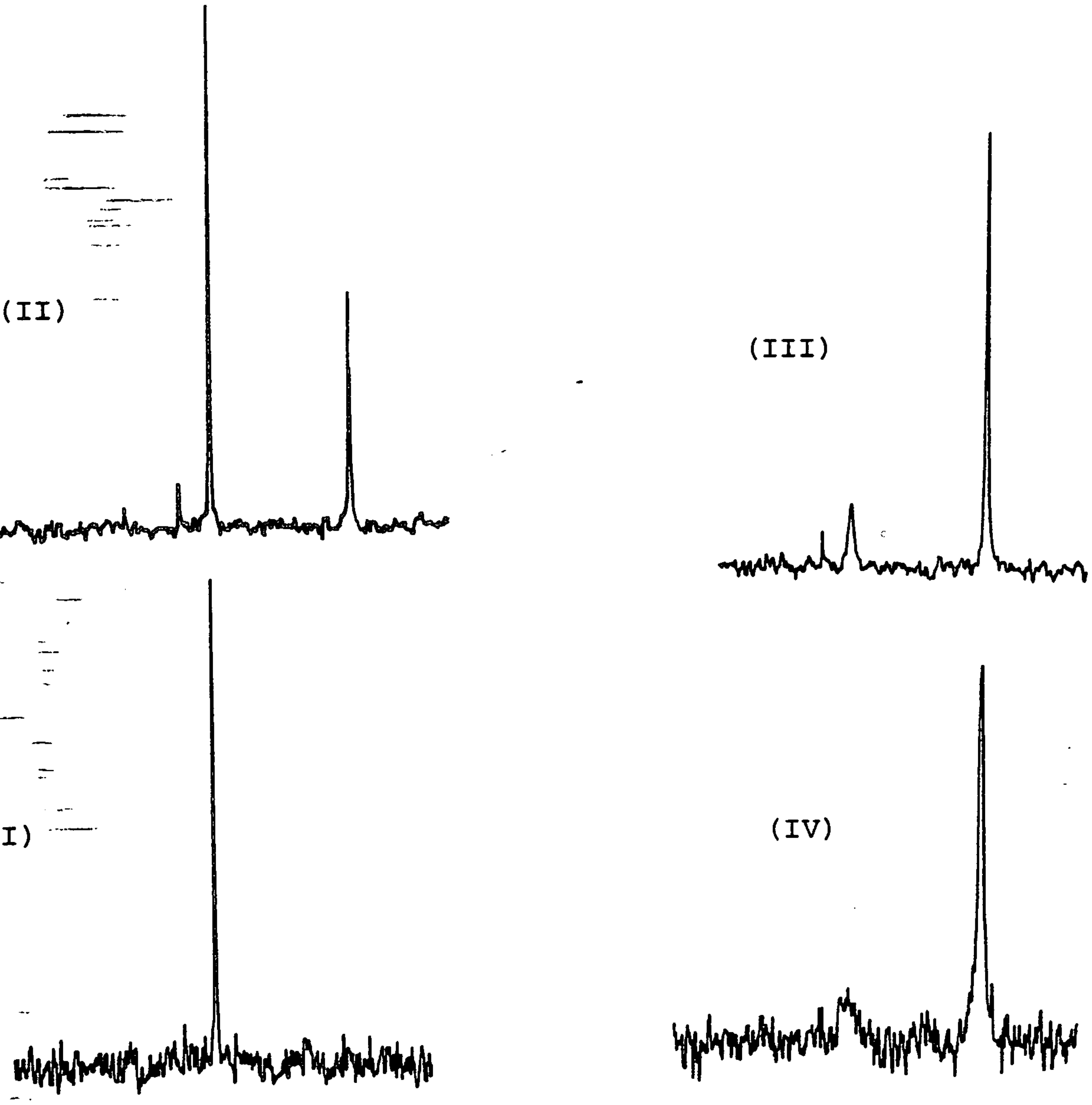


Fig. 2.5

Fig. 2.6

$^{31}P-\{^1H\}$ n.m.r. spectrum of $[Ni(SOCMe)_2(PPh_3)_2]$ + free PPh_3



(I) At 223 K without free PPh_3

(II) At 223 K with free PPh_3

(III) At 253 K with free PPh_3

(IV) At 263 K with free PPh_3

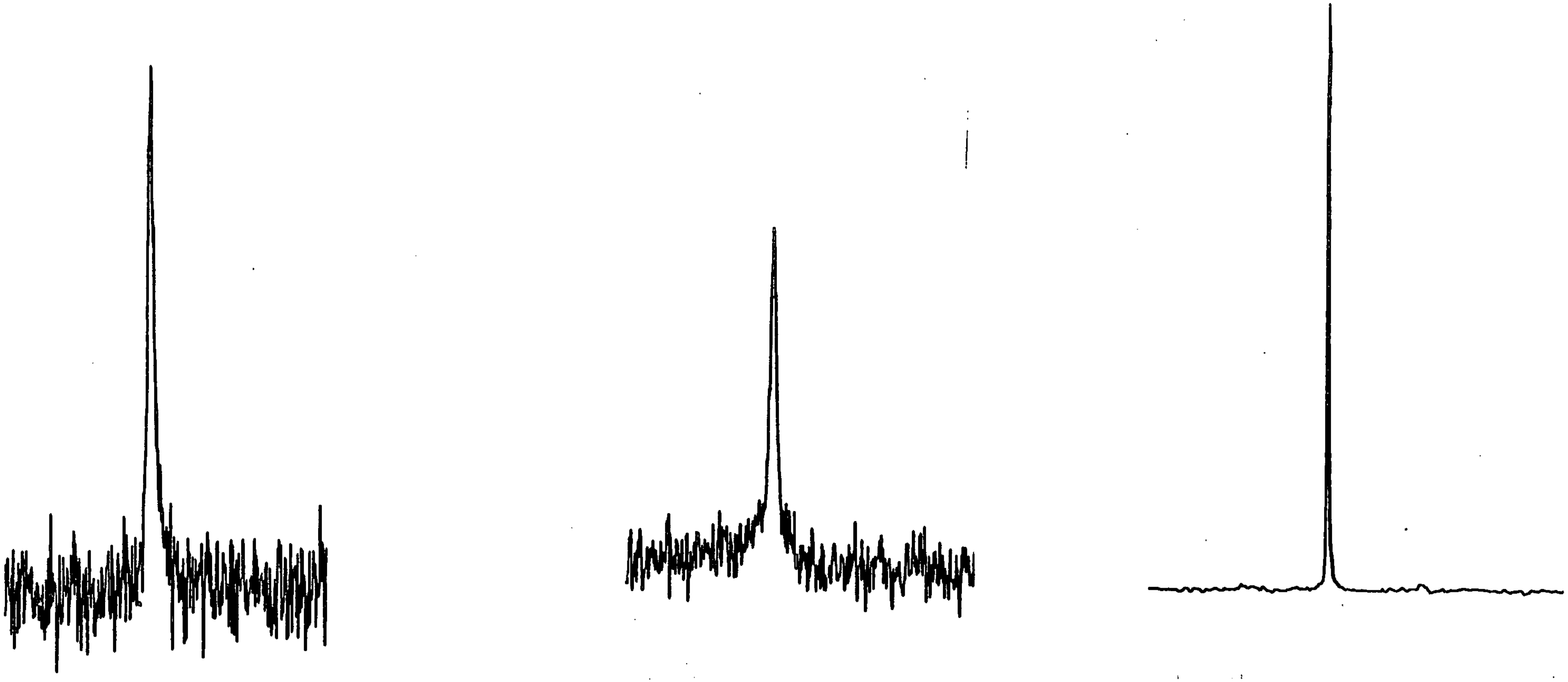
phosphorus-hydrogen coupling, at least below 273K, is not due to fast intermolecular PR_3' exchange (see ref. 79 for examples of this process) and also that the $[Ni(SOCR)_2(PR_3')_2]$ complexes do not dissociate significantly in solution below this temperature. Therefore the only explanation that can be offered for the loss of phosphorus-hydrogen couplings between 220 and 273K in compounds (26) is the generation of increasing amounts of paramagnetic isomers on raising the temperature, accompanied by facile exchange between these and the diamagnetic isomers (26) (cf. n.m.r. studies on the related $[NiX_2(PR_3')_2]$ complexes).[77]

Above 273K, broadening and subsequent loss of the ^{31}P n.m.r. signals can be attributed to a combination of facile intermolecular scrambling between $[Ni(SOCR)_2(PR_3')_2]$, $[Ni(SOCR)_2PR_3']$ and PR_3' and the formation of increasing amounts of paramagnetic isomer. Since the effect of the latter will be much less marked on the more distant protons, singlets are still observed at room temperature for the methyl resonances in their ^1H n.m.r. spectra.

In support of this explanation, the $^{31}P-\{^1H\}$ n.m.r. spectrum of $[Ni(SOCPh)_2(PPh_2(CH_2)_2PPh_2)]$ (where molecular weight and electronic spectral studies indicate no dissociation even at ambient temperature) shows a sharp singlet from 301 to 243K (Fig. 2.7).

Finally, on prolonged reaction of $[\{Ni(SOCR)_2 0.5\ EtOH\}_2]$ with an excess of $AsPh_3$ in ethanol at 253K, dark red solids of empirical formulae $[Ni(SOCR)_2(AsPh_3)]H_2O$ (R = Me,Ph) were isolated. Evidence that these are genuine products and not mixtures of starting material and $[Ni(SOCR)_2(AsPh_3)_2]$ is based on melting points, magnetic moments and the positions

Fig. 2.7



298 K

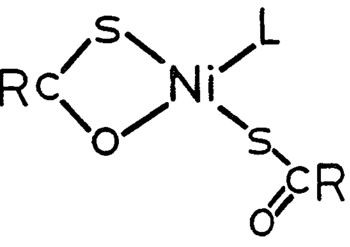
273 K

243 K

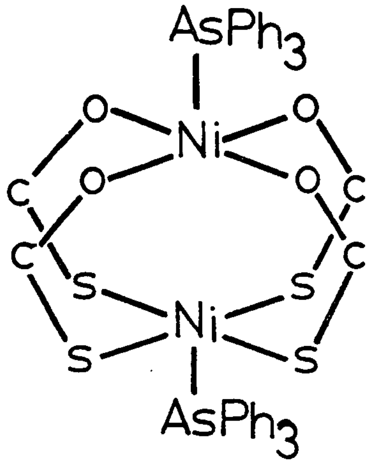
$^{31}P-\{^{1}H\}$ n.m.r. spectrum of $[Ni(SOCPh)_2(Ph_2P(CH_2)_2PPh_2)]$

of ν_{CO} and ν_{CS} vibrations in their infrared spectra (Table 2.1). Thus, for $[\{Ni(SOCPh)_2(AsPh_3)\}_n](H_2O)_n$, the observation that ν_{CO} 1510, ν_{CS} 950 cm^{-1}, together with the occurrence of typical infrared absorption bands of $AsPh_3$, is consistent with these 1:1 adducts having structure (28). Furthermore, although the compounds were too insoluble for molecular weight measurements, the magnetic moment of R = Ph is fairly similar to that of the parent dimer (17). Presumably, the high "class b" character of $AsPh_3$ inhibits further reaction with the "class a" nickel ion.

Similarily reaction of $[\{Ni(SOCMe)_2 0.5\ EtOH\}_2]$ with an excess of pyridine in ethanol was found to yield the dark red 1:1 adduct $[\{Ni(SOCMe)_2(C_5H_5N)\}_n]$ on work up (see experimental section for details). This formulation was based on melting points, magnetic moments and infrared spectral data (Table 2.1). This observation is in keeping with results obtained by Melson et al.,[42] who attempted to remove pyridine from the bis adducts by heating under high vacuum above the boiling point of the ligand for several hours. They found that the green 1:2 adducts turned red-brown characteristic of the original dimeric species, but these products did not analyse for the $[\{Ni(SOCR)_2 0.5\ EtOH\}_2]$ starting materials, and are more probably the 1:1 adducts.



(27)



(28)

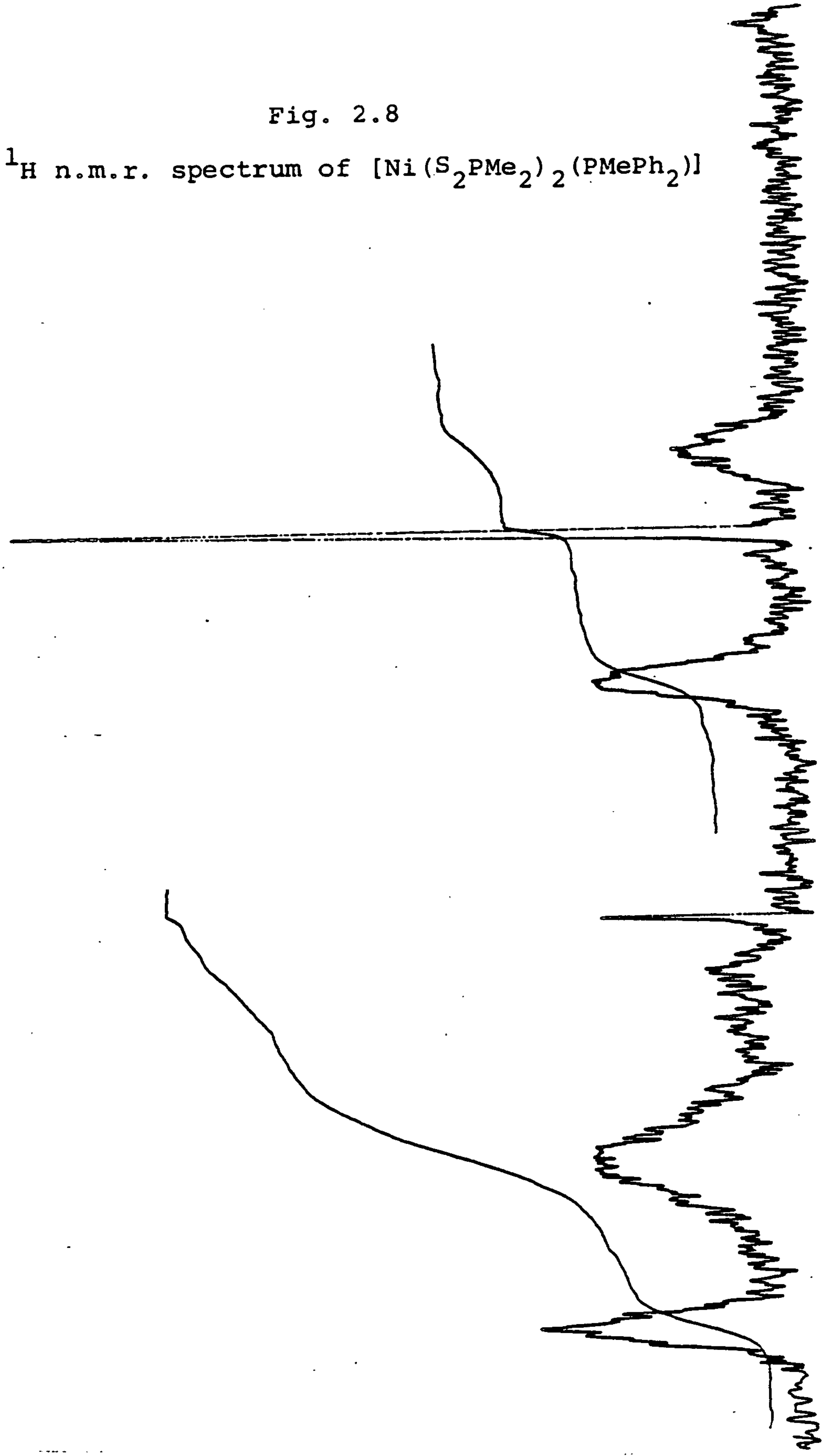
2.3.2 Reactions of $Ni(S-S)_2$ ($S-S = {}^-S_2PMe_2, {}^-S_2COEt$) with some tertiary phosphines

Since comparatively little work on reactions of $Ni(S-S)_2$ complexes with phosphorous containing Lewis bases has been published (see Section 2.2) a few reactions of $Ni(S-S)_2$ ($S-S = {}^-S_2PMe_2, {}^-S_2COEt$) with tertiary phosphines have been investigated and the results of these are described in this final section.

Thus, treatment of a suspension of $Ni(S_2PMe_2)_2$ in CH_2Cl_2 with an excess of L (L = $PMePh_2$,PMe_2Ph) produced an immediate reaction and after work-up (see experimental section 2.4.1) the resulting products were isolated as very dark blue-violet powders. On the basis of infrared data ν(P-S) values of 601 and 580 cm^{-1} for $[Ni(S_2PMe_2)_2(PMePh_2)]$ and 598 and 570 cm^{-1} for $[Ni(S_2PMe_2)_2(PMe_2Ph)]$ for the S_2PMe_2 groups indicate bidentate and elemental analyses (Table 2.3) these compounds were formulated as $Ni(S_2PMe_2)_2L$ complexes with probable structure of type (23) (cf. $Ni(S_2P\{OEt\}_2)_2PPh_3$).[64] This conclusion is supported by the proton n.m.r. spectrum (Fig. 2.8) of $Ni(S_2PMe_2)_2PMePh_2$ in $CDCl_3$ at 298°K which showed paramagnetic broadening and contact shifting of all the methyl peaks. Unfortunately attempts to grow single crystals of these compounds (for X-ray structural analysis) by allowing the solvent to slowly evaporate off at room temperature resulted only in the formation of dark blue crystals of $Ni(S_2PMe_2)_2$. It was also observed that even under reflux, no reaction

Fig. 2.8

^1H n.m.r. spectrum of $[Ni(S_2PMe_2)_2(PMePh_2)]$



occurred with the less basic triphenylphosphine (cf. the reaction of $Ni(S_2P\{OEt\}_2)_2$ with PPh_3).[68]

Similar reactions with $Ni(S_2COEt)_2$ were also carried out. Again reaction occurred immediately on mixing a CH_2Cl_2 suspension of $Ni(S_2COEt)_2$ with an excess of the tertiary phosphine L (L = $PMePh_2$, PMe_2Ph). However it proved to be much more difficult to isolate complexes from these reactions, because of the high solubility of the products and the apparent facile dissociation processes resulting in the formation of starting material and free tertiary phosphine. Hence, in the case of the dimethylphenylphosphine reaction, only oils were obtained (cf reaction of $Ni(S_2P(OR)_2)_2$ with $^nPBu_3$ gives $Ni(S_2P(OR)_2)_2PBu_3$ as stable purple oils which could not be recrystallised),[70] but for methyldiphenylphosphine a dark orange red solid was isolated which analysed closely for the 1:2 adduct (see Table 2.3). However at this point in time Zagal and Costamagna[71] published their results on the reactions of excess tributylphosphine with nickel (II) xanthates (see Section 2.2) and so work in this area was discontinued.

At this juncture, no explanation for this difference in behaviour of $Ni(S_2PMe_2)_2$ and $Ni(S_2COEt)_2$ towards phosphorous donor Lewis bases can be offered although other investigators have found analogous behaviour.[68,70,71].

2.4.1 Experimental

Microanalyses were by the University of Edinburgh Chemistry Department. Molecular weights were determined on a Hitachi Perkin Elmer vapour pressure osmometer (model 115) calibrated with benzil. Infrared, electronic and ^1H n.m.r. spectra, conductivity measurements and melting points were obtained as described in Chapter 1. Proton noise-decoupled ^{31}P spectra were recorded on a Jeol FX60 spectrometer operating in the pulse and Fourier transform modes at 24.21 M Hz (^{31}P chemical shifts quoted in ppm to high frequency of 85% H_3PO_4). Solution magnetic moments (Evans's method)[76,80] were obtained on a Varian Associates HA100 spectrometer and magnetic susceptibilities (solid) were measured on a Faraday balance at Dundee University.

Monothiobenzoic and monothioacetic acids (Aldrich), triphenylphosphine, (BDH) dimethylphenylphosphine and methyldiphenylphosphine (Maybridge Chemical Co.) were obtained as indicated. The compounds Na[SOCPh],[35] $Ph_2PCH_2PPh_2$,[49] $Ph_2P[CH_2]PPh_2$,[50] $[\{Ni(SOCPh)_2 0.5\ EtOH\}_2]$[42] $[\{Ni(SOCMe)_2 0.5\ EtOH\}_2]$[42] were prepared as described earlier.

Analytical data, characteristic i.r. bands and magnetic moments for various complexes are given in Table 2.1, ^1H and ^{31}P-$\{^1H\}$ n.m.r. data in Table 2.2. Reactions involving tertiary phosphines were carried out under a nitrogen atmosphere.

General Method of Preparation of [Ni(SOCR)$_2$L$_2$] and [Ni(SOCR)$_2$-(L-L)]Complexes:- The appropriate nickel (II) monothiocarboxylate compound was suspended in ethanol and treated with a 5 to 10 fold excess of an ethanolic solution of the monodentate ligand L. The resulting mixture was then gently warmed with stirring for 1 hour. On removal of some solvent, the product precipitated out in some instances. If not, precipitation was initiated by addition of light petroleum (bp 60-80°C). These products were filtered off, washed with light petroleum (bp 60-80°C) and dried *in vacuo* at 40°C. For the bidentate ligands (L-L) the molar ratio of ligand to complex used was 2:1 to help prevent complete displacement of the monothiocarboxylate groups.

For the preparation of $[\{Ni(SOCR)_2(AsPh_3)\}_n](H_2O)_n$, after reaction as above, the solution was reduced in volume and then stored at 253K for 5 days. At the end of this period, the reddish-brown products had precipitated out and these were dried as above. In all cases yields were between 60 and 90%.

The preparation of $[\{Ni(SOCMe)_2(C_5H_5N)\}_n]$ was carried out as before, and on addition of light petroleum the red-brown product precipitated out (Melson *et al*[42] reduced the solution to a minimum volume then stored at 0°C for 12 hours to obtain green crystals of the bis adduct).

General Method of Preparation of $Ni(S_2PMe_2)_2L$ and $Ni(S_2COEt)_2(PMePh_2)_2$ Complexes

The appropriate nickel (II) 1,1-dithiolate was suspended in methylene chloride and to this was added a 6 to 10 fold excess of the tertiary phosphine dissolved in methylene chloride. The resulting mixture was then stirred at room temperature of 1 hour. The solvent was then removed under vacuo to a minimum volume and a small amount of hexane added. The resulting mixtures were then sealed in flasks under nitrogen and stored at $-20^{o}C$ for 2-3 days, whereupon some product had precipitated out. Yields were between 35 and 55%.

2.4.2. Magnetic Measurements by the Evans's method

Many years ago it was found[76,80] that the position of a peak in the proton resonance spectrum of a molecule depends on the bulk susceptibility of the medium in which the molecule is situated. It was found that for an inert substance in the bulk solution, the shifts caused by paramagnetic ions are given by the theoretical expression,

$$\Delta H \neq H = (2\pi/3)\Delta k$$

where Δk is the change in the volume susceptibility. Thus, a simple method of measuring the paramagnetic susceptibilities of substances in dilute solutions was available. To obtain magnetic moments in solution in these studies the following procedure was employed. The solvent used was methylene chloride containing ca 2% tetramethylsilane as an inert reference and a sealed capillary containing the same solvent and concentration of tetramethylsilane was also made. A known quantity of the paramagnetic compound to be examined was then dissolved in 2 mls of the solvent and this was placed in an n.m.r. tube along with the sealed capillary. The spectrometer was "locked on" to the bulk solvent (methylene chloride) and the separation of the peaks from the methyl groups of the tetramethylsilane in bulk solvent and capillary were measured. Separate peaks were observed because of the difference in the volume susceptibilities of the two solutions, with the line from the more paramagnetic solution lying at higher frequencies. The gram magnetic susceptibility, χ_g, of the dissolved paramagnetic substance was then determined using the following expression:-

$$\chi_g = \frac{3\Delta f}{2\pi f m} + \chi_o + \frac{\chi_o(d_o - d_s)}{m}$$

where:- Δf is the frequency separation between the two lines measured in Hz; f is the frequency at which the proton resonances are being studied in Hz; m is the mass of the substance contained in 1 ml of solution and χ_o is the gram susceptibility of the solvent. The last part of the expression relates to the densities of the solvent and solution and for highly paramagnetic substances can be neglected without serious error.

In all measurements, values for diamagnetic correction factors were obtained from Modern Coordination Chemistry by Lewis and Wilkins.[81] The experimental molar susceptibility χ_m was then calculated since $\chi_m = \chi_g.M.$ (where M = molecular weight of the compound studied) and finally the effective magnetic moment of the complex (μ eff) was determined by use of the equation

$$\mu eff = 7.98 \times 10^2 [\chi_M T]^{\frac{1}{2}}$$

Complex	Colour	Mp (θc/°C)	Analyses (%)[a] C	H	N	M^c	Infrared bands(cm^{-1}) ν_{CO}	ν_{CS}	μ_{e}
$Ni(SOCPh)_2 0.5C_2H_5OH]_2$	Maroon	176-177	50.8(50.6)	3.7(3.6)	-	-	1508s	958vs	3.3
$Ni(SOCPh)_2(C_5H_5N)_2]$	Green	186-187	58.5(58.7)	4.1(4.1)	5.7(5.7)	365(490)	1600s	960vs	2.9 (3.
$Ni(SOCPh)_2(4\text{-}MeC_5H_4N)_2]$	Green	202-203	60.3(60.1)	4.7(4.6)	5.4(5.4)	431(519)	1610vs	965vs	(3.4
$Ni(SOCPh)_2(bipy)]$	Green	117-118	58.7(58.9)	3.7(3.7)	5.8(5.7)	-	1600s,1570w	960s	(3.
$Ni(SOCPh)_2(PPh_3)_2]$	Orange	154	68.7(68.4)	4.6(4.6)	-	317(877)	1590s,1570s	910vs	dia
$Ni(SOCPh)_2(PMePh_2)_2]$	Dark Red	151	65.3(65.5)	4.8(4.9)	-	-	1580s,1550vs	915s	dia
$Ni(SOCPh)_2(PMe_2Ph)_2]$	Red	157-159	59.3(59.1)	5.2(5.3)	-	417,634[e](609)	1590s,1560s	900vs[f]	dia
$Ni(SOCPh)_2(Ph_2PCH_2PPh_2)]$	Orange	160	65.2(65.3)	4.5(4.5)	-	-	1590m,1560w	910w	-
$Ni(SOCPh)_2(Ph_2P\{CH_2\}_2PPh_2)]$	Orange	180	65.5(65.7)	4.6(4.7)	-	760(731)	1580s,1555s	910s	-
$Ni(SOCPh)_2AsPh_3]_n(H_2O)_n$	Red-Brown	169-171	57.7(59.0)	3.9(4.1)	-	(too insoluble)	1510vs	950vs	-
$Ni(SOCMe)_2 0.5C_2H_5OH]_2$	Black	150(decomp)	25.6(25.8)	3.7(3.9)	-	-	1540s	975s	3.
$Ni(SOCMe)_2(4\text{-}MeC_5H_4N)_2]$	Dark Green	95(decomp)	48.8(48.6)	5.1(5.1)	7.0(7.1)	-	1610s	960(s)	(3.
$Ni(SOCMe)_2(bipy)]$	Green	140-150(decomp)	46.7(46.0)	3.9(3.8)	8.0(7.7)	-	1590s,1560m	965(s)	(2.
$Ni(SOCMe)_2(PPh_3)_2]$	Red-Orange	144-145(decomp)	65.3(65.5)	4.9(4.9)	-	265(733)	1600(vs)broad	940(s)	dia

Complex	Colour	mp (θc/°C)	C	H	N	M[c]	ν_{CO}	ν_{CS}	μ
$[Ni(SOCMe)_2(PMePh_2)_2]$	Red Orange	153(decomp)	59.2(59.1)	5.2(5.3)	-	362.(609)	1600vs	940(s)	di
$[Ni(SOCMe)_2(PMe_2Ph)_2]$	Red Orange	122-123	49.6(49.5)	5.8(5.8)	-	-	1600vs	938(s)	di
$[Ni(SOCMe)_2(Ph_2PCH_2PPh_2)]$	Dark red	130-132(decomp)	58.5(58.7)	4.7(4.7)	-	580(593)	1610vs(broad)	940(s)	di
$[Ni(SOCMe)_2(Ph_2P\{CH_2\}_2PPh_2]$	Orange yellow	201-203	59.1(59.3)	4.9(4.9)	-	-	1590(vs)(broad)	945(s)	-
$[Ni(SOCMe)_2AsPh_3]_n(H_2O)_n$	Dark red	135(decomp)	49.6(49.3)	4.1(4.3)	-	too insoluble	1605vs	970(s)	2
$[Ni(SOCMe)_2Py]_n$	Dark red	145(decomp)	37.6(37.5)	4.0(3.8)	4.9(4.9)	too insoluble	1565vs	705vs	

[a] Calculated values given in parentheses. [b] Magnetic moment measured by Faraday method (solid) at 295K; in parentheses, as measured by Evans' method in CH_2Cl_2 at 301K. [c] Osmometrically at 37°C in acetone; calculated values for monomer are given in parentheses. [d] Value taken from ref. 4; calculated per dimer. [e] Higher value measured on more concentrated solution. [f] Partially masked by strong PMe_2Ph vibration at 900 cm^{-1}. [g] Calculated assuming n = 2.

Complex	T/K	^{1}H nmr (δ)[a] Me (monothioacetate)	 Me (phosphine)	 Ph	T/K	^{31}P- {^{1}H} nmr (δ)[b]
$[Ni(SOCPh)_2(PPh_3)_2]$	221	-	-	7.0-7.5(m)	221	24.1(s)
$[Ni(SOCPh)_2(PMe_2Ph)_2]$	271	-	1.61(s)	7.0-8.0(m)	271	-5.7(s)
	218[c]	-	1.55(t)[d]		218[c]	-4.7(s)
$[Ni(SOCPh)_2(PMePh_2)_2]$	271	-	2.05(s)	7.0-7.8(m)	263	9.0(v.broad)
	243	-	1.98(s)(broad)		243	9.7(s)
	210[c]	-	1.97(s)v.broad		210[c]	10.7(s)
$[Ni(SOCPh)_2(Ph_2P(CH_2)_2PPh_2)]$	301	-	2.20(m)broad[e]	7.0-8.0(m)	301	56.7(s)
	243	-	2.15(m)broad[e]		243	58.3(s)
$[Ni(SOCPh)_2(Ph_2P(CH_2)PPh_2)]$	301	-	3.41(m)(broad)[f]	7.1-7.8(m)	-	-
$[Ni(SOCMe)_2(PMe_2Ph)_2]$	301	2.04(s)	1.63(s)	7.2-7.8(m)	233	−5.3(s)
$[Ni(SOCMe)_2(Ph_2P(CH_2)PPh_2)]$	301	2.06(s)	3.66(m)broad[f]	7.2-8.0(m)	223	26.1(s)

s = singlet, t = triplet, m = multiplet

[a] ±0.01 ppm

[b] ±0.05 ppm

[c] In CD_2Cl_2

[d] $|^{2}J(PH) + ^{4}J(PH)|$ 7.50Hz

[e] C_2H_4 resonance

[f] CH_2 resonance

Table 2.3

Analytical data for some nickel (II) dithioacid Complexes

	Analysis[a]	
	C	H
$i(S_2PMe_2)_2(PMePh)]$	41.1 (41.9)	4.9 (4.8)
$i(S_2PMe_2)_2(PMe_2Ph)]$	33.2 (32.2)	5.2 (5.1)
$i(S_2COEt)_2(PMePh_2)_2]$	53.9 (54.8)	5.1 (5.1)

alculated values given in parentheses

CHAPTER 3

REACTIONS OF $MCl_2(C_8H_{12})$ (M = Pd,Pt) COMPLEXES WITH Na[SOCPh] AND REACTIONS OF THE PRODUCTS WITH LEWIS BASES

3.1 Introduction

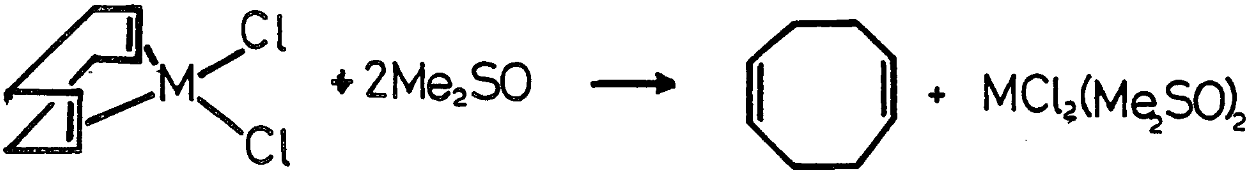
Over the past twenty years the reactions of nucleophiles with diene complexes of palladium and platinum (II) have attracted a great deal of attention mainly because of the importance of palladium-olefin[82,83] complexes in industrial olefin oxidation reactions.[84,85] During this period, reactions with dioxo- and, more recently, dithio-acid ions have been described but no studies with the corresponding monothio acid anions have been reported. For this reason, the reactions of Na[SOCPh] with MCl_2(1,5COD) (1,5COD = 1,5-cyclooctadiene; M = Pd,Pt) have been studied and these are discussed fully in this chapter. Some reactions of the products with various Lewis bases are also described. As in chapters 1 and 2, the aim of this work was to compare the structures and reactivities of these products with these of the previously established dioxo- and dithio-acid complexes.

Before discussing these results a short section outlining published reactions of nucleophiles in general with MX_2(diene) compounds is presented. This is followed by a more detailed account of the reactions of MX_2(diene) compounds with some sulphur and oxygen containing nucleophiles.

3.2.1 Reactions of MX_2(diene) complexes with nucleophiles in general

The reactions of MX_2(diene) complexes with nucleophiles can be divided into three groups:-[86]

a) The nucleophiles displace the diene. This is, in general, the favoured reaction with neutral nucleophiles especially soft (class b) ones with a high tendency to complex with the metal e.g. PR_3, C_5H_5N, Me_2SO etc. (see equation [8] and [9]). The platinum complexes usually react more slowly.



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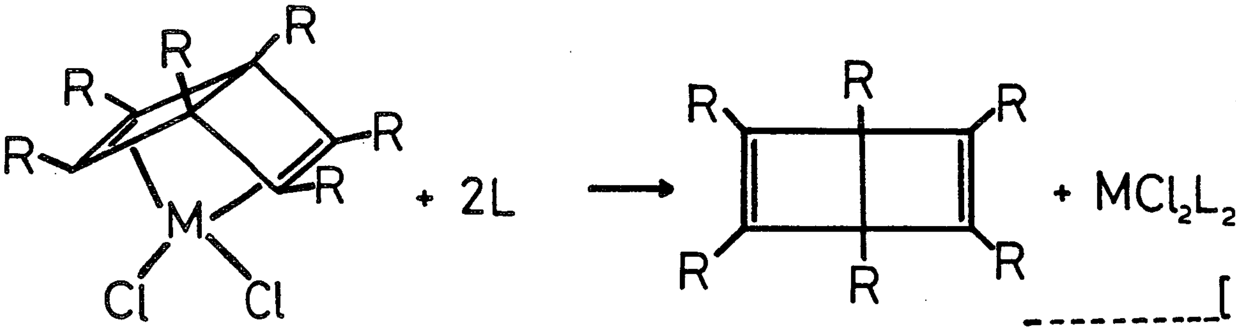
[8]

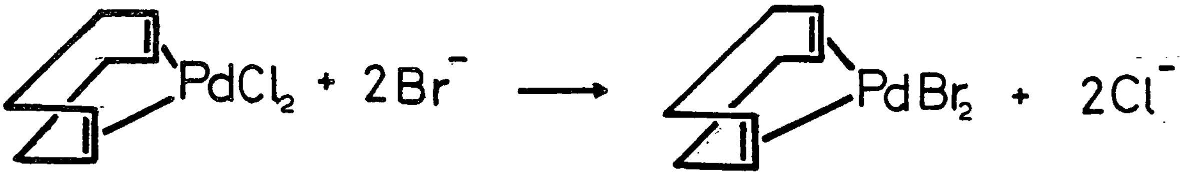


88, 89

[9]

($R=H,Me$; $L=PPh_3$, C_5H_5N)

b) Anionic nucleophiles such as halides, alkyl ions and $C_5H_5^-$ generally displace the anionic ligands. (See equations [10] and [11]).



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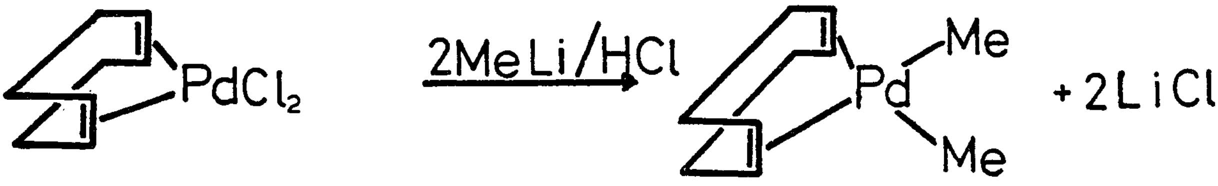
[10]



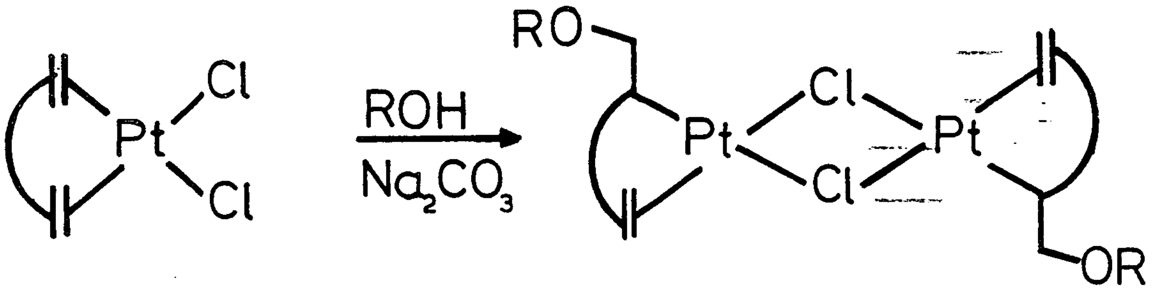
91

[11]

A large number of compounds of the type MR_2(cod) have been prepared by reaction of MX_2(cod), (X = I, Cl) with either MeLi or a Grignard reagent.[92] The subsequent displacement of a diene group from $Pt(Me)_2$(cod) by a Lewis base L,[93] (L = isocyanide, PR_3, 2,2'-bipyridyl, $AsMe_3$ etc.) then provides a useful route to complexes of the type cis $Pt(Me)_2L_2$.

c) The nucleophile attacks a carbon atom on the coordinated diene without displacement of the diene group. The first reaction of this type was reported in 1908 by Hofmann and Von Narbutt[94] who showed that dicyclopentadiene reacted slowly in alcohols with $K_2[PtCl_4]$ to give two types of product of empirical formulae $PtCl(ROC_{10}H_{12})$ and $PtCl_2(C_{10}H_{12})$ from ROH (R = Me,Et) and n-propanol respectively. They concluded that the first product was formed by addition of an RO^- ion and the PtCl group to a carbon-carbon double bond.

In 1957, this work was re-examined by Chatt et al[90,95] who showed that $PtCl_2$(diene) complexes reacted in basic alcoholic media to generate a dimeric complex containing both metal-ene and metal-alkyl linkages (equation [12]).

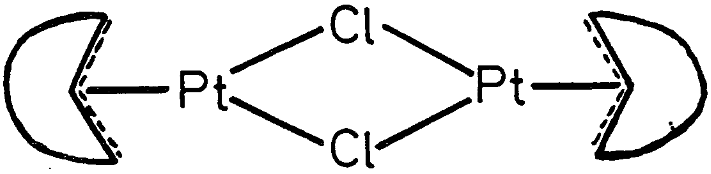


[12]

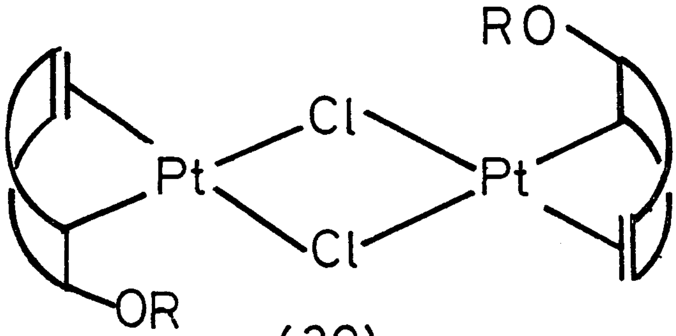
Since that date, reactions of a large number of nucleophiles such as hydroxide,[96] alkoxides,[90,87,98,99] carboxylates,[100-102] carbanions[103-105] and amines[99,105,106] with platinum (II) and palladium (II) diene complexes have been examined.

It has been proposed in all cases to date on the basis of spectroscopic data,[97,107,108] that the nucleophile attacks the double bond of the diene at an exo position resulting in the trans addition of the metal and nucleophile across the double bond. This suggestion has been verified by an X-ray structural analysis by Powell et al[109] on the methoxy-endo-dicyclopentadiene platinum (II) complex. The fact that attack occurs exo to the metal strongly indicates that initial attack on the metal followed by insertion of the carbon-carbon double bond into the metal-OR bond is not a very likely mechanism of formation.

The X-ray study by Powell et al[109] also excludes the possibility of an η^3-allyl structure (29) and confirms structure (30).

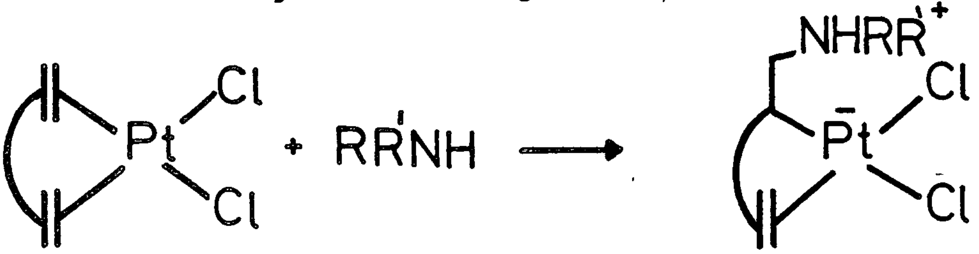


(29)

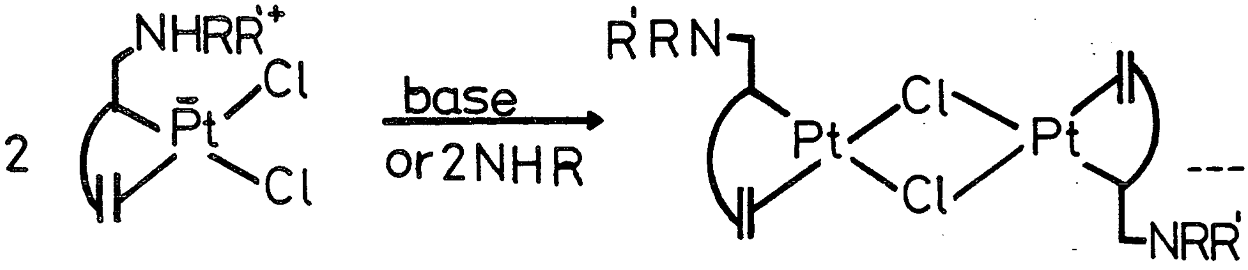


(30)

Paiaro et al[106] reported reactions of diene complexes of platinum (II) with NH_3, primary, secondary and tertiary amines. It was found that with more flexible dienes (e.g. 1,5-hexadiene and 4-vinylcyclohexene), monomers were obtained and could be isolated (equation [13]). Reaction with base or an equimolar amount of the same (or different) amine then resulted in elimination of HCl and formation of a chloride bridged dimer (equation [14]).



------[13]

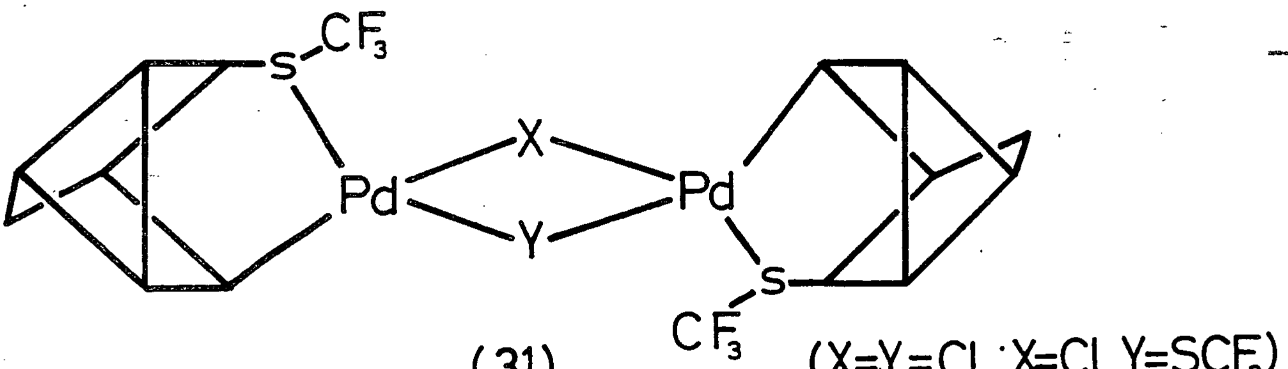


-----[14]

However, on reaction of platinum (II) complexes containing more rigid dienes (e.g. 1,5COD, norbornadiene) no monomeric complexes were isolated. This suggests that the initially formed species reacts with the amine more rapidly than does the diene starting material and a bridged dimeric complex is obtained. Therefore, more than an equimolar amount of amine was required for the complete reaction of the diene complex. It was suggested that for less rigid diene complexes only, intramolecular interactions between the amino group and the platinum atoms are possible. This interaction involving a hydrogen of the amine molecule and the non-bonding electron density of the metal is thought to be responsible for the higher stability of the monomer here.

3.2.2. Some reactions of oxygen and sulphur containing nucleophiles with MX_2(diene) complexes.

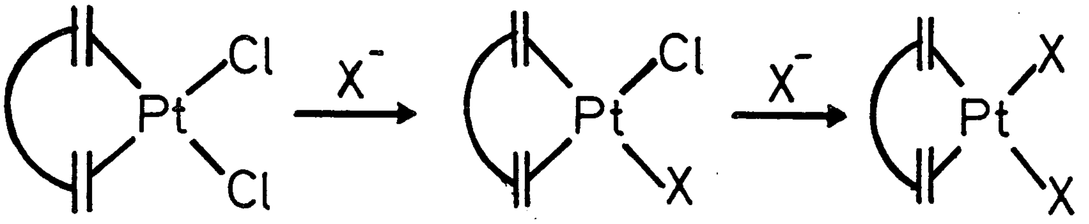
The first reported reaction of a sulphur containing nucleophile with an MCl_2 (diene) complex was by King and Efraty[110] in 1971 when they reacted MCl_2 (C_7H_8) with Ag[SCF_3]. For M = Pt, displacement of both chloride ions by $^-SCF_3$ groups occurred to give the while crystalline compound $Pt(SCF_3)_2(C_7H_8)$. However, the analogous reaction for M = Pd resulted in addition of SCF_3 groups to the norbornadiene ligand to give two products $[\{Pd(C_7H_8.SCF_3)\}_2]Cl_2$ and $[\{Pd(C_7H_8.SCF_3)\}_2]Cl.(SCF_3)$, shown by ^1H n.m.r. spectroscopy to be nortricyclyl derivatives (31).



(31)

The tendency for palladium (II) but not platinum (II) to undergo this type of reaction is most probably due to the lability of Pd-alkene bonds relative to Pt-alkene bonds.

More recently, Haszeldine _et al_[111] have published the results of the reactions of $PtCl_2$(diene), (diene = dicyclopentadiene; norbornadiene) with ^-SCN and ^-SPh nucleophiles. In the region of $PtCl_2(C_7H_8)$ with ^-SCN or ^-SPh, nucleophilic attack occurred _only_ at the _site_ of the metal and not at the coordinated diene (equation [15]).

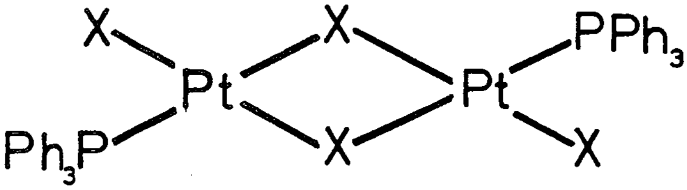


......[15]

(32)

(X=$^-$SCN, $^-$SPh)

Reaction of compound (32) with PPh_3 then resulted in complete displacement of the diene and formation of the thio-bridged complexes (33).

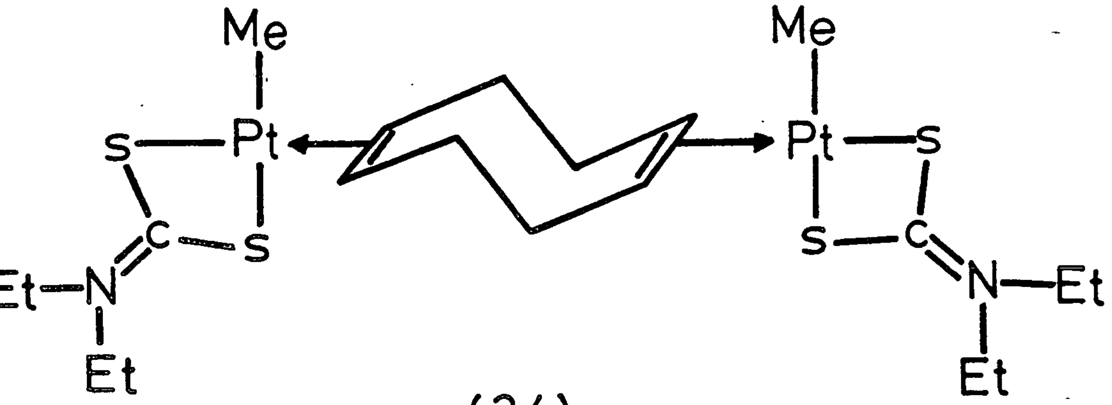


(33) (X=$^-$SCN, $^-$SPh)

In contrast, $PtCl_2(C_{10}H_{12})$ reacted with two molar equivalents of $^-$SCN or $^-$SPh to give products in which nucleophilic attack at both the metal and the diene had occurred i.e. $[\{Pt(alkenyl.X)X\}_2]$ (alkenyl = $C_{10}H_{12}$; X = $^-$SCN, $^-$SPh) was formed. When X = $^-$SCN, it was found by infrared studies that the organic substituent is bonded through nitrogen. This complex then reacted with PPh_3 without loss of the alkenyl ligand to give Pt(alkenyl.NCS)(SCN)PPh_3. However, the $^-$SPh derivative did not react with PPh_3.

Manzer et al prepared complexes of the type [Pt(diene)(Me)(solv)]PF_6 (solv = acetone,MeOH,THF) by reaction of Pt(diene)(Me)Cl with $AgPF_6$.[112] Treatment of [Pt(diene)(Me)(MeOH)]PF_6 with an equimolar amount of $NaS_2CNEt_2.3H_2O$ then gave an insoluble yellow product of probable structure

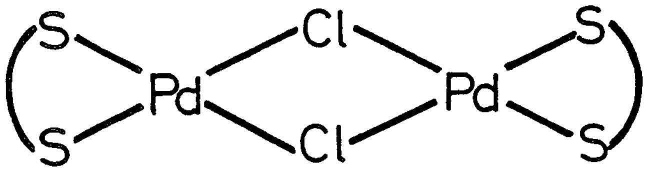
(34). Reaction of (34) with PPh_3 or $AsPh_3$ readily gave the



(34)

soluble neutral complexes $PtMe(S_2CNEt_2)L$ (L = PPh_3,$AsPh_3$).

Finally, Cornock and Stephenson[113] have made an extensive study of the reactions of $MCl_2(cod)$ (M = Pd,Pt; cod = 1,5 cyclooctadiene) with equimolar amounts of various alkali metal dithioacid salts Na(S-S) ($S\text{-}S^-$ = $^-S_2CNEt_2$, $^-S_2COEt$ and $^-S_2PMe_2$). When M = Pd, they found that the chlorobridged dimers $[\{PdCl(S\text{-}S)\}_2]$ (35) could be isolated.



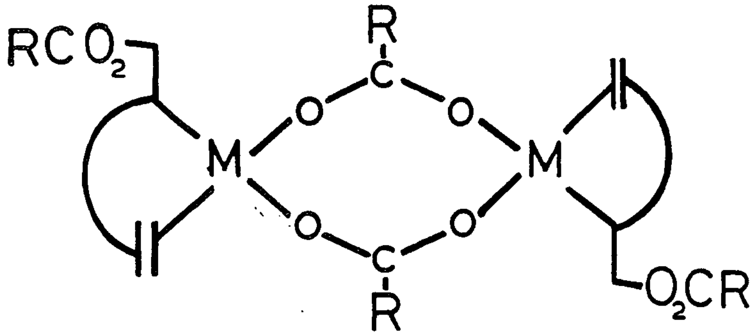
(35)

Also metathetical reactions of these gave the corresponding $[\{PdX(S_2CNEt_2)\}_2]$ (X = Br^-,^-SPh). Reaction of (35) with Lewis bases readily gave the monomeric neutral complexes PdCl(S-S)L (L = PPh_3; $S\text{-}S^-$ = $^-S_2CNEt_2$, ^-SCOEt, $^-S_2PMe_2$; L = $AsPh_3$, $SbPh_3$, C_5H_5N; $S\text{-}S^-$ = $^-S_2CNEt_2$), whereas reactions with MCl/HCl gave the ionic species $M[PdCl_2(S_2CNEt_2)]$ (M = Ph_4As^+, $Ph_3PhCH_2P^+$).

In contrast, reaction of $PtCl_2(C_8H_{12})$ and $NaS_2CNEt_2.3H_2O$ (1:1 molar ratio) gave $[\{PtCl(S_2CNEt_2)\}_2C_8H_{12}]$ (with a similar structure to (34)) which reacted with PPh_3 (1:1 molar ratio) to give $PtCl(S_2CNEt_2)PPh_3$, and with excess PPh_3 to give $[Pt(S_2CNEt_2)(PPh_3)_2]Cl.H_2O$ (2).

A study of the reactions of a range of MCl_2(diene) complexes with silver carboxylates (acetate, monofluoro- and monochloroacetate; benzoate) was made by Haszeldine and co-workers.[101] The complexes were characterised mainly by infrared spectroscopy where it was possible to distinguish between ester, unidentate and bridging carboxylate groups.

It was found that with four exceptions, all the complexes were dimers, the exceptions being $Pt(O_2CR)_2$(diene) (diene = C_7H_8, R = CH_2Cl, CH_2F; diene = 1,5COD, R = CH_2F) and $Pt(O_2CCH_2F)(C_8H_{12})$. The dimeric complexes (36) showed both bridging and ester carboxylate groups, the benzoate (37) both ester and bidentate, and the other monomers (38) contained only unidentate groups.



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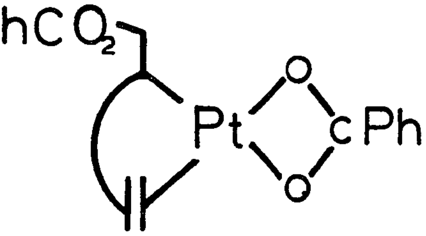

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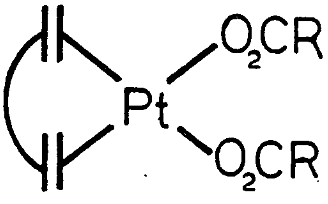
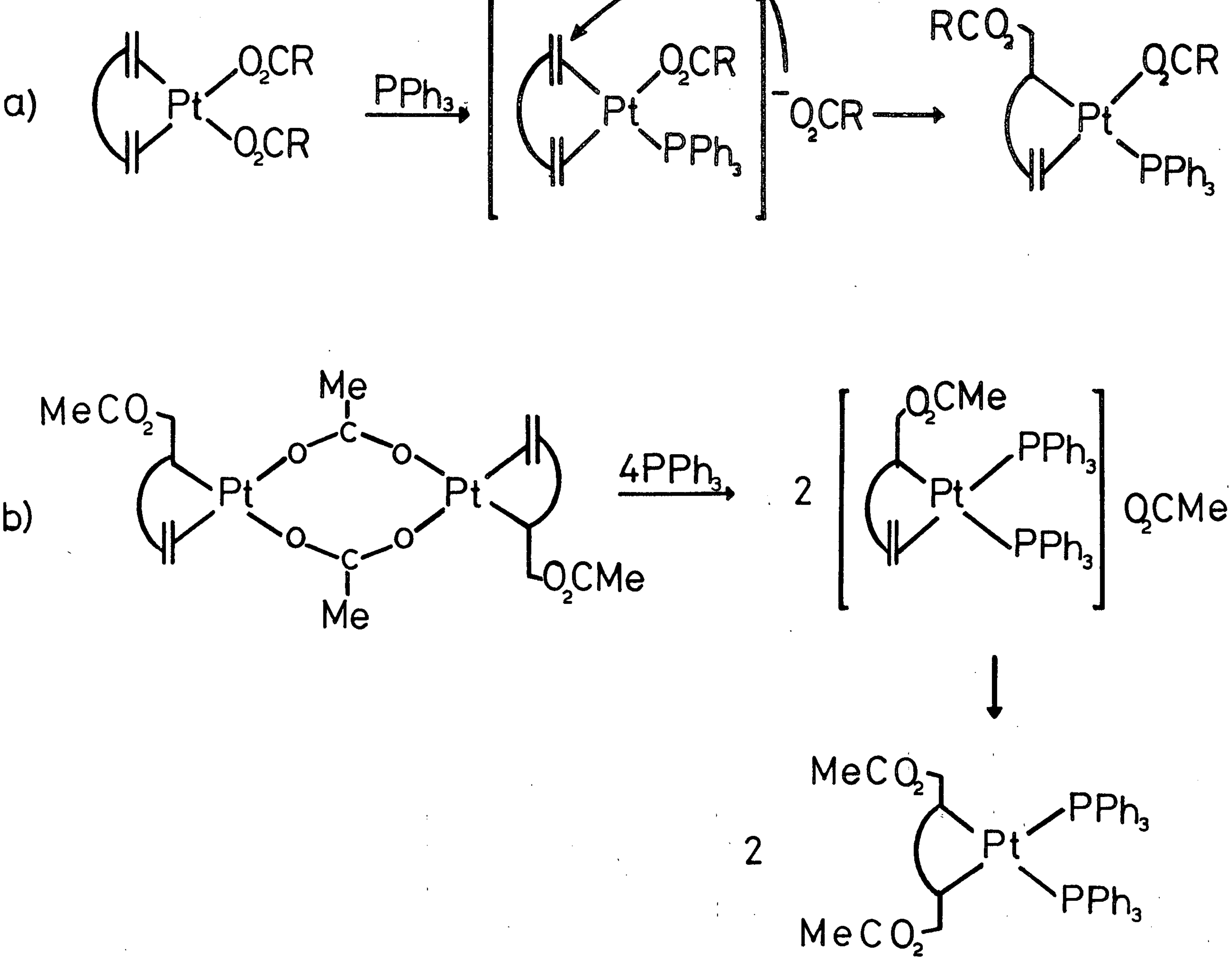


(38)

It was proposed that there is competition between nucleophilic attack at the coordinated double bond and at the metal. In the case of dicyclopentadiene and hexadiene, the configuration of the diene is strained and these systems react readily with all three carboxylates. Norbornadiene and 1,5 cyclooctadiene are less reactive since sterically they are better suited to chelation. The nucleophilicity of the carboxylate group is also an important feature, and is known to decrease in the order $CH_3CO_2^- > CH_2ClCO_2^- > CH_2FCO_2^-$. Hence a point is reached at which attack on the diene no longer occurs. Alkenes coordinated to palladium (II) however are generally more susceptible to nucleophilic attack and $[Pd(O_2CR)(RCO_2C_7H_8)]_2$ was formed with all three carboxylates.

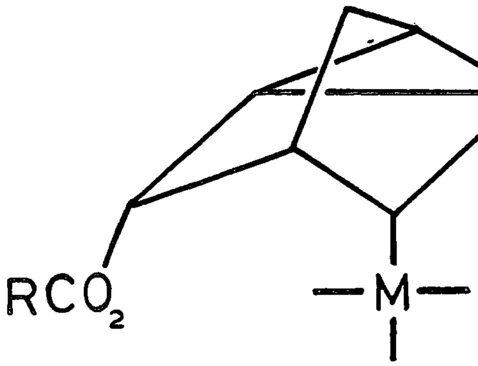
Reactions of these carboxylate complexes with tertiary phosphines were also reported. It was possible by this route to obtain platinum complexes where monochloro- or monofluoro-acetate groups had attacked the coordinated diene (see Scheme 3.1a) because the cation produced on reaction with PPh_3 was more susceptible to nucleophilic attack than is the neutral complex.

Similarily, addition of a 4-fold excess of PPh_3 to $[\{Pt(CH_3CO_2C_7H_8)(O_2CCH_3)\}_2]$ gave a product containing no acetate groups coordinated to the metal, but only acetoxy groups (see Scheme 3.1b). However, when the coordinated diene was norbornadiene, reaction with PPh_3 gave a dimeric product $[M(RCO_2C_7H_8)(O_2CR)PPh_3]_2$ in which the organic ligand had rearranged to a nortricyclene system (39).



Scheme 3.1

Reaction of a) $Pt(diene)(O_2CR_2)$ and b) $[Pt(alkenyl.\ O_2CMe)(O_2CMe)]_2$ with PPh_3



(39)

Lewis *et al*[104] also studied a series of metal carboxylates of general formulae [M(carboxycyclo-enyl)(OCOR)]$_2$ but placed greater emphasis on monitoring carboxylate exchange equilibria using the techniques of ^{1}H and ^{19}F n.m.r. spectroscopy. Thermodynamic parameters for the exchange of trifluoroacetic acid with other carboxylate moieties indicated that formation of the M-C bond is facilitated by electropositive substituents attached to the double bond.

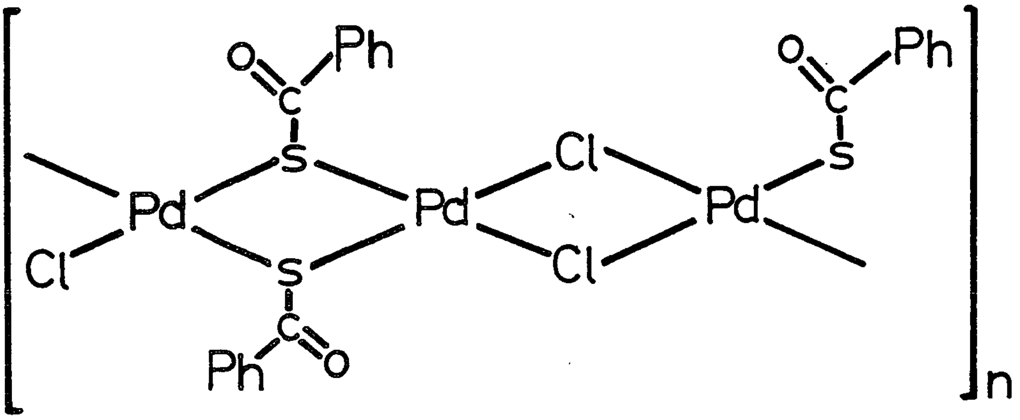
Finally, as mentioned earlier (section 3.2.1) there are numerous examples of reactions of MX$_2$(diene) complexes with unidentate oxygen nucleophiles and these all give complexes of type [M(diene-OR)X]$_2$. Furthermore, bridge splitting reactions of complexes of type [M(diene-OMe)X]$_2$ (M = Pd(II), Pt(II); diene = 1,5 cyclooctadiene, dicyclopentadiene; X = Cl,Br) by neutral ligands L (which contain nitrogen or phosphorus donor atoms) are reported to give M(diene-OMe)LX complexes.[114]

3.3 Results and Discussion

3.3.1 Reaction of $PdCl_2(C_8H_{12})$ with Na[SOCPh] (1:1 molar ratio)

Addition of an acetone solution of Na[SOCPh] to $PdCl_2(C_8H_{12})$ (C_8H_{12} = 1,5 cyclooctadiene) in dichloromethane (1:1 molar ratio) at ambient temperature gives a dark red solution and a precipitate of sodium chloride. Free 1,5 cyclooctadiene was also detected by its smell. However, after three to four minutes, the solution rapidly darkened and a black solid was deposited indicating that rapid decomposition of the initial product had occurred. If however, the reaction was carried out on a Schlenk line at 250 K using dried solvents and under dry nitrogen, an orange solid was obtained (see Experimental section for details). Once dried, this solid was completely air stable and elemental analysis showed it to have the empirical formula $[\{Pd(SOCPh)Cl\}_n]$. As discussed earlier,[113] Cornock <u>et al</u> made the analogous $[\{Pd(S_2CNEt_2)Cl\}_n]$ (35) (where n = 2) and then successfully reacted this with various Lewis bases to cleave the chloride bridges. However in that compound the dithio ligand was bonded in a bidentate manner, presumably because both donor atoms were soft in nature whereas in the monothiobenzoate group, there is a soft donor sulphur atom and a hard donor oxygen atom.

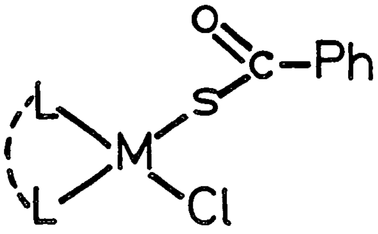
Infrared spectroscopic studies on $[\{Pd(SOCPh)Cl\}_n]$ revealed a band for $\nu(CO)$ at 1660 cm^{-1} and for $\nu(CS)$ at 865 cm^{-1} suggesting that the monothiobenzoate groups are coordinated in bridging fashion through the sulphur atoms only (see Chapter 1 for a full discussion). Since these bands were very similar in position to those found for the polymeric $[\{Pd(SOCPh)_2\}_n]$ (Chapter 1) and this compound also undergoes facile bridge splitting reactions with Lewis bases, a polymeric structure (40) was proposed. The presence of extra bands in the i.r. spectrum of (40) at 320 and 290 cm^{-1} compared to that of (16), supports the presence of MCl_2M bridging units (see refs 115 and 116). A similar compound containing alternative thiol and chloride bridges $[\{Pd(SPh)Cl\}_n]$ has previously been synthesised by reacting diphenyldisulphide with $Na_2[PdCl_4]$ in methanol or by refluxing $[\{Pd(S_2Ph_2)Cl_2\}_2]$ in methanol, and it has also been assigned a polymeric stucture.[117] Note that a molecular weight measurement on (40)



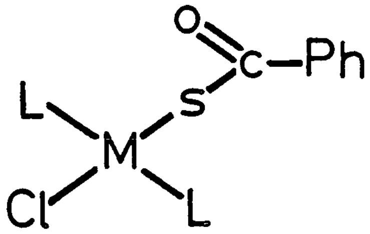
(40)

could not be obtained due to the low solubility of the compound.

Reaction of compound (40) with nitrogen and phosphorous containing Lewis bases in a 1:2 molar ratio led to cleavage of both the chloride and the monothiobenzoate bridges to give monomeric non-conducting complex $Pd(SOCPh)Cl(L)_2$ ($L = C_5H_5N$, 4-Me C_5H_4N, PPh_3, $PMePh_2$, PMe_2Ph). The infrared spectra of all these complexes show ν(CO) bands between 1550 and 1600 cm^{-1} and ν(CS) bands between 900 and 920 cm^{-1} (Table 3.1). The positions of these bands are indicative of strong M-S and weak M-O interactions (cf. Chapter 1). Furthermore, the ν(CO) bands are in similar positions to that found in <u>trans</u>-$Pt(PPh_3)_2H$ (SOCMe) (ν(CO) at 1595 cm^{-1}).[118] Finally, the electronic spectra of these complexes are analogous to those of other well established square-planar palladium and platinum (II) complexes, and this, together with molecular-weight measurements and the infrared evidence, suggests structures (41) and/or (42).



(41)



(42)

The $^{31}P-\{^1H\}$ n.m.r. spectra of the complex $Pd(SOCPh)Cl(L)_2$ (L = $PMePh_2$,PMe_2Ph) show only sharp singlets indicating that only the trans isomer is initially present (Table 3.2). Further support for this comes from the ^1H n.m.r. spectra which show a "virtually coupled" triplet pattern for the methyl resonances of the phosphine indicative of the trans structure.[44] It is interesting to note that there is little difference between the positions of the ^{31}P n.m.r. resonances in $Pd(SOCPh)Cl(L)_2$ [δ + 11.0($PMePh_2$) and -3.2(PMe_2Ph)] and $Pd(SOCPh)_2(L)_2$ [δ + 12.3($PMePh_2$) and -2.6 (PMe_2Ph)]. This is consistent with previous work on ^{31}P n.m.r. chemical shifts in which changes in the trans ligand produce much bigger effects than changes in the cis ligand.[119]

In the reaction of (40) with 2 moles of triphenylphosphine the following products were isolated; and characterised by i.r. and ^{31}P n.m.r. spectroscopy. The highly insoluble trans-$Pd(SOCPh)_2(PPh_3)_2$, trans-$PdCl_2(PPh_3)_2$ and trans-$Pd(SOCPh)Cl(PPh_3)_2$. Although trans-$Pd(SOCPh)Cl(PPh_3)_2$ could be isolated on dissolution into organic solvents it rapidly dissociated as shown in equation [16]. Presumably the insolubility of the bis(monothiobenzato)-compound here drives the equilibrium to the right hand side.

$$2[Pd(SOCPh)Cl(PPh_3)_2] \rightleftharpoons Pd(SOCPh)_2(PPh_3)_2 + Pd(Cl)_2(PPh_3)_2 \quad ....[16]$$

Even for $Pd(SOCPh)Cl(L)_2$ ($L = PMe_2Ph, PMePh_2$) which are virtually pure leaving for 2-3 days in solution gives small amounts of the bischloro- and bis(monothiobenzato)-complexes.

Structure (42) has been confirmed recently for $Pd(SOCPh)Cl(PMePh_2)_2$ by X-ray analysis (Fig. 3.1). Again it can be seen that there is no interaction between the oxygen of the monothiobenzoate group and the palladium atom i.e. Pd.....O 3.286(9)Å, (cf Chapter 1, <u>trans</u>-$Pd(SOCPh)_2(PMe_2Ph)_2$ Pd....O 3.313(3)Å). A list of bond lengths, angles and cell constants can be found in Table 3.3. Also in this molecule, the four ligands are coplanar and the palladium is not significantly out of the plane (cf. <u>trans</u>-$Pd(SOCPh)_2(PMe_2Ph)_2$ where symmetry constraints force coplanarity).

Similarly, reaction of $[\{Pd(SOCPh)Cl\}_n]$ with various bidentate Lewis bases (L-L) gave the monomeric non-conducting complexes Pd(SOCPh)Cl(L-L) (L-L = 2,2' bipyridyl, 1,10 phenanthroline, $Ph_2P(CH_2)_2PPh_2$) which must have the <u>cis</u> configuration (41).

Reactions of compound (40) with an excess of L($L = PPh_3$, C_5H_5N, $4MeC_5H_4N$) were found to yield the same products as were obtained from the reactions with only 2 moles of L. In contrast to this, the reactions with excess methyldiphenyl-

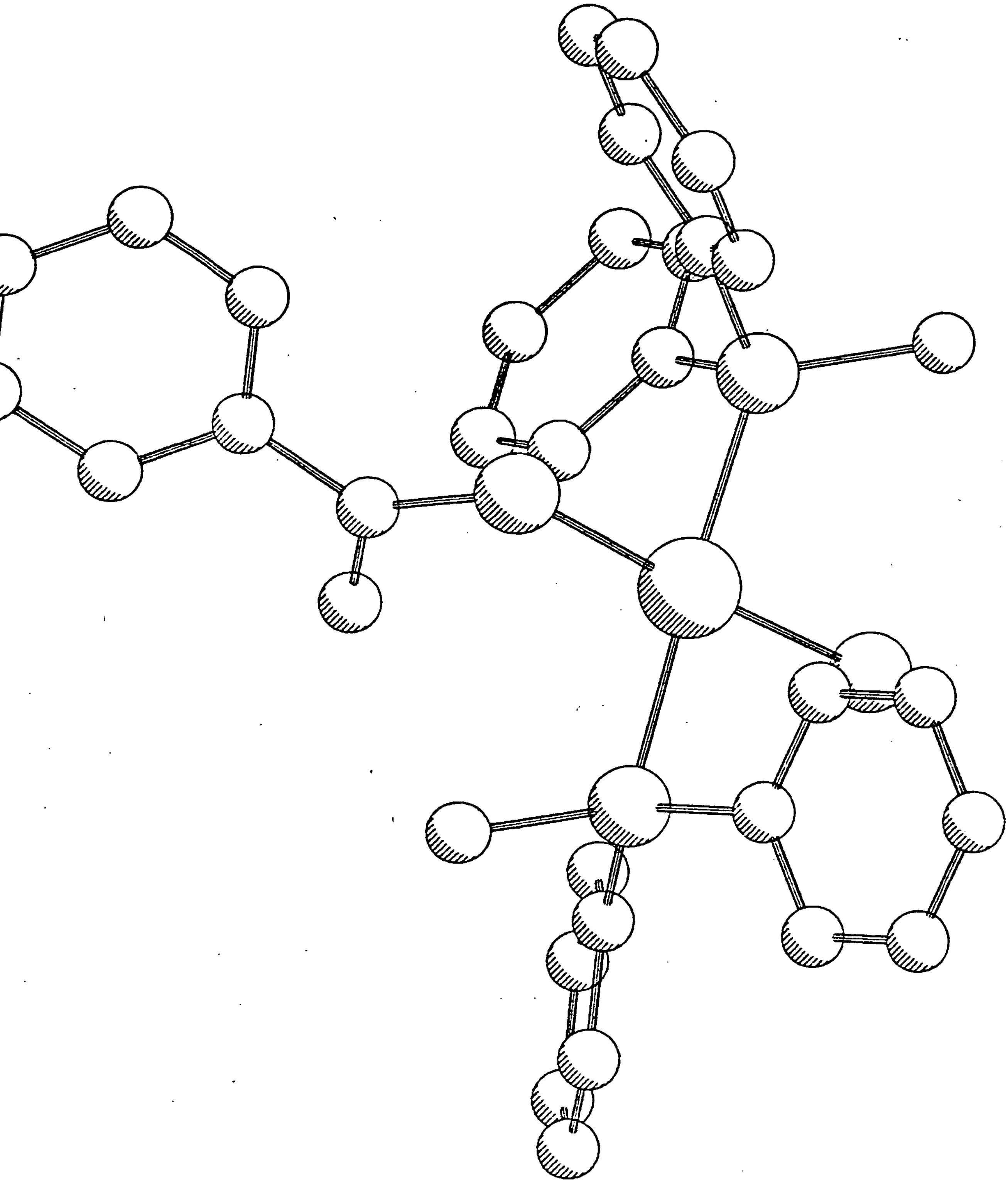
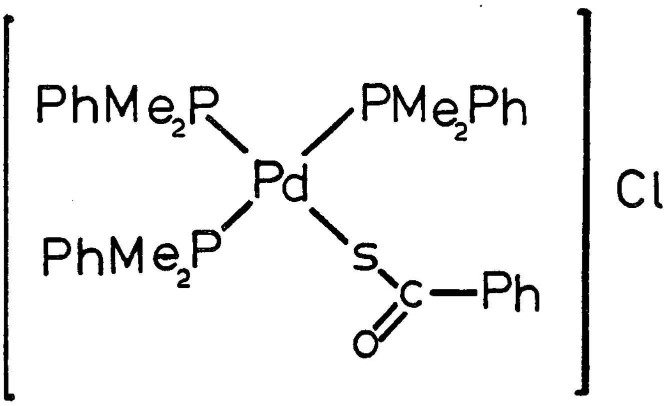


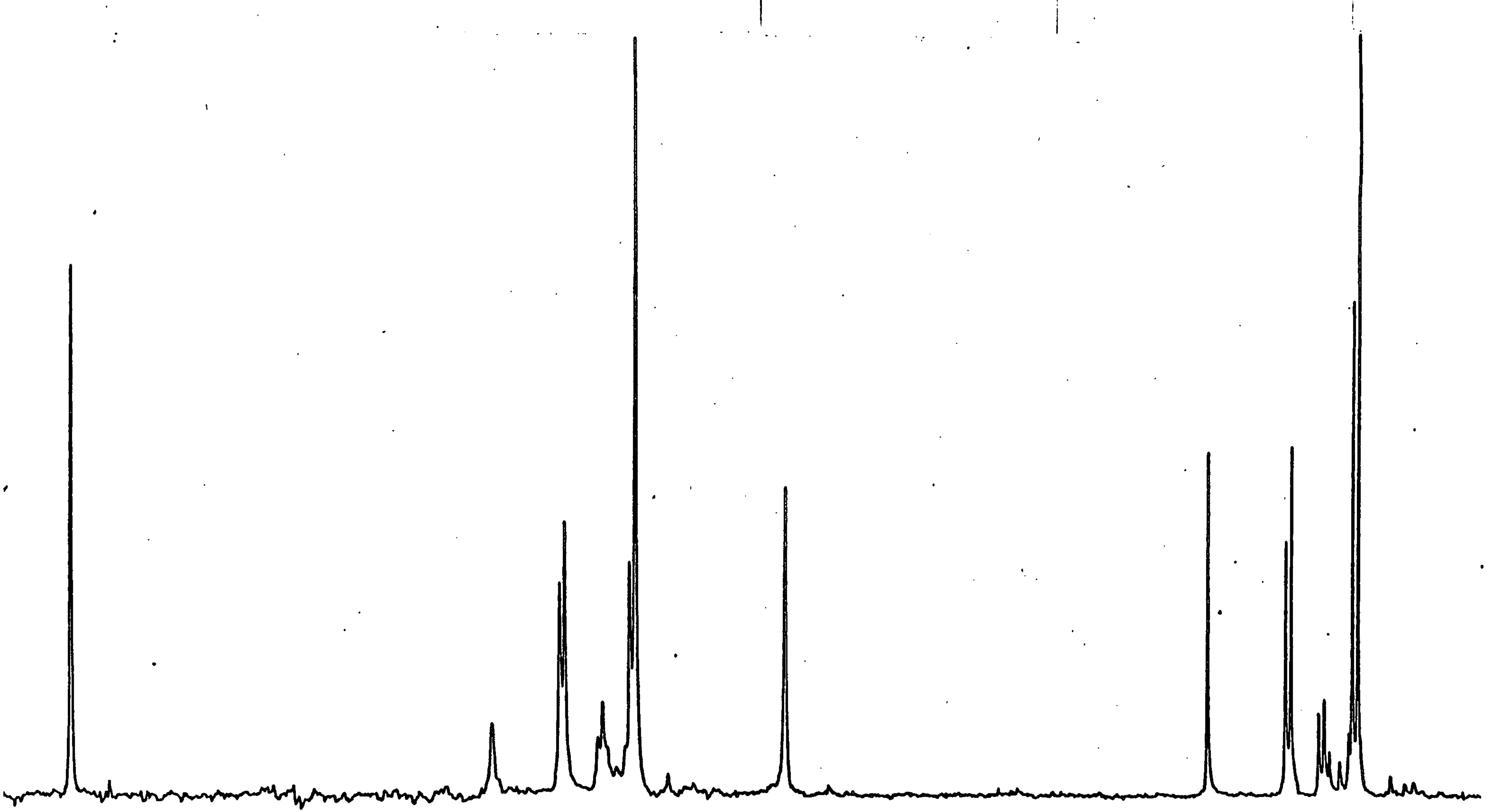
Fig. 3.1   X-ray structure of [Pd(SOCPh)Cl(PMePh$_2$)$_2$]

and dimethylphenyl-phosphine gave additional products. From the reaction with excess dimethylphenyl-phosphine, an orange-yellow solid was isolated and the $^{31}P-\{^{1}H\}$ n.m.r. spectrum of this material at 298 K showed two singlets at δ+34.1 and -2.5 ppm, the latter being very broad which suggests some form of exchange process is occurring in solution. A fresh sample was made up and a $^{31}P-\{^{1}H\}$ variable temperature n.m.r. study carried out. Starting at a temperature of *ca.* 203 K, the frozen-out spectrum was observed (Fig. 3.2a). This consisted of a singlet at δ+8.4 (assigned to ±$PdCl_2(PMe_2Ph)_2$), a singlet at δ-1.5 (assigned to ±-$Pd(SOCPh)_2(PMe_2Ph)_2$), and a singlet at δ-2.1 ppm (assigned to ±-$Pd(SOCPh)Cl(PMe_2Ph)_2$). In addition there was a doublet and triplet centred at δ+2.8 and +0.4 ppm respectively, assigned to the compound $[Pd(SOCPh)(PMe_2Ph)_3]Cl$ (43). Cations of type $[Pd(Cl)(PR_3)_3]^{+}$[120-122] are well known and show similar temperature variable n.m.r. behaviour to (43).



(43)

Thus, as the sample is warmed to 233 K, (Fig. 3.2b) the singlet due to *trans* $Pd(Cl)_2(PMe_2Ph)_2$ broadens and decreases in intensity, that arising from *trans* $Pd(SOCPh)_2(PMe_2Ph)_2$ also decreases in intensity whilst that from the mixed $Pd(SOCPh)Cl(PMe_2Ph)_2$ grows in intensity. At this temperature there is very little change in the resonances from the

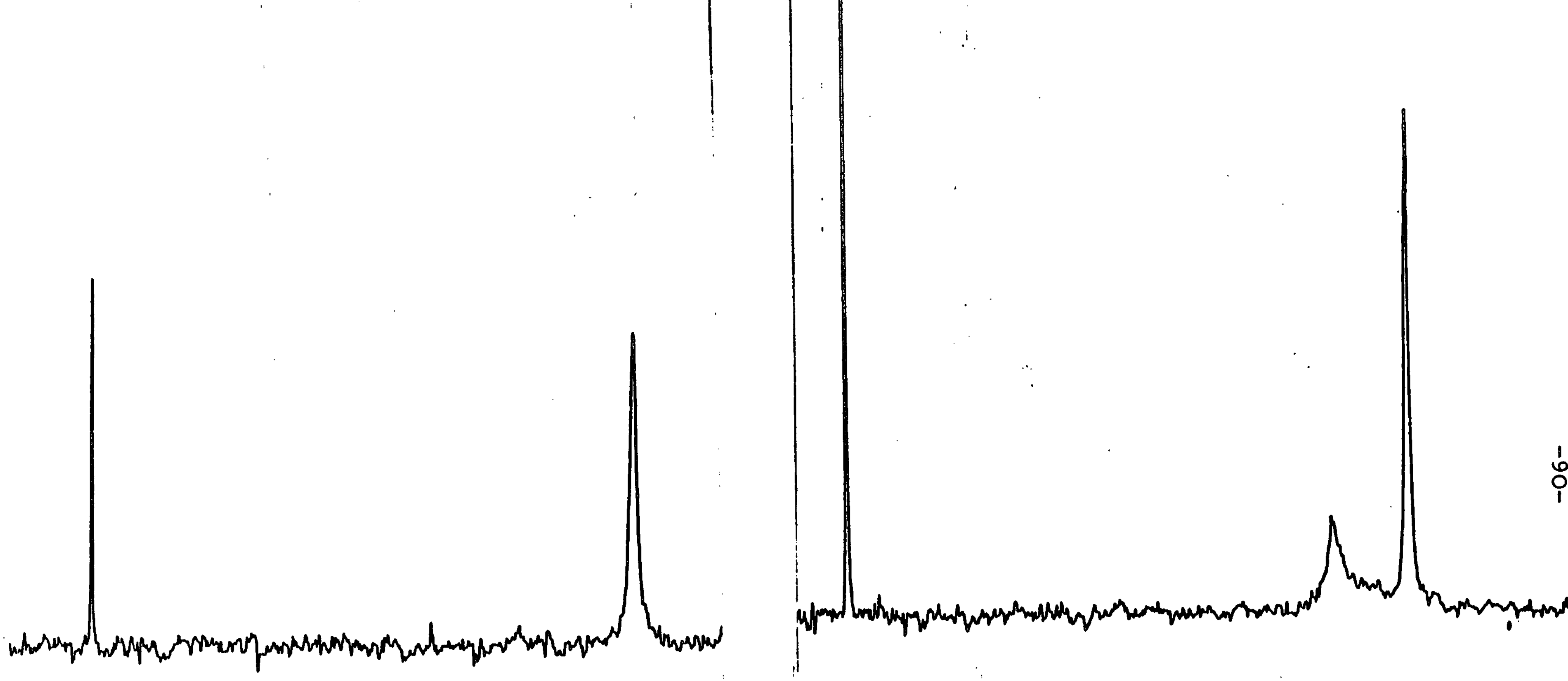


(b) 233 K

(a) 203 K

Fig. 3.2

$^{31}P-\{^1H\}$ n.m.r. spectrum of product isolated from the reaction of $[\{Pd(SOCPh)Cl\}_n]$ with a ten-fold excess of PMe_2Ph

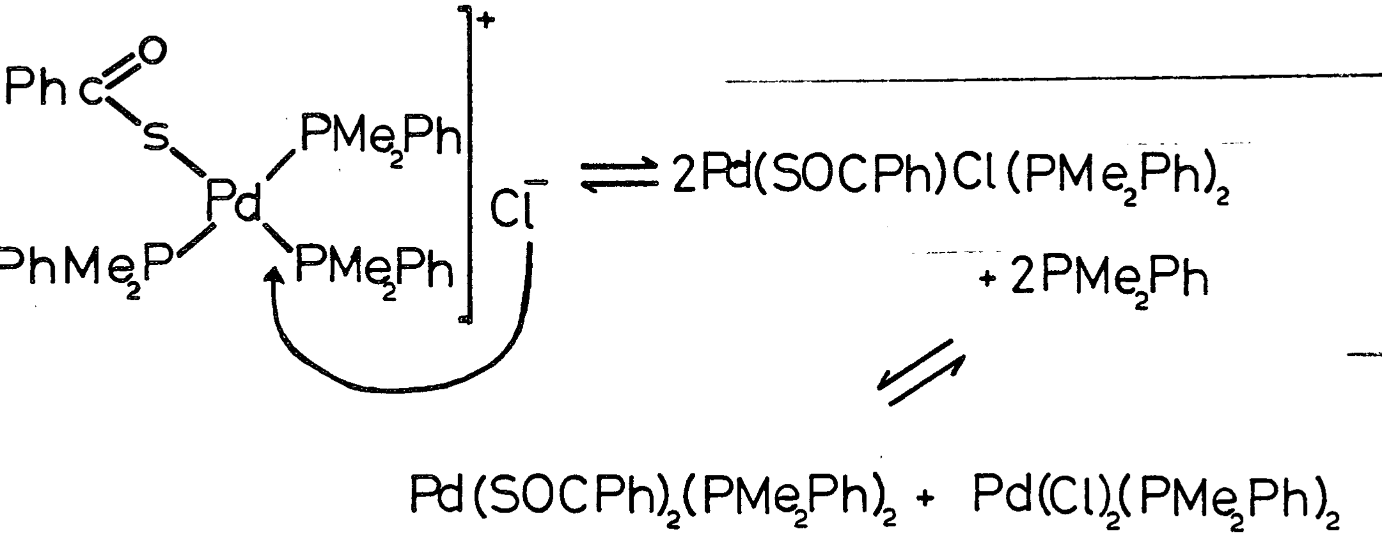


(d) 298 K

(c) 263 K

Fig. 3.2

$[Pd(SOCPh)(PMe_2Ph)_3]Cl$ complex apart from a slight broadening of the peaks. At 263 K, (Fig. 3.2c) the three singlets from the bisdichloro, the bismonothiobenzato and the chloromonothiobenzato complexes have collapsed into a broad singlet at -2.5 ppm indicative of the onset of a fast intermolecular process. The doublet and triplet pattern from the tris phosphine cation has also collapsed to a broad "hump" centred at 2.6 ppm. at 298 K, (Fig. 3.2d) all the peaks have collapsed to one broad singlet at -2.5 ppm indicating that facile exchange between all species in solution is occurring (eqn. 17). The singlet at +34.1 ppm (298 K) which moves only

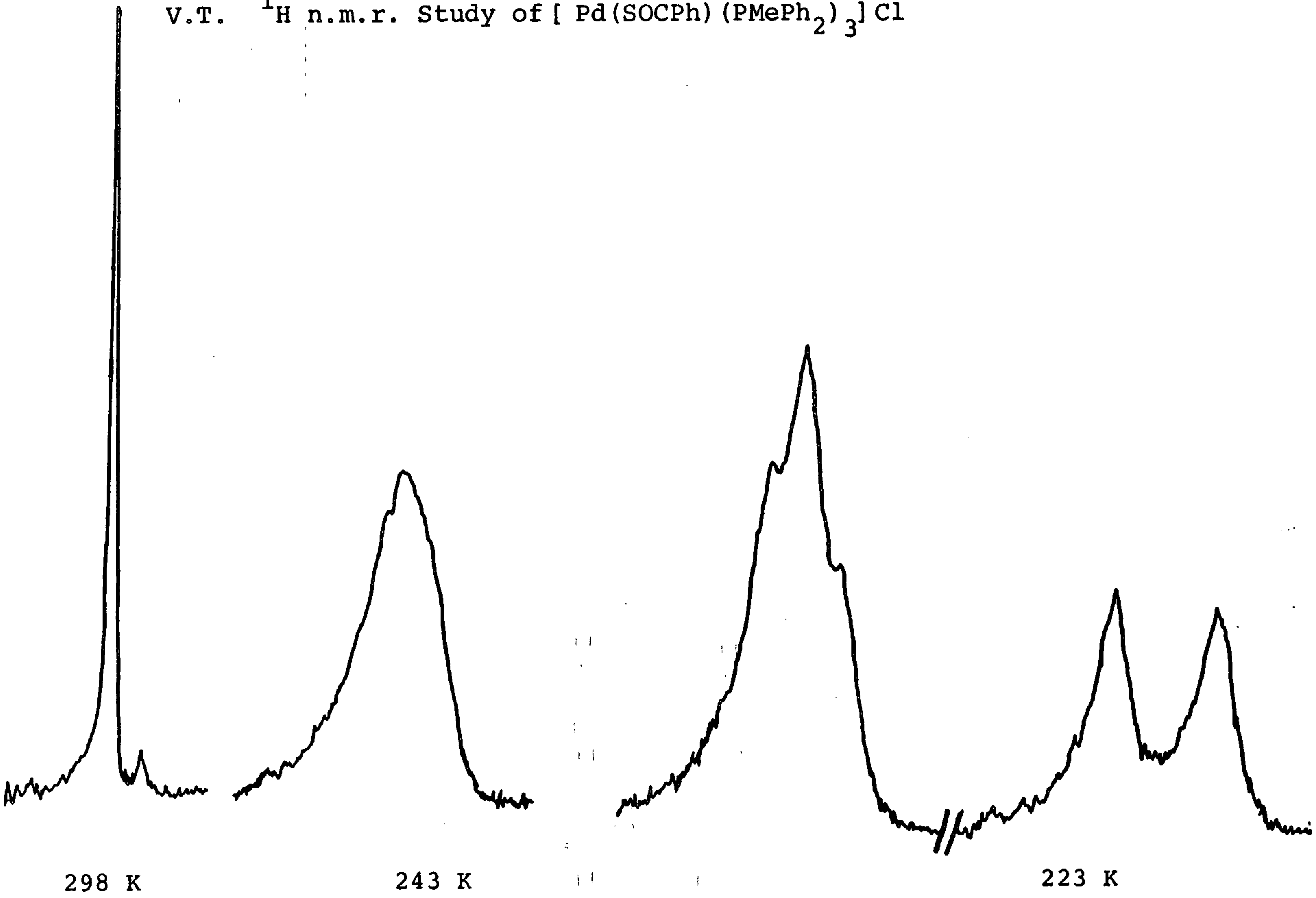


[17

slightly with temperature is assigned to the presence of some $OPMe_2Ph$ formed from the free PMe_2Ph present.

The analogous reaction with an excess of methyldiphenylphosphine also gives the orange cationic complex $[Pd(SOCPh)(PMePh_2)_3]Cl$. A variable temperature ^1H n.m.r. spectrum of this (Fig. 3.3) again reveals facile exchange processes

V.T. ^{1}H n.m.r. Study of [$Pd(SOCPh)(PMePh_2)_3$]Cl



at ambient temperature (broad singlet at 2.07 ppm) and a "frozen-out" spectrum at 223 K. The "frozen-out" spectrum consists of a "virtually-coupled" triplet centred at 2.61 ppm and a doublet at 1.94 ppm. This shows that only the $[Pd(SOCPh)(PMePh_2)_3]Cl$ is present in solution at this temperature If $Na[BPh_4]$ is added to this solution $[Pd(SOCPh)(PMePh_2)_3]BPh_4\ 2H_2O$ is precipitated and the ^1H nmr spectrum (Fig. 3.4) of this at 298 K shows a sharp "virtually-couplet" triplet centred at 1.81 ppm and a doublet at 1.22 ppm confirming structure (43). The weak resonance at 1.45 is assigned to a solvated water molecule (cf. $[Pt(S_2CNEt_2)(PR_3')_2]Cl$. The low temperature $^{31}P-\{^1H\}$ n.m.r. spectrum of $[Pd(SOCPh)(PMePh_2)_3]Cl$ also shows the expected doublet and triplet pattern (Table 3.2).

Reactions of $[\{Pd(SOCPh)Cl\}_n]$ with L (L = C_5H_5N, $PMePh_2$) in a 1:1 molar ratio have not been studied in great detail but preliminary results suggest that the chloride bridges are broken in preference to the monothiobenzoate bridges to form the complexes $[\{Pd(SOCPh)Cl\ L\}_2]$. Evidence for this comes from elemental analyses, and infrared data which show no bridging chloride stretches but still show ν(CO) and ν(CS) vibrations at 1670 and 870 cm^{-1} respectively. Furthermore the $^{31}P-\{^1H\}$ n.m.r. spectrum of the methyldiphenylphosphine complex contains a singlet at 20.4 ppm believed to be from a compound with structure (44). Belluco et al[114] also found that reaction of $[\{Pd(SPh)Cl\}_n]$ with L (1:1 molar ratio) (L = C_5H_5N,PPh_3,$AsPh_3$) gave sulphur bridged complexes $[\{Pd(SPh)LCl\}_2]$.

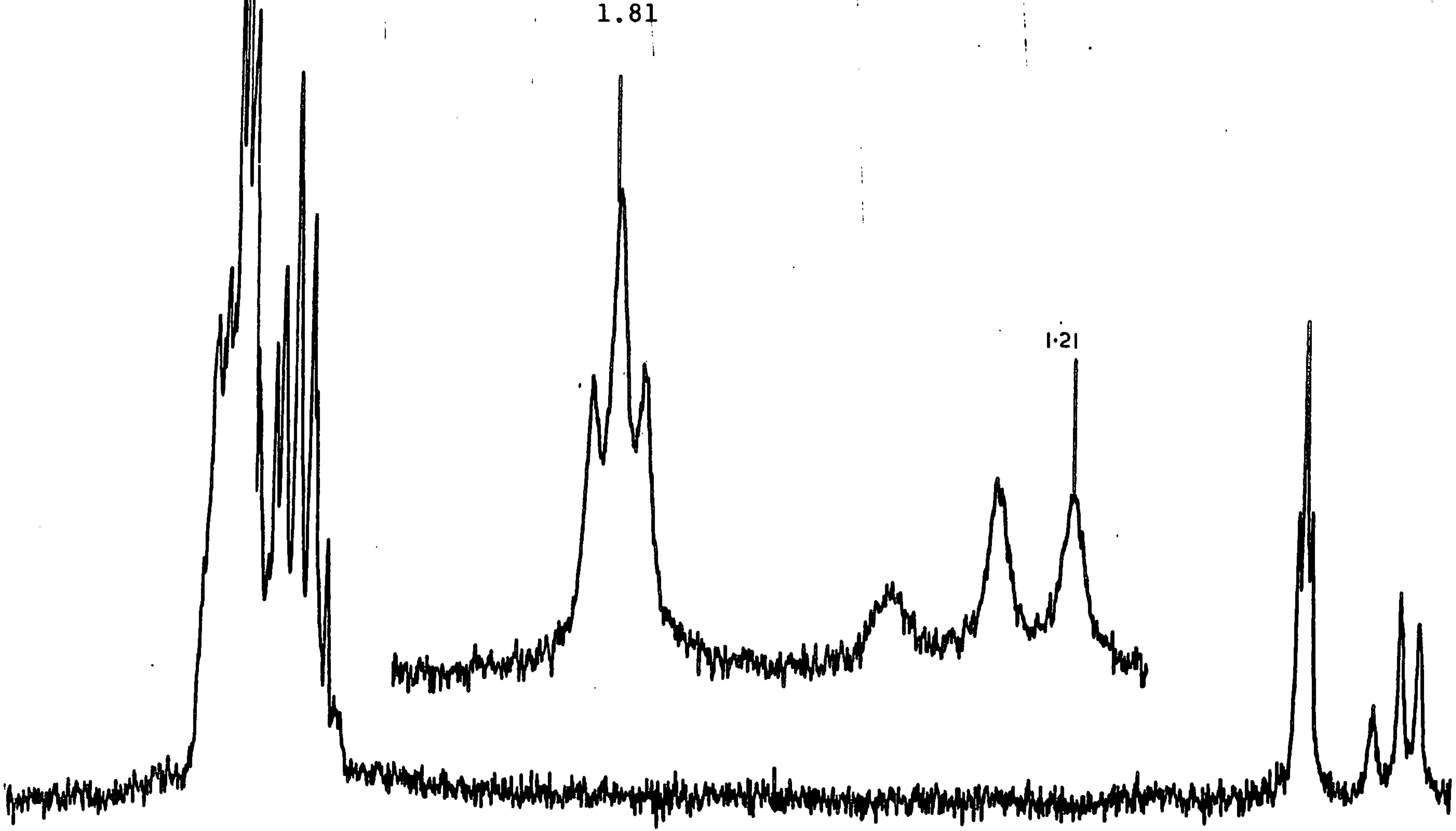
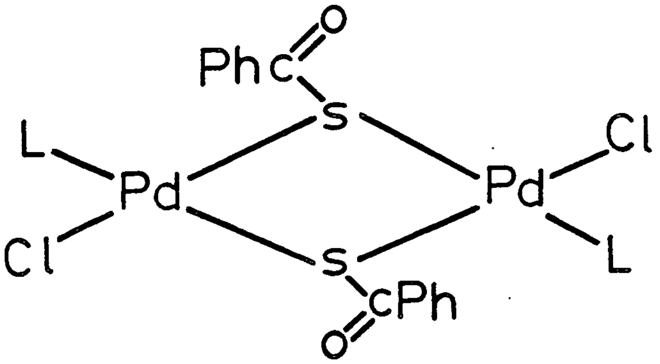


Fig. 3.4

^{1}H n.m.r. spectrum of [Pd(SOCPh)(PMePh)$_3$] BPh$_4$ at 298 K.



(44)

Finally, reaction of (44) (L = $PMePh_2$) with an excess of pyridine gave a yellow compound of empirical formula $Pd(SOCPh)Cl(C_5H_5N)(PMe_2Ph)$, and as would expected reaction of (44) (L = C_5H_5N) with 2 moles of PMe_2Ph gave $Pd(SOCPh)Cl(PMe_2Ph)_2$ where the pyridine had been displaced.

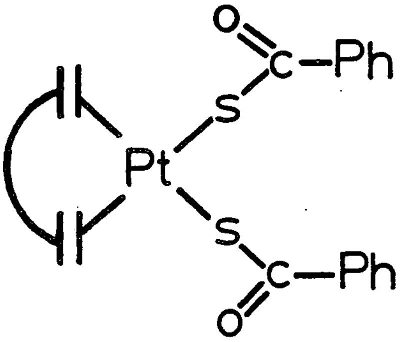
3.3.2 Reaction of $PdCl_2(C_8H_{12})$ with Na[SOCPh] (1:2 molar ratio)

Reaction of an excess or 2:1 molar ratio of Na[SOCPh] with $PdCl_2(C_8H_{12})$ was found to give the established $[\{Pd(SOCPh)\}_n]$ (see Chapter 1). This was confirmed by its infrared spectrum, melting point and by the products obtained on reaction with phosphorous and nitrogen containing Lewis bases.

3.3.3 Reaction of $PtCl_2(C_8H_{12})$ with Na[SOCPh] (1:2 molar ratio)

Reaction of the analogous $PtCl_2(C_8H_{12})$ in methylene chloride with Na[SOCPh] (1:2 molar ratio) dissolved in acetone gave a clear yellow solution and a precipitate of sodium chloride. No smell of free 1,5 cyclooctadiene was detected and on work-up, a pale sandy-coloured solid of empirical formula $Pt(SOCPh)_2(C_8H_{12})$ was obtained. The ^1H n.m.r.

spectrum of this compound confirmed the presence of both monothiobenzoate groups and coordinated diene, the integral of which showed that attack had not occurred on the diene. This information, together with the infrared spectrum which showed ν(CO) at 1620 and ν(CS) at 900 cm^{-1}, indicating terminal monothiobenzoate groups bonded only through sulphur, and a molecular-weight determination of 571 in acetone suggested structure (45). A test for chloride confirmed that this was not present.



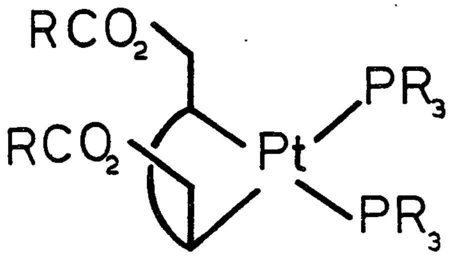
(45)

This behaviour is analogous to that found by King and Efraty[110] where reaction of $Ag[SCF_3]$ with $PtCl_2(C_7H_8)$ caused displacement of both chlorine atoms by SCF_3 groups to give $Pt(SCF_3)_2(C_7H_8)$. Similarly, it has been found that reaction of $PtCl_2(C_7H_8)$ with ^-SCN and ^-SPh ions gives only $Pt(X)_2(C_7H_8)$ ($X = {}^-SCN, {}^-SPh$).[111]

Therefore as noted earlier (Chapter 1), it would appear that the monothiobenzoate ion is again behaving as a pseudo thiol ligand rather than as a true bidentate ligand in these systems.

Reaction of compound (45) with phosphorous containing Lewis bases L (L = PMe_2Ph,$PMePh_2$,PPh_3) in either 1:2 or excess molar ratio readily gave the neutral monomeric complexes $Pt(SOCPh)_2L_2$. Although in the starting material (45) the monothiobenzoate groups were cis to one another, the ^1H n.m.r. spectra of $Pt(SOCPh)_2(L)_2$ (L = $PMePh_2$,PMe_2Ph) again showed the "virtually-coupled" triplet patterns indicative of trans isomers. The ^{31}P n.m.r. chemical shifts, $^1J_{Pt-P}$ coupling constants, ^1H n.m.r. data and melting points confirmed that the products obtained from these reactions are identical to those obtained by reaction of $[\{Pt(SOCPh)_2\}_n]$ with an excess of L (see Chapter 1). However, although reaction of $Pt(SOCPh)_2(C_8H_{12})$ with phosphorous containing Lewis bases readily gave the trans bis adducts, reactions with corresponding nitrogen containing Lewis bases such as pyridine at room temperature gave only starting materials on work-up.

This behaviour is in contrast to the previously reported reactions of $Pt(diene)(O_2CR)_2$ complexes (diene = C_7H_8, R = CH_2Cl,CH_2F; diene = 1,5 cod, R = CH_2F) with tertiary phosphines[101] where complexes (46), in which displaced carboxylate groups then attack the coordinated diene, are formed (see Scheme 3.1a). Presumably, the reason for this



(46)

difference is the inertness of Pt-S compared to Pt-O bonds with the result that the Pt-C bonds are preferentially broken by soft Lewis bases.

Reactions of compound (45) with various bidentate Lewis bases (L-L) gave the expected monomeric, non-conducting $Pt(SOCPh)_2(L-L)$ (L-L = 2,2'bipyridyl, $Ph_2P(CH_2)PPh_2$) complexes which must retain the cis configuration (18). This was confirmed by comparison of the ^{31}P chemical shifts, $^1J_{Pt-P}$ coupling constants, melting points and elemental analysis with those obtained in Chapter 1.

Although diene bridged complexes $[\{PtX(S_2CNEt_2)\}_2(C_8H_{12})]$ (34) (X = Me,Cl)[112,113] have been prepared, reaction of $Pt(SOCPh)_2(C_8H_{12})$ with stoichiometric amounts of L (L = PPh_3, PMe_2Ph) led only to the isolation of a mixture of $Pt(SOCPh)_2(L)_2$ and unreacted $Pt(SOCPh)_2(C_8H_{12})$. This was confirmed by thin layer chromatographic, $^{31}P-\{^1H\}$ n.m.r. and melting point studies.

Furthermore, reactions of $Pt(SOCPh)_2(C_8H_{12})$ with secondary amines HNR_2 (HNR_2 = $HNEt_2$, HN^+Pr_2) or alkoxides OR^- (OR^- = MeO^-) in an attempt to attack the diene without displacing it resulted only in isolation of starting materials on work-up. It should be noted that there have been no reports of nucleophilic attack on coordinated dienes bound to platinum (II) when the trans ligands are sulphur donors. One possible explanation for this may be that the sulphur ligands are donating electron density to the diene *via* π donation, making the diene less susceptible to nucleophilic attack.

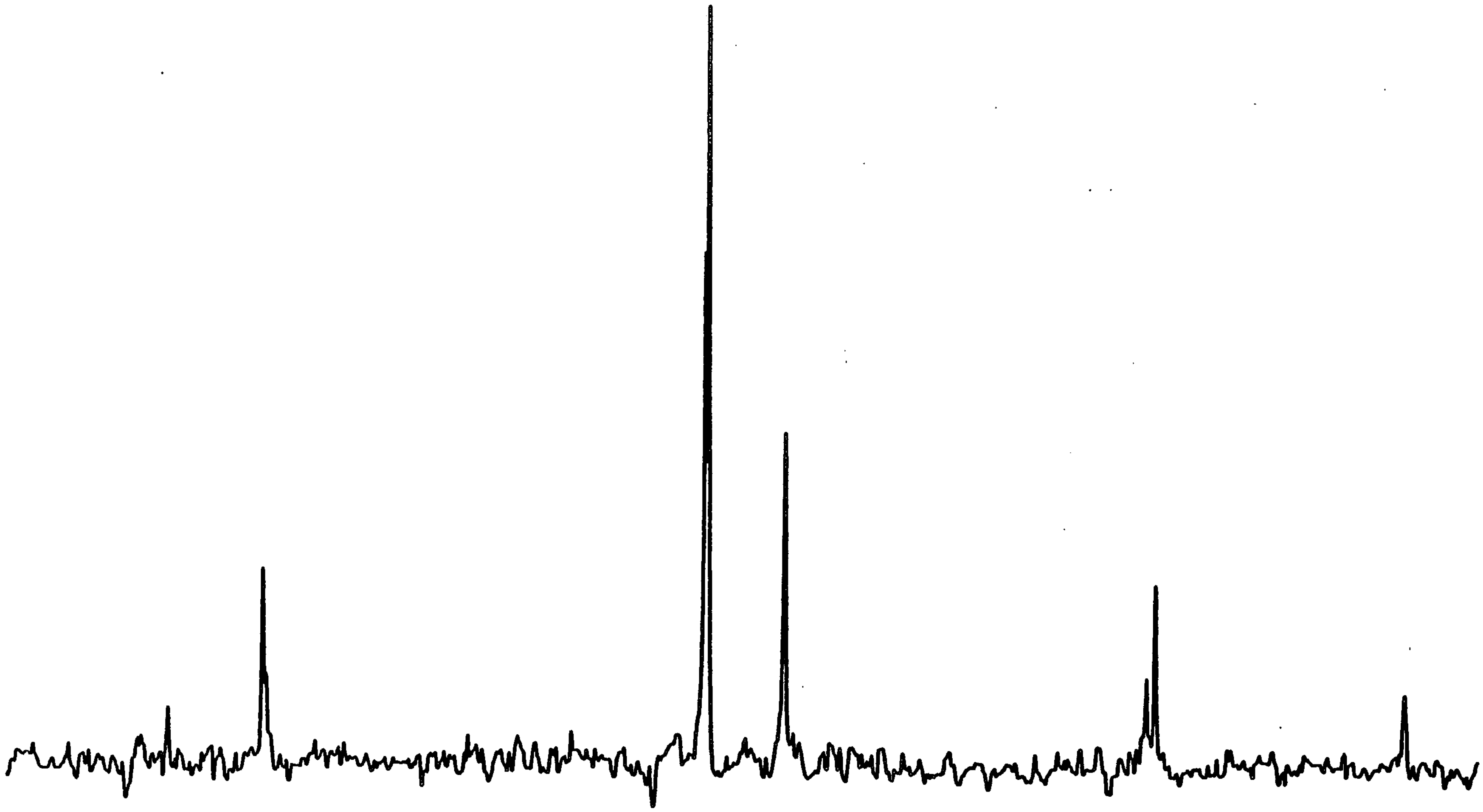
3.3.4 Reaction of $PtCl_2(C_8H_{12})$ with Na[SOCPh] (1:1 molar ratio)

Addition of an acetone solution of Na[SOCPh] to a stoichiometric amount of $PtCl_2(C_8H_{12})$ in dichloromethane again gave a pale yellow solution and a precipitate of sodium chloride. Once again no smell of free 1,5 cyclooctadiene was detected and this time the light brown solid isolated was found to be of empirical formula $Pt(SOCPh)Cl(C_8H_{12})$. However, a molecular-weight measurement of this compound in acetone was low (Found 210, required 475) suggesting that the product was probably either initially a mixture of $PtCl_2(C_8H_{12})$ and $Pt(SOCPh)_2(C_8H_{12})$ or that it was rapidly disproportionating to form these species when placed in solution. A melting point of the solid was reasonably sharp, suggesting that only one species was present initially and an ^1H n.m.r. spectrum of the compound appeared to be more complicated than a superposition of the spectra of $PtCl_2(C_8H_{12})$ and $Pt(SOCPh)_2(C_8H_{12})$. Also the mull infrared spectrum shows a few differences suggesting that it is not simply a composite spectrum of $PtCl_2(C_8H_{12})$ and $Pt(SOCPh)_2(C_8H_{12})$. Thus, on the basis of all of this data, it is believed that the product initially isolated is in fact $Pt(SOCPh)Cl(C_8H_{12})$ but on dissolution in organic solvents this disproportionates rapidly to form an equilibrium mixture of three complexes (see equation [18]), hence explaining the low molecular-weight value.

$$2Pt(SOCPh)Cl(C_8H_{12}) \rightleftharpoons Pt(SOCPh)_2(C_8H_{12}) + PtCl_2(C_8H_{12}) \quad \ldots[18]$$

Reaction of "$Pt(SOCPh)Cl(C_8H_{12})$" with phosphorous containing Lewis bases L (L = PPh_3,PMe_2Ph) in a 1:2 molar ratio gave off white to white coloured solids which analysed well for $Pt(SOCPh)Cl(L)_2$. However, as expected, the $^{31}P-^{1}H$ n.m.r. spectra of these products showed them to be mixtures. For L = PPh_3, two 1:4:1 triplets centred at δ+22.9 and +14.3 ppm with $^{1}J_{Pt-P}$ values of 2710 and 3672 respectively were found. These were assigned to trans-$Pt(SOCPh)_2(PPh_3)_2$ and cis-$PtCl_2(PPh_3)_2$ by comparison with the spectra of known pure samples of these compounds. No peaks which could be assigned to the mixed $Pt(SOCPh)Cl(PPh_3)_2$ were found here. However, when L = PMe_2Ph the $^{31}P-\{^{1}H\}$ n.m.r. spectrum showed three 1:4:1 triplets centred at δ-6.0, -6.4 and -15.5 ppm with $^{1}J_{Pt-P}$ values of 2524, 2544 and 3545 Hz, respectively (Fig. 3.5). The second and third resonances were assigned to trans-$Pt(SOCPh)_2(PMe_2Ph)_2$ and cis-$PtCl_2(PMe_2Ph)_2$ by comparison of known samples of these compounds and the 1:4:1 triplet centred at -6.0 ppm with a $^{1}J_{Pt-P}$ value of 2524 Hz was then assigned to the mixed chloromonothiobenzato complex trans-$Pt(SOCPh)Cl(PMe_2Ph)_2$. The same mixture of species was produced by reaction of "$Pt(SOCPh)Cl(C_8H_{12})$" with an excess of L. This is to be contrasted with the reactions of $[\{Pd(SOCPh)Cl\}_n]$ with excess $PMePh_2$ or PMe_2Ph (see section 3.3.1) which gave the compounds $[Pd(SOCPh)L_3]Cl$. The inability to form the corresponding platinum trisphosphine cations here is somewhat surprising since the related $[PtX(PR_3)_3]^+$ (X = Cl,H[47,121,123,124]) are well known.

Fig. 3.5 $^{31}P-\{^1H\}$ n.m.r. spectrum of "$[Pt(SOCPh)Cl(PMe_2Ph)_2]$"



Finally, reaction of "Pt(SOCPh)Cl(C_8H_{12})" with a stoichiometric amount of $Ph_2P(CH_2)_2PPh_2$ gave a product of stoichiometry "Pt(SOCPh)Cl($Ph_2P(CH_2)PPh_2$) but this was shown by $^{31}P-\{^1H\}$ n.m.r. spectroscopy to be a mixture.

3.4 Experimental

Microanalyses, i.r., ^1H n.m.r. spectra and melting points were obtained as described in Chapter 1. Molecular weights and $^{31}P-\{^1H\}$ n.m.r. spectra were obtained as described in Chapter 2. Analytical data and $^{31}P-\{^1H\}$ n.m.r. spectroscopic data for the compounds are given in Tables 3.1 and 3.2 respectively. Infrared bands diagnostic of the mode of coordination of the $^-$SOCPh groups are also given in Table 3.1.

Potassium tetrachloroplatinate (II), palladium (II) chloride, triphenylphosphine, dimethylphenylphosphine and methyldiphenylphosphine were obtained as indicated earlier. Sodium tetraphenylboron (BDH) and the compounds $PdCl_2(C_8H_{12})$,[90] $PtCl_2(C_8H_{12})$.[95] Na[SOCPh][35], $Ph_2P(CH_2)_2PPh_2$[50] were synthesised as described earlier.

3.4.1 Palladium Complexes

µ-Chloro-µ-monothiobenzato palladium (II)

$PdCl_2(C_8H_{12})$ (0.20g) was dissolved in methylenechloride in a Schlenk tube and to this was added an acetone solution of Na[SOCPh] (0.15g). Before mixing both samples were degassed and flushed with dry nitrogen several times. On mixing the solution turned red and a white precipitate of NaCl was deposited. The solution was stirred for 2 to 3 minutes and then filtered through celite. Solvent was removed under high vacuum, the sample being kept at a temperature of 250 K (CCl_4 slush bath). At a minimum volume a precipitate formed and precipitation was completed by the addition of degassed light petroleum (b.p. 60-80°C). The orange product was then filtered off, washed with light petroleum and dried under high vacuum in a desiccator over P_2O_5. All the work-up was done on a Schlenk line, but once isolated, the product was quite air stable (yield 70-80%) m.p. *ca* 100°C (decomp.).

General method of preparation of compounds $Pd(SOCPh)Cl(L)_2$

The easiest method of preparation was to make $[\{Pd(SOCPh)Cl\}_n]$ and then react it *in situ* rather than isolate it as a solid. For this reason, all the reactions described were with $[\{Pd(SOCPh)Cl\}_n]$ generated *in situ* and used within 1 to 2 minutes of its preparation. All the reactions here assume 100% yield of $[\{Pd(SOCPh)Cl\}_n]$ from the reaction of $PdCl_2(C_8H_{12})$ with Na[SOCPh] (which means *ca* 0.20 g of $[\{Pd(SOCPh)Cl\}_n]$ present in each reaction).

Bismethyldiphenylphosphinechloro/monothiobenzato palladium (II)

To a solution of $[\{Pd(SOCPh)Cl\}_n]$ (0.20 g) was added methyldiphenylphosphine (0.30 cm^3) dissolved in methylene chloride. On mixing, the solution turned bright yellow and after stirring for 1 hour was filtered through celite.

The clear yellow filtrate was then reduced to a small volume and diethylether slowly added until the solution just started to turn cloudy. The flask was then stoppered and left for 12 hours, after this time yellow crystals of the product had formed (yield 70%, m.p. 174°C). ^{1}H n.m.r. spectrum Me(phosphine) 2.6(†) Phenyl 7.0-8.0(m).

Bisdimethylphenylphosphine(chloro)monothiobenzato palladium(II)

This was prepared using the same method as for the methyldiphenylphosphine adduct, to give yellow crystals of the product (yield 60%, m.p. 130°C). ^{1}H n.m.r. spectrum Me(phosphine) 1.79(†) Phenyl 7.0-8.0(m).

Bistriphenylphosphine(chloro)monothiobenzato palladium (II)

Prepared as before using triphenylphosphine (0.36g) dissolved in methylene chloride. However on reducing the solution to a small volume, $PdCl_2(PPh_3)_2$ and $Pd(SOCPh)_2(PPh_3)_2$ precipitates out. This is filtered off and to the clear yellow filtrate is added diethyl ether until it just turns cloudy. The flask is then stoppered and after 12 hours yellow crystals of the product have formed (yield 60%, m.p. 215°C).

Bispyridine(chloro)monothiobenzato palladium (II)

To a solution of $[\{Pd(SOCPh)Cl\}_n]$ (0.20g) was added a slight excess of pyridine (0.15 cm^3) dissolved in methylene chloride. On mixing the solution turned yellow, and after stirring for a further hour it was filtered through celite.

The clear yellow filtrate was reduced to a minimum volume and on addition of light petroleum (b.p. 60-80°C), the yellow product precipitated out. The product was then filtered off, washed with light petroleum and dried under vacuo (yield 70% m.p. 120-123°C) (^{1}H n.m.r. spectrum 8.8-9.0(m) 7.0-8.0(m)).

Bis(p-methylpyridine)(chloro)monothiobenzato palladium(II)

This was prepared in the same manner as the pyridine adduct using p-MeC$_5$H$_4$N (0.20 cm^3) (yield 70%). ^{1}H n.m.r. spectrum Me(4-MeC$_5$H$_4$N) 2.34(5) 8.6-8.8(m) 7.0-8.2(m).

General method of preparation of Pd(SOCPh)Cl (L-L) complexes

To a solution of [{Pd(SOCPh)Cl}$_n$] was added 1 mole of L-L (L-L = 2,2'bipyridyl, 1,10 phenanthroline, Ph$_2$P(CH$_2$)$_2$PPh$_2$) dissolved in methylene chloride. In each case the solution slowly turned an orange-yellow colour. This was filtered through celite and the clear filtrate reduced to a minimum volume at which point the product precipitated out. The product was filtered off washed with light petroleum and dried under vacuo. Pd(SOCPh)Cl(Ph$_2$P(CH$_2$)$_2$PPh$_2$) (yield 80%, m.p. 208-209°C) Pd(SOCPh)Cl(2,2'bipyridyl) (yield 80%, m.p. ca. 240°C (decomp)). Pd(SOCPh)Cl(1,10 phenanthroline) (yield 80%, m.p. > 250°C).

Trismethyldiphenylphosphinemonothiobenzato palladium(II) chloride

To a solution of PdCl$_2$(C$_8$H$_{12}$) (0.18 g) in methylene chloride was added Na[SOCPh] (0.10 g) dissolved in acetone. On mixing a red solution of [{Pd(SOCPh)Cl}$_n$] was formed. This was stirred at 0°C for 2 minutes then excess methyldiphenylphosphine (0.5 cm^3) was added dropwise with stirring, and the solution turned orange-yellow. After stirring for a further 1 hour it was filtered through celite and the filtrate was reduced to a minimum volume to give a bright red solution. To this was added diethylether and the orange *product* precipitated out. The product was filtered off, washed with several portions of diethylether then dried under *vacuo* at 56°. (yield 60%, m.p. 137-140°C). ^{1}H n.m.r. (223 K) 2.61(†) 1.94(d) 7.0-8.0(m).

Trismethyldiphenylphosphinemonothiobenzato palladium(II) tetraphenylboronate

To a solution of $[Pd(PMePh_2)_3(SOCPh)]Cl$ dissolved in a minimum of methanol was added excess $Na[BPh_4]$ also dissolved in methanol. On mixing, the voluminous yellow *product* precipitated out. This was filtered off, washed with H_2O, MeOH and finally diethylether and then dried under *vacuo* at 56° (yield 80%). ^{1}H n.m.r. spectrum 1.81(†) 1.22(d) 7.0-8.0(m).

Reaction of $[\{Pd(SOCPh)Cl\}_n]$ with an excess of dimethylphenylphosphine

Mixing $PdCl_2(C_8H_{12})$ (0.18g) and Na[SOCPh] (0.10g) in methylene chloride gave a solution of $[\{Pd(SOCPh)Cl\}_n]$ (0.17g). After 1 minute, a 10 fold excess of dimethylphenylphosphine was added (0.87 cm^3). The yellow solution was filtered through celite and then reduced to a minimum volume.

Addition of light petroleum (b.p. 60-80°C) gave a precipitate of an orange-yellow solid (yield ca 40%). The composition of this solid is fully discussed in Section 3.3.1.

General method of preparation of $[Pd(SOCPh)ClL]_2$

The compound $[\{Pd(SOCPh)Cl\}_n]$ was generated in situ as before and to this was added very slowly and with constant stirring 0.5 mole of L(L = $PMePh_2$,C_5H_5N),(0.5 mole to each mole of Pd present), in a very dilute solution of methylene chloride. The resulting solution was then stirred for a further hour, filtered through celite, and the clear reddish filtrate was reduced to a minimum volume. On addition of light petroleum (b.p. 60-80°C) the orange-yellow product precipitated out and this was filtered off washed with light petroleum and dried under vacuo at 56°C (yield ca 50-60%).

Methyldiphenylphosphinepyridine(chloro)monothiobenzato palladium (II)

To a solution of $[Pd(SOCPh)Cl(PMePh_2)]_2$ (0.10 g) was added excess pyridine (0.10 cm^3). On mixing, the solution immediately lightened in colour, after 30 minutes the solution was reduced to a minimum volume. On addition of light petroleum (b.p. 60-80°C) the solution turned cloudy, this was stoppered and after an hour the yellow product had precipitated out. This was filtered off washed with diethyl-ether then dried under vacuo at 56°C (yield 70%, m.p. 111-114°C).

Bismonothiobenzato palladium (II)

To a methylene chloride solution of $PdCl_2(C_8H_{12})$ (0.20 g) was added Na[SOCPh] (0.22g) in acetone. On mixing the solution turned dark red and free 1,5 cyclooctadiene was detected by its smell. After 30 minutes, the solution was filtered through celite and the clear dark red filtrate reduced to a minimum volume. On addition of diethylether the reddish brown product $[\{Pd(SOCPh)_2\}_n]$ precipitated out. This was filtered off, washed with diethylether then dried under vacuo at 56°C (yield 75%, m.p. 118-121°C).

3.4.2 Platinum Complexes

1,5 cyclooctadienebismonothiobenzato platinum (II)

To a methylene chloride solution of $PtCl_2(C_8H_{12})$ (0.18 g) was added Na[SOCPh] (0.10 g) dissolved in acetone. On mixing, the solution turned pale yellow and a precipitate of sodium chloride formed. The solution was left to stand at room temperature for 2 hours and then filtered through celite. The clear lemon filtrate was reduced to a minimum volume and on addition of light petroleum (b.p. 60-80°C) the sandy coloured product precipitated out. The product was filtered off, washed with light petroleum then dried under vacuo at 56°C (yield 80-90%, m.p. 149-150°C).

General reaction of $Pt(SOCPh)_2(C_8H_{12})$ with phosphorous containing Lewis bases

To a solution of $Pt(SOCPh)_2(C_8H_{12})$ in methylene chloride was added either 2 moles or an excess of tertiary phosphine also dissolved in methylene chloride. On mixing, the solution turned bright clear yellow. After 30 minutes the solution was reduced to a minimum volume (free 1,5 cyclooctadiene was usually detected at this point by its smell) and on addition of light petroleum (b.p. 60-80°C) the product trans $Pt(SOCPh)_2L_2$ precipitated out. The product was purified as described elsewhere (Chapter 1) (yields 60 to 80%). When the same reaction was carried out using pyridine, only starting material was obtained on work-up. If the reaction was carried out using only 1 mole of tertiary phosphine then the product isolated was a mixture of trans $Pt(SOCPh)_2L_2$ and $Pt(SOCPh)_2(C_8H_{12})$.

Attempted reaction of $Pt(SOCPh)_2(C_8H_{12})$ with ^-OR ion

$Pt(SOCPh)_2(C_8H_{12})$ (0.15 g) was suspended in methanol with some Na_2CO_3 and the solution refluxed for 10 minutes. The solution was then quickly filtered hot to remove the insoluble Na_2CO_3. On leaving the solution to then cool a sandy coloured solid precipitated out. This was filtered off and on work-up (as described earlier) was found to be unreacted $Pt(SOCPh)_2(C_8H_{12})$.

1,2 Bis(diphenylphosphino)ethane bismonothiobenzato platinum (II)

A quantity of $Pt(SOCPh)_2(C_8H_{12})$ (0.12 g) was dissolved in methylene chloride and to this was added $Ph_2P(CH_2)_2PPh_2$ (0.08 g) also dissolved in methylene chloride. On mixing, the solution lightened in colour slightly and after 2 to 3 minutes free 1,5 cyclooctadiene could be detected by its smell. The solution was worked-up as before to give the product (yield 65%, m.p. 228°C).

1,5 cyclooctadiene(chloro)monothiobenzato platinum (II)

To a solution of $PtCl_2(C_8H_{12})$ (1.40 g) in methylene chloride was added a solution of Na[SOCPh] (0.59 g) in acetone. On mixing the solution immediately turned yellow and a precipitate of sodium chloride formed. After 30 minutes, it was filtered through celite and the clear yellow filtrate reduced to a minimum volume. Diethyl ether was then added until the solution just went cloudy and then the flask was stoppered and left for several hours. After this time a pale brownish solid had precipitated out. The solid was worked up as described earlier (yield 70%, m.p. 141-144°C).

Reaction of "$Pt(SOCPh)Cl(C_8H_{12})$" with phosphorous containing Lewis bases

To a solution of $Pt(SOCPh)Cl(C_8H_{12})$ was added 2 moles or an excess of tertiary phosphine dissolved in methylene chloride. On mixing the solution lightened in colour, after stirring for a further 20 minutes the solution is reduced in volume to a minimum and the white to off white products precipitate out on addition of diethylether (yields 60 to 90%). For a discussion of the nature of these products see Section 3.3.4. When only 1 mole of tertiary phosphine is used, then the product is found to be a mixture of the 2:1 adducts and unreacted $Pt(SOCPh)Cl(C_8H_{12})$.

Reaction of "Pt(SOCPh)Cl(C_8H_{12})" with $Ph_2P(CH_2)_2PPh_2$ (1:1 molar ratio)

To a solution of Pt(SOCPh)Cl(C_8H_{12}) (0.11 g) in methylene chloride was added $Ph_2P(CH_2)_2PPh_2$ (0.09 g) also dissolved in methylene chloride. On mixing the solution lightened slightly in colour, after stirring for 20 minutes the solution is reduced in volume and on addition of diethyl ether the cream coloured product precipitated out. This product was worked up as described earlier (yield 80%).

Analytical data and some characteristic I.R. bands for some mixed chloro/monothiobenzato and bis monothiobenzato palladium (II) and platinum (II) complexes

Compound	Colour	Analyses %			M.Wts.[a]	Infrared bands	
		C	H	N		$\nu(\mathrm{C} \underline{---} \mathrm{O})$	$\nu(\mathrm{C} \underline{---} \mathrm{S})$
$[\{Pd(SOCPh)Cl\}_n]$	Orange	30.9(30.2)	2.0(1.8)	-	-	1660(vs)	865(vs)
$[Pd(SOCPh)Cl(PPh_3)_2]$	Yellow	64.0(64.3)	4.4(4.4)	-	-	1600(s),1575(m)	910(s)
$[Pd(SOCPh)Cl(PMePh_2)_2]$	Yellow	58.5(58.4)	4.5(4.6)	-	667(678)	1595(s),1570(s)	910(s)
$[Pd(SOCPh)Cl(PMe_2Ph)_2]$	Yellow	49.9(50.0)	4.9(4.9)	-	598(554)	1595(s),1575(s)	910(s)
$[Pd(SOCPh)(PMePh_2)_3]Cl$	Orange	62.7(62.9)	5.1(5.0)	-	-	1575(w)	900(s),885(s)
$[Pd(SOCPh)(PMePh_2)_3]BPh_4 2H_2O$	Yellow	70.2(70.1)	5.6(5.7)	-	-	1580(m)	890(s)br
$[Pd(SOCPh)Cl(C_5H_5N)_2]$	Yellow	47.1(46.8)	3.4(3.4)	6.2(6.4)	480(436)	1595(m),1570(m)	910(s)
$[Pd(SOCPh)Cl(MeC_5H_4N)_2]$	Yellow	49.5(49.1)	4.0(4.1)	5.7(6.0)	-	1595(m),1575(m)	910(s)
[Pd(SOCPh)Cl(bipy)]	Pale orange	46.8(47.0)	3.0(3.0)	6.2(6.4)	-	1600(vs),1570(m)	930(s),905(s)
[Pd(SOCPh)Cl(1,10 Phenantholine)]	Pale orange	48.9(49.8)	2.6(2.8)	6.0(6.1)	-	1595(s),1575(m)	930(m),910(vs)

$[Pd(SOCPh)Cl(Ph_2P(CH_2)_2PPh_2)]$	Pale orange	58.7(58.6)	4.0(4.3)	-	-	1595(s),1570(s)	920(s)
$[Pd(SOCPh)Cl(PMePh_2)]_2$	Orange	50.9(50.2)	3.9(3.8)	-	-	1655(s)br	870(s)
$[Pd(SOCPh)Cl(C_5H_5N)]_2 \cdot 5CH_2Cl_2$	Orange	37.7(37.7)	2.5(2.5)	3.3(3.5)	-	1670(s)	870(s)
$[Pd(SOCPh)Cl(PMePh_2)(C_5H_5N)]$	Yellow	54.4(54.6)	4.4(4.4)	2.0(2.4)	525(557)	1595(s),1575(m)	905(s)
$[Pd(SOCPh)_2(PMe_2Ph)_2]$	Yellow	54.7(54.8)	5.1(4.9)	-	-	1595(s),1560(s)	910(vs)
$[Pd(SOCPh)_2(PPh_3)_2]$	Yellow	66.9(66.3)	4.3(4.4)	-	-	1595(s),1570(s)	910(vs)
$[Pd(SOCPh)_2(bipy)]$	Yellow	54.2(53.7)	3.4(3.4)	5.1(5.2)	-	1600(vs)1570(m)	930(s),910(vs)
$[Pd(SOCPh)_2(Ph_2P(CH_2)_2PPh_2)]$	Yellow	61.5(61.7)	4.0(4.1)	-	-	1590(s),1560(s)	925(sh,911(vs)
$[Pt(SOCPh)_2(C_8H_{12})]$	Sandy	45.5(45.8)	3.7(3.8)	-	571(567)	1620(vs)	900(vs)
$[Pt(SOCPh)Cl(C_8H_{12})]$	Pale brown	37.7(37.9)	3.6(3.6)	-	210(475)[b]	1625(vs)	900(vs)
$[Pt(SOCPh)_2(PPh_3)_2]$	Yellow	59.2(59.4)	4.1(4.0)	-	-	1600(s),1575(s)	915(vs)
$[Pt(SOCPh)_2(PMe_2Ph)_2]$	Yellow	48.2(48.3)	4.3(4.3)	-	-	1600(s),1570(m)	910(vs)
$[Pt(SOCPh)_2(Ph_2P(CH_2)PPh_2)]$	Yellow	55.2(55.4)	3.9(3.9)	-	-	1590(s),1565(s)	910(vs)
"$[Pt(SOCPh)Cl(PPh_3)_2]$"	white	57.9(57.9)	3.9(3.9)	-	-	1605(vs),1575(vs)	915(vs)915(vs)

"[Pt(SOCPh)Cl $(PMe_2Ph)_2$]"	white	42.8(42.9)	4.1(4.2)	-	-	1605(vs),1570(s)	945(m),905(vs) 915(vs)
"[Pt(SOCPh)Cl($Ph_2P(CH_2)_2PPh_2$)]"	white	52.0(51.8)	3.9(3.8)	-	-	1610(s)br,1570(M)	910(vs)

a. Osmometrically at 37°C in Acetone; calculated values are given in parentheses

b. Value low due to species being in equilibrium (see Section 3.3.4 for full discussion).

Table 3.2

$^{31}P-\{^1H\}$ n.m.r. data in $CDCl_3$ for various palladium (II) and platinum (II) complexes at 300 K.

	$^{31}P-\{^1H\}$ n.m.r.	
	δ	$^1J_{Pt-P}$/Hz
*$[Pd(SOCPh)Cl(PPh_3)_2]$	+26.1(s)	-
$[Pd(SOCPh)Cl(PMePh_2)_2]$	+11.0(s)	-
$[Pd(SOCPh)Cl(PMe_2Ph)_2]$	- 3.2(s)	-
$[Pd(SOCPh)_2(PPh_3)_2]$	+28.4(s)	-
*$[PdCl_2(PPh_3)_2]$	+23.1(s)	-
*$[Pt(SOCPh)_2(PPh_3)_2]$	+23.3(+)	2764
*$[PtCl_2(PPh_3)_2]$	+14.3(+)	3672
*$[Pt(SOCPh)_2(PMe_2Ph)_2]$	- 6.4(+)	2544
+$[Pt(SOCPh)Cl(PMe_2Ph)_2]$	- 6.0(+)	2524
*$[PtCl_2(PMe_2Ph)_2]$	-15.5(+)	3545
+$[Pt(SOCPh)_2(Ph_2P(CH_2)_2PPh_2)]$	+45.8(+)	3018
+$[PtCl_2(Ph_2P(CH_2)_2PPh_2)]$	+41.0(+)	3618

*Denotes that the values obtained were from reaction mixtures and where possible have been verified with values from known pure samples.

Table 3.3

Bond Lengths, Angles and Crystallographic data for $[\mathrm{Pd(SOCPh)Cl(PMePh_2)_2}]$

Distances

Pd—Cl	2.340 (10)
Pd—$\mathrm{P_1}$	2.325 (6)
Pd—$\mathrm{P_2}$	2.326 (5)
Pd—S	2.295 (10)
$\mathrm{C_1}$—S	1.732 (13)
$\mathrm{C_1}$—$\mathrm{O_1}$	1.224 (15)
$\mathrm{Pd_1}$----$\mathrm{O_1}$	3.286 (9)

Angles

$\mathrm{S_1}$—Pd—$\mathrm{P_1}$	88.39 (12)
$\mathrm{S_1}$—Pd—$\mathrm{P_2}$	93.60 (11)
$\mathrm{S_1}$—Pd—$\mathrm{Cl_1}$	176.64 (23)
$\mathrm{P_1}$—Pd—$\mathrm{P_2}$	177.81 (40)
$\mathrm{P_1}$—Pd—$\mathrm{Cl_1}$	88.26 (12)
$\mathrm{P_2}$—Pd—$\mathrm{Cl_1}$	89.75 (11)

Cell Dimensions

a = 15.2248 (18)

b = 9.6897 (210)

c = 21.3146 (25)

β = 83.829 (arcos .0095)

Z = 4

Space Group = $P2_{1/c}$

CHAPTER 4

SOME STUDIES ON BINUCLEAR MOLYBDENUM(II) DITHIOACID COMPLEXES

4.1.1 Introduction

In recent years there has been considerable interest shown in the chemistry of molybdenum complexes with 1,1 dithiolate ligands. This has been partially due to the increasing interest in the inorganic biochemistry of molybdenum, and also to the implications of Mo-S bonding in the active site of the enzyme nitrogenase.[125,126]

One result of this work has been to show that molybdenum 1,1 dithiolate complexes can exist in a number of oxidation states, namely Mo(II)-(VI). However, although the higher oxidation states have been studied in some detail[127-130] there has been little work until recently on the chemistry of the lower states (particularly that of molybdenum(II)). One reason for this may be due to the difficulties both in preparing and maintaining molybdenum in a +2 oxidation state.

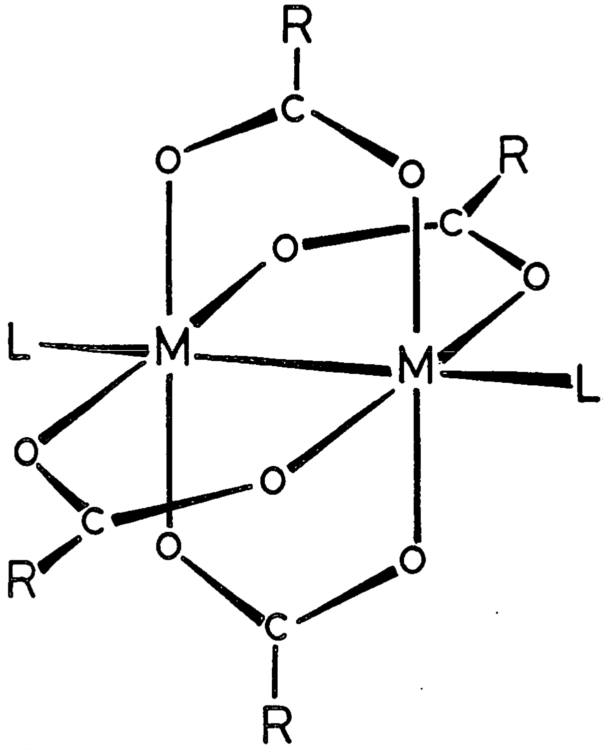
As previous work on the preparation and reactions of $Mo_2(S_2COR)_4$ complexes is not very extensive,[131-133] it was decided that this area merited further investigation. Since this chapter is primarily concerned with the +2 state of molybdenum, only complexes in this state will be considered in detail. A full discussion of molybdenum dithio-complexes in other oxidation states can be found however in a recent review by Coucouvanis.[60] Before discussing the results obtained a short introduction on the general chemistry and structures of molybdenum (II) binuclear complexes is given.

4.1.2 The general chemistry and structures of Mo(II) binuclear complexes

One of the most interesting features of d^4 metal systems [Cr(II), Mo(II), W(II), Re(III) and Tc(III)] is the formation of strong multiple metal-metal bonds.[134] This tendency is most marked in the series of compounds $Mo_2(O_2CR)_4$ (R = alkyl or aryl) first prepared by Stephenson et al by the reaction of $Mo(CO)_6$ with the appropriate carboxylic acid.[135] Structural studies on the acetate[136] and the trifluoroacetate[137] have shown that these compounds have the structure shown in Fig. 4.1 which is also the structure of Cr(II),[138] Rh(II)[138] and Cu(II)[139] acetates. More recently $Mo_2(S_2COEt)_4$-2THF[131] and $Mo_2(S_2CR)_4$ 2THF ($R = CH_3$, C_6H_5)[140] have also been shown by X-ray structural analysis to have a structure of the same type as that in Fig. 4.1. The interesting feature of all of these compounds is the interaction between the two metal centres which can vary from a very weak interaction as in $Cu_2(O_2CCH_3)_4$[139] (r(M-M) = 2.65 Å) to a very strong M-M bond as in $Mo_2(O_2CCH_3)_4$[136] (r(M-M) = 2.11 Å).

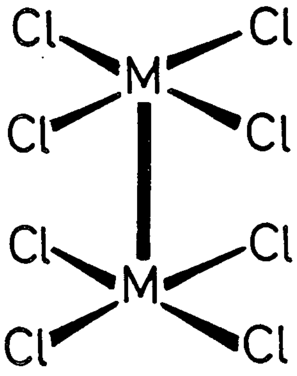
There are two important factors influencing the degree of metal-metal bond formation, namely oxidation state and valence shell configuration. The importance of low oxidation state is related to the size of the metal orbitals. High electron density on the metal centre can lead to orbitals of a size sufficient to produce good overlap with the orbitals on another metal centre at a distance which does not introduce too much repulsive interaction of the cores. For this reason,

Fig. 4.1



Dinuclear Carboxylate $M_2(O_2CR)_4L_2$ Structure

Fig. 4.2



Structures of $[Mo_2Cl_8]^{4-}$ and $[Re_2Cl_8]^{2-}$

most M-M bonded systems have metal atoms in a formal oxidation state of +2 or less. The valence shell configuration is important since too many electrons would result in occupancy of antibonding as well as bonding molecular orbitals, in spite of good overlap being possible. The most favourable configuration appears to be d^4 [Cr(II), Mo(II), W(II), Re(III), Tc(III) etc.] and the strongest M-M bonds are found in metal complexes with this configuration (cf. $Mo_2(O_2CCH_3)_4$). Cotton[134] has developed a semi-quantitative molecular orbital approach to this problem. Bonding molecular orbitals may be formed by overlap of d_{z^2} (σ), d_{xz} d_{yz} (π) and d_{xy} (δ) orbitals on one metal centre with those on the other. Thus the d^4 configuration can lead to complete filling of all the bonding orbitals, resulting in a quadruple bond between the metal centres. Good supporting evidence for this scheme arises from the structures of $[Mo_2Cl_8]^{4-}$ [141] and $[Re_2Cl_8]^{2-}$ [142] (both d^4) which have an eclipsed configuration of the two MCl_4 units (Fig 4.2) which is necessary for maximum overlap of the d_{xy} orbitals.

This criterion cannot be rigorously applied to the dinuclear carboxylates since the molecules are constrained to be in the eclipsed configuration by the bridging ligands. In these cases, the M-M bond length must be used to estimate the extent of the interaction. Another useful technique for the study of these systems in Raman spectroscopy.

The totally symmetric M-M stretching mode would be expected to be Raman active and various studies have confirmed this[137,143,144]. There does not, however, appear to be a great deal of correlation between ν(MM) and the M-M bond length, although for Mo-Mo quadruple bonds, the absorptions all lie in the range 425-340 cm^{-1}.[143] These results are summarised in Table 4.1.

In Fig. 4.1, the general dinuclear carboxylate structure, with the vacant co-ordination position at each end of the molecule filled by a donor ligand L (often the solvent in which the preparation is carried out) is shown. Molybdenum(II) carboxylates are unusual in this respect since they are quite difficult to obtain with the ligand L whereas the other dinuclear carboxylates are difficult to obtain in a crystalline form <u>without</u> it. Over the past 10 years Cotton and co-workers have worked extensively in this area and have published several papers discussing the implications and resistance of dimolybdenum(II) species to attach axial ligands.[145,146] The same group however have succeeded in generating and studying by X-ray structural analysis a number of $Mo_2(O_2CR)_4L_2$ complexes. This work was undertaken to determine the response of the Mo-Mo bond, as monitored by its bond length, to (a) the presence or absence of axial ligands and (b) changes in the inductive strength of the R group of the carboxylate ligands. The results that they have obtained are summarised in Table 4.2.

Table 4.1

Metal-Metal bond lengths and stretching frequencies for some Mo(II) dinuclear Compounds

Compound	ν_{MoMo} (cm^{-1})	r(Mo-Mo) Å	Ref.
$[Mo_2(O_2CCH_3)_4]$	406	2.093(1)	136/156
$[Mo_2(O_2CCH_3)_4]2Py$	363		143
$[Mo_2(O_2CCF_3)_4]$	397	2.090(4)	147
$[Mo_2(O_2CCF_3)_4]2MeOH$	386		143
$[Mo_2(O_2CCF_3)_4]2PPh_3$	377		143
$[Mo_2(O_2CCF_3)_4]2Py$	367	2.129(2)	137
$[Mo_2(O_2CEt)_4]$	400		143
$[Mo_2(O_2C^nPr)_4]$	402		143
$[Mo_2(O_2CPh)_4]$	404	2.096(1)	143/148
$[Mo_2(O_2CPh)_4]2$ Diglyme		2.100(1)	153
$[Mo_2(O_2CC_6H_{11})_4]$	397		143
$[Mo_2(O_2CH)_4]$	410	2.093(1)	149
$[Mo_2$(diphenylbenzamidinato)$_4]$	410	2.090(1)	150
$[Mo_2(Glycine)_4]2SO_4$	393	2.115(1)	151
$[Mo_2(S_2COEt)_4]2THF$		2.125(1)	131
$[Mo_2(S_2CPh)_4]2THF$		2.139(2)	140
$[Mo_2(S_2CMe)_4]2THF$		2.133(2)	140
$[Mo_2$(2-amino-6-methylpyridine)$_4]2THF$		2.070	154
$[Mo_2$(6-methylpyridine)$_4]$	425	2.065	153
$K_4[Mo_2Cl_8]2H_2O$	345	2.14	155
$[EnH_2]_2[Mo_2Cl_8]2H_2O$	348	2.13	155
$[NH_4]_5[Mo_2Cl_8]Cl.2H_2O$	350	2.15	155
$K_4[Mo_2(SO_4)_4]$	370	2.110(1)	155

Table 4.2

Structures of some $Mo_2(O_2CR)_4L_2$ Compounds

Carboxylate Group	Axial Ligand[a]	Mo....L	Mo-Mo	Ref
$C(CH_3)_3$	a	2.90	2.088(1)	148
CH_3	a	2.65	2.093(1)	156
H	a	2.65	2.091(2)	149
C_6H_5	a	2.88	2.096(1)	148
C_6H_5	Diglyme	2.66	2.100(1)	152
$CH_2NH_3^+$	SO_4^{2-}	2.93	2.115(1)	151
CF_3	a	2.72	2.090(4)	142
CF_3	C_5H_5N	2.55	2.129(2)	137

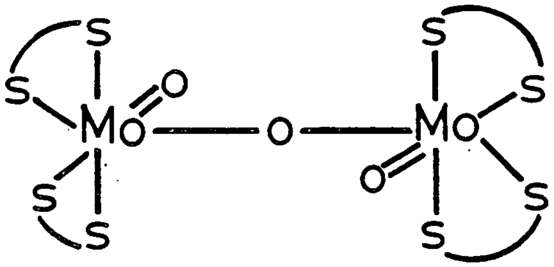
a. In all cases where there is no separate ligand L, the crystal packing places oxygen atoms of neighbouring molecules in axial positions.

From these results it is apparent that changing the R group from the most strongly electron withdrawing ($R = CF_3$) through those of intermediate character ($R = H, CH_3$) to the highly electron donating tert-butyl group ($R = C(CH_3)_3$) has virtually no effect on the Mo-Mo bond lengths. On the other hand the evidence suggests a small but apparently real effect due to axial ligand coordination. The first,[137] and still the most persuasive, evidence that there is an effect was provided by comparison of $Mo_2(O_2CCF_3)_4$ and $Mo_2(O_2CCF_3)_4(C_5H_5N)_2$.

Here, the replacement of weak intermolecular axial interactions (Mo....O, 2.72 Å) by considerably shorter bonds to a stronger base (Mo....N, 2.55 Å) is accompanied by an increase of 0.039 (4) Å in the Mo-Mo bond length. This effect is not however observed in a comparison of $Mo_2(O_2CC_6H_5)_4$ and $Mo_2(O_2CC_6H_5)_4$2 diglyme and from this Cotton has concluded that axial coordination can affect the strength of the Mo-Mo bond but only in special cases, (i.e. where R is a good electron withdrawing group and L is a good donor ligand), will the lengthening of the Mo-Mo bond be more than marginal.

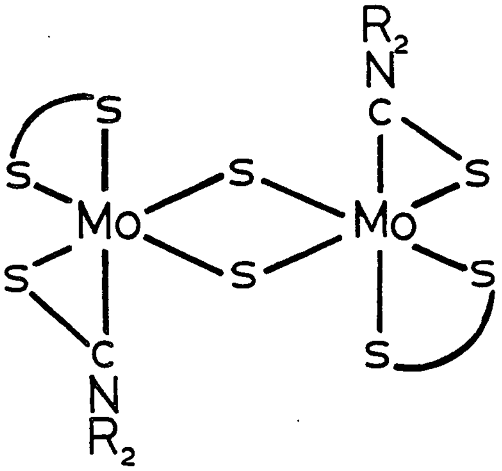
It is of interest to note here that a similar study on several $Cr_2(O_2CR)_4L_2$ complexes[157] has shown the Cr-Cr bond to be sensitive to both parameters.

In contrast to this extensive study on $Mo_2(O_2CR)_4$ complexes there has been little work on the analogous dinuclear Mo(II) dithioacid bridged complexes. The first Mo(II) dithio- and monothio-acid complexes, $Mo_2(S_2COEt)_4$ and $Mo_2(SOCPh)_4$ respectively, were prepared by Steele and Stephenson[132] by reaction of the appropriate Na[(S-X)] (X = S or O) salt with $Mo_2(O_2CCH_3)_4$. The same workers also made $Mo_2(S_2CNEt_2)_4$, by the reaction of $Na[S_2CNEt_2]$ with $Mo_2(O_2CCH_3)_4$ in methanol, although this compound very rapidly oxidised to the purple $[Mo_2O_3(S_2CNEt_2)_4]$ (47). On the other hand if the same starting materials were reacted in either ethanol solution or left for extended periods in very dilute methanol solution, green solids also of empirical



(47)

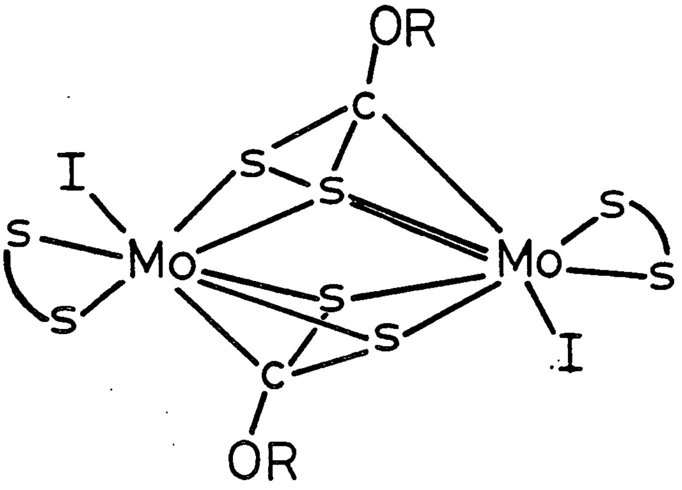
formula $Mo_2(S_2CNEt_2)_4$ were isolated which gave more complicated ^1H n.m.r. spectra than would be expected for the structure shown in Fig. 4.1. Weiss et al[158] independently reported an X-ray analysis on the product from the analogous reaction of $Mo_2(O_2CCH_3)_4$ with $NH_4[S_2CN^iPr_2]$ in ethanol and their results revealed that the product was the dimeric Mo(IV) complex (48) with bridging sulphido groups and a "carbene" ligand.



(48)

Von Holste[159] has also reported the synthesis of $Mo_2(SOCCH_3)_4$ and $Mo_2(S_2CPh)_4$ and more recently Cotton <u>et al</u>[140] have succeeded in making $Mo_2(S_2CR)_4 2THF$ (R = Ph,Me) by a more facile route.

Although several of these dinuclear Mo(II) dithio- and monothio-acid complexes have now been prepared little work has been published on their reactions with donor ligands. Steele and Stephenson did show that $Mo_2(S_2COEt)_4$ readily reacted with various donor ligands L (L = C_5H_5N, $CH_3C_5H_4N$, $AsEt_3$ <u>etc</u>.) to give dimeric compounds of empirical formula $Mo_2(S_2COEt)_4L_2$ where the ligands L were coordinated in the apical positions.[132] They also discovered that the analogous $Mo_2(SOCPh)_4$ readily reacted in solution with various donor ligands but on removal of solvent only starting material was recovered. Cotton <u>et al</u>[133] have also shown that $Mo_2(S_2COR)_4$ (R = Et, ^{i}Pr) reacts with Br_2 or I_2 to give neutral products of empirical formulae $Mo_2(S_2COR)_4X_2$ (R = Et, ^{i}Pr; X = Br, I). A full X-ray structural analysis of the $Mo_2(S_2COEt)_4I_2$ complex (49) has shown that in these reactions the Mo-Mo bond order has been reduced from 4 to 1 because the oxidative addition of I_2 is accompanied by a rearrangement of the xanthate groups relative to the metal atoms. A similar study of the reactions of Br_2 and I_2 with $Mo_2(S_2CCH_3)_4$ in THF or $CHCl_3$ has revealed that stable addition products are not obtained.[140]



(49)

These differences in reactivity are probably due to the fact that any ligand bonding to the molybdenum atoms has to do so initially in the apical position and therefore has to use an orbital which is already involved in the Mo-Mo bond, which will tend to weaken this bond. In the case of Mo(II) dinuclear bridged complexes, where all four d electrons are located in bonding molecular orbitals, it would appear that in most cases the requirements of the Mo-Mo bond take precedence and any interaction with a donor ligand L is weak. As stated earlier direct evidence for this has been difficult to obtain and the best example of this has come from a comparison of Mo-Mo bond lengths and Raman stretching frequencies of $Mo_2(O_2CCF_3)_4$ and $Mo_2(O_2CCF_3)_4(C_5H_5N)_2$. Also Cotton and Norman[137] have studied the Raman spectra of $Mo_2(O_2CCF_3)_4$ in various solvents and found that ν(Mo-Mo) varied from 397 cm^{-1} in CH_2Cl_2 to 343 cm^{-1} in pyridine, <u>i.e.</u> the stretching frequency decreased as the donor ability of the solvent increased. Finally further support for these proposals comes from an X-ray structural analysis of $Cs_2[Re_2Cl_8]H_2O$[160] in which the unit cell contains four $Re_2Cl_8{}^{2-}$ anions, two of which are anhydrous and have a

Re-Re bond length of 2.237(2) Å whilst the other two have molecules of H_2O coordinated at both axial positions and have a Re-Re bond length of 2.252(2) Å.

In conclusion it would appear that the ability of dinuclear molybdenum tetradithio-and monothio-acid compounds to form complexes with donor ligands must be dependent to some extent on the bridging ligands. This is shown by the ease with which $[Mo_2(S_2COR)_4]$ compounds react whilst the $[Mo_2(S_2CR)_4]$ ones do not. However, at this time it is not possible to explain these differences and more work in this area is required before they can be fully understood.

4.2. Results and Discussion

Several years ago[131,132] it was reported that the reaction of molybdenum(II) acetate with an excess of $K[S_2COEt]$ in degassed alcohol led to the precipitation of the red crystalline solid $Mo_2(S_2COEt)_4$, shown by X-ray structural analysis[131] to have the well known "acetate-type" structure (see Fig. 4.1). This red compound was isolated from a green solution, claimed by Weiss _et al_[131] to contain another complex of probable composition $Mo_2(S_2COEt)_4$, which reacted in the manner expected of an alkoxycarbonyl complex[161] and whose n.m.r. spectrum indicated the presence of two electronically non-equivalent ligands. Recently, Cotton _et al_[133] mentioned this green "impurity" and showed that it was _not_ formed when equivalent amounts of xanthate ion were used in the preparation of $Mo_2(S_2COR)_4$ (R = Et, ^{i}Pr).

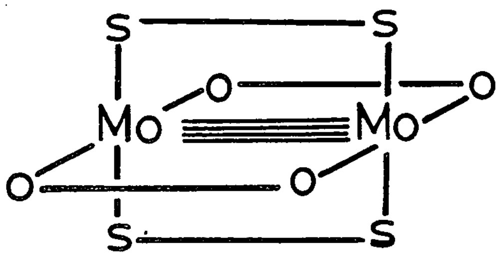
Both Cotton and Weiss prepared their $Mo_2(S_2COR)_4$ complexes by stirring $Mo_2(O_2CCH_3)_4$ with $K[S_2COR]$ in degassed alcohol for 6 to 12 hours whereas Steele and Stephenson refluxed the starting materials in methanol for approximately 20 minutes to obtain the required product. However, all three groups of workers found that on mixing the two reactants the solution very rapidly turned dark green and it was from this dark green solution that the red $Mo_2(S_2COR)_4$ products precipitated. Similarly, they all found that as the molar ratio of $K[S_2COR]$ to $Mo_2(O_2CCH_3)_4$ was increased (above 4:1) then the amount of $Mo_2(S_2COR)_4$ obtained decreased.

Initially both methods of preparation were investigated and compared (see Experimental Section). It was found that Steele and Stephenson's[132] method worked well for the ethyl and methyl xanthates but was less successful when the R group was longer e.g. ^{i}Pr. This is because of rapid decomposition of the product at the higher temperatures used. Cotton's method however proved suitable for preparing all $Mo_2(S_2COR)_4$ (R = Me, Et, ^{i}Pr) compounds in high yield. One disadvantage found with this latter method of preparation which was not mentioned in the literature was that if the reaction mixture was not stirred for long enough, then the red product was found to contain a yellow material. This was most clearly seen in the reaction with the ethyl xanthate and it was found that this yellow solid could be separated from the $Mo_2(S_2COEt)_4$ by adding it to a small amount of cold acetone in which only the latter was soluble. At first this yellow solid was assumed to be unreacted $Mo_2(O_2CCH_3)_4$ but its insolubility in most solvents soon suggested that this was not the case. The i.r. spectrum of this compound showed bands at 1510 cm^{-1} and 1245 cm^{-1} which were assigned to ν C-O of the acetate and ν C-O of the xanthate respectively, suggesting the presence of both of these ligands, whilst elemental analysis gave the empirical formula as $[\{Mo(O_2CCH_3)(S_2COEt)\}_n]$. Both the melting point (205°C decomp) which was reasonably sharp and thin layer chromatography implied that this was not a mixture of compounds. Attempts to obtain a ^1H n.m.r. spectrum failed due to low solubility of the compound, but a mass spectrum was obtained. This showed a pattern characteristic of a Mo_2^+ containing ion at m/e 552 (most abundant peak) which is consistent with the formulation $[Mo_2(O_2CCH_3)_2(S_2COEt)_2]$ (M = 552, based on ^{98}Mo). The structure of this compound could be both or either of the two possible isomers (50) and (51) (see Fig. 4.3). Unfortunately, all attempts to date to grow single crystals of this compound for a full X-ray structural analysis have been unsuccessful.

It is of interest to note here that Steele and Stephenson[132] found that the reaction of $Mo_2(O_2CCH_3)_4$ with an excess of $NH_4[S_2PPh_2]$ in ethanol gave a very insoluble orange precipitate of composition $[Mo(O_2CCH_3)(S_2PPh_2)]_n$. Similarly the reaction of $Mo(CO)_6$ with HO_2PPh_2 has been reported to give an insoluble salmon-pink complex formulated as $[Mo(O_2PPh_2)_2]_n$.[135] Due to the high insolubility of these compounds it has been suggested that they may in fact be polymeric, possible structures (52) and (53) are shown in Fig. 4.3. Obviously this area needs to be studied more

Fig. 4.3

Possible Structures for $[Mo(O_2CCH_3)(S-S)]_n$ Complexes



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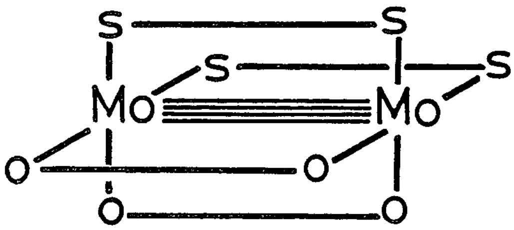

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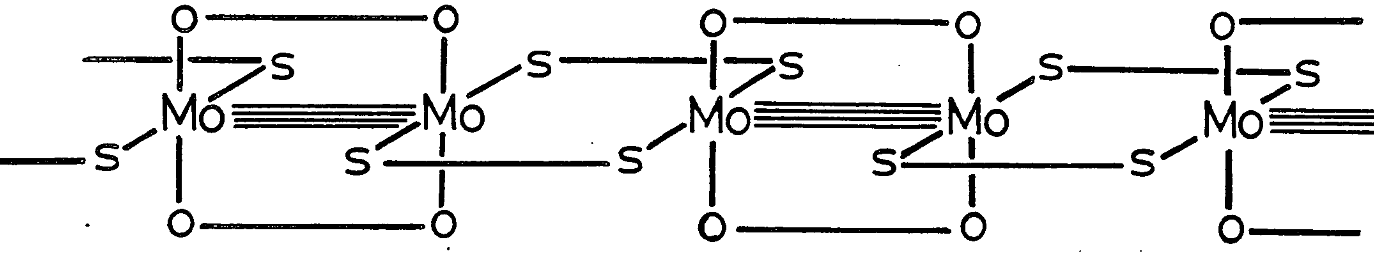

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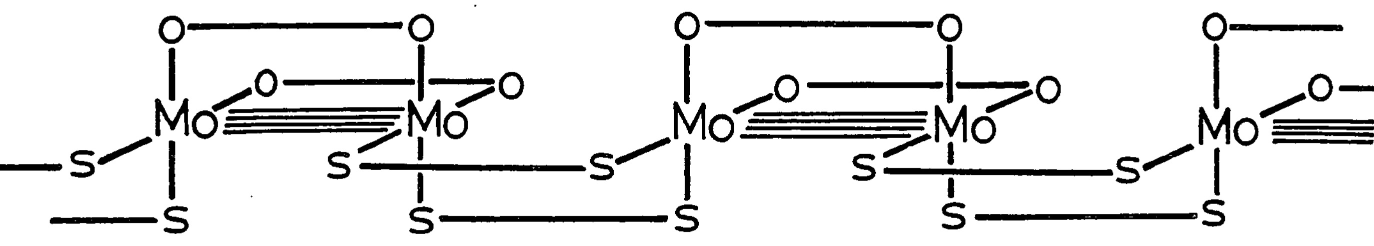
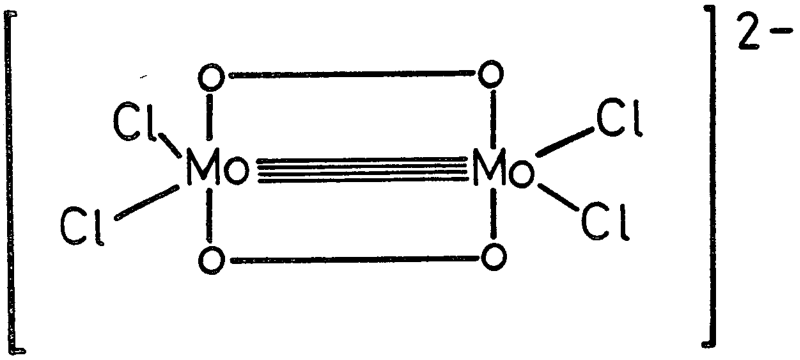


(53)

fully but at this stage it would appear that in the reactions of $Mo_2(O_2CCH_3)_4$ with dithioacid ligands products can be isolated in which only partial replacement of the acetate ligands has occurred.

Further support for this comes from the work of Garner et al[162] who reacted $Mo_2(O_2CCH_3)_4$ with an excess of $[AsPh_4]ClHCl$ in dilute hydrochloric acid and isolated $[AsPh_4]_2[Mo_2(O_2CCH_3)_2Cl_4]2MeOH$ which was shown by X-ray analysis to have structure (54).



(54)

4.2.1 Reaction of $Mo_2(S_2COR)_4$ compounds with $K[S_2COR]$ (1:1 Molar ratio).

~~In an~~ attempt to identify the green "impurity" which is always produced in the preparation of $Mo_2(S_2COR)_4$ compounds, the reaction of $Mo_2(S_2COR)_4$ with more ^-S_2COR (in a 1:1 molar ratio) was investigated.

Reaction of a solution of $Mo_2(S_2COR)_4$ with a stoichiometric amount of $K[S_2COR]$ in degassed acetone led immediately to the formation of a dark green solution. If this solution was slowly evaporated to dryness only unreacted starting materials were isolated. However, if a methanolic solution of $[PPh_3(PhCH_2)]Cl$ or $[AsPh_4]Cl.HCl$ was added, (see Experimental section for full details), then a green product could be isolated. Elemental analysis showed these compounds to be of empirical formulae $[M]_n[\{Mo_2(S_2COR)_5\}_n]$ (R = Me,Et,^{i}Pr; M = $AsPh_4^+$, $(PPh_3PhCH_2)^+$). Attempts to isolate these compounds with K^+ or Cs^+ as the counterion failed.

These compounds were characterised by elemental analysis, and high resolution ^1H n.m.r. spectroscopy (see Table 4.4). For $[M]_n[\{Mo_2(S_2COR)_5\}_n]$ (R = Me,Et), three sets of alkyl resonances of relative intensity 1:2:2 were clearly observed.* (See Fig. 4.4 for (R = Et, M = $PPh_3PhCH_2^+$)), which is consistent with either structure (55) or (56) (assuming n = 1). For R = ^{i}Pr, three methyl doublets also of relative intensity 1:2:2 were found but the methine proton region was too weak and complicated to analyse fully.

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* As all ^1H n.m.r. spectra were obtained by Fourier Transform methods, several spectra were obtained using long time intervals between each pulse to ensure correct peak intensities.

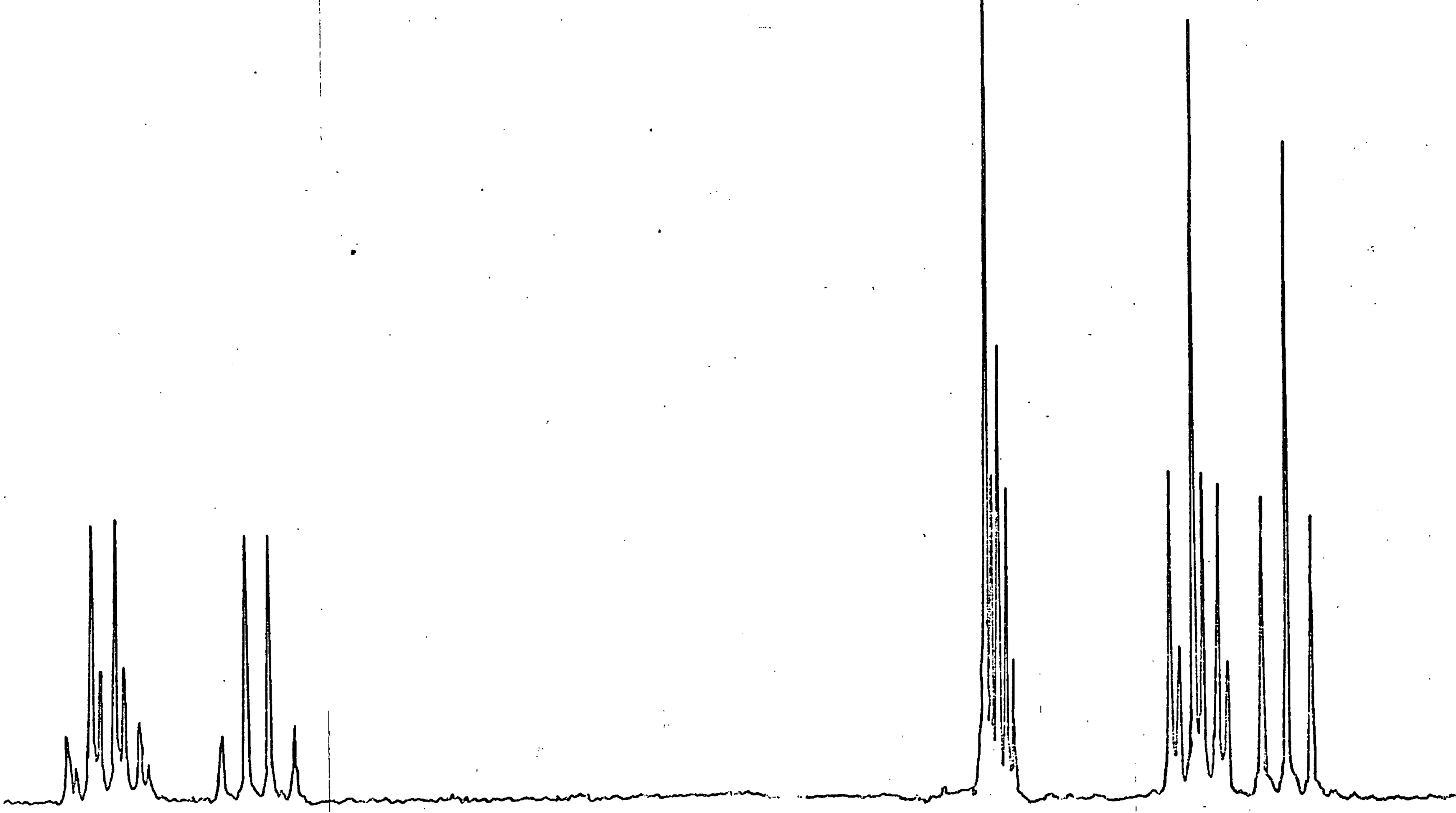
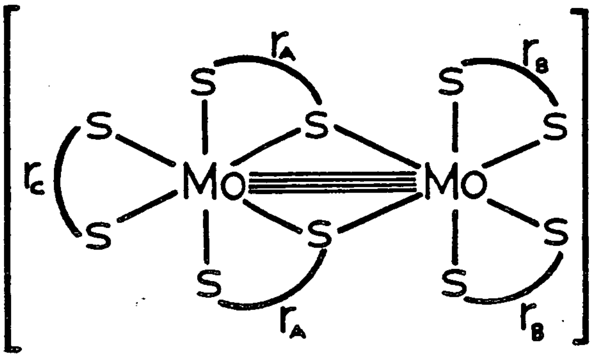
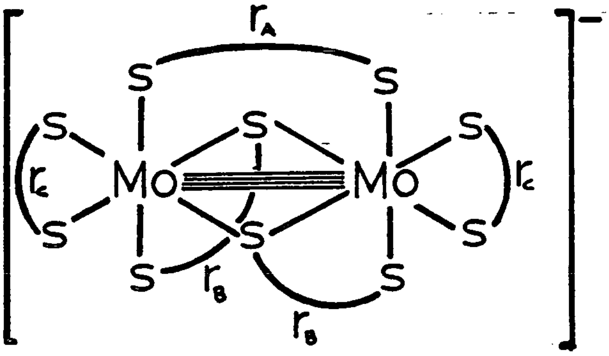


Fig. 4.4 High Resolution ^1H n.m.r. spectrum of $[Ph_3PhCH_2P][\{Mo_2(S_2COEt)_5\}_n]$ (ethyl region) in d^6-acetone at 300 K.



(55)



(56)

Since two of the n.m.r. signals are very close together such that at lower resolution, two sets of peaks of relative intensity 3;2 were initially observed (Fig. 4.5), (cf. the observation in reference 140), structure (55) in which alkyl groups R_B and R_C are in very similar environments was believed to be the more likely.

Structures of type (55) and (56) have been found for other dithioacid transition metal complexes. For example, Hendrickson and Martin[163a,163b] found that the reaction of $Co(S_2CNR_2)_3$ with $Et_2O.BF_3$ in benzene in the presence of air or O_2 afforded green-brown complexes of general formula $[Co_2(S_2CNR_2)_5]BF_4$ (where R_2 = Me_2; Et_2; pyrrolidyl; Me,Bu^n; Benzyl$_2$). An X-ray structural analysis of the $[Co_2(S_2CNEt_2)_5]BF_4$ complex has shown it to have a structure of type (55).[163b] Similarly, Raston and White[164] have prepared and obtained X-ray structures of two of the analogous ruthenium dithiocarbamate cations. They solved the crystal structures of $[Ru_2(S_2CN(^iPr)_2)_5]Cl.\ 2.5\ C_6H_6$ and

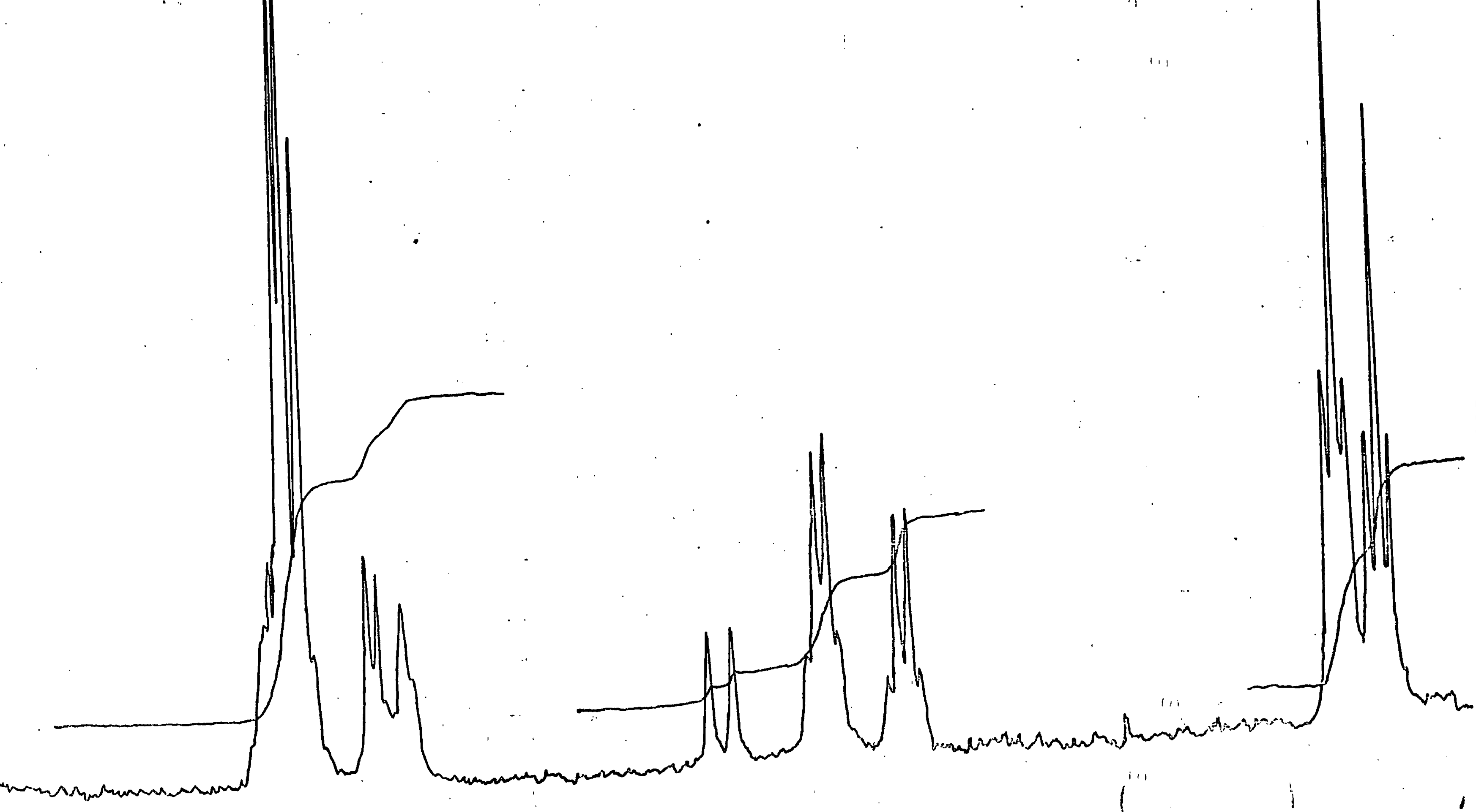


Fig. 4.5 Low resolution ^{1}H n.m.r. spectrum of $[Ph_3PhCH_2P]_n[\{Mo_2(S_2COEt)_5\}_n]$ at 298K in d^6-acetone

$[Ru_2(S_2CN(^iPr)_2)_5][Ru_2Cl_6]2CHCl_3$ and found both cations to again have a structure of type (55). However, Pignolet and Mattson[165] prepared $[Ru_2(S_2CNEt_2)_5]BF_4$ and found by X-ray analysis that the cation here was in the form of the other isomer (56). Finally the structure of the analogous $[Rh_2(S_2CNMe_2)_5]BF_4\ 0.5CH_2Cl_2$[166] complex has been solved and the cation shown to have a structure of type (55).

To investigate the effect of the cation on the isomeric form of the $[\{Mo_2(S_2COR)_5\}_n]^{n-}$ anions, high resolution ^1H n.m.r. spectra were obtained in the presence of different cations (e.g. K^+, Cs^+, $AsPh_4^+$). In all cases only the formation of configuration (55) was indicated.

The analogous reactions of $Mo_2(S_2COR)_4$ (R = Me, Et, ^{i}Pr) with stoichiometric amounts of $K[S_2COR']$ (R = Me,Et,^{i}Pr) in the presence of a large cation were also studied and again green products of empirical formulae $[M]_n[\{Mo_2(S_2COR)_4(S_2COR')\}_n]$ were isolated. Form the ^1H n.m.r. spectrum of $[PPh_3PhCH_2]_n$–$[\{Mo_2(S_2COEt)_4(S_2COMe)\}_n]$ it was possible to determine the coordinating position of the methylxanthate group. As it was the resonance assigned to the ethyl bridging groups R_A in (55) which was halved in intensity, this suggested that the fifth xanthate group was occupying one of the bridging positions in (55). In all cases where it was possible to obtain good high resolution ^1H n.m.r. spectra of these mixed anions the fifth ligand was always found to be in one of the bridging positions (see Table 4.6).

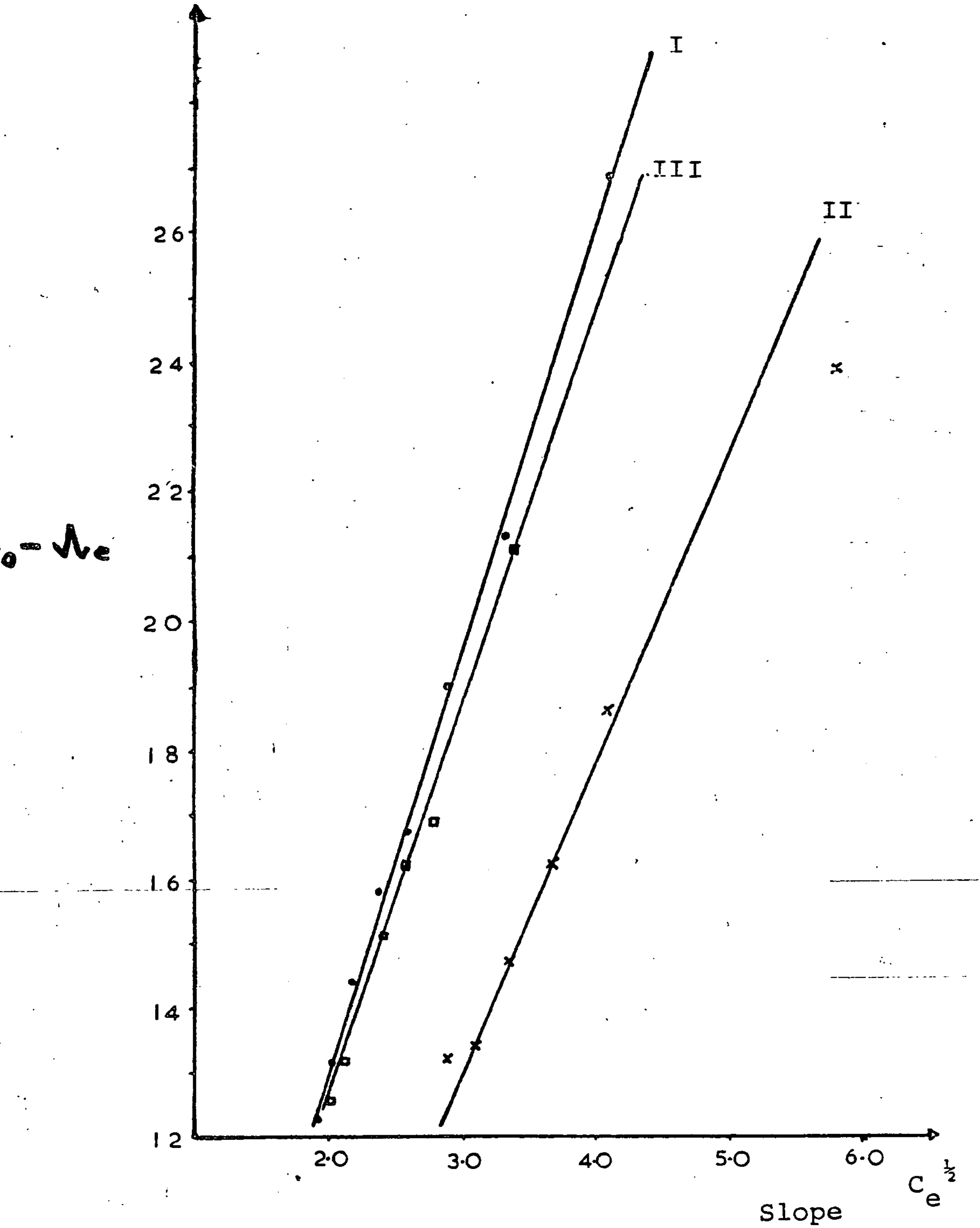
At this stage all the data obtained suggested that the formulation $[M]_n[\{Mo_2(S_2COR)_5\}_n]$ (with n = 1), was correct. However, although conductivity measurements in nitromethane or acetone (<u>ca</u>. 10^{-3} dm^{-3} mol, assuming n = 1) gave values expected for 1:1 electrolytes (75-95 S cm^2mol^{-1}),[167-170] measurements over a wide range of concentrations for all of these complexes and subsequent plots of $\Lambda_o-\Lambda_e$ (equivalent conductance) <u>vs</u> $C_e^{\frac{1}{2}}$ (concentration in equivalents dm^{-3})[168,169] (Fig. 4.6) revealed unequivocally that all of these complexes were <u>2:1</u> and <u>not</u> 1:1 electrolytes (for calculations see Appendix). This is because in all cases, the gradients of these plots were larger than 300 (Table 4.4) and comparison of these values with those found for known types of electrolyte in nitromethane (see Table 4.3), confirmed that they were not 1:1 electrolytes.

<u>Table 4.3</u>

<u>Conductivity data for various types of electrolytes in nitrometha</u>

<u>Compound</u>	Λ_m	<u>Slope of $\Lambda_o-\Lambda_e$ vs $C_e^{\frac{1}{2}}$ plot</u>	<u>Ion Type</u>	<u>Ref.</u>
$[Ru_2Cl_3(PEt_2Ph)_6]Cl$	85.5	151	1:1	168
$NaBPh_4$	100	216	1:1	168
$[Pd_2(PPh_2)_2(Ph_2P(CH_2)_2PPh_2)_2][ClO_4]_2$	192	560	2:1	169
$[Ni(1,10\ phenanthroline)_3]Cl_2$	118	420	2:1	169
$[Co(bipy)_3][ClO_4]_3$	144	1020	3:1	169
$[(\eta^6-C_6H_6)_2Ru_2Cl_3]PF_6$	82	207	1:1	171
$[Ru_2Cl_3(PMe_2Ph)_6]PF_6$	75	190	1:1	171

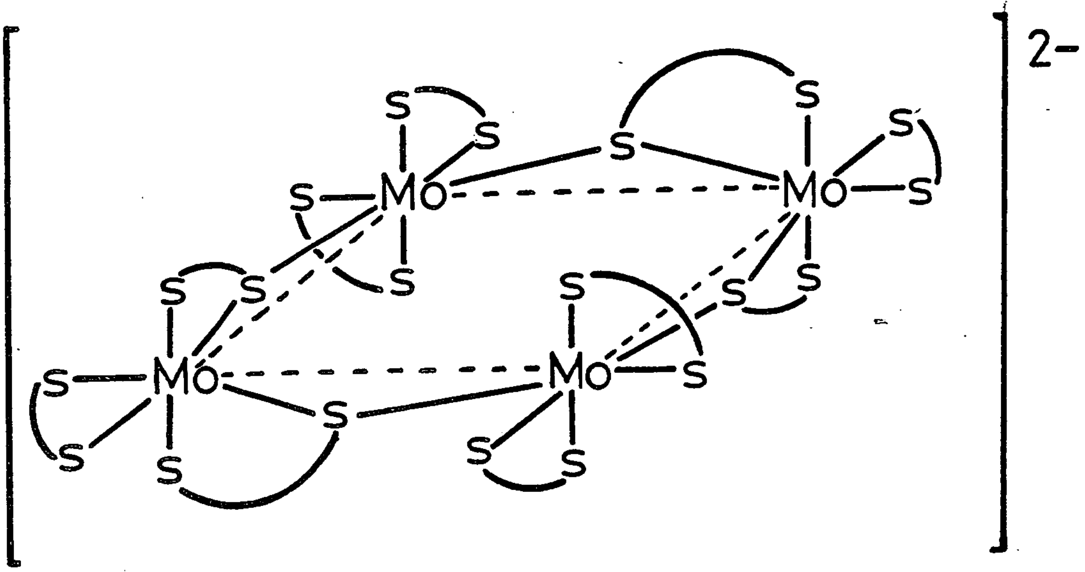
Plot of $\Lambda_o-\Lambda_e$ vs $C_e^{\frac{1}{2}}$ for various $[M]_n[\{Mo_2(S_2COR)_5\}_n]$ electrolytes in acetone



	Slope
$P[Ph_3PhCH_2]_n[\{Mo_2(S_2COEt)_5\}_n]$	650
$P[Ph_3PhCH_2]_n[\{Mo_2(S_2COEt)_4(S_2COMe)\}_n]$	500
$P[Ph_3PhCH_2]_n[\{Mo_2(S_2COMe)_5\}_n]$	600

Fig. 4.6

Therefore, it would appear that in solution these molybdenum compounds should be formulated as tetrameric $[M]_2[Mo_4(S_2COR)_{10}]$ and $[M]_2[Mo_4(S_2COR)_8(S_2COR^1)_2]$ complexes (i.e. n = 2) and a possible structure which maintains the xanthato ligand arrangement shown in (55) is given in (57).



(57)

Although X-ray structural analyses are now essential to verify the detailed configurations of these tetrameric structures, the recent X-ray[172] of the related $[Mo_4Cl_8(PEt_3)_4]$ complex showing it to be a rectangular cluster containing two short and two long Mo-Mo bonds is most encouraging.

Unfortunately attempts to verify this tetrameric formulation from molecular weight measurements using vapour pressure osmometry failed. The main reason for this is the rapid decomposition of these compounds in solution especially at the higher temperatures (308 K) required in the osmometric study.

4.2.2 Reaction of $Mo_2(S_2COR)_4$ with $Na[S_2CNR_2]$ and Na[SOCPh] (1:1 molar ratios)

Reaction of $Mo_2(S_2COEt)_4$ in degassed acetone with $Na[S_2CNR_2]$ (R = Me,Et) in stoichiometric amounts resulted in the immediate formation of a green solution from which the green product could be "trapped out" with a large cation. The products isolated from these reactions were not as stable as those isolated from the analogous reactions with $K[S_2COR]$ and were found to slowly decompose over a period of several days in air, turning brown and giving off a foul sulphurous smell. However, elemental analysis did suggest that the products were of empirical formulae $[PPh_3PhCH_2]_n$-$[\{Mo_2(S_2COEt)_4(S_2CNR_2)\}_n]$ (R = Me,Et) and the i.r. spectra showed bands at 1575 cm^{-1} (Me) and 1580 cm^{-1} (Et) which were assigned to $\nu(C\overset{\cdots}{=}N)$ of the dithiocarbamate ligand. Also conductivity measurements on $[PPh_3PhCH_2]_n[\{Mo_2(S_2COEt)_4$-$(S_2CNMe_2)\}_n]$ in nitromethane gave a gradient of 540 (Table 4.4), suggesting n = 2 and the formation of a tetrameric anion.

The corresponding reaction of $Mo_2(S_2COR)_4$ (R = Me,Et,^{i}Pr) with stoichiometric amounts of Na[SOCPh] in degassed acetone again resulted in immediate reaction on mixing. This time the reaction mixtures turned a deep red-wine colour from which maroon solids could be isolated. These compounds however proved to be rather unstable in the solid state decomposing to form sticky dark red tars after several days exposure to air. They could however be kept longer if stored under vacuo over P_2O_5. In solution decomposition proved to be very rapid and all attempts to obtain either good ^1H n.m.r. spectra or conductivity data failed. The proton spectra obtained did show inequivalence of the Et groups of the xanthate ligands and along with i.r. spectra which showed no bands above 1460 cm^{-1} suggested that the monothiobenzoate ligand was bound in a bidentate manner in one of the bridging positions (see Chapter 1 for discussion of i.r. correlations). However at this time it is not possible to say whether the anion is a dimer (55) or a tetramer (57) but as all the other complexes have been shown to be tetramers by conductivity plots it would seem reasonable to assume that these complexes are also tetramers.

4.2.3 Reaction of $Mo_2(S_2COEt)_4$ with $NH_4[S_2PPh_2]$ (1:1 molar ratio)

Reaction of $Mo_2(S_2COEt)_4$ with $NH_4[S_2PPh_2]$ in a 1:1 molar ratio resulted in a deep red solution from which an orange product could be isolated by "trapping out" with $[PPh_3PhCH_2]Cl$. Elemental analysis again showed the product to be of empirical formula $[PPh_3PhCH_2]_n[\{Mo_2(S_2COEt)_4-(S_2PPh_2)\}_n]$. However the ^1H n.m.r. spectrum (Fig. 4.7) shows only one quartet and one triplet for the ethyl groups of the xanthate ligands indicating that they are all magnetically equivalent. On the basis of this data structure (58) is suggested where the dithiophosphinate ligand is bound only in a unidentate fashion behaving in the same manner as a halide group (see d).

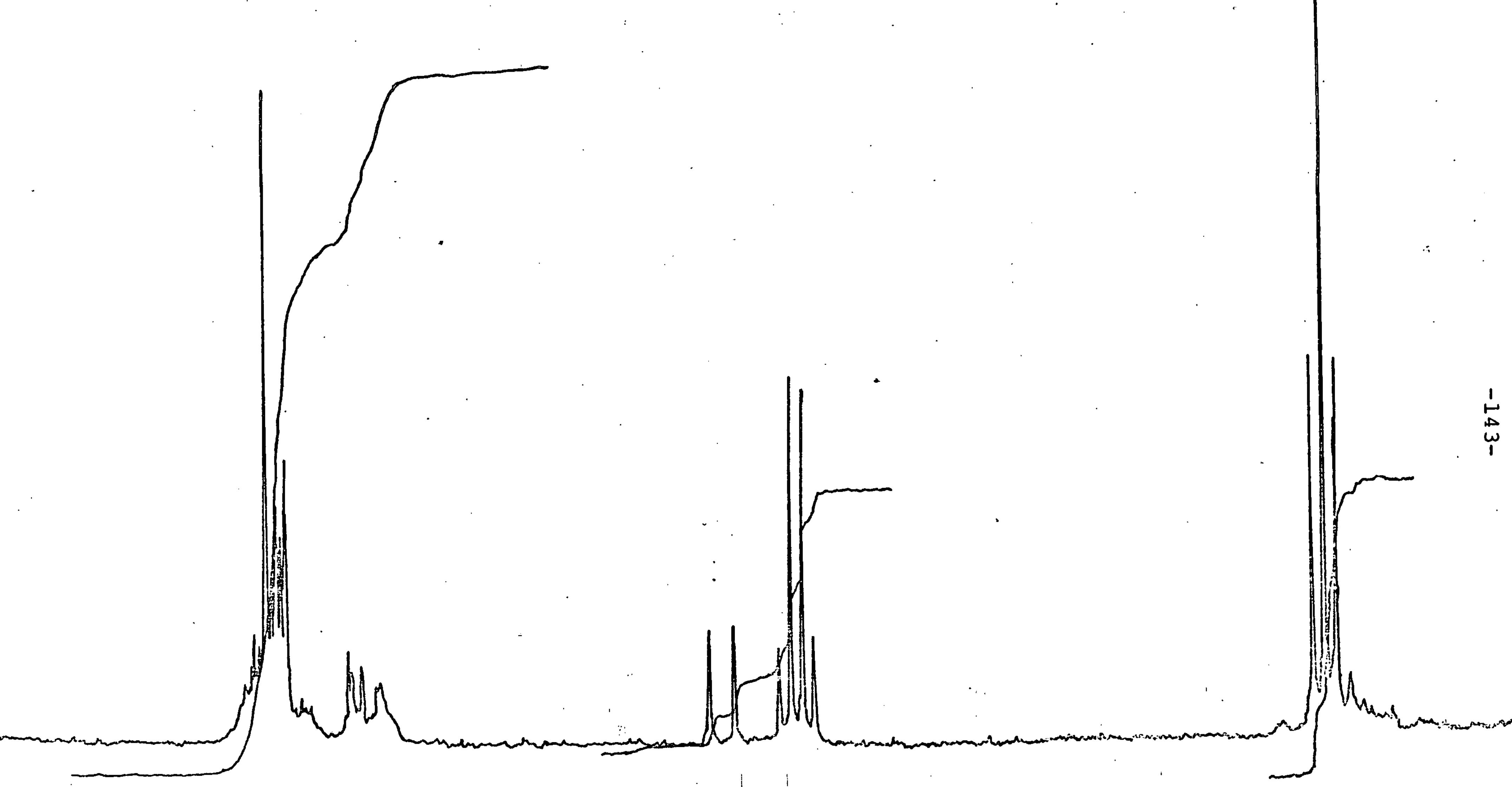
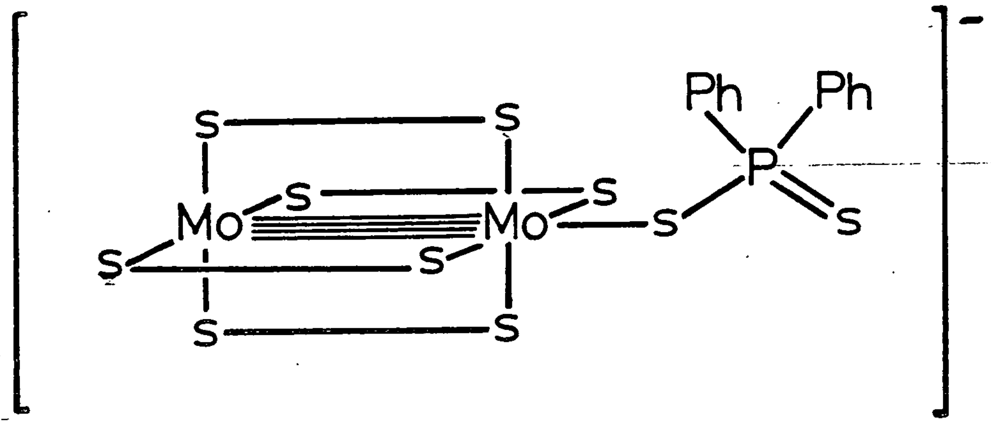


Fig. 4.7 ^1H n.m.r.spectrum of $[Ph_3PhCH_2P][Mo_2(S_2COEt)_4(S_2PPh_2)]$ at 298K in d^6-acetone



(58)

4.2.4 Reaction of $Mo_2(S_2COEt)_4$ with X^- ($X^- = Cl^-, Br^-, I^-$).

Reaction of $Mo_2(S_2COEt)_4$ in degassed acetone with LiX ($X = Br^-, I^-$) in either 1:1 or 1 to excess molar ratios followed by treatment with a methanolic solution of $[Ph_3(PhCH_2)P]Cl$ was found by elemental analysis (see Table 4.5) to yield compounds of empirical formulae $[Ph_3(PhCH_2)P][Mo_2(S_2COEt)_4X]$ and $[Ph_3(PhCH_2)P]_2[Mo_2(S_2COEt)_4X_2]$ respectively. High resolution ^1H n.m.r. spectroscopy (see Table 4.6) in all cases showed that the halide groups had simply added at the apical positions and that no rearrangement of the xanthate ligands had occurred (see Fig. 4.8 for ^1H n.m.r. spectrum of $[Ph_3PhCH_2P]_n[\{Mo_2(S_2COEt)_4Cl\}_n]$). The analogous reactions with LiCl in 1:1 or 1 to excess molar ratio in the presence of a large cation, however, only gave products of empirical formula $[Ph_3PhCH_2P]_n[\{Mo_2(S_2COEt)_4Cl\}_n]$. Although elemental analysis, i.r. and ^1H n.m.r. spectroscopy suggested that the same product was obtained from both reactions differing solubilities suggested that the products were not the same. In the reaction where stoichiometric amounts of reactants were used the product obtained was only

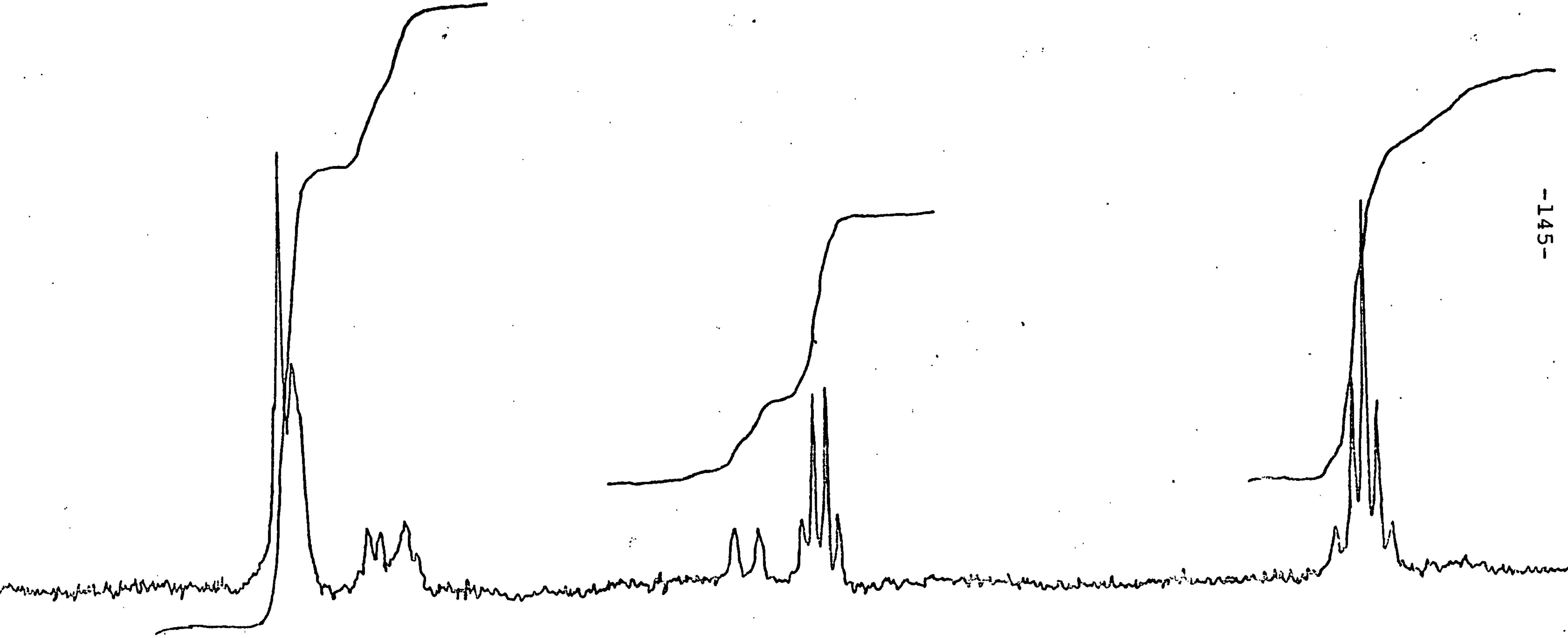
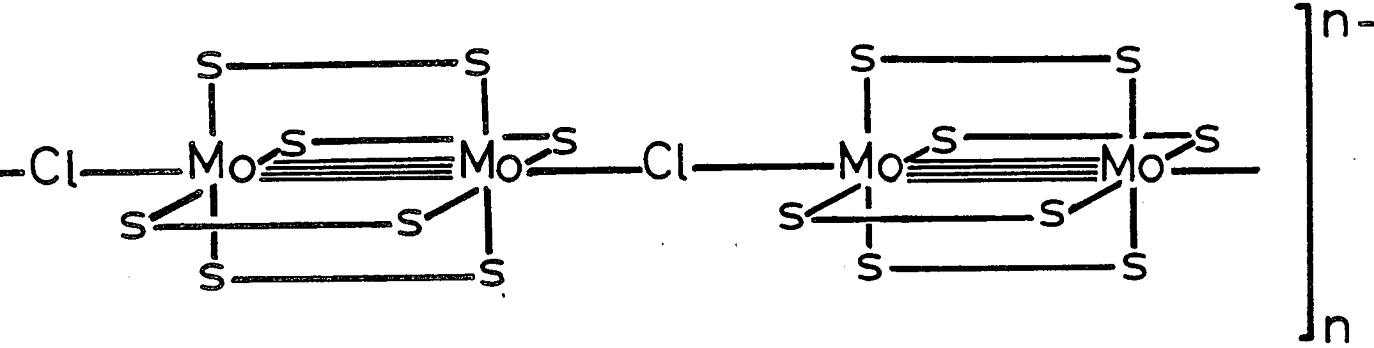
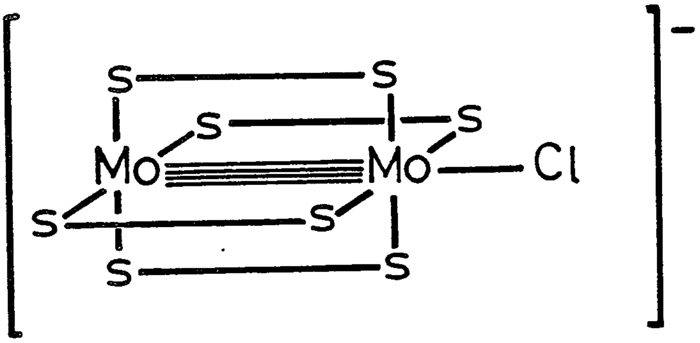


Fig. 4.8 ^{1}H n.m.r. spectrum of $[Ph_3PhCH_2P]_n[\{Mo_2(S_2COEt)_4Cl\}_n]$ at 298K in d^6-acetone

sparingly soluble whereas the product obtained from the reaction with excess LiCl was found to be reasonably soluble in most organic solvents. One possible explanation for this is that in the first case, the compound is a polymer (59) whereas in the second case the product isolated exists in discrete monomeric units (60).



(59)

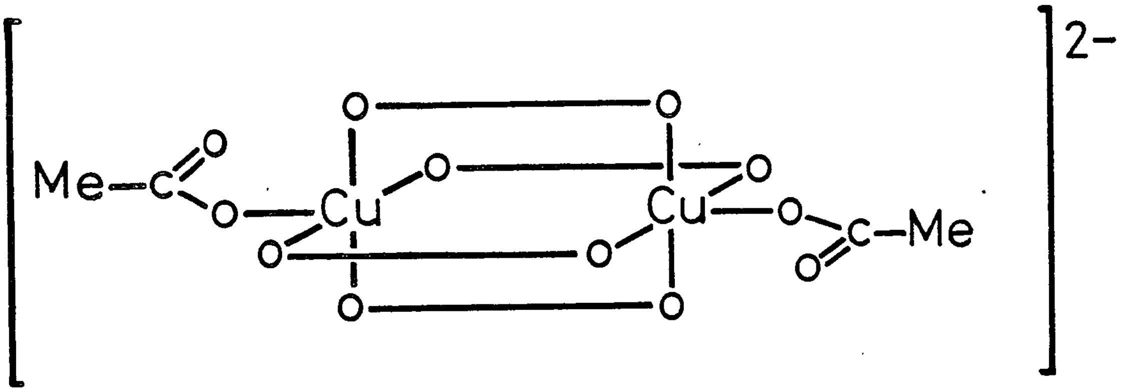


(60)

Both structures (59) and (60) have previously been found for this type of compound. Cotton <u>et al</u>[172] reported an X-ray analysis of $Ru_2(O_2CC_3H_7)_4Cl$ and showed it to have structure (59), where the molecules existed in infinite zigzag chains.

More recently Garner and Senior[173] have made an extensive study of the reactions of $Mo_2(O_2CCF_3)_4$ with $[Et_4N]X$ and isolated a range of compounds of empirical formula $[Et_4N]_n^+$–$[Mo_2(O_2CCF_3)_4X_n]^{n-}$ (n = 1, X = Cl^-, Br^-, I^-, $^-O_2CCF_3$, $SnCl_3^-$; n = 2, X = Br^-, I^-). They have suggested from vibrational spectral data that the 1:1 adducts exist as discrete asymmetric units with a structure of type (60).

In general however most published work in this area has been on the bisadducts. Cotton et al[174] have reported the X-ray structure of $Re_2(O_2CPh)_4Cl_2.2CHCl_3$ and shown it to be analogous to that of $Cu_2(O_2CCH_3)_42H_2O$ (see Fig. 4.1). Similarly the preparation of the analogous $[Rh_2(O_2CCF_3)_4X_2]^{2-}$ (X = Br^-, I^-) anions has been reported.[175] The corresponding $[Me_4N]_2[Cu_2(O_2CR)_4(NCS)_2]$ (R = H,Me)[176] complexes have also been prepared and more recently the crystal structures of $[Cu_2(O_2CCH_3)_4(OMe)_2]^{2-}$ and $[Cu_2(O_2CCH_3)_6]^{2-}$ (61) have been reported.[177] The latter again maintain the $Cu_2(O_2CCH_3)_4$ core with the fifth and sixth acetate groups only bonded in a unidentate manner.



(61)

This structure has also been suggested for the transient $[Mo_2(O_2CCF_3)_6]^{2-}$ anion on the basis of ^{19}F n.m.r. spectroscopy.[178]

However a more facile route to preparing complexes of the type $[M]_n[Mo_2(S_2COEt)_4X_n]$, similar to that used by Garner and Senior[173] was then tried and found to be very successful. This method involved reacting $Mo_2(S_2COEt)_4$ with $[M]X$($M = Ph_3PH^+$, $^nBu_4N^+$; $X = Br^-, I^-$) (where M was the large cation used to "trap out" the anion generated) in either 1:1 or 1:2 molar ratio, thus eliminating the need to add a large cation at a later stage to isolate the product.

4.3 Experimental

Microanalyses, i.r., ^1H n.m.r. spectra and melting points were obtained as described in Chapter 1. Conductivity data and $^{31}P-\{^1H\}$ n.m.r.spectra were obtained as described in Chapter 2. Mass spectra were obtained on an AEI MS9 spectrometer. Analytical data and ^1H n.m.r. spectroscopic data are given in Tables 4.4, 4.5 and 4.6 respectively. Gradients obtained from the plots of $\Lambda_o-\Lambda_e$ vs $C_e^{\frac{1}{2}}$ obtained from conductivity measurements are also given in Tables 4.4 and 4.5. All solvents were degassed before use by refluxing under a stream of oxygen-free nitrogen (BOC) and all manipulations were carried out under nitrogen under normal Schlenk conditions. ^1H n.m.r. spectra and conductivity measurements were all measured in degassed solvents. Molybdenum was determined by ignition to the oxide at 500-550°C.

Materials:- Molybdenum hexacarbonyl, K[S_2COEt] and Na[S_2CNEt$_2$]$3H_2O$ (BDH), Na[S_2CNMe$_2$]$2H_2O$ (Ralph-Emanuel), [AsPh$_4$]ClHCl (Koch Light Ltd.). The salts K[S_2COR] (R = Me, ^{i}Pr) were synthesised as described earlier,[179] [Ph$_3$PhCH$_2$P]Cl was prepared by reaction of Ph$_3$P with PhCH$_2$Cl in dmf,[180] NH$_4$[S_2PPh$_2$] was prepared from Ph$_2$PS$_2$H and ammonia in benzene[181] and [Mo$_2$(O_2CCH$_3$)$_4$] was prepared as described elsewhere.[182]

μ_4-tetrakis (O-ethyldithiocarbonato)dimolybdenum(II)

Method A (Prepared as described by Steele and Stephenson[132]). A suspension of [Mo$_2$(O_2CCH$_3$)$_4$] (1.00 g) in methanol (50 cm^3) was heated to 333 K with constant stirring and treated with K[S_2COEt] (1.70 g; 2:1 molar ratio). The yellow suspension rapidly dissolved to give a green solution from which a dark red crystalline solid was deposited after a few minutes; heating and stirring were continued for a further 30 minutes to ensure complete reaction. The dark red product was filtered off, washed with H_2O, MeOH and Et$_2$O then dried by suction [ν(CO) 1200 (vs); ν(CS) 1045 (vs) cm^{-1}].
The same compound was obtained if the reaction was carried out in ethanol. The complex could be recrystallised from acetone as the acetone adduct (ν(CO) acetone 1680 cm^{-1}); however this rapidly lost acetone at room temperature. (Yield ca 60%).

Method B (Prepared as described by Cotton et al[133])
To a suspension of $[Mo_2(O_2CCH_3)_4]$ (1.10 g) in 120 cm^3 of absolute ethanol was added $K[S_2COEt]$ (1.60 g). The resulting mixture was then stirred for 6 to 12 hours at room temperature during which time the red product precipitated out. The product was filtered off, washed with ethanol, then redissolved in a minimum of acetone and any remaining yellow solid filtered off. The purified product was then recrystallised from the acetone filtrate. (Yield *ca* 70%).

μ_4-bis(O-ethyldithiocarbonato)bis(acetato)dimolybdenum (II)

To a suspension of $Mo_2(O_2CCH_3)_4$ (1.20 g) in absolute ethanol was added $K[S_2COEt]$ (1.60 g). The resulting mixture was stirred for 6 hours then the orange precipitate was filtered off. This orange solid was redissolved in a minimum of acetone to give a deep red solution of $[Mo_2(S_2COEt)_4]$ and the insoluble yellow product. The yellow product was filtered off, washed with ethanol then diethyl ether and dried *in vacuo* at 60°C.
(ν(CO) acetate 1510, ν(CO) xanthate 1195, ν(CS) 1040 cm^{-1})
(Yield *ca* 30%).

μ_4-tetrakis(O-methyldithiocarbonato)dimolybdenum (II)

Method A:- To a suspension of $Mo_2(O_2CCH_3)_4$ (0.70g) in 70 cm^3 of methanol was added $K[S_2COMe]$ (0.96 g) suspended in 70 cm^3 of methanol. The reaction mixture was stirred and heated at 333 K for 1 hour, then cooled to room temperature to give a red solid and a red solution. The product was filtered off, washed with H_2O (40 cm^3), MeOH (40 cm^3) and diethyl ether and then dried *in vacuo* at 56°C. (Yield *ca* 45%).

Method B:- To a suspension of $Mo_2(O_2CCH_3)_4$ (0.64 g) in 100 cm^3 of absolute ethanol was added $K[S_2COMe]$ (0.88 g). After 2 to 3 minutes the solution turned a dark green colour but after stirring for a further 3 hours it had turned a bright orange/red colour and an orange solid had formed. This orange product was filtered off washed with absolute ethanol and then diethyl ether. The product was dried *in vacuo* at 56°C. (Yield, 70-75%).

μ_4-tetrakis (O-isopropyldithiocarbonato)dimolybdenum (II)

Method A:- $Mo_2(S_2COCH(Me)_2)_4$ was prepared using the same method as for the O-methyl- and O-ethyldithiocarbonato complexes. (Yield, 20-25%).

Method B:- As for the O-methyl- and O-ethyldithiocarbonato complexes. (Yield, *ca* 60%).

Triphenylbenzylphosphonium[decakis(O-ethyldithiocarbonato) tetramolybdate (II)]

To a solution of $[Mo_2(S_2COEt)_4]$ (0.26 g) dissolved in acetone (40 cm^3) was added $K[S_2COEt]$ (0.06 g) also dissolved in acetone (40 cm^3). On mixing the solution immediately turned very dark green; after stirring for a further 5 minutes a methanolic solution of triphenylbenzylphosphonium chloride was added. The resulting solution was stirred and slowly reduced in volume (to ca 10 cm^3) over a period of 2 hours. The reaction vessel was then filled with dry N_2, sealed and stored at 253 K for 24 hours. During this period very dark green micro crystals of the product formed. These were filtered off, washed with ice-cold methanol then light petroleum (b.p. 60-80°C) and dried in vacuo at 50°C.M.p. 152-153°C. (Yield ca 60%).

The same compound was obtained by the reaction of $[Mo_2(S_2COEt)_4]$ with excess $K[S_2COEt]$ except that washing the product with methanol was necessary to remove any traces of excess $K[S_2COEt]$. Similarly rather than storing for 24 hours at 253 K, if excess diethylether was added to the solution the product was precipitated as an amorphous green powder. This product was identical to the micro crystalline one in every way but for the fact that it melts 3 to 4°C lower. M.p. 149-150°C (Yield ca 65%).

Tetraphenylarsonium[decakis(O-ethyldithiocarbonato)tetramolybdate (II)]

To a solution of $Mo_2(S_2COEt)_4$ (0.17 g) dissolved in acetone (30 cm^3) was added a solution of $K[S_2COEt]$ (0.04 g) also dissolved in acetone (20 cm^3). On mixing, the solution immediately turned a very dark green colour. After 5 minutes a methanolic solution of $[Ph_4As]ClHCl$ was added. The resulting mixture was stirred and slowly reduced in volume (to ca 5 cm^3) over a period of 2 hours. On addition of diethylether the green product precipitated out; this was filtered off, washed with methanol and then dried *in vacuo* at 56°C. (Yield *ca* 70%).

Potassium[decakis(O-ethyldithiocarbonato)tetramolybdate (II)]

(Performed as an n.m.r. tube experiment). To a solution of $[Mo_2(S_2COEt)_4]$ (0.015 g) in d^6-acetone (0.20 cm^3) was added a mole equivalent of $K[S_2COEt]$ (0.0035 g) also dissolved in d^6-acetone. The solutions were mixed to give a green solution of the product and the ^1H n.m.r. spectrum was run immediately.

Attempted preparation of Caesium [decakis(O-ethyldithiocarbonato)tetramolybdate (II)]

To a solution of $[Mo_2(S_2COEt)_4]$ (0.12 g) dissolved in acetone (25 cm^3) was added $K[S_2COEt]$ (0.03 g) also in acetone (25 cm^3), to give a dark green solution. After 5 minutes a methanolic solution of CsCl was added. On work-up however only the starting material $[Mo_2(S_2COEt)_4]$ was isolated. This was confirmed by elemental analysis. [*Found*: C 20.9; H 3.0%. Required for $Mo_2(S_2COEt)_4$ C 21.2; H 2.9%] and by comparison of i.r. spectra; ν(CO) 1200 (vs), ν(CS) 1045 cm^{-1} (vs).

Triphenylbenzylphosphonium[decakis(O-methyldithiocarbonato) tetramolybdate (II)]

To a suspension of $[Mo_2(S_2COMe)_4]$ (0.12 g) in acetone (20 cm^3) was added $K[S_2COMe]$ (0.03 g) also in acetone (20 cm^3).

On mixing the solution immediately turned a dark green colour. After 5 minutes a methanolic solution of $[Ph_3PhCH_2P]Cl$ was added, and then worked up as previously described, the very dark green <u>micro crystals</u> of product forming after storage at 253 K for 20 hours. (Yield <u>ca</u> 50%).

<u>Triphenylbenzylphosphonium[octakis(O-ethyldithiocarbonato)bis(O-methyl-dithiocarbonato)tetramolybdate (II)]</u>

To a suspension of $[Mo_2(S_2COEt)_4]$ (0.25 g) in acetone (45 cm^3) was added $K[S_2COMe]$ (0.06 g) also in acetone (20 cm^3). On mixing the solution immediately turned dark green and after 5 minutes an ethanolic solution of $[Ph_3PhCH_2P]Cl$ was added. The resulting solution was then stirred and slowly reduced in volume (to <u>ca</u> 5 cm^3), by which time a large amount of product had precipitated out. The dark green <u>product</u> was filtered off, washed with MeOH, light petroleum (b.p. 60-80°C) and then dried <u>in vacuo</u> at 56°C. (Yield <u>ca</u> 70%).

<u>Triphenylbenzylphosphonium[bis(O-ethyldithiocarbonato)octakis(O-methyl-dithiocarbonato)tetramolybdate (II)]</u>

This was prepared using the same method as for the last complex, using $[Mo_2(S_2COMe)_4]$ (0.12 g) and $K[S_2COEt]$ (0.03 g). (Yield <u>ca</u> 60%).

<u>Triphenylbenzylphosphonium[octakis(O-ethyldithiocarbonato bis(dimethyl-dithiocarbamato)tetramolybdate (II)]</u>

To a suspension of $[Mo_2(S_2COEt)_4]$ (0.14 g) in acetone (15 cm^3) was added $Na[S_2CNMe_2]2H_2O$ (0.04 g) also dissolved in acetone (15 cm^3). On mixing, the solution turned a dark green colour and after 5 minutes an ethanolic solution of $[Ph_3PhCH_2P]Cl$ was added. Over a period of 2 hours the resulting solution was stirred and slowly reduced to a minimum volume (<u>ca</u> 10 cm^3). At this point some of the product had precipitated out and precipitation was completed by the addition of diethylether (25 cm^3). The product was then worked up as described earlier. (Yield <u>ca</u> 60%).

Triphenylbenzylphosphonium[octakis(O-ethyldithiocarbonato)-bis(diethyldithiocarbamato)tetramolybdate (II)]

This compound was prepared as described previously using $[Mo_2(S_2COEt)_4]$ (0.17 g) and $Na[S_2CNEt_2]3H_2O$ (0.06 g). The product was obtained on precipitation as a dark green solid. (Yield *ca* 65%).

Triphenylbenzylphosphonium[μ_4-tetrakis(O-ethyldithiocarbonato)-diphenyldithiophosphinatodimolybdate (II)]

To a solution of $Mo_2(S_2COEt)_4$ (0.10 g) in acetone (40 cm^3) was added $NH_4[S_2PPh_2]$ (0.05 g) also in acetone (20 cm^3). On mixing there was no apparent colour change but after a few minutes the solution darkened and after 5 minutes it had become very deep red. An ethanolic solution of $[Ph_3PhCH_2P]Cl$ was then added and the total volume reduced to *ca* 5-10 cm^3. The reaction mixture was then stored at 253 K for 48 hours and the product precipitated out. The product was filtered off, washed with EtOH, diethylether and dried *in vacuo* at 56°C. (Yield *ca* 50%).

Triphenylbenzylphosphonium[octakis(O-ethyldithiocarbonato)-bis(monothiobenzoato)tetramolybdate (II)]

To a suspension of $Mo_2(S_2COEt)_4$ (0.11 g) in acetone (20 cm^3) was slowly added Na[SOCPh] (0.05 g) also dissolved in acetone (15 cm^3). On mixing, the solution immediately turned a deep wine colour. To this was added an ethanolic solution of $[Ph_3PhCH_2P]Cl$, the total volume reduced to approximately 5 mls and on addition of light petroleum (b.p. 60-80°C) the maroon-coloured product precipitated out. The product was filtered off and worked up as described previously. (Yield *ca* 60%).

Triphenylbenzylphosphonium[octakis(O-methyldithiocarbonato) bis(monothiobenzoato) tetramolybdate (II)]

This compound was prepared as above using $Mo_2(S_2COMe)_4$ (0.11 g) and Na[SOCPh] (0.04 g). (Yield *ca* 60%).

Triphenylbenzylphosphonium[octakis(O-isopropyldithiocarbonato)-bis(monothiobenzoato) tetramolybdate (II)]

This compound was prepared as above using $Mo_2(S_2CO^iPr)_4$ (0.11 g) and Na[SOCPh] (0.03 g). (Yield *ca* 50%).

Triphenylbenzylphosphonium[μ_4-tetrakis(O-ethyldithiocarbonato)-μ-chloro-dimolybdate (II)]

To a suspension of $Mo_2(S_2COEt)_4$ (0.10 g) in acetone (15 cm^3) was added LiCl (0.007 g) dissolved in an acetone/ethanol mixture. On addition all the $Mo_2(S_2COEt)_4$ went into solution and it turned dark red. After 5 minutes an ethanolic solution of $[Ph_3PhCH_2P]Cl$ was added. The reaction mixture was then slowly reduced in volume to approximately 5 cm^3 and at this stage the orange product precipitated out. The product was filtered off, washed with a small amount of ice-cold MeOH then several portions of diethyl ether, and finally dried *in vacuo* at 56°C. (Yield *ca* 85%).

Triphenylbenzylphosphonium[μ_4-tetrakis(O-ethyldithiocarbonato) chlorodimolybdate (II)]

To a suspension of $Mo_2(S_2COEt)_4$ (0.14 g) in acetone (15 cm^3) was added a 20 fold excess of LiCl (0.19 g) dissolved in acetone (25 cm^3). After mixing, the reaction mixture was stirred for 20 minutes and then an ethanolic solution of $[Ph_3PhCH_2P]Cl$ was added. The reaction mixture was reduced to a minimum volume (*ca* 10 cm^3) over a period of 1 hour. At this stage a small amount of solid had precipitated out and precipitation of the *product* was completed by addition of diethyl ether. The orange product was worked up as earlier described. (Yield *ca* 70%).

Triphenylbenzylphosphonium[μ_4-tetrakis(O-ethyldithiocarbonato)-iododimolybdate (II)]

To a sample of $Mo_2(S_2COEt)_4$ dissolved in an acetone/ethanol mixture was added a 3 to 5 fold excess of LiI dissolved in absolute ethanol. The resulting mixture was stirred for 20 minutes and then an excess of $[Ph_3PhCH_2P]Cl$ dissolved in ethanol was added. The reaction mixture was then stirred and slowly reduced in volume and the yellow-orange *product* precipitated out. The product was worked up as previously described. (Yield *ca* 60%).

Triphenylbenzylphosphonium[μ_4-tetrakis-(O-methyldithiocarbonato)iododimolybdate (II)]

This compound was prepared as for the O-ethyldithiocarbonate complex. (Yield *ca* 70%).

Triphenylbenzylphosphonium[μ_4-tetrakis(O-ethyldithiocarbonato) bisbromodimolybdate (II)]

To a suspension of $Mo_2(S_2COEt)_4$ (0.17 g) in acetone (15 cm^3) was added a 10 fold excess of LiBr (0.22 g) dissolved in acetone (15 cm^3). After 5 minutes the reaction mixture had turned a deep red colour and then an ethanolic solution of $[Ph_3PhCH_2P]Cl$ was added. The reaction mixture was stirred and slowly reduced in volume to ca 10 cm^3 and on addition of diethyl ether the orange product precipitated out. The product was worked up as previously described. (Yield ca 70%).

Triphenylphosphonium[μ_4-tetrakis(O-ethyldithiocarbonato)-bromodimolybdate (II)]

To an acetone (120 cm^3) solution of $Mo_2(S_2COEt)_4$ (0.17 g) was added a stoichiometric amount of $[Ph_3PH]Br$ (0.08 g) dissolved in a mixture (1:1 v/v) of acetone/ethanol (20 cm^3). On mixing, the solution darkened slightly in colour. The reaction mixture was then stirred and slowly reduced in volume (to ca 5 cm^3) over a period of 2 hours. On addition of diethyl ether the orange red product precipitated out. The product was worked up as described earlier. (Yield 60%).

Tetra-n-butylammonium[μ_4-tetrakis(O-methyldithiocarbonato)-iododimolybdate (II)]

This compound was prepared as above using $Mo_2(S_2COEt)_4$ (0.23 g) and $[nBu_4N]I$ (0.11 g). (Yield ca 55%).

Tetra-n-butylammonium[μ_4-tetrakis(O-ethyldithiocarbonato)bisiododimolybdate (II)]

This compound was prepared in the same manner as the mono iodo adduct using $Mo_2(S_2COEt)_4$ (0.17 g) and a 2.5 fold excess of $[^nBu_4N]I$ (0.24 g). (Yield *ca* 60%).

Some Analytical and Conductivity Data on Molybdenum (II) Dithioacid Complexes

Complex	M.P. °C	Colour	Analysis (%)[a]			Gradient of $\Lambda_o - \Lambda_e$ vs $C_e^{\frac{1}{2}}$ plot[b]
			C	H	N	
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COEt)_5\}_n]$[c]	152-153	Dark green	41.5(41.7)	4.0(4.1)		650[d]; 780[e]
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COMe)_5\}_n]$	117-119	Dark green	38.4(38.9)	3.5(3.4)		600[d]; 646[e]
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COCH(Me)_2)_5\}_n]$	77-78	Dark green	44.0(44.2)	4.4(4.7)		
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COEt)_4-(S_2COMe)\}_n](CH_2Cl_2)_n$	146-148decomp	Dark green	39.3(39.3)	3.8(3.8)		500[d]
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COMe)_4(S_2COEt)\}_n]$	90-91	Dark green	39.8(39.5)	3.4(3.6)		
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COEt)_4-(SOCPh)\}_n](CH_2Cl_2)_n$	78-81	Purple	43.4(43.2)	3.7(3.9)		
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COMe)_4-(SOCPh)\}_n]$	112-114	Purple	43.5(43.2)	3.4(3.5)		
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COCH(Me)_2)_4-(SOCPh)\}_n]$	80-82	Purple	47.2(47.1)	4.5(4.6)		
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COEt)_4-(S_2CNMe_2)\}_n]$	137-138	Dark Green	41.2(41.8)	4.3(4.2)	1.2(1.2)	540[e]
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COEt)_4-(S_2CNEt_2)\}_n]$	116-119	Dark Green	42.6(42.8)	4.2(4.4)	1.1(1.2)	
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COEt)_4-(S_2PPh_2)\}_n]$	129-131	Orange Brown	44.9(46.0)	3.8(4.1)		

[a] Calculated percentages in parentheses; [b] Measured at 291 K;

[c] Found Mo 16.7; P 2.8; S 27.5%. Required Mo 16.7; P 2.7; S 27.8%.

[d] In acetone; [e] In nitromethane.

Some Analytical and Conductivity Data on Molybdenum (II) Dithioacid Halide Complexes

Complex	M.P. °C	Colour	Analysis (%)[a]			Gradient of $\Lambda_o-\Lambda_e$ vs $C_e^{\frac{1}{2}}$ plot[b]
			C	H	N	
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COEt)_4Cl\}_n]$[c]	ca 190(decomp)	Orange	41.8(41.7)	4.0(4.0)		
$[Ph_3(PhCH_2)P][Mo_2(S_2COEt)_4Cl]$	ca 190(decomp)	Orange	41.7(41.7)	4.0(4.0)		260[d]
$[Ph_3(PhCH_2)P][Mo_2(S_2COEt)_4I]$	ca 190(decomp)[e]	Yellow Orange	38.5(38.4)	3.7(3.6)		300[d]
$[Ph_3(PhCH_2)P][Mo_2(S_2COMe)_4I]H_2O$	ca 160(decomp)	Yellow Orange	32.8(33.0)	3.3(3.2)		
$[^nBu_4N][Mo_2(S_2COEt)_4I]$	120-121	Yellow Orange	32.0(32.2)	5.4(5.4)	1.3(1.3)	
$[Ph_3PH][Mo_2(S_2COEt)_4Br]$	>200	Brown	35.4(35.3)	3.5(3.5)		
$[Ph_3(PhCH_2)P]_2[Mo_2(S_2COEt)_4Br_2]$[f]	180	Reddish Brown	48.0(48.2)	4.1(4.2)		400[d]
$[^nBu_4N]_2[Mo_2(S_2COEt)_4I_2]$	153-154	Reddish orange	37.3(37.3)	6.5(6.5)	1.9(2.0)	450[d]

[a] Calculated percentages in parentheses

[b] Measured at 291 K.

[c] Found Cl 3.4% required; 3.3%.

[d] In nitromethane.

[e] Darkens in colour above 150°C; melts with decomposition at ca 190°C.

[f] Found Br, 10.4% required 10.4%.

Complex	^{1}H n.m.r. (δ)[a,b]				
	CH_3	CH_2	CH	Ph	$Ph_3(PhCH_2)P^+$
$Mo_2(S_2COEt)_4$	1.48(t)	4.67(q)			
"$[K]_n[\{Mo_2(S_2COEt)_5\}_n]$"	1.21(t) [2] 1.45(t) [1] 1.48(t) [2]	4.21(q) [2] 4.45(q) [1] 4.80(q) [2]			
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COEt)_5\}_n]$	1.17(t) [2] 1.42(t) [1] 1.43(t) [2]	4.17(q) [2[4.62(q) [3]		7.0-8.0(m)	5.02(d)
$[AsPh_4]_n[\{Mo_2(S_2COEt)_5\}_n]$	1.17(t) [2] 1.41(t) [1] 1.43(t) [2]	4.17(q) [2] 4.60(q) [1] 4.62(q) [2]		7.86(m)	
$Mo_2(S_2COMe)_4$	4.31(s)				
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COMe)_5\}_n]$	3.77(s) [2] 4.22(s) [1] 4.25(s) [2]			7.0-8.0(m)	5.12(d)
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COCH[Me]_2)_5\}_n]$	1.35(d) [2] 1.36(d) [2] 1.41(d) [1]		5.43[c]	6.7-7.8(m)	4.66(d)
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COMe)_4(S_2COEt)\}_n]$	1.46(t) [1] 3.75(s) [1] 4.22(s) [1] 4.25(s) [2]	4.67(q) [1]		7.0-8.0(m)	5.02(d)
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COEt)_4(S_2COMe)\}_n][CH_2Cl_2]_n$	4.21(s) [1] 1.17(t) [1] 1.43(t) [2] 1.42(t) [1]	4.18(q) [1] 4.62(q) [2] 4.64(q) [1]		7.0-8.0(m)	5.03(d)
$Mo_2(S_2COCH[Me]_2)_4$	1.54(d)		5.54(sep)		
$[Ph_3PhCH_2P]_n[\{Mo_2(S_2COEt)_4Cl\}_n]$	1.40(t)	4.54(q)		7.0-8.0(m)	4.97(d)
$[Ph_3PhCH_2P][Mo_2(S_2COMe)_4I]$	4.16(s)			7.0-8.0(m)	5.08(d)
$[Ph_3PhCH_2P]_2[Mo_2(S_2COEt)_4Br_2]$	1.44(t)	4.59(q)		7.0-8.0(m)	5.18(d)

[a] ±0.01. [b] Relative intensities in parentheses. [c] ^{1}H n.m.r. of this compound is very poor due to rapid decomposition in solution.

4.4 Electrochemical Studies

4.4.1 Introduction

The possibility of discrete redox changes in metal-metal bonded binuclear complexes is of intrinsic interest for a number of reasons; one-electron transfer steps should generate mixed valence compounds and if the redox active orbital is intimately involved in metal-metal bonding relaxation of the structure should accompany electron transfer. In particular, there have been a number of brief reports from Cotton's group on the electrochemistry of binuclear molybdenum complexes containing quadruple bonds and for this reason it was decided to study the redox potentials of some of the related carboxylate and dithiolate compounds mentioned earlier in this chapter. Before discussing the results obtained there is by way of introduction a short section on the relevant electrochemistry of M-M quadruple bonds and on the various electrochemical techniques used.

4.4.2 The relevant electrochemical studies of M-M quadruple bonds and the electrochemical techniques used.

The first electrochemical study[183] on M-M quadruple bonds was on the $[Re_2X_8]^{2-}$ ions. ($X = Cl^-$, Br^-, SCN^-) when it was reported that they could all be polarographically reduced to yield $[Re_2X_8]^{3-}$ and possibly also $[Re_2X_8]^{4-}$. A more recent study of the $[Re_2Cl_8]^{2-}$ anion,[184] however, has shown that it only undergoes a one electron quasi-reversible reduction and that the $[Re_2Cl_8]^{3-}$ species formed is very unstable and rapidly decomposes. A similar study of the analogous $[Tc_2Cl_8]^{2-}$ ion[184] has also shown it to undergo a one-electron quasi-reversible reduction, but in this case the product $[Tc_2Cl_8]^{3-}$ is more stable and its lifetime in solution has been measured as >300 s. This data has been used to explain why attempts to isolate salts of $[Tc_2Cl_8]^{3-}$ and $[Re_2Cl_8]^{3-}$ have failed.

Cotton et al[185] have also studied the electrochemical behaviour of $[Mo_2Cl_8]^{4-}$ and shown by cyclic voltammetry a single oxidation peak at +0.50V vs SCE with a shape for the forward scan very close to that expected for a reversible reaction. However, the corresponding reduction peak could only be observed at sweep rates of 0.5 V s^{-1} and above, and was completely absent for lower sweep rates. This has been postulated as being due to the formation of the very short lived $[Mo_2Cl_8]^{3-}$ anion. A similar study[186] of the $[Mo_2(SO_4)_4]^{3-}$ and $[Mo_2(SO_4)_4]^{4-}$ anions has shown that these can be interconverted electrochemically but again both species are found to decompose in solution especially the $[Mo_2(SO_4)_4]^{3-}$ anion. The only other study in this area has been on the neutral $Mo_2(O_2CC_3H_7)_4$ complex[185] which has been claimed to undergo a quasi-reversible oxidation to $[Mo_2]^+$ (see section 4.4.3 for a full discussion of this work).

Before discussing our results a short description of the particular electrochemical techniques used, cyclic voltammetry and a.c. voltammetry, are presented.*

Voltammetry is an electrochemical method of analysis involving an electrolysis of short duration at a microelectrode ('polarography' for the dropping mercury electrode), such that the currents are very small and the changes produced by electrolysis are normally not measurable; hence the solution can be recovered virtually unchanged. The microelectrode is polarised to different potentials by a voltage applied from an outside source between it and a reference electrode. By plotting the currents obtained when the applied voltage is gradually altered a current-voltage curve is produced in which the characteristic redox processes are indicated as 'waves' or peaks.

Two of the more modern techniques are alternating current (a.c.) polarography and cyclic voltammetry, both of which, for the most part, provide access to the same information. Both techniques deal with three parameters, current, potential and time.

(a) Cyclic voltammetry

Consider a redox couple, the oxidant form of which is present in a solution containing an excess of supporting electrolyte (present to prevent the migration of charged test species in the presence of an electric field). A stationary working electrode is employed, the potential of which is

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*No one text was used for reference for this section but references 187-192 were found very useful.

varied at a finite rate as a linear function of time. After reaching the required limiting value the potential is brought back to zero at the same rate. A current-potential curve similar to that in Fig. 4.9 is obtained (except for irreversible processes where there is no reverse wave), which provides four measurable parameters; the net current ($i_p{}^c$) and potential ($E_p{}^c$) at the peak of the cathodic response, and the corresponding parameters ($i_p{}^a$ and $E_p{}^a$) for the anodic response. These parameters can be used to determine whether the charge transfer process (i.e. transfer of electron to species at electrode) is reversible, quasi-reversible or irreversible. If the charge transfer is "reversible" the process occurs at a significantly more rapid rate than the rate of diffusion. A reaction in which the transfer process is governed by both diffusion

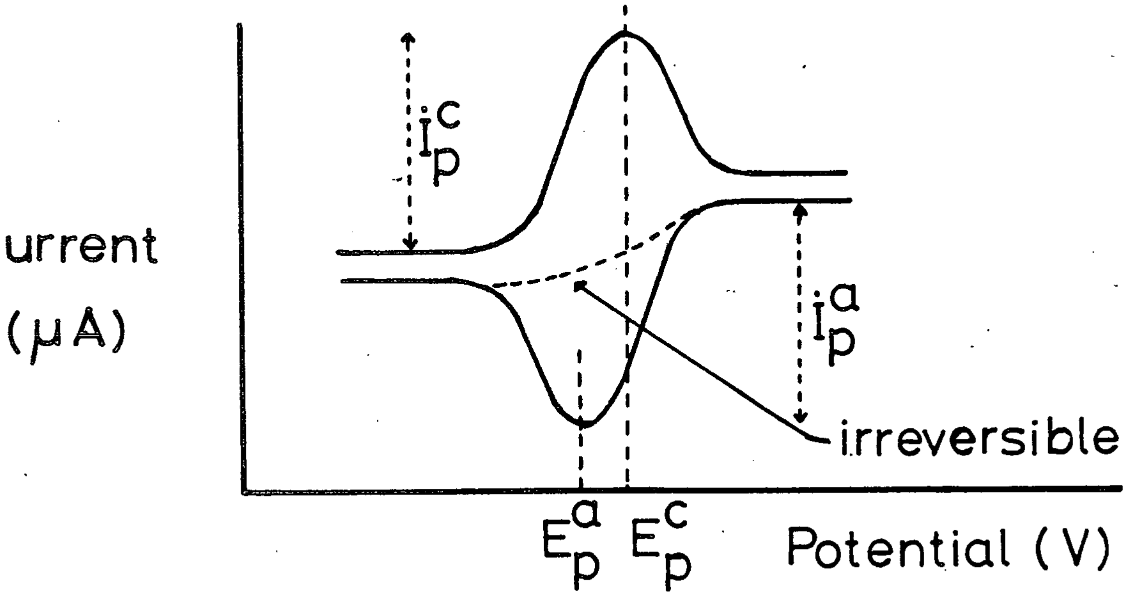


Fig. 4.9. Example of a cyclic voltammetric curve

and charge transfer kinetics is termed "quasi-reversible", and a reaction in which the charge transfer process is much slower than the diffusion rate is called "irreversible". The criteria for each of these three types are tabulated in Table 4.7. Note that the midpoint potential $(E_p{}^c + E_p{}^a)/2$ coincides with E_o, the formal electrode potential in the reversible case.

(b) a.c. Polarography

To obtain an a.c. polarogram, a d.c. potential is applied to the electrode and is varied linearly as a function of time, and at the same time a small potential periodic in time, such as a sine wave, is also applied to the electrode. The net alternating current is monitored as a function of d.c. potential to give a typical symmetric peak wave form as shown in Fig. 4.10. In this case for rapid charge transfer the peak potential coincides with the classical dc $E_{\frac{1}{2}}$ parameter and can be taken as E_o in the fully reversible case. Strictly speaking, this account only applies to experiments at the dropping mercury electrode or rapidly rotating solid electrodes. However in practice it is found that very well defined waves are obtained at a stationary Pt wire.

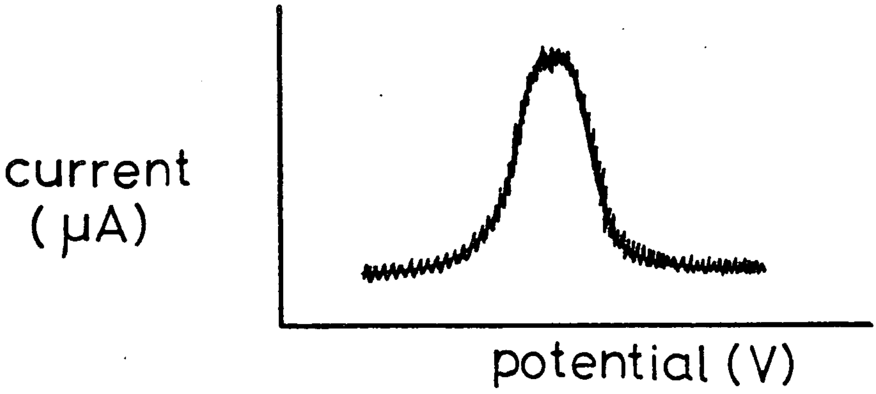


Fig. 4.10. Example of an a.c. voltammogram

Table 4.7

Cyclic Voltammetric Criteria for reversible, quasi-reversible and irreversible charge transfer processes

Reversible	E_p is independent of ν $E_p^c - E_p^a$ = 59/n mv at 25°C and is independent of ν $i_p/\nu^{\frac{1}{2}}$ (current function) is independent of ν i_p^a/i_p^c is unity and independent of ν
Quasi-reversible	E_p shifts with ν $E_p^c - E_p^a$ increases as ν increases $i_p/\nu^{\frac{1}{2}}$ is independent of ν $i_p^a/i_p^c \neq 1$
Irreversible	E_p shifts with ν $i_p/\nu^{\frac{1}{2}}$ is constant with scan rate There is no current on the reverse scan

ν is the sweep rate in volts sec^{-1}

n = number of electrons involved in oxidation or reduction process.

4.4.3 Results and discussion

Cotton and Pedersen[185] studied the electrochemical behaviour of $Mo_2(O_2CC_3H_7)_4$ with the view that the butyrate complex was representative of the tetracarboxylatodimolybdenum complexes. Their reason for not studying the tetraacetate complex was the relative insolubility of that species and the possible difficulties there would be in the eventual characterisation of oxidised products. The results of cyclic voltammetry on the acetate were asserted to be very similar to those obtained for the butyrate complex although no actual values or details were quoted. In the light of this situation, and bearing in mind the close relationship between $Mo_2(O_2CCH_3)_4$ and our own binuclear complexes it was felt that this was a valuable and interesting starting point to our own studies.

Cyclic voltammetry on $Mo_2(O_2CCH_3)_4$ was performed using a platinum electrode in acetone with a potential range from -1.8 V to +1.4 V vs Ag/AgCl. With the equipment at our disposal (PAR 170) the solubility of the compound in our chosen solvent was well within the workable range. At +0.51 V a quasi-reversible oxidation was observed (see Fig. 4.11) and at sweep rate $\nu > 20$ m V sec^{-1} the ratio between the cathodic and anodic peak currents, i_p^c/i_p^a, was unity. A plot of I_p vs $\nu^{\frac{1}{2}}$ as shown in Fig. 4.12 gave a straight line showing that the process was diffusion controlled. Similarily it was found that ΔE_p distends with increasing scan rate, as shown in Table 4.8, confirming

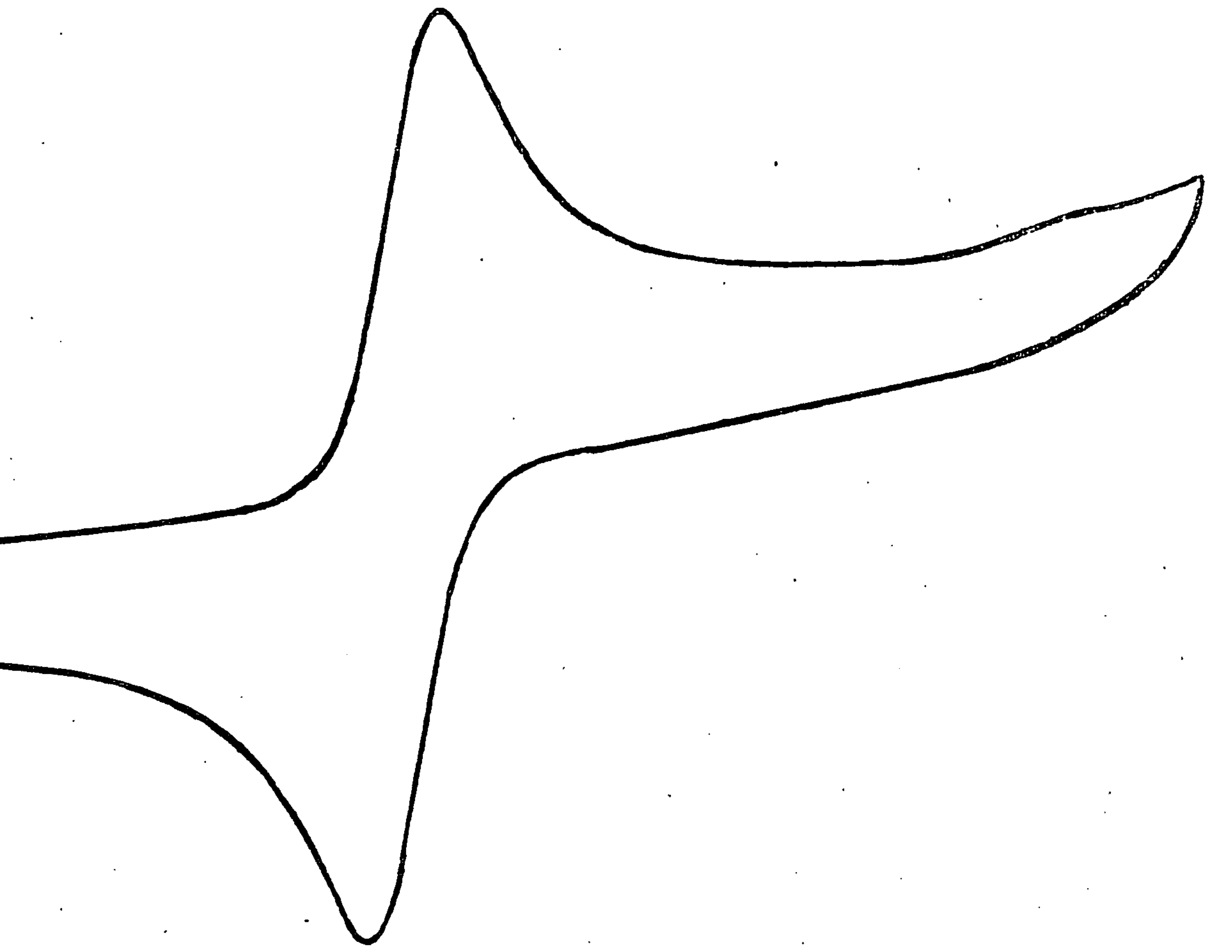


Fig. 4.11   Cyclic Voltammogram of $Mo_2(O_2CCH_3)_4$

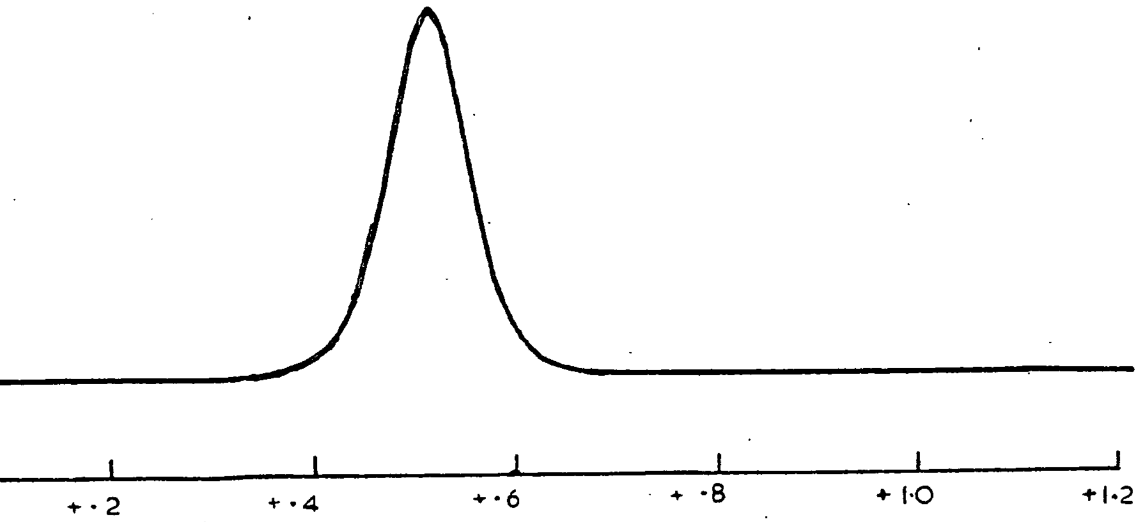
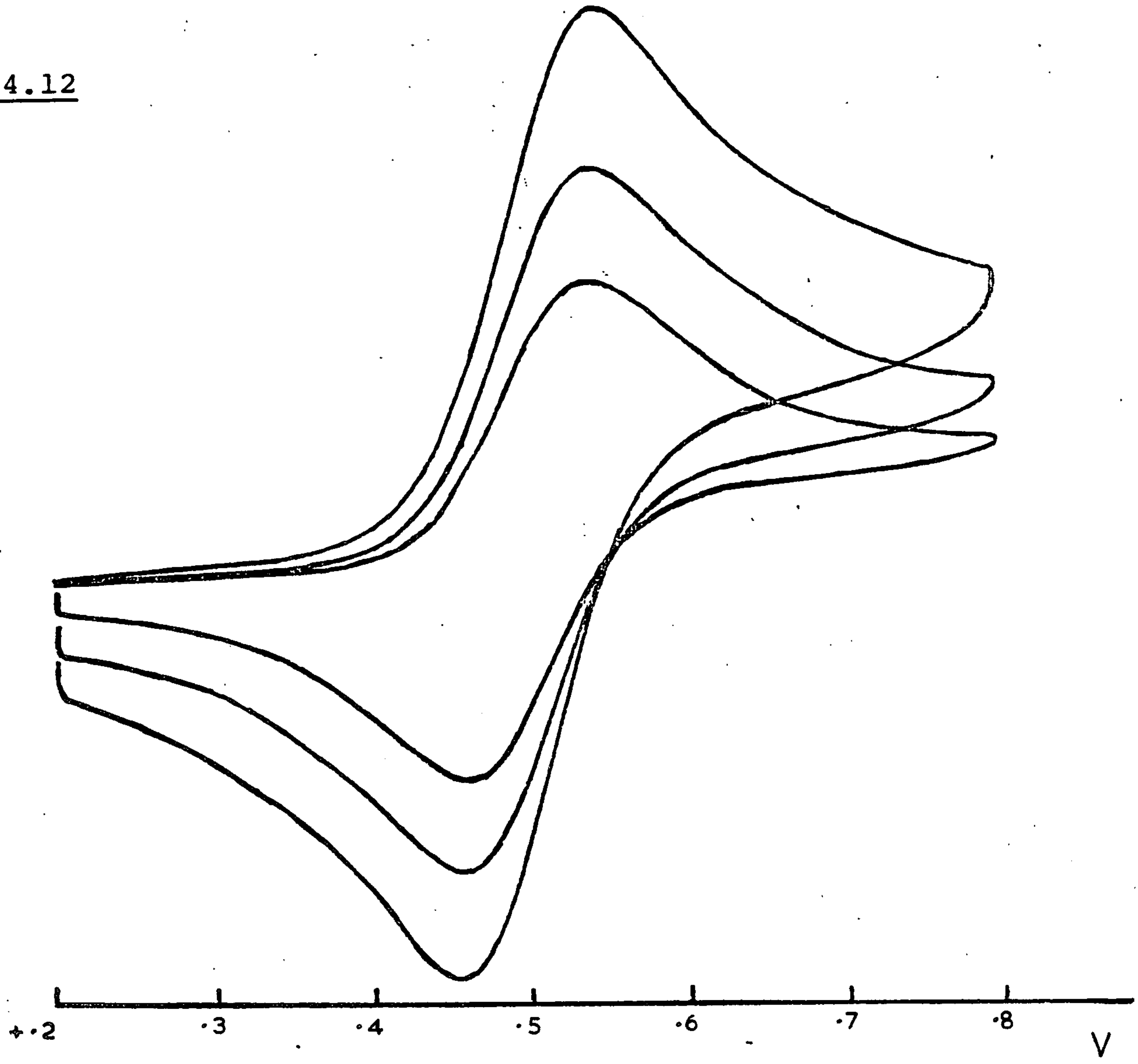
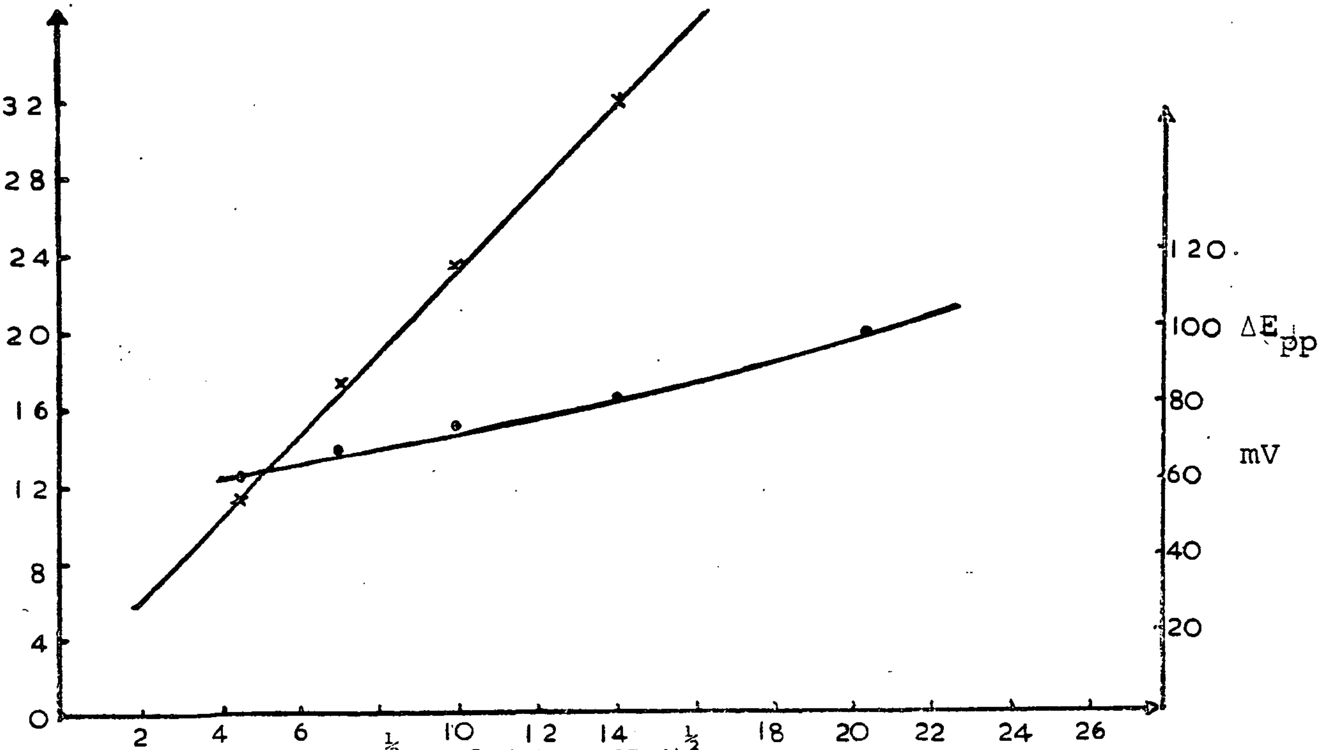


Fig. 4.12   A.C. voltammogram of Mo (O CCH)

4.12



Cyclic Voltammograms of $Mo_2(O_2CCH_3)_4$ at different scan speeds



Plots of I_p vs $\nu^{\frac{1}{2}}$ and ΔE_{pp} vs $\nu^{\frac{1}{2}}$

Table 4.8

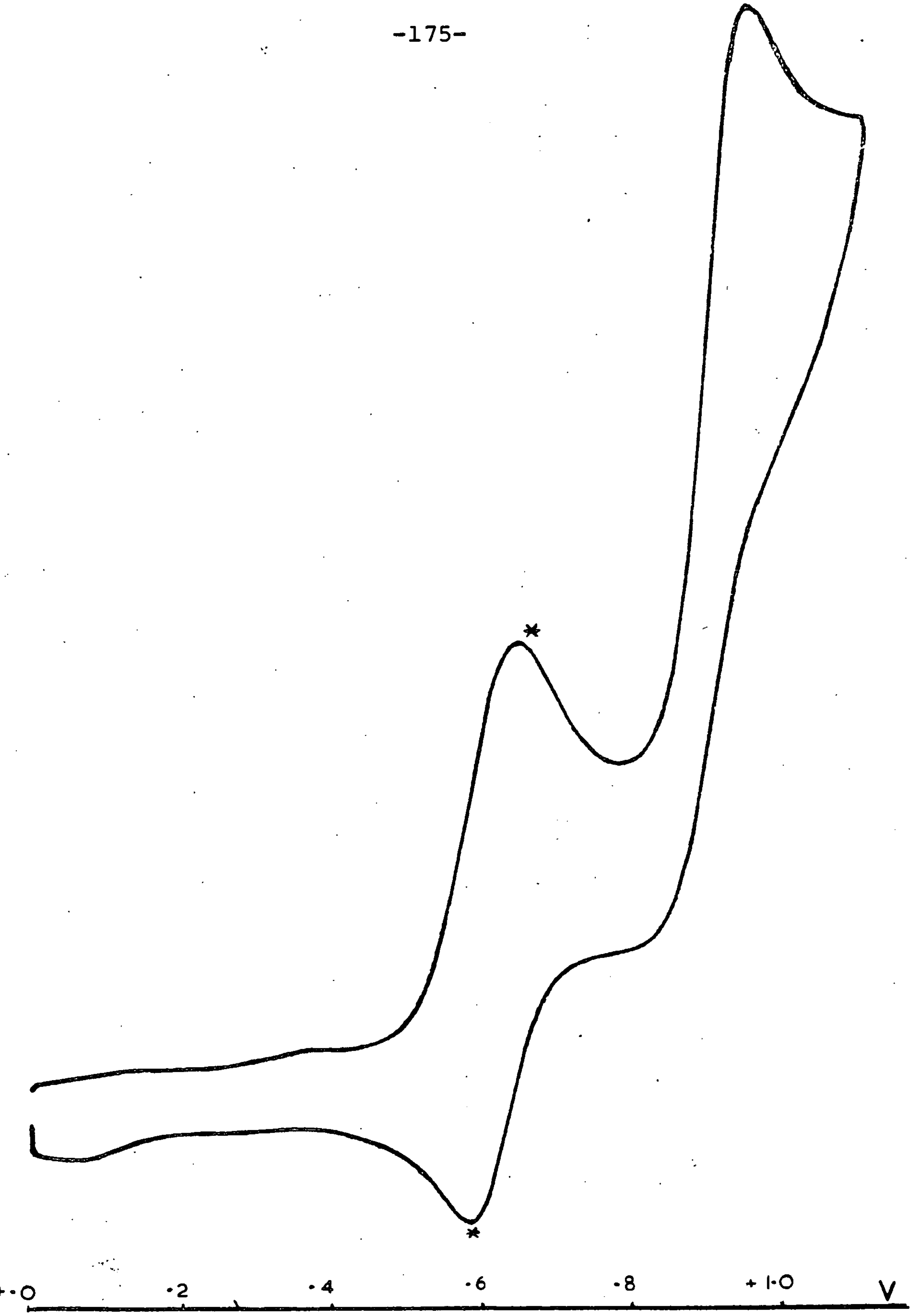
Electrochemical data for $Mo_2(O_2CCH_3)_4$

Scan Rate ν mv/sec	$\nu^{\frac{1}{2}}$	I_p^f	I_p^r	I_p^f/I_p^r	ΔE_{pp} mV
20	4.5	11.5	11.2	1.03	62
50	7.1	17.5	16.8	1.04	70
100	10.0	23.5	22.5	1.04	77.5
200	14.1	32	30	1.07	82.5
500	22.4	(20)	18.5	1.08	100

that the process was strictly only quasi-reversible. It is of interest to note here that in the study of the butyrate complex Cotton et al[185] state that at values of $\nu = 100$ m V sec^{-1} in dichloromethane and ethanol solutions values for ΔE_p of 380 and 290 mV respectively were found which would suggest far more sluggish charge transfer. Alternatively uncompensated cell resistance could attenuate the voltage axis contributing to these very large values, though of course we have no evidence that this has occurred. Cotton et al also note that for $\nu = 5$ m V sec^{-1} in ethanol $i_p^c/i_p^a = 0$. In all they interpret these results as showing an almost irreversible charge-transfer process. However, our results obtained for the acetate complex in acetone show that at $\nu = 100$ m V sec^{-1} $\Delta E_p = 77$ m V and at sweep rates as low as $\nu = 20$ m V sec^{-1} i_p^c/i_p^a was unity. Therefore it would appear that with the acetate complex we observe a much closer approach to fully reversible charge transfer. Recalling that Cotton found little differences between the acetate and butyrate, we tentatively suggest that in the latter case also that the lifetime of the oxidised butyrate species is longer than Cotton and Pedersen calculated. One possible explanation for this is that Cotton et al used too slow scan rates in their cyclic voltammograms, because at very slow scan rates the anodic peak moves towards the origin whilst the cathodic peak disappears and at $\nu = 5$ m V sec^{-1} (as Cotton used) the cyclic voltammogram effectively becomes a stirred voltammogram as convection processes in solution remove the product from the electrode before scanning in the opposite direction occurs. There is in any event a clear anomaly in that Cotton et al were able to record e.s.r. spectra of $[Mo_2(O_2CC_3H_7)_4]^+$ after bulk electrogeneration notwithstanding the short lifetime attributed to it. Therefore it appears that $Mo_2(O_2CCH_3)_4$ undergoes a quasi reversible oxidation at +0.51 V to generate the mixed II/III cationic species. From the results obtained there is no indication of decomposition down to scan rates of ν = 20 m V sec^{-1} (the practical limit for C.V. detection) and an ac voltammogram, shown in Fig. 4.13, (The first recorded for this type of compound) shows that the electron transfer step is relatively fast.

A study of the redox behaviour of the analogous $Mo_2(O_2CCF_3)_4$ complex in acetone showed no oxidations or reductions in our accessible range i.e. -1.8 V to +1.5 V. As the $Mo_2(O_2CCH_3)_4$ complex oxidised at +0.51 V this suggests that, in substituting trifluoroacetate groups for acetate ones, the energy of the highest occupied molecular orbital has been lowered by one eV or more.

The cyclic voltammogram of the $Mo_2(S_2COEt)_4$ complex again showed only an oxidation at +0.97 V vs Ag/AgCl but this time there was no return wave (see Fig. 4.14). In fact even at scan rates of ν = 500 m V sec^{-1} no return wave was observed showing that the $[Mo_2(S_2COEt)_4{}^+]$ complex formed was very unstable and decomposed immediately on formation. However an a.c. voltammogram of the product



. 4.14 Cyclic Voltammogram of $Mo_2(S_2COEt)_4$ plus Ferrocene

*Denotes Ferrocene Wave

was obtained, with the peak potential centred on the mid-point of the cyclic voltammogram, showing that although the oxidised form was short-lived the actual electron transfer process must be fast.

Therefore it can be seen that binuclear molybdenum complexes can undergo one-electron oxidations to generate the mixed II/III dimers but that the relative stability of these cations is dependent on the bridging ligands. Also as would be expected there are no indications of corresponding one electron reductions to form the mixed I/II anions. These results are broadly consistent with the previous electrochemical studies[185,186] on binuclear molybdenum (II) complexes though the tendency to decomposition of the carboxylate cations has clearly been exaggerated hitherto. From the data obtained in these studies it appears that the oxidations fit into a series:-

$Mo_2(O_2CCH_3)_4$	<	$Mo_2(S_2COEt)_4$	<	$Mo_2(O_2CCF_3)_4$
+0.51 V		+0.97 V		> +1.50 V

which is consistent with the resistance of these complexes to substitution.

Finally an electrochemical study of the $[Ph_3PhCH_2P]_n$-$[\{Mo_2(S_2COEt)_5\}_n]$ complex was undertaken. Cyclic voltammetry revealed independent reduction and oxidation waves at -1.8 V and +0.5 V respectively. However in both cases no return wave was observed showing that both the reduced and oxidized species formed decomposed very quickly. The waves were of equal height and measurements in stirred solution confirmed that the same number of electrons was involved in each step. In the a.c. mode reduction could

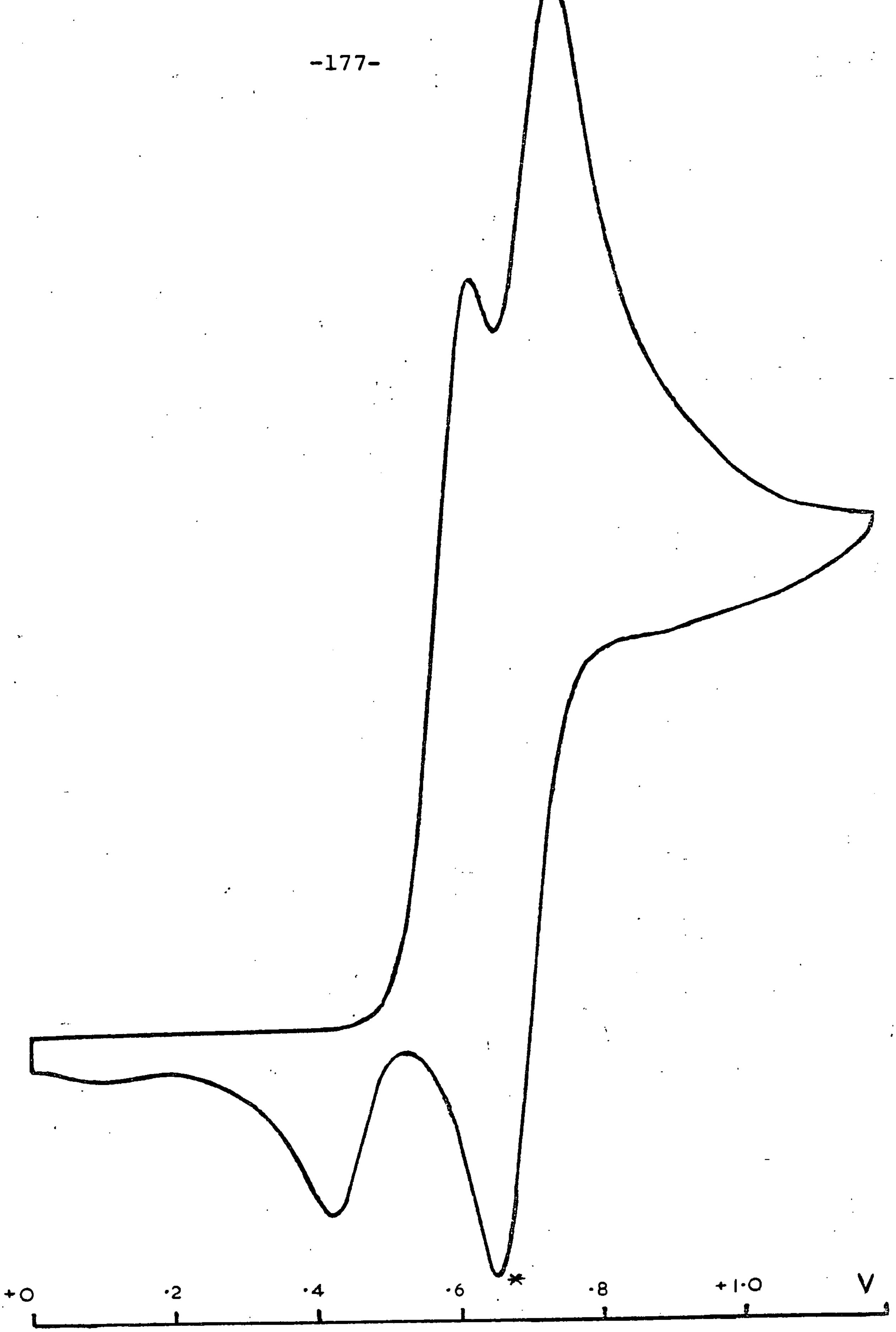
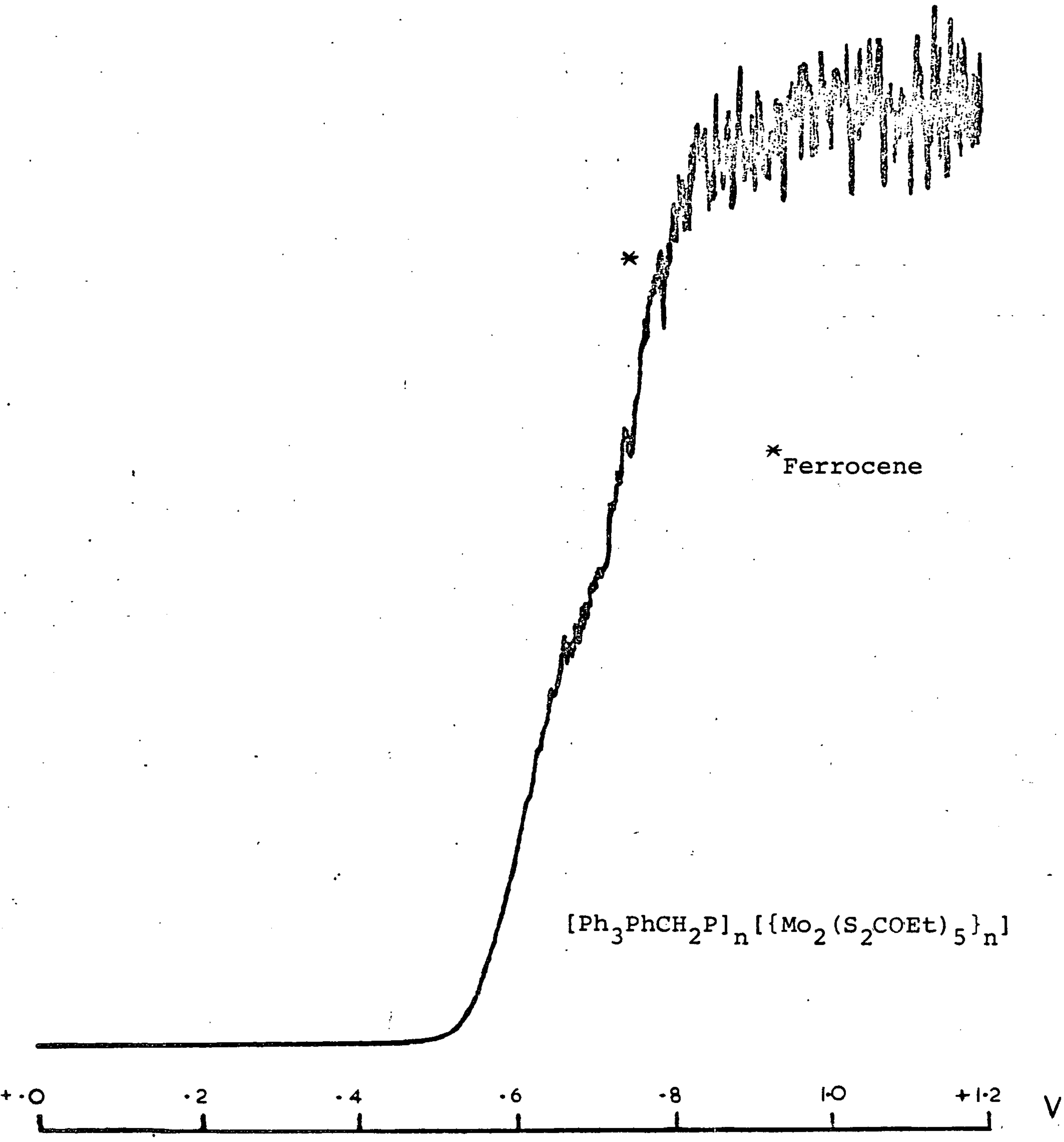


Fig. 4.15 Cyclic Voltammogram of $[Ph_3PhCH_2P]_n[\{Mo_2(S_2COEt)_5\}_n]$ plus Ferrocene

*Denotes Ferrocene wave

always be obtained but the appearance of the oxidation wave was highly non-reproducible and dependent on the history of the electrode. In the case of non-reversible wave forms the number of electrons involved in the redox step cannot be determined simply from the wave shape. However, a carefully controlled experiment was run in an attempt to define the molecular weight of this complex (i.e. dimer or tetramer) from the quantity of charge transferred. In this case the oxidations of known concentrations of ferrocene and the molybdenum complex in equimolar(Mo_2) amounts were compared, as shown in Fig. 4.15. However, a stirred voltammogram of this mixture showed equivalent amounts of ferrocene and $[Mo_2]_n$ had been added implying a one-electron transfer per Mo_2 unit or a two-electron transfer per Mo_4 unit (see Fig. 4.16). These two were indistinguishable. It had been hoped that the occurrence of a one-electron transfer on $[Mo_2]_n$ would lead to an apparent fractional electron transfer per Mo_2 unit, proving $n > 1$.

Two-electron transfers are sufficiently uncommon as to make it rather a coincidence to encounter two such processes for one molecule as demanded by the tetrameric formulation, but it may be that at the electrode the electroactive form of the complex is present in the form of dimers i.e. the tetramer has dissociated and one-electron steps are occurring. Another possible explanation is that in this unusual tetramer as the Mo centres are identical and remote from another, two one-electron transfers might occur essentially simultaneously at the same potential.



. 4.16 Stirred Voltammogram of $[Ph_3PhCH_2P]_n[\{Mo_2(S_2COEt)_5\}_n]$ plus Ferrocene

Denotes Ferrocene wave

4.4.4 Experimental

All measurements were made with a three electrode Princeton Applied Research model 170 instrument, on ca 3×10^{-3} moles dm^{-3} solutions in degassed analar acetone with supporting electrolyte $[Et_4N][ClO_4]$ or $[^nBu_4N][BF_4]$ (0.5 mol dm^{-3}). For cyclic voltammetry, potentials were measured at a stationary Pt electrode with reference to a Ag/AgCl electrode and scan speeds varied from 50 to 500 mV/sec. The potentials for a.c. polarography were measured at a dropping mercury electrode with reference to a Ag/AgCl electrode at a scan speed of 20 mV/sec.

Appendix 1

The determination of magnetic moments by the Evan's method

As stated earlier (see Chapter 2 section 2.4.2) the position of a peak in the proton resonance spectrum of a molecule depends on the bulk susceptibility of the medium in which the molecule is situated. The theory behind the calculation of magnetic moments by n.m.r. techniques is also well covered in the same section. However, in this short section by way of clarification a worked example of one of the compounds discussed in Chapter 2 is now given.

Example 1 $[Ni(SOCPh)_2(NC_6H_7)_2]$ M.Wt. = 519

Solvent used was CH_2Cl_2 + 3% Tetramethylsilane (T.M.S.)

Spectrometer "locked on" to the solvent (CH_2Cl_2) and shifts observed in the T.M.S. peaks. See spectrum A.1.1

Quantity of sample used 0.0074 i.e. m = 0.0074 g

For CH_2Cl_2 $\chi_o = -0.549 \times 10^{-6}$

Temperature (^oK)	Δf	m	$\chi_g \times 10^{-6}$
301	14.9	0.0074	9.06
273	16.2	0.0074	9.90
249	18.6	0.0074	11.45
223	20.7	0.0074	12.81

$\chi_g \times 10^{-6}$	$\chi_m \times 10^{-6}$	$\chi_m^{corr} \times 10^{-6}$	μ_{eff}
9.06	4702	4851	3.43
9.90	5138	5287	3.41
11.45	5942	6091	3.49
12.81	6648	6797	3.49

These calculations are from

$$\chi_g^{corr} = \frac{3\Delta f}{2\pi f m} + \chi_o$$

$$\chi_m = \chi_g^{corr} \times \text{m.wt.}$$

and $\chi_m^{corr} = \chi_m$ + Diamagnetic correction for ligands

In this case the Diamagnetic correction for

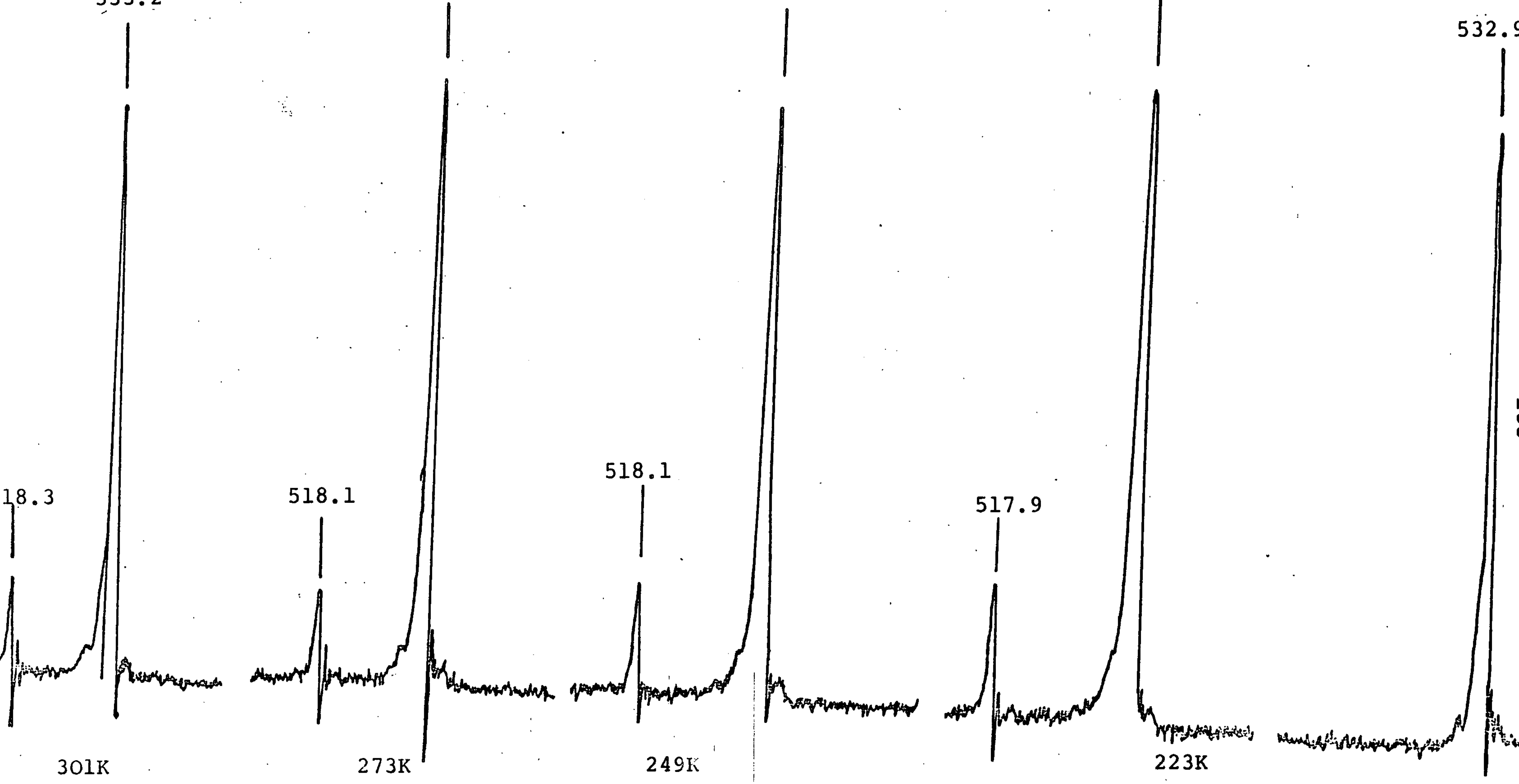
$[Ni(SOCPh)_2(NC_6H_7)_2] = 149 \times 10^{-6}$ see ref. 193

Finally

$$\mu_{eff} = 2.84\sqrt{\chi_m^{corr} \times T}$$

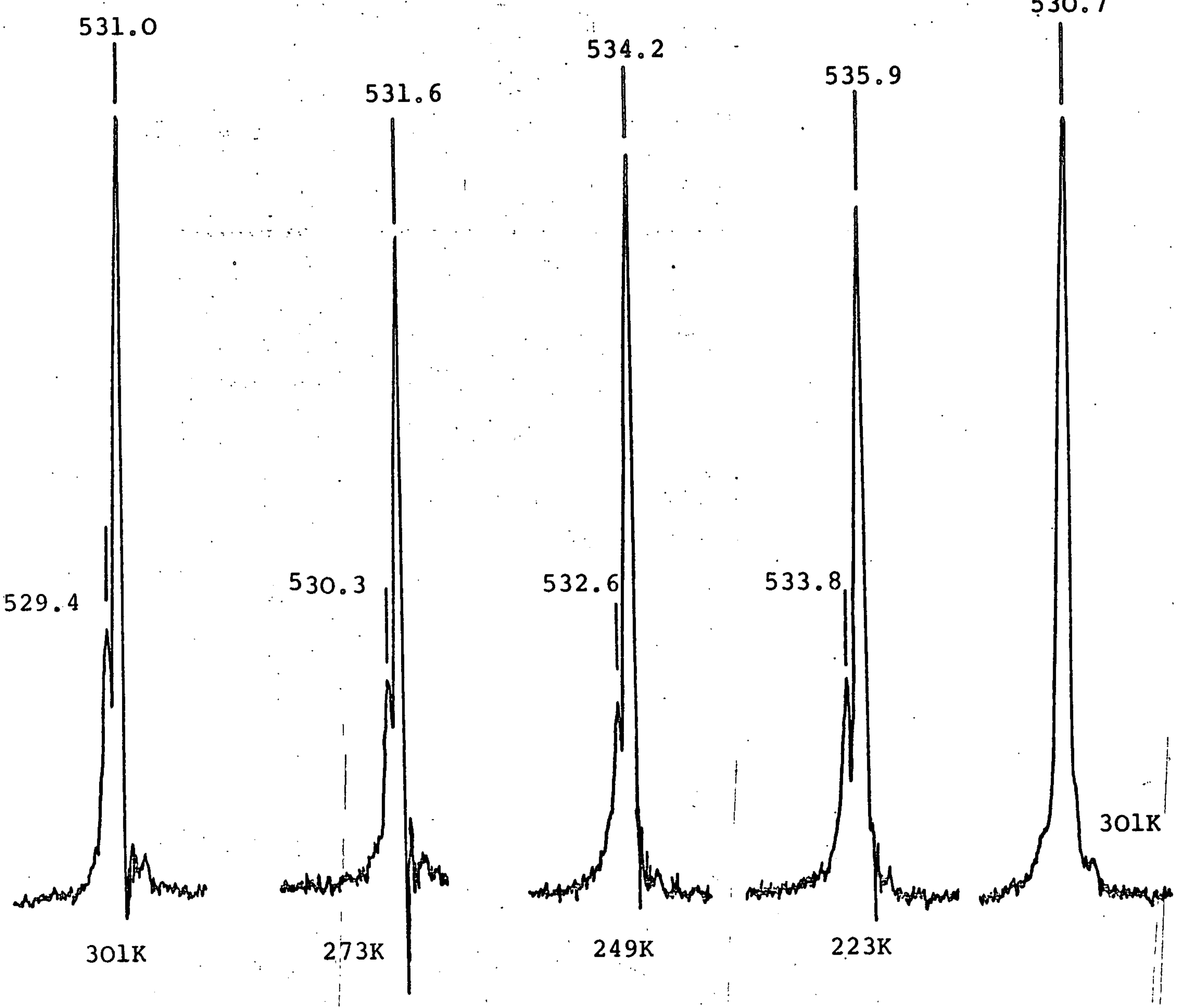
<u>Example 2</u> $[Ni(SOCPh)_2(PMe_2Ph)_2]$ m.wt. = 609

In this case the separation between the T.M.S. peaks Δf was not large enough to calculate a sensible value for the magnetic moment. However, as a separation was observed (see spectrum A.1.2) this showed that there must have been some paramagnetic material present in solution.



Sample at room
temp. with no
capillary
present

Spectrum A.1.1 of $Ni(SOCPh)_2(NC_6H_7)_2$



Spectrum A.1.2. of Ni(SOCPh)$_2$(PMe$_2$Ph)$_2$

Appendix 2

The determination of electrolyte type by conductivity measurements

The interpretation of conductivity data for coordination compounds in terms of possible structures has been widely used in the past. The most commonly adopted procedure is to determine the specific conductivity K, of a solution by measuring the resistance R, in an experimental cell of known cell constant. K can then be calculated from the expression

$$K = \text{cell constant}/R$$

The Portland Electronics conductivity bridge used in this work, measures K directly.

The expressions used for the comparison of electrolyte types are either the molar conductivity Λ_m, or the equivalent conductivity Λ_e, which are related to K by the defining expressions

$$\Lambda_m = 1000\ K/C_m \qquad \Lambda_e = 1000\ K/C_e$$

where C_m and C_e are the concentration of the solute in mol dm^{-3} or equiv. dm^{-3} respectively. These expressions are derived by considering one equivalent of electrolyte to be enclosed by the two electrodes in the bridge, placed 1 cm apart. If the concentration of the solution is c equivalents dm^{-3}, the volume of solution required is 1000 cm^3/C, so that this is the area of the electrodes.

Across each 1 cm^3 of solution the conductance is K, hence the conductance between the electrodes is 1000 K/C. In practice, Λ_m is usually calculated at a single concentration from an assumed molecular weight and this is compared with particular ranges of Λ_m found for other known electrolytes in the same solvent and at the same concentration (see Table A2.1).[194]

Table A2.1

Range of Λ_m for some electrolytes

Electrolyte type	Ranges of Λ_m for 10^{-3} mol dm^{-3} solutions in nitromethane
1:1	75-95 ohm^{-1} cm^2 mol^{-1}
2:1	150-180
3:1	220-260
4:1	290-330

The main drawback to this method is that it requires the assumption of a molecular weight which may be erroneous. A better method is that described by Feltham and Hayter,[168] in which the conductivity is measured over a range of concentrations. This method allows the application of the Onsager Law.[195]

$$\Lambda_o - \Lambda_e = (A + w\ B\ \Lambda_o)C_e^{\frac{1}{2}}$$

where Λ_o is the equivalent conductance at zero concentration; A and B are constants depending on the dielectric constant and viscosity of the solvent, temperature and the ionic charges, and w is a function of the ionic charges and mobilities. Thus, Λ_e is initially plotted against $C_e^{\frac{1}{2}}$ and extrapolation to zero concentration gives Λ_o as the intercept. The factor, $(\Lambda_o - \Lambda_e)$ is then plotted against $C_e^{\frac{1}{2}}$ to obtain a straight line of slope $(A + w\ B\ \Lambda_o)$. Since the term $(A + w\ B\ \Lambda_o)$ depends, amongst other factors, on the charges of the ions concerned, it will reflect directly the electrolyte type of the complex. The electrolyte type can then be found by comparison of the experimental $(A + w\ B\ \Lambda_o)$ value for the unknown sample with the experimental values for electrolytes of known type in the same solvent (see Table 4.3, page 138, for examples).

The most widely used solvent for the determination of the molar conductivity data of coordination compounds is nitromethane. The advantages of this solvent include the relatively high conductivity values obtained for a given electrolyte; the absence of unpleasant working conditions; its low viscosity and its relatively low donor capacity. The latter prevents problems arising through dissociation of the complex under investigation, caused by coordination of the solvent. This often occurs with solvents such as water and acetonitrile.

There now follows a short section showing a worked example of one of the compounds synthesised in Chapter 4. Conductivity measurements of $[Ph_3(PhCH_2)P]_2[Mo_2(S_2COEt)_4Br_2]$ in nitromethane were made at 295 K, 10 dm^{-3} aliquots of solution were used for each measurement and the results obtained are shown in Table A2.2.

Table A2.2

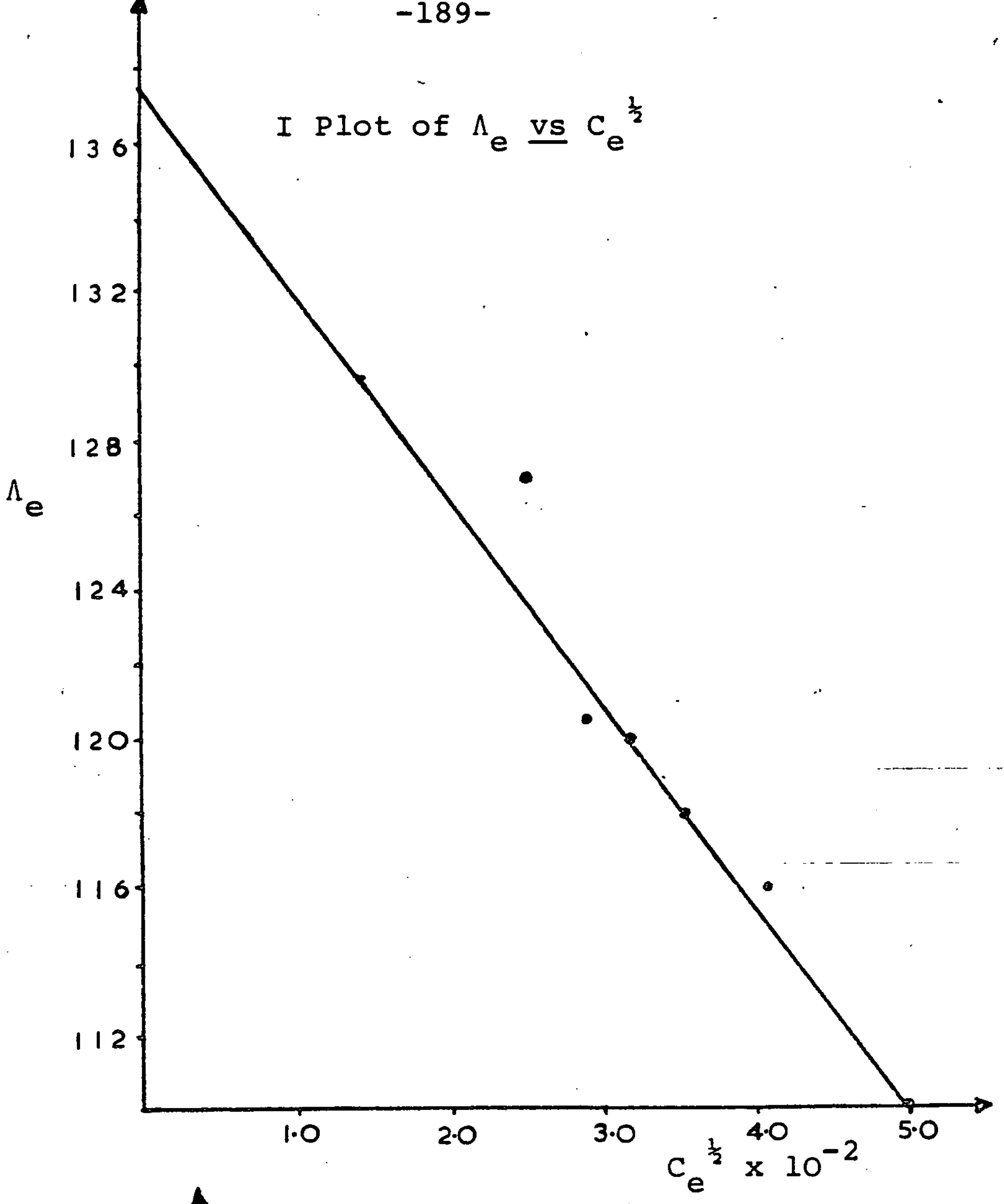
Conductivity data for $[Ph_3PhCH_2P]_2[Mo_2(S_2COEt)_4Br_2]$ in nitromethane

Vol in dm^{-3}	K x 10^{-6}	C_e x 10^{-3}	$C_e^{\frac{1}{2}}$x10^{-2}	Λ_e	$\Lambda_o-\Lambda_e$
10	275	2.49	4.99	110	27.4
15	192	1.66	4.07	116	21.4
20	147	1.24	3.53	118	19.4
25	120	1.00	3.16	120	17.4
30	100	.83	2.88	120.5	16.9
40	79	.62	2.50	127	10.4

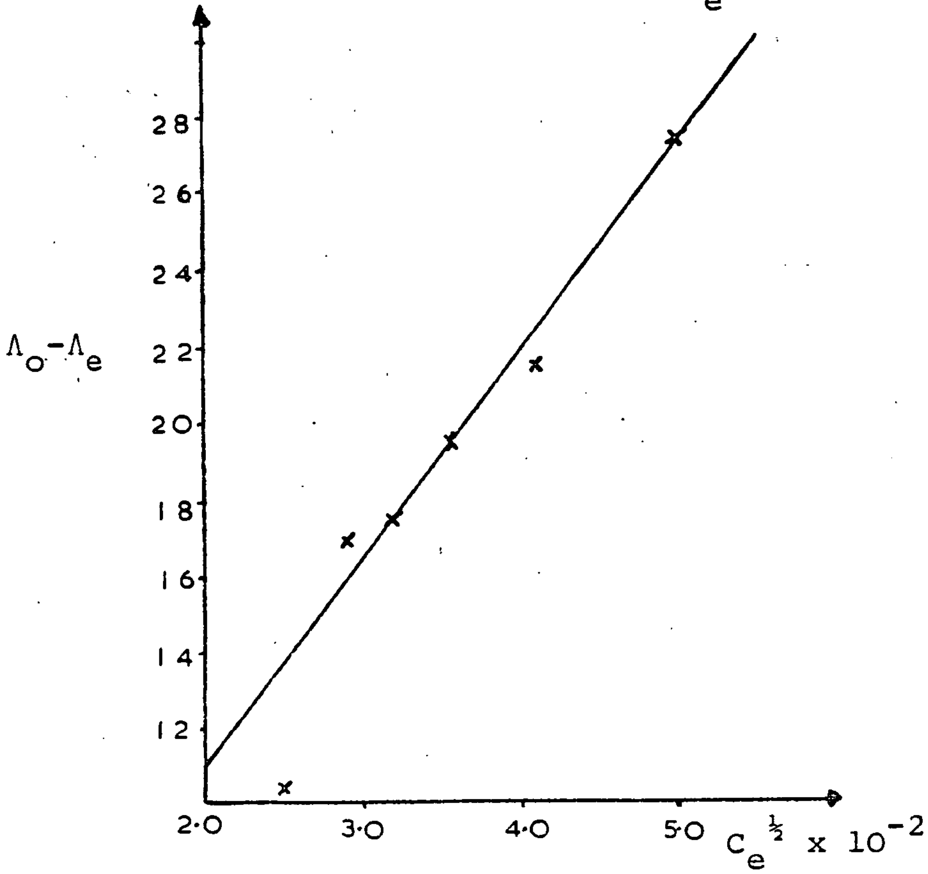
From the plot (I) of Λ_e vs $C_e^{\frac{1}{2}}$, Λ_o = 137.4

From the plot (II) of $\Lambda_o-\Lambda_e$ vs $C_e^{\frac{1}{2}}$

Slope = $5/1.25 \times 10^{-2}$ = 400



I Plot of Λ_e vs $C_e^{\frac{1}{2}}$



II Plot of $\Lambda_o - \Lambda_e$ vs $C_e^{\frac{1}{2}}$

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Post Graduate Courses Attended

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"Inorganic Biochemistry"	Dr. G.A. Heath
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