"COMPLEXES OF RUTHENIUM, RHODIUM AND OSMIUM WITH SOME DITHIOACID LIGANDS".

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To my father, my step-mother and my wife.

In memory of my mother.

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ABSTRACT

Chapter 1. The chemistry of transition metal complexes of dithioacid ligands is reviewed group by group, with reference both to complexes with and without other ligands.

Chapter 2. The synthesis and properties of complexes of general formula $Ru(S\text{-}S)_2L_2$ (S-S = S_2PR_2 (R = Me, Et, Ph), S_2CNMe_2; L = PPh_3, PMe_2Ph, $PMePh_2$, $P(OPh)_3$, CO, etc. or L_2 = diene, diars, diphos or $(Ph_2P)_2CH_2$) are reported. For S-S = S_2PR_2, the complexes are carbonylated to $Ru(S\text{-}S)_2LCO$. Although for S-S = S_2CNMe_2 the complexes are more inert to carbonylation, all the complexes undergo ligand exchange with L to give either $Ru(S_2PMe_2)_2LL'$ or $Ru(S_2PMe_2)_2L_2$ or, in some cases, both. Most of the compounds show temperature variable ^1H n.m.r. spectra which for S-S = S_2PMe_2 are attributable to a facile inversion of optical isomers via a solvent assisted bond rupture mechanism which is discussed in detail; whereas for S-S = S_2CNMe_2, they are attributable to facile rotation about the C$\cdots$N bond at higher temperatures. Finally, carbonylation of $Ru(S_2PR_2)_2(PMe_2Ph)_2$ gives rise to two other complexes of formula $Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$ whose spectra and structures are discussed.

Chapter 3. The formation of $Rh(S\text{-}S)_3(PMe_2Ph)_2$ (S-S = S_2PR_2, (R = Me or Ph) or S_2CNMe_2) from mer-$RhCl_3(PMe_2Ph)_3$ and Na S-S in refluxing ethanol has been shown to occur via stepwise displacement of chloride ions and phosphine ligands and, by varying the reaction conditions, many of the intermediates have been isolated. The reaction with KS_2COEt proceeds along similar lines although attack on coordinated xanthato groups leads to the formation of various dithiocarbonato complexes, such as mer-$Rh(S_2CO)Cl(PMe_2Ph)_3$, cis and trans $Rh(S_2COEt)(S_2CO)(PMe_2Ph)_2$ and K[trans-$Rh(S_2CO)_2(PMe_2Ph)_2$].

The spectroscopic properties of the complexes are discussed.

Chapter 4. The reactions of mer-$OsCl_3(PMe_2Ph)_3$ with $S\text{-}S^-$ ($S\text{-}S = S_2PR_2$ (R = Ph, Me), S_2CNMe_2, S_2COEt) are discussed. With KS_2COEt, the sole product is mer-$Os(S_2COEt)Cl(PMe_2Ph)_3$ whereas with S_2CNMe_2 and S_2PR_2, the final products are cis-$Os(S\text{-}S)_2(PMe_2Ph)_2$. As for ruthenium, those complexes show temperature variable ^1H n.m.r. spectra which are similarly interpreted although for $S\text{-}S = S_2PMe_2$, the optical inversion appears to occur via a non solvent assisted bond rupture mechanism. The formation of cis-$Os(S\text{-}S)_2(PMe_2Ph)_2$ appears to go via a series of Os^{III} ionic intermediates with reduction to Os^{II} as the last step whilst for $Os(S_2CNMe_2)_2(PMe_2Ph)_2$, a parallel mechanism operates which involves an Os^{II} intermediate of the form mer-$Os(S_2CNMe_2)Cl(PMe_2Ph)$ which isomerises to the facial isomer before reaction with more $^-S_2CNMe_2$. This facial isomer also reacts with solvent (EtOH) to give fac-$Os(S_2CNMe_2)OEt(PMe_2Ph)_3$.

Finally, carbonylation of cis-$Os(S_2PMe_2)_2(PMe_2Ph)_2$ gives the analagous products to the ruthenium system except that they are less labile and $Os(S_2PMe_2)_2(PMe_2Ph)(CO)_2$ is also formed.

Appendix 1 outlines the method of obtaining activation parameters from experimental and computed spectra at different temperatures and lifetimes respectively.

Appendix 2 The crystal structure of cis-$Ru(S_2PEt_2)_2(PMe_2Ph)_2$ is presented.

CHAPTER 1

A Survey of Transition Metal Complexes with Dithioacid Ligands

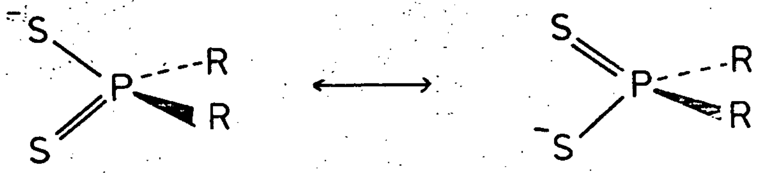
Dithioacids may be regarded as being derived from any oxoacid having two or more functional oxygen atoms by replacing two of the functional oxygen atoms in that acid with sulphur atoms. Since the results presented in the later chapters of this thesis refer to complexes of N,N-disubstituted dithiocarbamates ($^{-}S_2CNR_2$), O-substituted dithiocarbonates ($^{-}S_2COR$) (hereafter referred to as xanthates), and P,P disubstituted phosphinodithioates, it is considered of interest to review the results that have already been published on transition metal complexes of these ligands.

1) Bonding in transition metal dithioacid complexes.

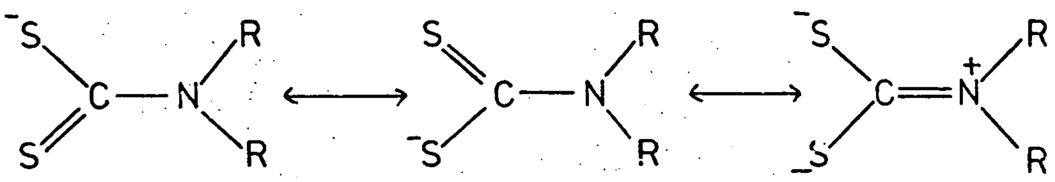
The versatility of dithioacid ligands is evidenced by the fact that they are able to stabilize wide ranges of oxidation states for many metals. This phenomenon is perhaps best explained because, apart from being σ-donors, the sulphur atoms are also capable of acting as weak π-donors (from the filled 3p orbitals), thus stabilizing high oxiation states, or π-acceptors (to empty 3d orbitals) thus stabilizing lower oxidation states. This π-donor ability has also been used to explain the change in the mode of bonding of thiocyanate ions from N- to S- bonded when potassium ethyl xanthate is reacted[1] with $[Cr(NCS)_6]^{3-}$ to give $[Cr(SCN)_4(S_2COEt)]^{2-}$, whilst the π-acceptor properties are confirmed by the covalency of the out of plane π-bonds in $Cu(S-S)_2$ (S-S = S_2CNR_2 or S_2COR), as detected by e.s.r. spectroscopy.[2,3]

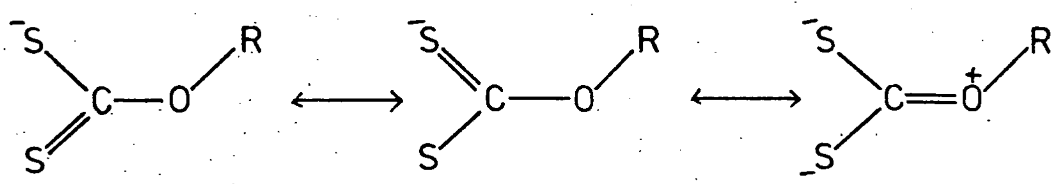
There are differences, however, between the dithioacid ligands; e.g. lower oxidation states tend to be better stabilized by phosphinodithioates than by xanthates or dithiocarbamates. Thus, whereas the xanthates and dithiocarbamates of Mn(II), Fe(II) and Co(II)[4] are relatively difficult to prepare since they are readily oxidised to the M(III) complexes, the phosphinodithioates of the divalent ions are easier to prepare and more stable than their corresponding M(III) compounds[5,6]. An explanation of this is forthcoming from a consideration of the different resonance structures that can be exhibited by the various ligands, and of the effect of these on the donor and acceptor properties of the ligands.

Since all the dithioacid anions have two terminal sulphur atoms, either of these may be doubly bonded to the neighbouring atom (C or P), in the free ion, while the other supports the uninegative charge. i.e.



For $^-S_2CNR_2$ and ^-S_2COR, however, a further resonance form is possible in which a lone pair from the oxygen or nitrogen atom is donated to the carbon atom and each sulphur atom supports a uninegative charge[7,8]. i.e.





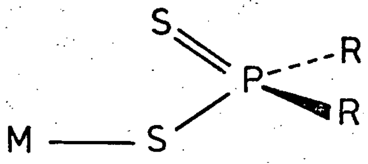
On account of the greater electronegativity of oxygen compared with that of nitrogen, it has been suggested[7] that donation of the lone pair from the oxygen atom is less likely and therefore this resonance structure will be less important for $^{-}S_2COR$ than for $^{-}S_2CNR_2$, and this has been shown by infra-red (i.r.)[7,9] and x-ray techniques[10,11] to be experimentally the case.

Thus, the following order of negative charge density on the sulphur atoms of the dithioacid ligands may be drawn up, and this order will correlate directly with the donor properties of the ligands but inversely with their acceptor properties[8] and consequently directly with their ability to stabilize higher oxidation states of metals:

$$^{-}S_2CNR_2 > {}^{-}S_2COR > {}^{-}S_2PR_2$$

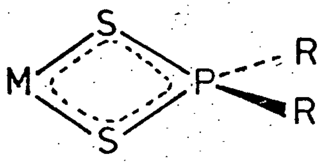
Another facet of the versatility of dithioacid anions as ligands arises from the different ways in which they may coordinate to metals. Thus, apart from acting as simple counter anions, they may act as unidentate one electron donors,

i.e.



or a lone pair of the uncoordinated sulphur atom may then donate either to the same metal atom or to another one, forming a bidentate or bridging ligand.

i.e.



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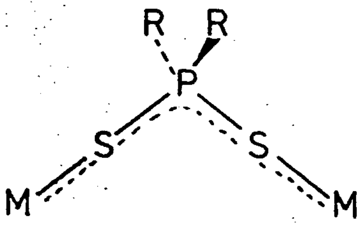
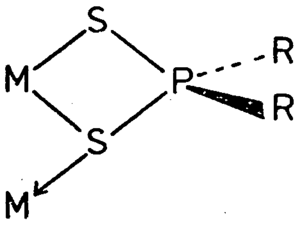


Occasionally, a further two electrons may then be donated to another metal atom to form a five electron donor ligand bridging either two or three metal atoms.

i.e.



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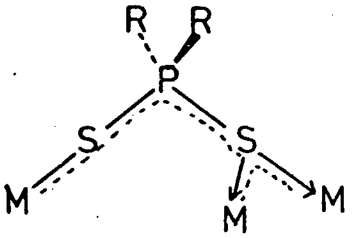
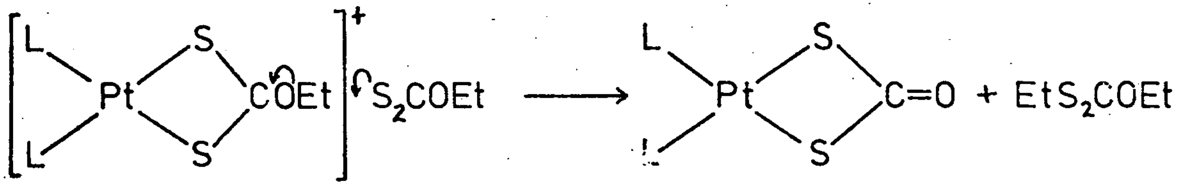


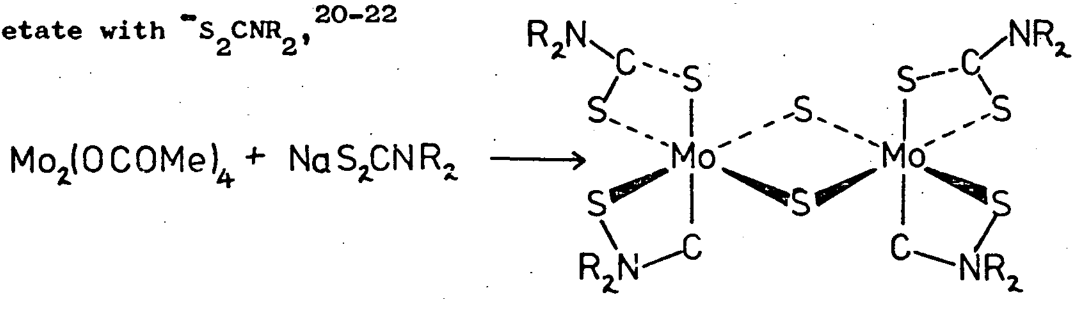
Complexes which exhibit all these types of bonding have been made (vide infra) and i.r.$^{12-16}$ and n.m.r.^{17} techniques have been developed to distinguish between them.

Finally, some reactions occur in which modification of the dithioacid ligand takes place. These include attack on the alkoxy group of S_2COR by nucleophiles to give dithiocarbonates;^{18,19}

e.g.



and the formation of coordinated carbenes by the reaction of Mo(II) acetate with $^{-}S_2CNR_2$,$^{20-22}$



in which a molybdenum atom apparently inserts into a C-S bond.

Transition metal complexes of these three dithioacid ligands will now be examined triad by triad.

2) Complexes of Copper, Silver and Gold.

a) Binary compounds.

The coinage metals are the only transition elements for which univalent dithioacid complexes are known. These metals all have a d^{10} electronic configuration in their +1 oxidation state and the stability of the closed sub-shell presumably accounts for the formation of these complexes. There are two main modes of preparation of Cu(I) dithioacid complexes. Dithiocarbamates may be prepared by oxidation of the metal with tetraalkylthiuram disulphides, $(S_2CNR_2)_2$, in cold benzene[23] or chloroform[24], although in the latter solvent, some $Cu(S_2CNR_2)_2$ is also formed. Xanthates[25] and phosphinodithioates[26], on the other hand, are best prepared by the reduction of Cu(II) salts with the appropriate dithioacid anion. $\{Cu(S_2PF_2)\}_n$ has also been prepared, by the action of HS_2PF_2 on copper in toluene at 70°C[27].

Since silver and gold both have stable + 1 chlorides, direct reaction of these with dithioacid anions leads to the formation of $\{M(S\text{-}S)\}_n$ (S-S = S_2CNR_2[28], S_2COR[29,30] or S_2PR_2[26,31]). $\{Au(S\text{-}S)\}_2$ (S-S = S_2COR[28], S_2PR_2[26]) may also be prepared by the interaction of Au(III) salts with Na(S-S), whereas oxidation of metallic gold with xanthates leads to the isolation of $\{Au(S_2COR)\}_2$. However, since higher oxidation states of silver are relatively unstable, Ag(I) salts are not oxidised by $(S_2CNR_2)_2$ but react with them or $Ni(S_2CNR_2)_2$ to produce $\{Ag(S_2CNR_2)\}_6$[32,33].

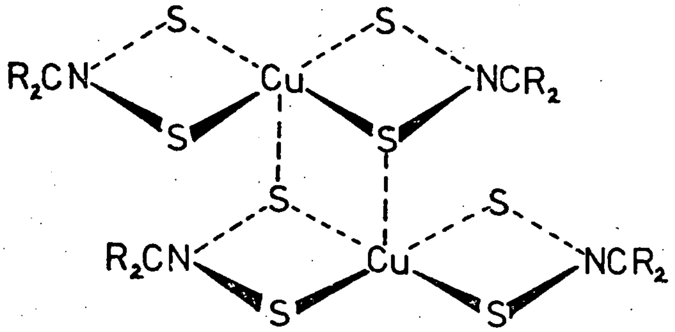
All these dithioacid complexes are found to be associated both in solution and in the solid state and, although the degree of association is not always easy to determine, it appears that at least for the dithiocarbamates[34-36] and phosphinodithioates[26], the gold complexes are dimeric, the copper complexes tetrameric and the silver complexes hexameric or of higher association.

The only x-ray crystallographic data available on these complexes pertain to the dithiocarbamates and these are shown to have interesting structures and unusual bonding modes for the ligands. Thus, $\{Cu(S_2CNEt_2)\}_4$[34] has the copper atoms arranged at the corners of a somewhat distorted tetrahedron with a dithiocarbamate ligand situated above each face of this tetrahedron and coordinated to all three metal atoms of the face such that each copper atom is bound to three sulphur atoms in an almost planar fashion. Although it is evident that one sulphur atom of each ligand binds to one copper atom whilst the other is coordinated to two copper atoms, the electronic nature of the bonding in this compound is not entirely clear, but it is presumably similar to that in the complex $\{Ag(S_2CNPr_2)\}_6$[35], in which the silver atoms are arranged at the apices of a distorted octahedron with the dithiocarbamate ligands again situated above six of the faces of the octahedron and coordinated to all three sulphur atoms of that face so that the silver atoms are trigonally coordinated although not quite planar. $\{Au(S_2CNPr_2)\}_2$[36] is rather different, with both of the dithiocarbamate ligands bridging the two gold atoms and acting as three electron donors. However, the molecule is twisted in such a way that the coordination of each gold atom by sulphur is essentially linear, as in most other complexes of Au(I). It is also interesting to note that in all three complexes some of the metal-metal distances are shorter than those found in the free metal, but this need not necessarily be due to direct metal-metal bonding[36].

Oxidation of these univalent dithiocarbamate complexes by $(S_2CNR_2)_2$ leads to $M(S_2CNR_2)_2$ (M = Cu,Ag) and, whilst the gold compound is oxidised slowly to $Au(S_2CNR_2)_3$ under these conditions, the Au(II) complex has been detected as an intermediate by E.S.R.[38] $Cu(S_2CNR_2)_2$ may also be prepared by the reaction of Cu or $CuSO_4$ with $(S_2CNR_2)_2$ in refluxing solvents[23,24], or by reaction between $CuCl_2$ and $(Me_2NCS)_2S$.[39] Attempts to oxidise $Cu(S_2PF_2)$ to $Cu(S_2PF_2)_2$ with $(S_2PF_2)_2$ were unsuccessful, yielding only unchanged starting material.[27]

$Cu(S_2COR)_2$[40] and $Cu(S_2PR_2)_2$[41] have been prepared by the reaction of stoichiometric amounts of the dithioacid anions with $CuSO_4$ in water followed by extraction of the product with CCl_4. However, facile reduction to the Cu(I) complexes (vide supra) means that yields of the Cu(II) complexes are low.

Very little structural information is available for the phosphinodithioates or xanthates of the divalent coinage metals except that e.s.r. experiments on $Cu(S_2PR_2)_2$[42] have shown that the hyperfine splitting of the signals arises from coupling of the unpaired electron on the copper ion with the ^{31}P nucleus of the ligand via delocalisation through the coordinated sulphur atoms. This indicates that the unpaired electron is in the $d_{x^2-y^2}$ orbital of the copper ion (as predicted by simple crystal field theory) and contrasts with the mechanism for the interaction of the unpaired electron with the phosphorus atoms in $VO(S_2PR_2)_2$, which occurs by a direct interaction between the $3d_{xy}$ orbital on vanadium and the 3s orbital on phosphorus. However, the structures of $Cu(S_2CNR_2)_2$ have been very extensively studied and they have been shown to be monomeric square-planar species in solution[43], the gas phase[44], and at high temperatures in the solid state[45] when they are isomorphous with $Ni(S_2CNR_2)_2$. At normal temperatures in the solid state, however, the complexes are isomorphous with $\{Zn(S_2CNR_2)_2\}_2$[46], i.e. dimeric with the two planes of sulphur atoms parallel to one another, and each copper atom in a distorted square- pyramidal environment (1). For R = Pr[47] or Et[48], it is found that



(1)

the sixth coordinating position of the copper atoms is occupied by a hydrogen atom of a neighbouring dimer. E.s.r. and magnetic measurements also indicate that, apart from a weak anti-ferromagnetic interaction between dimers[49], the individual dimers each have a triplet (S=1)[50] ground state because of a ferromagnetic[49] exchange interaction between the two halves of the dimer which occurs through the out of plane orbitals[51] and the bridging sulphur atoms[50]. This has also been confirmed for the dimeric $\{Ag(S_2CNPr)_2\}_2$[52]. The only non dimeric compound of this kind is $Cu(S_2CNMePh)_2$ which is monomeric in the crystal[53]. This is rationalised in terms of a steric interaction between the methyl group and the phenyl ring on each dithiocarbamate ligand which leads to the plane of the ring being inclined at 87° to the plane of the four sulphur atoms, thus making it sterically unfavourable for dimerisation to occur[53].

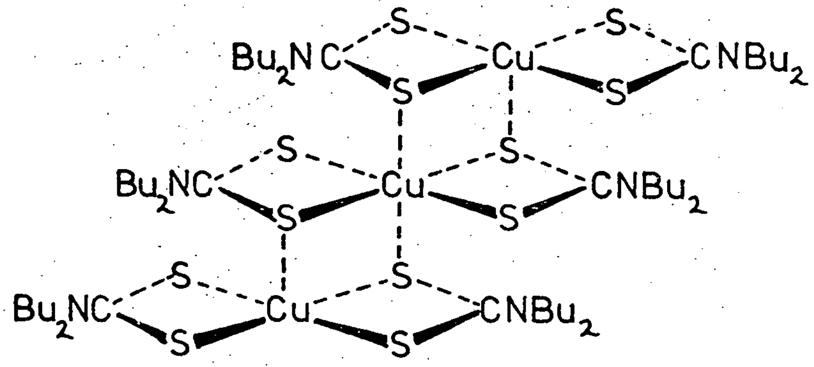
As has already been noted, $\{Au(S_2CNR_2)\}_2$ slowly give $Au(S_2CNR_2)_3$ when treated with $(S_2CNR_2)_2$. These Au(III) complexes may also be prepared by the reaction of $AuCl_3$ with NaS_2CNR_2 in slightly acid solution[54]. This reaction occurs by stepwise displacement of the chloride ions by dithiocarbamate ligands[54] but if carried out in basic solution or if excess dithiocarbamate is used, $\{Au(S_2CNR_2)\}_2$ is the only product[55]. A similar technique has been employed to isolate $Au(S_2PPh_2)_3$[56].

Cationic dithiocarbamate complexes of Au(III), $[Au(S_2CNR_2)_2]$-$[AuBr]$ have also been prepared, by the interaction of one equivalent of $\{Au\ (S_2CNR_2)\}_2$ with half a mole of bromine[57]. Other anions may then replace the $AuBr^-$ either by the use of an ion exchange column or by precipitation[58]. In the case of $[Au(S_2CNR_2)_2][AuBr_4]$, this decomposes on heating to yield $Au(S_2CNR_2)Br_2$ which may also be prepared by the action of one mole of bromine with one equivalent of $\{Au(S_2CNR_2)\}_2$ and which reacts with excess $^-S_2CNR_2$ to give $[Au(S_2CNR_2)_2]Br$. These Au(III) complexes ($5d^8$) are isoelectronic with Pt(II) complexes and would therefore be expected to be spin-paired, square-planar compounds. This is indeed the case and an x-ray structure of $Au(S_2CNEt_2)_3$[59] has shown that one of the dithiocarbamate ligands is bidentate whilst the other two are unidentate (c.f. the xanthate ligands in $[AsPh_4]$-$[Pt(S_2COEt)_3]$)[60]. The ionic Au(III) complexes are also square-planar but an interesting feature of their crystal structures[61] is that the anions often pack close to the nitrogen atoms of the dithiocarbamate ligands and hence have an effect on the position of $\nu\ C\overset{\cdots}{-}N$ in the solid state i.r. spectra[61].

An analagous series of cationic copper complexes has also been prepared, by the oxidation of $\{Cu(S_2CNR_2)\}_4$ or $\{Cu(S_2CNR_2)_2\}_2$

with iodine or metal chlorides[62] and a crystal structure of $[Cu(S_2CNBu_2)_2]I_3$[63] has revealed that the copper atom is in a square-planar environment of sulphur atoms, with the Cu-S bond length being ca 0·08Å shorter than in neutral $\{Cu(S_2CNBu_2)_2\}_2$ which is consistent with there being a greater positive charge on the metal in the former complex.

Finally, if three moles of $Cu(S_2CNBu_2)_2$ are treated with one mole of bromine and one of MBr_2 (M = Zn,Cd or Hg), compounds of formula $[Cu_3(S_2CNBu_2)_6][M_2Br_3]$ can be isolated[64]. An x-ray crystal structure[64] of the compound (M = Cd) shows that the cation consists of three square-planar $Cu(S_2CNBu_2)_2$ units bound together in such a way that their planes are parallel (2); the two outer copper



(2)

atoms are in distorted square pyramidal environments whilst the environment of the central copper atom is a distorted octahedron. On the basis of Cu - S bond lengths, the outer two copper atoms are assigned a +3 oxidation state, whereas the central atom is in +2 oxidation state.

b) <u>Compounds containing other ligands.</u>

(i) <u>Nitrogen donors.</u>

No complexes of the coinage metals containing <u>both</u> dithioacid ligands and nitrogen donor ligands have been isolated but solutions of $Cu(S_2CNR_2)_2$ containing pyridine[65], piperidine[65], n-hexylamine[65], 3-, 4- picolines[66], 3, 4- and 2,6- lutidines[67] in various solvents have been studied by e.s.r. techniques. All these ligands form 1:1 adducts, the base being in the apical[68] position of a square-pyramid, and thermodynamic and kinetic parameters have been calculated for adduct formation. A similar study on $Ag(S_2CNR_2)_2$[69] has shown that this too forms 1:1 adducts with pyridine, 2-, 3-, 4-picolines and triethylamine.

(ii) Phosphorus donors.

Complexes containing both a dithioacid ligand and phosphorus donor ligands may either be prepared by the action of tertiary phosphines or phosphites on $\{M(S-S)\}_n$, or by reaction of $(S-S)^-$ with a complex of the metal which already contains the phosphorus ligand. Thus, the reactions between $\{M(S-S)\}_n$ (M=Ag, S-S=S_2CNR_2[70] or S_2COEt[20]; M=Cu, S-S=S_2CNR_2[70]) and triphenylphosphine yield $M(PPh_3)_2$ (S-S) which are definitely ionic for S-S= S_2CNR_2[70] and probably ionic for S-S= S_2COEt[29]. In contrast, reaction of $\{M(S_2CNR_2)\}_n$ (M = Cu, Ag)[70] with triethylphosphine leads to the formation of $M(PEt_3)$ (S_2CNR_2) which, for M = Cu, is rapidly oxidised by air to $Cu(S_2CNR_2)_2$. Similar compounds, AuL (S-S) (L = PPh_3, S-S = S_2COEt[29]; L = PEt_3, S-S = S_2CNR_2[70] or S_2COR[29]) have also been prepared by the action of $(S-S)^-$ on AuL Br, although for S-S = S_2CNMe_2 or S_2CNEt_2, both Br^- and triethylphosphine are replaced to yield Au $(S_2CNR_2)_2$[70].

Finally, reaction of M (S_2PF_2) (M = Cu[71], Ag[72]) with tri-o-tolylphosphine or triphenylphosphite leads, at low temperature, to the tetrahedral L_3 $M(SP(S)F_2)$ complex with the anion bound through only one sulphur atom; on heating, this expels a phosphorus donor ligand with concomitant chelation of the S_2PF_2 ligand.

(iii) Halogen and alkyl ligands.

Oxidation of $\{M(S_2CNR_2)\}_n$ (M = Au[73], Cu[74]) with halogens (1:1 molar ratios) leads to the formation of square-planar[75] $M(S_2CNR_2)X_2$, which react with Grignard or alkyl cadmium reagents to produce $M(S_2CNR_2)R'_2$[73]. These compounds may also be prepared by the interaction of $AuCl_4$ with NaS_2CNR_2 in the presence of a Grignard or alkyl cadmium reagent. If excess halogen is used in the reaction with $\{Cu(S_2CNR_2)\}_n$, the monomeric compound CuX_3-(S_2CNR_2) is formed[76]. Magnetic measurements indicate that this molecule has one unpaired electron which could be explained either by invoking the presence of Cu(IV) ($3d^7$) or by assuming Cu(II) ($3d^9$) and a coordinated halogen molecule; either of these situations would be extremely unusual.

$Cu(S_2CNR_2)Cl$ has been prepared by direct exchange between $Cu(S_2CNR_2)_2$ and $CuCl_2$[77], a reaction that has also been used to form compounds containing more than one dithioacid ligand e.g. $Cu(S_2CNEt_2)(S_2PPr_2)$[78] and $Cu(S_2CNEt_2)(S_2P(OEt)_2)$[79].

Finally, the anions $Au(S_2CNR_2)(S_2C_2(CN)_2)$ have been prepared[80] and shown to have the square-planar configuration expected for Au(III) ($5d^8$).

3. Complexes of Titanium, Zirconium and Hafnium.

a) Binary compounds.

Only one dithioacid complex of hafnium has been reported ($Hf(S_2CNMe_2)_4$)[81] but the dithiocarbamates of Ti(IV) and Zr(IV) are relatively well known. They may be prepared either by reaction of $TiCl_4$ with NaS_2CNR_2[82], in which case stepwise substitution of chloride ions by S_2CNR_2 occurs, or by insertion of CS_2 into the

M-N bonds of $M(NR_2)_4$[14,81]. It has also been shown that reaction of $Ti(NR_2)_3$ with CS_2 yields $Ti(S_2CNR_2)_4$[83] along with a brown powder, tentatively formulated as $Ti(S_2CNR_2)_2$[84]. This reaction presumably involves initial formation of $Ti(S_2CNR_2)_3$ followed by disproportionation to yield the products.

The compounds $M(S_2CNEt_2)_4$ (M = Ti or Zr) are isomorphous[85], and a single crystal study of $Ti(S_2CNEt_2)_4$ reveals that all eight sulphur atoms are coordinated to titanium in a dodecahedral arrangement[85]. This is not inconsistent with its behaviour in solution[86], although both Ti(IV) and Zr(IV) compounds have been shown by ^1H, ^{13}C [87,88] and, in the case of $Zr(S_2CNMeC_6F_5)_4$, ^{19}F n.m.r.[88] to be stereochemically non-rigid down to -130°C.

b) <u>Compounds containing other ligands.</u>

Reactions of $TiCl_4$ with dithioacids or their sodium salts in refluxing benzene lead to complexes which contain both chlorine and dithioacid ligands. Thus, $Ti(S_2CNR_2)_n Cl_{4-n}$[82] (n = 2,3 or 4) all of which contain only bidentate S_2CNR_2 ligands and show rapid metal centred rearrangements down to -90°C, may be isolated from the reaction with NaS_2CNR_2, whilst HS_2PF_2 and HS_2PPh_2 yield only $TiCl_3(S_2PF_2)$[89] and $TiCl_2(S_2PPh_2)_2$[90] respectively. This last compound reacts with phenol to give $Ti(OPh)_2(S_2PPh_2)_2$[90].

The only other complexes of titanium containing dithioacid and other ligands are $(\eta^5\text{-}C_5H_5)_2Ti(S\text{-}S)$ (S-S = S_2CNR_2[83,91] or S_2COR[92]) which may either be prepared by the action of the appropriate dithioacid anion on $(\eta^5\text{-}C_5H_5)_2TiCl_2$[91,92] or, for S-S = S_2CNR_2, by insertion of CS_2 into the Ti-N bonds of $(\eta^5\text{-}C_5H_5)_2Ti(NMe_2)_2$[83].

4. Complexes of Vanadium, Niobium and Tantalum.

a) Binary compounds.

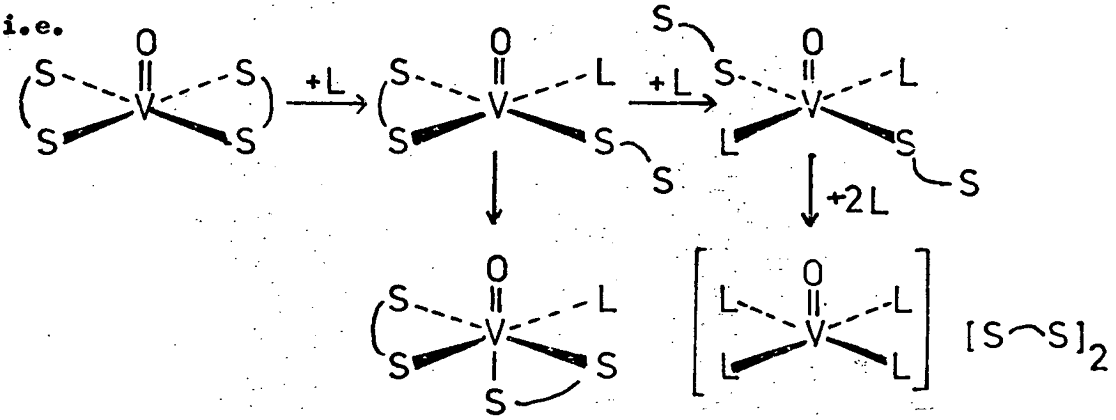
Both dithiocarbamates and phosphinodithioates are known for V(III) and are presumably tris chelates with distorted octahedral stereochemistries. $V(S_2CNR_2)_3$[86] are prepared by heating $V(S_2CNR_2)_4$ in vaccuo, whilst $V(S_2PR_2)_3$[93,94] are made by the action of $^-S_2PR_2$ on VCl_3 under anaerobic conditions. These compounds are all air-sensitive solids, being readily oxidised to $VO(S\text{-}S)_2$[95]. $V(S_2PF_2)_3$ can also be prepared, by reaction of HS_2PF_2 with either VCl_3[95] or VCl_4[89].

As with titanium, reaction of $M(NR_2)_n$ (M = V or Nb, n=4; M=Ta, n=5) with CS_2 yield $M(S_2CNR_2)_n$[14] which for the M(IV) species are dodecahedral[96], fluxional[87] compounds. Although $V(S_2CNEt_2)_4$ is isostructural with $Ti(S_2CNEt_2)_4$[85], an aged solution of $V(S_2CNEt_2)_4$ appears to contain only unidentate ligands. These are presumably arranged in a distorted tetrahedral configuration; c.f. $V(S_2COEt)_4$ which has been shown by e.s.r. experiments to add phosphorus donor ligands to its coordination sphere at high temperatures[98]. $M(S_2CNR_2)_n$ (M=Nb, n=4; M=Ta, n=5) have also been prepared from MCl_n and NaS_2CNR_2[99], but the structure of the Ta(V) complex is unknown.

b) Compounds containing other ligands.

Reactions of $VOSO_4$ with dithioacid ligands lead to the formation of $VO(S\text{-}S)_2$ ($S\text{-}S=S_2CNR_2$[100], S_2COR[101] or S_2PR_2[102]) which have been extensively studied by e.s.r. spectroscopy[103] and have been shown to have square-pyramidal structures with the oxygen atom in the apical position of the pyramid[104]. These compounds all interact with solvents[100], pyridine[94,100], 4-methylpyridine[104] or dimethyl sulphoxide[100] to yield 1:1 trans octahedral adducts, some of which (S-S=S_2CNR_2, L=pyridine or 4-methylpyridine) have been isolated[104]. A more recent study of the reaction of $VO(S_2PR_2)_2$ with pyridine, dimethyl formamide or hexamethyl phosphoramide has shown that several products are formed by stepwise cleavage of the V-S bonds[105].

i.e.



The interesting $VO(S_2CNR_2)_3$ may also be prepared by the reaction of VO SO_4 with NaS_2CNR_2, but only in the presence of hydrogen peroxide[106]. This compound, like its niobium analogue, prepared by the reaction of $NbCl_5$ with NaS_2CNR_2 in cold, anhydrous methanol[106], has a pentagonal-bipyramidal configuration with the oxygen atom in an axial position[107].

The reaction of $NbCl_5$ or $TaCl_5$ with NaS_2CNR_2 in cold, anhydrous methanolhas, however, been shown by other workers to produce $MCl(OMe)_2(S_2CNR_2)_2$[108], another pentagonal-bipyramidal molecule with axial methoxy groups, whilst in less polar solvents (C_6H_6 or CH_2Cl_2), $M(S_2CNR_2)_4Cl$, $M(S_2CNR_2)_3S$ or $M(S_2CNR_2)_2Cl_3$ are formed, depending upon the relative ratios of the starting materials[109].

The only other dithioacid complexes that have been isolated are the ionic $[(\eta^5\text{-}C_5H_5)_2VS_2COR]$ (S_2COR)[110], prepared by reaction of S_2COR with $(\eta^5\text{-}C_5H_5)_2VCl_2$ and these complexes with BPh_4^- or BF_4^- as counter anions, $[(\eta^5\text{-}C_5H_5)V(S_2COR)]X$.[111]

5. Complexes of Chromium, Molybdenum and Tungsten.

a) Binary compounds.

Dithiocarbamate complexes of Cr(II) may be prepared by interaction of hydrated chromous chloride with NaS_2CNR_2 in carefully degassed water[4]. The resulting yellow-green complexes are pyrophoric in air and oxidise readily in solution to yield Cr(III) species[4]. However, they have been shown to be isomorphous with $\{Cu(S_2CNR_2)_2\}_2$ and are thus dimeric with each chromium ion surrounded by five sulphur atoms in a square-pyramidal arrangement. Magnetic measurements indicate that the complexes are low-spin d^4 systems which, in contrast to their Cu(II) analogues, have rather low magnetic moments on account of an anti-ferromagnetic interaction between unpaired electrons on the two chromium ions of a dimer[112].

$Mo_2(OCOMe)_4$, on the other hand, reacts with NaS_2CNR_2[22], NaS_2COR[21,113] or NaS_2PPh_2[22] to give dimeric, diamagnetic complexes with four bridging dithioacid ligands and very significant metal-metal interaction[113]. Care must, however, be exercised in the preparation of $Mo_2(S_2CNR_2)_4$ since prolonged reaction in alcohols leads to the sulphur bridged carbene complex mentioned earlier[21,22] (page 4) and, in air, oxidation to the oxo-bridged $Mo_2O_3(S_2CNR_2)_4$ readily occurs[22].

Reaction of $CrCl_3$ with dithioacid ligands leads to the formation of $Cr(S\text{-}S)_3$ (S-S = S_2CNR_2[114,115], S_2COR[115], S_2PR_2[31,116,117] or S_2PF_2[27]), all of which are monomeric compounds with magnetic moments close to their spin-only values[118,119], as expected for a d^3 configuration. An x-ray crystal structure of $Cr(S_2COEt)_3$[120], as well as low temperature absorption and emission spectra[121,122] and solution electronic spectra[119,123], indicates that all these complexes have trigonally distorted octrahedral stereochemistries. These distortions towards trigonal prismatic geometry are perhaps best explained in terms of the steric nature of the ligands, which seem to require that the S-Cr-S angle (both sulphur atoms in the same chelate) be ca. 75°, somewhere between that for an octahedron (90°) and a trigonal prism (ca 70°). $Mo(S_2PF_2)_3$ may also be prepared, by the reaction of $MoCl_5$ with HS_2PF_2, which again indicates the reducing nature of the $^-S_2PF_2$ anion[124].

The dodecahedral complex $Mo(S_2CNR_2)_4$ may be prepared either by treatment of $Mo(CO)_6$ with $(S_2CNR_2)_2$[125] or by insertion of CS_2 into the Mo-N bonds of $Mo(NR_2)_4$[126], whilst $W(S_2CNR_2)_4$ is best prepared by reaction of $WCl_4(MeCN)_2$ with NaS_2CNR_2[99]. Both these M(IV) species (R=Et) may be oxidised by iodine or bromine to $[M(S_2CNEt_2)_4]X$ (X=I,Br)[127], in which the cation again posesses dodecahedral stereochemistry[128].

b) Compounds containing other ligands.

(i) Oxygen.

Oxygen containing complexes of these metals with dithioacid ligands are limited to those of molybdenum in relatively high oxidation states (IV, V and VI). Reactions of $[MoO_4]^{2-}$ with NaS_2CNR_2 in alkaline solution yield $MoO_2(S_2CNR_2)_2$[114] whereas if the reactions are carried out in neutral or slightly acid solution, the singly oxo-bridged $Mo_2O_3(S_2CNR_2)_4$ are isolated[129]. These may also be prepared by the action of NaS_2CNR_2 on $[MoOCl_5]^{2-}$ [106,130] or $[MoO_4]^{3-}$ [114] in acid solution. If 1:1 ratios of NaS_2CNR_2 and $[MoO_4]^{3-}$ are employed, the product is the doubly oxo-bridged

$Mo_2O_4(S_2CNR_2)_2$[131a]. Similar compounds but with sulphur bridges, $Mo_2\,O_2\,S_2\,(S_2COR)_2$ have recently been prepared by the reaction of $Mo_2\,O_3\,(S_2COR)_4$ with alcohols[131b]. With xanthates, however, both $[Mo\,O_4]^{2-}$ and $[Mo\,O_4]^{3-}$ give $Mo_2\,O_3\,(S_2COR)_4$, the former requiring three moles of KS_2COR per mole of molybdenum so that reduction can occur[132]. Reaction of $[MoO_4]^{2-}$ with HS_2PPh_2 yields $MoO_2(S_2PPh_2)_2$[93].

The monomeric Mo(VI) species $MoO_2(S-S)_2$ have been shown by x-ray[133], dipole moment measurements[134] and i.r. spectroscopy (two ν Mo = O near 900 cm)[130,134] to have a cis arrangement of oxygen atoms, although the dimeric species $[MoO_2\,(S_2CNR_2)_2]_2$ have also been reported, as arising from the oxidation of $Mo(CO)_2$-$L(S_2CNR_2)$ (L = PPh_3, $AsPh_3$ or $SbPh_3$) in non-polar solvents[135]. However, in the Mo(V) species, although the terminal oxygen atoms are always cis to the bridging oxygen, they may be either mutually cis (S-S = S_2COR[136] or S_2CNR_2[130]) or trans (S-S = $S_2P(OEt)_2$[137]) and their diamagnetism has been explained in terms of interaction between the unpaired electrons on each molybdenum ion via the linear oxygen bridge[136].

Reductions of $Mo_2O_3\,(S_2CNR_2)_4$ with zinc[138], or of $MoO_2\,(S_2CNR_2)_2$ with triphenylphosphine[139] produce $MoO\,(S_2CNR_2)_2$, which readily coordinate unsaturated C=C bonds in their vacant position[140] and are presumably isostructural with the corresponding $VO\,(S_2CNR_2)_2$[103]. The analagous $MoO\,(S_2PF_2)_2$ is formed by the reaction of $MoOCl_4$ with HS_2PF_2[124], and reacts with pyridine to give $[MoOpy_4\,]\,[\,S_2PF_2]_2$[124] (c.f. reaction of $VO\,(S_2PR_2)_2$ with pyridine)[105].

(ii) Nitric oxide.

Complexes containing nitric oxide and dithioacid ligands are known for all the group VIa metals; thus, the monomeric cis - $M(NO)_2(S_2CNR_2)_2$ are readily prepared either by reaction of $\{M(NO)_2Cl_2\}_n$ (M = Mo or W)[141] with Na S_2CNR_2, or by interaction of $Cr_2(OCOMe)_4$, NO and Na S_2CNR_2 at low temperatures[142]. In all these complexes, the NO ligand acts as a three electron donor making them eighteen electron systems. The molybdenum and tungsten species both show temperature dependent n.m.r. spectra which have been interpreted in terms of a rupture of a metal - sulphur bond, followed by recombination of the ligand with the environments of the R groups interchanged[143]. $Cr(NO)_2(S_2CNEt_2)_2$ may also be prepared by reaction of $[Cr(NO)_2(MeCN)_4][PF_6]_2$ with As $(S_2CNEt_2)_3$[144]. In contrast, reactions of $\{MoNOCl_3\}_n$ with NaS_2CNR_2 give the interesting pentagonal-bipyramidal $Mo(NO)(S_2CNR_2)_3$[145] which are also eighteen electron systems and their temperature variable n.m.r. spectra have been explained in a similar fashion to those of $M(NO)_2(S_2CNR_2)_2$ (M = Mo or W)[143].

A series of e.s.r. experiments on compounds containing $[Cr(H_2O)_3NO(S-S)]^+$ (S-S = S_2CNR_2[146], S_2COR[146] or S_2PR_2[147]) has revealed that the water molecules in this cation are facially arranged, and that reactions with nitrogen[148], phosphorus[149-151] and arsenic[153] donor ligands only produce substitution of the water molecule trans to the nitric oxide ligand, which is an effective demonstration of the much lower six-coordinate trans effect of the sulphur ligand than of NO. The only exception to this pattern occurs for the very nucleophilic trialkylphosphites which also replace one of the water molecules trans to sulphur, but only with some difficulty[154,155].

Finally, $(C_5H_5)_2$ $MoNO(S_2CNMe_2)$[156] has been prepared and at low temperature contains one η^5- and one η^1- cyclopentadienyl ring, as required for the molydbenum atom to be an eighteen electron system. However, on warming, the η^1- ring first becomes fluxional and this is followed by site exchange of the two cyclopentadienyl rings together with interconversion of the environments of the two methyl groups on the dithiocarbamate ligand[156].

(iii) Carbon monoxide.

Reaction of $Mo(CO)_4Cl_2$ with NaS_2CNR_2 under anaerobic conditions has been shown to yield $Mo(CO)_3(S_2CNR_2)_2$[157] which loses carbon monoxide reversibly under high vaccuum to give $Mo(CO)_2(S_2CNR_2)_2$ and can thus act as a carbon monoxide carrier[158]. The similar stabilities of the two complexes presumably arises from less steric crowding in the dicarbonyl counter-balanced by the preferable eighteen electron system of the tricarbonyl.

The complexes $(\eta^5-C_5H_5)M(CO)_2(S-S)$ have been extensively studied, being prepared from $(\eta^5-C_5H_5)M(CO)_3Cl$ and Na(S-S) (M = Mo[159] or W[160,161], S-S = S_2CNR_2; M = Mo, S-S = S_2PEt_2[162]), reaction of $\{(\eta^5-C_5H_5)Mo(CO)_3\}_2$ with $(S_2CNR_2)_2$[163] or from the interaction of $(S_2CNR_2)_2$ on $\{(\eta^5-C_5H_5)M(CO)_3\}_2$ Hg (M = Cr, Mo or W)[164]. In the last reaction, $(\eta^5-C_5H_5)M(CO)_3$ Hg (S_2CNR_2) is also isolated[164].

Photolysis if $M(CO)_6$ with $[(Ph_3P)_2N][F_2PS_2]$ gives only $[(Ph_3P)_2N][M(CO)_4(S_2PF_2)]$ (M = Cr, Mo or W)[165], whilst the products of the reactions of $Mo(CO)_3L_2Cl_2$ and $[M(CO)_3NO\ diphos]PF_6$ with NaS_2CNR_2 are $Mo(CO)_2L(S_2CNR_2)_2$ (L = PPh_3, $AsPh_3$ or $SbPh_3$)[135] and cis M(CO)(NO) diphos (S_2CNR_2) (M = Mo or W, diphos = $Ph_2PCH_2CH_2PPh_2$)[166]. All these complexes contain only bidentate dithioacid ligands and are eighteen electron systems. However, cis - Mo(CO)(NO) diphos(S_2CNR_2) exhibit temperature variable n.m.r. spectra[166] which have been explained by the same mechanism as that invoked for $Mo(NO)_2(S_2CNR_2)_2$[143].

6. Complexes of Manganese, Technetium and Rhenium.

a) Binary compounds.

Reactions of $MnCl_2$ or $MnSO_4$ with dithioacid anions under anaerobic conditions lead to the formation of $Mn(S\text{-}S)_2$ (S-S = S_2CNR_2[4,167], S_2COEt[168], S_2PR_2[31,169] or S_2PF_2[27]), whose stabilities are very dependent upon the nature of the dithioacid ligand. The dithiocarbamates, like their chromium analogues, are very unstable, being pyrophoric in air[4] and being oxidised readily in solution to $Mn(S_2CNR_2)_3$[170]. The xanthates and phosphinodithioates, however, are relatively stable to oxidation and $Mn(S\text{-}S)_3$ (S-S = S_2COEt or S_2PR_2) have not been isolated, although reaction of three moles of KS_2COEt with one mole of $MnCl_2$ in the presence of $[Et_4N]Cl$ leads to the formation of $[Et_4N][Mn(S_2COEt)_3]$[168], presumably a distorted octahedral Mn(II) anionic species.

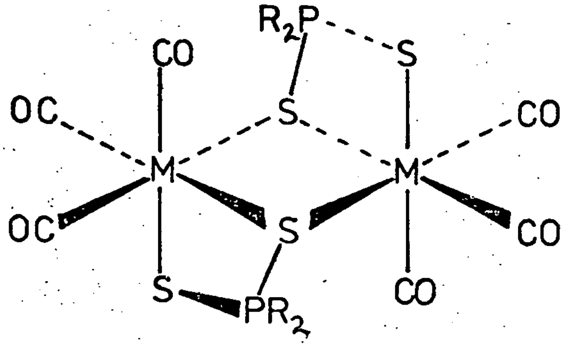
The structures and magnetic properties of these ligands also seem to be dependent upon the dithioacid ligand present and sometimes, even on the ligand substituents. There seems to be conflicting evidence about the crystal structure of $Mn(S_2CNEt_2)_2$ as it has been reported[4,171] to be isostructural with $\{Cu(S_2CNEt_2)_2\}_2$[48] (i.e. dimeric with a square-pyramidal arrangement of sulphur atoms around the metal) and with $Ni(S_2CNEt_2)_2$[172] (i.e. a monomeric square-planar species). However, whichever of these two structures is correct, it is clear that the tetragonal distortion from octahedral symmetry is sufficient for $Mn(S_2CNEt_2)_2$ to have a ^4E ground state[171] which, although unusual for Mn(II)($3d^5$), may be explained in terms of simple crystal field theory by the presence of three electrons in the d_{xz} and d_{yz} orbitals, one in each of the d_{xy} and d_{z^2} orbitals and no electrons in the $d_{x^2-y^2}$ orbital. In contrast, $Mn(S_2PR_2)_2$ all have $^6A_1$ ground states and are isostructural with their Co(II) analogues[6], which for R = Me is polymeric with S_2PMe_2 bridges and each metal atom in a tetrahedral environment, whilst for R = Et, the compounds are dimeric, again with tetrahedral coordination but with two bridging and two bidentate S_2PEt_2 ligands per dimer[6]. $Mn(S_2PF_2)_2$ is monomeric and probably tetrahedral in solution but, in the solid state its pale pink colour is indicative of octahedral geometry, which can be achieved by forming a layer type of polymeric structure[27].

As has been noted earlier $Mn(S_2CNR_2)_2$ are not very stable in solution and are readily oxidised to $Mn(S_2CNR_2)_3$[170]. The magnetic moments of these Mn(III) compounds are temperature invariant and are close to the spin-only values expected for a high-spin d^4 configuration[118]. This is consistent with a ^5E ground state with the first excited state ($^3T_1$) being not-too-low-lying[173,174]. The structures of $Mn(S_2CNR_2)_3$, as indicated by x-ray analysis (R = Et)[175] and electronic spectra[123], deviate widely from octahedral geometry in a way which is best explained by a Jahn-Teller distortion arising from the high-spin d^4 configuration (O_h approximation) superimposed upon the trigonal distortion noted elsewhere for $Cr(S_2CNR_2)_3$ and attributable to the steric requirements of the ligands. This deviation from octahedral geometry, together with the change in ligand field stabilization energy on changing from octahedral to trigonal-prismatic symmetry, has been correlated with the activation energy of inversion of the two possible optical enantiomorphs by means of a trigonal twist mechanism via a trigonal-prismatic intermediate, which has been invoked to account for the temperature variable ^{1}H n.m.r. spectra of $Mn(S_2CNR_2)_3$[176].

These Mn(III) complexes have been shown to oxidise slowly in air to give Mn(IV) species[170] whose structures are not known; and eight coordinate Re(V) cationic species $[Re(S_2CNEt_2)_4]^+$ have been isolated along with other products from the reaction of $(S_2CNEt_2)_2$ with $Re(CO)_5Cl$ in benzene or acetone[177(a)].

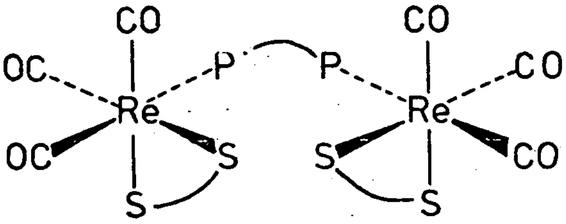
b) Compounds containing other ligands.

The most extensively studied non binary dithioacid complexes of group VIIa metals are $M(CO)_4(S\text{-}S)$ (M = Mn[160,163] or Tc[178], S-S = S_2CNR_2; M = Mn[179,180] or Re[180], S-S = S_2PR_2), which are prepared by the interaction of $M(CO)_5X$ (X = Cl or Br) with dithioacid anions. For S-S = S_2PR_2, these complexes have been shown to undergo reversible loss of carbon monoxide with concomitant dimerisation under high vaccuum to yield $\{M(CO)_3(S_2PR_2)\}_2$[180] (3), in which the phosphinodithioate ligands act as bridging five electron donors[181]. Reactions

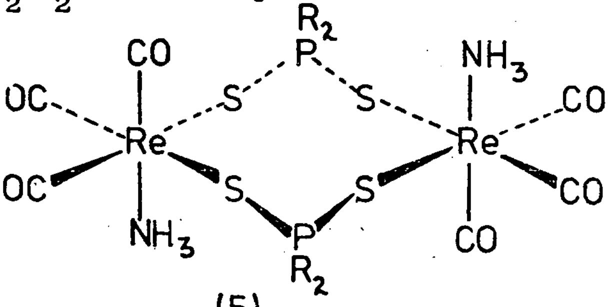


(3)

of $M(CO)_4(S_2PR_2)$ with various ligands have also been studied and it is found that with monodentate non π - acceptor ligands, such as ammonia, a stepwise displacement of S_2PR_2 occurs to give first $M(CO)_4(NH_3)(SP(S)R_2)$ and then $M(CO)_4(NH_3)_2$ S_2PR_2 [182]. In contrast, monodentate ligands which are capable of back bonding simply replace one carbon monoxide molecule to yield fac- $M(CO)_3$-$L(S_2PR_2)$ (L = pyridine, PPh_3, $AsPh_3$ or $SbPh_3$)[182], which, for L = PPh_3, is also the product of reaction of $\{M(CO)_3(S_2PR_2)\}_2$ with triphenylphosphine[183]. If bidentate π- acceptor ligands are reacted with $M(CO)_4(S_2PR_2)$, one carbon monoxide molecule is lost and the S_2PR_2 ligand becomes unidentate so as to accommodate the chelating ligand, the product being fac-$M(CO)_3(L\text{-}L)(SP(S)R_2)$ (L-L = 2,2'-bipyridyl or $Ph_2PCH_2CH_2PPh_2$ (diphos))[182]. For L-L = diphos, it has been shown that this reaction occurs via a dimeric species with a diphos bridge (4). Finally, reactions of $\{Re(CO)_3$-$(S_2PR_2)\}_2$ with ammonia at low temperatures give $\{Re(CO)_3(NH_3)$-$(S_2PR_2)\}_2$ (5) with the bridging S_2PR_2 groups acting as three electron donors, which convert to $Re(CO)_3(NH_3)(S_2PR_2)$ on warming[184].



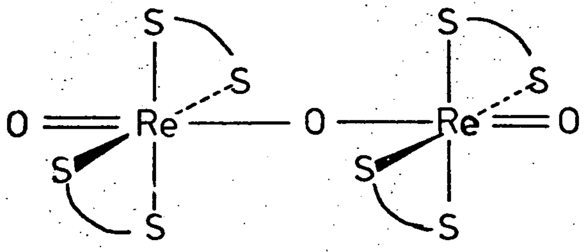
(4)



(5)

If $Re(CO)_5Cl$ is treated with $(S_2CNEt_2)_2$, no $Re(CO)_4(S_2CNEt)$ is isolated, but various other dithioacid species are produced and their natures depend upon the conditions for the reaction. Thus, if the reaction is carried out in benzene, the main products are $ReCl_2$-$(S_2CNEt_2)_4$, $Re(S_2CNEt_2)_4$ $ReCl_4(S_2CNEt_2)$ and $ReCO(S_2CNEt_2)_3$,[177(a)] whose x-ray structure indicates a pentagonal-bipyramidal structure with an axial CO group[177(b)]. In acetone, however, $Re(CO)(S_2CNEt_2)_3$ is again isolated along with $Re(S_2CNEt_2)_4$ $ReCl(CO)_3(S_2CNEt_2)$ [177(a)]. In contrast, $Re(CO)_5Cl$ and $Tl(S_2CNEt_2)$ react together to give the dimeric $\{Re(CO)_3(S_2CNEt_2)\}_2$, which is similar in structure and properties to $\{Re(CO)_3(S_2PR_2)\}_2$, e.g. reacting with PPh_3 to give $Re(CO)_3(PPh_3)(S_2CNEt_2)$ which may also be prepared by reaction of $Tl(S_2CNEt_2)$ on $ReCl(CO)_3(PPh_3)_2$ [177(a)].

$Re_2O_3(S_2CNR_2)_4$ have been prepared by the action of NaS_2CNR_2 on $\{ReCl(OCOMe)_2\}_2$ [185], $ReOCl_3$ [185,186] or $Re_2O_3Cl_4py_4$ [185] and, in contrast to their molybdenum analogues, have a linear O = Re-O-Re = O backbone (6); whereas reaction between $ReNCl_2(PPh_3)_2$ and NaS_2CNEt_2 leads to the monomeric square-pyramidal $ReN(S_2CNEt_2)_2$ with an apical nitrogen atom.



(6)

The only non binary xanthate complexes of manganese that have been reported are $Mn(S_2COR)_2(N-N)$ [168] and $[Mn(N-N)_3](S_2COR)_3$ [187] (N-N = 2,2'-bipyridyl or 1,10-phenanthroline) prepared from stoichiometric amounts of $MnCl_2$, (N-N) and KS_2COR; and $MnNO(S_2COR)_2$ which, like their dithiocarbamate analogues are square pyramidal (apical NO) and have only one unpaired electron[188].

Finally, the nitrosyl complexes $(\eta^5-RC_5H_4)MnNO(S_2CNR^1_2)$ have been prepared by the reaction of $NaS_2CNR^1_2$ with $[(\eta^5-RC_5H_4)MnNO(CO)_2]PF_6$ [189] (R = H or alkyl); and the reaction of $ReCl_3$ with NaS_2CNEt_2 gives the diamagnetic $ReCl_2(S_2CNR_2)$[190], which was originally formulated as an unusual low-spin tetrahedral complex[190] but may in fact be a trimer derived from the well known Re_3Cl_9 cluster[103].

7. Complexes of Iron, Ruthenium and Osmium.

Reactions of $FeSO_4$ with NaS_2CNR_2 in oxygen-free water yield $Fe(S_2CNR_2)_2$[4], high-spin complexes which are isomorphous with $\{Cu(S_2CNR_2)_2\}_2$, being dimeric with each iron atom exhibiting square-pyramidal coordination[4,48]. These complexes are readily air oxidised, whilst the complexes $Fe(S_2PR_2)_2$ (prepared similarly)[169] are remarkably stable. $Fe(S_2PR_2)_2$ are isostructural with the corresponding manganese complexes, being polymeric for R = Me and dimeric for R = Et[169]. $Fe(S_2PF_2)_2$ is monomeric (tetrahedral) in solution but, again like its manganese analogue, appears to be polymeric in the solid state with each iron atom surrounded by an octahedral arrangement of sulphur atoms[27]. If the reactions of $FeSO_4$ with Na(S-S) are carried out in the presence of a large cation, e.g. Et_4N^+, the interesting high-spin[191] distorted octahedral complex anions $[Et_4N][Fe(S\text{-}S)_3]$ (S-S = S_2CNR_2 or S_2COR) are isolated[168].

In contrast to the Fe(II) complexes, Fe(III) dithiocarbamates are much more stable than the phosphinodithioates. All these trivalent complexes are prepared by reaction of $FeCl_3$ with Na(S-S) (S-S = S_2CNR_2[192], S_2COR[193] or S_2PR_2[26(b),194]) but $Fe(S_2PR_2)_3$ readily decompose in air[194]. These Fe(III) complexes have interesting structural and magnetic properties which are very dependent on the ligand. In general, all $Fe(S_2PR_2)_3$ are high-spin complexes[6], all $Fe(S_2COR)_3$[195] are low-spin and $Fe(S_2CNR_2)_3$ represent spin cross-over systems, the magnetic properties of which are dependent upon R and the temperature of measurement[196].

It is clear from simple crystal field theory considerations, that since for a high-spin d^5 system there are two electrons in the e_g set of metal orbitals of an octahedral complex, whereas in the low-spin system the five electrons are all in the t_{2g} set of metal orbitals, the coordinating atoms of the ligands are more shielded from the positive charge on the metal ion and hence, the metal-ligand bonds are longer in high-spin complexes than in low-spin complexes. On account of this, there is more interaction between the ligands and the e_g orbitals for the low-spin case and hence Δ (low-spin) is greater than Δ(high-spin) for a given set of ligands. If it happens that the energy required to pair two electrons in a t_{2g} orbital lies between Δ (low-spin) and Δ (high-spin), it is difficult to predict which of the two spin states will produce the lowest energy system. It has been shown by semi-empirical calculations that this is, in fact, the situation in certain Fe(III) dithiocarbamates[195], and this has been used to explain both their temperature[197] and pressure[197] variable magnetic moments, and the contraction of Fe-S bond length of $Fe(S_2CNEt_2)_3$[198] from when the structure is measured at 279K (high-spin) to when it is measured at 79K (low-spin), as well as the difference of ca.0·1Å in the Fe-S bond lengths of known high-spin ($Fe(S_2CNBu_2)_3$[199], $Fe(S_2CN(CH_2)_4)_3$[200]) and known low-spin ($Fe(S_2COEt)_3$[201], $Fe(S_2CNMePh)_3$[200]) compounds. However, it has not been possible to decide whether the electronic structures of the iron atoms in these cross-over systems are in a rapid spin state equilibrium ($^2T_2 \rightleftharpoons {}^6A_1$), or whether they represent genuine mixed spin state systems[198]. Correlations have, however, been noted between μ_{eff} and both the steric size of the R groups[195] and the pK_a of the parent secondary amine (NHR_2)[202].

These have been rationalised in terms of the effect of the R - N - R angle or the donor properties of the NR_2 group on the bond order of the C$\overset{\cdots}{-}$N bond, which, in turn, affects the electronic properties of the sulphur atoms and their capacity to act as π-acceptors from the filled t_{2g} orbitals on the metal, which acceptor capacity is greater for low-spin systems[195,202].

M $(S\text{-}S)_3$ (M = Ru [203] or Os[204], S-S - S_2CNR_2; M = Ru[205], S-S = S_2PR_2) have also been prepared, by the reaction of $RuCl_3$ or $[NH_4]_2[OsCl_6]$ with Na (S-S) but, being of 2nd and 3rd row elements, these complexes do not exhibit variable magnetic properties and are all low-spin d^5 compounds[203].

Like the trivalent complexes of Cr, Mn and Co, the iron complexes exhibit substantial deviations from octahedral geometry. Thus, Fe $(S_2CNBu_2)_3$ has a distortion towards trigonal prismatic geometry in the crystal[199] which was originally thought to be due to crystal packing forces because of the large difference between solid state and solution magnetic moments[103]. However, distortions of this kind have since been shown to occur both in the solid state[200,201] and in solution[123] for other similar iron complexes and are attributable to the steric requirements of the ligands[200]. It is interesting to note that the distortions of the high-spin complexes from octahedral geometry (ca.30°) are significantly greater than those of the low-spin complexes (ca.20°)[200].

$[Fe(S_2CNR_2)_3]X$ cations have also been prepared, by oxidation of $Fe(S_2CNR_2)_3$ with BF_3 in air ($X = BF_4$)[206], by the action of $(S_2CNR_2)_2$ on $FeCl_3$ in ether ($X = FeCl_4$)[62], or by electrolytic oxidation of $Fe(S_2CNR_2)_3$ in the presence of BF_4^- ($X = BF_4$)[207].

The complexes $[Fe(S_2CNR_2)_3]X$, $M(S_2CNR_2)_3$ (M = Fe or Ru[208]) and

$Fe(S_2CNR_2)_2$ (phen)[168], made by the interaction of $FeCl_2$, NaS_2CNR_2 and 1,10-phenanthroline, have all been shown to be steriochemically non-rigid on the n.m.r. time scale and, as for the analagous $Mn(S_2CNR_2)_3$, this has been attributed to an interconversion of the two possible optical isomers of the complexes via a trigonal twist mechanism. The activation energies ($\Delta G^{\ddagger}$) for this process follow the order of the M - S bond strengths, i.e. Fe(II) (S = 2) $<$ Fe(III) ($S = {}^5/_2 \rightleftharpoons S = {}^1/_2$) $\overset{\frown}{=}$ Fe (IV) (S = 1) with Fe(III) ($S = {}^5/_2$) $<$ Fe(II) ($S = {}^1/_2$)[209]. $Ru(S_2CNR_2)_3$ are less labile than any of the iron compounds[208]. The activation parameters for the racemisation have also been correlated with structural factors of the ground state and changes in ligand field stabilization energies on passing from the ground state to the trigonal-prismatic transition state[209].

Finally, $[Ru(S_2CNMe_2)_3]\,BF_4$ has been prepared by the oxidation of $Ru(S_2CNMe_2)_3$ with BF_3 in air but, unlike the iron analogue, this compound is strongly associated in solution and diamagnetic[210].

b) Compounds containing other ligands.

The most extensively studied non-binary dithioacid complexes of iron are $FeNO(S{-}S)_2$ ($S{-}S = S_2CNR_2$ or S_2COR) which have the iron in a formal oxidation state of +1 and, as such have a doublet[211] ground state characteristic of a low-spin d^7 configuration. Several methods have been devised for preparing these complexes, including reaction of $Fe(S{-}S)_2$ with $(NH_2OH)_2SO_4$ or nitric oxide[213]. The green crystalline complexes[212] have been shown by e.s.r.[214] and x-ray[215-217] methods to have the iron atom in a square-pyramidal environment with the nitric oxide group at the apex bound through the nitrogen atom. Disorder in the positions of the oxygen atoms at room temperature in certain of the crystals[216] has led to some doubt as to whether the Fe - N - O group is linear, but this has been resolved by a low temperature x-ray study of $FeNO(S_2CNMe_2)_2$[217] which shows the Fe - N - O angle to be 170°. This small deviation from linearity is attributed to an electrostatic attraction between a lone pair on the oxygen atom and the $N^{\delta+}$ on a dithiocarbamate moiety[217]. This explanation is supported by the observation that changing from $^-S_2CNR_2$ to ^-S_2COR causes a shift in ν NO which is attributed to the smaller positive change on the oxygen atom of the xanthate group producing less attraction to it of the nitric oxide oxygen atom[218].

I.r.[219,220] and e.s.r.[220] studies on $Fe\,NO(S_2CNR_2)_2$ in different solvents have shown shifts in ν NO as well as in the e.s.r. parameters g_{av} and A_{iso} (^{14}N) which correlate well with the coordinating ability of the solvent. This has been interpreted in terms of coordination of the solvent in the vacant site of the iron atom (trans to NO) and the large changes in e.s.r. parameters are due to the presence of the unpaired electron in the d_{z^2} orbital[220].

Since the compounds $Fe\,NO(S_2CNR_2)_2$ are seventeen electron systems, they easily form adducts with one electron donors. However, in contrast to the solvated species, these adducts are all cis-$Fe(NO)\,X\,(S_2CNR_2)_2$ (X = I, Br or NO_2)[221]. The original reports of addition of NO to FeNO $(S\text{-}S)_2$ to yield cis-$Fe(NO)_2$ $(S\text{-}S)_2$[142,213,222] have now been shown to be incorrect; the correct formulation of the products being $FeNO(NO_2)\,(S_2CNR_2)_2$[221], which is more consistent with their diamagnetism[222].

$Ru(S_2CNR_2)_3$ reacts with nitric oxide under mild conditions to yield $RuNO\,(S_2CNR_2)_3$[223], the first complex to be isolated containing a unidentate dithiocarbamate ligand[224], which can also be prepared byreaction of NaS_2CNR_2 with K_2 $RuNO(CN)_5$ at 0°C[223].

Square-pyramidal complexes of Fe(III), $FeX(S_2CNR_2)_2$ (X = Cl, Br, I or NCS) have been prepared either by the reaction of FeX_3 with $Fe(S_2CNR_2)_3$, NaS_2CNR_2 or $(S_2CNR_2)_2$[225], or by the reaction of $Fe(S_2CNR_2)_2$ with the appropriate haloacid[226]. These complexes are interesting in that they have a ^4A ground state (three unpaired electrons)[225] and one, $FeCl(S_2CNEt_2)_2$ exhibits ferromagnetism[227,228]. The zero-field quadrapole splitting of Fe X $(S_2CNR_2)_2$ has been shown to be dependent upon the nature of X[225] and is reduced markedly on passing from the solid state to solution, presumably because the asymmetry of the iron atom is decreased by coordination of a solvent molecule in the position <u>trans</u> to X.[229]

Reactions of $FeCl(S_2CNR_2)_2$ with sodium dithiolates give $[Fe(S_2CNR_2)_2\ (S\text{-}S)']^-$ ($S\text{-}S' = S_2C_2(CN)_2$ or $S_2C_2(CF_3)_2$) which can be oxidised to $Fe(S_2CNR_2)_2\ (S\text{-}S)'$[230]. These Fe(IV) complexes, which may also be prepared by reaction of $Fe(S_2CNR_2)_n$ (n = 2 or 3) and $Na_2(S\text{-}S)'$ followed by oxidation by air or Cu(II) in acetonitrile[231,232], exhibit magnetic properties of spin cross-over systems and their temperature variable, contact shifted, n.m.r. spectra have been interpreted as arising from two processes, the one of lower activation energy being an inversion of optical isomers via a trigonal twist mechanism (as for $Fe(S_2CNR_2)_3$), and the other a fast rotation about the $C\overset{\text{---}}{=}N$ bond of the dithiocarbamate ligands at higher temperatures[231,232].

Other non-binary dithioacid complexes of metals in the iron group are all prepared by the action of dithioacid anions on compounds already containing other ligands. Thus, $Fe(CO)_4\ Br_2$ reacts with NaS_2CNR_2 to yield <u>cis</u> - $Fe(CO)_2\ (S_2CNR_2)_2$[163] whilst $Fe(CO)_3I_2$ gives rise to $Fe(CO)_3I\ (S_2CNR_2)$[160]. Reaction of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2$

with NaS_2CNR_2 gives $(\eta^5\text{-}C_5H_5)FeCO(S_2CNR_2)$[160] whilst the reaction with HS_2PF_2 yields $(\eta^5\text{-}C_5H_5)Fe(CO)_2\ (SP(S)F_2)$, a rare example of a complex containing a unidentate S_2PF_2 ligand[159]. $(\eta^3\text{-}C_3H_5)Fe(CO)_{3\ 2}$ yields $(\eta^3\text{-}C_3H_5)\ Fe(CO)_2(S_2CNR_2)$ when reacted with NaS_2CNR_2[160].

In ruthenium chemistry, fewer complexes have been made. However, $RuCl_2(PPh_3)_3$ reacts which Na(S-S) to produce $Ru(S\text{-}S)_2(PPh_3)_2$ (S-S = S_2CNR_2 or S_2COR)[233], $\{(C_8H_{12})\ RuX_2\}_n$ and NaS_2CNMe_2 give $(C_8H_{12})Ru(S_2CNMe_2)_2$[234], reaction of the red solution (obtained by passing CO through an ethanolic solution of $RuCl_3$) with $(S_2CNR_2)_2$ gives $Ru(CO)_n\ (S_2CNR_2)_2$ (n = 1 or 2)[235] and the reaction between $K_3\ [Ru_2NCl_8\ (H_2O)_2]$ and NaS_2CNEt_2 has recently been shown to yield the interesting nitrogen bridged compound $Ru_2(N)\ (S_2CNEt_2)_4Cl$ which is thought to be polymeric, at least in the solid state[236]. Finally, apart from a brief mention of $OsO_2\ (S_2CNR_2)_2$[237], the only osmium complex of this kind to have been prepared is $Os(bipy)_2(S_2CN(CH_2)_5)Cl$, made from the interaction of $Os(bipy)_2Cl_2$ and $KS_2CN(CH_2)_5$ (bipy = 2,2'-bipyridyl)[204].

8. Complexes of Cobalt, Rhodium and Iridium.

The stabilities of complexes of cobalt with dithioacid ligands depend very much on the particular dithioacid ligand involved. Thus, whereas $Co(S_2CNR_2)_2$[23] and $Co(S_2COR)_2$[238] have only been briefly reported, being prepared from reaction of Co(II) salts with the appropriate dithioacid anion in strongly acid solutions, $(Co(S\text{-}S)_3$[238,239] are isolated from solutions of pH2.2 to 10.1), the phosphinodithioate complexes $Co(S_2PR_2)_2$ are well known and quite stable. These are prepared by reaction of $CoCl_2$ with NaS_2PR_2[5,26(b)] or HS_2PF_2[27] and, for R = Ph[240] or S-S = S_2PF_2[27], are monomeric, tetrahedral high-spin $3d^7$ species. As with $M(S_2PR_2)_2$ (M = Mn or Fe), $Co(S_2PMe_2)_2$[6] is polymeric with dithioacid ligands bridging the cobalt atoms in such a way that the environments of the cobalt atoms are tetrahedral, whilst $Co(S_2PEt_2)_2$[6] is dimeric, again with tetrahedrally coordinated cobalt atoms and two bridging and two bidentate S_2PEt_2 groups.

The dithiocarbamate and xanthate complexes of Co(III), on the other hand, are much more stable than their phosphinodithioate analogues. $Co(S_2PEt_2)_3$ decomposes even under nitrogen at room temperature to yield $Co(S_2PEt_2)_2$[5]; $Co(S_2PR_2)_3$[6] (R = Me or Ph) decompose on mild heating whilst $Co(S_2CNR_2)_3$ are indefinitely stable in air. $M(S-S)_3$ are prepared by the reaction of MCl_n with Na S-S (M = Co, S-S = S_2CNR_2[239] or S_2COR[208], n = 2; M = Rh or Ir, S-S = S_2CNR_2[203,241], S_2PR_2[242] or S_2PF_2[27], n = 3) or for $Co(S_2COR)_3$ by reaction of $[Co(NH_3)_6]Cl_3$ with KS_2COR to give first $[Co(NH_3)_6][S_2COR]_3$ which loses ammonia on heating to give the product[243]. $Co(S_2PR_2)_3$ are best prepared by reaction of NaS_2PR_2 with $Na_3[Co(NO_2)_6]$[5] whilst $Co(S_2PF_2)_3$ is obtained from the oxidation of $Co(S_2PF_2)_2$ with $(S_2PF_2)_2$[27].

All the complexes $Co(S-S)_3$ have been shown both by their electronic spectra[6,123] and by x-ray studies[10,11] to have the sulphur atoms arranged in a distorted octahedron around the cobalt atom, as has been described for $M(S-S)_3$ (M = Fe and Cr). Also, $Co(S_2CNR_2)_3$[208] are stererchemically non-rigid on the n.m.r. time scale (in contrast to $Rh(S_2CNR_2)_3$[209] which are rigid up to 200°C), and this has again been attributed to a metal centred inversion of optical isomers occurring via a trigonal twist mechanism[208]. Excellent support for the theory that an interconversion of optical isomers is occurring is available because, on account of the high activation energy ($\Delta G^{\ddagger}$), the optical isomers can be obtained in an optically pure state by reaction of NaS_2CNR_2 with optically active K[CoEDTA] or K[CoPDTA][244]. The racemisation of $Co(S_2CNR_2)_3$ may then be followed by the more usual technique of monitoring the loss of optical activity of a solution of one of the isomers with time, and this produces an activation energy for the racemisation of $Co(S_2CN(CH_2)_5)_3$[244] of 99.5 KJ $mole^{-1}$, very close to that obtained from n.m.r. data for $Co(S_2CNBz_2)_3$ (99.1 KJ $mole^{-1}$)[208].

Finally, oxidation of $M(S_2CNMe_2)_3$ (M = Co or Rh) with BF_3 in air leads to the formation of $[M(S_2CNMe_2)_3]\ BF_4$ which, like the ruthenium analogue are diamagnetic and probably polymeric[210].

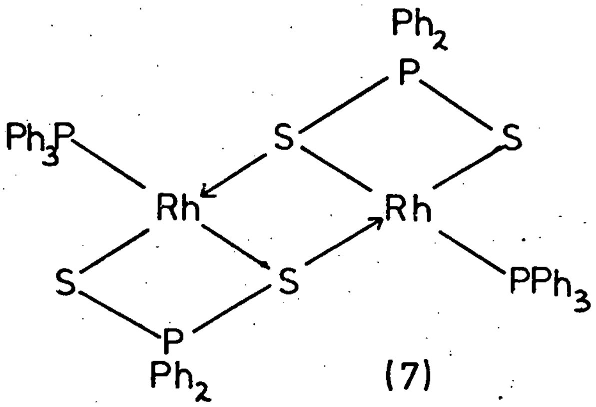
b) Compounds containing other ligands.

Being a coordinatively unsaturated fifteen electron system, $Co(S_2CNMe_2)_2$ readily reacts with nitric oxide (a three electron donor) to form the square-pyramidal $CoNO(S_2CNMe_2)_2$[245] in which the NO group is at the apex and the Co-N-O angle is 135°[246,247]. As in $FeNO(S_2CNMe_2)_2$, there is some disorder of the oxygen atoms in the crystal but for the cobalt complex, the oxygen atom lies alternately over the two C-S bonds of one dithiocarbamate ligand[247]. $Co(S_2PF_2)_2$ also reacts with NO to form an eighteen electron system but in this case the tetrahedral $Co(NO)_2\ (S_2PF_2)$ is the product, which also arises from the reaction of $Co(S_2PF_2)_3$ with nitric oxide[27]. $Co(S_2PR_2)_2$ react with pyridine[5,26(b)] or 2,2'-bipyridyl[248] in dimethyl formamide to yield $Co(S_2PR_2)_2L_2$ (L = pyridine; L_2 = 2,2'bipyridyl).

On account of the inertness of the eighteen electron tris-chelates, $M(S\text{-}S)_3$ (M = Co,Rh or Ir), few reactions have been carried out between them and donor ligands, although mixtures of $Co(S_2CNEt_2)_3$ and $Co(S_2COEt)_3$ have been shown to produce $Co(S_2CNEt_2)_2\ (S_2COEt)$[249].

Other cobalt complexes of mixed sulphur ligands include $[Co(bi)_2(S\text{-}S)]^{2-}$, $[Co(bi)(S\text{-}S)_2]^-$ (bi = bisbiuretate, S-S = S_2CNR_2 or S_2COR) prepared from $K[Co(bi)_2]$ and Na(S-S)[249], and $Co(S_2CNR_2)_2(S_2C_2(CF_3)_2)$, a low-spin, distorted octahedral complex of Co(IV), prepared from the interaction of $CoCl_2$, NaS_2CNR_2 and $NaS_2C_2(CF_3)_2$[231]. The anionic $[Co(CN)_2(CO_3)_2]^{3-}$ complex reacts with NaS-S to give anionic cis - $[Co(CN)_2(S\text{-}S)_2]^-$ (S-S = S_2CNR_2 or S_2COR)[250].

Interesting differences are observed in the reactions of Rh(I) complexes with different dithioacid ligands; for example, $\{RhCl(CO)_2\}_2$ reacts with NaS_2CNR_2 to afford the monomeric $Rh(CO)_2(S_2CNR_2)$[163], whilst with CsS_2PF_2, the chloride bridges are replaced by S_2PF_2 bridges producing the dimeric $\{Rh(CO)_2(S_2PF_2)\}_2$[251] which reacts with triphenylphosphine to give monomeric $Rh(CO)(PPh_3)$-(S_2PF_2)[251]. A similar compound $Rh(CO)(PPh_3)(S_2CNMe_2)$[233] may be prepared by the interaction of stoichiometric amounts of trans $RhCl(CO)(PPh_3)_2$ and NaS_2CNMe_2, whilst excess of the latter reagent gives $Rh(S_2CNMe_2)_3(CO)(PPh_3)$[233], a Rh(III) complex with one bidentate and two unidentate dithiocarbamate ligands. Reaction of $RhCl(PPh_3)_3$ with excess NaS_2CNMe_2 yields $Rh(S_2CNMe_2)_3(PPh_3)$[233], with two bidentate and one unidentate dithiocarbamate ligands whilst if 1:1 ratios of the reactants are used, the Rh(I) complex, $Rh(S_2CNMe_2)(PPh_3)_2$ is isolated[233]. The reaction of stoichiometric amounts of $RhCl(PPh_3)_3$ and HS_2PPh_2, on the other hand, yields the dimeric $\{Rh(S_2PPh_2)(PPh_3)\}_2$[252](7), which is thought to contain bridging S_2PPh_2 ligands acting as five electron donors.



(7)

Some other interesting rhodium complexes, $Rh(S_2PPh_2)_3PPh_3$ and $[Rh(S_2CNR_2)_2(PPh_3)_2]BF_4$, have been prepared by the reaction of dithioacid anions with a solution containing $[Rh_4]^{2+}$ in the presence of PPh_3[253].

The only non-binary dithioacid complexes of iridium that have been reported are cis-$IrH_2(S\text{-}S)(EPh_3)_2$ (E = P or As, S-S = S_2CNR_2[254], S_2COR[254] or S_2PR_2[255]), prepared by the action of Na(S-S) on IrH_3 $(EPh_3)_2$.

9. Complexes of Nickel, Palladium and Platinum.

a) Binary compounds.

Since $NiSO_4$ is often used in the extraction of dithioacids during their preparations[41,256], nickel complexes of almost all dithioacid ligands have been reported. However, they are more usually prepared by reaction of Ni(II) salts with the appropriate free dithioacid or its sodium salt. The complexes so formed are all of stoichiometry $Ni(S\text{-}S)_2$ (S-S = S_2CNR_2[257], S_2COR[243], S_2PR_2[169] or S_2PF_2[27]). Many of these complexes have been studied by x-ray diffraction and all of them have planar NiS_4 skeletons. In general, the atoms which make up the chelate rings (C or P) are coplanar with this skeleton but in $Ni(S_2PMe_2)_2$[258], the phosphorus atoms are slightly out of plane. The degree of interaction between molecules, in the solid state, varies from none for $Ni(S_2CNEt_2)_2$[259], via weak intermolecular hydrogen bonding interactions ($CH_2\cdots S$) in $Ni(S_2CNPr_2)_2$[260], to fairly strong Ni-S interactions which give the nickel atom a distorted octahedral environment in $Ni(S_2COEt)_2$[261]. $Ni(S_2CNR_2)_2$ have also been prepared by insertion of CS_2 into the Ni-N bonds of $Ni(NR_2)_4$[262] but it is interesting to note that CS_2 will not insert in to the Ni-O bonds of alkoxy complexes of nickel to form xanthates[262].

Square-planar dithioacid complexes of Pt(II) and Pd(II) may also be prepared, by the action of Na(S-S) on $K_2[PtCl_4]$ or $PdCl_2$ to give $M(S\text{-}S)_2$ (S-S = S_2CNR_2[203], S_2COR[243], S_2PR_2[169] or S_2PF_2[27]). NaS_2CNR_2 also give $Pt(S_2CNR_2)_2$ with $K_2[PtCl_6]$ but in this case, it may be shown conductimetrically that the displacement of chloride ions occurs in a stepwise manner[263].

The dithioacid complexes of these metals are diamagnetic in the solid state and the Pd(II) and Pt(II) complexes remain so in solution. The Ni(II) complexes, however, become paramagnetic on dissolution in strongly coordinating solvents and this has been attributed to solvent addition to the complexes forming distorted octahedral complexes in which the energy separation of the d_{z^2} and $d_{x^2-y^2}$ orbitals is less than the energy required to pair two electrons in the d_{z^2} orbital and thus each of these orbitals holds one unpaired electron[264].

Anionic $[M(S\text{-}S)_3]^-$ have also been prepared, by the action of KS_2COEt on $NiCl_2$ in the presence of a large cation (M = Ni, S-S = S_2COEt)[265], by the reaction of $Pd(S_2PF_2)_2$ with $[Pr_4N][S_2PF_2]$ (M = Pd, S-S = S_2PF_2)[27] or by the interaction of $[Ph_4As][S_2COR]$ with $Pt(S_2COR)_2$ (M = Pt, S-S = S_2COEt or S_2CO^iPr)[266]. The nickel complex has been shown to be octahedral with two unpaired electrons whilst $[Pd(S_2PF_2)_3]^-$[27] and $[Pt(S_2COR)_3]^-$[60] are diamagnetic square-planar anions containing one bidentate and two unidentate dithioacid ligands (c.f. $Au(S_2CNEt_2)_3$[59]).

Some dithioacid complexes of nickel, palladium and platinum in higher oxidation states have been prepared but, apart from $Ni(S_2CNEt_2)_3$[267], detected at low temperature by its e.s.r. spectrum in solutions of $Ni(S_2CNEt_2)_2$ with an 80-fold excess of $(S_2CNEt_2)_2$, they are all ionic complexes with the metal in oxidation state +4. This interesting complex of Ni(III) has a low spin d^7 electronic configuration and, presumably on account of the Jahn-Teller distortion that arises from this configuration is a square-pyramidal complex[267].

The diamagnetic, low-spin, d^6 complexes $[M(S_2CNR_2)_3]X$ (M = Ni, Pd or Pt, X = Cl, Br or I_3) are prepared by the action of halogens on $M(S_2CNR_2)_2$ (M = Ni)[76,268], reaction of NiX_2 with $(S_2CNR_2)_2$ at elevated temperatures (M = Ni)[76,268] or by oxidation of $M(S_2CNR_2)_2$ (M = Ni, Pd or Pt)[269] with $M'(S_2CNR_2)X_2$ (M' = Cu or Au). The crystal structure of $[Ni(S_2CNBu_2)_3]Br$ indicates that the complex is a genuine example of a distorted octahedral complex of Ni(IV) rather than a complex of Ni(II) in which oxidation of the ligand to give a coordinated tetrabutylthiuram disuphide unit has occurred[270].

b) Complexes containing other ligands.

Apart from reactions of NiX_2 with dithioacid ligands in the presence of triphenylphosphine, which yield $NiX(PPh_3)$ (S-S) (X = Cl or Br, S-S = S_2CNR_2[271] or S_2COR[272]), all non binary dithioacid complexes of elements of the nickel group are prepared by addition of neutral molecules to $M(S-S)_2$, either with or without simultaneous oxidation. Thus, $M(S_2CNR_2)_2$ react with halogens to give cis and trans oxidative addition products, $MX_2(S_2CNR_2)_2$ (M = Pd or Pt, X = Br or I)[273] although at low temperatures the reaction with iodine gives $NiI(S_2CNR_2)_2$ which disproportionate in ethanol to give $Ni(S_2CNR_2)_2$ and $[Ni(S_2CNR_2)_3]I_3$[274]. The reactions in which oxidation does not occur are of two kinds; for nickel, stepwise addition to form five and six coordinate products is the most usual reaction pathway, whereas for palladium and platinum, on account of the strongly antibonding character of the $d_{x^2-y^2}$ 'metal' orbital, reactions involving the stepwise cleavage of metal sulphur bonds tend to occur.

(i) Nitrogen donors.

Although there appears to be no reaction when $Ni(S_2CNR_2)_2$ is treated with pyridine[265], heterocyclic bases form high-spin trans - NiL_2 $(S\text{-}S)_2$ (L = pyridine, S-S = S_2COR[275] or S_2PR_2[276]; L = thiophene, S-S = S_2PR_2[5]) when reacted with $Ni(S\text{-}S)_2$. These reactions are thought to occur in a stepwise manner but none of the five coordinate intermediates have been isolated although there is some spectroscopic evidence for the existence of $Ni(S_2PPh_2)_2py$ in solution[277]. Quinoline, on the other hand, only forms 1:1 adducts with $Ni(S_2PEt_2)_2$[278]. Tertiaryaliphatic amines do not react with $Ni(S\text{-}S)_2$ but primary amines form both 1:1 and 1:2 adducts with $Ni(S\text{-}S)_2$ (S-S = S_2COR or S_2PR_2)[279] and this has led to the use of $Ni(S_2PR_2)_2$ as paramagnetic shift reagents in interpreting the ^{1}Hn.m.r. spectrum of $NH_2{}^iPr$[280]. The reactions of secondary amines depend very much on the nature of the dithioacid ligand present in the metal complex; thus, NHR'_2 react with $Ni(S\text{-}S)_2$ (S-S = S_2CNR_2 or S_2COR) to give $Ni(S_2CNR'_2)_2$ by attack on the ligand[281] whilst with $Ni(S_2PEt_2)_2$, 1:1 square-pyramidal adducts are formed[279]. In the reaction of $Ni(S_2PEt_2)_2$ with ammonia, both addition and displacement of S_2PEt_2 occur, the product being $[Ni(NH_3)_6][S_2PEt_2]_2$[5].

Bidentate nitrogen donors also react with $Ni(S-S)_2$, to produce cis - $Ni(S_2COR)_2$ (N-N) (N-N = 2,2'-bipyridyl, pyrazine or 1,10-phenanthroline)[282], or coordination polymers (S-S = S_2PR_2, N-N = 2,2'-bipyridyl or pyrazine)[283]. Solvent molecules are often clathrated by cis- $Ni(S_2COR)_2$ (N-N) on cyrstallisation, but they may be removed by pumping[282].

The reactions of nitrogen donors with $M(S-S)_2$ (M = Pd or Pt) have been less extensively studied; but, as for the Ni(II) complexes, $M(S-S)_2$ (S-S = S_2CNR_2 or S_2COR) react with secondary amines (NHR'_2) to give $M(S_2CNR'_2)_2$[281]. A brief report of the reactions of $M(S_2COEt)_2$ (M = Pd or Pt) with pyridine indicates that compounds $M(S_2COEt)_2py_2$, with unidentate xanthate ligands occur in solution, but these could not be isolated[284].

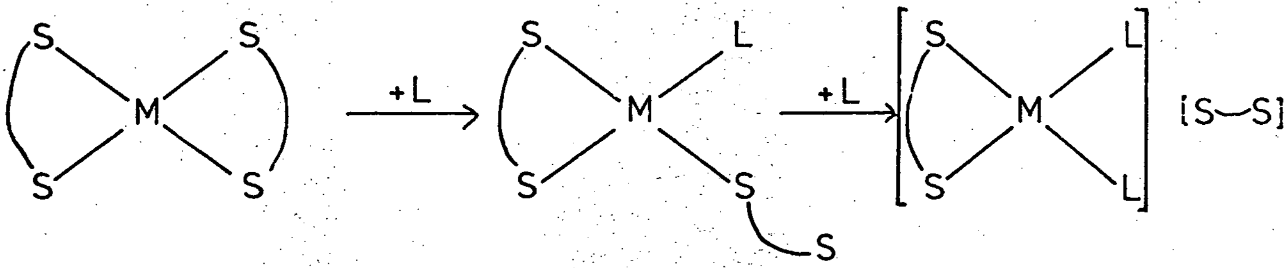
(ii) Phosphorus donors.

The reaction between $Ni(S_2COEt)_2$ and PPh_3 to produce the square-pyramidal $Ni(S_2COEt)_2$ (PPh_3)[275] represents the only example of adduct formation by $Ni(S-S)_2$ with phosphorus donor ligands, but reactions of $M(S-S)_2$ (M = Pd or Pt) with phosphines have been more extensively studied.

In general, interactions of $M(S-S)_2$ (M = Pd or Pt, S-S = S_2CNR_2[18,19], S_2COR[18,19], S_2PR_2[15,16] or S_2PF_2[27]) with tertiary phosphines (L) lead to the stepwise displacement of a dithioacid ligand giving first $M(S-S)_2L$ which contain both unidentate and bidentate dithioacid ligands (1:1 adduct), followed by

$[M(S\text{-}S)L_2]$ S-S (1:2) adduct.

i.e.



1:1 adduct 1:2 adduct

For S-S = S_2COR, the 1:2 adducts react further to give $ML_2(S_2CO)$ and RS_2COR by attack of ^-S_2COR on the coordinated xanthate ligand[18,19] (see page 4). All these 1:1 and 1:2 complexes undergo interconversions both inter - and intra-molecular in origin which give rise to interesting temperature variable n.m.r. spectra[16].

A related study on reactions of $(\eta^3\text{-}C_3H_5)Pt(S\text{-}S)$ (S-S = S_2CNR_2 or S_2COR) with tertiary phosphines (L) shows that, although the final products in each case are $[(\eta^3C_3H_5)PtL_2][S\text{-}S]$, the intermediate (1:1) complexes can have either a η^1-allyl group and bidentate dithio ligand or a unidentate dithio ligand and an η^3-allyl group, and which of these occurs depends upon the dithioacid ligand and the position of any substituents on the allyl group[285].

CHAPTER 2

Dialkyl, Diaryl-phosphinodithioato and N,N- Dialkyldithiocarbamato Complexes of Ruthenium (II)

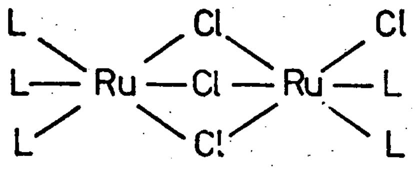
Introduction

Following the work carried out on the reactions of $M(S-S)_2$ (M = Pd or Pt, S-S = S_2CNR_2[19], S_2COR[19] or S_2PR_2[15,16]) with tertiary phosphines, in which stepwise displacement of a (S-S) ligand occurs (see page 41), it was considered of interest to extend this work to cover complexes of ruthenium, and this chapter details the results of this investigation. A short survey of some of the chemistry of halo- and hydrido- complexes of ruthenium containing phosphorus donor ligands is included in order that the results presented may be better understood[286].

The reactions of $RuCl_3$ with tertiary phosphines give several different products, depending not only on the particular phosphine used for the reaction but also on the reaction conditions. Thus, shaking $RuCl_3$ with triphenylphosphine in methanol (1:2 molar ratio) produces $RuCl_3(PPh_3)_2MeOH$[287], whereas if excess PPh_3 is employed, the product is $RuCl_2(PPh_3)_4$[287]. However, if the reaction is carried out under reflux conditions, $RuCl_2(PPh_3)_3$[287], a square-pyramidal complex with trans basal chloride ions and the sixth position blocked by an ortho-hydrogen atom from one of the phenyl rings of a basal phosphine group, is formed[288]. Similar compounds $RuCl_2(L)_n$ ($L_2 = R_2PCH_2CH_2PR_2$[289] or o-phenylenebisdimethylarsine[290], n = 4) are similarly prepared but complexes of this type containing monotertiary phosphines (not PPh_3) have only recently been prepared, by the reaction of $RuCl_2(PPh_3)_{3 \text{ or } 4}$ with excess of the phosphorus ligand in non-polar solvents (L = PMe_2Ph[291], $PMePh_2$[291] or $P(OPh)_3$[292], n = 4; L = $PEtPh_2$[291] or PEt_2Ph[291], n = 3). In polar solvents, these compounds ($L \neq P(OPh)_3$)

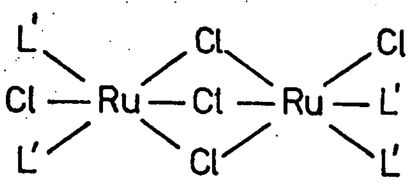
rearrange rapidly to the triply bridged cationic species $[Ru_2Cl_3L_6]Cl$[291] which are also formed from the long-term reaction of $RuCl_3$ and L in refluxing ethanol[289]. Short term reactions between $RuCl_3$ and L in EtOH/HCl mixtures produce mer - $RuCl_3L_3$[293] ($L \neq P(OPh)_3$) which again give $[Ru_2Cl_3L_6]Cl$ on warming in polar solvents[293].

The dimeric cationic species are fairly stable to reaction with other Lewis bases (although reactions with CO under pressure or in 2-methoxyethanol give $Ru(CO)_2L_2Cl_2$[294] and $RuCOL_3Cl_2$[295] respectively) but heating $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ in methylacetate produces $[Ru_2Cl_3(PEt_2Ph)_6][RuCl_3(PEt_2Ph)_3]$, in which the anion has a meridional configuration[297], whilst, if the same compound is heated in n-propylpropionate, $Ru_2Cl_4(PEt_2Ph)_5$[296] (1) results, in which the anion replaces a phosphine group in the co-ordination sphere.



$L = PEt_2Ph$

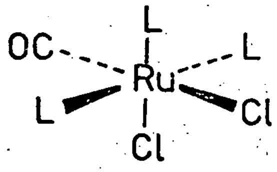
(1)



$L' = PBu_3$

(2)

A related compound which formally contains Ru(II) and Ru(III), $Ru_2Cl_5(PBu_3)_4$ (2) has been obtained, along with the doubly bridged $\{RuCl_3(PBu_3)_2\}_2$, from the reaction of $RuCl_3$ with PBu_3 in 1:2.2 ratios[298]. An interesting feature of the crystal structures of $Ru_2Cl_4(PEt_2Ph)_5$[299] and $Ru_2Cl_5(PBu_3)_4$[300] is the observation that the bridging Ru-Cl bonds are significantly shorter when trans to chloride than when trans to a phosphine, a reflection of the greater trans-influence of tertiary phosphines than of chloride in both Ru(II) and Ru(III) complexes. A similar effect is responsible for the different rates of replacement of the chloride ions in $RuCl_2CO(PMe_2Ph)_3$ (3). The chloride ion trans to phosphine is replaced relatively easily by shaking with a 20-fold excess of NaI in acetone, the maximum amount of $RuIClCO(PMe_2Ph)_3$ (ca. 85%) being reached after eleven hours, whilst conversion to the diiodo complex under the same conditions takes six weeks, indicating the much lower trans-effect of CO than of PMe_2Ph in ruthenium chemistry[295].



L = PMe_2Ph

(3)

Many reactions of these halo-ruthenium phosphine complexes, particularly those involving direct exchange of phosphines with other Lewis bases, have been studied, but since the results presented concern reactions in which replacement of chloride ion occurs, this review will be confined to reactions in which halide ion is replaced, either with or without simultaneous loss of all or some of the phosphine groups.

The reactions of $RuCl_2(PPh_3)_3$ with either β-diketones in the presence of triethylamine, sodium carboxylates or Na(S-S) yield $Ru(PPh_3)_2(L-L)_2$ (L-L = β-diketone[301], RCO_2[301], S_2CNR_2[233] or S_2COR[233]) which for the oxygen donor ligands have cis-stereochemistry, whereas in the reaction of $RuCl_3(AsPh_3)_2MeOH$ with NaS_2PPh_2, all the arsine ligands are replaced and $Ru(S_2PPh_2)_3$ is the sole product[302]. If the reactions between $RuCl_2(PPh_3)_3$ and carboxylate ions are carried out in the presence of hydrogen or any other source of hydride ion, the only products are $RuH(OCOR)(PPh_3)_3$[303] and the reaction between $RuCl_2(PPh_3)_3$ or $[Ru_2Cl_3(PMePh_2)_6]Cl$ and TlC_5H_5 produces $(\eta^5\text{-}C_5H_5)RuClL_2$

(L = PPh_3 or $PMePh_2$)[304].

Reduction of $RuCl_2(PPh_3)_3$ with $NaBPh_4$ in benzene produces $RuHCl(PPh_3)_3$[305] which can also be prepared by reaction of $RuCl_3$, HCHO and PPh_3[306] and this is thought to be the active catalyst when $RuCl_2(PPh_3)_3$ is used to catalyse the hydrogenation of unsaturated substrates[305]. The cis-dihydrido species, RuH_2L_4 may be prepared either from Et_3Al reduction of $RuCl_3$ in the presence of triphenylphosphine (L = PPh_3)[307], or from the reaction of $[Ru_2Cl_3(PMePh_2)_6]Cl$ with hydrazine, $PMePh_2$ and hydrogen under pressure (L = $PMePh_2$)[308], whilst reaction of $\{RuCl_2(PPh_3)_2\}_2$ with Et_3N and hydrogen in benzene yields Ru $H_4(PPh_3)_3$[309,310] which undergoes various interesting reactions; e.g. with NOCl, $RuH_4(PPh_3)_3$ gives $Ru(NO)(PPh_3)_2Cl_3$[309] whilst with NO or SO_2 the products are $RuL_2(PPh_3)_2$ (L = NO or SO_2)[309]. The interesting reaction of cis-$RuH_2(PPh_3)_4$ with CS_2 has recently been reported to produce cis-$Ru(S_2CH)_2(PPh_3)_2$ by insertion of CS_2 into the Ru-H bonds[310]. RuH_2L_4 (L = PEt_2Ph, PMe_2Ph, $PMePh_2$ or PPh_2OMe) have been shown to be stereochemically non-rigid on the n.m.r. time scale and the mechanism for the exchange of the environments of the phosphine groups and of the hydride ions is said to involve a pseudotetrahedral transition state in which the hydride ions exchange via face and edge tunnelling[311].

Finally, it is interesting to note that the only complexes of Ru(IV) containing phosphorus donor ligands that have been isolated are the unusual mer-Ru $(NPR_3)Cl_3$ $(PR_3)_2$ (R_3 = Ph_2Et, $PhEt_2$, Ph_2Me or Et_3) which are formed by attack of PR_3 on a co-ordinated nitride ligand[312].

Results and discussion

1. Preparations of $Ru(S\text{-}S)_2L_2$.

Although there has recently been an increasing interest in the chemistry of ruthenium as well as in the chemistry of complexes of sulphur-containing ligands with various metals, research into ruthenium complexes containing dithioacid ligands has been confined to relatively few papers and most of these have been concerned with complexes containing N,N-dialkyldithiocarbamato groups. Thus, to recap, complexes such as $Ru(S_2CNRR^1)_3$ ($R = R^1$ = Me, Et, ^{n}Bu[203]; R = Me, $R^1 = PhCH_2$[208]), $[Ru(S_2CN(PhCH_2)_2)_2(CO)_2]Cl$[235], $Ru(S_2CNR_2)_2CO$ (R = Me,Et)[235], $Ru(S_2CNR_2)_2(CO)_2$ (R = Me, $PhCH_2$)[235], $Ru(S_2CNR_2)_2(PPh_3)_2$ (R = Me, Et, Ph)[233], $Ru(S_2CNEt_2)_2(Me_2SO)_2$[313], $Ru(S_2CNRR^1)_2(S_2C_2(CF_3)_2)$ ($R = R^1$ = Me, Et; R = Me, R^1 = Ph)[231] and $RuNO(S_2CNR_2)_3$ (R = Me, Et)[223] have been reported (for details see pages 28 - 32) but the latter is the only example to date of a ruthenium compound containing a 'dangling' dithioacid group. Related 1,2-dithiolene complexes of ruthenium of type $Ru(S_2C_2(CF_3)_2)(CO)_n(ER_3)_{3-n}$ (n = 1,0; E = P,As) have also been recently reported[314,315].

In contrast, apart from brief references to the syntheses of $Ru(S_2PR_2)_3$ (R = Et,[205] Ph[302]), no investigation of ruthenium dialkyl (or diaryl) phosphinodithioates has been made.

By analogy with earlier palladium and platinum studies[15,16,19], our first attempts to synthesise a range of ruthenium dithioacid compounds were made either by reacting tertiary phosphines directly with $Ru(S_2PR_3)_3$ or by refluxing an ethanolic solution of $RuCl_3.nH_2O$, NaS_2PR_2 and PMe_2Ph. In both cases, the main product was $Ru(S_2PR_3)_3$ which provides an effective demonstration of the substitutional inertness of the Ru(III) (d^5) co-ordination sphere in this instance. This contrasts with the behaviour of $Ru(S_2CNR_2)_3$ towards NO, which reacts to give $RuNO(S_2CNR_2)_3$ even at low temperatures[223]. However, this can be rationalised in terms of the loss of entropy in going from reactants to product being more than compensated for by the

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reduction in enthalpy of the system produced by the greater strength of the Ru-N bond than of the Ru-S bond, and the more favourable eighteen electron configuration of the product. Since tertiary phosphines are only two electron donors, the products of reactions of $Ru(S_2PR_2)_3$ with them would only be seventeen electron systems (like $Ru(S_2PR_2)_3$) and the reduction in enthalpy of the system would not be nearly as great as in the formation of $RuNO(S_2CNR_3)_3$. This is evidently not sufficient to compensate for the loss of entropy by the systems, at least at the temperatures at which the reactions were attempted, and hence no reaction occurred.

Therefore, we attempted to prepare complexes of ruthenium containing both phosphine and dithioacid ligands from reactions of halo-complexes of ruthenium which already contained phosphines with alkali metal salts of dithioacid ligands. As previously pointed out (page 44) this method had already been shown to be successful in the preparation of $Ru(S\text{-}S)_2(PPh_3)_2$ from $RuCl_2(PPh_3)_3$ and Na(S-S) (S-S = S_2CNR_2 or S_2COR)[233] and proved to be extendable to other related systems. Thus, when $RuCl_2(PPh_3)_n$ (n= 3 or 4)[287], $RuCl_3(PPh_3)_2$ $MeNO_2$ [315], $RuCl_2(PEtPh_2)_3$[291], $[Ru_2Cl_3(PMePh_2)_6]Cl$[289] or mer-$RuCl_3(PMe_2Ph)_3$[293] are gently refluxed in ethanol with an excess of NaS_2PR_2 (R = Me,Et or Ph) for ca. two hours, orange solutions are formed. Cooling the orange solutions, after filtration to remove any sodium chloride formed, causes orange crystals of composition $Ru(S_2PR_2)_2L_2$ (L = PPh_3, PPh_2Me, PMe_2Ph or $PEtPh_2$)(A) to be deposited in high yield.* Similar products are formed using acetone or methanol as solvent, except that reaction of $[Ru_2Cl_3(PMePh_2)_6]Cl$ with NaS_2PMe_2

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* Shorter reaction times with stoichiometric amounts of NaS_2PR_2 give paramagnetic species which have not been characterised, but they are probably similar to some of the Rh(III) and Os(III) complexes reported in Chapters 3 and 4.

in methanol also produces a red solid, believed to be of composition $Ru_2Cl_3(PMe_2Ph)_5$ (S_2PMe_2) which is similar to the complexes obtained by pyrolysis of $[Ru_2Cl_3(PR_3)_6][S_2PR_2]$ [317] (c.f. the pyrolysis of $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ in n-propylpropionate (see page 43))[296]. In this instance, the dimer is readily separated from $Ru(S_2PMe_2)_2$ $(PMePh_2)_2$ by the technique of dry column chromatography[318]. For $RuCl_2(PPh_3)_3$ and NaS_2PPh_2, $Ru(S_2PPh_2)_2$-$(PPh_3)_2$ is only obtained in a pure form in the presence of excess PPh_3; with no added PPh_3, analytical and molecular weight data (see experimental section) indicate that a mixture of $Ru(S_2PPh_2)_2(PPh_3)_2$ and $Ru(S_2PPh_2)_2PPh_3$ is formed (other reactions in which similar results occur include the formation of mono- and bis- carbonyl dithiocarbamato complexes of ruthenium[235] and of $RuCl_2(PPh_3)_n$ (n = 3 or 4)[287] by slight changes in the experimental conditions). However, by reaction in the presence of excess sulphur (an effective tertiary phosphine scavenger), pure $Ru(S_2PPh_2)_2PPh_3$ can be isolated.

$Ru(S_2CNMe_2)_2L_2$ (L = PPh_3, PMe_2Ph or $P(OPh)_3$) (B) are prepared in a similar fashion to (A) by reaction of $RuCl_2(PPh_3)_3$,[287] <u>mer</u>-$RuCl_3(PMe_2Ph)_3$[293] or $RuCl_2(P(OPh)_3)_4$[292] with NaS_2CNMe_2.

Compounds A and B have been fully characterised by elemental analyses (Tables 2.2) and the usual spectroscopic techniques (see later), and the monomeric formulation has been confirmed by osmometry and by an x-ray analysis of $Ru(S_2PEt_2)_2$ $(PMe_2Ph)_2$ (see Appendix 2). The compounds are non electrolytes and diamagnetic (by Evans' method)[319], and exhibit sharp ^1H n.m.r. resonances. However, exposure of solutions of A to air rapidly produces broadening of the n.m.r. signals and the growth of a weak e.s.r. signal, both of which are attributed to facile oxidation to paramagnetic ruthenium (III) species.

The rate of oxidation which can be substantially reduced by addition of excess tertiary phosphine is also dependent on the nature of L, a qualitative order being $PPh_3 > PMePh_2 > PMe_2Ph$. The solvent medium is also important, since studies indicate that increasing the percentage of $CDCl_3$ in $CDCl_3/CS_2$ mixtures increases the rate of oxidation. After several weeks, sharp resonances are again seen in the n.m.r. spectra of compounds A, but, since identical signals are obtained from aged solutions of $Os(S_2PMe_2)_2L_2$ (see chapter 4), they cannot arise from metal containing species and, since for L = PMe_2Ph, one of the signals (a doublet at $\tau 8{\cdot}03$, J_{PH} = 13 Hz) corresponds to $PhMe_2PS$, substantial decomposition of the complexes probably occurs.

In the reaction of $RuCl_2(P(OPh)_3)_4$ with excess NaS_2PR_2, the product formed depends critically upon both reaction time and solvent medium. Thus, in refluxing ethanol for one hour, reaction with excess NaS_2PMe_2 gives a sample of $Ru(S_2PMe_2)_2(P(OPh)_3)_2$. However, if refluxing is continued for a further hour, a mixture of products is obtained which proved impossible to separate by chromatographic or sublimation techniques. However, the mass spectrum of the mixture reveals the parent ion and fragmentation pattern peaks expected for $Ru(S_2PMe_2)_2(POEt(OPh)_2)_2$ together with a peak at $^m/_e$ 780 (^{102}Ru isotope) which can only arise from the species $Ru(S_2PMe_2)_2(P(OEt)_2OPh)_2$ since there is no way of obtaining a fragment of this mass number by degradation of $Ru(S_2PMe_2)_2(POEt(OPh)_2)_2$. Consistent with this interpretation, the ^1H n.m.r. spectrum of the mixture shows two sets of ethyl resonances of approximate intensity 3:1 (the ratio varied from sample to sample) attributable to the mono- and bis- ethoxy phosphite complexes respectively. The experimental carbon and hydrogen percentages for the mixture are also in good agreement with calculated data based on this ratio.

Further refluxing (24 hours) gives a yellow solution from which no solid product could be isolated but a mass spectrum of the resultant oil shows peaks attributable to $Ru(S_2PMe_2)_2(P(OEt)_3)_2$, together with a number of other tertiary phosphite compounds (see experimental section). However, if the reaction between $RuCl_2(P(OPh)_3)_4$ and excess NaS_2PMe_2 is carried out in refluxing methanol, even for comparatively short reaction times, a pure sample of $Ru(S_2PMe_2)_2(P(OMe)_3)_2$ can be isolated and phenol and trimethylphosphite can be identified in the filtrate. All these phosphite compounds are more resistant to oxidation in solution than the corresponding tertiary phosphine complexes.

Muetterties <u>et al</u>[320] have reported that triphenylphosphite, when co-ordinated to ruthenium, does not appear to undergo transesterification by alcohols, whereas such reactions readily occur with the free ligands. Therefore, at first sight, the transesterification of the tertiary phosphite groups in $Ru(S_2PMe_2)_2(P(OPh)_3)_2$ appears surprising. However, since the starting material has four phosphites per ruthenium and the product only two, then two must be released during the reaction, presumably as free tertiary phosphite. This free triphenylphosphite may then be transesterified giving, in the case where methanol is solvent, trimethylphosphite. The trimethylphosphite, being a stronger nucleophile than its triphenyl-analogue[321], (as well as less bulky), can then replace the co-ordinated $P(OPh)_3$ groups to give $Ru(S_2PMe_2)_2(P(OMe)_3)_2$. This conclusion is supported by the observation that $Ru(S_2PMe_2)_2(P(OPh)_3)_2$ may be recovered unchanged after refluxing in degassed methanol for 24 hours.* Presumably the

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* In a recent paper[322] Roundhill <u>et al</u> suggest that transesterification of tertiary phosphites occurs when the phosphites are co-ordinated to platinum. However, since in each case where transesterification occurs, there is free phosphite present in the system, a better explanation (in view of Muetterties work[320]) might be that the free phosphite is transesterified and then this replaces a bound phosphite which is, in turn, transesterified etc.

ease of formation of the $P(OMe)_3$ complex, compared with the $P(OEt)_3$ complex, is a reflection of the greater nucleophilicity of the methoxide ion compared to the ethoxide ion.

Finally, reaction of $\left\{RuCl_2(diene)\right\}_n$ with NaS_2PMe_2 in dimethyl formamide or ethanol gives $Ru(diene)(S_2PMe_2)_2$ (diene = C_7H_8 or C_8H_{12}), analogous to $Ru(C_8H_{12})(S_2CNMe_2)_2$ which is prepared by a similar method[234] (see page 32).

2. <u>Reactions of $Ru(S\text{-}S)_2L_2$ complexes</u>.

All the compounds of type (A) readily react with carbon monoxide under very mild conditions to give the monocarbonyl species $Ru(S_2PR_2)_2LCO$ (C). For L = PPh_3, $AsPh_3$; R = Me, the same compounds are also formed by prolonged interaction of <u>cis</u> - $RuCl_2(CO)_2L_2$ [287] with NaS_2PMe_2. In contrast, in agreement with earlier work[233], attempted carbonylation of the corresponding $Ru(S_2CNR_2)_2(PR'_3)_2$ compounds (PR'_3 = PMe_2Ph,PPh_3), even under pressure, gives only unchanged starting material. Furthermore, attempts to displace the remaining L group from $Ru(S_2PR_2)_2LCO$ to give $Ru(S_2PR_2)_2(CO)_2$ have also proved unsuccessful. However, the dicarbonyl complexes $Ru(S_2PR_2)_2(CO)_2$ (R = Me,Ph) have been synthesised from $Cs_2[RuCl_4(CO)_2]$[323], NaS_2PMe_2 and from $Ru_3(CO)_{12}$*, Ph_2PS_2H combinations respectively. Similarly, reaction of $Ru_3(CO)_{12}$ with tetramethylthiuramdisulphide gives the previously characterised $Ru(S_2CNMe_2)_2(CO)_2$. A small amount of this product is also formed by prolonged reaction of <u>cis</u>- $RuCl_2(CO)_2(PPh_3)_2$ with NaS_2CNMe_2. Although $Ru(S_2CNR_2)_2(CO)_2$ does not react with PR'_3, the corresponding $Ru(S_2PR_2)_2(CO)_2$ are readily converted to $Ru(S_2PR_2)_2(PR'_3)CO$. Thus, it appears that the products $Ru(S_2PR_2)_2LCO$ are thermodynamically very stable, being readily formed from either $Ru(S_2PR_2)_2L_2$ or $Ru(S_2PR_2)_2(CO)_2$ whereas with (S-S) = S_2CNR_2, no

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* We thank Dr. J.R. Jennings of I.C.I. (P. and P.) Ltd. for a sample of this compound.

evidence has been found for the mixed species. For L = PMe_2Ph, reactions of $Ru(S_2PR_2)_2(PMe_2Ph)_2$ and carbon monoxide give, in addition of $Ru(S_2PR_2)_2(PMe_2Ph)CO$, two other complexes which both analyse for $Ru(S_2PR_2)_2(PMe_2Ph)_2CO$. Compounds of this type have not been observed with other tertiary phosphines. A detailed spectroscopic analysis of these compounds, together with proposed structures and a possible general mechanism for these carbonylation reactions are presented later in this chapter.

All the $Ru(S\text{-}S)_2L_2$ compounds undergo ligand exchange reactions with other phosphorus ligands of greater basicity. Thus, for $Ru(S_2PR_2)_2L_2$ where L = PPh_3 or $PMePh_2$, reaction with $PMe_2Ph(L')$ gives $Ru(S_2PR_2)_2L'_2$; similarly, both L groups are displaced by L' when L = PPh_3, L' = $PMePh_2$ and also with $Ru(S_2CNMe_2)_2(PPh_3)_2$ and excess PMe_2Ph, $Ru(S_2CNMe_2)_2(PMe_2Ph)_2$ is exclusively formed. These results can be readily rationalised on the basis that the compounds $Ru(S\text{-}S)_2L'_2$ are both sterically <u>and</u> electronically favoured compared with the mixed ligand complexes $Ru(S\text{-}S)_2LL'$. However, when the phosphine complexes are treated with $P(OPh)_3$, steric effects become more important. Thus, $Ru(S_2PR_2)_2(PMe_2Ph)_2$ and $P(OPh)_3$ give only the mixed ligand complex $Ru(S_2PR_2)_2(PMe_2Ph)(P(OPh)_3)$ whereas with $Ru(S\text{-}S)_2(PPh_3)_2$ (S-S = S_2PMe_2, S_2CNMe_2), both $Ru(S\text{-}S)_2(PPh_3)(P(OPh)_3)$ and $Ru(S\text{-}S)_2(P(OPh)_3)_2$ can be isolated, the amount of each depending on the conditions employed. This is presumably because there is a fine balance between the large difference in basicity of PPh_3 and $P(OPh)_3$ (which will favour the bis-phosphite complex) and the greater steric crowding in the bis-phosphite complex compared with the mixed phosphine-phosphite species.

On account of the lability of ruthenium-olefin bonds, the complexes $Ru(S_2PMe_2)_2$diene (diene = C_7H_8 or C_8H_{12}) have proved very useful as starting materials for exchange reactions and react with CO or PPh_3 to give $Ru(S_2PMe_2)_2L_2$ (L = CO or PPh_3). The diene complexes also react with ditertiary phosphines to give $Ru(S_2PMe_2)_2$ (P-P) (P-P = $Ph_2PCH_2CH_2PPh_2$ (diphos) or $Ph_2PCH_2PPh_2$) which, because of the insolubility of <u>trans</u> - $RuCl_2(P\text{-}P)_2$ [289] are only obtained in low yield from the reactions of these compounds with NaS_2PMe_2. With o-phenylenebisdimethyl-arsine (diars), $Ru(S_2PMe_2)_2$ (C_7H_8) gives an off white compound which analyses for $Ru(S_2PMe_2)_2(diars)_2$ after refluxing in ethanol, but recrystallisation of this compound from toluene either in the presence or absence of elemental sulphur gives orange $Ru(S_2PMe_2)_2(diars)$. Unfortunately, $Ru(S_2PMe_2)_2(diene)$ do not react with triphenylarsine and since attempts to prepare $Ru(S_2PPh_2)_2(AsPh_3)_2$ from $RuCl_3(AsPh_3)_2$ MeOH[287] or $Me_4N[RuBr_4(AsPh_3)_2]2Me_2CO$[316] and NaS_2PPh_2 only gave rise to the formation of $Ru(S_2PPh_2)_3$, we have not succeeded in preparing any complexes of ruthenium which contain both dithioacid ligands and triphenylarsine, apart from <u>cis</u>-$Ru(S_2PMe_2)_2(AsPh)_3CO$ (see above).

3. <u>Spectroscopic Properties of Dithioacid Complexes.</u>

(a) <u>Infrared Spectra</u>:- The infra-red (ir) spectra of all the complexes reported are rather complicated, showing absorptions due to the tertiary phosphine or phosphite groups, as well as the phosphinodithioate ligands. However, recent work in this laboratory[15], indicates that for platinum and palladium (II) diphenylphosphinodithioate complexes, there appears to be an empirical i.r. method of distinguishing between bidentate, ionic and unidentate co-ordination of the S_2PPh_2 group. Thus, bidentate co-ordination is characterised by two bands at 603, 570 cm^{-1}; ionic, 650, 560 cm^{-1} and unidentate, 645, 540 cm^{-1}. Similarly, platinum and palladium (II) dimethylphosphinodithioates have characteristic bands at 570-585 cm^{-1} (bidentate); 610 cm^{-1} (ionic) and 600 cm^{-1} (unidentate). In this instance, the lower energy band (ca 500 cm^{-1}) is masked by strong ligand vibrations[16].

An examination of Table 2.3 reveals that all the $Ru(S_2PR_2)_2L_2$, $Ru(S_2PR_2)_2LL'$ and $Ru(S_2PR_2)_2(L-L)$ complexes contain only i.r. absorptions characteristic of bidentate S_2PR_2 co-ordination. Similarly, in spite of complications arising from the presence of carbonyl bending modes (δ_{CO}) in the region 600-500 cm^{-1}, all the compounds of type $Ru(S_2PR_2)_2LCO$ and $Ru(S_2PR_2)_2(CO)_2$ show only 'bidentate' S_2PR_2 co-ordination. The latter also have two ν_{CO} bands indicating a cis-configuration. For the compounds $Ru(S_2PR_2)_2(PMe_2Ph)_2CO$, in addition to the 'bidentate' bands, there are absorptions at 645, 540 cm^{-1} (S_2PPh_2) and ca 600 cm^{-1} (S_2PMe_2), indicative of unidentate co-ordination, although the presence of a carbonyl bending vibration in this region is a complicating factor. In the i.r. spectrum of $Ru(S_2PMe_2)_2(diars)_2$, the only band in the 700-500 cm^{-1} region is a strong peak at 600 cm^{-1} with a shoulder at 595 cm^{-1}, which suggests that both S_2PMe_2 groups are unidentate. This observation, which is supported by n.m.r. data (see later) together with the rest of the data in Table 2.3 clearly indicate the generality of these empirical methods for distinguishing between different types of S_2PR_2 co-ordination in platinum metal complexes.

(b) Mass Spectra:- The complexes of formula $Ru(S_2PR_2)_2(PR'_3)_2$ are all of high melting point and decompose at low enough temperatures to make it impossible to obtain mass spectra for these complexes. However, the phosphine/phosphite, bisphosphite, diphos and diene compounds are more volatile and excellent mass spectra may be recorded at ca 440K. These consist of well-defined parent ion peaks together with fragmentation patterns e.g. the spectrum of $Ru(S_2PMe_2)_2(P(OMe)_3)_2$ (Table 2.4) which shows successive loss of methyl groups and oxygen atoms from the phosphite groups.

The carbonyl-containing compounds, $Ru(S_2PR_2)_2LCO$ and $Ru(S_2PR_2)_2(PMe_2Ph)_2CO$, are also more volatile than their bis-phosphine parent compounds and thus give reasonable mass spectra. For L = tertiary phosphine, parent ion peaks together with fragmentation patterns corresponding to loss of carbonyl, loss of tertiary phosphine and loss of both carbonyl and phosphine groups are observed. There are also metastable ions corresponding to the loss of carbonyl groups and in some cases, doubly positively charged species $[Ru(S_2PR_2)_2L]^{2+}$ are observed. For the $Ru(S_2PR_2)_2(PMe_2Ph)_2CO$ compounds, exactly the same parent ion and fragmentation pattern is observed as for $Ru(S_2PR_2)_2(PMe_2Ph)CO$ due to ready loss of a PMe_2Ph group. The phosphite complexes containing a carbonyl group give more complicated mass spectra e.g. the spectrum of $Ru(S_2PMe_2)_2(P(OPh)_3)CO$ (Table 2.5) which shows successive loss of carbonyl, phenoxy and S_2PMe_2 groups.

(c) <u>^1H n.m.r. spectra</u>.

i) <u>Complexes of formula $Ru(S_2PR_2)_2L_2$</u> :- For L = $PMePh_2$ or PMe_2Ph, the room temperature resonance arising from the methyl groups on the phosphines (a $H_nPP'H'_n$ second order type spectrum n = 3 or 6[324]) consists of a sharp doublet with a broad hump situated between the doublet* (see Figure 2.1b, page 57). Comparison with other similar ruthenium tertiary phosphine complexes is of interest. Thus, for trans- $RuCl_2CO(PMe_2Ph)_3$, the ^1H n.m.r. spectrum consists

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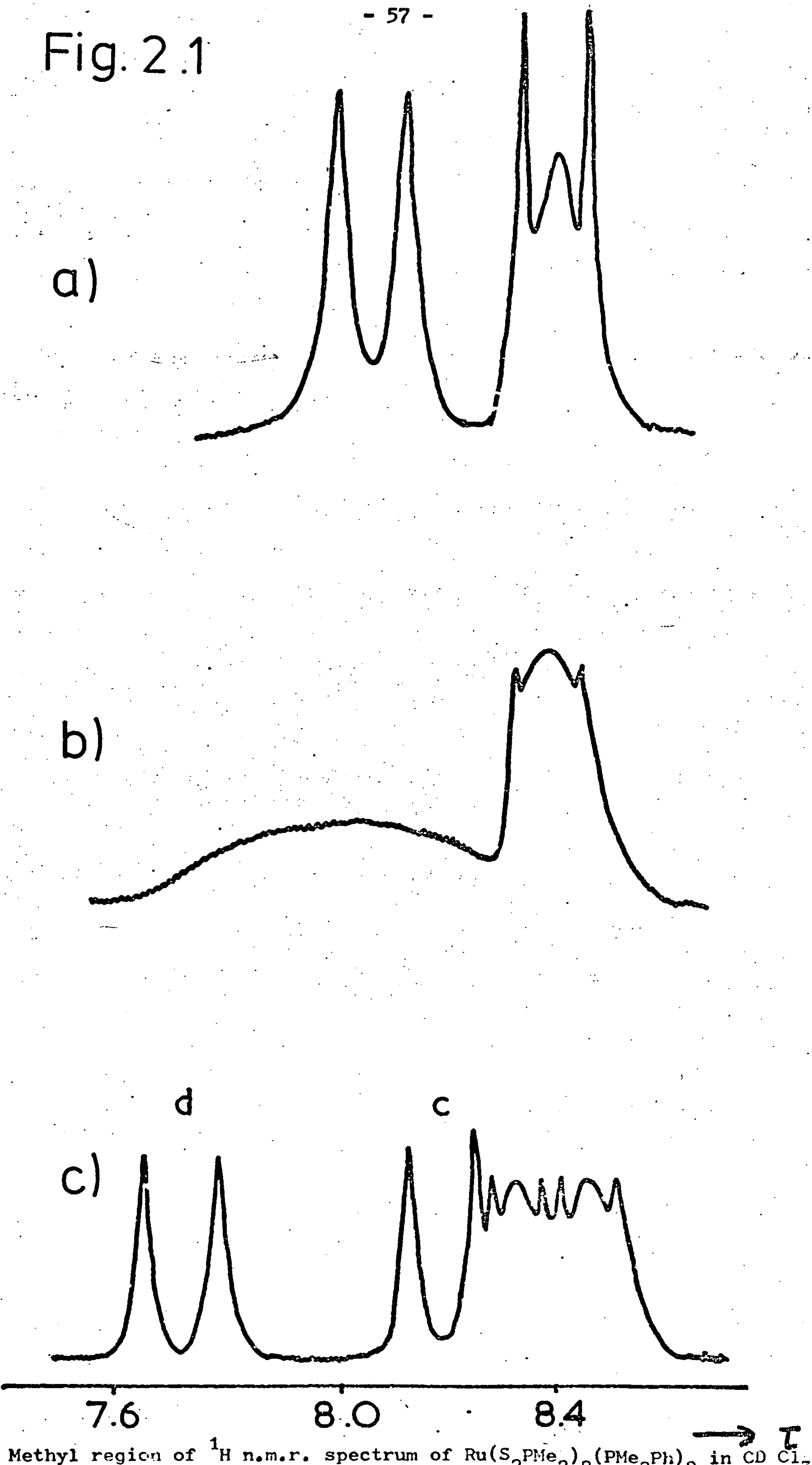
* Referred to hereafter as a 'pseudo-triplet' pattern.

of a 'virtually' coupled 1:2:1 triplet from the trans phosphines and a doublet arising from the cis-phosphine, due to the fact that in this compound, $J_{PP'}$(trans) is very large and $J_{PP'}$(cis) is effectively zero[325]. However, in some complexes, where the cis-phosphines are in equivalent chemical environments e.g. $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ and cis- $RuCl_2(PMe_2Ph)_4$ [291], the methyl ^1H n.m.r. signal is a pseudo-triplet, very similar in shape to those observed here for $Ru(S_2PR_2)_2L_2$ (L = PMe_2Ph,$PMePh_2$). This however is not true in every case, e.g. the cis-phosphines in cis- $RuH_2(PMe_2Ph)_4$ (which are also in equivalent chemical environments) give rise to a single sharp doublet[308] (i.e. $J_{PP'}$ is effectively zero). Thus, the pseudo-triplet pattern could arise either from cis-phosphines with a relatively large $J_{PP'}$ or trans phosphines with a relatively low $J_{PP'}$[324] and hence no definitive conclusion about stereochemistry can be drawn from these peak contours at room temperature.

However, on cooling the PMe_2Ph complex, the methyl resonance signal broadens and at 250K, consists of two pseudo-triplets separated by ca 13Hz (Figure 2.1c, page 57); raising the temperature reverses the process. The best explanation for these observations is that the complex has a cis-configuration and at lower temperatures, rotation about the ruthenium-phosphorus bond is slow and the inequivalence of the chemical environments of the two methyl groups (a and b) is seen in the n.m.r. spectrum (Figure 2.2 page 58). This non-equivalence has also been noted for the trans phosphines of cis- $RuCl_2CO(PMe_2Ph)_3$ [325]. If A (L = PMe_2Ph) had a trans-configuration, then the two methyl groups on the one PMe_2Ph ligand would be in identical chemical environments, giving rise to one resonance, irrespective of the rate of rotation about the ruthenium-phosphorus bond.

Fig. 2.1



Methyl region of ^{1}H n.m.r. spectrum of $Ru(S_2PMe_2)_2(PMe_2Ph)_2$ in CD Cl_3 at different temperatures.

a) 338K b) 301K c) 253K

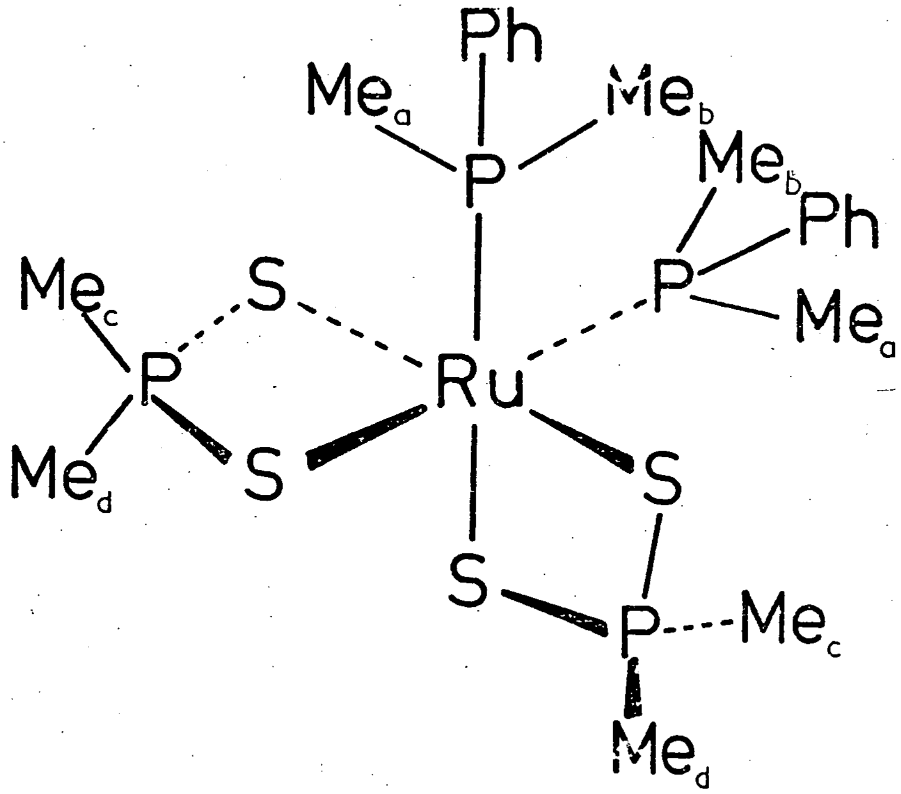


Fig. 2.2

Diagrammatic representation of cis - configuration for $Ru(S_2PMe_2)_2(PMe_2Ph)_2$.

The process by which the phosphine methyl groups of cis-$Ru(S_2PR_2)_2(PMe_2Ph)_2$ exchange at higher temperatures cannot, however, be simply an increase in the rate of rotation about the Ru-P bonds since this does not lead to coalescence behaviour, but rather to a gradual decrease in the separation of the two phosphine methyl resonances until they coincide (see for example:- cis-$Ru(S_2CNMe_2)_2(PMe_2Ph)_2$ (page 73) and cis-$Ru(S_2PMe_2)_2(PMe_2Ph)CO$ (page 66)). Hence, the dynamic process which equilibrates the environments of the phosphine methyl groups is probably the same as that which equilibrates the environments of the S_2PMe_2 methyl groups at higher temperatures, namely an interconversion of the two optical enantiomorphs of cis - $Ru(S_2PMe_2)_2(PMe_2Ph)_2$ - (see below). For L = $PMePh_2$, the similarity of the shape of the pseudo-triplet to that for L = PMe_2Ph, and for L = $P(OMe)_3$, the close similarity of the observed second-order spectrum with that obtained for cis- Pt $X_2(P(OMe)_3)_2$ [326] is further evidence for cis-stereochemistry in these compounds.

However, full confirmation of cis stereochemistry for all these tertiary phosphine and phosphite complexes comes from an examination of the low temperature ^1H n.m.r. spectra of the methyl groups of the S_2PMe_2 ligands. For cis- $Ru(S_2PMe_2)_2L_2$, two types of inequivalent dithioacid methyl groups (c and d in Figure 2.2. page 58) are present, which should give two signals, each split into a doublet by the ^{31}P nuclei, whereas for trans stereochemistry, only one doublet should be observed. Experimentally, the low temperature, ^1H n.m.r. spectra of all the bisphosphine and bis-phosphite compounds consist of two doublets, indicative of cis stereochemistry, at least at low temperature.* (see Figure 2.1c, page 57 and Table 2.6).

However, on warming to room temperature or above, these two doublets first coalesce and then sharpen to a single doublet (with a very similar J_{PH}) (Figure 2.1a, page 57 and Table 2.6). This process, which occurs at different rates for different L, is completely reversible. At first sight, these observations are consistent with either a reversible cis-trans isomerism or a rapid interconversion of the two possible optical enantiomers of the cis compounds at elevated temperatures. There are several reasons why the latter explanation is preferred. First the shape of the resonance due to the methyl groups on the phosphines remains almost unchanged throughout the temperature changes whereas cis-trans isomerism should produce large changes in $J_{PP'}$ and hence in the shape of this resonance[324]. In general, it has been found that the more stable isomers of ruthenium complexes have a cis-configuration and that quite often on heating, the trans isomer undergoes an irreversible conversion to the cis isomer[287,328]. This is the reverse of the behaviour found in these complexes. Furthermore, the related $Ru(S_2PR_2)_2(CO)_2$ complexes, which have a cis configuration in both solid and solution state (two ν_{CO}), show no evidence for formation of the trans isomer at higher temperatures (no change in i.r. spectra).

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* X-ray analysis has confirmed the cis-configuration for $Ru(S_2PEt_2)_2(PMe_2Ph)_2$ (see Appendix 2), and the related compounds $Ru(HCS_2)_2(PPh_3)_2$ [310(b)] and $Ru(pyS)_2(PPh_3)_2$ (pyS = pyridine - 2 - thiolato) also possess cis stereochemistry in the solid state.

Finally, the high temperature doublet is approximately halfway between the positions of the doublets at low temperature, irrespective of L (Table 2.6). This phenomenon is characteristic of a process such as rapid inversion which averages the two chemical environments of the methyl groups c and d but not of an interconversion of geometrical isomers where it is extremely unlikely that the chemical shift of the methyl groups of the trans isomer will always coincide with the mean of those of the cis isomer.

Therefore, all the evidence suggests that the variation in ^1H n.m.r. spectra of these complexes cis-$Ru(S_2PR_2)_2L_2$ with temperature is due to the facile interconversion of optical isomers and the mechanism of this process is discussed in detail later in this chapter.

The chemical shifts of the methyl resonances of the S_2PMe_2 ligands are also of interest in that the position of the lower field doublet remains almost unaltered by changing L whereas that of the higher field doublet is very sensitive to changes in L, varying from τ8.08 (L = $P(OMe)_3$) to τ8.94 (L = PPh_3) Table 2.6). A possible explanation of this is that the lower field doublet arises from the methyl groups anti to the phosphorus ligands (d in Figure 2.2, page 58) and the higher field doublet from the methyl groups (c) syn to the phosphorus ligands. Then, the syn methyl groups are more influenced by the ring currents of the phenyl rings on the phosphorus ligand, causing them to be more shielded than the anti methyl groups which accounts for their higher field position. Furthermore, increasing the number of phenyl groups on the tertiary phosphine leads to increased shielding of the syn methyls, making them resonant at even higher fields. Similar effects have been observed in the compounds $[M(S\text{-}S)(PR^1_3)_2]\,BPh_4$ (M = Pt or Pd; S-S = S_2CNR_2 or S_2COR) where the R and R^1 resonances are shifted ca.0.2-0.4τ upfield with respect to their positions in the corresponding PF_6^- and Cl^- salts[16,19], as well as in recent studies on the interaction of benzene with arsenic, antimony and bismuth dithiocarbamates[329]. For L = $P(OPh)_3$, the higher field doublet resonates at τ8.35. This is lower than that in the PPh_3 complex, presumably because the phenyl groups are further away from the syn methyl groups and hence produce less efficient shielding.

(ii) Complexes of formula $Ru(S_2PMe_2)_2(L\text{-}L)$.

In all of these tris-chelate complexes (L-L = C_7H_8, C_8H_{12}, $Ph_2PCH_2PPh_2$, diphos or diars), the stereochemistry of the molecules is confined by steric factors to be cis and, although for L-L = C_8H_{12}, the resonances from the diene protons are difficult to see and for L-L = diphos, only the phenyl resonances are clearly seen on account of the complicated nature of the ^1H n.m.r. signals arising from a $PH_2H'_2P'$ spin system, the resonances arising from (L-L) in the other complexes are easily distinguished and are all consistent with cis stereochemistry (Table 2.6). Thus, for L-L = C_7H_8, signals arising from the three distinct sets of protons (Figure 2.3, page 63) are seen and are assigned as arising from H_2,H_3,H_5 and H_6 at τ6.15, H_1 and H_4 at τ5.9 and H_7 and H_8 at τ8.7; for L-L = diars, a poorly resolved $AA'BB'$[330] type spectrum arising from the phenylprotons is observed, centred at τ2.40, whilst the methyl groups of the diarsine give rise to two sharp singlets at τ8.24 and τ8.60; and for L-L = $Ph_2PCH_2PPh_2$, apart from the phenyl resonances, a sharp triplet at τ5.03 is seen which arises from the

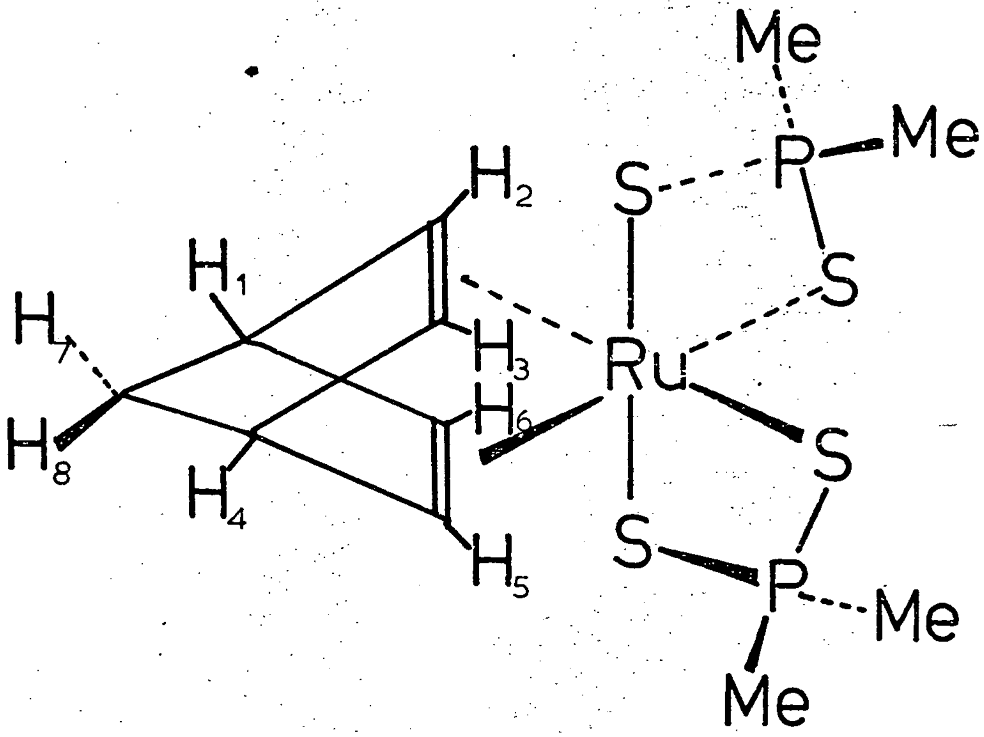


Fig. 2.3

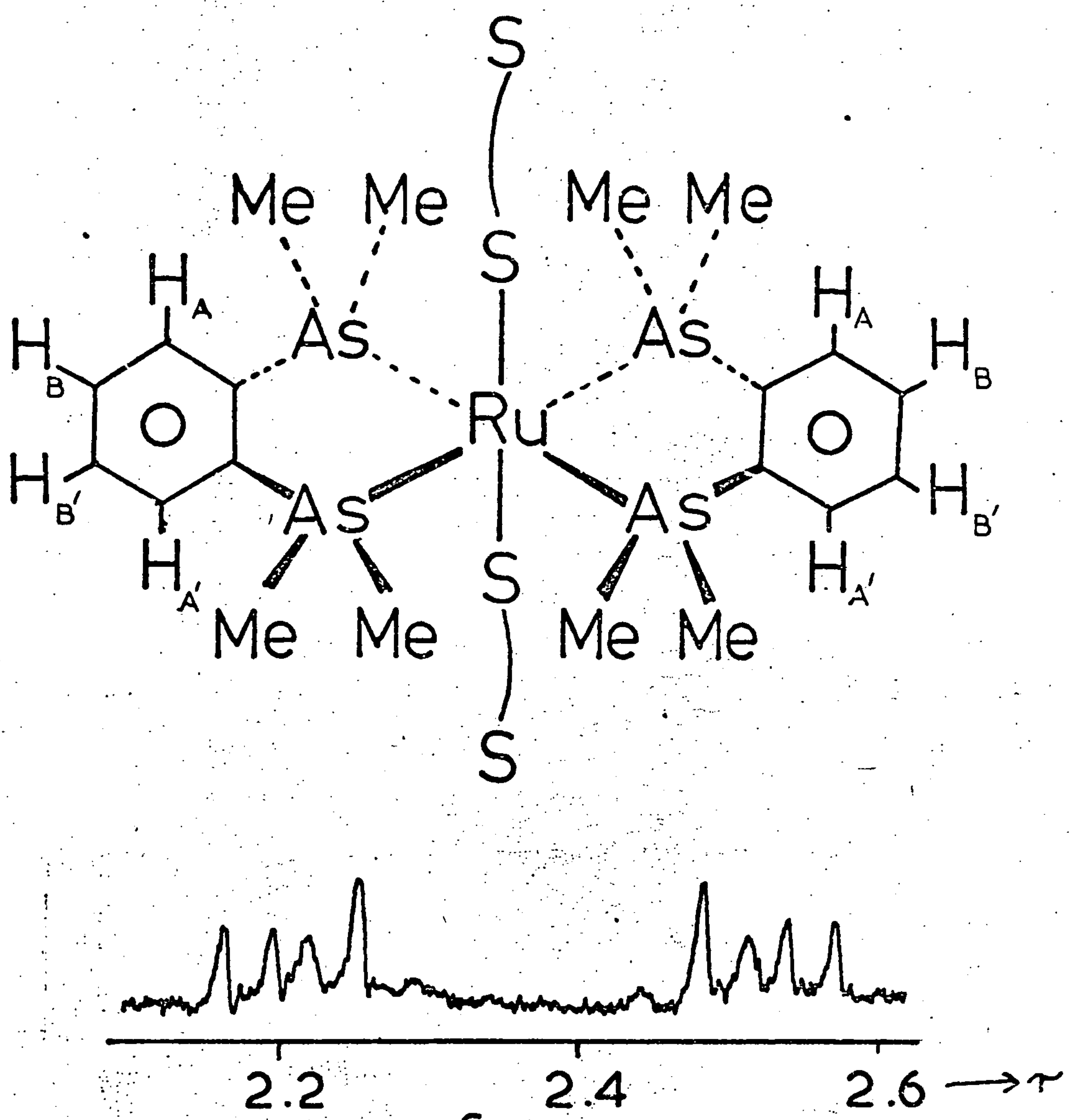
Diagrammatic representation of $Ru(S_2PMe_2)_2\ (C_7H_8)$.

splitting of the methylene proton resonance by the two chemically equivalent ^{31}P nuclei. As for $Ru(S_2PMe_2)_2L_2$, the methyl groups on the S_2PMe_2 ligands give rise to two doublets at low temperatures; however, in contrast to the behaviour of $Ru(S_2PMe_2)_2L_2$, the resonances remain sharp on warming up to 373K in C_6H_5Cl. Above this temperature, for L-L $\neq$ diene, the signals begin to broaden but since the boiling point of C_6H_5Cl is 403K, the condition in which fast exchange of the environments of the S_2PMe_2 methyl groups is occuring, is never reached (Table 2.6).

Finally, $Ru(S_2PMe_2)_2(diars)_2$ gives rise to a well resolved AA'BB'[330] type set of resonances in the phenyl region (Figure 2.4, page65) as well as a sharp singlet from the diars methyl groups (τ8.02) and a sharp doublet from the methyl groups of the S_2PMe_2 ligands (τ8.46). This spectrum is invariant from 233K to 333K and this is best explained if the two S_2PMe_2 groups are both unidentate and mutually <u>trans</u>, since if they were <u>cis</u>, two resonances would be expected from the methyl groups of the diarsine ligands.

(iii) Complexes of formula $Ru(S_2PR_2)_2LCO$ and $Ru(S_2PR_2)LL'$.

In all the $Ru(S_2PR_2)LCO$ complexes, the methyl group(s) of the phosphorus ligand produce a single doublet at high temperature in the ^1H n.m.r. spectrum, an observation consistent with either cis or trans stereochemistry. However, in the low temperature spectrum of $Ru(S_2PR_2)_2$ $(PMe_2Ph)CO$, two doublets from the phosphine methyl groups are seen which, on warming gradually move together without broadening until they are coincident.



$\delta\nu = 30.1$ Hz

$J_{AA'} = 0$

$J_{BB'} = 6.5$ Hz

$J_{AB} = 7.6$ Hz

$J_{AB'} = 1.4$ Hz

Fig. 2.4

Diagrammatic representation and low field (AA′BB′) type ^1H n.m.r. spectrum of <u>trans</u> - $Ru(S_2PMe_2)_2$ (diars)$_2$.

The only type of mechanism that could give rise to this behaviour is one in which the chemical environments of the two methyl groups on one phosphine become more equivalent at higher temperatures, without there being any exchange of methyl groups between the two environments (since no coalescence phenomenon is observed).

One such mechanism could arise from the fact that at low temperatures (when rotation about the metal-phosphorus bond is slow) there will be one* or more preferred, discrete orientations of the phosphine moiety with respect to the rest of the molecule. These preferred orientations will be determined by a combination of steric and electronic factors. Since there is no symmetry element of the molecule that incorporates the metal-phosphorus bond, then, under these conditions, the environments of the two methyl groups on one phosphine will be different and two different signals will therefore be seen in the ^1H n.m.r. spectrum.

Now, when the orientation of the phosphine ligand differs from that preferred, each methyl group will be in a different chemical environment from that in the preferred configuration. Thus, as the temperature is raised and the rate of rotation about the metal-phosphorus bond is increased, each methyl group will spend less time in its preferred environment and more in other environments.

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* In this instance, there is probably only one preferred rotamer since further cooling does not give rise to additional signals which is what would be expected if, when no rotation is possible, the phosphine group could take up more than one preferred configuration.

Its chemical shift will then be an average of the chemical shifts of each environment, weighted according to the amount of time spent in each environment. When, at higher temperatures, the phosphine group is rotating freely, each methyl group will spend an equal amount of time in all environments, hence, the average environment of each is the same and a single resonance is expected.

It is important to note that exchange of the environments of the methyl groups does not occur in this process since, although at different times, each may occupy the same position relative to the non-phosphine part of the molecule, their environment with respect to the orientation of the other methyl group and the phenyl group attached to the phosphorus atom will always be different.

For the compounds $Ru(S_2PR_2)_2LL'$, the methyl groups on the phosphine exhibit a single sharp doublet which is temperature independent except for R = Ph; L = PMe_2Ph; L' = $P(OPh)_3$ (Table 2.6). However, as for the $Ru(S_2PMe_2)_2L_2$ compounds, examination of the S_2PMe_2 methyl resonances provides an unequivocal demonstration of cis stereochemistry. If the complexes $Ru(S_2PMe_2)_2LL'$ or $Ru(S_2PMe_2)_2LCO$ had a trans configuration, the methyl groups of the S_2PMe_2 ligands would occupy two different environments, either syn to the ligand L or syn to L' (or CO), which would give rise to two signals, each split into a doublet by coupling with a ^{31}P nucleus. For a cis configuration, all four methyl groups will be in different chemical environments (Figure 2.5, page 68) and four resonances (each a doublet) should appear in the ^1H n.m.r. spectrum.

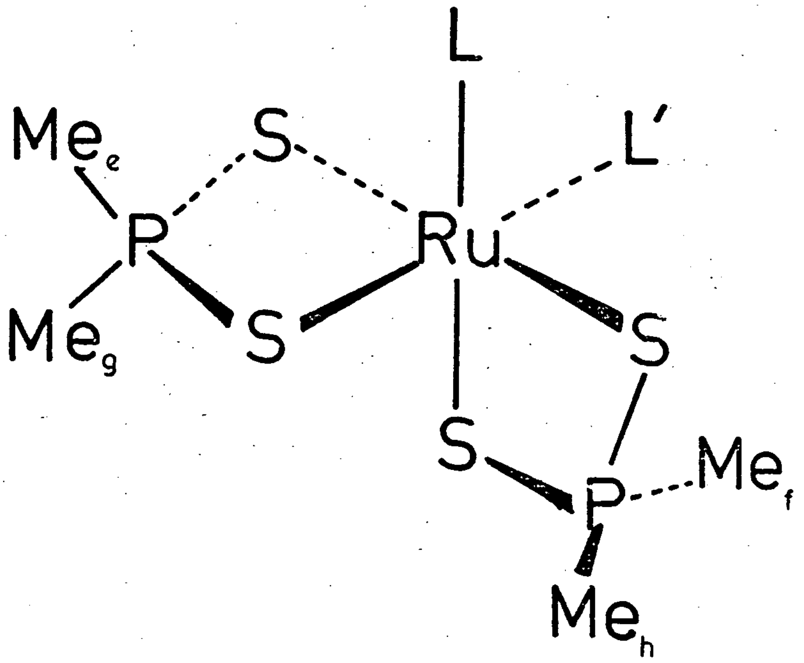

Fig.2.5

Diagrammatic representation of cis-configuration for $Ru(S_2PMe_2)_2LL'$

a) $L = PMe_2Ph$, $L' = P(OPh)_3$; b) $L = P(OMe)_3$, $L' = CO$; c) $L = PPH_3$, $L' = P(OPh)_3$

At low temperature, the ^1H n.m.r. spectra of all these complexes (with the exception of $Ru(S_2PMe_2)_2(PMe_2Ph)(P(OPh)_3)$ and $Ru(S_2PMe_2)_2(P(OMe)_3)CO$) consist of four doublets arising from the S_2PMe_2 groups. For $Ru(S_2PMe_2)_2(PMe_2Ph)(P(OPh)_3)$ the two higher field doublets are superimposed (Table 2.5). These two resonances presumably arise from the methyl groups syn to the phosphine and syn to the phosphite ligands (e and f respectively - Figure 2.5a, page 68). In this instance, although the PMe_2Ph group has fewer phenyl rings than $P(OPh)_3$, those on the phosphite are further removed from the methyl group f by the presence of the oxygen atoms, thus producing similar shielding effects and hence identical chemical shifts for e and f. This conclusion is supported, in part, by the observation that the chemical shifts of the methyl groups (c) in the bis - PMe_2Ph and bis - $P(OPh)_3$ complexes are fairly close, being τ8.14 and 8.35 respectively.

For $Ru(S_2PMe_2)_2(P(OMe)_3)CO$, the two lower field doublets are superimposed (i.e. g and h in Figure 2.5b, page68). This is not unexpected since the chemical shifts of the low field doublets in the bis - $P(OMe)_3$ and bis - carbonyl compounds occur at τ8.89 and 7.86 respectively (Table 2.5). In support of this interpretation, heteronuclear phosphorus-hydrogen spin decoupling experiments confirm that two methyl groups attached to different phosphorus atoms are accidentally superimposed.

The methyl resonances of the dithio ligands of the cis - $Ru(S_2PMe_2)_2LCO$ and cis - $Ru(S_2PMe_2)_2(CO)_2$ complexes are temperature invariant up to ca 330K (although measurements on cis - $Ru(S_2PMe_2)_2(PPh_3)(CO)$ at higher temperatures in chlorobenzene indicate similar behaviour to that described below for $Ru(S_2PMe_2)_2(PPh_3)(P(OPh)_3)$). However, those of the $Ru(S_2PMe_2)_2LL'$

compounds show marked changes at lower temperatures. For example, on warming $Ru(S_2PMe_2)_2(PPh_3)(P(OPh)_3)$, the four methyl doublets present at low temperature (Figure 2.6a, page 71) begin to broaden, the inner two coalescing at ca 280K (Figure 2.6b page 71) and the outer two continuing to broaden until at 320K, the spectrum consists of a slightly broadened doublet superimposed on a broad signal which represents the coalesced peak of the outer doublets (Figure 2.6c, page 71). At even higher temperatures (in chlorobenzene), the spectrum consists of two doublets situated halfway between the original inner and outer doublet positions respectively (Figure 2.6d, page 71) (Table 2.5). This behaviour is attributed to the facile interconversion of optical isomers at higher temperatures, the different coalescence temperatures for the two pairs of doublets being due to their different separations.

At this juncture, it is of interest to consider which resonances in the low temperature spectrum of this compound correspond to which methyl groups of the complex because such information will be important when the detailed mechanism of the inversion process is considered. According to the theory propounded earlier in which the ring currents of the phenyl rings on L (or L$'$) shield the methyl groups nearest to them, the methyl resonances of $Ru(S_2PMe_2)_2(PPh_3)(P(OPh)_3)$ are assigned as h, g, f and e respectively (Figure 2.5c, page 68) in ascending order of chemical shift (Figure 2.6a page 71). This is based on the fact that methyl groups e and g are closer to the PPh_3 group (which has the greater shielding effect) than are f and h. These conclusions are supported by the fact that irradiating the phosphorus spectrum at 40481983 Hz collapses the doublets labelled e and g whereas irradiation at 40482100 Hz decouples f and h.

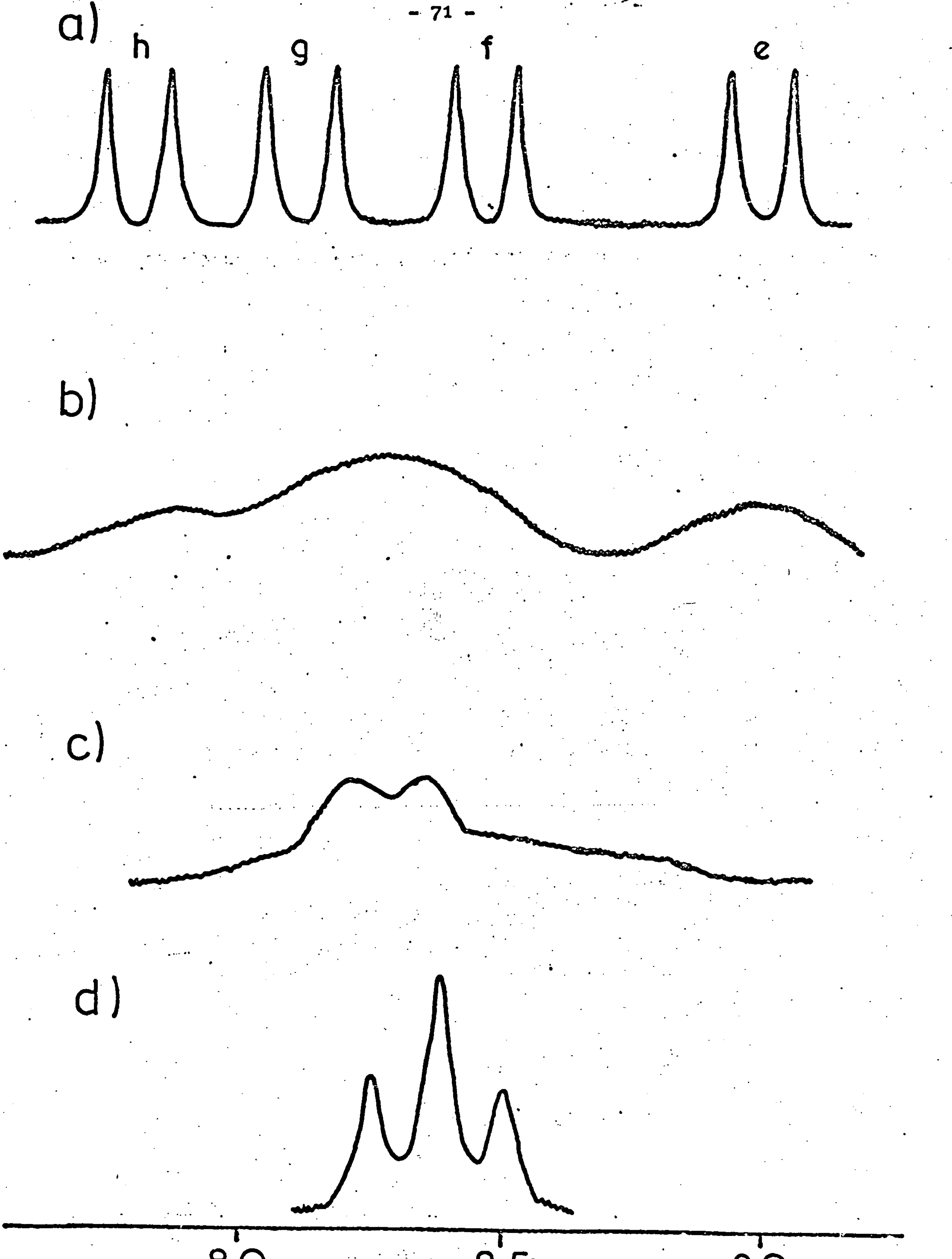

Fig. 2.6

Methyl region of ^1H n.m.r. spectrum of $Ru(S_2PMe_2)_2(PPh_3)(P(OPh)_3)$ at different temperatures.

(a) 233K in CH_2Cl_2; (b) 283K in CH_2Cl_2; (c) 310K in CH_2Cl_2; (d) 363K in C_6H_5Cl.

This confirms that the methyl groups giving rise to resonances e and g are attached to the same phosphorus atom whereas those giving rise to resonances f and h are attached to the other phosphorus atom. Thus at higher temperature, the chemical environments of groups h, e and of g, f are interchanged but there is <u>no</u> exchange between any of the other environments.* A possible interpretation of these observations is presented later in this chapter.

(iv) <u>Complexes of Formula $Ru(S_2CNMe_2)_2L_2$</u> .

It was reported earlier[233] that the ^1H n.m.r. spectrum of $Ru(S_2CNMe_2)_2(PPh_3)_2\ Me_2CO$ shows S_2CNMe_2 methyl resonances at τ 7.18 and 7.30 (with an intensity ratio of 1:2). The authors concluded that the structure was <u>trans</u>, attributing the methyl group splitting to different orientations of the methyl groups, which they suggested is probably caused by steric effects emanating from the bulky PPh_3 groups. However, on repeating this experiment, (in both cold and refluxing acetone), a crystalline yellow solid, analysing for $Ru(S_2CNMe_2)_2(PPh_3)_2\ Me_2CO$ was formed, whose n.m.r. spectrum contains two methyl resonances of the <u>same</u> intensity at τ 7.06 and 7.25; there is also a peak at τ 7.86 (acetone). This spectrum is consistent with a <u>cis</u> - configuration. Similarly, for $Ru(S_2CNMe_2)_2(PMe_2Ph)_2$, prepared from <u>mer</u> - $RuCl_3(PMe_2Ph)_3$, the

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* Homonuclear double resonance experiments at low temperature, in which irradiation at the resonant frequency of one of the lines of doublet h causes partial collapse of the corresponding line in doublet e but no collapse of doublets f and g, confirm that exchange is only occurring between methyl groups e, h and f, g.[331]

low temperature ^1H n.m.r. spectrum consists of two pseudo-triplets (PMe_2Ph groups) and two singlets (S_2CNMe_2 groups) which is indicative of a cis - configuration. On warming, the two pseudo triplets move together without broadening until at 263K they are coincident whilst the methyl doublet coalesces to a singlet at ca 300K. A similar behaviour is observed at 318K for the bis - PPh_3 complex (Table 2.6). For these compounds, the coincidence of the pseudo-triplets at higher temperatures is again attributed to the free rotation around the Ru-P bonds. However, the process equilibrating the methyl groups at higher temperatures is probably due to facile $C \cdots N$ bond rotation rather than inversion of optical isomers. This conclusion is based on the results of a kinetic line shape analysis on the compound $Ru(S_2CNMe_2)_2(PPh_3)(P(OPh)_3)$ which reveals different rates of exchange for the two sets of methyl groups. This is discussed in more detail later in this chapter.

Finally, the reaction of cis - $Ru(S_2CNMe_2)_2(PPh_3)_2$ with excess PMe_2Ph in ethanol gives two products which both analyse for $Ru(S_2CNMe_2)_2(PMe_2Ph)_2$. The ^1H n.m.r. spectrum of the more soluble species (71% yield) is identical to that obtained from mer - $RuCl_3(PMe_2Ph)_3$ and NaS_2CNMe_2 (i.e. the cis isomer). However, the ^1H n.m.r. spectrum of the minor product (21%), which is temperature invariant up to 315K, has a single, sharp peak at τ7.20 (S_2CNMe_2 groups) and a broader peak of the same intensity at τ8.27 (PMe_2Ph groups), indicative of a trans configuration, with $J_{PH} \simeq -J_{PH'}$ and a large value of $J_{PP'}$. On further heating, this compound rearranges irreversibly to the cis isomer. Therefore, in this instance, there is evidence for the irreversible trans - cis isomerism found elsewhere[287,328], and on this evidence, it is also possible to interpret the ^1H n.m.r. spectrum of

$Ru(S_2CNMe_2)_2(PPh_3)_2$ observed earlier[233] as a 50/50 cis/trans mixture of isomers with the trans methyl resonance accidentally superimposed on one of the cis methyl resonances.

4. Mechanism of Inversion of Optical Isomers of $Ru(S_2PMe_2)_2L_2$.

A great deal of interest has been shown in recent years in the mechanisms of interconversions of optical isomers of metal complexes and a comprehensive review of the publications in this field has recently appeared[332]. Most of the results which have been presented pertain to tris-chelate complexes although complexes of general formula cis-M(chelate)$_2$X$_2$ have also been studied[332]. In ruthenium chemistry, the only stereochemically labile complexes for which optical inversions have been reported are $Ru(S_2CNMeBz)_3$[208] (see page 29) and $RuH_2(L)_4$[311] (page 45).

Apart from the tunnelling of hydride ions in RuH_2L_4, two main first-steps have been postulated for the inversion of optical isomers. First, an extension of the normal vibrations of a molecule can lead to a twist of one half of the molecule with respect to the other half about an imaginary C_3 axis, as has been noted for $M(S_2CNR_2)_3$(M = Fe,Mn or CO) (see chapter 1); or second, rupture of a metal - ligand bond to give rise to a square-pyramidal or trigonal-bipyramidal transition state may occur, followed by some form of rearrangement of the transition state, and recombination to give the optical isomer, as in Al(acac)(hfac)$_2$ (acac = acetylacetonate, hfac = hexafluoroacetyl-acetonate[333]).

In Table 2.7, the activation parameters for the inversion of the optical isomers of $Ru(S_2PMe_2)_2L_2$, as calculated by full line-shape analyses, are given and a detailed example of how these parameters are obtained from variable temperature ^1H n.m.r. and computer simulated spectra is included in Appendix 1. The results are presented graphically in Figure 2.7 (page 76). For cis - $Ru(S_2PMe_2)_2(PPh_3)(P(OPh)_3)$, where four methyl groups are present at low temperature, inversion rates and activation parameters were determined by separate line-shape analyses on the exchange of the inner methyl doublets (g and f) and the outer doublets e and h (Figure 2.6, page 71). The close similarity of the calculated values for these rates and activation parameters (see Table 2.7) indicates that the same process is responsible for the interchange of the chemical environments of these two sets of methyl protons. For cis - $Ru(S_2PMe_2)_2(PPh_3)CO$, the activation parameters given in the Table were calculated by using rate data obtained from the exchange of both the inner and outer doublets respectively, which again suggests that a common kinetic process is in operation.

From Table 2.7, several other points of interest emerge which must be considered when contemplating possible mechanisms of inversion. For example, the rate and associated activation parameters are dependent upon the solvent medium in which the measurements are made. For cis - $Ru(S_2PMe_2)_2(PMe_2Ph)_2$, measurements in C_6H_6, C_6H_5Cl and $CDCl_3$ respectively (Figure 2.8, page 77) show an increasing inversion rate accompanied by a substantial decrease in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, particularly on changing from C_6H_6 to C_6H_5Cl (or $CDCl_3$). In addition, measuring the rate of inversion (by line shape analysis) at 301K for $CS_2/CDCl_3$ solutions of cis - $Ru(S_2PMe_2)_2(PMe_2Ph)_2$ in which the $CDCl_3$ component is increased from 0 to ca. 40% reveals a first order dependence on $CDCl_3$ concentration (Figure 2.9, page 78). Solvent dependences have been noted in the inversion of other complexes by bond rupture

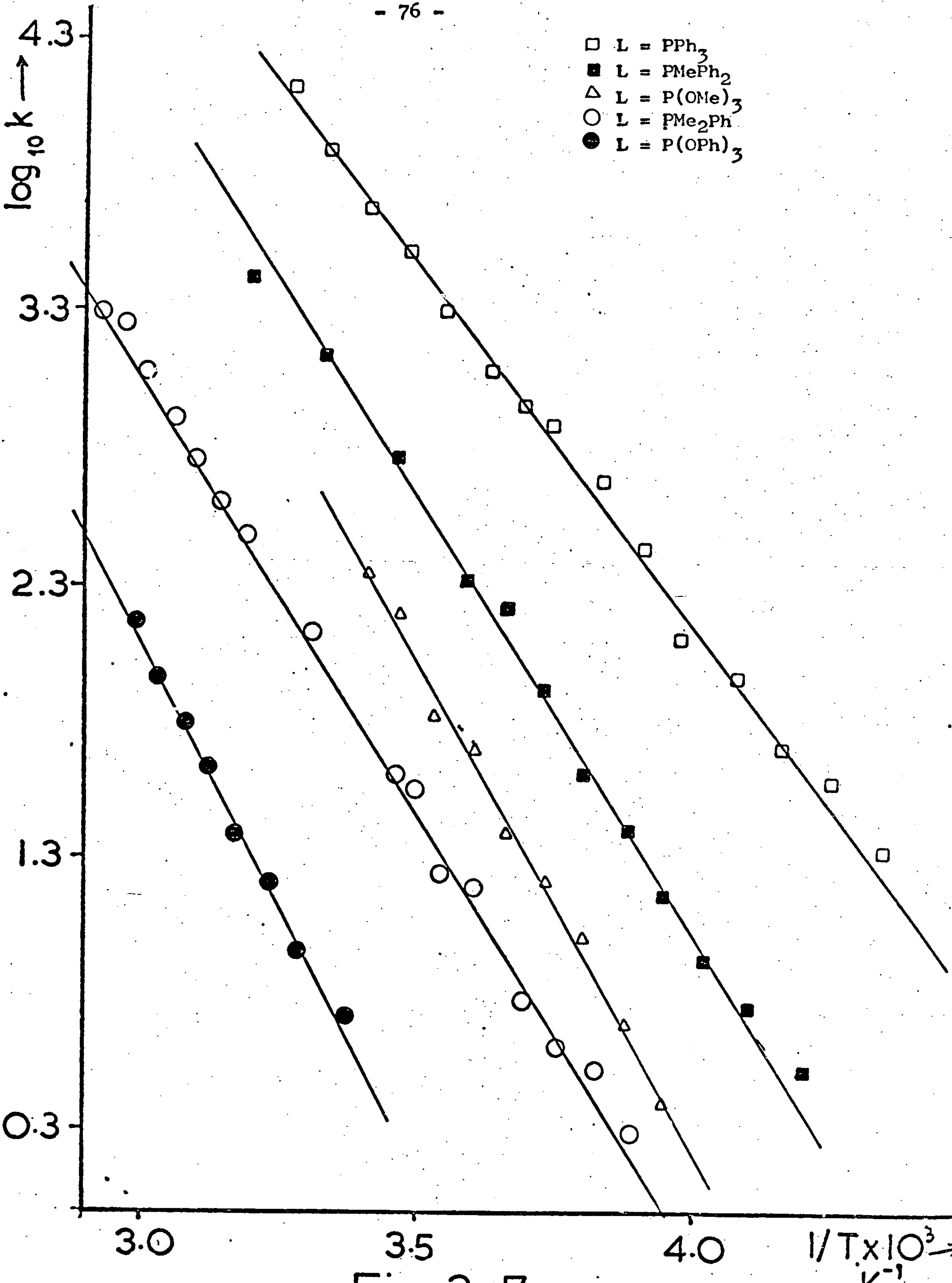


Fig. 2.7

Arrhenius plots ($\log_{10}$ k vs. $^1/_T$) for various cis - $Ru(S_2PMe_2)_2L_2$.

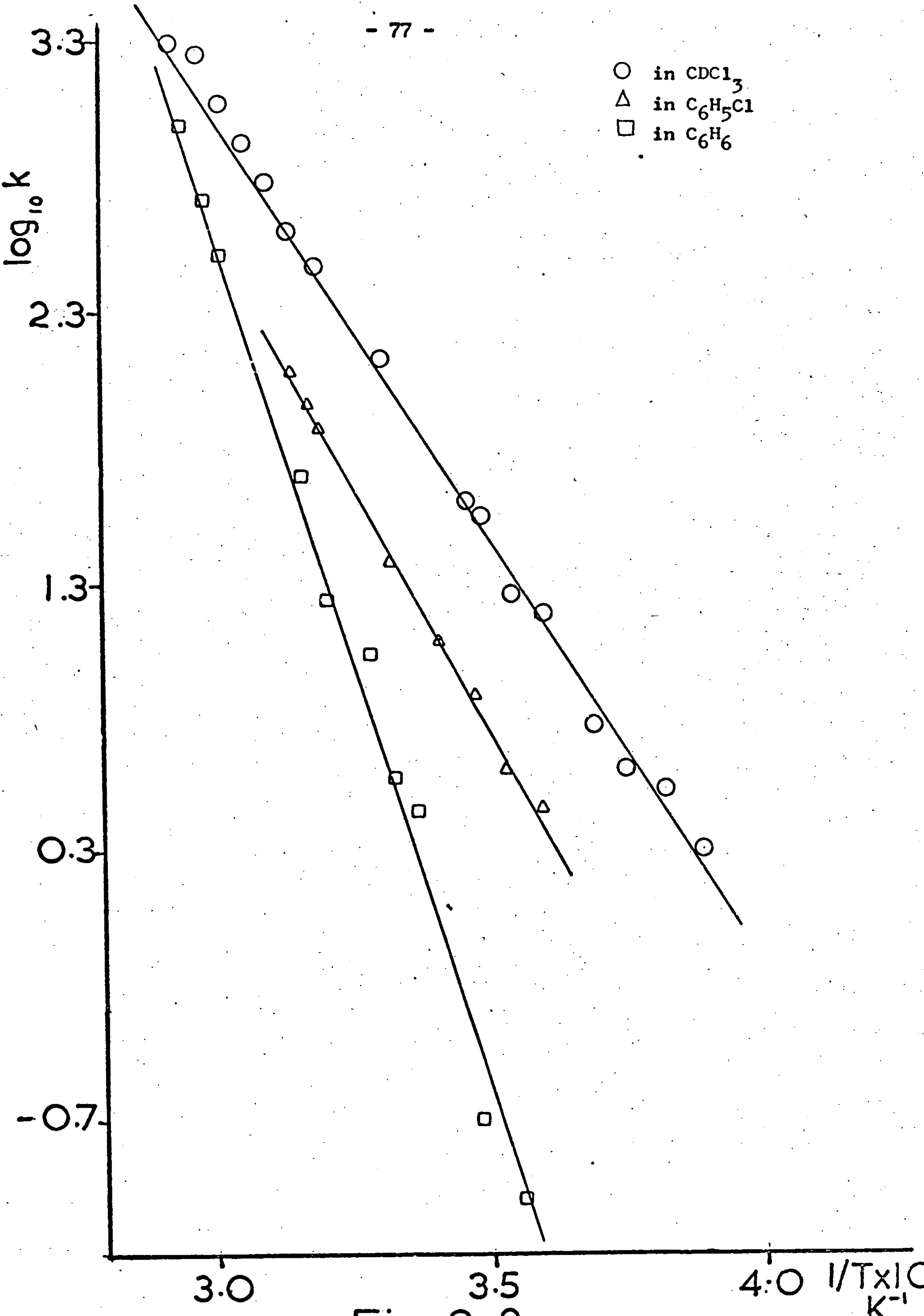


Fig. 2.8

Arrhenius plots ($\log_{10}$ k vs. $^1/_T$) for <u>cis</u> - $Ru(S_2PMe_2)_2(PMe_2Ph)_2$ in various solvents.

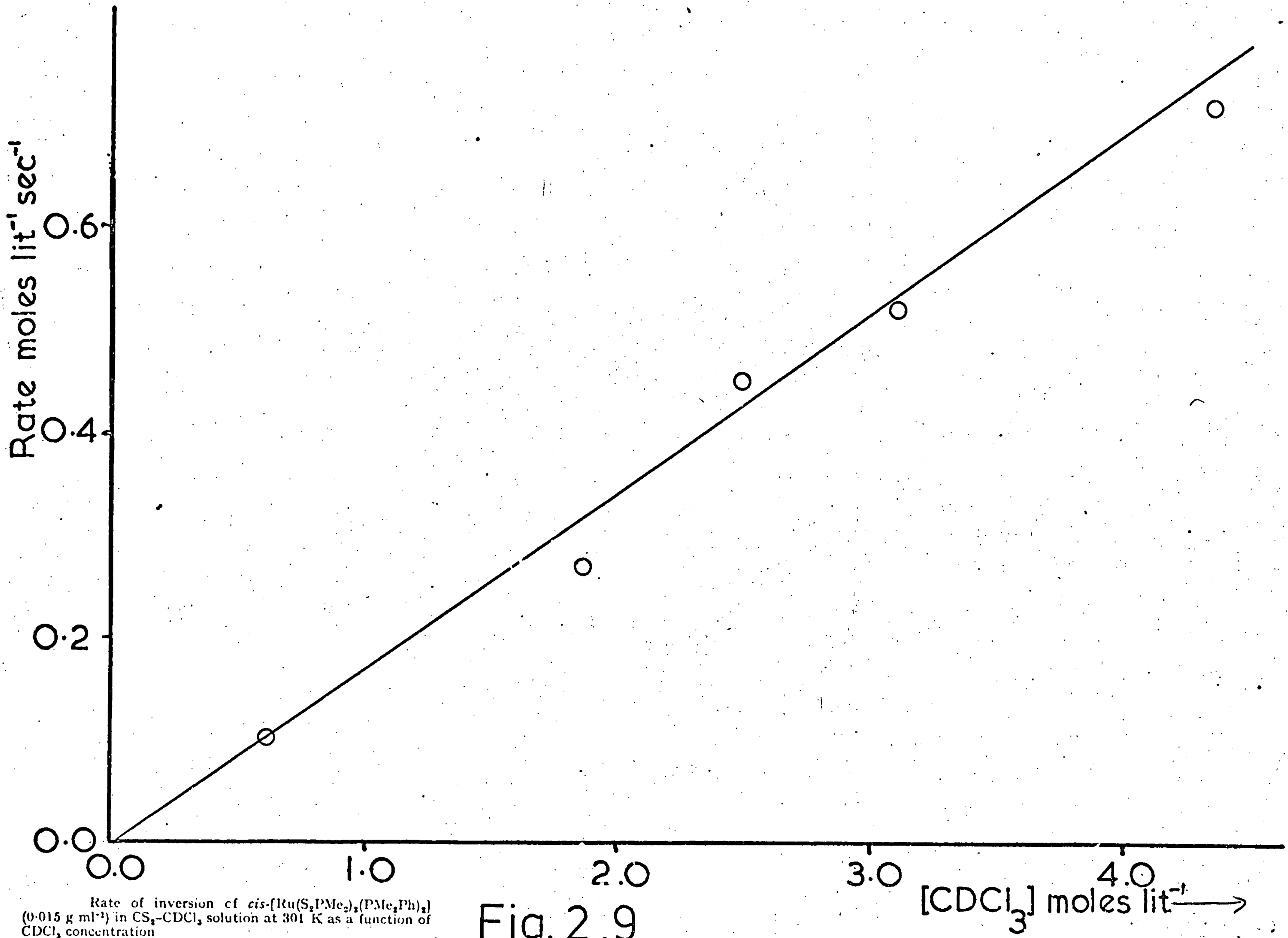


Fig. 2.9

Rate of inversion of *cis*-[Ru(S_2PMe_2)$_2$(PMe_2Ph)$_2$] (0·015 g ml^{-1}) in CS_2–$CDCl_3$ solution at 301 K as a function of $CDCl_3$ concentration mechanisms but in general they are relatively insignificant, producing small changes in $\Delta S^{\ddagger}$ and negligible changes in $\Delta H^{\ddagger}$. They are attributed to the different charge separations and degrees of solvation in passing from the ground state of a molecule to the transition state with a dangling ligand[333]. However, the mechanism for exchange of the phosphine methyl groups in $(PhMe_2P)$ Cl M $(OOCH_3)_2$ (M = Pt,Pd) has been postulated as involving a solvent assisted rupture of the M-O bond of a bridging carboxylate group followed by rotation of one half of the molecule about the other bridging ligand and reformation of the M-O bond with expulsion of solvent[334].

In a given solvent ($CDCl_3$), the inversion rate is also dependent on the group L, the relative order being $PPh_3 > PMePh_2 > P(OMe)_3 > PMe_2Ph > P(OPh)_3 \gg$ diphos $\sim Ph_2PCH_2PPh_2 \sim$ diars $>$ CO $\sim C_7H_8 \sim C_8H_{12}$, which is qualitatively the same as the order found for the rates of oxidation of <u>cis</u> - $Ru(S_2PMe_2)_2L_2$ in solution (page 49).

Finally, for the compounds <u>cis</u> - $Ru(S_2PR_2)_2(PMe_2Ph)_2$ (R = Me or Ph), the two pseudo-triplets arising from the PMe_2Ph methyl groups at low temperature in $CDCl_3$ are separated by 13Hz and 8Hz and these coalesce at ca 278K and 273K respectively. From this data, the free energies of activation for the processes which average the methyl protons are estimated to be 57.4 and 58.6 $kJmol^{-1}$ respectively. Although the value of $\Delta G^{\ddagger}_{278}$ for this process for <u>cis</u> - $Ru(S_2PMe_2)_2(PMe_2Ph)_2$ is different from that obtained by line shape analysis for the exchange of the S_2PMe_2 methyl groups, (63.4 $KJmol^{-1}$) the coalescence approach assumes a small line width compared with the separation of the peaks[334]. In this case, the assumption is invalid since the line width of each pseudo-triplet is ca. 12.0Hz which is comparable with their separation (13.0Hz). This fact coupled with the observation that fast rotation around the metal phosphorus bond does not lead to coalescence phenomena (see page 66) indicates that there is probably only one kinetic exchange process occurring (inversion of optical enanticmers) and this exchanges both the phosphine methyl groups, and the methyl groups of the S_2PMe_2 ligands.

The possible mechanisms for the inversion process in cis - $Ru(S_2PMe_2)_2L_2$ will now be considered, starting with intramolecular twisting mechanisms.

(a) Bailar (or trigonal) Twists[335]:- In this mechanism, the three atoms comprising one face of these octahedral complexes are rotated through 120° about the imaginary three-fold axis ($i-C_3$) which passes through that face, whilst keeping the opposite face fixed. In the complexes cis - $Ru(S_2PMe_2)_2LL'$, there are four such axes as illustrated in Figure 2.10 (page 81) and diagrams of the complex as viewed along those axes are given in Figure 2.11 (page 82). The positions of the methyl groups e, f, g and h shown in these Figures are consistent with the detailed assignments made earlier for $L = PPh_3$, $L' = P(OPh)_3$ (page 72) and the starting configuration arbitarily chosen is designated cis -Δ on the basis of rules suggested by the recent IUPAC commission[336].

The problem is now to consider the effect of a trigonal twist around each axis in turn (clockwise and anticlockwise) in order to determine if such a process gives the optical isomer and also interchanges only the chemical environments of the methyl groups e, h and g, f respectively. Examination of Figure 2.11a (page 82)

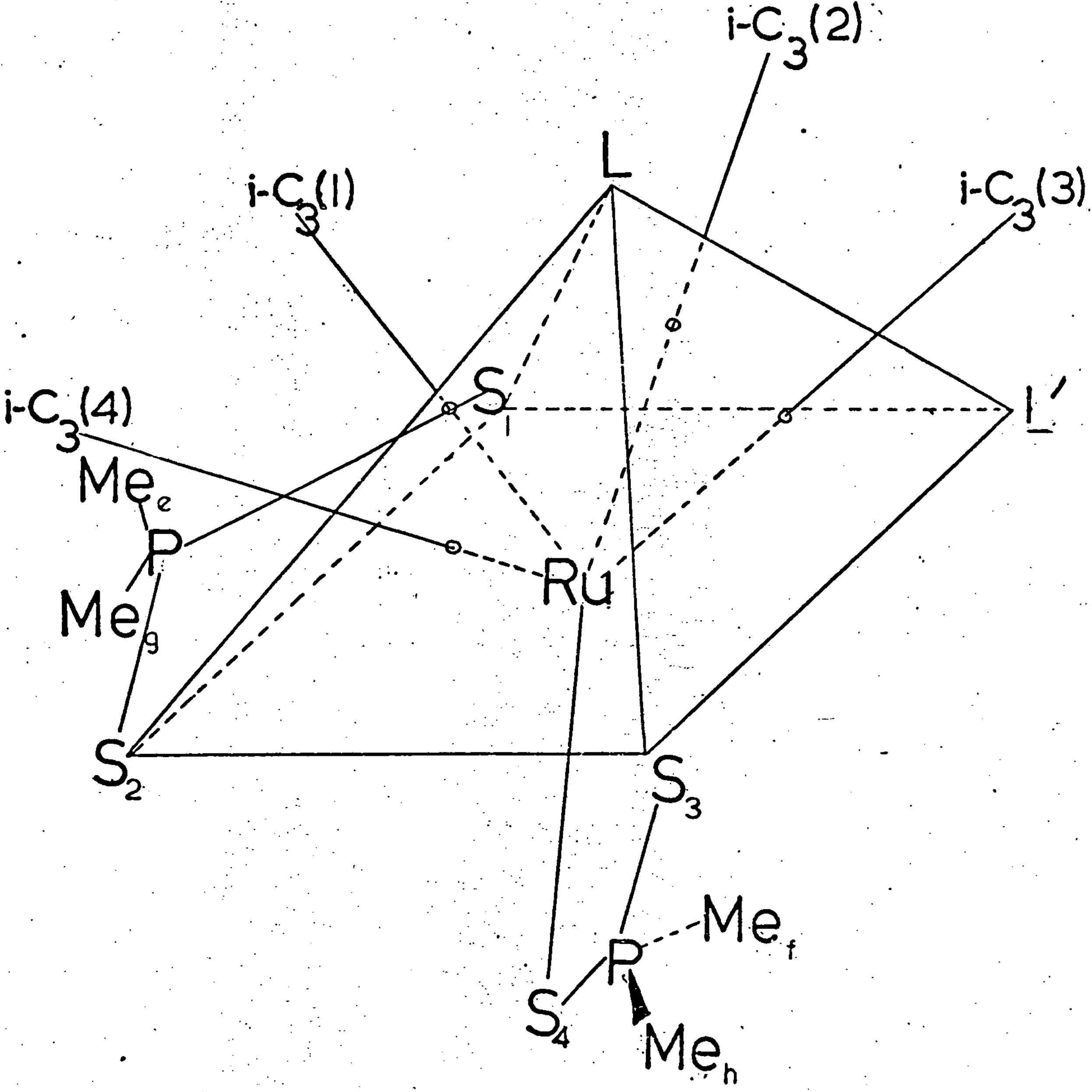


Fig. 2.10

Labelling of the four imaginary C_3 axes (i-C_3) for the

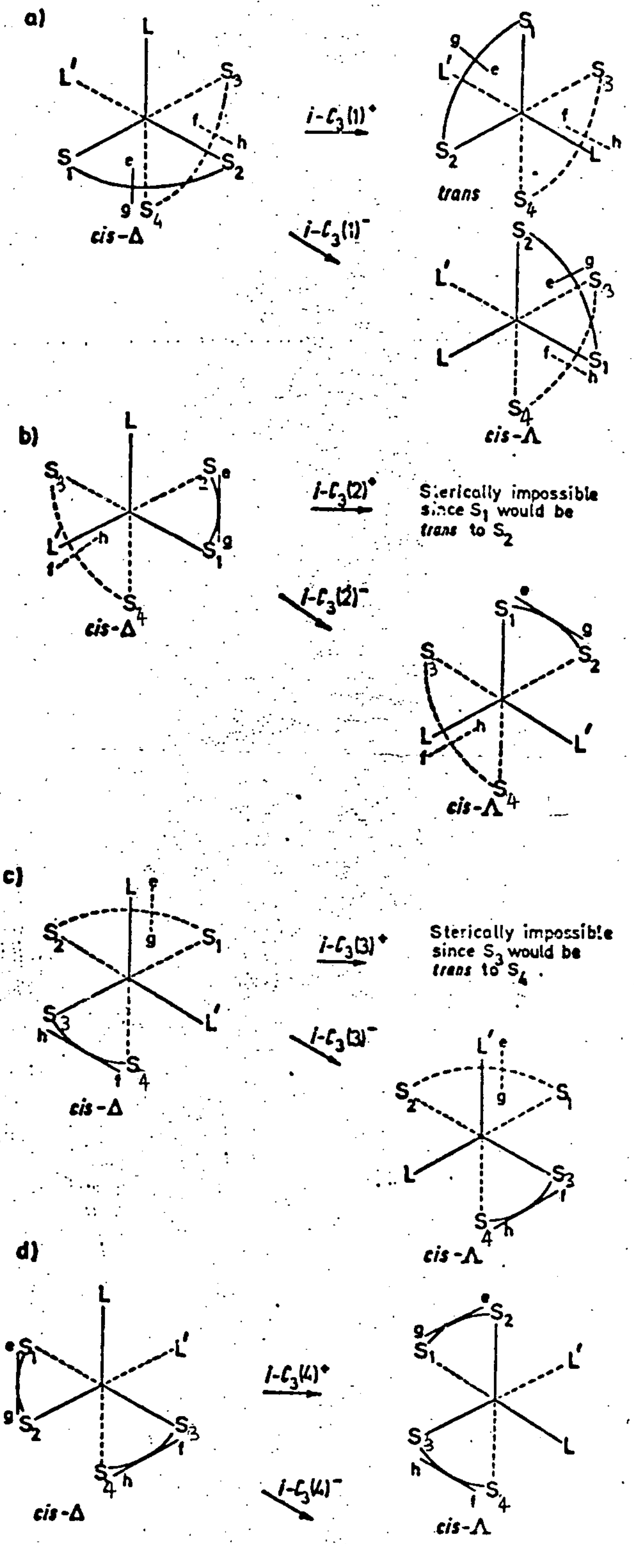
<u>cis</u> - Δ - $Ru(S_2PMe_2)_2LL'$ complex.

i-C_3 (1) axis through plane of atoms S_1, L, S_2.

i-C_3 (2) " " " " " L′, L, S_1.

i-C_3 (3) " " " " " S_3, L, L′.

i-C_3 (4) " " " " " S_2, L, S_3.



Sterically impossible since S_1 would be *trans* to S_2

Sterically impossible since S_3 would be *trans* to S_4.

Sterically impossible since S_1 would be *trans* to S_2 and S_3 would be *trans* to S_4

Fig. 2.11

Bailar (trigonal) twists for a *cis*-Δ-[Ru(S_2PMe_2)$_2$LL'] compound about the four *i*-C_3 axes in clockwise (+) and anticlockwise (−) directions. For ease of interpretation, the direction of the P–Me bonds are drawn as the same as those of the Ru–L (or L') bonds to which they are *syn* or *anti* and Table 2.8 shows that the rotation about the i-C_3(1) axis in a clockwise direction gives the trans isomer whereas an anticlockwise twist gives the cis - isomer. However, the $^-S_2PMe_2$ methyl groups will finish in the same chemical environment as they started and hence this twisting motion predicts inversion without any scrambling of methyl resonances. Rotation about i-C_3(2) or i-C_3(3) in a clockwise direction is impossible because it leads to a configuration in which a S_2PMe_2 group would have to span trans positions. Anticlockwise rotation about these axes gives the optical isomer together with scrambling of all methyl groups. Hence, if this were the inversion mechanism, a single methyl resonance should be observed at elevated temperatures and careful experiments with cis - $Ru(S_2PMe_2)_2(PPh_3)(P(OPh)_3)$ and cis - $Ru(S_2PMe_2)_2(PPh_3)CO$ (see pages 69 and 70) show that this is not the case. Finally, rotation about i-C_3(4) is sterically impossible in an anticlockwise direction but in a clockwise direction gives the cis -Λ isomer and only partial scrambling of methyl groups. Thus, groups e, f and g, h respectively are interchanged (Figure 2.11d, page 82 and Table 2.8). However, examination of Figure 2.5 (page 68) shows that for L = L$'$, groups e and f and groups g and h are chemically equivalent and, therefore, if this were the inversion mechanism, the ^1H n.m.r. spectra of the compounds cis - $Ru(S_2PMe_2)_2L_2$ should be temperature invariant. This is not the case and therefore a mechanism involving a trigonel twist about this axis is also rejected.

(b) Ray Dutt (or rhombic) Twist[337]:- For cis - $Ru(S_2PMe_2)_2L_2$, this inversion mechanism may be visualised as follows:- the two L groups remain fixed while the two chelate rings rotate in their planes in different directions through an angle of 90° about axes which are perpendicular to their respective planes and pass through the ruthenium ion. For cis - $Ru(S_2PMe_2)_2L_2$ this does not produce any scrambling of the methyl resonances and so this twisting mechanism can also be discarded.

Final rejection of a trigonal or rhombic twist mechanism comprising rotation about one or several of these axes is based on a consideration of steric effects on the expected trigonal prismatic transition state. If a twisting mechanism is important, the activation energy for the process should be dependent on the size of L, being higher the bulkier the ligand[338]. However, the results given in Table 2.7 reveal no apparent correlation with the size of L e.g. the bis - PPh_3 complex has a smaller activation energy than the bis - PMe_2Ph complex which is smaller than the bis - $P(OPh)_3$ compound. The large dependence of rate and associated activation parameters on solvent composition is also not compatible with a twist mechanism[339].

Therefore, it is necessary next to consider inversion mechanism arising from initial cleavage of a ruthenium-ligand bond.

(c) Cleavage of a ruthenium-phosphorus bond:- Since the activation energies for the optical isomerism of the compounds cis - $Ru(S_2PMe_2)_2L_2$ depend on the ligand L, it seems reasonable, at first sight, to postulate that the inversion mechanism might involve dissociation of a phosphorus ligand to give a square pyramidal or trigonal bipyramidal intermediate followed by recombination as the optical isomer. However, if this were the mechanism, the ^1H n.m.r. spectrum of a mixture of two complexes containing different L groups should show scrambling of all the methyl resonances of the $^-S_2PMe_2$ groups. This is not the case for a mixture of cis - $Ru(S_2PMe_2)_2(PPh_3)_2$ and cis - $Ru(S_2PMe_2)_2(PMe_2Ph)_2$ in $CDCl_3$ which shows only the unchanged ^{1}H n.m.r. spectral patterns of the two components. Furthermore, the ^{1}H n.m.r. spectrum of a mixture of cis - $Ru(S_2PMe_2)_2(PMe_2Ph)_2$ and free PMe_2Ph in $CDCl_3$ at ca 330K indicates no exchange of free and bound phosphine. Thus, cleavage of a ruthenium-phosphorus bond may be eliminated as a possible first step in the inversion process.

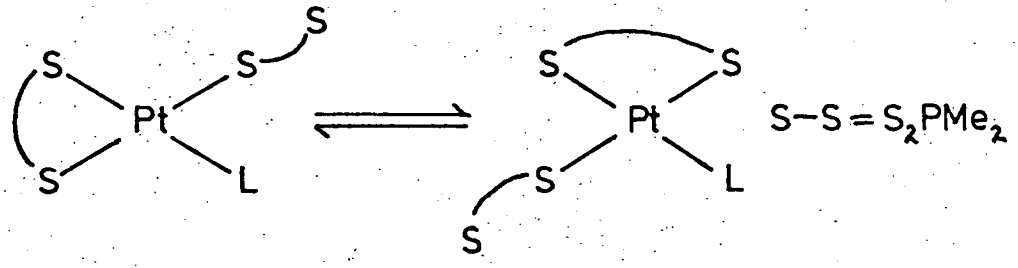
(d) Complete dissociation of a dithioacid ligand:- If this was an important process, a mixture of the two compounds cis - $Ru(S_2PR_2)_2L_2$ and cis - $Ru(S_2PR^1{}_2)_2L_2$ should give some of the mixed ligand species cis - $Ru(S_2PR_2)(S_2PR_2{}^1)L_2$ under exchange conditions. This does not occur and therefore, the racemisation mechanism cannot involve complete dissociation of a dithioacid ligand.

(e) Cleavage of a ruthenium-sulphur bond:- In the symmetrical complexes cis - $Ru(S_2PR_2)_2L_2$, there are two types of ruthenium-sulphur bond; those which are trans to another sulphur atom and those trans to a phosphorus ligand. If optical isomerism occurred via a cleavage of a ruthenium sulphur bond trans to another sulphur atom, then the activation energy for the reaction would be relatively insensitive to changes in L. Thus, if a bond rupture mechanism is correct, it must involve cleavage of a ruthenium-sulphur bond, which is trans to a phosphorus ligand. This statement can be rationalised on the basis that the larger trans influence (the extent to which a ligand weakens the bond trans to itself in the equilibrium state of a complex)^{340} of the phosphorus ligands, as compared with the S_2PR_2 groups, should preferentially weaken the ruthenium-sulphur bonds trans to them. This suggestion is supported by the bond length in cis - $Ru(S_2PEt_2)_2(PMe_2Ph)_2$ (Appendix 2) where the Ru-S bonds trans to the PMe_2Ph groups are ca. 0.2Å longer than those trans to another sulphur atom.

Since a first order dependence on solvent concentration is found for the inversion of cis - Ru(S_2PMe_2)$_2$(PMe_2Ph)$_2$, it follows that, if the first step of the inversion process is rate determining, that step must involve an S_N2 attack on the complex by a molecule of solvent to form a seven co-ordinate transition state. Furthermore, since the activation parameters (Table 2.7) for the inversion of cis - Ru(S_2PMe_2)$_2$(PPh_3)(P(OPh)$_3$) are of the same order of magnitude as those for cis - Ru(S_2PMe_2)$_2$(PPh_3)$_2$, it is probable that the mechanism of inversion for these two compounds is the same. Thus, the mechanism which is postulated for cis - Ru(S_2PMe_2)$_2$LL$'$ must obey the principle of microscopic reversibility, not only for the case where L = L$'$, but also for complexes in which L and L$'$ are different. Thus, no mechanism which involves an attack by solvent on the complex to form a seven co-ordinate intermediate, rupture of a Ru-S bond then reattack by the dangling sulphur ligand followed by expulsion of solvent to give the optical isomer, can be correct since for L $\neq$ L$'$, if the Ru-S bond which is originally trans to L were the one to break in the second step, the Ru-S bond formed in the third step would be that of the sulphur atom which ends up trans to L$'$ in the optical isomer, hence violating the principle of microscopic reversibility.

Thus, the mechanism must involve at least five steps; the first two, as before, involve the formation of a seven co-ordinate transition state and rupture of a metal sulphur bond trans to L (say), then, at this point an exchange of bidentate and unidentate sulphur ligands similar to that found in Pt(S_2PMe_2)$_2$L must occur[16].

i.e.



This is then followed by reattack of the free sulphur atom in such a position that, when the solvent is expelled, it (the S atom) becomes trans to L. There are two main ways in which this can occur; one (Figure 2.12a, page 88) involves attack of a solvent molecule (Y) in a position close to the Ru-S bond to be broken, so that the solvent simply takes the place of the dissociating sulphur atom in the co-ordination sphere; the other involves a pentagonal-bipyramidal intermediate in which the leaving sulphur atom and the attacking solvent molecule are in the two axial positions (Figure 2.12b, page 88). As can be seen in Figure 2.12, (page 88), L and L$'$ in this seven co-ordinate transition state may be next to one another in the plane of the pentagon or they may be separated by a sulphur atom and after cleavage of the Ru-S bond, either L or L$'$ may be trans to the co-ordinated solvent molecule (if any of the sulphur atoms takes up the position trans to Y, the mechanisms which ensue can all be shown to disobey the principle of microscopic reversibility). From Figure 2.12a it is clear that only the environments of methyl groups e and h and of f and g are exchanged (as required for cis - $Ru(S_2PMe_2)_2(PPh_3)(P(OPh)_3)$) and that this only occurs if the positions of S_2 and S_4 are interchanged, the other two sulphur atoms remaining in their original positions. Thus, the last mechanism in Figure 2.12b may be discarded because it averages the environments of different methyl groups than observed experimentally for cis - $Ru(S_2PMe_2)_2(PPh_3)(P(OPh)_3)$ (see page 72).

These mechanisms are also consistent with many of the other experimental observations. Thus, the solvent attack on the complex is consistent with the first order dependence on $CDCl_3$ concentration in $CS_2/CDCl_3$ mixtures, although this does not necessarily mean that

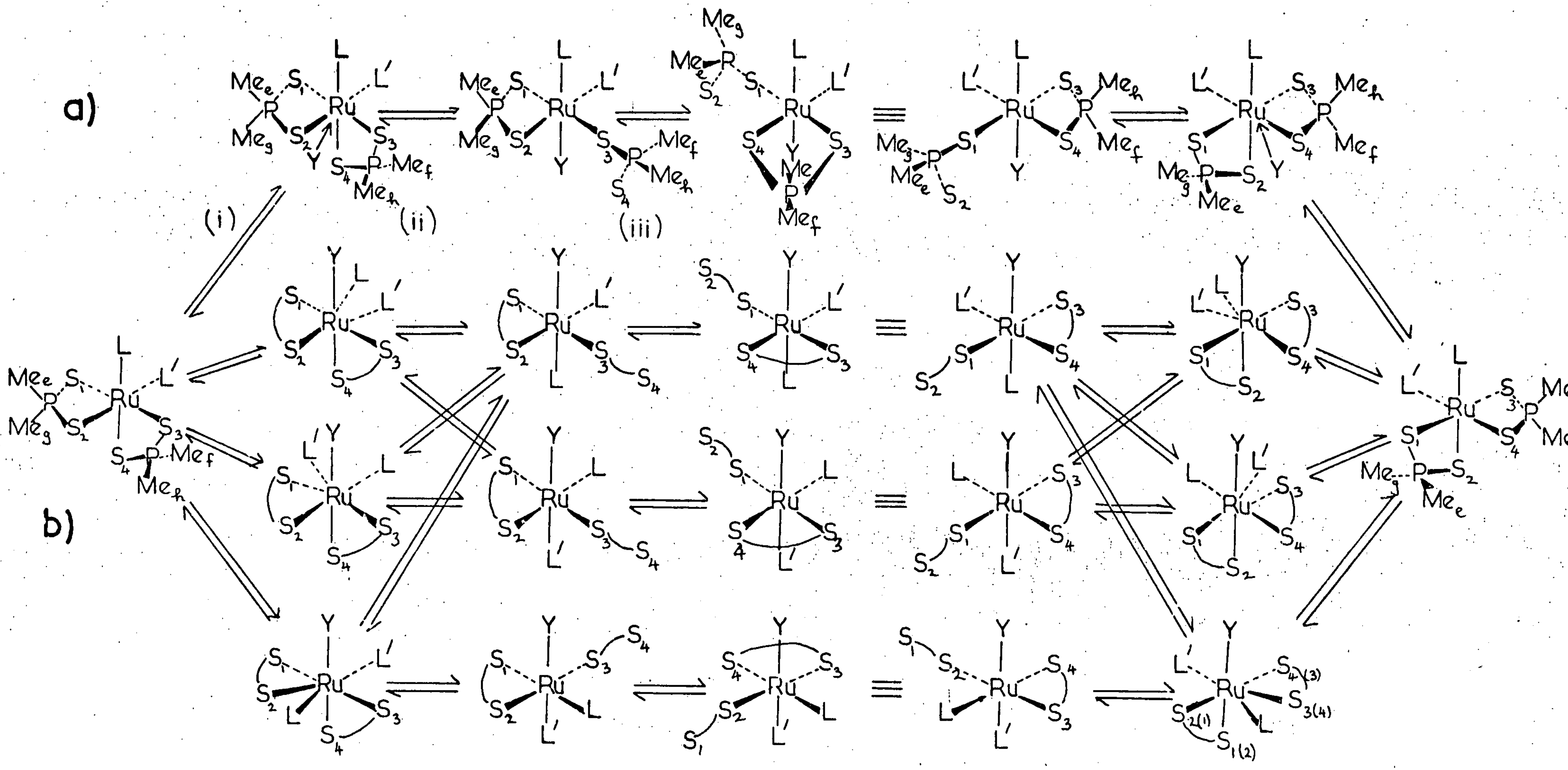


Fig. 2.12

Possible solvent (Y) assisted bond-rupture mechanisms for inversion of cis - $Ru(S_2PMe_2)_2LL'$

(a) cis attack by solvent (b) trans attack by solvent.

the first step is rate determining, since if any later steps (apart from the last) were rate determining, a first order dependence on solvent would still be seen[341]. On changing to a less solvating medium such as benzene, the first step should be slower and the overall inversion rate should decrease, as is observed experimentally. Also, since the main factor influencing the rate of sub-step(i) (apart from the choice of solvent) should be the steric size of the ligands, being slower the bulkier the ligands, and since a direct correlation between inversion rate and bulk of L is not observed, it is evident that step (i) alone is probably not rate determining. Since a good correlation is found between the rates of inversion of <u>cis</u> - $Ru(S_2PMe_2)_2L_2$ and the <u>trans</u>-influence[*] of L as established independently by ^1H n.m.r. and i.r. studies[342], <u>viz</u> $PPh_3 > PMePh_2 > PMe_2Ph > P(OMe)_3 \sim P(OPh)_3 > CO$, it is likely that step (iii) also contributes to the determination of the rate of inversion since this step involves the rupture of a Ru-S bond trans to L, whose strength is directly influenced by L. The anomalous position of $P(OMe)_3$ in the order of inversion rates is probably best explained by its small steric size making step (i) easier and speeding up the inversion process. Thus, it appears that both steps (i) and (iii) contribute to the rate expressions for this reaction and it remains to determine the relative contributions of these two steps.

From Table 2.7, the activation parameters for <u>cis</u> - $Ru(S_2PMe_2)_2(PPh_3)CO$ in C_6H_5Cl are $\Delta H^{\ddagger}$, 119.3kJmol^{-1}; $\Delta S^{\ddagger}$, 125KJ^{-1}mol^{-1}.

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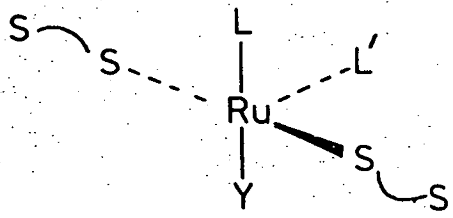
[*] There is a 1:1 correlation between <u>trans</u> influence and <u>trans</u> effect in six co-ordinate complexes[342].

Since the second step of any of the mechanisms postulated for the inversion is likely to involve rupture of the weakest Ru-S bond in the molecule (that originally trans to PPh_3 in cis - $Ru(S_2PMe_2)_2(PPh_3)CO$), it is likely that the rate of this step should not vary greatly with L′, although a small decrease in rate might be expected in changing L′ from PPh_3 to CO on account of the smaller size of the CO group. However, since the overall rate is considerably slower for cis - $Ru(S_2PMe_2)_2(PPh_3)CO$ than for cis - $Ru(S_2PMe_2)_2(PPh_3)_2$, the rate of step (iii) must be considerably slower* and hence the observed activation parameters for cis - $Ru(S_2PMe_2)_2(PPh_3)CO$ must correspond quite closely to those for step (iii) alone. This indicates that step (iii) is characterised by large positive $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, which are consistent with the exchange of unidentate and bidentate S_2PMe_2 ligands occurring by a dissociative mechanism[339] to form a five co-ordinate transition state in which the two unidentate S_2PMe_2 ligands are mutually trans (4), (c.f. one isomer of $VO(S_2PR_2)_2py_2$ (page 15)), the breaking of a Ru-S



(4)

bond trans to L′ being rate determining.

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* This rules out an intermediate in which L′ is trans to Y since in this case, the rate of step (iii) should be insensitive to changes in L′.

For ligands of higher trans influence than CO, it is reasonable to assume that $\Delta H^{\ddagger}$ for this process would be much lower but that the value of $\Delta S^{\ddagger}$ should not be very different since $\Delta S^{\ddagger}$ depends on the breakdown of the solvation sphere of the molecule by the dangling S_2PMe_2 groups. Thus, the inversion rates for cis - $Ru(S_2PMe_2)_2L_2$ in $CDCl_3$ must have an appreciable contribution from sub-step (i) since $\Delta S^{\ddagger}$ for these complexes are close to zero. Since the first step is associative, a large negative $\Delta S^{\ddagger}$ should be associated with it and thus if there are contributions from both steps (i) and steps (iii), the positive $\Delta S^{\ddagger}$ from step (iii) and the negative $\Delta S^{\ddagger}$ from step (i) will cancel one another out.

The overall rate decrease, accompanied by substantial increases in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ which are observed when cis - $Ru(S_2PMe_2)_2(PMe_2Ph)_2$ is examined in C_6H_6 rather than $CDCl_3$ (or C_6H_5Cl) (Table 2.7) is explicable on the basis that in such a poor solvating medium, step (i) not only becomes considerably slower because it is no longer a solvent assisted process, but also becomes dissociative in nature. However, the similarity of the high temperature n.m.r. spectra of cis - $Ru(S_2PMe_2)_2(PPh_3)(P(OPh)_3)$ in C_6H_6 and C_6H_5Cl (two methyl doublets) is consistent with retention of the same overall mechanism (Figure 2.13(b), page 92).

It only remains to explain the activation parameters found for the tris-chelate complexes $Ru(S_2PMe_2)_2(L-L)$. The high positive values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ found for $Ru(S_2PMe_2)_2$ diphos (Table 2.7) (and presumably for the other tris chelate complexes although insufficient data could be obtained for an Arrhenius plot) could be explained by either sub-step (i) or sub-step (iii) being slow and therefore rate-determining. That is, either the chelating ligands have low trans influences, thus making step (iii) slow, or they

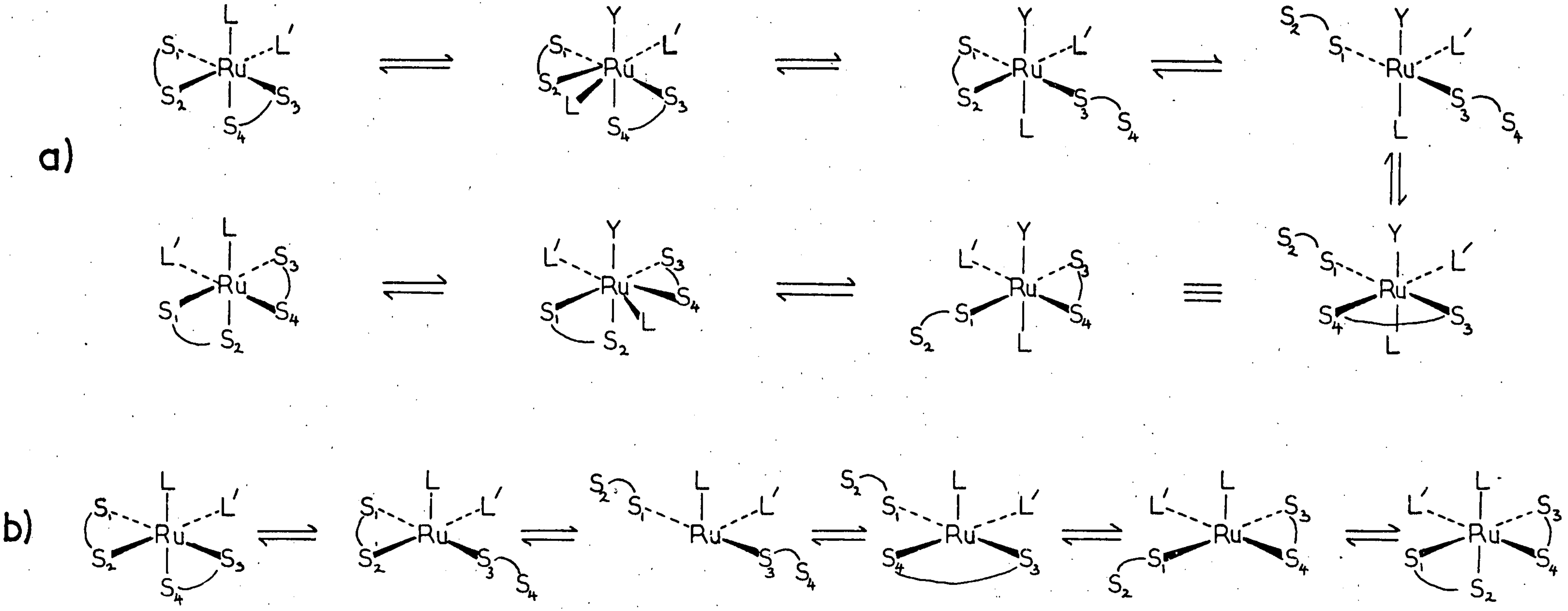

Fig. 2.13

Postulated mechanisms of inversion for $Ru(S_2PMe_2)_2LL'$

a) in a polar solvent b) in a non-polar solvent prevent the solvent from entering the co-ordination sphere for steric reasons, thus making step (i) dissociative and slow. The literature available on the trans-influences of these ligands is somewhat erratic since, although dienes all appear to have low trans-influences, diphos can have a high or a low trans-influence, depending upon how it is measured. Diars, on the other hand, is generally considered to have a high trans-influence[342]. However, examination of the seven co-ordinate transition state in the last mechanism in Figure 2.12b, (page 88) shows that L and L' are separated by a sulphur atom, and this is not, of course, sterically possible if L and L' are joined as opposite ends of a chelate. Thus, it appears that this mechanism (Figure 2.13a, page 92) best fits the observations that we have made and it should be pointed out that the seven co-ordinate transition state in which L and L' are not adjacent in the plane of the pentagonal-bipyramid is the least sterically hindered of the possible transition states postulated.

Finally, support for the fact that the six co-ordinate intermediate with a unidentate S_2PMe_2 ligand in fact has the stereochemistry postulated comes from the carbonylation under mild conditions of cis - $Ru(S_2PMe_2)_2(PMe_2Ph)_2$. The product from this reaction has the formula $Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$ and has been shown to have the same stereochemistry as that of the intermediate postulated ($L = L' = PMe_2Ph$; Y = CO) (see later). Unfortunately, however, this does not show exchange of bidentate and unidentate sulphur ligands on the n.m.r. time scale even at 323K. The reason for this is not clear although it may be that a six co-ordinate complex in which all co-ordination sites are occupied by fairly strong donor ligands is generally less labile than one in which one of the sites is occupied by a loosely co-ordinated solvent molecule.

This might also explain why step (iii) (a non solvent assisted rupture of an Ru-S bond trans to L) has a comparable rate to step (i) (a solvent assisted rupture of an Ru-S bond trans to L) in the postulated mechanism, when L = $L' \neq$ CO.

5. C=N bond rotation in cis - $Ru(S_2CNMe_2)_2L_2$

For cis - $Ru(S_2CNMe_2)_2L_2$ (L = PMe_2Ph, PPh_3 or $P(OPh)_3$), the low temperature ^1H n.m.r. spectra consist of two S_2CNMe_2 methyl singlets which coalesce at higher temperatures (see page 72 and Table 2.6). The rates and activation parameters at 298K for this process are given in Table 2.9. The room temperature ^1H n.m.r. spectrum of cis - $Ru(S_2CNMe_2)_2(PPh_3)(P(OPh)_3)$ consists of three methyl singlets of relative intensity 1:2:1, indicating accidental superposition of two of the methyl resonances. At higher temperatures, the highest field singlet at τ7.37 and one of the superimposed resonances at τ7.13 coalesce to give a singlet at τ7.23 (Tc = 318K) whilst the lowest field signal at τ6.86 and the remaining resonance at τ7.13 broaden considerably and move towards each other (see Table 2.6). Thus, the high field pair of singlets and the low field pair of singlets are undergoing exchange and the rates and activation parameters at 298K for these exchange processes are given in Table 2.9). These data clearly show that although the rates are fairly similar at 298K, the activation parameters are very different. This can only mean that the kinetic processes exchanging these two sets of methyl signals are independent of each other and the best explanation of this is that these n.m.r. changes are produced by fast rotation about the $C\overset{\cdots}{-}N$ bonds of the S_2CNMe_2 groups syn to PPh_3 and syn to $P(OPh)_3$ and not by a facile inversion process. In support of this conclusion, the two sets of activation parameters found for cis - $Ru(S_2CNMe_2)_2(PPh_3)(P(OPh)_3)$ are reasonably similar to those found for the bis-PPh_3 and bis-$P(OPh)_3$ complexes respectively. The large difference in $\Delta S^{\ddagger}$ values for the C$\overset{\cdots}{-}$N bond rotation process is probably caused by substantial differences in the degree of solvation of the complexes which might arise as a consequence of replacing phenyl with phenoxy groups.

Finally, further heating of cis - $Ru(S_2CNMe_2)_2(PPh_3)(P(OPh)_3)$ to 403°K in C_6H_5Cl causes both exchanging sets of methyl groups to give rise to sharp singlets which do not, however, show any sign of broadening or coalescence phenomena with one another. Thus, the activation energy for the inversion of this complex is very high, which is probably due to the much greater strength of the Ru-S bonds in S_2CNMe_2 complexes than in S_2PR_2 complexes[16].

6. Mechanism of carbonylation of cis - $Ru(S_2PR_2)_2(PMe_2Ph)_2$.

When cis - $Ru(S_2PR_2)_2(PMe_2Ph)_2$ (A) (R = Me, Ph) is carbonylated in refluxing ethanol or acetone for a prolonged period, a mixture of cis - $Ru(S_2PR_2)_2(PMe_2Ph)CO$ (C) and $Ru(S_2PR_2)_2(PMe_2Ph)_2CO$ (D) is always formed although these can be separated by dry column chromatography. However, when D is redissolved, partial rearrangement to C slowly occurs whereas if the reaction of A and CO is carried out in the presence of excess sulphur, only C is formed. Conversely reaction of A and CO in the presence of excess PMe_2Ph gives pure D. In addition, another complex of formula $Ru(S_2PR_2)_2(PMe_2Ph)_2CO$ (E) may be isolated if the carbonylation reaction is carried out in the cold for a very short time (ca one minute). In solution, E slowly and irreversibly gives first C and then some of D. This process can be monitored by both ^1H n.m.r. (since all the compounds have different spectra) or by observing the change in ν_{CO} position since for R = Me; $\nu_{CO}(E)$ = 1967cm^{-1}; $\nu_{CO}(C)$ = 1945 cm^{-1}; $\nu_{CO}(D)$ = 1940cm^{-1} (all measured in $CHCl_3$). Measurement of the rate of loss of the carbonyl band intensity for E gives a rate constant for this rearrangement reaction of $1.7 \times 10^{-4} sec^{-1}$ at 323K ($t_{1/2}$ = 65 mins) and also confirms that the process is first order with respect to E.

Thus, these observations are consistent with the carbonylation mechanism shown below:- viz. facile formation of E followed by a slower conversion to C which then undergoes a partial reversible rearrangement to D.

$$\begin{tikzcd}
\underset{(A)}{Ru(S_2PR_2)_2(PMe_2Ph)_2} + CO \arrow[r, "fast"] & \underset{(E)}{Ru(S_2PR_2)_2(PMe_2Ph)_2CO} \arrow[dl, "slow"'] \\
\underset{(C)}{Ru(S_2PR_2)_2(PMe_2Ph)CO}\ (C) + PMe_2Ph \arrow[r, shift left, harpoon] & \underset{(D)}{Ru(S_2PR_2)_2(PMe_2Ph)_2CO} \arrow[l, shift left, harpoon]
\end{tikzcd}$$

It now only remains to determine the structures of D and E in order to establish the stereochemical pathway of the mechanism.

Assuming that ruthenium (II) retains its usual six-co-ordinate stereochemistry+, and we therefore have unidentate and bidentate S_2PR_2 groups*, there are four possible isomers for compounds of formulae $Ru(S_2PR_2)_2(PMe_2Ph)_2CO$ (Figure 2.14, page 97). For R = Me, the room temperature ^1H n.m.r. spectrum of D consists of

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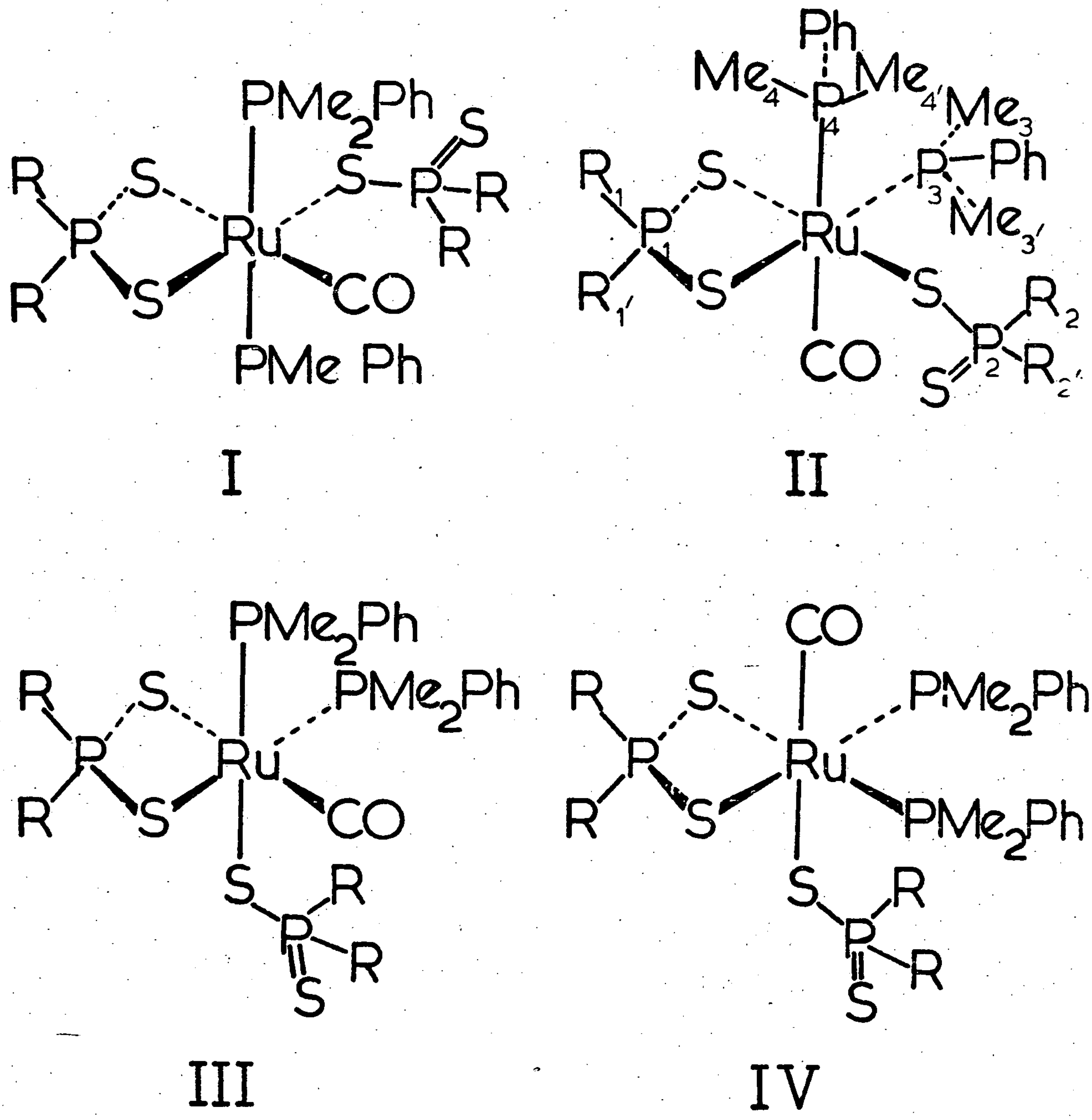
+ A reasonable assumption since to our knowledge only one ruthenium (II) seven co-ordinate compound has been claimed i.e. $RuCl_2(CO)_2(MeC(CH_2SEt)_3)$[343].

* This is suggested by the i.r. spectra of D and E (see earlier) (cf. $Ru(NO)(S_2CNR_2)_3$[223].



I II

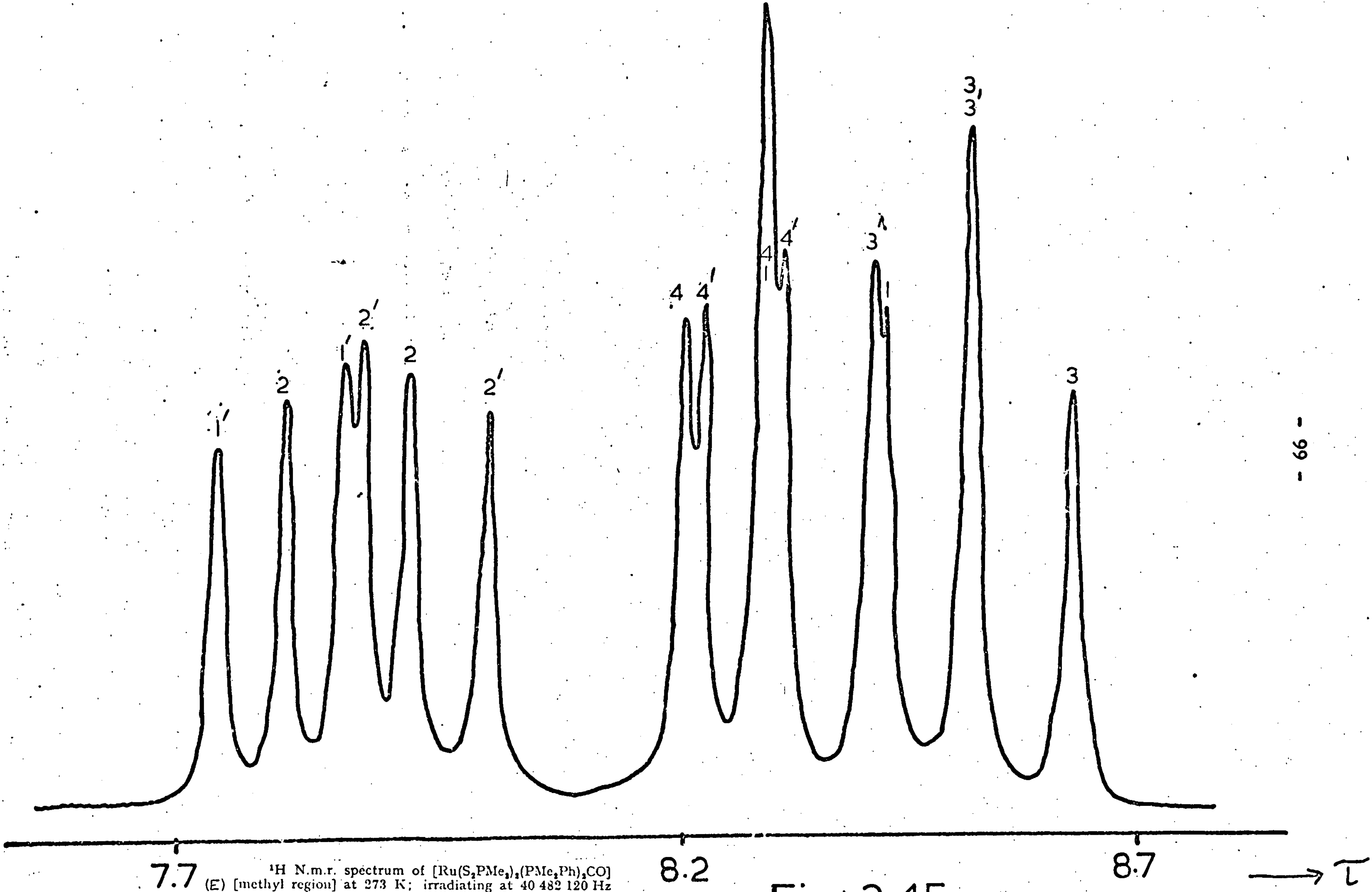
III IV

Fig. 2.14

Possible isomeric forms for $Ru(S_2PR_2)_2(PMe_2Ph)_2CO$ assuming bidentate and unidentate S_2PR_2 co-ordination.

two doublets (from the S_2PMe_2 groups) and a 1:3:3:1 quartet for the PMe_2Ph groups (i.e. two overlapping 1:2:1 'virtually-coupled' triplets as is seen for R = Ph) Table 2.6). At higher temperatures, these collapse to a single triplet although a detailed observation of this process is obscured (for R = Me) by the increased tendency to rearrange to compound C at these higher temperatures. In contrast, the two S_2PMe_2 doublets are almost temperature invariant, except for a slight broadening at ca 330K which again is obscured because of the facile rearrangement to C at this temperature. Examination of Figure 7 reveals that this n.m.r. spectrum corresponds to that expected for structure I i.e. trans PMe_2Ph groups with slow exchange of uni/bidentate S_2PR_2 groups. Assignment of this structure to D would also account for the similarity in the position of ν_{CO} to that observed for C (Table 2.3) since in each case, the carbonyl group is situated trans to a sulphur atom of a bidentate dithioacid ligand.

The ^1H n.m.r. spectrum of E (R = Me), which is temperature invariant from 220 to 320K, (although over longer periods, it slowly converts to a mixture of C and D), consists of fourteen lines (Figure 2.15, page 99). By means of heteronucleur spin decoupling experiments it can be shown that the four phosphorus atoms in the molecule are all in inequivalent chemical environments and this is confirmed by measuring the proton noise decoupled ^{31}P n.m.r. spectrum of the complex (Figure 2.16, page 100). The decoupling studies (see Figure 2.15, page 99) also indicate that the 14 line ^1H n.m.r. spectrum is comprised of 8 doublets (with four of the doublets



^{1}H N.m.r. spectrum of $[Ru(S_2PMe_2)_2(PMe_2Ph)_2CO]$ (E) [methyl region] at 273 K; irradiating at 40 482 120 Hz decouples 1 and 1', at 40 480 770 Hz decouples 2 and 2', at 40 478 777 Hz decouples 3 and 3', and at 40 477 700 Hz decouples 4 and 4' (*note* Assignments of 2 and 2', 3 and 3', 4 and 4' are arbitrary.)

Fig. 2.15

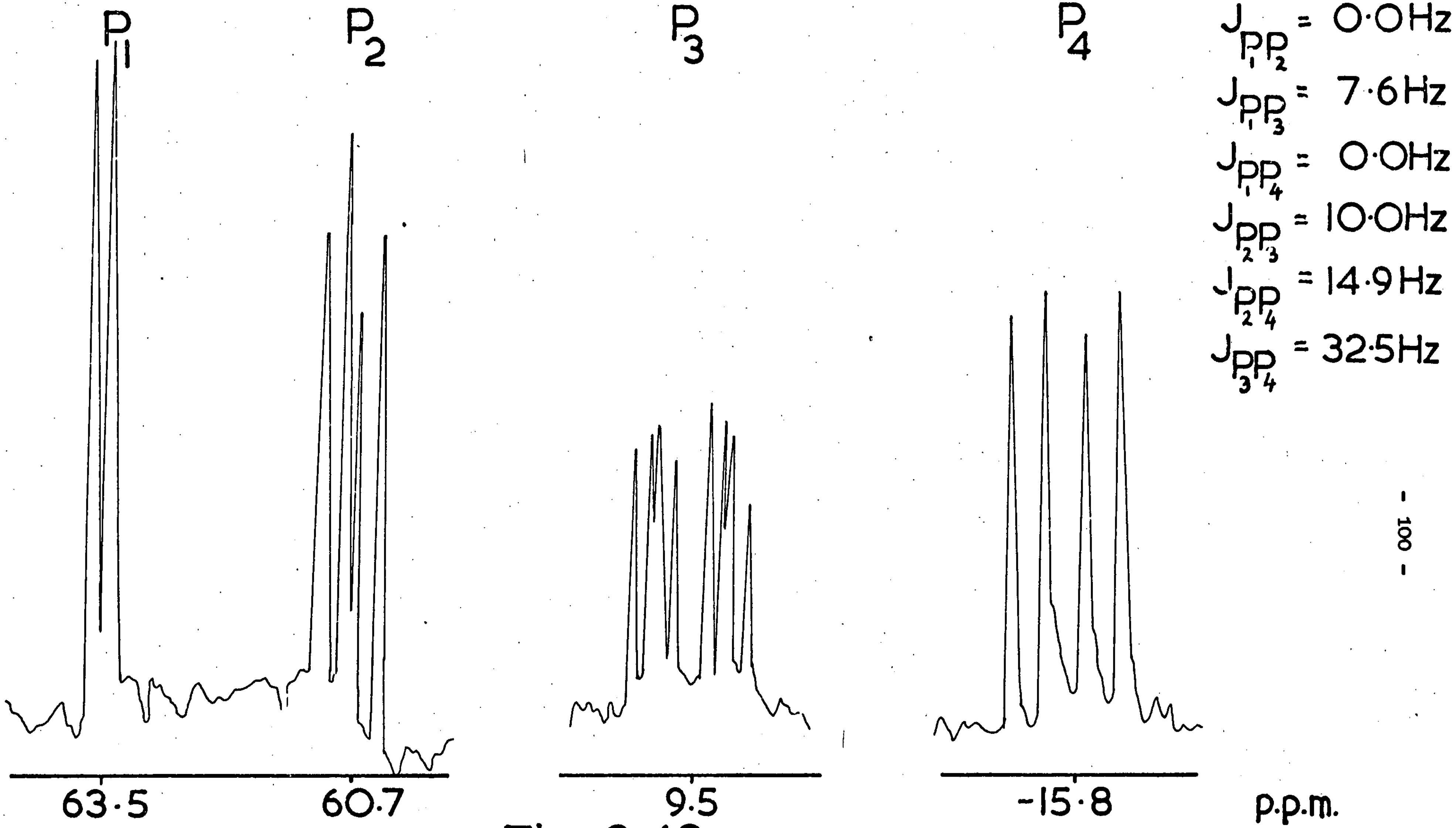


Fig. 2.16

^{31}P n.m.r. spectrum of Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$CO (E) Chemical shifts are in p.p.m. to high frequency of 85% H$_3$PO$_4$.

c.f. *cis* - Ru(S$_2$PMe$_2$)$_2$(CO)$_2$ + 92.6; *cis*-Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$ + 88.1, + 21.4.

partially superimposed)*. Thus, all the methyl groups are in inequivalent chemical environments, and there is restricted rotation (even at 320K) about the Ru-P bonds. This n.m.r. evidence is, in fact, compatible with a seven co-ordinate complex with only bidentate dithioacid groups. However, addition of methyl iodide to a dichloromethane solution of E produces an immediate increase in conductivity. A similar increase is observed for $Pt(S_2PMe_2)_2PMe_2Ph$ (where uni/bidentate co-ordination is well established)[16] and compound D, but with $Pt(S_2PMe_2)_2$ and $Ru(S_2PMe_2)_2(PMe_2Ph)_2$ there is no change. This conductivity increase is attributed to the formation of the complex $[Ru(S_2PMe_2)(MeS_2PMe_2)(PMe_2Ph)_2CO]I$ by methylation of the unco-ordinated sulphur atom. Furthermore, the ^1H n.m.r. spectrum of the conducting solution is not significantly different from that of E, except for extra signals at τ6.46 (-SMe group) and τ7.93 (excess MeI) which strongly suggests that MeI is <u>not</u> reacting with a bound sulphur atom of a labile seven-co-ordinate species.

Examination of Figure 2.14 (page 97) indicates that neither structure I (already assigned to D) not structure IV (which has a plane

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* The irradiation frequencies given in Figure 2.15 (page 99) are different from the frequencies of the phosphorus nuclei obtained from the Fourier transform spectrum (Figure 2.16, page 100) because the former are obtained from the HA100 spectrometer (with Schlumberger FS30 frequency synthesiser attachment) whereas the latter are directly measured on the XL100 machine, and these have slightly different reference frequencies.

of symmetry making the PMe_2Ph groups equivalent) fit the ^1H and ^{31}P n.m.r. data. However, II and III are both possible structures since in both cases, hindered rotation about the ruthenium-phosphorus bonds is reasonable on steric grounds and furthermore, the ruthenium atom is potentially a chiral centre and thus, no matter how rapid the rotation about the Ru-S bond of the unidentate S_2PMe_2 ligand, the two Me groups will always remain inequivalent. However, III would be expected to have a ν_{CO} band in a similar position to that found in compounds C and D since the CO group is <u>trans</u> to a sulphur atom of a bidentate $^-S_2PR_2$ ligand whereas II should have a higher ν_{CO} since the CO group is <u>trans</u> to a stronger π-acceptor ligand and hence back donation into the π^* orbitals of the CO group will be reduced. The latter is experimentally the case (Table 2.3) and hence structure II is preferred. The analagous compounds $Ru(OCOR)_2(PPh_3)_2CO$ have recently been prepared[344] and are also thought (i.r. evidence) to have structures similar to II.

The heteronuclear decoupling information given in Figure 2.15, (page 99) determines which sets of methyl protons in E are attached to phosphorus atoms 1 to 4 (which are labelled in the order they occur in the ^{31}P n.m.r. spectrum (Figure 2.16, page 100). Assuming structure II is more feasible than III, then these phosphorus atoms can be assigned as follows:- P_1 and P_2 belong to the S_2PMe_2 groups and P_3 and P_4 to the PMe_2Ph groups. This assignment is based on the chemical shift positions of the ^{31}P nuclei compared with those in $Ru(S_2PMe_2)_2(CO)_2$ and $Ru(S_2PMe_2)_2(PMe_2Ph)_2$ (Figure 2.16, page 100) together with the fact that the lower field methyl doublets (which correspond to the S_2PMe_2 methyl resonances) are decoupled by irradiating at frequencies corresponding to phosphorus atoms

P_1 and P_2. In $Ru(S_2PMe_2)_2(PMe_2Ph)CO$, the separation between the methyl dithioacid group syn to PMe_2Ph and that syn to CO is 33Hz, which is close in value to the separation of the methyl groups 1 and $1'$ attached to P_1 (44Hz). In contrast, those attached to P_2 (2 and $2'$) are only separated by 6Hz. We therefore assign P_1 to the phosphorus atom of the bidentate S_2PMe_2 group and P_2 to the unidentate S_2PMe_2 group. Finally, since P_3 couples to P_1 whereas P_4 does not (Figure 2.16, page 100) it seems likely that P_3 is more nearly trans to P_1 than is P_4 and therefore P_3 and P_4 are assigned accordingly (see Figure 2.14, page 97, structure II).

The stereochemical pathway of the carbonylation mechanism is given in Figure 2.17 (page 104). Thus, E is formed by cleavage of the weakest Ru-S bond i.e. that trans to a PMe_2Ph group. This is consistent with the bond lengths found in cis - $Ru(S_2PEt_2)_2(PMe_2Ph)_2$, where the Ru-S bonds trans to the PMe_2Ph groups are ca 0.2Å longer than those trans to another sulphur atom (Appendix 2). This, incidentally, is another reason why structure II rather than III is preferred for E since to form the latter, the Ru-S bond trans to a sulphur atom must be broken. Next, steric repulsions, together with the favourable energy change associated with the conversion of unidentate to bidentate S_2PMe_2 co-ordination, results in the expulsion of a PMe_2Ph group and the formation of C. Finally, the high affinity of PMe_2Ph for ruthenium(II)[321] is demonstrated by its attack on the Ru-S bond trans to PMe_2Ph to give D. The inability of cis - $Ru(S_2PR_2)_2(PMe_2Ph)CO$ to give cis - $Ru(S_2PR_2)_2(CO)_2$ is presumably a reflection of the fact that the favourable steric change is more than offset by the unfavourable electronic change of replacing a $Ru\text{-}PMe_2Ph$ bond with a

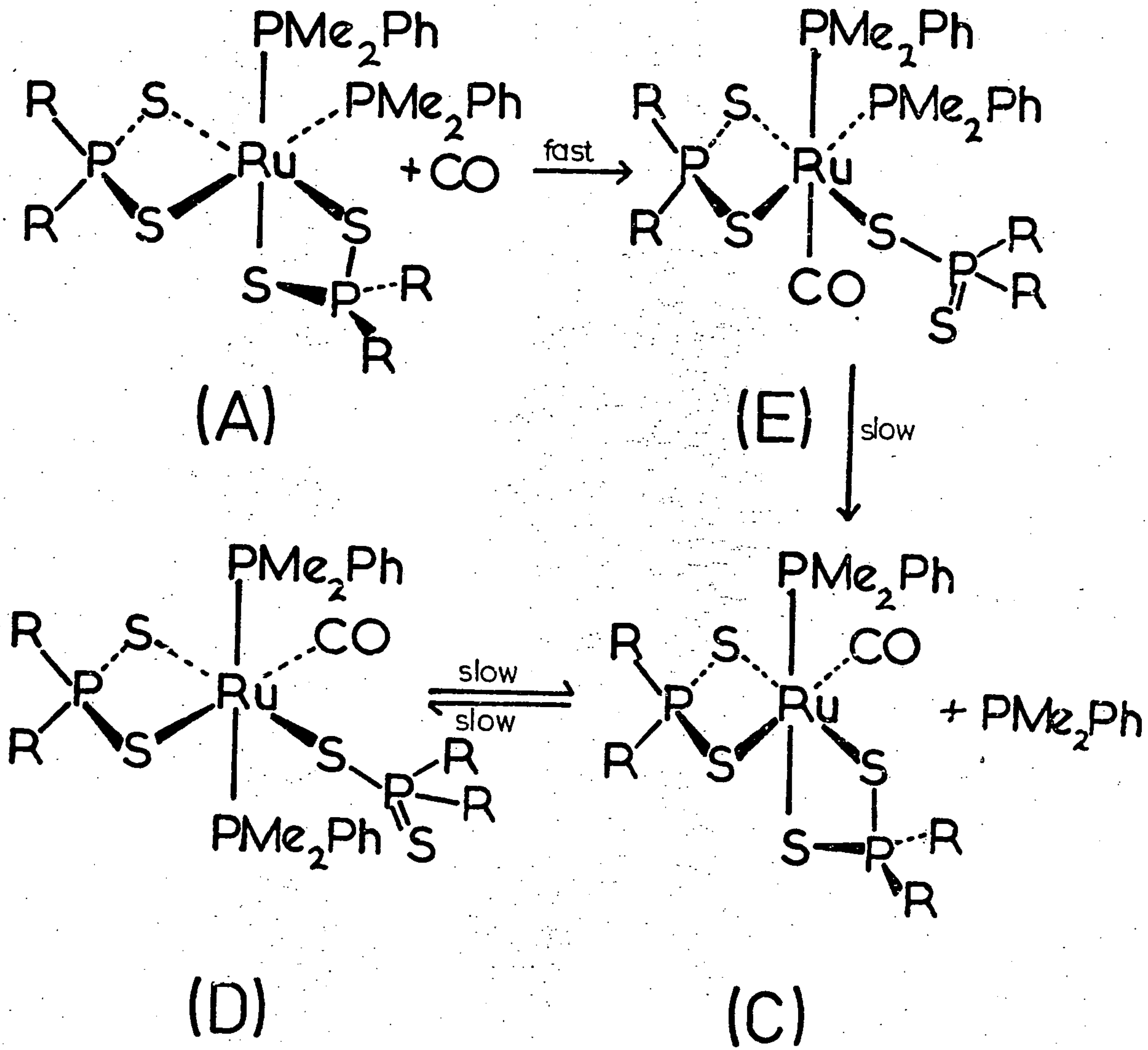

Fig. 2.17

Proposed mechanism for carbonylation of <u>cis</u> - $Ru(S_2PR_2)_2(PMe_2Ph)_2$

Ru-CO bond. This rationale is supported by the fact that <u>cis</u> - $Ru(S_2PMe_2)_2(CO)_2$ reacts with excess PMe_2Ph, even in the presence of CO to give D and with excess PPh_3 to give <u>cis</u> - $Ru(S_2PMe_2)_2(PPh_3)CO$. The failure to observe compounds of type D or E with ligands other than PMe_2Ph* is probably due to the smaller <u>trans</u> effects (tertiary phosphites) and nucleophilicities (tertiary phosphines) towards ruthenium (II) of these other ligands compared to PMe_2Ph[26], although doubtless a similar mechanism of carbonylation is applicable. It is also reasonable to postulate a similar mechanistic scheme for formation of the mixed ligand species $Ru(S_2PR_2)_2LL'$ although, again no intermediates of <u>type</u> E (or D) have been observed.

Finally, the unsuccessful attempts to carbonylate the <u>cis</u> - $Ru(S_2CNR_2)_2L_2$ complexes are probably due to the stronger nucleophilicity of S_2CNR_2 compared to S_2PR_2 (see page 95), preventing formation of a compound of type E.

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* The one possible exception is with $Ru(S_2PMe_2)_2(P(OMe)_3)_2$ where carbonylation gives a transient species with ν_{CO} 1997 cm^{-1} (type E!) but unfortunately, this could not be separated from starting material.

Experimental.

Microanalyses were by the National Physical Laboratory, Teddington, A. Bernhardt, West Germany and the University of Edinburgh Chemistry Department. Molecular weights were determined on a Perkin-Elmer Hitachi osmometer (model 115) at 37°. Infra-red spectra were recorded in the region 4000-250 cm^{-1} on a Perkin-Elmer 457 Grating Spectrometer using nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. Mass spectra were obtained on an AEI MS9 mass spectrometer and conductivity measurements on a model 310 Portland electronics conductivity bridge. ^{1}H n.m.r. spectra and solution magnetic moments (Evans' method)[319] were obtained on a Varian Associates HA-100 Spectrometer with variable temperature attachment. Accurate temperatures were determined using the separation of the two resonances of methanol (low temperature) and ethylene glycol (high temperature). Spectra were simulated using a computer program based on that of Nakagawa[345]. The exchange process was considered for the purpose of computation as consisting of n two site exchanges where n is the multiplicity of the resonances being monitored. The single line simulated spectra were then superimposed with suitable weighting for intensities and the results plotted out on the line printer. Thus, a doublet is considered as two two site exchanges of intensity ratio 1:1. The experimental spectra were fitted to the computed spectra either by finding the best fit between the ratio of maximum to minimum heights in the doublets (above and below coalescence) or the width of the signal at half height (around coalescence). Spin-spin relaxation times (T_2) were obtained for each compound by measurement of the peak width at half height under slow exchange conditions.

The same value of T_2 was used for all line-shape calculations on a given compound because for L = PMe_2Ph and $P(OMe)_3$, the widths at half height in the slow and fast exchange limits differed by less than 0.25Hz. Lifetimes obtained by these fitting procedures were then used to construct Arrhenius plots ($\log_{10}k$ vs $^1/_T$) to which straight lines were fitted by the least squares method. Activation parameters and errors were then calculated as in Appendix 1.

^{31}P n.m.r. spectra were recorded on a Varian XL100 spectrometer operating in the Pulse and Fourier Transform mode at 40.5M Hz. Heteronuclear decoupling experiments were carried out on the HA100 spectrometer using a second radio frequency field provided by the Schlumberger FS30 frequency synthesiser. Melting points were determined with a Köfler hot stage microscope and are uncorrected.

Materials: - Ruthenium trichloride trihydrate (Johnson Matthey); triphenylphosphine, dimethylphenylphosphine, triphenylphosphite, (BDH); methyldiphenylphosphine (strem); $PEtPh_2$, 1,2 bisdiphenylphosphinomethane[347] and 1,2 bisdiphenylphosphinoethane[346] were made by standard literature methods; carbon monoxide (Air products); bicyclo(2,2,1)-hepta-2,5-diene (Koch-Light); 1,5 cyclooctadiene (Ralph Emanuel); o-phenylenebisdimethylarsine (Aldrich); $NaS_2CNMe_2 2H_2O$ (Ralph Emanuel). Sodium diethyl[347]- and dimethylphosphinodithioates[119] were prepared by published methods and ammonium diphenylphosphinodithioate from Ph_2PS_2H and ammonia in benzene[119]. Operations involving free tertiary phosphines and phosphites (with the exception of $P(OPh)_3$ and PPh_3) were carried out under nitrogen. The various ruthenium (II) and (III) tertiary phosphine and phosphite complexes which were used as starting materials were synthesised by published methods.

Dialkyl (aryl) phosphinodithioate Complexes

cis - Bis(diphenylphosphinodithioato)bis(triphenylphosphine) ruthenium (II) -

$RuCl_2(PPh_3)_3$ (0.10g), $NH_4S_2PPh_2$ (0.12g) and PPh_3 (0.20g) were shaken in acetone (25ml) for 30 min. and then the resulting red crystals filtered off, washed with water, acetone and n-pentane. (Yield 0.10g, 85%). However, if the reaction is carried out in the absence of excess PPh_3, the resulting red, crystalline precipitate gave a consistently low analysis for the bis-phosphine complex. Found:- C,60.1; H,4.2%; $Ru(S_2PPh_2)_2(PPh_3)_2$ requires C,64.1; H,4.5% and Bis(diphenylphosphinodithioato) (triphenylphosphine) ruthenium (II) 0.5 acetone requires C,58.6; H,4.3% . Furthermore, the molecular weight of the product in benzene, over a short period of time, decreased from 697 to 649, values indicative of the facile dissociation of $Ru(S_2PPh_2)_2(PPh_3)_2$ (M,1123) to $Ru(S_2PPh_2)_2PPh_3$ (M.861) and free PPh_3 in solution. However, by refluxing a mixture of $RuCl_2(PPh_3)_3$ (0.10g), $NH_4S_2PPh_2$(0.12g) and sulphur (0.003g) in acetone, a pure sample of $Ru(S_2PPh_2)_2PPh_3$ (0.06g, 72%) was isolated. Found: - C,58.1; H,4.1% .

cis - Bis(dimethylphosphinodithioato)bis(triphenylphosphine) ruthenium (II):- $RuCl_3(PPh_3)_2MeNO_2$ (0.04g), NaS_2PMe_2(0.04g) and PPh_3(0.04g) were shaken overnight in ethanol (10 ml). The resultant brown, crystalline precipitate was filtered off, washed with water, ethanol and n-pentane to give red-brown needles of the complex (0.04g, 90%). The same compound was also prepared from $RuCl_2(PPh_3)_3$ (0.25g) and NaS_2PMe_2(0.15g) in acetone solution (0.21g, 92%). Similarly, cis - Bis(diethylphosphinodithioato)bis(triphenylphosphine) ruthenium (II) was prepared from $RuCl_2(PPh_3)_3$ (0.25g) and NaS_2PEt_2 (0.12g).

cis-Bis(dimethylphosphinodithioato)bis(ethyldiphenylphosphine) ruthenium (II) $RuCl_2(PEtPh_2)_3$ was shaken in ethanol for 12 hours with a three fold excess of NaS_2PMe_2 to give the orange crystalline complex (73%).

The compounds in Table 2.1 were prepared by the following general method. The starting materials were refluxed in ethanol for the time shown and then the solution cooled and filtered. The crystals obtained were washed with water, ethanol, n-pentane and dried in vacuo (40^o).

If $[Ru_2Cl_3(PMePh_2)_6]Cl$(0.60g) and NaS_2PMe_2(0.30g) are refluxed in methanol (15 ml) for 24 hours, an orange crystalline solid is precipitated. Dissolution in a minimum volumn of benzene and chromatography on a dry alumina column gives an orange and a red band. Both bands may be extracted with diethylether, evaporated to dryness and recrystallised from CH_2Cl_2/n-pentane, the orange band giving cis - $Ru(S_2PMe_2)_2(PMePh_2)_2$ whilst the red gives $Ru_2Cl_3(PMePh_2)_5(S_2PMe_2)$ (0.07g, 11.0%) Found: - C,56.1, H5.0%; Required C,56.1; H5.0% .

cis-Bis(dimethylphosphinodithioato)bis(methyldiphenylphosphine) ruthenium (II) may also be prepared by the reaction of cis - $Ru(S_2PMe_2)_2$-$(PPh_3)_2$(0.05g) with $PMePh_2$(0.10 ml) in refluxing ethanol (15 ml) for 12 hours. Cooling the solution gives orange crystals of the complex (0.03g; 70%).

cis-Bis(dimethylphosphinodithioato)bis(dimethylphenylphosphine) ruthenium (II) may be prepared in two other ways:- a) cis - $Ru(S_2PMe_2)_2(PMePh_2)_2$ (0.05g) and PMe_2Ph (0.05 ml) were refluxed in ethanol (20 ml) for 4 hours. Cooling the solution and partial removal of solvent gave orange crystals of the complex which were filtered off, washed with n-pentane and dried in vacuo (0.02g; 48%). b) cis - $Ru(S_2PMe_2)_2(PPh_3)_2$ (0.10g) and PMe_2Ph (0.03 ml) were refluxed in acetone for one hour. Removal of the solvent gave an orange oil from which the product was obtained by recrystallisation from CH_2Cl_2/n-pentane (0.05g; 70%)

Bis(dimethylphosphinodithioato)(bicyclo(2,2,1)hepta-2,5-diene) ruthenium (II) was also prepared by addition of $\{RuCl_2(C_7H_8\}_n$(0.26g) to a hot solution of NaS_2PMe_2(0.29g) in dimethylformamide (8 ml). After cooling and addition of water, the brown solid was filtered off and recrystallised from aqueous acetone as orange crystals (0.17g, 41%).

Bis(dimethylphosphinodithioato)(cyclo-octa-1,5-diene) ruthenium (II) was prepared similarly from $\{RuCl_2C_8H_{12}\}_n$ (0.28g) and NaS_2PMe_2 (0.29g) as orange crystals.

Bis(dimethylphosphinodithioato)(1,2-bisdiphenylphosphinoethane) ruthenium (II) was also prepared by refluxing $Ru(S_2PMe_2)_2(C_7H_8)$(0.11g) with diphos (0.1g) in degassed acetone for 24 hours. After cooling, the orange solution was concentrated and the orange crystals collected and recrystallised from CH_2Cl_2/n-hexane (1.0g, 58%). Similarly, Bis(dimethylphosphinodithioato)(bisdiphenylphosphinomethane) ruthenium (II) was prepared by shaking $Ru(S_2PMe_2)_2(C_7H_8)$ (0.05g) with $(Ph_2P)_2CH_2$ (0.1g) in ethanol (20 ml) under Nitrogen. The orange crystalline solid was filtered and dried (0.13g, 80%); and trans-bis(dimethylphosphinodithioato) bis(o-phenylenebisdimethylarsine) ruthenium (II) was prepared by refluxing $Ru(S_2PMe_2)_2(C_7H_8)$(0.05g) and diars (0.2 mls) in degassed ethanol (10 mls) for 10 minutes. The complex separated as pink crystals (0.085g, 97%) but recrystallisation from boiling toluene gave orange crystals of bis(dimethylphosphinodithioato)(o-phenylenebisdimethylarsine) ruthenium II in 100% yield.

Reaction of $RuCl_2(P(OPh)_3)_4$ (0.60g) and NaS_2PMe_2 (0.48g) in ethanol (25 ml) under reflux for 5 hours gave a yellow solution. The solution was filtered hot, concentrated and allowed to crystallise overnight to give a yellow solid. Mass spectrum:- $^m/_e$ 876, (^{102}Ru isotope) $[Ru(S_2PMe_2)_2(P(OPh)_2OEt)_2]^+$; 828, $[Ru(S_2PMe_2)_2(P(OPh)_2OEt)-(P(OPh)(OEt)_2]^+$; 780, $[Ru(S_2PMe_2)_2(P(OEt)_2OPh)_2]^+$ etc.

<u>^{1}H n.m.r.</u> (223K); $Ru(S_2PMe_2)_2(P(OPh)_2OEt)_2$; τ 7.89 (12.5), 8.20 (12.5) S_2PMe_2 ; τ 6.08, 8.97 (6.0) Et groups : $Ru(S_2PMe_2)_2(P\ OPh(OEt)_2)_2$; τ 7.91, 8.13 ($^-S_2PMe_2$); τ 5.93, 8.80 (6.0) Et groups - Intensity ratio 6:1.

<u>Analysis</u>:- Found:- C,42.9; H,4.9% $Ru(S_2PMe_2)_2(P(OPh)_2OEt)_2$ requires C,43.9; H,48%: $Ru(S_2PMe_2)_2(POPh(OEt)_2)_2$ requires C,37.0; H,5.4%. For 6:1 ratio, calculated analysis is C,42.9; H,4.9%.

Reaction of $RuCl_2(P(OPh)_3)_4$ with NaS_2PMe_2 in refluxing ethanol for 24 hours gives, on solvent removal, an oil with mass spectral peaks $^m/_e$ 828, $[Ru(S_2PMe_2)_2(P(OPh)_2OEt)_2]^+$; 780, $[Ru(S_2PMe_2)_2(P(OEt)_2OPh)_2]^+$; 732, $[Ru(S_2PMe_2)_2(P(OEt)_2CPh)(P(OEt)_3)]^+$; 684, $[Ru(S_2PMe_2)_2(P(OEt)_3)_2]^+$ <u>etc.</u>

<u>cis-Bis(dimethylphosphinodithioato)bis(trimethylphosphite) ruthenium (II)</u>:- $RuCl_2(P(OPh)_3)_4$ (0.50g) and NaS_2PMe_2 (0.30g) were refluxed in methanol (30 ml) for 3 hours. The resultant yellow solution was filtered hot, and after concentration, allowed to slowly crystallise at 273K for 10 days. The orange crystals so formed were filtered and washed with water, methanol and n-pentane (0.06g, 28%). On further solvent removal from the filtrate, an oily white solid was deposited which on recrystallisation was identified as phenol (by its ^{1}H n.m.r. spectrum). The ruthenium complex rapidly decomposed on air exposure to give a black solid.

<u>cis - Bis(dimethylphosphinodithioato)(triphenylphosphine)(triphenylphosphite) ruthenium (II)</u> <u>cis</u> - $Ru(S_2PMe_2)_2(PPh_3)_2$ (0.08g) and $P(OPh)_3$ (0.05 ml) were refluxed in ethanol (15 ml) for 3 hours. The solution was cooled and the precipitated orange <u>solid</u> washed with ethanol and n-pentane (0.03g, 35%). The yellow filtrate was allowed to crystallise overnight to give a sample of <u>cis</u> - $Ru(S_2PMe_2)_2(P(OPh)_3)_2$ (0.04g, 45%).

cis - Bis(dimethylphosphinodithioato)(dimethylphenylphosphine)(triphenylphosphite) ruthenium (II):- cis - $Ru(S_2PMe_2)_2(PMe_2Ph)_2$ (0.20g) was refluxed with $P(OPh)_3$ (1.2 ml) in ethanol for 1 hour. Then, after concentration and standing for two days at 273K, orange crystals were deposited which were filtered off and washed with ethanol and n-pentane (0.10g, 39%).

cis - Bis(diphenylphosphinodithioato)(dimethylphenylphosphine)(triphenylphosphite) ruthenium (II):- cis - $Ru(S_2PPh_2)_2(PMe_2Ph)_2$ (0.20g) and $P(OPh)_3$ (0.3 ml) were shaken in dichloromethane (20 ml) for 7 days. After filtration and addition of n-pentane, the resultant orange solution was concentrated until orange crystals were deposited. These were filtered off and washed with n-pentane (0.07g, 29%).

cis - Bis(dimethylphosphinodithioato)carbonyl(triphenylphosphine) ruthenium (II):-

a) cis - $Ru(S_2PMe_2)_2(PPh_3)_2$ (0.10g) and PPh_3(0.40g) were carbonylated in refluxing ethanol for two hours. The resulting orange solution was evaporated to dryness and the residue recrystallised from CH_2Cl_2/light petroleum (bp60-80°) to give orange crystals of the complex (0.03g, 41%).

b) cis - $Ru(S_2PMe_2)_2(CO)_2$ (0.02g) and PPh_3(0.04g) were refluxed in ethanol (25 ml) for two hours. Removal of solvent gave an orange oil which was redissolved in diethylether and after leaving at 273K for 12 hours, orange crystals of the product were deposited (0.03g, 92%).

c) cis - $RuCl_2(CO)_2(PPh_3)_2$ (0.13g) and NaS_2PMe_2(0.26g) were refluxed in acetone (20 ml) for 60 hours. The resultant solution was filtered, evaporated to dryness and then chromatographed on a dry silica column[22], using benzene as eluent. One orange band was observed and the central portion of the band was extracted with diethylether. The resulting yellow solution was evaporated to dryness and the residue recrystallised from CH_2Cl_2/n-pentane to give orange crystals of the complex (0.08g, 73%).

cis - Bis(dimethylphosphinodithioato)carbonyl(triphenylarsine) ruthenium (II):- cis - $RuCl_2(CO)_2(AsPh_3)_2$ (0.06g) and NaS_2PMe_2 (0.09g) were refluxed in acetone (25 ml) for 4 days with no apparent reaction. The mixture was then shaken for 3 weeks to give an orange solution and a white precipitate. After filtration, the solution was evaporated to dryness and the resulting orange oil chromatographed on a dry alumina column[22] using benzene as eluent and washing off the orange band with diethylether. Evaporation of the ethereal solution and recrystallisation from CH_2Cl_2/n-pentane gave the orange complex (0.03g, 61%).

cis - Bis(dimethylphosphinodithioato)carbonyl(methyldiphenylphosphine) ruthenium (II):- cis - $Ru(S_2PMe_2)_2(PMePh_2)_2$ (0.10g) was carbonylated in cold CH_2Cl_2 for one minute. The yellow orange solution was evaporated to dryness and the product recrystallised from CH_2Cl_2/n-pentane to give the orange crystalline complex (0.03g, 37%). Similarly, carbonylation of cis - $Ru(S_2PMe_2)_2(P(OMe)_3)_2$ (0.05g) in CH_2Cl_2 for 10 minutes and recrystallisation from CH_2Cl_2/hexane gave yellow crystals of cis - Bis(dimethylphosphinodithioato)carbonyl (trimethylphosphite) ruthenium (II) (0.01g, 25%) whereas carbonylation of cis - $Ru(S_2PMe_2)_2(P(OPh)_3)_2$ (0.07g) in refluxing acetone for 4 hours gave after recrystallisation from CH_2Cl_2/n-pentane, yellow crystals of cis - Bis(dimethylphosphinodithioato)carbonyl(triphenylphosphite) ruthenium (II) (0.03g, 60%).

cis-Bis(dimethylphosphinodithioato)carbonyl(dimethylphenylphosphine) ruthenium (II) (C) and Bis(dimethylphosphinodithioato)carbonyl bis (dimethylphenylphosphine) ruthenium (II) (D)

cis - $Ru(S_2PMe_2)_2(PMe_2Ph)_2$ (0.20g) was carbonylated in refluxing acetone for ca 1 hour and the resulting solution evaported to dryness.

The residue was chromatographed on a dry alumine column using benzene and gave a yellow band (r.f. value ca 0.5) and an orange band (r.f. value ca 0.1) which were removed separately with diethyl ether, evaported to dryness and recrystallised from CH_2Cl_2/n-pentane. The yellow band consisted of cis - $Ru(S_2PMe_2)_2(PMe_2Ph)CO$ (0.01g, 6%) and the orange $Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$ (configuration D) (0.15g, 80%).

If cis- $Ru(S_2PMe_2)_2(PMe_2Ph)_2$ (0.10g) and sulphur (0.05g) were carbonylated in refluxing benzene for 6 hours, a t.l.c. of the resulting orange solution showed a single orange band together with a yellow band with the same r.f. value as sulphur. The solution was evaporated to dryness to give an orange oil. This was dissolved in diethylether and after filtering off excess sulphur, left overnight at 273K when orange crystals of cis - $Ru(S_2PMe_2)_2(PMe_2Ph)CO$ (0.05g, 60%) were deposited.

cis- $Ru(S_2PMe_2)_2(CO)_2$ (0.10g) was suspended in ethanol (50 ml), presaturated with carbon monoxide and PMe_2Ph (0.14 ml) added. The solution was then refluxed in a stream of CO for 2 hours to give an orange solution which on leaving overnight at 273K gave only $Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$ (D) (0.08g, 50%).

Bis(dimethylphosphinodithioato)carbonyl bis(dimethylphenylphosphine) ruthenium (II) (E):- cis - $Ru(S_2PMe_2)_2(PMe_2Ph)_2$ (0.20g) was dissolved in CH_2Cl_2 (10 ml) and carbon monoxide passed through the solution for 45 secs. The resulting yellow solution was evaporated to dryness under vacuum at 273K and the residue recrystallised by dissolving in a minimum amount of CH_2Cl_2 and adding excess diethylether (0.15g, 80%).

cis-Bis(diphenylphosphinodithioato)carbonyl(dimethylphenylphosphine) ruthenium (II) (C):- cis- $Ru(S_2PPh_2)_2(PMe_2Ph)_2$ (0.35g) was dissolved in CH_2Cl_2 (30 ml) and carbonylated for 1 hour at room temperature. The yellow solution formed was evaporated to dryness and eluted from a dry silica column with CH_2Cl_2. Two yellow bands were found and the first was extracted with CH_2Cl_2 and the solution evaporated to dryness to give the crystalline product (0.04g, 13%). The other band was removed with diethylether, the solution evaporated to dryness and the residue recrystallised from CH_2Cl_2/light petroleum (bp 40-60°) to give $Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$ (mixture of isomers D and E) (0.05g, 14%).

Bis(diphenylphosphinodithioato)carbonyl bis(dimethylphenylphosphine) ruthenium (II) (D):- cis- $Ru(S_2PPh_2)_2(PMe_2Ph)_2$ (0.30g) was carbonylated in refluxing ethanol (40 ml) for two hours to give a yellow solution. Concentration to dryness, followed by chromatography on a dry alumina column with benzene gave two bands. The first was eluted with diethylether, evaporated to dryness and the residue recrystallised from benzene/light petroleum (bp 100-120°) to give a very small amount of cis- $Ru(S_2PPh_2)_2(PMe_2Ph)CO$. The second (more intense) orange band was also eluted with diethylether and after evaporation to dryness (in the cold) was recrystallised from benzene/n-pentane to give the required product (0.10g, 31%).

Bis(diphenylphosphinodithioato)carbonyl bis(dimethylphenylphosphine) ruthenium (II) (E):- *cis*- $Ru(S_2PPh_2)_2(PMe_2Ph)_2$ (0.20g) was carbonylated for one minute in cold CH_2Cl_2. Then, pentane was added and the resulting orange solution evaporated to dryness and the orange solid collected without further purification (0.21g, 100%).

cis-Bis(dimethylphosphinodithioato)bis(carbonyl)ruthenium (II):-

a) *cis*-$Cs_2[RuCl_4(CO)_2]$ (0.50g) and NaS_2PMe_2 (0.50g) were refluxed in ethanol (20 ml) for six hours to give a yellow solution. After filtration, this was cooled giving yellow *crystals* which were washed with water, ethanol and n-pentane (0.14g, 39%). b) CO was passed through a solution of $Ru(S_2PMe_2)_2(C_7H_8)$ (0.19) for three hours. The resulting yellow solution was concentrated and allowed to crystallise to give the complex (0.065g, 70%).

cis-Bis(diphenylphosphinodithioato)bis(carbonyl)ruthenium (II):-

$Ru_3(CO)_{12}$ and excess Ph_2PS_2H were refluxed together in tetrahydrofuran for 18 hours. The resulting yellow solution was evaporated to dryness, the residue extracted with diethylether and crystallised at 273K to give the yellow *product*.

N.N.- Dimethyldithiocarbamate Complexes

cis-Bis(dimethyldithiocarbamato)bis(triphenylphosphine)ruthenium (II) Acetone:- $RuCl_2(PPh_3)_3$ (0.26g) and $NaS_2CNMe_22H_2O$ (0.15g) were shaken in acetone (25 ml) for two days. The solution was then filtered and the orange crystals washed with water, diethylether and dried in *vacuo* at 40°.

cis-Bis(dimethyldithiocarbamato)bis(dimethylphenylphosphine)ruthenium (II):-

mer- $RuCl_3(PMe_2Ph)_3$ (0.16g) and $NaS_2CNMe_22H_2O$ (0.16g) were shaken in degassed CH_2Cl_2 under nitrogen for eight hours. The resulting greenish-yellow solution was filtered to remove any precipitated sodium chloride and evaporated to dryness. Chromatography on a dry alumina column with benzene gave an intense yellow band (ca r.f. value 0.6) together with a number of weaker bonds of lower r.f. value. The yellow band was removed with diethyl ether, giving on removal of solvent the yellow product (0.13g, 88%).

trans-Bis(dimethyldithiocarbamato)bis(dimethylphenylphosphine) ruthenium (II):- cis- $Ru(S_2CNMe_2)_2(PPh_3)_2$ (0.20g) was refluxed with PMe_2Ph (0.15 ml) in ethanol (20 ml) for 12 hours. The resulting yellow solution was filtered hot and allowed to crystallise. The first crop of yellow crystals were filtered off, washed with ethanol and n-pentane to give the desired product (0.03g, 21%). The yellow filtrate later deposited more crystals shown to be cis- $Ru(S_2CNMe_2)_2(PMe_2Ph)_2$ (0.10g, 71%).

cis-Bis(dimethyldithiocarbamato)bis(triphenylphosphite)ruthenium (II):- $RuCl_2(P(OPh)_3)_4$ (0.20g) and $NaS_2CNMe_2 2H_2O$ (0.16g) were refluxed in ethanol (15 ml) for one hour. The resulting yellow solution was filtered hot and on cooling give yellow crystals of the product (0.06g, 41%).

cis-Bis(dimethyldithiocarbamato)(triphenylphosphine)(triphenylphosphite) ruthenium (II):- cis- $Ru(S_2CNMe_2)_2(PPh_3)_2$ (0.10g) and $P(OPh)_3$ (0.04 ml) in refluxing CH_2Cl_2 gave an orange solution. Addition of ethanol and evaporation of CH_2Cl_2 gave the yellow crystalline product which was washed with ethanol and n-pentane (0.07g, 69%).

cis-Bis(dimethyldithiocarbamato)biscarbonyl ruthenium (II):-

a) $Ru_3(CO)_{12}$ (0.20g) and tetramethylthiuramdisulphide (0.40g) were refluxed in ethanol (15 ml) for 2 hours. On cooling, the yellow solution gave the yellow crystalline product (0.20g, 54%).

b) <u>cis</u>- $RuCl_2(CO)_2(PPh_3)_2$ (0.10g) and $NaS_2CNMe_22H_2O$ (0.20g) were refluxed in ethanol (20 ml) for seven days. The resulting pale yellow solution was filtered, chromatographed on a dry alumina column with benzene and the yellow band extracted with diethylether. Removal of solvent and recrystallisation from hexane gave the <u>product</u> (0.001g, 2%).

TABLE 2.1

Preparative methods for some ruthenium complexes (see page 108)

Starting materials	Vol. EtOH	Reaction Time	Yield	Product
mer- $RuCl_3(PMePh_2)_3$ (0.20g) and $NH_4S_2PPh_2$(0.25g)	50 ml	4 h	0.14g (56%)	*cis*- $Ru(S_2PPh_2)_2(PMePh_2)_2$
$[Ru_2Cl_3(PMePh_2)_6]Cl$(0.08g) and NaS_2PMe_2(0.10g)	20 ml	1 h	0.05g (62%)	*cis*- $Ru(S_2PMe_2)_2(PMePh_2)_2$
mer- $RuCl_3(PMe_2Ph)_3$ (0.5g) and $NH_4S_2PPh_2$(1.0g)	70 ml	3 h	0.70g (100%)	*cis*- $Ru(S_2PPh_2)_2(PMe_2Ph)_2$
mer- $RuCl_3(PMe_2Ph)_3$ (0.70g) and NaS_2PMe_2(0.70g)	70 ml	15 m	0.70g (100%)	*cis*- $Ru(S_2PMe_2)_2(PMe_2Ph)_2$
$RuCl_2(P(OPh)_3)_4$ (0.80g) and NaS_2PMe_2(0.60g)	20 ml	1 h	0.25g (46%)	*cis*- $Ru(S_2PMe_2)_2(P(OPh)_3)_2$
mer- $RuCl_3(PMe_2Ph)_3$ (0.50g) and NaS_2PEt_2(0.90g)	25 ml	3 h	0.39g (71%)	*cis*- $Ru(S_2PEt_2)_2(PMe_2Ph)_2$
$\{RuCl_2C_7H_8\}_n$(0.2g) and NaS_2PMe_2(0.4g)	25 ml	5 h	0. 2g (60%)	$Ru(S_2PMe_2)_2(C_7H_8)$
trans $RuCl_2(diphos)_2$(0.2g) and NaS_2PMe_2 (0.2g)	25 ml	24 h	0.06g (39%)	$Ru(S_2PMe_2)_2$ diphos

TABLE 2.2

Analytical Data for Some Ruthenium Complexes

Complex	Colour	Mp(°C)	Found % C	Found % H	Found % Others	Found % M	Required % C	Required % H	Required % Others	Required % M
cis- $Ru(S_2PPh_2)_2(PPh_3)_2$	Red	193-195	64.2	4.7			64.1	4.5		
cis- $Ru(S_2PPh_2)_2(PMePh_2)_2$	Orange	116-118	60.1	4.4			60.1	4.6		
cis- $Ru(S_2PPh_2)_2(PMe_2Ph)_2$	Orange	247-248	54.7	4.7	S,14.8;P.14.2		54.7	4.8	S,14.6;P,14.2	
cis- $Ru(S_2PMe_2)_2(PPh_3)_2$	Red-Brown	139-142	54.7	4.7			54.9	4.8		
cis- $Ru(S_2PMe_2)_2(PMePh_2)_2$	Orange	279-280(d)	47.8	5.0			47.9	5.1		
cis- $Ru(S_2PMe_2)_2(PMe_2Ph)_2$	Orange	212(d)	38.3	5.2	S,20.6;P.19.6	618[a]	38.3	5.4	S,20.6;P,19.8	627
cis- $Ru(S_2PMe_2)_2(P(OPh)_3)_2$	Yellow	145-147	49.3	4.6		973±5[b]	49.4	4.3		971
cis- $Ru(S_2PMe_2)_2(P(OMe)_3)_2$	Yellow	213-214	20.1	5.0		599[a]	20.0	5.0		599
cis- $Ru(S_2PMe_2)_2(PEtPh_2)_2$	Orange	158	48.7	5.6			49.3	5.4		
$Ru(S_2PMe_2)_2$(diphos)	Orange	228-230	47.7	4.9		749[b]	48.0	4.8		749
$Ru(S_2PMe_2)_2(Ph_2PCH_2PPh_2)$	Orange	230-233(d)	47.5	4.8			47.3	4.6		
$Ru(S_2PMe_2)_2$(diars)	Orange	238-240(d)	28.6	4.3			26.4	4.4		
trans-$Ru(S_2PMe_2)_2(diars)_2$	Pink	236-237(d)	31.3	4.9			31.2	4.8		
cis-$Ru(S_2PEt_2)_2(PPh_3)_2$	Red	124-126	56.3	5.3			56.7	5.4		
cis- $Ru(S_2PEt_2)_2(PMe_2PH)_2$	Red	156-157	42.7	6.1	S,18.9		42.2	6.1	S,18.7	
cis- $Ru(S_2CNMe_2)_2(P(OPh)_3)_2$	Yellow	150-152	51.7	4.5			52.4	4.4		
cis- $Ru(S_2CNMe_2)_2(PPh_3)_2\ Me_2CO$	Yellow	168-169	58.1	4.8	N,3.3		58.3	4.9	N,3.2	
cis- $Ru(S_2CNMe_2)_2(PMe_2Ph)_2$	Yellow	204-206	42.8	5.5	N,4.7;S,20.6,P,10.1		42.8	5.5	N,4.5;S,20.7P,10.0	
trans- $Ru(S_2CNMe_2)_2(PMe_2Ph)_2$	Yellow		42.8	5.5	N,4.8		42.8	5.5		

TABLE 2.2 (CONTD.)

Complex	Colour	Mp (°C)	Found %				Required %			
			C	H	Others	M	C	H	Others	M
cis- $Ru(S_2PMe_2)_2(PPh_3)(P(OPh)_3)$	Orange	182-184	51.1	4.5			52.0	4.6		
cis- $Ru(S_2PMe_2)_2(PMe_2Ph)(P(OPh)_3)$	Orange	124-125	44.4	4.7			45.0	4.8		
cis- $Ru(S_2PPh_2)_2(PMe_2Ph)(P(OPh)_3)$	Orange	182-184	56.9	4.6			57.3	4.4		
cis- $Ru(S_2CNMe_2)_2(PPh_3)(P(OPh)_3)$	Yellow	201-204	55.0	4.6	N,3.1		55.2	4.6	N,3.1	
cis- $Ru(S_2PPh_2)_2(PMe_2Ph)CO$	Orange	194-195	51.6	4.0		763 ± 3^b	51.7	4.1		766
cis- $Ru(S_2PMe_2)_2(PPh_3)CO$	Orange	123-125	43.3	4.3		720^a 638 ± 3^b	43.1	4.2		641
cis- $Ru(S_2PMe_2)_2(PMePh_2)CO$	Orange	161-163	37.3	4.4		579 ± 1^b	37.3	4.3		579
cis- $Ru(S_2PMe_2)_2(PMe_2Ph)CO$	Yellow	43- 44	30.2	4.6		478^a 517 ± 1^b	30.2	4.5		517
cis- $Ru(S_2PMe_2)_2(P(OPh)_3)CO$	Yellow	193-194	40.0	3.9		689 ± 1^b	40.1	3.9		689
cis- $Ru(S_2PMe_2)_2(P(OMe)_3)CO$	Yellow	117-119	19.3	4.4		502 ± 1^b	19.1	4.2		503
cis- $Ru(S_2PMe_2)_2(AsPh_3)CO$	Orange	104-106	40.8	4.3		687 ± 2^b	40.3	3.9		685
$Ru(S_2PPh_2)_2(PMe_2Ph)_2CO$ [d]	Yellow	95-115(d)	53.9	4.7			54.5	4.7		
$Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$ [d]	Yellow	134-135(d)	38.2	5.2			38.5	5.2		
$Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$ [e]	Yellow	102-118(d)	38.7	5.1			38.5	5.2		
cis- $Ru(S_2PPh_2)_2(CO)_2$	Yellow	89- 90	47.8	3.2		655 ± 1^b	47.6	3.1		655
cis- $Ru(S_2PMe_2)_2(CO)_2$	Yellow	159-160	17.9	3.0		407 ± 1^b	17.7	2.9		407
cis- $Ru(S_2CNMe_2)_2(CO)_2$	Yellow	230-231[f]	24.5	3.1	N,7.2		24.8	3.0	N,7.1	
$Ru(S_2PMe_2)_2(C_7H_8)$	Orange	167-170	29.9	4.6		443 ± 1^b	29.8	4.5		443
$Ru(S_2PMe_2)_2(C_8H_{12})$	Orange	184-185	30.7	5.1		459 ± 1^b	31.3	5.2		459

a) Molecular weight measured osmometrically at 37° (C_6H_6)

b) Molecular weight from parent ion peak (^{101}Ru isotope) in mass spectrum

c) Sublimes at 160°C

d) Configuration D

e) Configuration E

f) Sublimes at 170°C

TABLE 2.3

Infrared Spectra of Various Ruthenium Dithioacid Complexes

(shoulders are underlined)

	$^-S_2PR_2$ bands (cm^{-1})			
Complex	Bidentate	Unidentate	ν_{CO} (cm^{-1})	δ_{CO} (cm^{-1})
cis- $Ru(S_2PMe_2)_2(PPh_3)_2$	583			
cis- $Ru(S_2PMe_2)_2(PMePh_2)_2$	587			
cis- $Ru(S_2PMe_2)_2(PMe_2Ph)_2$	588			
cis- $Ru(S_2PMe_2)_2(P(OPh)_3)_2$	589			
cis- $Ru(S_2PMe_2)_2(P(OMe)_3)_2$	589			
$Ru(S_2PMe_2)_2$(diphos)	585			
$Ru(S_2PMe_2)_2(Ph_2PCH_2PPh_2)$	589			
$Ru(S_2PMe_2)_2$(diars)	580			
trans-$Ru(S_2PMe_2)_2(diars)_2$	600,$\underline{595}$			
cis- $Ru(S_2PMe_2)_2(PPh_3)(P(OPh)_3)$	589			
cis- $Ru(S_2PMe_2)_2(PMe_2Ph)CO$	570		1933(1945)[a]	564
$Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$[b]	589,579	600	1939,$\underline{1929}$(1940)[a]	569
$Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$[c]	580	598	1961,1944(1967)[a]	569
cis- $Ru(S_2PMe_2)_2(PPh_3)CO$	581		1934	569
cis- $Ru(S_2PMe_2)_2(PMePh_2)CO$	581		1930	569
cis- $Ru(S_2PMe_2)_2(P(OMe)_3)CO$	581		$\underline{1955}$,1938	563
cis- $Ru(S_2PMe_2)_2(CO)_2$	582		2045,1989,1970 (2042,1967)[a]	610,562
$Ru(S_2PMe_2)_2(C_7H_8)$	589			
$Ru(S_2PMe_2)_2(C_8H_{12})$	591			
cis- $Ru(S_2PPh_2)_2(PPh_3)_2$	606,572,568			
cis- $Ru(S_2PPh_2)_2(PMePh_2)_2$	609,570			
cis- $Ru(S_2PPh_2)_2(PMe_2Ph)_2$	611,573			
cis- $Ru(S_2PPh_2)_2(PMe_2Ph)(P(OPh)_3)$	609,572,568			
cis- $Ru(S_2PPh_2)_2(PMe_2Ph)CO$	610,570		1920(1948)[d]	568
$Ru(S_2PPh_2)_2(PMe_2Ph)_2CO$[b]	611,570	645,540	1939(1946)[d]	579
$Ru(S_2PPh_2)_2(PMe_2Ph)_2CO$[c]	607,565	645,542	1989(1984)[d]	551
cis- $Ru(S_2PPh_2)_2(CO)_2$	608,568		(2030,1960)[a]	612,560

[a] Measured in $CHCl_3$ solution

[b] Configuration D

[c] Configuration E

[d] Measured in $CDCl_3$ solution

TABLE 2.4

Main peaks in the Mass Spectrum of $Ru(S_2PMe_2)_2(P(OMe)_3)_2$

Mass No. of Ru^{102} peak[a]		Probable Ion
600		$[Ru(S_2PMe_2)_2(P(OMe)_3)_2]^+$
585		$[Ru(S_2PMe_2)_2(P(OMe)_3)(P(OMe)_2O)]^+$
569		$[Ru(S_2PMe_2)_2(P(OMe)_3)(P(OMe)_2)]^+$
507		$[Ru(S_2PMe_2)_2(P(OMe)_3)P]^+$
492		$[Ru(S_2PMe_2)_2(P(OMe)_2O)P]^+$
476		$[Ru(S_2PMe_2)_2P(OMe)_3]^+$
	or	$[Ru(S_2PMe_2)_2P(OMe)_2P]^+$
461		$[Ru(S_2PMe_2)_2P(OMe)_2O]^+$
	or	$[Ru(S_2PMe_2)_2P(OMe)OP]^+$
445		$[Ru(S_2PMe_2)_2P(OMe)_2]^+$
	or	$[Ru(S_2PMe_2)_2(P(OMe))P]^+$
383		$[Ru(S_2PMe_2)_2\ P]^+$
377 (metastable)		600 ⟶ 476
352		$[Ru(S_2PMe_2)_2]^+$

[a] All peaks show the characteristic ruthenium isotopic pattern

TABLE 2.5

Main Peaks in the Mass Spectrum of $Ru(S_2PMe_2)_2(P(OPh)_3)CO$

Mass No. of Ru^{102} peak[a]	Probable Ion
690	$[Ru(S_2PMe_2)_2(P(OPh)_3)CO]^+$
662	$[Ru(S_2PMe_2)_2(P(OPh)_3)]^+$
635 (metastable)	690 ⟶ 662
597	$[Ru(S_2PMe_2)_2(P(OPh)_2)CO]^+$
569	$[Ru(S_2PMe_2)_2(P(OPh)_2)]^+$
537	$[Ru(S_2PMe_2)(P(OPh)_3)]^+$
476	$[Ru(S_2PMe_2)_2(P(OPh))]^+$
435 (metastable)	662 ⟶ 537
412	$[Ru(P(OPh)_3)]^+$
380	$[Ru(S_2PMe_2)_2CO]^+$
352	$[Ru(S_2PMe_2)_2]^+$
331	$[Ru(S_2PMe_2)_2(P(OPh)_3)]^{2+}$

[a] All peaks show the characteristic ruthenium isotopic pattern.

TABLE 2.6

^{1}H n.m.r. Data for Various Ruthenium Dithioacid Complexes

Complex	Solvent	Temp(K)	Dithioligand(Me groups) τ Value^{a}(J_{PH})^{b}		Tc(K)^{c}	Me(phosphorus ligand) τ Value^{a}		Tc(K)^{d}	Phenyl groups τ Value^{a}
cis- $Ru(S_2PMe_2)_2(PPh_3)_2$	$CDCl_3$	319	8.34(12.0)		256			-	2.4-3.1
		215	7.73(12.0)	8.94(12.0)					
cis- $Ru(S_2PMe_2)_2(PMePh_2)_2$	$CDCl_3$	329	8.28(12.5)		278	$8.05^{e}(8.0)^{f}$		-	2.4-3.0
		213	7.83(12.5)	8.61(12.5)		8.01^{e}			
cis- $Ru(S_2PMe_2)_2(PMe_2Ph)_2$	$CDCl_3$	341	8.01(12.5)		298	$8.38^{e}(9.0)^{f}$		278	2.7-3.1
		232	7.69(13.0)	8.14(12.0)		$8.30^{e}(9.0)^{f}$	$8.43^{e}(9.0)^{f}$		
cis- $Ru(S_2PMe_2)_2(P(OPh)_3)_2$	$CDCl_3$	297	7.95(12.5)	8.35(12.5)	330	-	-	-	2.6-3.1
cis- $Ru(S_2PMe_2)_2(P(OMe)_3)_2$	$CDCl_3$	301	8.03(12.5)		278	$6.27^{e}(10.0)^{f}$		-	-
		243	7.89(12.5)	8.08(12.5)		$6.27^{e}(10.0)^{f}$		-	
cis- $Ru(S_2PPh_2)_2(PMePh_2)_2$	$CDCl_3$	301	-	-	-	$8.08^{e}(8.0)^{f}$		-	2.2-3.1
cis- $Ru(S_2PPh_2)_2(PMe_2Ph)_2$	CH_2Cl_2	301	-	-	-	$8.45^{e}(3.0)^{f}$			
		253	-	-	-	$8.41^{e}(8.0)^{f}$	$8.49^{e}(8.0)^{f}$	273	2.0-3.2

TABLE 2.6 (CONTD.)

Complex	Solvent	Temp(K)	Dithioligand(Me group)	Tc(K)	Me(Phosphorus Ligand)	Tc(K)	Phenyl Groups
cis- $Ru(S_2PMe_2)_2(PPh_3)CO$	C_6H_5Cl	373	8.21[j] 8.68[k]	353[l]			
	C_6H_5Cl	301	8.10[i](13.0) 8.33(12.5) 9.04(12.5)	368[m]		-	2.3-2.8
	$CDCl_3$	301	7.94 (13.0) 8.00(13.0) 8.04(12.5) 9.04(12.5)				
cis- $Ru(S_2PMe_2)_2(AsPh_3)CO$	$CDCl_3$	298	7.90 (13.0) 7.96(13.0) 8.00(12.5) 9.07(12.5)	>330		-	2.4-2.9
cis- $Ru(S_2PMe_2)_2(PMePh_2)CO$	$CDCl_3$	301	7.88 (13.0) 7.94(13.0) 8.05(13.0) 8.62(13.0)	>330	7.83[g](9.0)[h]	-	2.2-3.0
cis- $Ru(S_2PMe_2)_2(PMe_2Ph)CO$	$CDCl_3$	301	7.83(13.0) 7.96(13.0) 8.06(12.5) 8.33(12.5)	>330	8.11[g](9.5)[h]	-	2.2-2.8
		243	7.80 (13.0) 7.94(13.0) 8.05(12.5) 8.35(12.5)		8.10[g](9.5)[h]8.12[g](10.0)[h]		
cis- $Ru(S_2PMe_2)_2(P(OPh)_3)CO$	$CDCl_3$	301	7.89 (13.0) 7.96(13.0) 8.09(13.0) 8.20(12.5)	>330	-	-	2.6-3.0
cis- $Ru(S_2PMe_2)_2(P(OMe)_3)CO$	$CDCl_3$	301	7.91[i](12.5) 8.00(12.5) 8.10(13.0)	>330	6.25[g](10.5)[h]	-	-
cis- $Ru(S_2PMe_2)_2(CO)_2$	$CDCl_3$	301	7.86(12.5) 7.99(12.5)	>330	-	-	-
cis- $Ru(S_2PPh_2)_2(PMe_2Ph)CO$	$(CD_3)_2CO$	333	-	-	8.19[g](10.0)[h]		
		301	-	-	8.16[g](10.0)[h]8.21[g](10.0)[h]	-	2.0-3.0
cis- $Ru(S_2PMe_2)_2(PPh_3)(P(OPh)_3)$	C_6H_5Cl	363	8.32[j](12.5) 8.45[k](12.5)	283[l]			
	CH_2Cl_2	298	8.28[n]	313[m]	-	-	2.2-3.3
	CH_2Cl_2	233	7.83(13.0) 8.12(13.0) 8.45(12.5) 8.97(12.5)				
cis- $Ru(S_2PMe_2)_2(PMe_2Ph)(P(OPh)_3)$	$CDCl_3$	333	8.19(12.5)	301[o]	8.05[g](9.5)[h]		
		253	7.86(8.0) 8.03(8.0) 8.41[i](12.5)		7.99[g](8.0)[h]	-	2.3-3.2
cis- $Ru(S_2PPh_2)_2(PMe_2Ph)(P(OPh)_3)$	$CDCl_3$	301	-		8.04[g](9.0)[h]		
		233	-		7.99[g](9.0)[h]8.02[g](9.0)[h]	-	2.1-3.2
$Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$ (Configuration D)	$CDCl_3$	301	8.11(12.5) 8.91(12.5)	-	7.86[p](8.0)[f]7.90[p](8.0)[f]	-	2.2-2.8

TABLE 2.6 (CONTD.)

Complex	Solvent	Temp(K)	Dithioligand (Me group)			Tc(K)	Me(Phosphorus Ligand)	Tc^d(K)	Phenyl Groups
$Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$ (configuration E)	$CDCl_3$	273	7.80(12.5)	7.87(12.5) 7.93(12.5)	8.36(11.8)	-	$8.24^g(8.0)^h$ $8.26^g(8.0)^h$ $8.43^g(9.5)^h$ $8.48^g(10.0)^h$	-	2.4-3.0
$Ru(S_2PPh_2)_2(PMe_2Ph)_2CO$ (configuration D)	$(CD_3)_2CO$	333		-		-	$8.34^p(7.0)^f$		
		273					$8.34^p(7.0)^f$ $8.39^p(7.0)^f$	-	1.8-3.0
$Ru(S_2PPh_2)_2(PMe_2Ph)_2CO$ (configuration E)	$CDCl_3$	301		-		-	$8.25^g(7.0)^h$ $8.33^g(9.0)^h$ $8.34^g(9.0)^h$ $8.36^g(8.0)^h$	-	1.8-3.0
cis- $Ru(S_2CNMe_2)_2(PPh_3)_2$ Me_2CO^q	$CDCl_3$	333		7.14^r					
		288	7.06^r		7.25^r	318	-	-	2.3-3.2
cis- $Ru(S_2CNMe_2)_2(PMe_2Ph)_2$	$CDCl_3$	313		6.76^r			$8.51^e(8.0)^f$		
		240	6.67^r		6.75^r	303	$8.48^e(8.0)^f$ $8.53^e(8.0)^f$	-	2.7-3.0
trans- $Ru(S_2CNMe_2)_2(PMe_2Ph)_2$	$CDCl_3$	313		7.20^r		-	8.27^s	-	2.3-3.0
cis- $Ru(S_2CNMe_2)_2(P(OPh)_3)_2$	$CDCl_3$	330		7.10^r					
		301	7.07^r		7.20^r	225	-	-	2.7-3.2
cis- $Ru(S_2CNMe_2)_2(PPh_3)(P(OPh)_3)$	$CDCl_3$	330	6.94	7.10	7.23^v				
		301	6.86^r	7.13^t	7.37^r	318^w	-	-	2.0-3.2
cis- $Ru(S_2CNMe_2)_2(CO)_2$	$CDCl_3$	298	6.72^r		6.75^r		-	-	-
$Ru(S_2PMe_2)_2(diphos)$	$CDCl_3$	301	7.90(13.0)		9.25(13.0)	$>403^x$	-	-	2.0-3.0
$Ru(S_2PMe_2)_2(Ph_2PCH_2PPh_2)$	$CDCl_3$	301	7.85(13.0)		8.88(12.5)	$>403^x$	$5.03^x(10.0)$	-	2.0-3.0
$Ru(S_2PMe_2)_2(diars)$	$CDCl_3$	301	7.65(13.0)		8.26(12.5)	$>403^x$	8.24^r 8.60^r	403^x	2.1-2.8
trans-$Ru(S_2PMe_2)_2(diars)_2$	$CDCl_3$	301		8.46(12.0)			8.02^r		2.1-2.6
$Ru(S_2PMe_2)_2(C_7H_8)$	$CDCl_3$	301	7.78(12.5)	8.15(13.0)		$>403^x$	See text		-
$Ru(S_2PMe_2)_2(C_8H_{12})$	$CDCl_3$	301	8.20(13.0)	8.75(12.5)		$>403^x$	-		-

TABLE 2.6 (CONTD.)

[a] $\pm$ 0.01

[b] Doublet; J_{PH} in parentheses ($\pm 0.2H_2$)

[c] Coalescence temperature of dithioacid methyl resonances

[d] Coalescence temperature of methyl groups attached to phosphorus ligands

[e] $H_nPP'H'_n$ type spectrum (pseudo-triplet)

[f] $J_{PH} + J_{PH'}$ in parentheses ($\pm 0.2H_2$)

[g] Doublet

[h] J_{PH} in parentheses ($\pm 0.2H_2$)

[i] Two doublets superimposed

[j] Doublet from coalescence of inner doublets

[k] Doublet from coalescence of outer doublets

[l] Coalescence temperature for inner doublets

[m] Coalescence temperature for outer doublets

[n] Broadened doublet superimposed on broad signal

[o] Coalescence temperature for doublets at τ8.03, 8.41 and τ7.86, 8.41

[p] Virtually coupled 1,2,1 triplet

[q] Methyl singlet (acetone) at 7.86

[r] Singlet

[s] Broad singlet

[t] Two singlets superimposed

[v] Singlet from coalescence of peaks at τ7.13 and 7.37

[w] Coalescence temperature for resonances at τ7.13 and 7.37

[x] In C_6H_5Cl

[y] Triplet from CH_2 protons

TABLE 2.7

Rates and Activation Parameters obtained by Line Shape Analysis for the Inversion Process cis-$\Delta \rightleftharpoons$ cis-Λ in some Ruthenium(II) Dimethylphosphinodithioate Complexes

Compound	Solvent	$\log_{10} k_{298}$[a]	Ea[b]	$\Delta H^{\ddagger}_{298}$[b]	$\Delta S^{\ddagger}_{298}$[c]	$\Delta G^{\ddagger}_{298}$[b]
cis- $Ru(S_2PMe_2)_2(PPh_3)_2$	$CDCl_3$	3.83 ± 0.02	49.6 ± 1	47.1 ± 1	-14 ± 3	51.1 ± 0.1
cis- $Ru(S_2PMe_2)_2(PMePh_2)_2$	$CDCl_3$	3.08 ± 0.02	60.5 ± 2	58.0 ± 2	9 ± 7	55.4 ± 0.2
cis- $Ru(S_2PMe_2)_2(P(OMe)_3)_2$	$CDCl_3$	2.53 ± 0.34	67.8 ± 2	65.3 ± 2	23 ± 13	58.6 ± 2
cis- $Ru(S_2PMe_2)_2(PMe_2Ph)_2$	$CDCl_3$	1.91 ± 0.12	62.0 ± 1	59.6 ± 1	-9 ± 4	62.1 ± 0.1
	C_6H_5Cl	1.31 ± 0.01	69.7 ± 1	67.2 ± 1	6 ± 4	65.5 ± 0.1
	C_6H_6	0.34 ± 0.12	126 ± 4	123.5 ± 4	176 ± 11	71.0 ± 0.1
cis- $Ru(S_2PMe_2)_2(P(OPh)_3)_2$	$CDCl_3$	0.71 ± 0.01	73.7 ± 2	71.2 ± 2	8 ± 8	68.9 ± 0.1
cis- $Ru(S_2PMe_2)_2(PPh_3)(P(OPh)_3)$	CH_2Cl_2	1.99 ± 0.05[d]	47.3 ± 4[d]	44.8 ± 4[d]	-56 ± 15[d]	61.6 ± 0.3[d]
		1.92 ± 0.03[e]	42.5 ± 3[e]	40.0 ± 3[e]	-74 ± 9[e]	62.0 ± 0.2[e]
cis- $Ru(S_2PMe_2)_2(PPh_3)CO$[f]	C_6H_5Cl	-1.62 ± 0.08[g]	121.8 ± 2[g]	119.3 ± 2[g]	125 ± 7[g]	82.0 ± 0.4[g]
$Ru(S_2PMe_2)_2(diphos)$	C_6H_5Cl	-3.2 ± 0.3	113.4 ± 7	110.9 ± 7	65 ± 20	91.4 ± 2

[a] sec^{-1}

[b] $kJmol^{-1}$

[c] $JK^{-1}mol^{-1}$

[d] Obtained from analysis of exchange of inner doublets g and f

[e] Obtained from analysis of exchange of outer doublets e and h

[f] For cis- $Ru(S_2PMe_2)_2(CO)_2$, no scrambling of methyl groups at 330K

[g] Obtained from analysis of exchange of inner and outer doublets

TABLE 2.8

Assignment of Methyl Group Stereochemistries for <u>cis</u> -Δ- $Ru(S_2PMe_2)_2LL'$ after Twisting and Bond Rupture operations

	Methyl Group Stereochemistries[b]			
	syn(to L)	anti(to L)	syn(to L$'$)	anti(to L$'$)
For <u>cis</u>- Δ isomer[a]	e	g	f	h
Established experimentally for <u>cis</u>-$\Delta \rightleftharpoons$ <u>cis</u>-Λ	e $\rightleftharpoons$ h	g $\rightleftharpoons$ f	f $\rightleftharpoons$ g	h $\rightleftharpoons$ e

See figures 2.10 and 2.11

Operation (on <u>cis</u>-)	Product	Methyl Group Stereochemistries of Product			
		syn(to L)	anti(to L)	syn(to L$'$)	anti(to L$'$)
a) $i-C_3(1)^+$	<u>trans</u>-isomer	e,h	g,f	g,f	e,h
$i-C_3(1)^-$	<u>cis</u>-Λ	e	g	f	h
b) $i-C_3(2)^+$	d				
$i-C_3(2)^-$	<u>cis</u>-Λ	f	h	g	e
c) $i-C_3(3)^+$	d				
$i-C_3(3)^-$	<u>cis</u>-Λ	h	f	e	g
d) $i-C_3(4)^+$	<u>cis</u>-Λ	f	h	e	g
$i-C_3(4)^-$	d				
Bond Rupture mechanism (Figure 2.13)	<u>cis</u>-Λ	h	f	g	e

[a] Δ and Λ isomers defined on basis of rules suggested by I.U.P.A.C. commission[336].

[b] See Figure 2.5 for assignment of e,g,f and h groups in <u>cis</u>-Δ isomer.

[c] By variable temperature ^1H n.m.r. studies for <u>cis</u>- $Ru(S_2PMe_2)_2(PPh_3)(P(OPh)_3)$

[d] These twist operations are sterically impossible since they produce a configuration in which a $^-S_2PMe_2$ group would have to span <u>trans</u> positions.

TABLE 2.9

Rates and Activation Parameters obtained by Line Shape Analysis for the interchange of Methyl groups in some Ruthenium (II) N,N-Dimethyldithiocarbamato Complexes

Compound	Solvent	$\log_{10} k_{298}$ a	Ea b	$\Delta H^{\ddagger}_{298}$ b	$\Delta S^{\ddagger}_{298}$ c	$\Delta G^{\ddagger}_{298}$ b
cis- $Ru(S_2CNMe_2)_2(PMe_2Ph)_2$	$CDCl_3$	1.01 ± 0.01	94.0 ± 2	91.5 ± 2	81 ± 7	67.3 ± 0.02
cis- $Ru(S_2CNMe_2)_2(PPh_3)_2$	$CDCl_3$	0.52 ± 0.02	105.7 ± 2	103.2 ± 2	111 ± 6	70.0 ± 0.2
cis- $Ru(S_2CNMe_2)_2(P(OPh)_3)_2$	$CDCl_3$	0.31 ± 0.02	79.2 ± 3	76.7 ± 3	18 ± 9	71.3 ± 0.07
cis- $Ru(S_2CNMe_2)_2(PPh_3)(P(OPh)_3)$	$CDCl_3$	0.53 ± 0.01[d]	109.9 ± 2[d]	107.4 ± 2[d]	126 ± 5[d]	70.0 ± 0.07[d]
		0.45 ± 0.05[e]	57.8 ± 3[e]	55.3 ± 3[e]	-54 ± 11[e]	71.5 ± 0.07[e]

a sec^{-1}

b $kJmol^{-1}$

c $JK^{-1}mol^{-1}$

d Obtained from exchange of high field pair of singlets

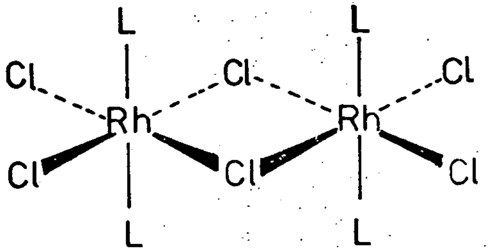
e Obtained from exchange of low field pair of singlets

Chapter 3

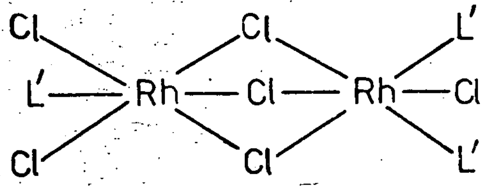
Reactions of mer - $RhCl_3(PMe_2Ph)_3$ with Dithioacid Ligands.

Introduction

As has already been noted (page 47), reactions of mer-$RuCl_3(PMe_2Ph)_3$ with NaS_2PR_2 (R = Me or Ph) lead to the formation of paramagnetic (presumably Ru (III)) species which proved impossible to isolate and which were thought to be intermediates in the formation of cis - $Ru(S_2PR_2)_2(PMe_2Ph)_2$. In order to gain more information on complexes of this type, it was decided to investigate the complexes formed from the reactions of Rh (III) complexes with dithioacid anions since, not only is Rh (III) generally considered to be less labile than Ru (III)[208,286b] but it does not have a stable +2 oxidation state and it forms phosphine containing complexes in the +3 oxidation state which are comparable with those of Ru (III)[286b]. Thus, reactions of $RhCl_3$ with excess tertiary phosphine in refluxing ethanol lead to the formation of mer-$RhCl_3L_3$ (L = alkyl or alkyl-aryl tertiary phosphine)[343] with fac-$RhCl_3L_3$, which has been shown (L = PEt_2Ph) to be formed on irradiation of mer-$RhCl_3(PEt_2Ph)_3$[349], often occurring as a by-product[348]. The meridional isomers, which have three terminal νRh-Cl in their i.r. spectra[350], (as predicted by group theory), have been shown to undergo metathesis with other anions and the chloride ion trans to a phosphine group is more labile than the other two although refluxing with excess X^- in ethanol gives mer-RhX_3L_3 (X = NCO, SCN, Br or I)[350]. In contrast to the behaviour of alkyl and alkyl-aryl tertiary phosphines towards $RuCl_3$, prolonged reactions with $RhCl_3$ do not give complexes of the type $[Rh_2Cl_3L_6]Cl$, on account of the instability of Rh (II) complexes, but binuclear species with double halide bridges, $\{RhCl_3L_2\}_2$(1) have been isolated from the reaction of 1:2 molar ratios of $RhCl_3$ and L, or from stoichiometric quantities of $RhCl_3$ and <u>mer</u>-$RhCl_3L_3$[348]. For L = $P(Bu)_3$, a further dimeric species, $Rh_2Cl_6(P(Bu)_3)_3$, has been isolated and is thought to have the triple halide bridged structure (2)[351].

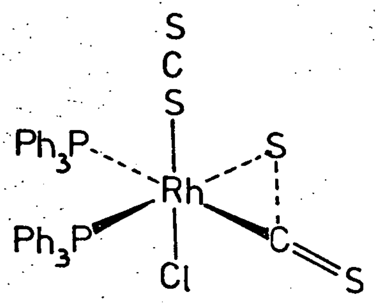


(1)



(2) L′= PBu_3

In contrast, to the alkyl and alkyl-aryl tertiary phosphines, triphenylphosphine reacts with $RhCl_3$ to give purple, or orange, $RhCl(PPh_3)_3$[352,353]. This complex has been very fully investigated since it has been shown to be an excellent catalyst for the homogeneous hydrogenation of olefins[353]. $RhCl(PPh_3)_3$ also undergoes oxidative addition with many other substrates including $[Ph_4As]Cl.HCl$ which gives $[Ph_4As][RhCl_4(PPh_3)_2]$[316]. Similar Rh (III) anions containing more basic phosphines may be prepared by exchange of PPh_3 for L[316]. The reaction of $RhCl(PPh_3)_3$ with CS_2 is also interesting since the product, $Rh(CS_2)_2(PPh_3)_2Cl$ contains two CS_2 groups which are differently bonded (3)[354].



(3)

Since rhodium does have a stable +1 oxidation state, it was considered possible that reactions of Rh (III) complexes with dithioacid anions, which are usually considered to be reducing in nature, might lead to the formation of Rh (I) species. However, this is unlikely since reactions of Rh (I) complexes such as $RhCl(PPh_3)_3$ and $RhClCO(PPh_3)_2$ with excess NaS_2CNR_2 have been shown to cause oxidation to Rh (III) species[233] (page 35).

The reactions of rhodium complexes with $^-S_2CNR_2$, ^-S_2COR and $^-S_2PR_2$ have already been discussed (pages 32 - 36) but other interesting compounds of rhodium with sulphur donor ligands should be noted. Reaction of a solution containing $[Rh_4]^{2+}$ (page 36) with $NaS_2P(OEt)_2$ in the presence of PPh_3 yields the very unusual $Rh\ (S_2POEt)_3(PPh_3)_3$ which is said to contain three unidentate dithioacid ligands[253], and reactions of $RhCl_3$ with NaS_2CR give $Rh\ (S_2CR)_3$ (R = Ph or Bz) whilst the ionic $NH_4[RhCl_2(S_2CBz)_2]$ is isolated from the reaction of $[NH_4]_3\ [RhCl_6]$ with NaS_2CBz[355].

Results and discussion

Since mer-$RhCl_3(PMe_2Ph)_3$ is readily prepared from $RhCl_3$ and PMe_2Ph[348] (see above), its reactions with various dithioacid anions were investigated and the results of this investigation are presented in this chapter.

Reactions of mer-$RhCl_3(PMe_2Ph)_3$ with an excess of an alkali metal, or ammonium, dithioacid salt under reflux for one hour lead to the formation of several different products in every case. These products may be separated by fractional recrystallisation or dry column chromatography[318] or, in general, each may be synthesised as the sole product by slight changes in the conditions of the reaction. Analytical data for all these new compounds are given in Table 3.1 and spectroscopic properties in Tables 3.2 and 3.3.

1. <u>NN-dimethyldithiocarbamato complexes</u>:- Refluxing <u>mer</u>-$RhCl_3(PMe_2Ph)_3$ with an axcess of $NaS_2CNMe_2 2H_2O$ in ethanol for one hour leads to the formation of two products. These are readily separated, since one of them, $RhCl_2(S_2CNMe_2)(PMe_2Ph)_2$ (I), is insoluble in cold ethanol whereas the other is very soluble. After removal of (I), the other is precipitated in high yield as a yellow crystalline complex by addition of excess $NaBPh_4$ or NH_4PF_6. These complexes are strongly conducted in CH_2Cl_2 and analyse for $[Rh(S_2CNMe_2)_2(PMe_2Ph)_2]$ Y(IIa,Y = BPh_4^-; IIb, Y = PF_6^-). Longer reaction times in ethanol lead exclusively to this ionic product on addition of Y^-.

However, if a suspension of <u>mer</u>-$RhCl_3(PMe_2Ph)_3$ and $NaS_2CNMe_2 2H_2O$ is shaken in methanol for 10m, the orange, methanol-insoluble complex $RhCl_2(S_2CNMe_2)(PMe_2Ph)_3$ (III) is formed, but on recrystallisation from CH_2Cl_2/hexane, this is converted into (I). If (III) is shaken in methanol with a mixture of $NaBPh_4$, and PMe_2Ph for 24h, (I) is again formed together with a new compound of formula $[RhCl(S_2CNMe_2)(PMe_2Ph)_3]$ BPh_4 (IV). Attempts to prepare (IV) directly from <u>mer</u>-$RhCl_3(PMe_2Ph)_3$ by reaction with $NaS_2CNMe_2 2H_2O$, $NaBPh_4$ and PMe_2Ph have proved abortive. Instead, the yellow, conducting solid $[RhCl_2(PMe_2Ph)_4]$ BPh_4[356] is formed which, on leaving in $CDCl_3$ for 48h, reverts to <u>mer</u>-$RhCl_3(PMe_2Ph)_3$ and free PMe_2Ph.

Finally, if <u>mer</u>-$RhCl_3(PMePh_2)_3$ is used instead of <u>mer</u>-$RhCl_3(PMe_2Ph)_3$, the long-term reaction in refluxing ethanol with excess $NaS_2CNMe_2 2H_2O$, followed by addition of $NaBPh_4$ gives <u>two</u> ionic compounds, both of formula $[Rh(S_2CNMe_2)_2(PMePh_2)_2]$ BPh_4 (Va and VIa) together with very small amounts of $Rh(S_2CNMe_2)_3$. Similar ionic compounds $[Rh(S_2CNMe_2)_2(PMePh_2)_2]PF_6$ (Vb and VIb) are formed by addition of NH_4PF_6.

2. Diphenyl- and dimethyl-phosphinodithioato complexes:- If mer-$RhCl_3(PMe_2Ph)_3$ is refluxed in ethanol for 60m with an excess of $NH_4S_2PPh_2$, addition of excess $NaBPh_4$ or NH_4PF_6 leads to precipitation of the expected $[Rh(S_2PPh_2)_2(PMe_2Ph)_2]$ Y(VIIa, Y = BPh_4^-; VIIb, Y = PF_6^-). In addition, very small amounts of an ethanol-insoluble compound analysing for $RhCl_2(S_2PPh_2)(PMe_2Ph)_2$ (VIII) are obtained. However, if the reaction is carried out using $NaS_2PMe_22H_2O$, the analogous compounds are not formed. Instead, a red solid of uncertain composition is obtained since this exhibited variable analyses (carbon and hydrogen) each time the reaction was attempted. The ^1H n.m.r. spectrum of this material contains only broad peaks, which are temperature invariant. The broadness of these signals probably arises from a paramagnetic impurity since the substance exhibits a weak esr signal (cf the preparation of $RhCl(PPh_3)_3$)[353]

The compound $[Rh(S_2PMe_2)_2(PMe_2Ph)_2]BPh_4$(IX) can however, be prepared as a yellow, microcrystalline solid either by excluding oxygen completely from the reaction in ethanol or by reaction of fac-$RhCl_3$ $(PMe_2Ph)_3$[348] with excess $NaS_2PMe_22H_2O$ in acetone, followed by addition of $NaBPh_4$. Compound (IX) is, in fact, stable both in the solid state and in solution. However, a red solution is rapidly formed when (IX) is dissolved in ethanol or methanol in the presence of excess $NaS_2PMe_22H_2O$ and air.

Short term reactions between mer-$RhCl_3(PMe_2Ph)_3$ and $NaS_2PMe_22H_2O$ or $NH_4S_2PPh_2$ also differ slightly from one another. The dimethylphosphinodithioato ion behaves like the NN-dimethyldithiocarbamato ion, giving, after shaking for 10m in methanol, orange $RhCl_2(S_2PMe_2)(PMe_2Ph)_3$ (X) which, on recrystallisation from $CDCl_3$/

hexane, gives $RhCl_2(S_2PMe_2)(PMe_2Ph)_2$ (XI). Recrystallisation of (XI) from hot toluene gives mainly (XI), together with a small amount of another compound (XII) with the same analytical data but different spectral properties from (XI).

In contrast, shaking mer-$RhCl_3(PMe_2Ph)_3$ and $NH_4S_2PPh_2$ in ethanol for 10m gives only $RhCl_2(S_2PPh_2)(PMe_2Ph)_2$ (XIII). Compound (XIII) has different spectral properties from (VIII) although recrystallisation of (XIII) from hot ethanol gives small amounts of (VIII).

Finally, attempts to prepare the compound $[RhCl(S_2PMe_2)(PMe_2Ph)_3]BPh_4$ by reaction between $RhCl_2(S_2PMe_2)(PMe_2Ph)_3$ (X), $NaBPh_4$ and PMe_2Ph in methanol yield only $[RhO_2(PMe_2Ph)_4]BPh_4$[357] (XIV) or, if oxygen is excluded, a mixture of $[RhCl_2(PMe_2Ph)_4]BPh_4$[356] (XV) and $RhCl_2(S_2PMe_2)(PMe_2Ph)_2$ (XI). Compound (XIV) is also formed as the sole product from the reaction of $Rh(S_2PMe_2)_3$, PMe_2Ph and $NaBPh_4$.

3. O-ethyldithiocarbonate (xanthate) and dithiocarbonate complexes:- The reaction of KS_2COEt with mer-$RhCl_3(PMe_2Ph)_3$ leads to an even wider range of products than those found with the other dithio ligands, since there is the added possibility of attack on a co-ordinated xanthate ligand by a nucleophile to yield dithiocarbonato complexes (e.g. the formation of $PtL_2(S_2CO)$ from $[PtL_2(S_2COR)][S_2COR]$ (see page 4))[18,19].

Thus, when mer-$RhCl_3(PMe_2Ph)_3$ is refluxed in ethanol with excess KS_2COEt for 60m, no fewer than four different compounds, which may be separated by dry column chromatography, are isolated. Analytical and spectroscopic analyses indicate the formulations

$RhCl(S_2CO)(PMe_2Ph)_3$ (XVI), $K[RhCl_2(S_2CO)(PMe_2Ph)_2]$* (XVII) and two isomers of $Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2$ (XVIII) and (XIX).

However, if the reaction is carried out in a less polar solvent such as acetone, or an ethanol/$CHCl_3$ mixture, none of these products are obtained but instead, orange $RhCl_2(S_2COEt)(PMe_2Ph)_2$ (XX) is isolated.

As for (S-S) = S_2CNMe_2, shaking mer-$RhCl_3(PMe_2Ph)_3$ and KS_2COEt in methanol for 10m gives the dark orange complex $RhCl_2(S_2COEt)(PMe_2Ph)_3$ (XXI) which yields (XX) on recrystallisation from hot methanol or $CHCl_3$/hexane. This interconversion can also be affected by heating (XXI) to its melting point (120-123°C) whereupon PMe_2Ph is evolved and the orange residue consists largely of compound (XX).

Finally, if $RhCl_2(S_2COEt)(PMe_2Ph)_3$ (XXI) is shaken in ethanol with excess $NaBPh_4$ for several weeks, a small amount of $[RhCl(S_2COEt)(PMe_2Ph)_3]BPh_4$ (XXII) is deposited. This compound can also be prepared in high yield by reaction of mer-$RhCl_3(PMe_2Ph)_3$ and KS_2COEt (1:1 molar ratios) in refluxing methanol for 60m, followed by addition of $NaBPh_4$. Longer reaction times (5h) give yellow solutions from which compounds (XVI) and (XVIII) have been isolated.

4. Spectroscopic properties of dithioacid complexes.

a) Infrared spectra:- The three infrared active νRhCl stretching vibrations for the compound mer-$RhCl_3(PMe_2Ph)_3$ have been assigned to the peaks at 339, 313 and 273 cm^{-1} with the band at lowest energy arising (predominantly) from the stretch of the rhodium-chloride bond trans to a PMe_2Ph group[350]. Thus, an analysis of the RhCl stretching region of some of these new complexes should yield information about their structures. Also as previously

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* See Erratum (page 205)

pointed out (page 53), the position of the sulphur ligand absorption bands should give some information about the mode of bonding of the dithioacid group.

For each of the complexes $RhCl_2(S-S)(PMe_2Ph)_3$ ($S-S$ = S_2CNMe_2, S_2PMe_2, S_2COEt), the $\nu RhCl$ region is similar to that of mer-$RhCl_3(PMe_2Ph)_3$ (Table 3.2) except that the lowest $\nu RhCl$ band has disappeared, indicating that the chloride ion trans to phosphine has been replaced. This is in agreement with the larger trans labilising effect of PMe_2Ph compared to chloride ion and is consistent with the results of other exchange reactions[350], (see page 132). In addition, for ($S-S$) = S_2PMe_2, the absorption at 601 cm^{-1} [16] and for ($S-S$) = S_2CNMe_2 the position of νCN below 1470 cm^{-1} [14,233] both suggest that the sulphur ligands are co-ordinated through only one sulphur atom.

Since there is little change in the $\nu RhCl$ region from $RhCl_2(S-S)(PMe_2Ph)_3$ to $RhCl_2(S-S)(PMe_2Ph)_2$ and since all the dithio ligand absorptions now have characteristic frequencies for bidentate co-ordination (see Table 3.2), it seems reasonable to infer that the chloro groups remain mutually trans and that chelation of the dithio ligand occurs with concomitant loss of a PMe_2Ph group. From an i.r. standpoint, there is very little difference between the $\nu RhCl$ region or between the νPS region for the different isomers of $RhCl_2(S_2PR_2)(PMe_2Ph)_2$ although other parts of their i.r. spectra and their ^1H n.m.r. spectra are substantially different (see later).

The remaining compounds all appear to contain only chelated dithio groups and have only one or no $\nu RhCl$ bands and hence, little stereochemical information can be gleaned from i.r. studies. N.m.r. spectroscopy has, however, proved an invaluable tool in assigning structures to all these compounds.

b) N.m.r. spectra:- The only differences between the ^1H n.m.r. spectra of $RhCl_2(S-S)(PMe_2Ph)_3$ and mer-$RhCl_3(PMe_2Ph)_3$ is that dithio-ligand resonances occur in the former and that the positions of the triplet and the doublet arising from the phosphine groups are very slightly different (Table 3.3), presumably because of the different shielding effects of the dithio ligands from that of the chloride ion. In agreement with the i.r. data, this confirms the structure of these compounds to be A, (see Scheme 3.1) since if either of the other chloride ions had been replaced, the plane of symmetry passing through the three phosphorus atoms would have been removed and because of hindered rotation about the rhodium-phosphorus bonds, two triplets should arise from the methyl groups of the mutually trans phosphines (cf cis-$RuCl_2CO(PMe_2Ph)_3$[325]).

In fact, the ^1H n.m.r. spectra of the complexes $[RhCl(S_2CNMe_2)-(PMe_2Ph)_3]BPh_4$ (IV) and $RhCl(S_2CO)(PMe_2Ph)_3$ (XVI) do show two triplets arising from the trans phosphine groups, indicating that there is no plane of symmetry through these phosphines and hence the former is assigned structure B (see Scheme 3.1).

Further evidence that compound (IV) has structure B stems from the fact that at 301K, there are two resonances arising from the methyl groups on the dithiocarbomato ligand which can only be explained if there is no plane of symmetry perpendicular to the S_2CN plane in the molecule and if rotation about the $C\overset{\cdot\cdot\cdot}{-}N$ bond is hindered. Since the two resonances remain sharp up to 320K, it appears that free rotation about the $C\overset{\cdot\cdot\cdot}{-}N$ bond is not occuring, even at this temperature. The dithiocarbonate complex (XVI) which can be assigned structure C is most likely formed from $[RhCl(S_2COEt)(PMe_2Ph)_3]BPh_4$ (XXII) by attack of a previously displaced chloride ion, or excess $^-S_2COEt$, on the co-ordinated xanthato group.

The complexes $RhCl_2(S-S)(PMe_2Ph)_2$ (S-S = S_2CNMe_2 (I) S_2PMe_2(XI), S_2PPh_2(XIII) and S_2COEt(XX))show only one dithio ligand resonance in each case, together with one $H_6PP'H'_6$ pseudo-doublet* which arises from the PMe_2Ph groups. Since $J_{PP'}$ is small and there is only one phosphine methyl resonance, the phosphine groups must be mutually cis and the phosphorus atoms must lie on the plane of symmetry of the molecule. The sulphur ligand must also have planes of symmetry both in the S-Rh-S plane and perpendicular to it, since if either of these were absent, either the compound with (S-S) = S_2PMe_2 or that with (S-S) = S_2CNMe_2 would give rise to two dithio ligand resonances.

Thus, the only possible structure for these compounds is one with trans chloride groups (as suggested by i.r. studies) as in structure D.

For $RhCl_2(S_2PMe_2)(PMe_2Ph)_2$ (XII), since the ^1H n.m.r. spectra contains no triplet patterns, the compound cannot contain trans-PMe_2Ph groups. The only possible structure for this isomer is one containing cis-chlorides and cis-phosphines (structure E). This structure should exhibit four phosphine methyl doublets but only two are observed (Table 3). This could be due to fast rotation about the metal phosphorus bonds at room temperature but since the solutions used for this n.m.r. study were very weak (because of the small yield of XII), it is possible that further small splittings are obscured by the high noise level. Further support for the correctness of this cis, cis,

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* A 'pseudo-doublet' is analagous to the 'pseudo-triplet' referred to in Chapter 2. However, in this case, the much lower signal intensity between the two main lines of the signal is indicative of a smaller but non-zero value for $J_{PP'}$, than is indicated by a pseudo-triplet[324].

cis-isomer formulation for (XII) comes from recent studies of the isomerisation reaction of $RuCl_2(CO)_2(EPh_3)_2$ (E = P,As) where recrystallisation of trans-$RuCl_2(CO)_2(EPh_3)_2$ gives the more stable cis, cis, cis-isomer[302].

The ^1H n.m.r. spectrum of K $[RhCl_2(S_2CO)(PMe_2Ph)_2]$ (XVII) consists of broad peaks in the phenyl region of the spectrum, together with a single sharp triplet at τ8.22 . This can only occur if the phosphine groups are mutually trans ('virtually-coupled' triplet with large $J_{PP'}$)[324] and thus the compound is assigned structure F. A possible mode of formation of this rather unusual compound is by attack of potassium chloride, formed from the reaction of mer- $RhCl_3(PMe_2Ph)_3$ and KS_2COEt on $RhCl(S_2CO)(PMe_2Ph)_3$ (XVI). The PMe_2Ph group released could then attack (XVII) to reproduce (XVI) with loss of potassium chloride. Since both compounds are found in the reaction mixture, it seems likely that in the presence of excess KCl and PMe_2Ph, an equilibrium is set up between the two compounds.

The ^1H n.m.r. spectra of the two compounds of formula $Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2$ both contain quartet and triplet signals in the positions expected for an -OEt group but the pattern arising from the methyl groups on the two phosphines is quite different in each case. Compound (XVIII) contains a single 'virtually-coupled' triplet indicative of trans phosphines (structure G) whereas (XIX) shows four doublets (Figure 3.1a, page 144) which suggests that the two phosphine groups are mutually cis, and in different chemical environments and that there is hindered rotation about the rhodium-phosphorus bonds. A similar phosphine methyl pattern is observed for isomer E of the compound $Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$ (page 99). For (XIX), the proton noise decoupled ^{31}P n.m.r. spectrum shows two resonances (indicating the phosphorus atoms are magnetically inequivalent) each split into a doublet of doublets by coupling to the rhodium^{103} nucleus and the other phosphorus atom. The ^{103}Rh n.m.r. spectrum of (XIX) has also been measured by decoupling the proton spectrum. Each peak arising from a methyl group in the ^{1}H n.m.r. spectrum is rather broad (2-3Hz) due to ^{103}Rh-^{1}H coupling and hence, irradiation in the rhodium range of frequencies sharpens some of the signals but not others (Figure 3.1, page 144). In this way, the rhodium spectrum may be seen to consist of four resonances *ie*. a doublet of doublets arising from coupling to two inequivalent phosphorus atoms. The only structure consistent with all this information is *H*.

The complexes $[Rh(S\text{-}S)_2(PMe_2Ph)_2]Y$ ($S\text{-}S = S_2CNMe_2$, $Y = BPh_4^-$ or PF_6^-; $S\text{-}S = S_2PMe_2$; $Y = BPh_4^-$) all have low temperature ^{1}H n.m.r. spectra which are consistent with *cis*-phosphines and hindered rotation about the rhodium-phosphorus bonds, (structure *J*), namely two resonances corresponding to the methyl groups on the dithio ligands and two pseudo-doublets arising from the phosphine methyl groups (Figure 3.2, page 145). The ^{1}H n.m.r. spectrum of *cis*-$[Rh(S_2PMe_2)_2(PMe_2Ph)_2]BPh_4$ (IX) is temperature invariant in chlorobenzene up to 360K but above this temperature, all the peaks begin to broaden and the solution turns dark, indicating that decomposition has probably occurred. Thus, unlike the related *cis*-$Ru(S_2PMe_2)_2(PMe_2Ph)_2$ complex, the inversion process *cis*-$\Delta \rightleftharpoons$ *cis*-Λ is very slow on the n.m.r. timescale. This indicates that these complexes are indeed much less labile than their ruthenium analogues but this is probably due mainly to the fact that they are ionic. Hence, the positive charge on the metal will tend to make the metal-ligand bonds stronger and it is probably this fact rather than any large, intrinsic differences in lability of the co-ordination spheres of rhodium (III) and ruthenium (II) which accounts for the difference in behaviour.

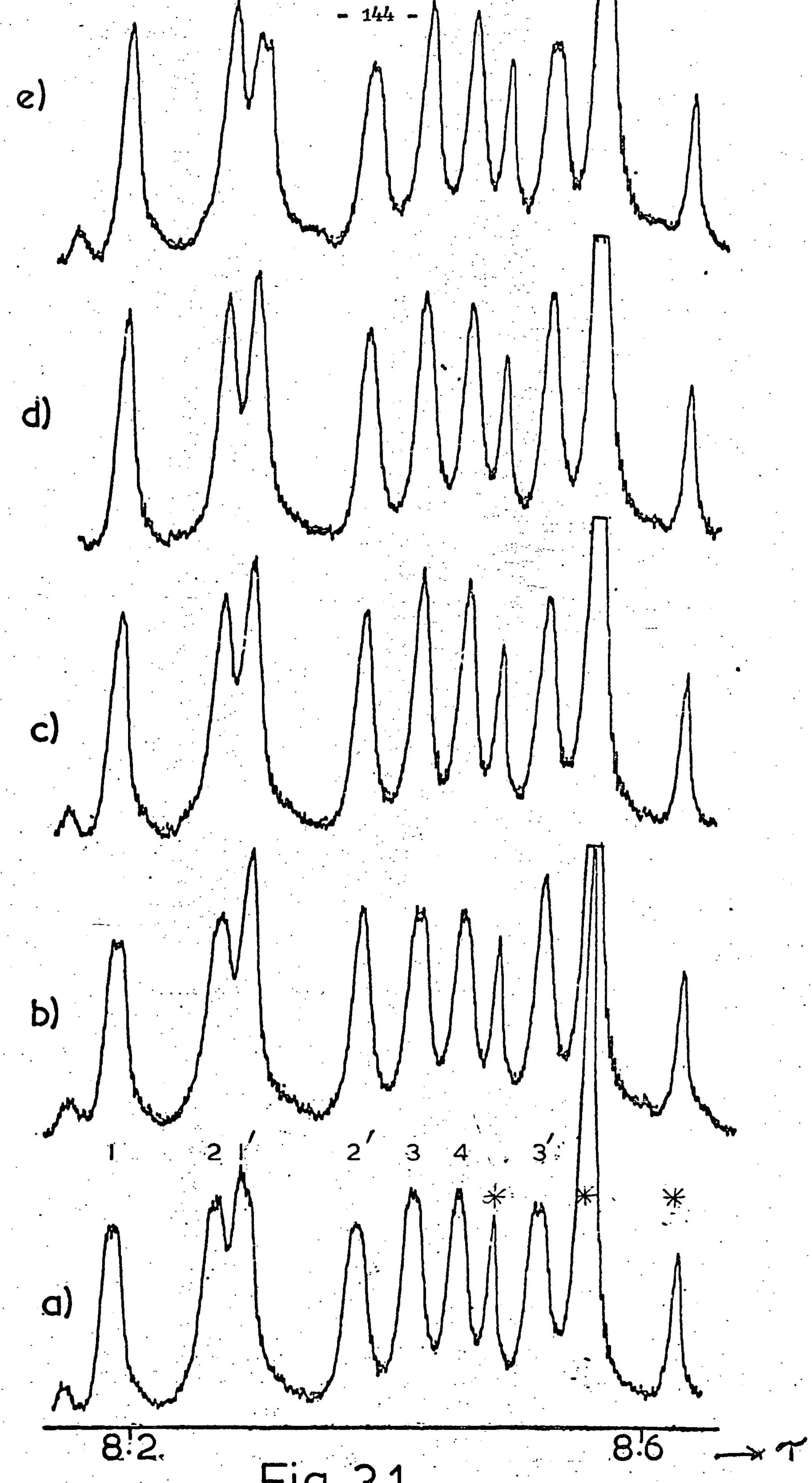

Fig. 3.1

Figure 3.1

Rhodium -103 decoupling of ^{1}H n.m.r. spectrum of cis-Rh(S_2CO)(S_2COEt)(PMe_2Ph)$_2$ (XIX)

a) No irradiation.

b) irradiation at 3,163,455Hz decouples 1′, 2′, 3′, 4′ rhodium-methyl doublets.

c) irradiation at 3,163,345Hz decouples 1′, 2′, 3′, 4′ more than 1,2,3 and 4. rhodium-methyl doublets.

d) irradiation at 3,163,337Hz decouples 1,2,3,4 more than 1′, 2′, 3′ and 4′ rhodium-methyl doublets.

e) irradiation at 3,163,227Hz decouples 1,2,3,4 rhodium-methyl doublets.

* Triplet from methyl group of $^-S_2$COEt. Centre peak totally masks 4′ rhodium-methyl doublet.

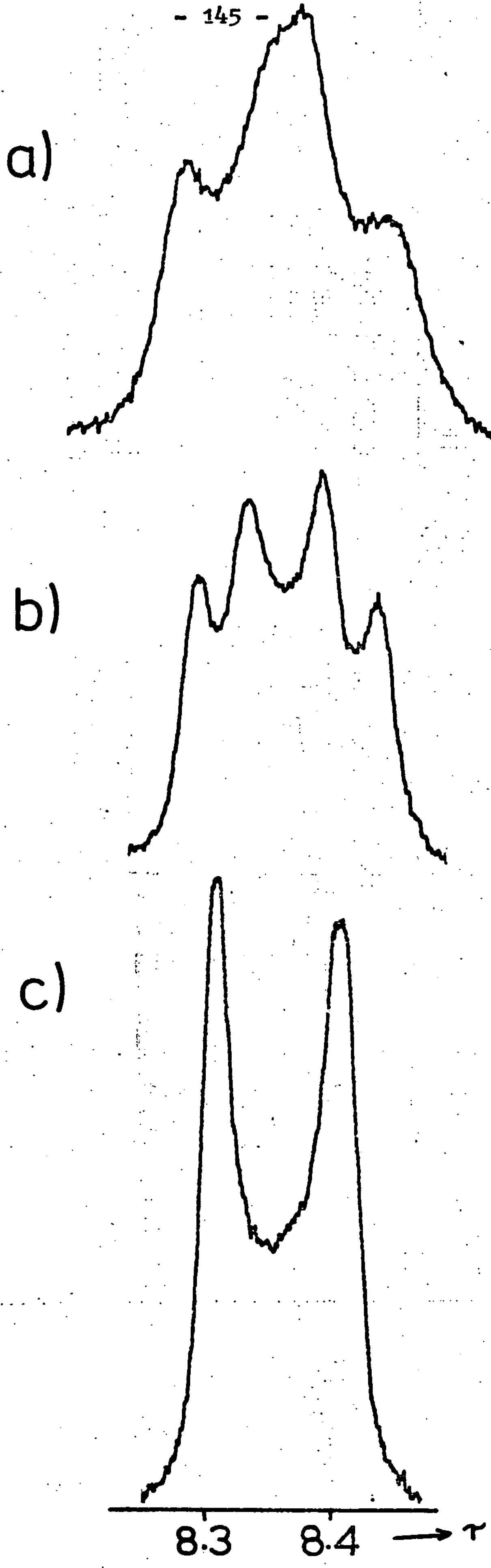

Fig.3.2

^{1}H n.m.r. spectrum of phosphine methyl groups of <u>cis</u>-$[Rh(S_2CNMe_2)_2(PMe_2Ph)_2]PF_6$ in $CDCl_3$ at different temperatures.

a) 223K b) 253K c) 300K

The compounds, cis - [$Rh(S_2CNMe_2)_2(PMe_2Ph)_2$] Y ($Y = BPh_4^-$ (IIa) or PF_6^- (IIb)) both give rise to a single doublet in the proton noise-decoupled ^{31}P n.m.r. spectrum due to coupling with the ^{103}Rh nucleus and this coupling is found to be temperature invariant in each case. In contrast, the ^1H n.m.r. spectrum of (IIb) does show marked variations with temperature giving only a singlet for the S_2CNMe_2 methyl resonance and a pseudo-doublet for the phosphine methyl resonance at 300K (Figure 3.2(c), page 145). As for cis - $Ru(S_2PMe_2)_2(PMe_2Ph)CO$ (page 64) and cis - $Ru(S_2CNMe_2)_2(PMe_2Ph)_2$ (page 72) the phosphine methyl resonances do not undergo coalescence on heating, but rather, gradually move together until they become coincident (Figure 3.2, page 145). Once again, this is attributable to fast rotation about the rhodium-phosphorus bond at high temperatures, which on account of the chiral nature of the cation does not lead to exchange of the magnetic environments of the two methyl groups on each phosphine ligand, but rather, to an average environment which is the same for both methyl groups. A similar process occurs on warming cis -[$Rh(S_2CNMe_2)_2(PMe_2Ph)_2$]$BPh_4$(II(a)) but in this case the separation of the pseudo doublets at lower temperatures is greater than for II(b), and superposition is not reached even at 335°K.

Finally, the ionic compounds formed by long-term reaction between mer- $RhCl_3(PMePh_2)_3$ and $NaS_2CNMe_22H_2O$ are, as expected, geometrical isomers of [$Rh(S_2CNMe_2)_2(PMePh_2)_2$]Y. Thus, the ^1H n.m.r. spectra of (VIa and b) consist of one S_2CNMe_2 methyl resonance and a 'virtually-coupled' triplet phosphine methyl resonance (structure K) whereas (Va and b), which cannot be satisfactorily separated from the trans isomer, have two S_2CNMe_2 resonances and one pseudo-doublet phosphine resonance in each case (structure J).

The fact that the trans isomer is formed more readily when the phosphine is $PMePh_2$ rather than PMe_2Ph* can presumably be attributed to the greater steric size of $PMePh_2$. It should be noted at this point that the analogous complex $[Rh(S_2CNEt_2)_2(PPh_3)_2]BF_4$ has been assigned a trans stereochemistry[253] and, although no evidence is cited to support this assignment, the result is consistent with the still greater steric size of triphenylphosphine.

Thus, this combination of i.r. and n.m.r. studies, together with the various interconversions of compounds noted earlier can be used to suggest a probable stereochemical pathway for the overall reaction between mer- $RhCl_3(PMe_2Ph)_3$ and these various dithioacid ligands and this is outlined in the Scheme 3.1.

Experimental: General experimental techniques and non-Rhodium containing materials were as for Chapter 2. Rhodium Chloride Trihydrate was from Johnson-Matthey Ltd.

mer- $RhCl_3(PMe_2Ph)_3$, fac- $RhCl_3(PMe_2Ph)_3$ and mer- $RhCl_3(PMePh_2)_3$ were synthesised by published methods[350].

NN- Dimethyldithiocarbamato Complexes

trans- Dichloro (N,N-dimethyldithiocarbamato) bis(dimethylphenylphosphine) rhodium (III) (I) and cis- Bis(N,N-dimethyldithiocarbamato) bis(dimethylphenylphosphine) rhodium (III) tetraphenylborate (IIa):- mer- $RhCl_3(PMe_2Ph)_3$ (0.25g) and excess $NaS_2CNMe_2 2H_2O$ (0.25g) were refluxed in

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* The presence of a small triplet at τ8.15 and a singlet at τ7.10 in the n.m.r. spectrum of cis-$[Rh(S_2CNMe_2)_2(PMe_2Ph)_2]PF_6$ indicates that some of the trans isomer is formed but it is only of the order of 7% of the total yield (as determined from peak areas).

ethanol (20ml) for 60m. and then, the resulting orange solution cooled and filtered. The residue was well-washed with water to remove sodium chloride and then with ethanol, pentane to give the orange solid (I) (0.07g, 30%). The yellow filtrate was treated with excess $NaBPh_4$ in ethanol, the resulting yellow precipitate filtered, washed with water, ethanol, pentane and then recrystallised from CH_2Cl_2/ethanol to give (IIa) (0.20g, 51%) ^{31}P n.m.r. (IIa) in $CDCl_3$; 4.5ppm (doublet; J_{RhP} = 112Hz).

If mer- $RhCl_3(PMe_2Ph_3$ and $NaS_2CNMe_22H_2O$ were refluxed in ethanol for 16h, only (IIa) (0.35g, 92%) was isolated on addition of $NaBPh_4$.

cis- Bis(N,N-dimethyldithiocarbamato) bis(dimethylphenylphosphine) rhodium(III) hexafluorophosphate (IIb) was similarly prepared except that excess NH_4PF_6 was added to the yellow ethanolic solution. No immediate precipitation occurred but large orange crystals were deposited when the solution was left for three days. These were filtered, washed with water, ethanol and pentane to give (IIb) (0.30g, 98%).

^{31}P n.m.r. (IIb) in $CDCl_3$; 4.57 ppm (doublet)(J_{RhP}= 114Hz); -147.2 ppm (heptet, J_{PF} = 727Hz).

cis- and trans- Bis(N,N-dimethyldithiocarbamato)bis(methyldiphenylphosphine) rhodium (III) tetraphenylborate (Va) and (VIa):- As above, refluxing mer- $RhCl_3(PMePh_2)_3$ (0.20g) and excess $NaS_2CNMe_22H_2O$ (0.15g) in ethanol (20ml) for 16h. Addition of $NaBPh_4$ then gave an immediate yellow precipitate consisting of a mixture of the cis and trans isomers (Va) and (VIa) (^1H n.m.r. and analytical evidence). On leaving the filtrate, yellow microcrystals of the pure trans isomer (VIa) were deposited. Total yield 90%; cis: trans ratio ca 1.5; 1.0.

Similarly, *cis* and *trans*- $[Rh(S_2CNMe_2)_2(PMePh_2)_2]\ PF_6$ (Vb) and (VIb) were prepared from *mer*- $RhCl_3(PMePh_2)_3$ and $NaS_2CNMe_2 2H_2O$ followed by addition of excess NH_4PF_6. The yellow crystals that separated first were the pure *trans* isomer (VIb) (^1H n.m.r. evidence). Later batches were orange and consisted of a mixture of *cis* and *trans* isomers. Total yield *ca* 70%.

mer- Dichloro(N,N-dimethyldithiocarbamato)tris(dimethylphenylphosphine) rhodium (III) (III):- A suspension of *mer*- $RhCl_3(PMe_2Ph)_3$ (0.25g) was shaken with excess $NaS_2CNMe_2 2H_2O$ (0.20g) in methanol (25ml) for 10m. The resulting orange *solid* (III) was filtered off and washed with water, methanol and pentane (0.25g, 88%). Recrystallisation from CH_2Cl_2/hexane gave *trans*- $RhCl_2(S_2CNMe_2)(PMe_2Ph)_2$ (I).

mer- Chloro(N,N-dimethyldithiocarbamato)tris(dimethylphenylphosphine) rhodium (III) tetraphenylborate (IV):- *mer*- $RhCl_2(S_2CNMe_2)(PMe_2Ph)_3$ (0.23g), $NaBPh_4$ (0.36g) and PMe_2Ph (0.20ml) were shaken in methanol for 24h under nitrogen. The resulting mixture of orange and yellow solids was treated with hot ethanol to leech out the yellow solid. On cooling, this solution gave yellow *crystals* which were recrystallised from methanol to give (IV) (0.20g, 55%). The remaining orange solid, which was insoluble in hot ethanol was *trans*- $RhCl_2(S_2CNMe_2)(PMe_2Ph)_2$ (I).

Diphenylphosphinodithioato Complexes

cis-cis-cis Dichloro(diphenylphosphinodithioato)bis(dimethylphenylphosphine) rhodium (III) (VIII) and *cis-Bis(diphenylphosphinodithioato)bis(dimethylphenylphosphine) rhodium (III) tetraphenylborate* (VIIa):- *mer*- $RhCl_3$-(PMe_2Ph)_3$ (0.30g) and excess $NH_4S_2PPh_2$ (0.40g) were refluxed in ethanol (20ml) for 60m. Filtration of the hot solution left a very small amount of orange *crystals* of (VIII), purified by washing with water, methanol and pentane. The orange filtrate was treated with excess $NaBPh_4$ to give an immediate orange precipitate (VIIa), which was recrystallised from CH_2Cl_2/methanol to remove any NH_4BPh_4 (0.46g; 80%) cis- $[Rh(S_2PPh_2)_2(PMe_2Ph)_2]PF_6$ (VIIb) was similarly prepared except that the orange, ethanolic solution was treated with excess NH_4PF_6 and the complex separated, slowly as large orange crystals (0.40g, 80%). (VIIa) could also be obtained in a pure state by dissolving (VIIb) in methanol and adding excess $NaBPh_4$.

trans-Dichloro(diphenylphosphinodithioato)bis(dimethylphenylphosphine) rhodium (III) (XIII):- mer- $RhCl_3(PMe_2Ph)_3$ (0.20g) and $NH_4S_2PPh_2$ (0.20g) were shaken in ethanol (25 ml) for 10m. Excess starting material was filtered off and after 3 days, large crystals of the complex were formed in the filtrate. These were filtered and washed with diethyl-ether and pentane (0.11g, 50%). Recrystallisation from ethanol gave a mixture of mainly (XIII) and small amounts of the cis, cis, cis isomer (VIII) (i.r. evidence).

Dimethylphosphinodithioato Complexes:-

cis-Bis(dimethylphosphinodithioato)bis(dimethylphenylphosphine) rhodium (III) tetraphenylborate (IX):- mer- $RhCl_3(PMe_2Ph)_3$ (0.30g) and NaS_2PMe_2-$2H_2O$ (0.35g) were refluxed in degassed ethanol (20ml) for 1H. with dry, oxygen-free nitrogen continuously bubbling through the mixture. The resulting orange solution was cooled (under nitrogen) and $NaBPh_4$ (0.20g) added. The resulting yellow solid was filtered off under nitrogen and washed with water, ethanol and pentane (0.30g, 61%). Omission of nitrogen from the reaction gave a red solution from which a red solid was precipitated by addition of excess $NaBPh_4$. This material had different analyses from ostensibly the same preparation e.g. C, 51.2; H, 5.6% and C, 37.3; H, 4.7%.

However (IX) may also be prepared by refluxing fac- $RhCl_3$-$(PMe_2Ph)_3$ (0.07g) and excess $NaS_2PMe_22H_2O$ (0,06g) in acetone/chloroform

(50; 50 v/v) (25ml) for 60m. Then, by evaporating to dryness, dissolving in CH_2Cl_2, filtering off excess $NaS_2PMe_22H_2O$, evaporating to dryness, dissolving in methanol and adding excess $NaBPh_4$, (IX) is obtained as yellow microcrystals.

mer- Dichloro(dimethylphosphinodithioato)tris(dimethylphenylphosphine)-rhodium (III) (X) was prepared by shaking mer- $RhCl_3(PMe_2Ph)_3$ (0.40g) and $NaS_2PMe_22H_2O$ (0.24g) in methanol (40ml) for 10m. (0.41g, 90%). Recrystallisation from $CDCl_3$/hexane gave trans-Dichloro(dimethylphosphinodithioato)bis(dimethylphenylphosphine) rhodium (III) (XI). This compound was also obtained by shaking mer- $RhCl_3(PMe_2Ph)_3$ (0.30g) and NaS_2PMe_2 - $2H_2O$ (0.30g) in ethanol (20ml) for two days. The orange crystals were filtered from the red-brown solution and washed with water, ethanol and pentane (0.22g, 80%). Recrystallisation of (XI) from toluene gave mainly (XI) together with small quantities of cis, cis, cis- $RhCl_2$--$(S_2PMe_2)(PMe_2Ph)_2$ (XII).

Reaction of mer- $RhCl_2(S_2PMe_2)(PMe_2Ph)_3$ (X) with $NaBPh_4$ and PMe_2Ph

(X) (0.32g), $NaBPh_4$ (0.32g) and PMe_2Ph (0.10ml) were shaken in degassed ethanol under nitrogen for two days to give a yellow precipitate of cis- Dichlorotetrakis(dimethylphenylphosphine)rhodium(III)tetraphenylborate (XV), purified by washing several times with water, methanol, diethylether and pentane (0.43g, 80%) mp 145-147°C (Found:- C,64.1; H,6.3% Calc for $C_{56}H_{64}BCl_2P_4Ru$; C,64.3; H,6.1%). The same compound was also formed by reaction of a mixture of mer- $RhCl_3(PMe_2Ph)_3$, NaS_2CNMe_2-$2H_2O$, $NaBPh_4$ and PMe_2Ph. ^1H n.m.r. (CH_2Cl_2)(233K) 8.26τ ('triplet') ($J_{PH}+J_{PH'}$, 48Hz); 8.94τ ('doublet') ($J_{PH}+J_{PH'}$, 40Hz); at 313K 8.40τ (singlet); Ph resonance at τ1.4-3.6 . Compound (XV) rearranges to mer- $RhCl_3(PMe_2Ph)_3$ and free PMe_2Ph on standing in $CDCl_3$ for 48h.

If the reaction between (X), $NaBPh_4$ and PMe_2Ph is carried out in the presence of air, the white solid cis-(oxygen)tetrakis-(dimethylphenylphosphine)rhodium (I) tetraphenylborate (XIV) is formed (0.40g, 80%) (νO-O , 841,860cm^{-1}; cf 841, 870 for $[RuO_2(PMe_2Ph)_4]$-ClO_4^{357}. The same compound is formed when $Rh(S_2PMe_2)_3$ is reacted with excess PMe_2Ph in the presence of $NaBPh_4$. mp 129-130°C (Found:- C,66.2; H,6.6% Calc. for $C_{56}H_{64}BO_2P_4Ru$; C,66.8; H,6.4%) ^{1}H n.m.r. (CH_2Cl_2)(300K) 8.88τ ('triplet') ($J_{PH}+J_{PH'}$ = 7Hz); 8.99τ ('doublet') ($J_{PH}+J_{PH'}$) = 8Hz) Ph resonance 2.2-3.6τ.

Reaction of potassium O-Ethyldithiocarbonate (xanthate) with mer- $RhCl_3$-$(PMe_2Ph)_3$.

mer- $RhCl_3(PMe_2Ph)_3$ (0.30g) and excess KS_2COEt (0.30g) were refluxed in ethanol for 60m and the resulting yellow solution filtered hot in order to remove potassium chloride. It was then evaporated to dryness and the yellow oil dissolved in CH_2Cl_2. Excess KS_2COEt was filtered off and the solution allowed to stand whereupon yellow needle-shaped crystals of potassium cis-dichloro(ditniocarbonato) trans-bis(dimethylphenylphosphine)rhodate (III) (XVII) were deposited. (0.02g, 7%). These were filtered off and recrystallised from CH_2Cl_2/methanol. The yellow filtrate was placed onto an alumina dry column and eluted with CH_2Cl_2 to give three poorly resolved bands coloured yellow, orange and yellow respectively. Each band was extracted with diethyl-ether and then hexane added. Slow evaporation of these solutions gave crystals in each case.

The first yellow band gave trans-(dithiocarbonato)(O -ethyldithiocarbonato)bis(dimethylphenylphosphine)rhodium (III) (XVIII) (0.05g, 17.5%). The orange band gave mer-chloro(dithiocarbonato)tris (dimethylphenylphosphine)rhodium (III) (XVI) (0.05g, 16%) and the second yellow band yielded cis-(dithiocarbonato)(O-ethyldithiocarbonato) bis(dimethylphenylphosphine)rhodium (III) (XIX) (0.10g, 35%)

^{31}P n.m.r.(XIX) in $CDCl_3$; 9.13ppm (doublet of doublets); 0.46ppm (doublet of doublets); J_{P_1Rh}, 118H; J_{P_2Rh} 110Hz; $J_{P_1P_2}$ = 18Hz.

If the initial ethanolic solution is allowed to evaporate slowly, the first product to crystallise out is (XIX) (0.20g, 70%). Then a mixture of (XIX) and (XVI) are deposited followed by small amounts of pure (XVI) (0.05g, 16%).

When mer- $RhCl_3(PMe_2Ph)_3$ (0.30g) and KS_2COEt (0.08g)(1.; 1.05 molar ratio) were refluxed in ethanol for 5h and the resulting yellow solution worked-up as before, two bands were eluted containing (XVI) (0.05g, 16%) and (XIX) (0.02g, 7%).

However, when mer- $RhCl_3(PMe_2Ph)_3$ (0.30g) and excess KS_2COEt (0.30g) were shaken in acetone (25ml) for 16 hours, and the resulting orange solution evaporated to dryness (after removing KCl by filtration) recrystallisation of the orange oil from CH_2Cl_2/hexane gave orange crystals of trans- Dichloro(O-ethyldithiocarbonato)bis (dimethylphenylphosphine)rhodium(III) (XX) (0.20g, 72%). This compound was also prepared by carrying out the same reaction in a refluxing solution of ethanol/$CHCl_3$ and working up the orange solution in the same way. Reaction of (XX) with KS_2COEt gave (XIX).

If mer- $RhCl_3(PMe_2Ph)_3$ (0.30g) and KS_2COEt(0.30g) were shaken in methanol (25ml) for 10m. the orange complex mer-Dichloro - (O-ethyldithiocarbonato)tris(dimethylphenylphosphine)rhodium(III) (XXI) (0.30g, 88%) was deposited. Recrystallisation of this compound from methanol (or $CHCl_3$/hexane) gave trans- $RhCl_2(S_2COEt)(PMe_2Ph)_2$ (XX).

Finally, if mer- $RhCl_2(S_2COEt)(PMe_2Ph)_3$ (XXI) (0.12g) is shaken for 4 weeks in ethanol (20ml) with $NaBPh_4$ (0.12g), a small amount of the orange compound mer-Chloro(O-ethyldithiocarbonato)tris(dimethylphenylphosphine)rhodium (III) tetraphenylborate (XXII) is deposited (0.02g, 9.5%).

However, this compound can be prepared in high yield by reaction of <u>mer</u>- $RhCl_3(PMe_2Ph)_3$ (0.37g) with KS_2COEt (0.09g, 1:1 molar ratio) in refluxing methanol (20ml) for 60m followed by addition of excess $NaBPh_4$. Recrystallisation of the resulting yellow solid from CH_2Cl_2/methanol gives (XXII) as orange microcrystals (0.45h, 80%).

TABLE 3.1

Analytical Data for some Rhodium Complexes

	Complex	Colour	M.p. (°C)	Found % C	Found % H	Found % N	Found % Cl	Required % C	Required % H	Required % N	Required % Cl	Λ^a (Conc. 10^{-4} M)
(I)	*trans*-$RhCl_2(S_2CNMe_2)(PMe_2Ph)_2$	Orange	207-208	39.9	4.9	2.6	12.5	40.0	4.9	2.5	12.5	
(IIa)	*cis*-$[Rh(S_2CNMe_2)_2(PMe_2Ph)_2]\ BPh_4$	Yellow	178-180	58.7	5.7	2.8	-	58.9	5.8	3.0	-	64.8(3.5)
(IIb)	*cis*-$[Rh(S_2CNMe_2)_2(PMe_2Ph)_2]\ PF_6$	Yellow	204-206	34.6	4.5	3.7	-	34.6	4.5	3.7	-	77.4(10.5)
(III)	*mer*- $RhCl_2(S_2CNMe_2)(PMe_2Ph)_3$	Orange	189-195(d)	45.4	5.5	1.7	-	45.8	5.5	2.0	-	
(IV)	*mer*-$[RhCl(S_2CNMe_2)(PMe_2Ph)_3]\ BPh_4$	Yellow	176-178	61.4	5.9	1.3	3.8	61.7	6.0	1.4	3.6	50.0(10.2)
(VIa)	*trans*-$[Rh(S_2CNMe_2)_2(PMePh_2)_2]BPh_4$	Yellow	192-195	62.4	5.6	2.7	-	63.3	5.5	2.6	-	53.2(5.4)
(VIb)	*trans*-$[Rh(S_2CNMe_2)_2(PMePh_2)_2]\ PF_6$	Yellow	230	43.3	4.3	3.1	-	43.2	4.3	3.2	-	68.1(8.7)
(Va),(VIa)	$[Rh(S_2CNMe_2)_2(PMePh_2)_2]BPh_4{}^b$	Yellow	-	62.1	5.6	2.4	-	63.3	5.5	2.6	-	
(VIIa)	*cis*-$[Rh(S_2PPh_2)_2(PMe_2Ph)_2]\ BPh_4$	Yellow	110-112	63.8	5.2	-	-	64.2	5.2	-	-	74.0(2.0)
(VIIb)	*cis*-$[Rh(S_2PPh_2)_2(PMe_2Ph)_2]\ PF_6$	Orange	128-130	47.3	4.2	-	-	47.0	4.1	-	-	74.0(10.5)
(VIII)	*cis*,*cis*,*cis* $RhCl_2(S_2PPh_2)(PMe_2Ph)_2$	Orange	208-210	48.0	4.5	-	-	48.1	4.6	-	-	
(IX)	*cis*-$[Rh(S_2PMe_2)_2(PMe_2Ph)_2]\ BPh_4$	Yellow	72-73	57.2	5.9	-	-	55.7	5.7	-	-	49.2(9.2)
(X)	*mer*- $RhCl_2(S_2PMe_2)(PMe_2Ph)_3$	Orange	140-142(d)	43.9	5.8	-	-	43.8	5.5	-	-	
(XI)	*trans*- $RhCl_2(S_2PMe_2)(PMe_2Ph)_2$	Orange	235-237(d)	37.8	4.9	-	12.5	37.6	4.9	-	12.4	
(XII)	*cis*,*cis*,*cis*-$RhCl_2(S_2PMe_2)(PMe_2Ph)_2$	Orange	184-186	37.8	4.9	-	-	37.6	4.9	-	-	
(XIII)	*trans*- $RhCl_2(S_2PPh_2)(PMe_2Ph)_2$	Orange	228-229(d)	48.1	4.8	-	-	48.1	4.6	-	-	
(XVI)	*mer*- $RhCl(S_2CO)(PMe_2Ph)_3$	Orange	150-155(d)	45.9	5.2	-	-	46.5	5.1	-	-	
(XVII)	$K[RhCl_2(S_2CO)(PMe_2Ph)_2]$	Yellow	195(d)	34.9	3.8	-	-	35.1	3.8	-	-	64.0(5.2)
(XVIII)	*trans*-$Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2$	Yellow	150-153(d)	40.5	4.6	-	-	40.5	4.6	-	-	

TABLE 3.1 (Contd.)

	Complex	Colour	M.p. (°C)	Found %				Required %			
				C	H	N	Cl	C	H	N	Cl
(XIX)	*cis*-Rh(S_2CO)(S_2COEt)(PMe_2Ph)$_2$	Yellow	172-173(d)	40.6	4.7	-	-	40.5	4.6	-	-
(XX)	*trans*-RhCl$_2$(S_2COEt)(PMe_2Ph)$_2$	Orange	155-157	40.1	4.8	-	12.2	39.9	4.7	-	12.5
(XXI)	*mer*-RhCl$_2$(S_2COEt)(PMe_2Ph)$_3$	Orange	120-123(d)	45.4	5.5	-	10.3	45.6	5.4	-	10.0
(XXII)	*mer*-[RhCl(S_2COEt)(PMe_2Ph)$_3$]BPh$_4$	Orange	89-91	59.6	5.8	-	-	61.7	5.8	-	-

[a] In $\Omega^{-1}cm^2mol^{-1}$; measured in CH_3NO_2 at 298K

[b] Mixture of *cis* and *trans* isomers (^{1}H n.m.r. evidence)

Table 3.2

Infrared Spectra of Various Rhodium Dithioacid Complexes

(shoulders underlined)

	Complex	RhCl	Dithioacid Ligand Absorptions
	mer-$RhCl_3(PMe_2Ph)_3$	339, 313, 273	-
(III)	*mer*-$RhCl_2(S_2CNMe_2)(PMe_2Ph)_3$	339, 319	1432^a
(X)	*mer*-$RhCl_2(S_2PMe_2)(PMe_2Ph)_3$	342, 309	601^b
(XXI)	*mer*-$RhCl_2(S_2COEt)(PMe_2Ph)_3$	342, 312	1200^c
(I)	*trans*-$RhCl_2(S_2CNMe_2)(PMe_2Ph)_2$	332, 320	$1520br^a$
(XIII)	*trans*-$RhCl_2(S_2PPh_2)(PMe_2Ph)_2$	340, 330	645, 580^d
(VIII)	*cis*-*cis*-*cis*-$RhCl_2(S_2PPh_2)(PMe_2Ph)_2$	339, 312	630, 576^d
(XI)	*trans*-$RhCl_2(S_2PMe_2)(PMe_2Ph)_2$	*330*, 321	589^e
(XII)	*cis*-*cis*-*cis*-$RhCl_2(S_2PMe_2)(PMe_2Ph)_2$	330, 318	580^e
(XX)	*trans*-$RhCl_2(S_2COEt)(PMe_2Ph)_2$	338, 325	1240^c
(IV)	[*mer*- $RhCl(S_2CNMe_2)(PMe_2Ph)_3]BPh_4$	320	$1549br^a$
(XXII)	[*mer*- $RhCl(S_2COEt)(PMe_2Ph)_3]BPh_4$	342	$1258br^c$
(XVI)	*mer*-$RhCl(S_2CO)(PMe_2Ph)_3$	312	$1680br^f$, 1600^f
(XVII)	$K[RhCl_2(S_2CO)(PMe_2Ph)_2]$	320	1640^f 1610^f
(XVIII)	*trans*-$Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2$	-	$1670br^f$, 1592^f, 1248^c
(XIX)	*cis*-$Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2$	-	$1680br^f$, 1598^f, 1255^c
(IIa)	*cis*-$[Rh(S_2CNMe_2)_2(PMe_2Ph)_2]BPh_4$	-	$1540br^a$
(IIb)	*cis*-$[Rh(S_2CNMe_2)_2(PMe_2Ph)_2]PF_6$	-	$1540br^a$
(VIIa)	*cis*-$[Rh(S_2PPh_2)_2(PMe_2Ph)_2]BPh_4$	-	$572^{d,g}$
(VIIb)	*cis*-$[Rh(S_2PPh_2)_2(PMe_2Ph)_2]PF_6$	-	$572^{d,g}$
(IX)	*cis*-$[Rh(S_2PMe_2)_2(PMe_2Ph)_2]BPh_4$	-	577^e

[a] νCN ($^-S_2CNMe_2$) (ref 14 and 233)

[b] unidentate band (for $^-S_2PMe_2$) (ref 16)

[c] $\nu C\text{-}O$ ($^-S_2COEt$) (ref 103)

[d] bidentate bands (for $^-S_2PPh_2$) (ref 15)

[e] bidentate band (for $^-S_2PMe_2$) (ref 16)

[f] $\nu C{=}O$ ($^{2-}S_2CO$) (ref 281)

[g] Higher energy band positions masked by BPh_4^- or PF_6^- vibrations.

TABLE 3.3

^{1}H n.m.r. data for various sulphur compounds (in $CDCl_3$)

	Compound	T/K	τ Value ^{a}		
			Dithio-ligand	Methyl(phosphine)	Phenyl Groups
	mer-$RhCl_3(PMe_2Ph)_3$	301	-	8.04t(8.0)^b 8.70d(11.0)^c	2.3-3.2
(III)	mer-$RhCl_2(S_2CNMe_2)(PMe_2Ph)_3$	301	6.83s.	8.02t(8.0)^b 8.76d(12.0)^c	2.2-3.0
(X)	mer-$RhCl_2(S_2PMe_2)(PMe_2Ph)_3$	301	7.72d(13.0)^c	7.88t(8.0)^b 8.74d(11.0)^c	2.2-3.2
(XXI)	mer-$RhCl_2(S_2COEt)(PMe_2Ph)_3$	301	5.47q(7.0)^e 8.56t(7.0)^e	8.18t(8.0)^b 8.80d(11.0)^c	2.3-3.2
(IV)	mer-$[RhCl(S_2CNMe_2)(PMe_2Ph)_3]BPh_4$	301	7.14s, 7.45s	8.20t(7.5)^b 8.34t(7.5)^{b}8.72d(10.5)^c	2.0-3.3
(XVI)	mer-$RhCl(S_2CO)(PMe_2Ph)_3$	301	-	7.98t(7.5)^b 8.33t(7.5)^{b}8.85d(10.0)^c	2.2-3.4
(I)	trans-$RhCl_2(S_2CNMe_2)(PMe_2Ph)_2$	301	6.54s	8.31^f(11.0)^b	2.2-2.8
(XI)	trans-$RhCl_2(S_2PMe_2)(PMe_2Ph)_2$	301	7.98d(13.0)^c	8.32^f(11.0)^b	2.2-2.8
(XIII)	trans-$RhCl_2(S_2PPh_2)(PMe_2Ph)_2$	301	-	8.34^f(11.0)^b	2.2-2.8
(XX)	trans-$RhCl_2(S_2COEt)(PMe_2Ph)_2$	301	5.50q(7.0)^e, 8.66t(7.0)^e	8.29^f(11.0)^b	2.2-2.8
(XII)	cis,cis,cis-$RhCl_2(S_2PMe_2)(PMe_2Ph)_2$	301	7.52d(13.0)^c, 8.26d(13.0)^c	8.10^f(11.0)^b 8.29^f(11.0)^b	2.4-3.2
(XVII)	$K[RhCl_2(S_2CO)(PMe_2Ph)_2]$ ^{g}	301	-	8.22t(8.0)^b	2.0-2.9
(XVIII)	trans-$Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2$	301	6.30q(7.0)^e, 8.90t(7.0)^e	8.16t(7.0)^b	2.4-2.8
(XIX)	cis-$Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2$	301	5.44q(7.0)^e, 8.57t(7.0)^e	8.24d(9.0)^c, 8.35d(9.0)^c, 8.48d(9.5)^c 8.53d(9.0)^c	2.6-3.2
(IX)	cis-$[Rh(S_2PMe_2)_2(PMe_2Ph)_2]BPh_4$	301	7.86d(13.0)^c, 8.30d(13.0)^c	8.32^f(8.0)^b, 8.42^f(8.0)^b	2.4-3.4
(VIIa)	cis-$[Rh(S_2PPh_2)_2(PMe_2Ph)_2]BPh_4$	301	-	8.38^f(10.0)^b, 8.48^f(10.0)^b	2.0-3.2
(VIIb)	cis-$[Rh(S_2PPh_2)_2(PMe_2Ph)_2]PF_6$	301	-	8.22^f(10.0)^b, 8.28^f(10.0)^b	2.0-3.2

TABLE 3.3

	Compound	T/K	τ Value [a] Dithio-ligand	Methyl(phosphine)	Phenyl Groups
(IIa)	*cis*-$[Rh(S_2CNMe_2)_2(PMe_2Ph)_2]BPh_4$	301	6.96s, 7.00s	8.46^f(8.0)^b; 8.56^f(8.0)^b	2.4-3.3
		333	6.93s, 6.96s	8.45^f(10.0)^b, 8.50^f(10.0)^b	
(IIb)	*cis*-$[Rh(S_2CNMe_2)_2(PMe_2Ph)_2]PF_6$	227	6.63s, 6.65s	8.32^f(9.5)^b; 8.38^f(9.5)^b	2.6-3.2
		264	6.67s, 6.68s	8.34^f(9.5)^b 8.38^f(10.5)^b	
		301	6.71s	8.37^f(9.5)^b	
(VIa)	*trans*-$[Rh(S_2CNMe_2)_2(PMePh_2)_2]BPh_4$	301	7.60s	7.92t(6.5)^b	2.4-3.4
(VIb)	*trans*-$[Rh(S_2CNMe_2)_2(PMePh_2)_2]PF_6$	301	7.33s	7.90t(7.0)^b	2.3-3.2
(Va)	*cis*-$[Rh(S_2CNMe_2)_2(PMePh_2)_2]BPh_4$[h]	301	7.22s, 7.40s	8.18^f (8.0)^b	2.4-3.4
(Vb)	*cis*-$[Rh(S_2CNMe_2)_2(PMePh_2)_2]PF_6$[h]	301	7.00s, 7.27s	8.08^f (8.0)^b	2.3-3.2

s(singlet); d(doublet); t(triplet); q(quartet)

[a] ± 0.01

[b] Since $H_nPP'H_n'$ type spectrum, coupling constant is $J_{PH} + J_{PH'}$ Hz

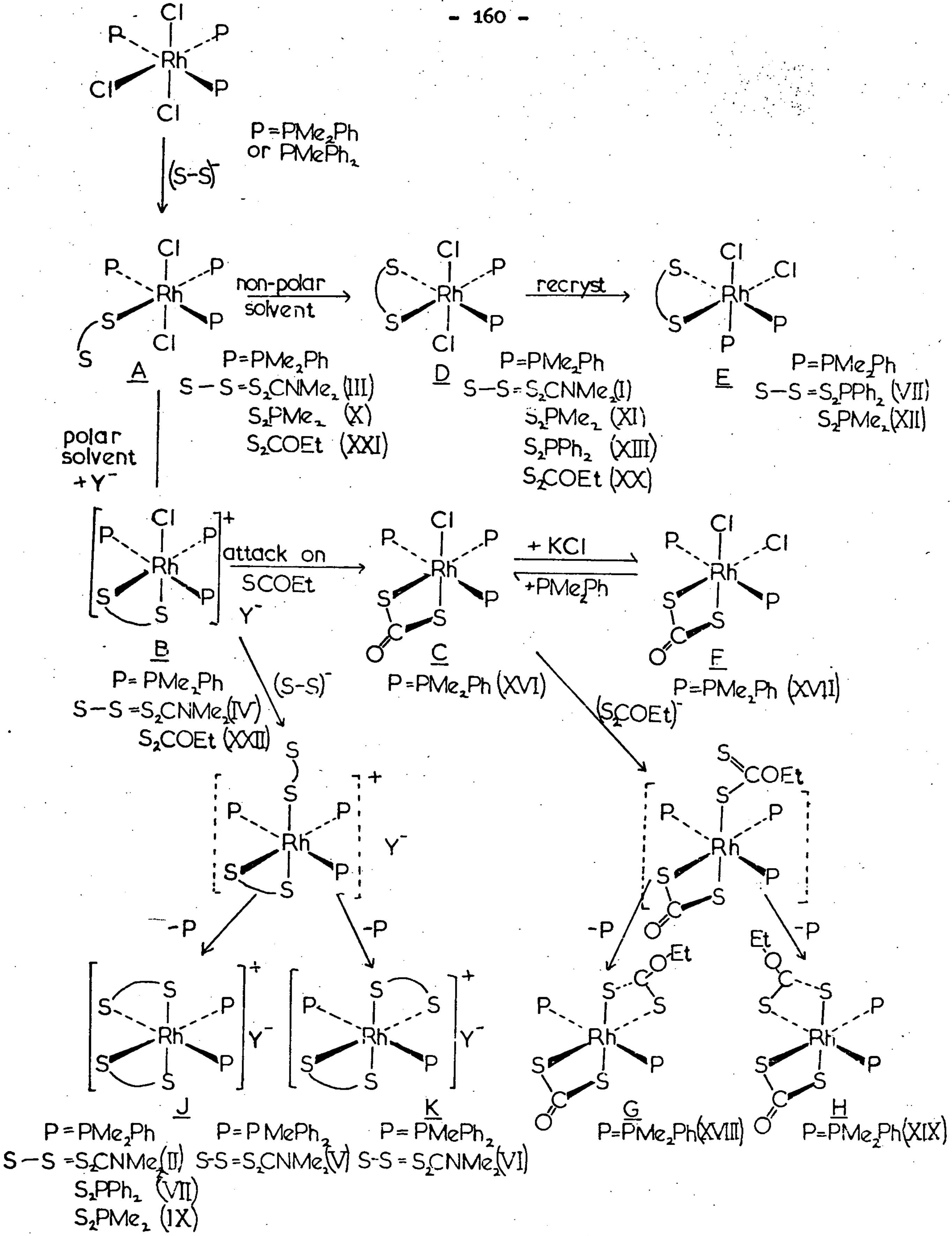
[c] J_{PH}(Hz)

[e] $J_{CH_3-CH_2}$ (Hz)

[f] Pseudo-doublet

[g] Measured in $(CD_3)_2CO$.

[h] Spectrum obtained from mixture of *cis* and *trans* isomers.



SCHEME 3.1

Proposed mechanism for reactions of <u>mer</u>-RhCl$_3$(PMe$_2$Ph)$_3$ with (S-S)$^-$

(Compounds in dashed brackets have not been isolated)

Chapter 4.

Reactions of mer-$OsCl_3(PMe_2Ph)_3$ with Dithioacid Ligands.

Introduction

The investigation of the reactions of mer-$RhCl_3(PMe_2Ph)_3$ with dithioacid ligands gave considerable insight into the possible nature of some of the paramagnetic intermediates which might be formed in the preparation of cis-$Ru(S_2PR_2)_2(PMe_2Ph)_2$ (R = Me or Ph) from mer-$RuCl_3(PMe_2Ph)_3$ but, on account of the stability of Rh(III) complexes with respect to reduction to Rh(II), no information can be gleaned about the step at which reduction to Ru(II) occurs, or the nature of any Ru(II) intermediates. However, it was felt that, since osmium not only has stable oxidation states of +2 and +3, but also is considered to be much less labile than ruthenium in both of these oxidation states[286b], an investigation of some of the reactions of halo-osmium complexes, containing phosphines, with dithioacid ligands might shed some extra light on the mechanism of formation of cis-$Ru(S_2PR_2)_2(PMe_2Ph)_2$ from mer-$RuCl_3(PMe_2Ph)_3$.

The phosphine chemistry of osmium, although less extensively studied than that of the other metals of the iron group, has been shown to be similar to that of ruthenium, except that higher oxidation states tend to be more stable and less labile than their ruthenium analogues[286]. Thus, although very few phosphine containing complexes of Ru(IV) have been isolated[286a], OsX_4L_2 (X = Cl or Br, L = PPr_3, PMe_2Ph, PPr_2Ph, PBu_2Ph) may be prepared either by oxidation of mer-$OsCl_3L_3$ with CCl_4[293], or chlorine in the presence of u.v. light[358], or by the controlled reduction of OsO_4 with L in the presence of HX[293]. Prolonged reaction of

OsO_4 with L in boiling HX gives stepwise reduction to mer-OsX_3L_3 and finally the triply bridged ionic species $[Os_2X_3L_6]X$ is formed[293]. The harsher condition required to form $[Os_2X_3L_6]X$[293] compared with the preparation of $[Ru_2X_3L_6]X$[289] (see page 43) is probably a reflection both of the higher stability to reduction of the Os(III) compound and the lower lability of the osmium complexes. $[Os_2X_3L_6]X$ may also be prepared by the reaction of $(NH_4)_2OsX_6$ with L in aqueous ethanol[289] or by reduction of mer-$OsCl_3(PMe_2Ph)_3$, but in the latter reaction, trans $OsCl_2(PMe_2Ph)_4$ is also isolated[359]. This is further evidence for the lower lability of Os(II) than of Ru(II) since under similar conditions, $RuCl_2(PMe_2Ph)_4$ rapidly rearranges to give $[Ru_2Cl_3(PMe_2Ph)_6]Cl$[291] (page 43).

Very little work has been carried out on the synthesis of osmium compounds containing sulphur donor ligands although, apart from the compounds mentioned in the review section (pages 26 - 32) some spectrophotometric investigations on the reactions of Os(III) and Os(IV) with HS_2CR (R = Bz or p-MeBz) have shown that complexes of stoichiometry $Os(S_2CR)_n$ (n = 3 or 4) are formed, depending upon the pH of the solution[360].

Results and discussion

As noted above, mer-$OsCl_3(PMe_2Ph)_3$ can be prepared by the reaction of OsO_4 with PMe_2Ph in HCl, or, in low yield by refluxing $(NH_4)_2OsCl_6$ with excess PMe_2Ph in 2-methoxyethanol[293]. We have been able to increase the yield of the latter reaction to ca. 100% by addition of HCl to the mixture and by prolonging the reflux for sixteen hours. On account of this facile preparation of mer-$OsCl_3(PMe_2Ph)_3$ in high yield, some reactions of the complex with dithioacid anions were carried out and the results of this investigation are detailed below. Table 4.1 contains analytical data for the complexes whilst their spectroscopic properties are given in Tables 4.2 and 4.3.

1. N,N-dimethyldithiocarbamato complexes

If mer-$OsCl_3(PMe_2Ph)_3$ is refluxed with excess NaS_2CNMe_2 for 90 mins. in ethanol, a yellow compound of composition $Os(S_2CNMe_2)_2$-$(PMe_2Ph)_2$ (I) is isolated in ca. 80% yield and the remaining solution may be shown by (t.l.c.) to contain three other coloured compounds which are present in small quantities, together with some white $(S_2CNMe_2)_2$. Shaking the two reactants in methanol for 10 mins produces a single yellow compound of formula $Os(S_2CNMe_2)Cl(PMe_2Ph)_3$(II) and a white solid, $(S_2CNMe_2)_2$, along with a very small quantity of (I). If, however, this latter reaction is carried out in the presence of excess PMe_2Ph, the previously known pale yellow complex, $OsCl_2(PMe_2Ph)_4$, is isolated and this is oxidised quantitatively to mer-$OsCl_3(PMe_2Ph)_3$ and Me_2PhPO on standing in $CDCl_3$ (c.f. the reaction of $[RhCl_2(PMe_2Ph)_4]^+$ with $CDCl_3$ to give mer-$RhCl_3(PMe_2Ph)_3$ (page 135)).

Attempts to prepare compounds of the form $Os(S_2CNMe_2)_2(PMe_2Ph)_3$ by the reaction of (II) with NaS_2CNMe_2 in the presence of excess PMe_2Ph were unsuccessful, giving only unchanged starting material. However, (II) does react with NaS_2CNMe_2 in refluxing ethanol and in the absence of excess PMe_2Ph to produce, after 90 mins, (I) and the other three coloured compounds that were prepared in the earlier preparation of (I) but in this case, (I) is only obtained in ca. 50% yield.

Reaction of (II) with KS_2COEt in refluxing ethanol again

produces several compounds, four of which are the same as those produced from the reaction of (II) with NaS_2CNMe_2 and the fifth is an orange compound of higher r.f. value than the others. In this case, the five complexes were separated on a dry alumina column and, after recrystallisation, were shown to have the following composition, in decreasing order of r.f value:
$Os(S_2CNMe_2)(S_2COEt)(PMe_2Ph)_2$ (III), (I), $Os(S_2CNMe_2)Cl(PMe_2Ph)_3$ (IV) (but with different spectral properties from (II))
$Os(S_2CNMe_2)(OEt)(PMe_2Ph)_3$ (V) and a red oil which could not be recrystallised or identified.

The stereochemistries of these complexes will be discussed in the spectroscopic section of this chapter but it is of interest to note that, although reaction of (II) with NaS_2CNMe_2 does give rise to the formation of (I), the yield of (I) is not as high as from the reaction of mer-$OsCl_3(PMe_2Ph)_3$ with (I). Thus, although (II) may be an intermediate in the formation of (I) from mer-$OsCl_3(PMe_2Ph)_3$, a parallel pathway which does not involve (II) as an intermediate must also be operating to form (I). The mechanistic implications of this observation will be discussed later in this chapter.

2. Diphenyl and dimethylphosphinodithioato complexes

As for the dithiocarbamate, reactions of mer-$OsCl_3(PMe_2Ph)_3$ with excess NaS_2PMe_2 or $NH_4S_2PPh_2$ in refluxing ethanol lead to the formation of orange solutions from which highly crystalline complexes of formula $Os(S_2PR_2)_2(PMe_2Ph)_2$(R = Me(VI) or Ph(VII)) may be isolated in high yield. Solutions of these complexes rapidly turn green in the presence of air and as with cis-$Ru(S_2PMe_2)_2(PMe_2Ph)_2$, broadening of the previously sharp ^1H n.m.r. signals is observed indicating that oxidation to a paramagnetic species is probably occurring. Again as for the ruthenium complexes, sharp peaks grow up in these spectra after several weeks but these are thought to arise from non-metal-containing decomposition products since the ruthenium and osmium spectra are superimposable and one of the doublets in the spectrum is assignable to Me_2PhPS. During one of the preparations of (VI), a pale yellow compound was isolated. This is the well known $[Os_2Cl_3(PMe_2Ph)_6]Cl$ which is formed when mer-$OsCl_3(PMe_2Ph)_3$ is refluxed in aqneous ethanol (see page 162).

As with mer-$RhCl_3(PMe_2Ph)_3$, shaking excess NaS_2PMe_2 with mer-$OsCl_3(PMe_2Ph)_3$ in methanol produces a compound of formula $Os(S_2PMe_2)Cl_2(PMe_2Ph)_3$ (VIII), but in this case, the compound is purple and a reaction time of 90 mins. (c.f. 10 mins. for Rh) is required for complete conversion. The analogous compound, $Os(S_2PPh_2)Cl_2(PMe_2Ph)_3$ (IX) may also be prepared, but by interaction of a methanolic solution of NaS_2PPh_2 with a solution of mer-$OsCl_3(PMe_2Ph)_3$ in CH_2Cl_2, followed by evaporation of the CH_2Cl_2 and collection of the methanol insoluble product. Since (IX) is more difficult to prepare than (VIII), and less amenable to ^1H n.m.r. studies, its reactions were not investigated further, but those of (VIII) were studied in some detail.

Thus, (VIII) may be recovered unchanged if it is recrystallised quickly from CH_2Cl_2/n-Hexane in the cold (contrast the facile formation of trans-$Rh(S_2PMe_2)Cl_2(PMe_2Ph)_2$ on recrystallisation of mer-$Rh(S_2PMe_2)Cl_2(PMe_2Ph)_3$) but if the solution is warmed and allowed to stand, quantitative conversion to the red mer-$OsCl_3(PMe_2Ph)_3$ occurs, whilst prolonged reaction of (VIII) with PMe_2Ph in cold CH_2Cl_2 produces a yellow solution from which $[Os_2Cl_3(PMe_2Ph)_6]Cl$ may be isolated. Recrystallisation of (VIII) from boiling benzene in air gives a red compound of formula $Os(S_2PMe_2)Cl_2(PMe_2Ph)_2$(X) together with some Me_2PhPO, whereas if (VIII) is allowed to stand in cold benzene for two weeks, three compounds may be isolated from the resulting brown solution by fractional crystallisation with n-Hexane. These are, a purple, strongly conducting oil, which is thought to contain the cationic $[Os(S_2PMe_2)Cl(PMe_2Ph)_3]^+$(XI), a brown crystalline solid of formula $Os(S_2PMe_2)Cl(PMe_2Ph)_3$(XII) and <u>mer</u>-$OsCl_3(PMe_2Ph)_3$. Longer reaction times in cold benzene (4 weeks) produce only (XII) and <u>mer</u>-$OsCl_3(PMe_2Ph)_3$. Finally, shaking (VIII) in acetone for several days again produces a highly conducting purple oil, as well as <u>mer</u>-$OsCl_3(PMe_2Ph)_3$, but, in this instance, none of (XII).

As in the case of <u>cis</u>-$Ru(S_2PMe_2)_2(PMe_2Ph)_2$, $Os(S_2PMe_2)_2(PMe_2Ph)_2$ reacts with carbon monoxide under mild conditions. Thus, reaction of $Os(S_2PMe_2)_2(PMe_2Ph)_2$ with CO in refluxing ethanol, in the presence of a small amount of elemental sulphur, produces a compound of formula $Os(S_2PMe_2)_2(PMe_2Ph)CO$ (XIII) together with a brown oil which contains (i.r. and n.m.r. evidence) both Me_2PhPS and a compound with two cis CO groups, of probable formula, $Os(S_2PMe_2)_2(PMe_2Ph)(CO)_2$ (XIV). If the reaction is carried out in the presence of excess PMe_2Ph, a yellow crystalline complex of formula $Os(S_2PMe_2)_2(PMe_2Ph)_2CO$ (XV) is exclusively formed. Finally, reaction of $Os(S_2PMe_2)_2(PMe_2Ph)_2$ with CO in cold CH_2Cl_2/n-hexane gives another yellow complex, probably of formula $Os(S_2PMe_2)_2(PMe_2Ph)_2CO$ (XVI), which rapidly becomes green on exposure to air and whose structure will be discussed later in this chapter.

3. O-ethyldithiocarbonato(xanthato) complexes

The reaction of mer-$OsCl_3(PMe_2Ph)_3$ with KS_2COEt is rather different from those with the other dithioacid anions studied since both refluxing the reactants in ethanol for one hour and shaking them together in methanol for 10 mins. produce only one compound, which has the formula $Os(S_2COEt)Cl(PMe_2Ph)_3$(XVII), Attempts to react this compound further with either KS_2COEt or NaS_2CNMe_2 proved abortive yielding only unchanged starting materials in both cases. An attempt to prepare compounds of the type $Os(S_2COR)_2(PMe_2Ph)_2$ by reaction of mer-$OsBr_3(PMe_2Ph)_3$ (made by metathetical halide exchange of mer-$OsCl_3(PMe_2Ph)_3$) with KS_2COEt also proved fruitless since, although no solid product could be isolated, an n.m.r. spectrum of the resultant orange oil indicated that $Os(S_2COR)Br(PMe_2Ph)_3$ (XVIII) was the only identifiable product.

4. Spectroscopic properties of dithioacid complexes

a) Infra-red spectra

Like mer-$RhCl_3(PMe_2Ph)_3$ (page 138), mer-$OsCl_3(PMe_2Ph)_3$ has three i.r. active Os-Cl stretching vibrations and these are assigned to the absorptions at 350, 312 and 270 cm^{-1}. Again by analogy with the rhodium complex, the band of lowest energy (270 cm^{-1}) is assigned as arising predominantly from the Os-Cl bond trans to the highest trans-influence ligand (PMe_2Ph). Then, the two absorptions at 350 and 312 cm^{-1} are assigned as arising predominantly from the symmetric and asymmetric Cl-Os-Cl stretches. Although the exact assignment of these two stretches to ν_s and ν_{as} is not possible[361], since in a molecule of this size mixing with other vibrations of the same symmetry may be occurring, this region may be used as a 'finger-print' in assigning stereochemistries to similar molecules.

Analysis of the Os-Cl stretching regions of $Os(S_2PR_2)Cl_2(PMe_2Ph)_3$ (R = Me or Ph) (Table 4.2) indicates that in both cases the chloride ion trans to phosphine has been removed, which is expected in view of the greater trans-influence of PMe_2Ph as compared with chloride. This fact, coupled with the observations that absorptions in the P=S stretching regions indicate that only unidentate S_2PR_2 groups are present, and that $Rh(S_2PMe_2)Cl(PMe_2Ph)_3$ has the meridional configuration (see page 140) leads to the conclusion that compounds (VIII) and (IX) both have the structure A (see Scheme 4.1). The compound $Os(S_2PMe_2)Cl_2(PMe_2Ph)_2$ has a strong absorption at 300 cm^{-1} and the strength of this absorption together with its position indicates that it probably arises from a trans-Cl-Os-Cl group (C).

The similar νOs-Cl frequencies of complexes (XII), (II) and (XVII), all of which have formula $Os(S-S)Cl(PMe_2Ph)_3$ (S-S = S_2PMe_2, S_2CNMe_2 or S_2COR), indicate that these complexes probably have a common stereochemistry. Since the other isomer of $Os(S_2CNMe_2)Cl(PMe_2Ph)_3$ (IV) has a lower νOs-Cl, it is likely that in this compound, the chloride ion is trans to a phosphine group (F) and is thus more labile, whilst the other compounds ((XII), (II) and (XVII)) probably have a meridional configuration (E). The other complexes, apart from those containing CO, all have dithioacid absorptions characteristic of bidentate co-ordination (Table 4.2) and little information as to their stereochemistries can be gleaned from their i.r. spectra, although the presence of a C-O stretching frequency at 1030 cm^{-1} in $Os(S_2PMe_2)\ OEt(PMe_2Ph)_3$ is in the region of an ethoxy group which is directly bound to a metal(1000-1100 cm^{-1})[362].

For the carbonyl containing species, although once again the region from 700-500 cm^{-1} in their i.r. spectra is complicated by the presence of C=O bending modes, it can be seen from Table 4.2 that the two complexes of formula $Os(S_2PMe_2)_2(PMe_2Ph)_2CO$ as well as $Os(S_2PMe_2)_2(PMe_2Ph)(CO)_2$ probably contain both unidentate and bidentate S_2PMe_2 groups and that the last compound has the two CO groups in a <u>cis</u> configuration (two νCO). The higher value of νCO for $Os(S_2PMe_2)_2(PMe_2Ph)_2CO$ (XVI) than for the other two monocarbonyl species indicates that the CO groups in (XVI) may be trans to PMe_2Ph (c.f. $Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$(E) (page 104)). Finally, the absence of a peak at 600 cm^{-1}, in the i.r. spectrum of $Os(S_2PMe_2)_2(PMe_2Ph)CO$ (XIII) indicates that this compound probably does not contain unidentate S_2PMe_2 groups.

b) <u>Mass spectra</u>

The mass spectra of $Os(S_2PMe_2)_2(PMe_2Ph)CO$ (XIII) and $Os(S_2PMe_2)_2(PMe_2Ph)_2CO$ (XV) are identical since (XV) readily loses PMe_2Ph at high temperatures to form (XIII). Their mass spectra show well defined, intense osmium isotope patterns which correspond to $[Os(S_2PMe_2)_2(PMe_2Ph)CO]^+$ (608)[*], $[Os(S_2PMe_2)_2(PMe_2Ph)]^+$ (580), $[Os(S_2PMe_2)_2(PMe_2Ph)]^+$ (580), $[Os(S_2PMe_2)_2]^+$ (442) and $[Os(S_2PMe_2)_2(PMe_2Ph)]^{2+}$ (290), as well as several weaker patterns corresponding to loss of methyl groups and large metastable ion signals at 560 and 347 a.m.u. which correspond to the loss of CO from $[Os(S_2PMe_2)_2(PMe_2Ph)CO]^+$ and of PMe_2Ph from $[Os(S_2PMe_2)_2(PMe_2Ph)]^+$ respectively.

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[*] Numbers in brackets refer to $^m/_e$ ratio of Os^{192} peak.

The mass spectrum of $Os(S_2CNMe_2)Cl(PMe_2Ph)_3$(II) is also of interest since it not only shows the parent ion and fragmentation pattern corresponding to this compound, but also those for two other compounds, $Os(S_2CNMe_2)_2(PMe_2Ph)_2$(I) and $Os(S_2CNMe_2)Cl_2(PMe_2Ph)_3$ (see Table 4.3). Since there is no evidence for (I), or an isomer of (I), in the n.m.r. spectrum of (II) and since the relative intensities of the mass spectral signals arising from these two compounds are comparable in two different samples, it seems likely that (I) is formed from (II) under the extreme conditions of the mass spectrometer (200°C). However, since the intensities of the mass spectral signals arising from $Os(S_2CNMe_2)Cl_2(PMe_2Ph)_3$ vary considerably relative to those of (II) from one sample to another, it is likely that this compound is an impurity in (II). This is quite possible since the mode of preparation of (II) is similar to that of $Os(S_2PMe_2)Cl_2(PMe_2Ph)_3$, and the presence of this Os(III) impurity might also explain the broadness of the signals observed in the n.m.r. signals of (II) (see later).

c) ^{1}H n.m.r. spectra

The ^{1}H n.m.r. spectra of mer-$Os(S_2PR_2)Cl_2(PMe_2Ph)_3$ (R = Me(VIII) or Ph(IX)) and of trans-$Os(S_2PMe_2)Cl_2(PMe_2Ph)_2$(X) all show ill defined, contact shifted resonances from which very little structural data may be obtained. These spectra are indicative of paramagnetic species and solution magnetic moments (see Table 4.1) (by Evans' method)[319] lie well within the range expected for one unpaired electron and are consistent with the formulation of these complexes as containing Os(III). On account of the broadness of the signals, little structural data may be obtained from these ^{1}H n.m.r. spectra but the structures of (VIII), (IX) (A) and (X) (C) indicated by their i.r. spectra are consistent with those of the analagous diamagnetic Rh(III) complexes (page 160) as well as with their modes of preparation which involve replacement of the most labile chloride ion in mer-$OsCl_3(PMe_2Ph)_3$ by a unidentate (S-S) ligand ((VIII), (IX)) followed by chelation of this dithioacid ligand with concomitant loss of phosphine to form (X) (see Scheme 4.1). The remaining complexes are all diamagnetic and give rise to sharp n.m.r. signals from which their structures in solution may be unequivocally assigned.

The methyl groups on the phosphine ligands of $Os(S-S)X(PMe_2Ph)_3$ (X = Cl, S-S = S_2PMe_2(XII) or S_2COEt(XVII); X = Br, S-S = S_2COEt(XVIII)) give rise to two virtually coupled triplets and a sharp doublet in their ^1H n.m.r. spectra. The doublet must arise from a single phosphine group which has a plane of symmetry passing through the Os-P bond (since the methyl groups on that phosphine are equivalent), whereas the fact that two triplets are observed is indicative of two trans phosphines with no plane of symmetry through the Os-P bonds. This, together with the presence of only one methyl doublet from the S_2PMe_2 group of (XII), confirms that these complexes have the meridonal structure (E).

At low temperature, the ^1H n.m.r. spectra of complexes $Os(S_2CNMe_2)X(PMe_2Ph)_3$ (X = Cl(IV) or OEt(V)) consist of two pseudo-doublets and a sharp doublet arising from the methyl groups of the phosphines as well as a sharp singlet at lower field from the methyl groups of the dithiocarbamate ligand. For (V), there are also a quartet and a triplet arising from the OEt group. This information indicates that the complexes do not contain mutually trans phosphine groups and hence must have a facial configuration (F,G). Then, the phosphines trans to the sulphur atoms are chemically equivalent and give rise to the pseudo-doublets (there are two such pseudo-doublets since, there being no plane of symmetry through the Os-P bonds, hindered rotation about these bonds makes the two methyl groups on one phosphine inequivalent). The phosphine trans to X is unique and, since a plane of symmetry passes through that Os-P bond, gives rise to a single methyl doublet. At higher temperatures, the two pseudo-doublets of (V) become coincident, indicative of fast rotation about the Os-P bonds.

The ^1H n.m.r. spectrum of $Os(S_2CNMe_2)Cl(PMe_2Ph)_3$(II) is more difficult to interpret since, although immediately after the solution is made up, the resonances are relatively sharp, they rapidly become broad. This is presumably because the compound is rapidly air oxidised or, more likely, because a paramagnetic impurity is present in the solution.* (II) is assigned a meridional configuration partly on the basis of decoupling studies and partly because it is different from (IV) which definitely is the facial isomer. Irradiation in the region of ^{31}P resonances causes sharpening of the slightly broad singlets at τ8.20 and

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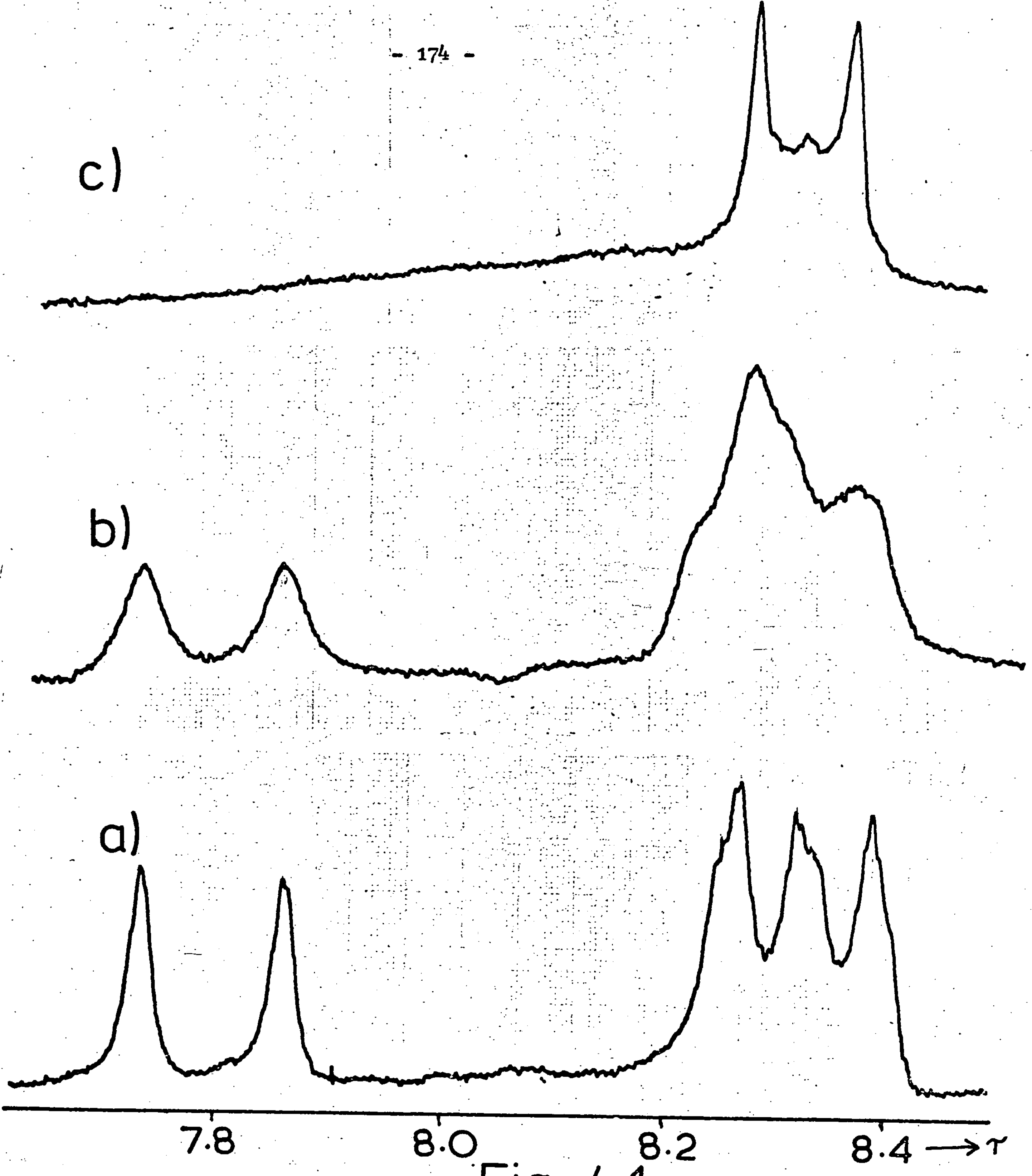
* A weak e.s.r. signal is observed in the solid, but, since its position is not reproducible it is probably due to a small amount of paramagnetic impurity in the sample rather than any inherent paramagnetism of the compound itself. The nature of this impurity is unclear although the presence of $[Os(S_2CNMe_2)Cl_2(PMe_2Ph)_3]^+$ in the mass spectrum of (II) could indicate that $Os(S_2CNMe_2)Cl_2(PMe_2Ph)_3$ is the impurity but this could also be formed in the mass spectrometer (see page 170).

8.34 which indicates that these are separate resonances with some P-H coupling. Irradiating at a different frequency in the same region decouples the doublet at τ8.66 to a singlet and thus it is most likely that the ^{1}H n.m.r. spectrum of the phosphine methyl groups is similar to those of the meridional complexes (XII), (XVII) and (XVIII) and that (II) also has the meridional configuration (E).

The low temperature ^{1}H n.m.r. spectra of $Os(S\text{-}S)_2(PMe_2Ph)_2$ (S-S = S_2PMe_2(VI), (Figure 4.1(a), page 174), S_2PPh_2(VII) or S_2CNMe_2(I) (Figure 4.2(a), page 175)) are all consistent with cis stereochemistry although the non-equivalence of the methyl groups of (VII) is not seen even at 213K. As for cis-$Ru(S_2PMe_2)_2(PMe_2Ph)_2$ (page 59), the two doublets arising from the S_2PMe_2 groups of VI broaden and coalesce on warming (Figure 4.1 (b and c), page 174) but in this case, the coalescence temperature is ca. 328K and the fast exchange limit is not reached in $CDCl_3$. The two pseudo-doublets from the phosphine methyl groups also coalesce on warming (Figure 4.1 (b), page 174) to give a sharp signal at higher temperatures (Figure 4.1(c), page 174). This behaviour is again attributed to a rapid interconversion of the two possible optical isomers of (VI) and Arrhenius plots together with related activation parameters for the inversion in $CDCl_3$ and C_6H_6 are given in Figure 4.3, (page 176). Since there is negligible difference in $\Delta H^{\ddagger}$ for this inversion on changing the solvent from $CDCl_3$ to C_6H_6, it is unlikely that a solvent assisted process is operating in this case[333,339]. However, the large positive values of $\Delta S^{\ddagger}$ together with the comparable values of the activation parameters for the inversions of cis-$Ru(S_2PMe_2)_2(PMe_2Ph)_2$ and of cis-$Os(S_2PMe_2)_2(PMe_2Ph)_2$ in C_6H_6 lead us to conclude that a



Methyl region of ^1H n.m.r. spectrum of cis-Os$(S_2PMe_2)_2(PMe_2Ph)_2$(VI) in $CDCl_3$ at different temperatures.

a) 273K b) 306K c) 333K

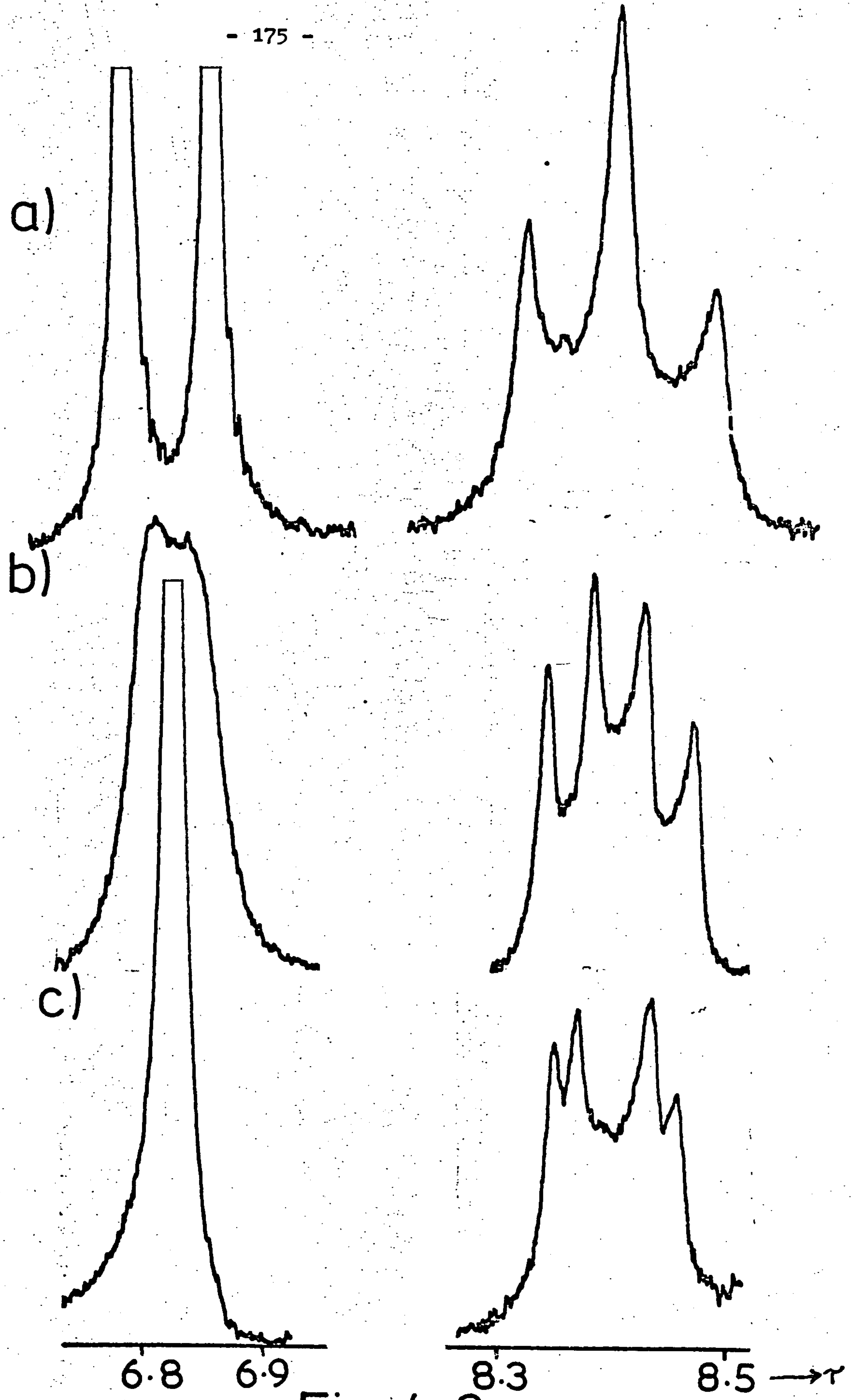
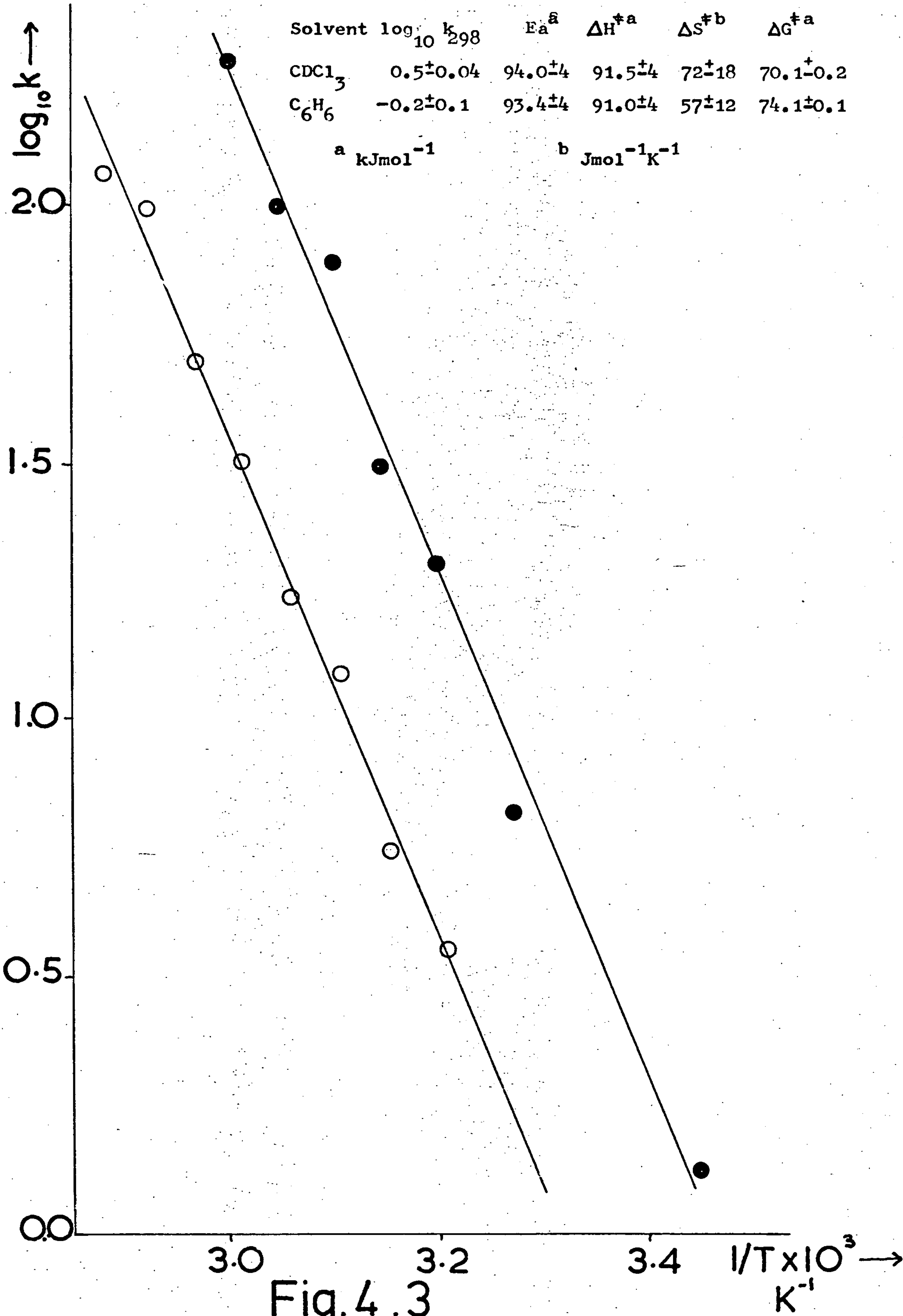


Fig.4.2

Methyl region of ^1H n.m.r. spectrum of <u>cis</u>-Os$(S_2CNMe_2)_2(PMe_2Ph)_2(I)$ in $CDCl_3$ at different temperatures.

a) 253K b) 303K c) 333K



Solvent	$\log_{10} k_{298}$	Ea^a	$\Delta H^{\ddagger a}$	$\Delta S^{\ddagger b}$	$\Delta G^{\ddagger a}$
$CDCl_3$	0.5 ± 0.04	94.0 ± 4	91.5 ± 4	72 ± 18	70.1 ± 0.2
C_6H_6	-0.2 ± 0.1	93.4 ± 4	91.0 ± 4	57 ± 12	74.1 ± 0.1

[a] $kJmol^{-1}$ [b] $Jmol^{-1}K^{-1}$

Fig. 4.3

Arrhenius plots ($\log_{10}$ k vs $^1/_T$) and activation parameters for <u>cis</u>-$Os(S_2PMe_2)_2(PMe_2Ph)_2$(VI) in different solvents.

similar mechanism to that shown in Figure 2.13(b) (page 92) is operating for the inversion of cis-$Os(S_2PMe_2)_2(PMe_2Ph)_2$ in both $CDCl_3$ and C_6H_6.

On raising the temperature, the ^1H n.m.r. spectrum of I also undergoes interesting changes (Figure 4.2, page 175). The two S_2CNMe_2 methyl singlets undergo coalescence behaviour to give a sharp singlet at higher temperatures (Figure 4.2(c), page 175), whilst the two pseudo doublets from the phosphine methyl groups gradually move together without broadening. This behaviour is similar to that found for cis-$Ru(S_2CNMe_2)_2(PMe_2Ph)_2$ (page 73) and cis-$[Rh(S_2CNMe_2)_2(PMe_2Ph)_2]$ BPh_4 (page 146) and once again cannot be explained in terms of a metal centred inversion, but rather by separate processes involving increases in the rates of rotation about the $C\underline{...}N$ bonds of the S_2CNMe_2 ligands and about the Os-P bonds at higher temperatures.

The low temperature ^1H n.m.r. spectrum of $Os(S_2PMe_2)_2(PMe_2Ph)CO$(XIII) consists of six doublets arising from the six inequivalent methyl groups in the molecule and indicative of cis stereochemistry (Figure 4.4(a), page 178). However, on warming, the two doublets arising from the methyl groups on the phosphine (c and c$'$) become coincident, presumably because of fast rotation about the Os-P bond, but also, more surprisingly, two of the dithioacid doublets (b and b$'$) move together until at ca. 283K they are exactly coincident (Figure 4.4(b), page 178). The large doublet so formed broadens on further heating (Figure 4.4(c), page 178) which presumably indicates that the chemical shifts of these two doublets are no longer identical. ^{31}P decoupling studies indicate that these two doublets arise from two methyl groups attached to the same phosphorus

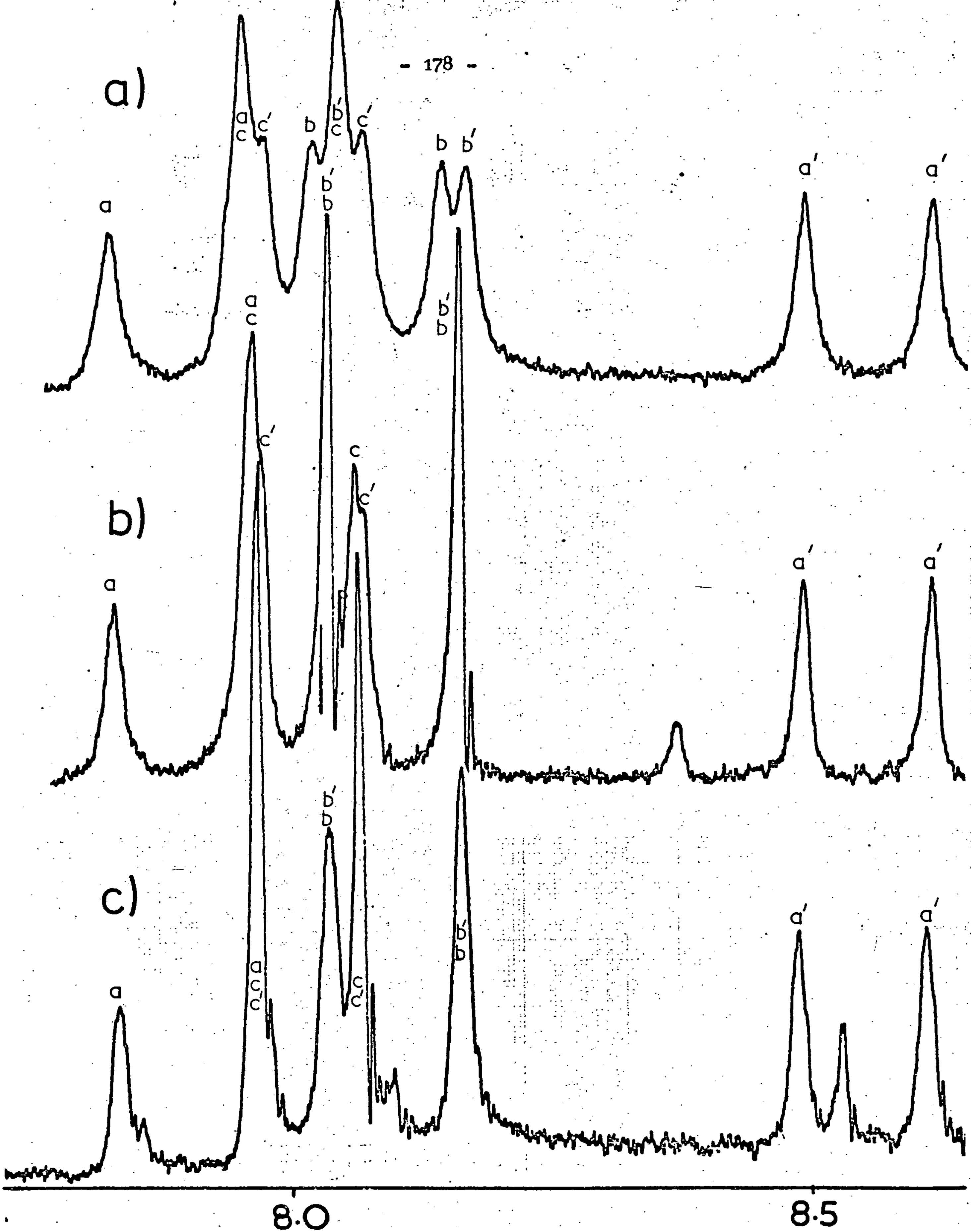


Fig. 4.4

Methyl region of ^{1}H n.m.r. spectrum of cis-Os$(S_2PMe_2)_2(PMe_2Ph)CO$(XIII) in $CDCl_3$ at different temperatures.

a) 233K b) 283K c) 333K

(for assignments of resonances see Scheme 4.2) atom (presumably with one of the methyl groups syn to CO) and the only explanation for this behaviour appears to be that small structural changes occur on warming the compound and these give rise to differing shielding effects on the two methyl groups at different temperatures.*

The presence of a triplet from the methyl groups of the phosphines and two doublets from the S_2PMe_2 methyl groups in the ^1H n.m.r. spectrum of $Os(S_2PMe_2)_2(PMe_2Ph)_2CO$ (XV) is consistent with a structure containing trans phosphines, as shown in Scheme 4.2, provided that there is free rotation about the metal phosphorus bonds. For the analagous $Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$ (compound D, Figure 2.17, page 104), the ^1H n.m.r. spectrum indicates that in this compound, rotation about the Ru-P bonds is slow at room temperature. Another important difference between these two compounds is that whereas at elevated temperatures $Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$ readily loses PMe_2Ph to give cis-$Ru(S_2PMe_2)_2(PMe_2Ph)CO$, (XV) may be kept in solution at 323K for several hours or may be recovered unchanged on recrystallisation from CH_2Cl_2/n-hexane. This is presumably a reflection of the greater inertness of Os(II) than of Ru(II).

* Since the four-membered rings in cis-$Ru(S_2PEt_2)_2(PMe_2Ph)_2$ are not planar in the solid state (Appendix 2), it may be that this is also the case at low temperatures for cis-$Os(S_2PMe_2)_2(PMe_2Ph)CO$ in solution, and that on warming, fast 'inversion' of these rings occurs which fortuitously causes equal shielding effects of the two methyl groups on one S_2PMe_2 ligand at 283K.

The other isomer of $Os(S_2PMe_2)_2(PMe_2Ph)_2CO$ (XVI) gives rise to seven doublets in the ^1H n.m.r. spectrum and apart from small changes in chemical shift, this spectrum is temperature invariant up to 323K and again shows no detectable decomposition at this temperature. ^{31}P decoupling studies indicate that the doublet at τ8.26, which has twice the intensity of the other doublets is made up of two accidentally degenerate resonances from methyl groups on different phosphine ligands. Thus, all the methyl groups in this complex are inequivalent, and in view of the similarity of preparation of this compound and that of $Ru(S_2PMe_2)_2(PMe_2Ph)_2CO$ (compound E, Figure 2.17, page 104) as well as the similarity in their spectroscopic properties, (XVI) is assigned the structure shown in Scheme 4.2.

Finally, ^{31}P decoupling studies on the ^1H n.m.r. spectrum of the brown oil (XIV) obtained from carbonylation of cis-$Os(S_2PMe_2)_2(PMe_2Ph)_2$ in the presence of sulphur (Figure 4.5(a) page 181) shows that it consists of a mixture of (XIII), Me_2PhPS and a compound whose n.m.r. spectrum is shown in Figure 4.5(b). The best interpretation of this spectrum is that the compound contains one PMe_2Ph ligand, in which the methyl groups are inequivalent and two S_2PMe_2 ligands in one of which the methyl groups are inequivalent whilst in the other they are equivalent. We assign this compound the structure shown in Scheme 4.2 because this fits the evidence and is the most likely dicarbonyl compound to be formed from further carbonylation of cis-$Os(S_2PMe_2)_2(PMe_2Ph)CO$(XIII). It is also the only isomer with no plane of symmetry through the Os-P bond in which there is a methyl group syn to PMe_2Ph on the bidentate S_2PMe_2 ligand, which is required to explain the large

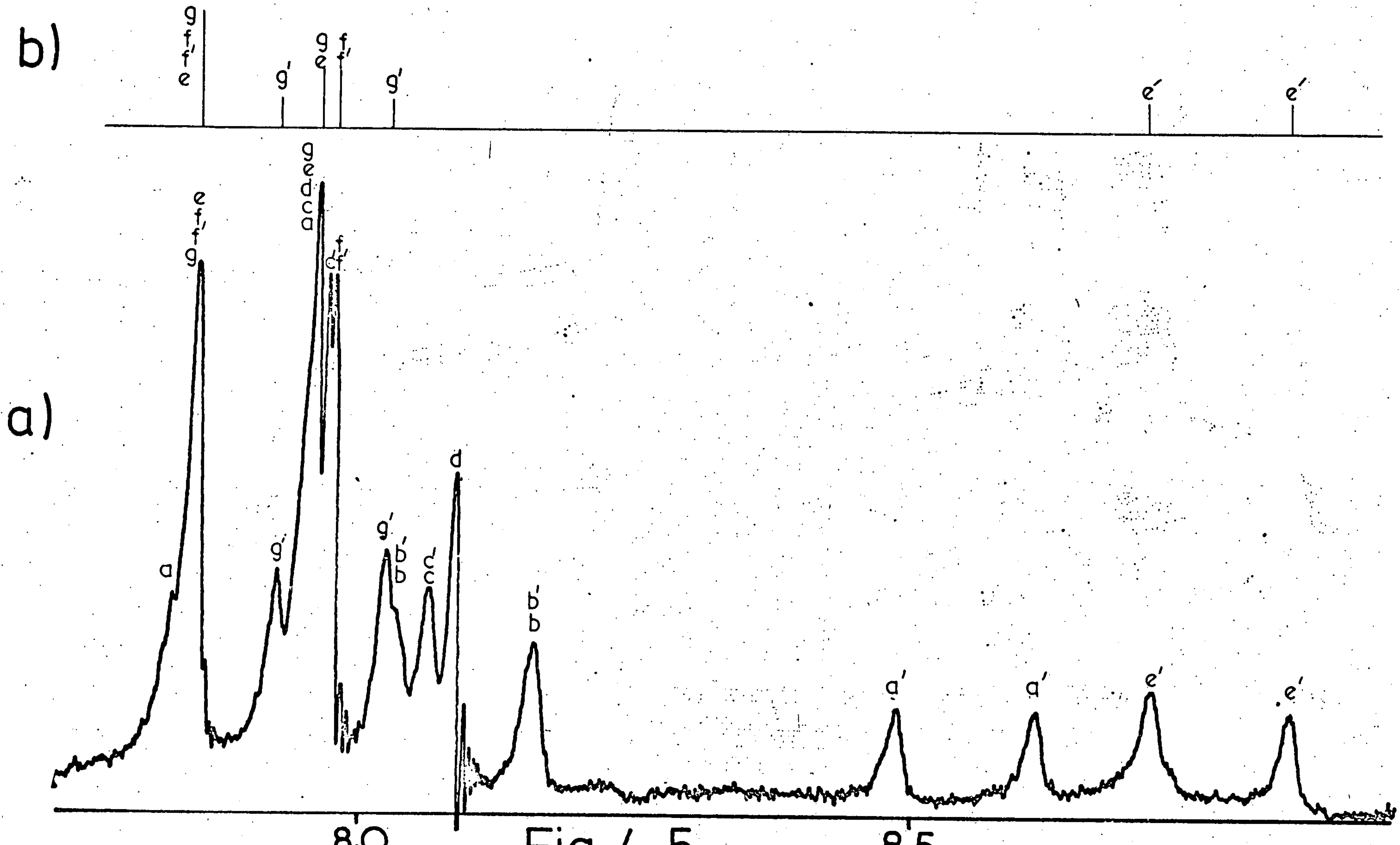


Fig. 4.5

a) Methyl region of ^{1}H n.m.r. spectrum of a mixture of cis-Os$(S_2PMe_2)_2(PMe_2Ph)_2$ (XIII)(a-c), $PhMe_2PS$(d) and $Os(S_2PMe_2)_2(PMe_2Ph)(CO)_2$(XIV) (e-g).

b) line spectrum of XIV (for assignments see Scheme 4.2).

shift to high field of one of these methyl groups (e′). Since the osmium atom in this compound is a chiral centre, the two methyl groups of the unidentate S_2PMe_2 ligand would be expected to be inequivalent (as in (XVI)) but in this case it appears that the chemical shift difference is only very small.

d) ^{31}P n.m.r. spectra

The proton-noise-decoupled ^{31}P n.m.r. spectra of mer-$Os(S-S)Cl(PMe_2Ph)_3$ (S-S = S_2CNMe_2(II)(a) and S_2COEt(XVII)(b)) are reproduced in Figure 4.6 (pages 183-185), along with that of mer-$RhCl_3(PMe_2Ph)_3$(c). The difference between the essentially first order AMX_2 spectrum of the rhodium complexes and those of the osmium complexes is striking but may easily be explained since the osmium spectra can be shown to be second order arising from AB_2 spin systems. From the spectra it is possible to calculate the positions of ν_A and ν_B as well as the coupling constant J_{AB}[363] and these are included alongside each spectrum. The reason why the relative positions of ν_A and ν_B reverse from (II) to (XVII) is unclear but presumably reflects the sensitivity of ^{31}P chemical shifts to small changes in environment.

5. Stereochemical pathway for conversion of mer-$OsCl_3(PMe_2Ph)_3$ to cis-$Os(S\frown S)_2(PMe_2Ph)_2$

Since the only compound obtainable from the reaction of mer-$OsCl_3(PMe_2Ph)_3$ with KS_2COEt is mer-$Os(S_2COEt)Cl(PMe_2Ph)_3$, it is clear that this compound does not react with KS_2COEt and that the chloride ion in this complex is inert. This indicates that the sulphur atom of the S_2COEt moiety has a low trans-effect and is not able to labilise the chloride ion trans to it to any large extent.

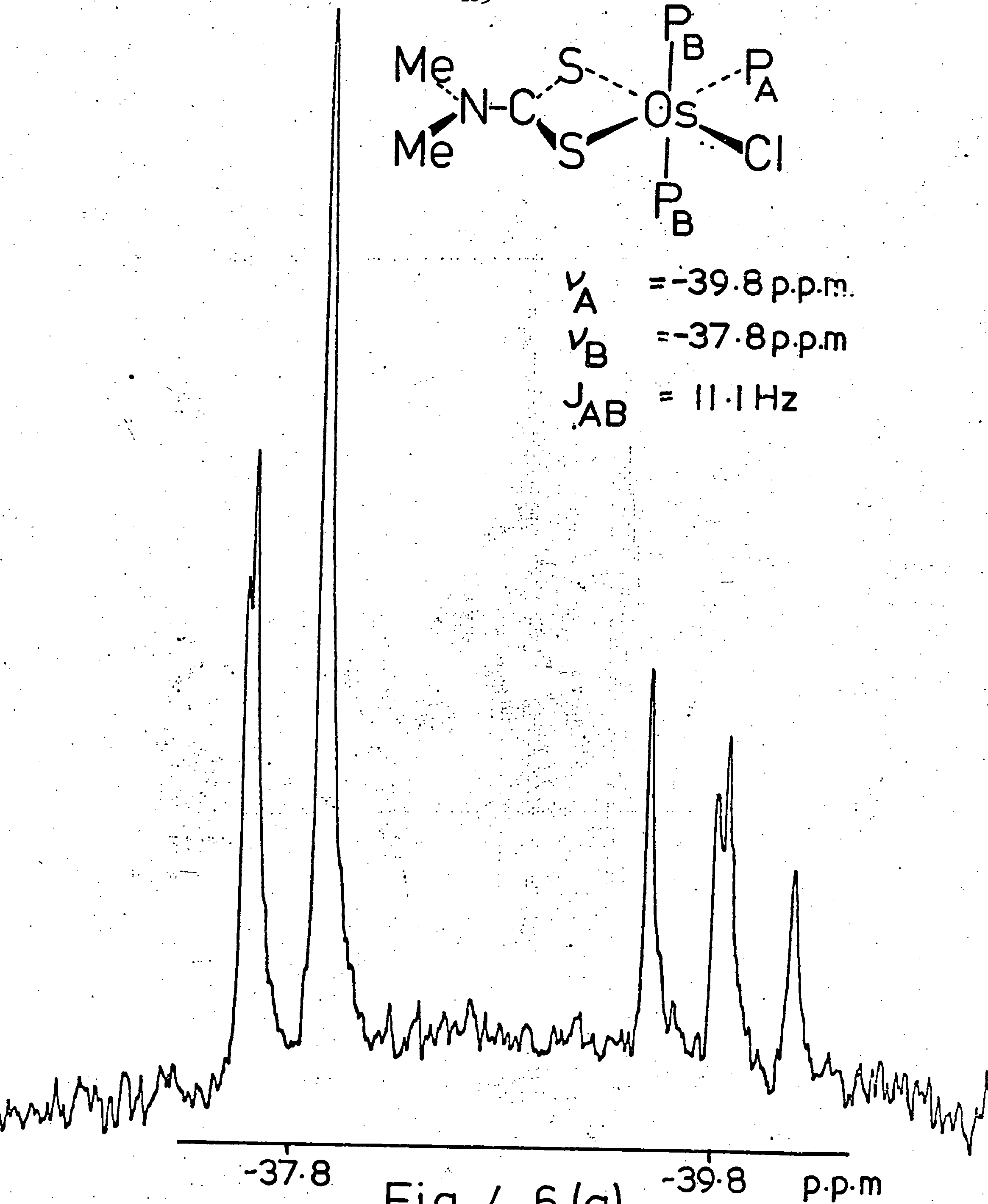


Fig. 4.6 (a)

^{31}P n.m.r. spectrum (AB_2 type) of mer-Os(S_2CNMe_2)Cl(PMe_2Ph)$_3$ (II)

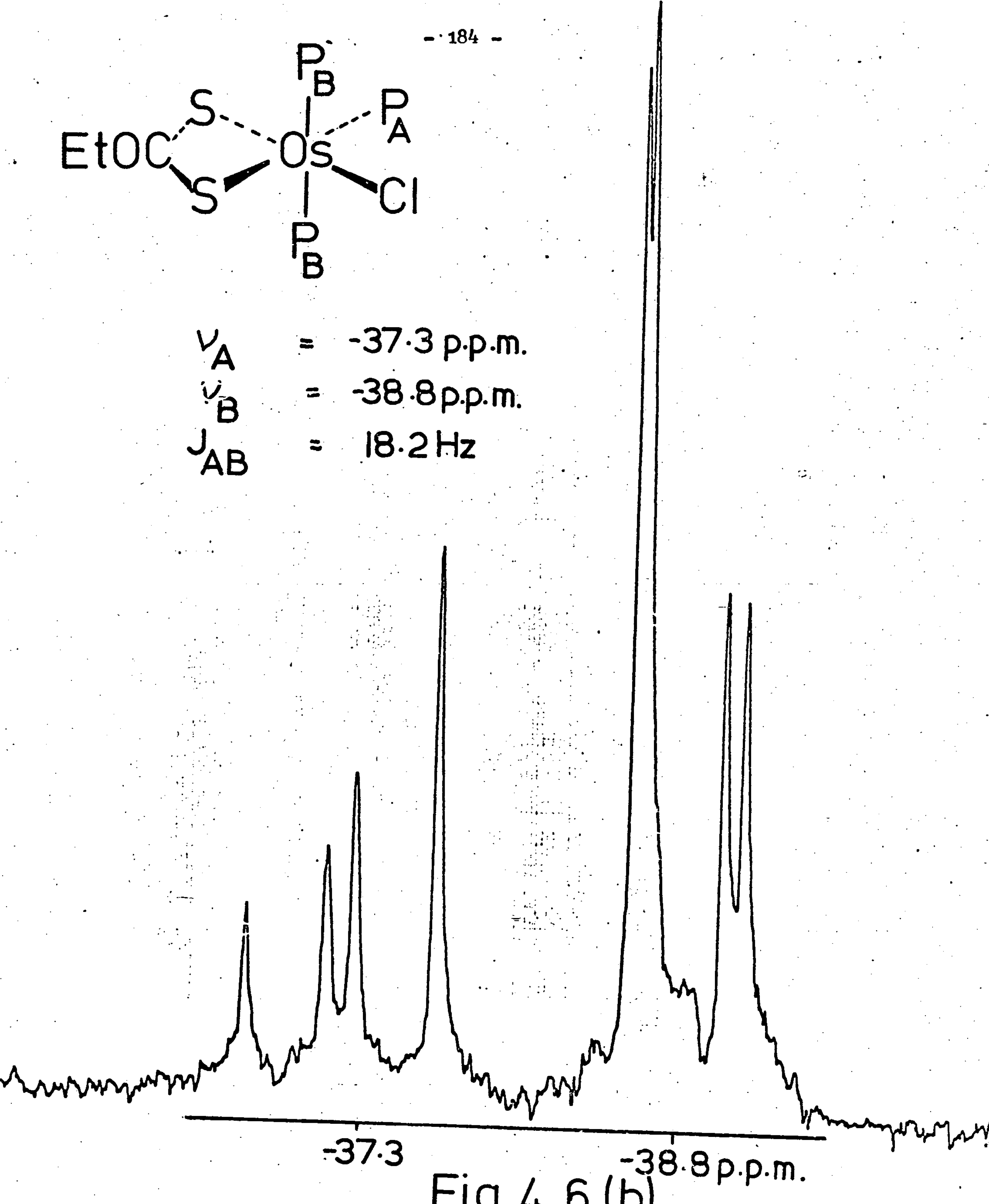


Fig. 4.6 (b)

^{31}P n.m.r. spectrum (AB_2 type) of mer-Os(S_2COEt)Cl(PMe_2Ph)$_3$ (XVII)

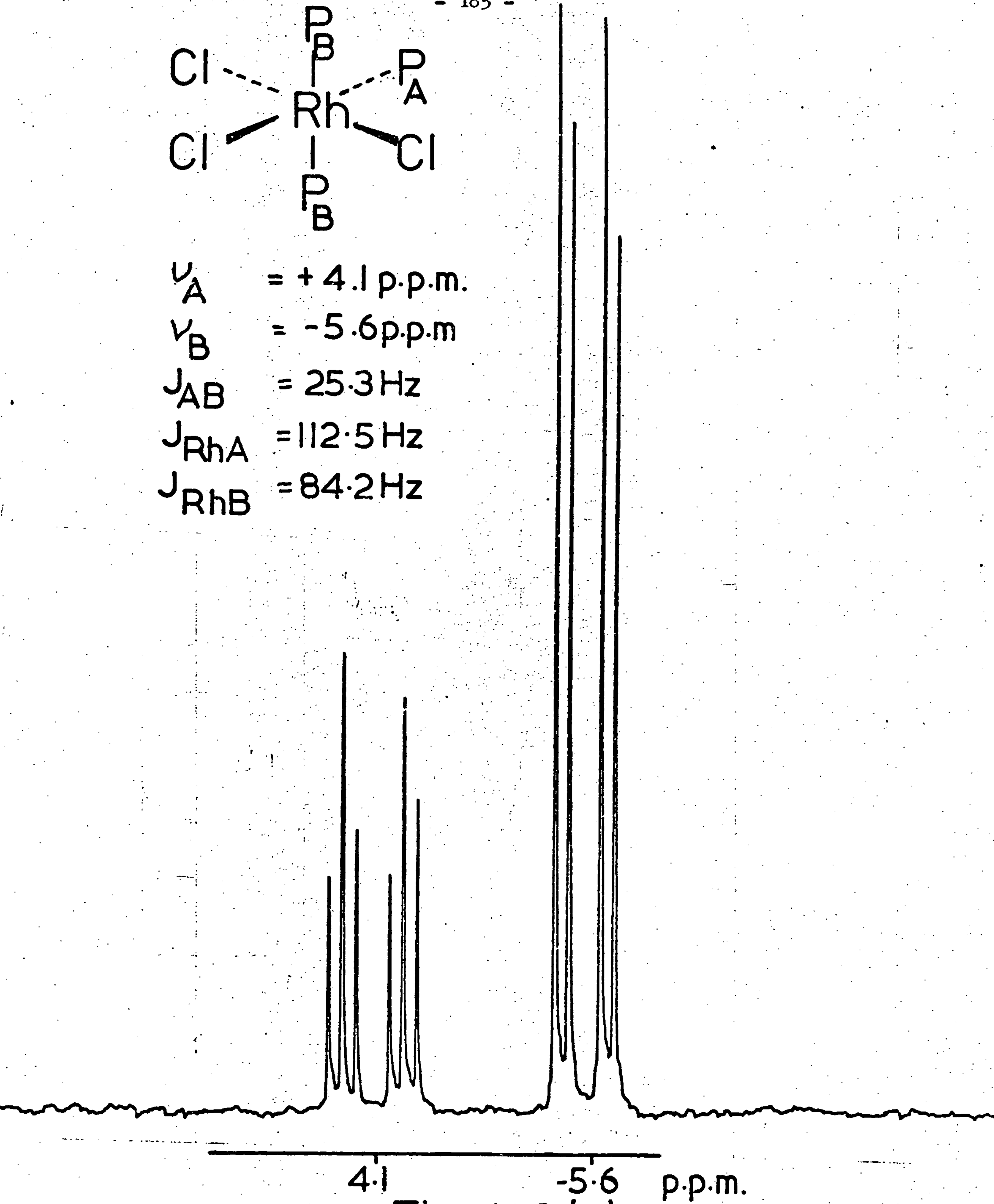


Fig. 4.6(c)

^{31}P n.m.r. spectrum (AMX_2 type) of <u>mer</u> $RhCl_3(PMe_2Ph)_3$

Chemical shifts are in p.p.m. to high frequency of 85% H_3PO_4

Although little information is available on the trans-effects of sulphur containing ligands, work on the reactions of fac-Cr(S-S)$(H_2O)_3$NO (S-S = S_2CNR_2, S_2COR and S_2PR_2)[146-155] (see page 19) with Lewis bases has shown that the trans-effects of these dithioacid ligands are low but of comparable magnitude. Thus, since mer-Os(S_2CNMe_2)Cl(PMe_2Ph)$_3$(II) reacts with $(S-S^1)^-$ to give cis-Os(S_2CNMe_2)$(S-S^1)$(PMe_2Ph)$_2$ ($S-S^1$ = S_2CNMe_2(I) or S_2COR(III)), the mechanism of these reactions cannot involve direct displacement of chloride ion by $(S-S^1)^-$. However, since fac-Os(S_2CNMe_2)Cl(PMe_2Ph)$_3$(IV) is also obtained from these reactions, it is probable that they proceed by an isomerisation of (II) to give (IV) followed by displacement of Cl^- by $(S-S^1)^-$ since in the facial isomer the chloride ion is trans to the high trans-effect ligand, PMe_2Ph. The formation of fac-Os(S_2CNMe_2)OEt(PMe_2Ph)$_3$ is then explained as arising from interaction of (IV) with solvent ethanol and loss of HCl gas.

As has already been noted (page 163), the reaction of mer-$OsCl_3$(PMe_2Ph)$_3$ with NaS_2CNMe_2 gives higher yields of (I) than does the reaction of (II) with NaS_2CNMe_2. This can only mean that another pathway which does not involve (II) as an intermediate is operative in the formation of (I) from mer-$OsCl_3$(PMe_2Ph)$_3$. This pathway probably involves ionic Os(III) intermediates with the reduction to Os(II) occurring as the last step (see Scheme 4.1).

Since mer-Os(S_2PMe_2)Cl(PMe_2Ph)$_3$(XII) is only formed on prolonged standing of mer-Os(S_2PMe_2)Cl_2(PMe_2Ph)$_3$(VIII) in non-polar solvents and since none of (XII) but only a purple ionic oil and mer-$OsCl_3$(PMe_2Ph)$_3$ are formed from (VIII) in polar solvents, it seems likely that the formation of cis-$Os(S_2PMe_2)_2(PMe_2Ph)_2$ from mer-$OsCl_3(PMe_2Ph)_3$ in refluxing ethanol does not involve (XII) as an intermediate but rather goes by the pathway which involves Os(III) cations outlined above. Then, the purple ionic oil probably contains $[Os(S_2PMe_2)Cl(PMe_2Ph)_3]^+$(XI) and the formation of mer-$OsCl_3(PMe_2Ph)_3$ on allowing (VIII) to stand in polar or non-polar solvents is easily explained since the chloride ion released in the formation of (XI) from (VIII) might attack further (VIII) to release $^-S_2PMe_2$ and give mer-$OsCl_3(PMe_2Ph)_3$.

It still remains to explain why neither of these pathways is open to the reaction of mer-$OsCl_3(PMe_2Ph)_3$ with KS_2COEt in boiling methanol. The latter is thought to be excluded because the strongly reducing nature of $^-S_2COEt$ causes reduction to Os(II) before $[Os(S_2COEt)Cl(PMe_2Ph)_3]^+$ can react with more $^-S_2COEt$. Since it is well documented that the ease with which isomerisations of complexes occur is dependent upon the substituents in the molecule[364], we propose that mer-$Os(S_2COEt)Cl(PMe_2Ph)_3$(XVII) isomerises less easily to its facial isomer than does (II) and that, in fact, harsher conditions than refluxing in ethanol are required to effect this isomerisation for (XVII) and thus to allow further reaction to occur. These results are summarised in Scheme 4.1.

Experimental

General experimental methods were as in Chapter 2, and magnetic moments were obtained in CH_2Cl_2 at 301K from measurements of the chemical shift difference of the tetramethylsilane (T.M.S.) peak arising from a solution containing a known concentration of paramagnetic ion and that arising from an internal capillary containing the same concentration of T.M.S. in CH_2Cl_2 but no paramagnetic ion. All solutions were degassed before use and reactions were carried out under a nitrogen atmosphere unless otherwise stated.

mer-trichlorotris(dimethylphenylphosphine)osmium(III)-$(NH_4)_2OsCl_6$(2g) and PMe_2Ph(3mls) were refluxed in 2-methoxyethanol(50mls) containing concentrated hydrochloric acid(5mls) for 16 hours. The resulting red solution was filtered hot to remove NH_4Cl and allowed to crystallise. The red crystals were collected and washed with water, ethanol and n-pentane(3.0g, 93%).

mer-tribromotris(dimethylphenylphosphine)osmium(III) - mer-$OsCl_3(PMe_2Ph)_3$(0.35g) and LiBr(2.0g) were refluxed in ethanol(20mls) for 36 hours and allowed to cool. The resulting purple needles were filtered off and washed with water, ethanol and n-pentane(0.3g, 72%).

mer-dichloro(diphenylphosphinodithioato)tris(dimethylphenylphosphine) - osmium(II) (IX) - Solutions of mer-$OsCl_3(PMe_2Ph)_3$(0.15g) in CH_2Cl_2(10mls) and NaS_2PPh_2(0.2g) in methanol(10mls) were mixed and after passing N_2, the purple solution was evaporated to half volume. The purple product was collected and washed with water, methanol and n-pentane(0.1g, 51%).

mer-dichloro(dimethylphosphinodithioato)tris(dimethylphenylphosphine) osmium(III)(VIII) mer-$OsCl_3(PMe_2Ph)_3$(0.3g) and NaS_2PMe_2(0.3g) were shaken in methanol(25mls) for 90 mins. The resulting purple crystals were collected and washed with water, methanol and n-pentane (0.31g, 92%). Slow recrystallisation of (VIII) from CH_2Cl_2/n-pentane gave red crystals of mer-$OsCl_3(PMe_2Ph)_3$.

mer-chloro(dimethyldithiocarbamato)tris(dimethylphenylphosphine) osmium(II) (II) From mer-$OsCl_3(PMe_2Ph)_3$(0.3g) and NaS_2CNMe_2(0.25g) in 25mls of methanol for 10 mins. as yellow crystals (0.22g, 69%);

and mer-chloro(O-ethyldithiocarbonato)tris(dimethylphenylphosphine) osmium (II) (XVII) from mer-$OsCl_3(PMe_2Ph)_3$(0.15g) and KS_2COEt(0.1g) in methanol(15mls) for 10 mins. and evaporation to near dryness, as orange crystals (0.11g,70%), were similarly prepared.

(XVII) was also prepared by refluxing mer-$OsCl_3(PMe_2Ph)_3$(0.15g) with KS_2COEt (0.1g) in ethanol (20 mls) for 60 mins, evaporating to dryness and recrystallising the orange oil from CH_2Cl_2/n-hexane (0.1g, 62%).

mer-bromo(O-ethyldithiocarbonato)tris(dimethylphenylphosphine) osmium(II) (XVIII) mer-$OsBr_3(PMe_2Ph)_3$(0.1g) and KS_2COEt(0.07g) were refluxed in ethanol (15mls) for 60 mins. and the orange solution evaporated to dryness. The resulting orange oil could not be recrystallised.

mer-chloro(dimethylphosphinodithioato)tris(dimethylphenylphosphine) osmium(II) (XII) mer-$Os(S_2PMe_2)Cl_2(PMe_2Ph)_3$ (0.1g) was dissolved in benzene (5mls) and allowed to stand in air for 2 weeks. Addition of n-hexane to the solution precipitated a purple oil (XI) from which the brown solution was decanted and allowed to crystallise slowly. The complex precipitated in low yield as brown needles and after filtration the filtrate deposited red crystals of mer-$OsCl_3(PMe_2Ph)_3$. If the reaction is allowed to proceed for 4 weeks, no purple oil is formed but approximately equal mole ratios of (XII) and mer-$OsCl_3(PMe_2Ph)_3$.

The purple oil (XI) may also be prepared by allowing mer-$Os(S_2PMe_2)Cl_2(PMe_2Ph)_2$ to stand in acetone in the presence of air for several days. (XI) and mer-$OsCl_3(PMe_2Ph)_3$ are then the sole products.

trans dichloro(dimethylphosphinodithioato)bis(dimethylphenylphosphine) osmium(III) (X) was prepared by refluxing mer-$Os(S_2PMe_2)Cl_2(PMe_2Ph)_3$ (0.07g) in benzene (10mls) for 30 mins. and evaporating to near dryness. The red needles were collected and washed with n-pentane (0.063g, 97%).

cis-bis(dimethylphosphinodithioato)bis(dimethylphenylphosphine) osmium (II) (VI) mer-$OsCl_3(PMe_2Ph)_3$ (0.6g) and NaS_2PMe_2 (0.5g) were refluxed in ethanol (25mls) for 60 mins. The orange solution was cooled with nitrogen bubbling through it and the resulting orange crystals were collected and washed with water, ethanol and n-pentane (0.4g, 66%). On one occasion, the filtrate deposited a small quantity of yellow $[Os_2Cl_3(PMe_2Ph)_6]Cl$.

Similarly prepared were cis-bis(diphenylphosphinodithioato)-bis(dimethylphenylphosphine) osmium (II) (VII) from mer-$OsCl_3(PMe_2Ph)_3$ (0.15g) and $NH_4S_2PPh_2$ (0.2g) as orange crystals (0.1g, 50%) and cis-bis(dimethyldithiocarbamato)bis(dimethylphenylphosphine) osmium (II) (I) from mer-$OsCl_3(PMe_2Ph)_3$ (0.1g) and NaS_2CNMe_2 (0.1g) in ethanol (10mls) for 90 mins, as yellow crystals (0.08g, 80%). A thin layer chromatograph of the filtrate from (I) (toluene on alumina)showed 4 weak bands, one of which corresponded to (I) .

cis-$Os(S_2CNMe_2)_2(PMe_2Ph)_2$(I) was also prepared by the reaction of mer-$Os(S_2CNMe_2)Cl(PMe_2Ph)_3$ (0.026g) with NaS_2CNMe_2 (0.02g) in refluxing ethanol (5mls) for 90 mins. the yellow solid crystallised on cooling (0.01g, 37%). A thin layer chromatograph (toluene on alumina) of the resulting solution showed four bands of approximately equal intensity identical in r.f. values and colours to those obtained from the reaction of mer-$OsCl_3(PMe_2Ph)_3$ with NaS_2CNMe_2. Thus, the total yield if I is c.a. 50%.

cis-(dimethyldithiocarbamato)(O-ethyldithiocarbonato)bis(dimethylphenylphosphine) osmium (II) (III), fac-chloro(dimethyldithiocarbamato)tris(dimethylphenylphosphine) osmium (II) (IV) and fac-ethoxy(dimethyldithiocarbamato)tris(dimethylphenylphosphine) osmium (II) (V). mer-$Os(S_2CNMe_2)Cl(PMe_2Ph)_3$ (0.147g) and KS_2COEt (0.031g) were refluxed in 15 mls of ethanol for 90 mins. A thin layer chromatograph of the resulting orange solution (toluene on alumina) revealed that it consisted of five compounds, four of which were identical to those produced in the reaction of mer-$OsCl_3(PMe_2Ph)_3$ with NaS_2CNMe_2, and the fifth, orange, band was of higher r.f. value than the other four. After evaporation of the solution to dryness, the orange oil was dissolved in toluene and eluted from a dry alumina column with toluene. The five bands were washed off with ether and after evaporation to dryness, the complexes were recrystallised from CH_2Cl_2/n-hexane. The products, in order of decreasing r.f. value were (III) (orange), (I) (yellow), (IV) (yellow) and (V) (yellow). The band of lowest r.f. value produced an orange oil whose identity is unknown.

cis-bis(dimethylphosphinodithioato)carbonyl(dimethylphenylphosphine) osmium (II) (XIII):- cis-$Os(S_2PMe_2)_2(PMe_2Ph)_2$ (0.1g) and S_8 (0.01g) were refluxed in ethanol (15mls), with CO bubbling, for 30 mins. The yellow solution was cooled, filtered through celite and evaporated to dryness. The resulting yellow oil was recrystallised from CH_2Cl_2/n-hexane to give a brown oil which contains (XIV), (XIII) and Me_2PhPS (see text). The yellow supernatant liquid was decanted and allowed to crystallise to give the product as yellow crystals (0.04g, 47%).

bis(dimethylphosphinodithioato)carbonylbis(dimethylphenylphosphine) osmium (II) (XV) cis-Os$(S_2PMe_2)_2(PMe_2Ph)_2$(0.1g) and 0.2mls PMe_2Ph were carbonylated in refluxing ethanol (15mls) for 30 mins. On cooling the resulting yellow solution gave yellow crystals of the product (0.07g, 67%).

bis(dimethylphosphinodithioato)carbonylbis(dimethylphenylphosphine) osmium (II) (XVI) cis-Os$(S_2PMe_2)_2(PMe_2Ph)_2$ (0.05g) was carbonylated in 1:1 CH_2Cl_2 n-hexane at room temperature for two minutes. The solvent was evaporated by passing N_2 and the yellow solid collected in quantitative yeild.

TABLE 4.1

Analytical data for some osmium dithioacid complexes

			required %			Found %			
Complex	Colour	M.p.(^{o}C)	C	H	N	C	H	N	Meff (B.M.)
mer-$\mathrm{Os(S_2PMe_2)Cl_2(PMe_2Ph)_3}$(VIII)	purple	140-142	39.0	4.9	-	39.8	4.9	-	1.82
mer-$\mathrm{Os(S_2PPh_2)Cl_2(PMe_2Ph)_3}$(IX)	purple	104-105	46.7	4.7	-	46.6	4.6	-	1.81
trans-$\mathrm{Os(S_2PMe_2)Cl_2(PMe_2Ph)_2}$(X)	red	207-210^{d}	32.6	4.2	-	32.6	4.3	-	1.97
mer-$\mathrm{Os(S_2PMe_2)Cl(PMe_2Ph)_3}$(XII)	brown	198-200	40.8	5.10	-	39.9	4.7	-	
mer-$\mathrm{Os(S_2CNMe_2)Cl(PMe_2Ph)_3}$(II)	yellow	140-150^{d}	42.7	5.1	1.8	42.6	5.3	1.7	
fac-$\mathrm{Os(S_2CNMe_2)Cl(PMe_2Ph)_3}$(IV)	yellow	172-174^{d}	42.7	5.1	1.8	42.4	5.2	1.9	
fac-$\mathrm{Os(S_2CNMe_2)OEt(PMe_2Ph)_3}$(V)	yellow	206-210^{d}	45.3	5.7	1.8	41.5	5.2	1.7	
mer-$\mathrm{Os(S_2COEt)Cl(PMe_2Ph)_3}$(XVII)	orange	123-125	42.6	5.0	-	42.5	5.2	-	
cis-$\mathrm{Os(S_2PMe_2)_2(PMe_2Ph)_2}$(VI)	orange	189-190^{d}	33.5	4.8	-	33.5	4.9	-	
cis-$\mathrm{Os(S_2PPh_2)_2(PMe_2Ph)_2}$(VII)	orange	238^{d}	49.7	4.4	-	49.5	4.5	-	
cis-$\mathrm{Os(S_2CNMe_2)_2(PMe_2Ph)_2}$(I)	yellow	172-174	37.4	4.8	4.0	37.5	4.9	4.1	
cis-$\mathrm{Os(S_2CNMe_2)(S_2COEt)(PMe_2Ph)_2}$(III)	orange	84- 86	37.3	4.7	2.0	37.1	4.6	1.8	
cis-$\mathrm{Os(S_2PMe_2)_2(PMe_2Ph)CO}$(XIII)	yellow	120-122	25.7	3.8	-	25.8	3.8	-	
$\mathrm{Os(S_2PMe_2)_2(PMe_2Ph)_2CO}$(XV)	yellow	155-158^{d}	33.9	4.6	-	34.0	4.7	-	

TABLE 4.2

Infra-red spectra of some osmium dithioacid complexes (cm^{-1})

Complex	Dithioacid vibrations	ν M-Cl	Others
mer-$OsCl_3(PMe_2Ph)_3$	-	350(m),312(s),270(m)	-
mer-$Os(S_2PMe_2)Cl_2(PMe_2Ph)_3$(VIII)	600(vs)[a]	350(w),310(s)	-
mer-$Os(S_2PPh_2)Cl_2(PMe_2Ph)_3$(IX)	645(s)[a],540(s)[a]	350(w),318(m)	-
trans-$Os(S_2PMe_2)Cl_2(PMe_2Ph)_2$(X)	582(m)[b]	300(s,br)	-
mer-$Os(S_2PMe_2)Cl(PMe_2Ph)_3$(XII)	580(m)[b]	340(w)	-
mer-$Os(S_2CNMe_2)Cl(PMe_2Ph)_3$(IV)	1510(m)[c]	348(w)	-
fac-$Os(S_2CNMe_2)Cl(PMe_2Ph)_3$(IV)	1505(m)[c]	330(vw)	-
fac-$Os(S_2CNMe_2)OEt(PMe_2Ph)_3$(V)	1515(m)[c]	-	1040(vs)[d]
mer-$Os(S_2COEt)Cl(PMe_2Ph)_3$(XVII)	1250(vs)[e]	350(w)	-
cis-$Os(S_2PMe_2)_2(PMe_2Ph)_2$(VI)	583(m)[b]	-	-
cis-$Os(S_2PPh_2)_2(PMe_2Ph)_2$(VII)	608(w)[b],571(vs)[b]	-	-
cis-$Os(S_2CNMe_2)_2(PMe_2Ph)_2$(I)	1510(vs,br)[c]	-	-
cis-$Os(S_2CNMe_2)(S_2COEt)(PMe_2Ph)_2$(III)	1520(m,br)[c],1230(s,br)[e]	-	-
cis-$Os(S_2PMe_2)_2(PMe_2Ph)CO$(XIII)	580(s)[b]	-	1908(vs)[f]
$Os(S_2PMe_2)_2(PMe_2Ph)(CO)_2$(XIV)	600(s)[a,g]	-	2010(s)[f],1950(s)[f]
$Os(S_2PMe_2)_2(PMe_2Ph)_2CO$(XV)	602(s)[a],570(m)[b]	-	1923(vs)[f]
$Os(S_2PMe_2)_2(PMe_2Ph)_2CO$(XVI)	602(s)[a],575(m)[b]	-	1942(vs)[f],1923(vs)[f] 1941(vs)[fmh]

a) Coupled νP=S characteristic of a unidentate S_2PR_2 group[15,16].

b) Coupled νP=S characteristic of a bidentate S_2PR_2 group[15,16].

c) ν $C\cdots N$ characteristic of bidentate S_2CNMe_2 group[14,233].

d) νC-O of OEt group[362].

e) νC-O of S_2COEt group[103].

f) νC=O of CO group.

g) Spectrum is of a mixture of (XIII) and (XIV) so lower P=S is obscured.

h) In $CDCl_3$ solution.

TABLE 4.3

Main osmium containing fragments observed in the mass spectrum of $mer\text{-}Os(S_2CNMe_2)Cl(PMe_2Ph)_3$ (II) at 200°C

$^m/_e$ for Os^{192} peak[a]	Probable ion
795	$[Os(S_2CNMe_2)Cl_2(PMe_2Ph)_3]^+$
761	$[Os(S_2CNMe_2)Cl(PMe_2Ph)_3]^+$
708	$[Os(S_2CNMe_2)_2(PMe_2Ph)_2]^+$
658	$[Os(S_2CNMe_2)Cl_2(PMe_2Ph)_2]^+$
623	$[Os(S_2CNMe_2)Cl(PMe_2Ph)_2]^+$
570	$[Os(S_2CNMe_2)_2(PMe_2Ph)]^+$
520	$[Os(S_2CNMe_2)Cl_2(PMe_2Ph)]^+$
485	$[Os(S_2CNMe_2Cl(PMe_2Ph)]^+$
458[b]	$708 \longrightarrow 570$
432	$[Os(S_2CNMe_2)_2]^+$
354	$[Os(S_2CNMe_2)_2(PMe_2Ph)_2]^{++}$
328[b]	$570 \longrightarrow 432$

a - all peaks show the characteristic osmium isotopic pattern.

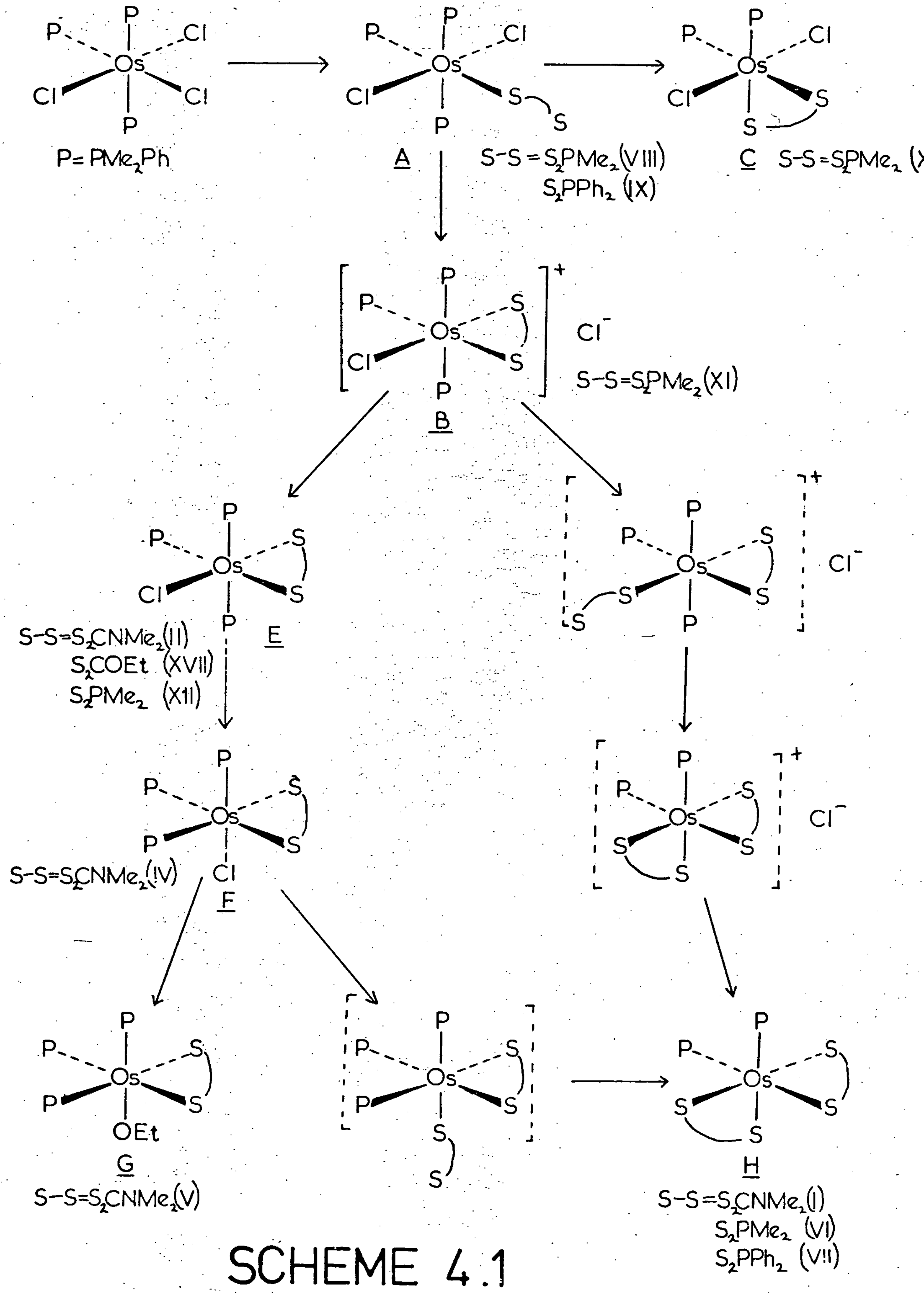
b - metastable ions (broad signals).

TABLE 4.4

^{1}H n.m.r. spectra of some osmium(II) dithioacid complexes in CDCl$_3$

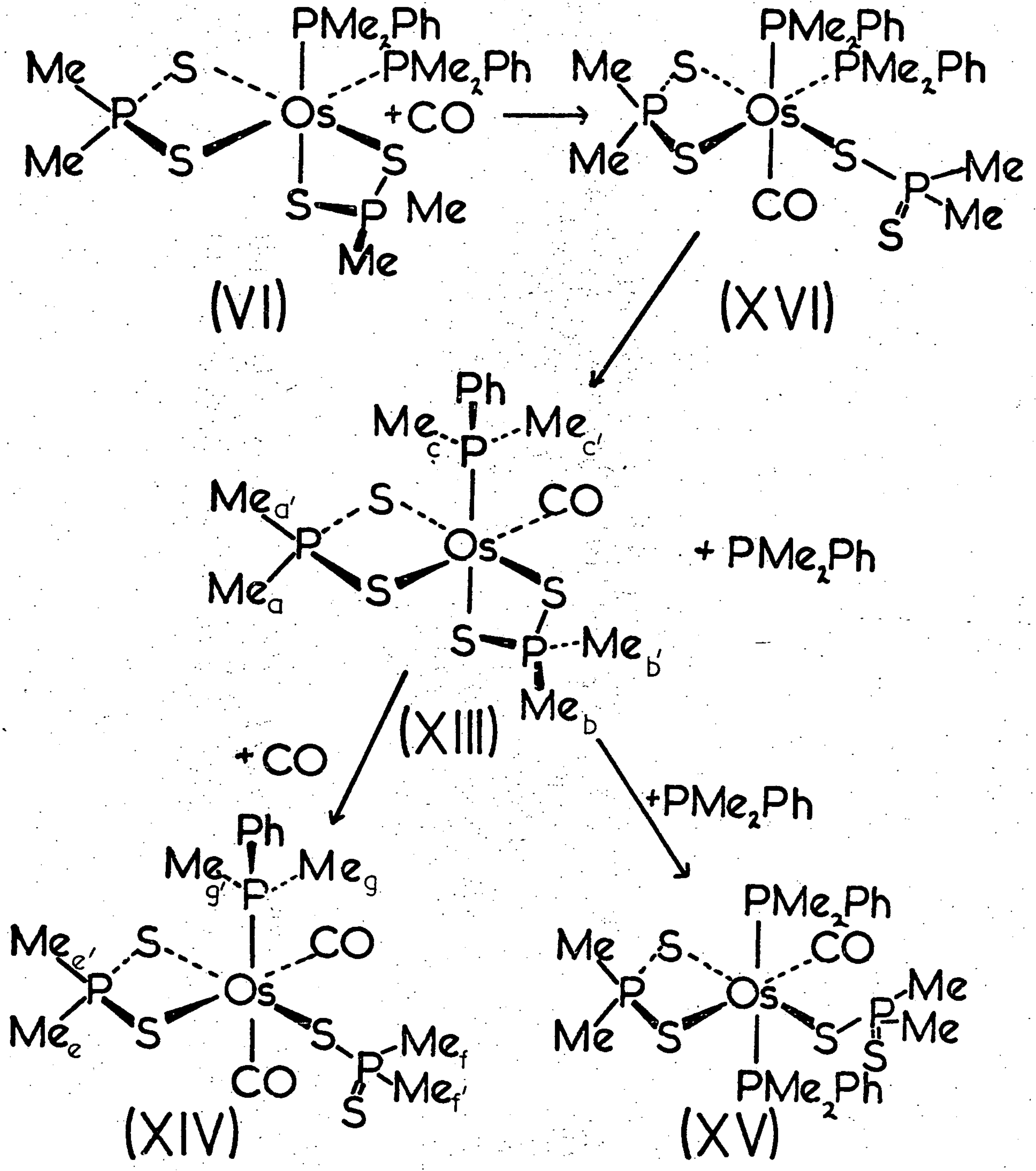
		τ value			Other
Complex	T/K	Dithioacid ligand	Phosphine Me groups	Phenyl	resonances
mer-Os(S$_2$PMe$_2$)Cl(PMe$_2$Ph)$_3$(XII)	301	$8.47^{d}(14.5)^{a}$	$8.00^{t}(8.0)^{b}$ $8.18^{t}(8.5)^{b}$ $8.64^{d}(10.5)^{a}$	2.1-3.0	-
mer-Os(S$_2$CNMe$_2$)Cl(PMe$_2$Ph)$_3$(II)	301	6.92^{c}	8.20^{s} 8.34^{s} $8.66^{d}(7.0)^{a}$	2.4-3.4	-
fac-Os(S$_2$CNMe$_2$)Cl(PMe$_2$Ph)$_3$(IV)	301	7.10^{s}	$8.00^{e}(8.0)^{b}$ $8.03^{e}(9.0)^{b}$ $8.45^{d}(12.0)^{a}$	2.2-3.2	-
fac-Os(S$_2$CNMe$_2$)OEt(PMe$_2$Ph)$_3$(V)	253	7.24^{s}	$8.02^{e}(7.0)^{b}$ $8.04^{e}(7.0)^{b}$ $8.65^{d}(8.0)^{a}$	2.2-3.3	$5.36^{q}(7.0)^{f}$ $8.67^{t}(7.0)$
	301	7.21^{s}	$8.08^{e}(8.0)^{b}$ $8.68^{d}(8.0)^{a}$	2.2-3.3	$5.39^{q}(7.0)^{f}$ $8.72^{t}(7.0)$
mer-Os(S$_2$COEt)Cl(PMe$_2$Ph)$_3$(XVII)	301	$5.70^{q}(7.0)^{f}$ $8.57^{t}(7.0)^{f}$	$8.18^{t}(6.5)^{b}$ $8.35^{t}(6.5)^{b}$ $8.59^{d}(8.5)^{a}$	2.4-3.2	-
mer-Os(S$_2$COEt)Br(PMe$_2$Ph)$_3$(XVIII)	301	$5.80^{q}(7.0)^{f}$ $8.61^{f}(7.0)^{f}$	$8.15^{t}(6.5)^{b}$ $8.25^{t}(6.5)^{b}$ $8.50^{d}(8.0)^{a}$	2.4-3.4	-
cis-Os(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$(VI)	273	$7.90^{d}(12.5)^{a}$ $8.32^{d}(12.5)^{a}$	$8.29^{e}(8.5)^{b}$ $8.36^{e}(8.5)^{b}$	2.7-3.3	-
	333	8.11^{c}	$8.33^{e}(8.5)^{b}$	2.7-3.3	-
cis-Os(S$_2$PPh$_2$)$_2$(PMe$_2$Ph)$_2$(VII)	301	-	$8.43^{e}(12.5)^{b}$	1.9-3.3	-
cis-Os(S$_2$CNMe$_2$)$_2$(PMe$_2$Ph)$_2$(I)	253	6.75^{s} 6.82^{s}	$8.38^{e}(8.0)^{b}$ $8.46^{e}(8.0)^{b}$	2.7-3.1	-
	313	6.84^{s}	$8.40^{e}(8.5)^{b}$ $8.45^{e}(8.5)^{b}$	2.7-3.1	-
cis-Os(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)CO(XIII)	233	$7.85^{d}(12.5)^{a}$ $8.04^{d}(12.5)^{a}$ $8.07^{d}(12.5)^{a}$ $8.52^{d}(12.5)^{a}$	$7.96^{d}(9.5)^{a}$ $7.98^{d}(9.5)^{a}$	2.3-2.7	-
	333	$7.91^{d}(13.0)^{a}$ $8.11^{d}(12.5)^{a}$ $8.56^{d}(12.5)^{a}$	$8.03^{d}(9.5)^{a}$	2.3-2.7	-
Os(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)(CO)$_2$(XIV)	301	$7.91^{d}(11.0)^{a}$ $7.93^{d}(12.0)^{a}$ $8.79^{d}(12.5)^{a}$	$7.91^{d}(11.0)^{a}$ $7.98^{d}(10.0)^{a}$	1.9-2.1	-
Os(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$CO(XV)	301	$8.09^{d}(12.0)^{a}$ $9.00^{d}(12.0)^{a}$	$7.79^{d}(7.0)^{a}$	2.2-2.8	-
Os(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$CO(XVI)	301	$7.94^{d}(12.5)$ $7.98^{d}(12.0)^{a}$ $7.99^{d}(12.5)^{a}$ $8.54^{d}(12.0)^{a}$	$8.22^{d}(9.5)^{a}$ $8.26^{d}(9.5)^{a}$ $8.38^{d}(9.5)^{a}$	2.4-3.2	-

a	J_{PH}	f	$J_{\underline{H}-C-C-\underline{H}}$
b	$J_{PH} + J_{PH'}$ for $H_6PP'H_6'$ spectrum	s	- singlet
c	Broad singlet	d	- doublet
e	Pseudo doublet	t	- triplet
		q	- quartet



SCHEME 4.1

Proposed mechanisms for reactions of mer-$OsCl_3(PMe_2Ph)_3$ with $(S\text{-}S)^-$ (compounds in dotted brackets have not been isolated).



SCHEME 4.2

Proposed mechanism of carbonylation of cis-$Os(S_2PMe_2)_2(PMe_2Ph)_2$(VI).

Appendix 1

Calculation of Activation Parameters for a Two Site Exchange

It can be shown[334] that when magnetic nuclei in two different magnetic environments exchange with one another, changes in the n.m.r. spectra arising from those nuclei occur. Under conditions of slow exchange, two sharp signals are seen whereas, if the exchange is fast, a single sharp resonance midway between the positions of the slow exchange signals results. Between these two limits, broadened spectra are observed whose shape may be predicted using the Bloch equations[334], as modified by Gutowsky and Holm[365]. The shape of the spectra may be shown to be dependent not only upon the rate of exchange of the nuclei between environments, but also on the separation of the resonances, the spin-spin relaxation time for the molecule, (which is related to the natural line width of the signals) and the coupling constant if each resonance is a multiplet, all under slow exchange conditions[334].

Nakagawa[345] has used these modified Bloch equations to write a program for calculating the line shape at a given lifetime for exchange between two nuclei (or sets of equivalent nuclei), provided that the exchanging nuclei are not coupled to other magnetic nuclei in the molecule, and this has been modified by D.F. Steele to allow for such coupling[366].

Thus, if the relative populations of the two sites between which exchange is occurring, the natural line width (at half peak height) of the resonances, the frequency separation of the signals of the exchanging nuclei and the coupling constant if they are multiplets are supplied to the computer, the print-out consists of different simulated spectra arising from the different lifetimes fed into the computer.

In the general situation where exchange between two sites A and B of different populations, is occurring.

$$A \rightleftharpoons B$$

we define P_A = population of site A

P_B = population of site B

τ_A = lifetime in A

τ_B = lifetime in B

Then the rate constants for the forward (k_A) and back (k_B) reactions are $\frac{1}{\tau_A}$ and $\frac{1}{\tau_B}$ respectively.

The equilibrium constant, $K = \frac{[B]}{[A]} = \frac{P_B}{P_A} = \frac{k_A}{k_B} = \frac{\tau_B}{\tau_A}$

$$\text{i.e. } P_B\tau_A = P_A\tau_B$$

The computer program is arranged so that the input lifetime is τ_A and the input population is P_A. Then, since for equal populations of sites A and B,

$$\tau_A = \tau_B$$

the rates of the forward and back reaction are equal so that the rate of exchange (k_r) may be found directly from the relationship

$$\frac{1}{\tau_A} = \frac{1}{\tau_B} = k_A = k_B = k_r$$

Thus, by comparing computed spectra with spectra obtained experimentally at different temperatures (T), the rates of exchange (k_r) at these temperatures may be found.

Then, using the Arrhenius equation[341]

$$\ln k_r = -\frac{E_A}{RT} + \text{const},$$

the activation energy, E_A, may be obtained from the slope of a graph of ln k_r against $\frac{1}{T}$ by multiplying by $-R$. (The slope and intercept of the graph are obtained by a least-squares method and the errors in these parameters are used to calculate errors in activation parameters.

$\Delta H^{\ddagger}_{298}$ may be obtained from E_A using the equation

$$\Delta H^{\ddagger}_{298} = E_A - R \times 298.$$

Also, since $G = -RT \ln (K^{\ddagger})$

and $K^{\ddagger} = \frac{k_r h}{kT}$ where

k = Boltzmann's oonstant
h = Planck's constant
T = Temperature

$$\Delta G^{\ddagger} = RT \ln \frac{k_r h}{kT}$$

Thus $\Delta G^{\ddagger}_{298}$ may be calculated

and $\Delta S^{\ddagger}_{298}$ follows from the relationship

$$\Delta G^{\ddagger}_{298} = \Delta H^{\ddagger}_{298} - T\Delta S^{\ddagger}_{298}$$

Appendix 2

The Crystal Structure of cis-Ru(S_2PEt_2)$_2$(PMe_2Ph)$_2$

The crystal structure of cis-Ru(S_2PEt_2)$_2$(PMe_2Ph)$_2$ has been determined by Dr. J.D. Owen. Table A2 lists some interatomic distances within the molecule and Figure A2 shows the molecule viewed down its approximate two-fold axis, which bisects the P-Ru-P angle.

Various features of the structure should be noted since they are relevant to the chemistry of this and similar molecules (see Chapters 2-4). Thus, the Ru-S bonds trans to PMe_2Ph have a mean distance of 2.584Å whereas those trans to a sulphur atom average 2.428Å. This large difference is explained by the higher trans-influence of PMe_2Ph than of the S_2PEt_2 ligand and confirms that, at least in the solid state, the Ru-S bonds trans to PMe_2Ph are the weakest in the molecule. The comparitively short Ru-P bonds (2.257Å, c.f. the range of 2.2-2.4Å found for Ru(II) complexes[288,327,367-369]) again reflect the low trans-influence of the S_2PEt_2 group. The M-S-P-S-M rings are found to be non-coplanar, and this is thought to be due to steric repulsions of the ethyl groups away from the phosphine ligand. Finally, although the individual molecules do not possess a centre of symmetry, the unit cell is found to be centro-symmetric and must, therefore, contain a racemic mixture of the two optical isomers of cis-Ru(S_2PEt_2)$_2$(PMe_2Ph)$_2$. This indicates that both isomers were present in the solution from which the compound was crystallised.

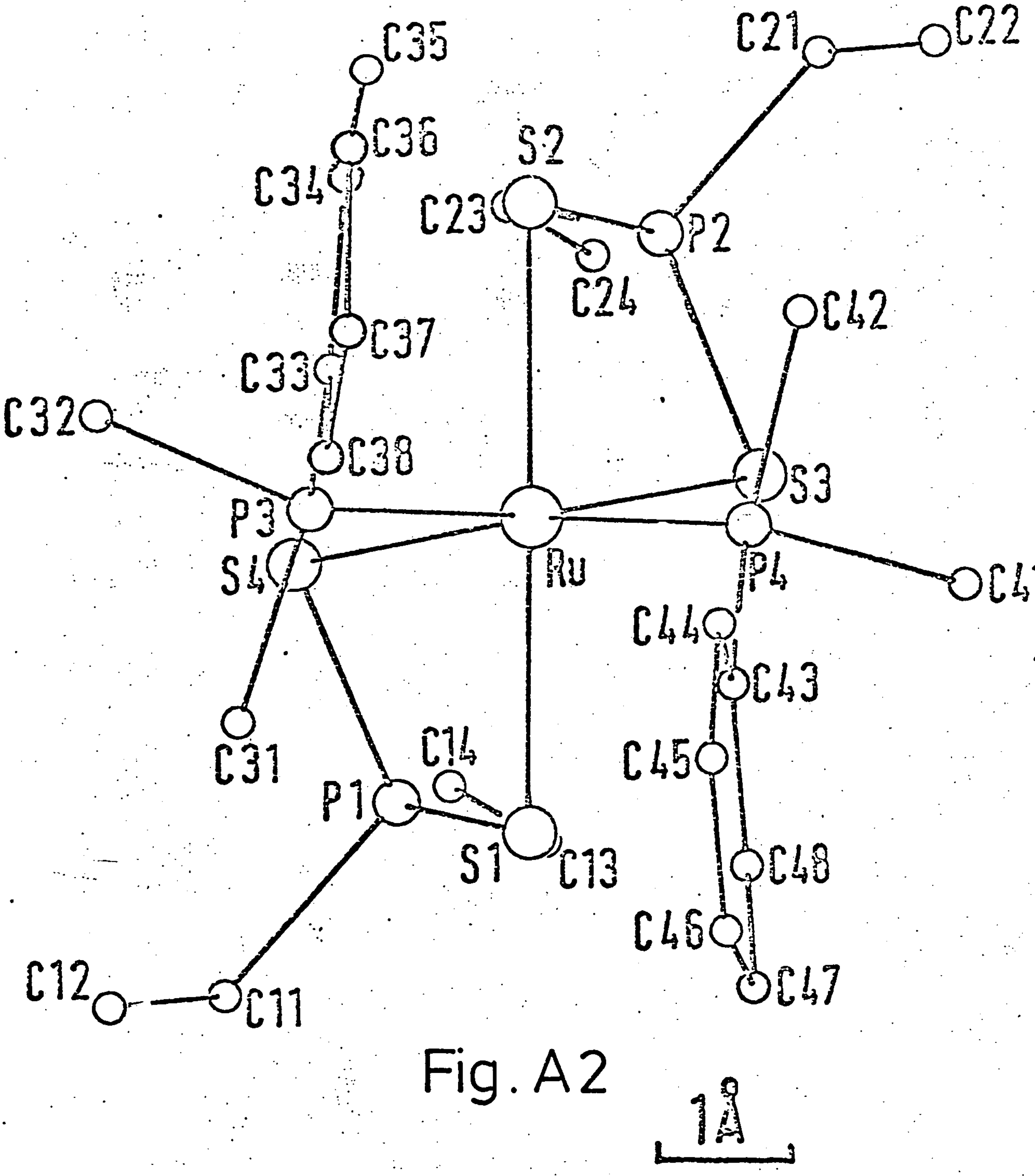


Fig. A2

Structure of cis-Ru$(S_2PEt_2)_2(PMe_2Ph)_2$ viewed down the approximate two-fold axis.

Table A2

Selected Interatomic distances (Å) and angles (degrees) for cis-Ru$(S_2PMe_2)_2$-$(PMe_2Ph)_2$

Ru - S1	2.423(7)
Ru - S2	2.433(8)
Ru - S3	2.575(7)
Ru - S4	2.592(8)
Ru - P3	2.251(7)
Ru - P4	2.262(7)
S1 - P1	1.986(13)
S4 - P1	1.999(11)
S2 - P2	1.973(13)
S3 - P2	1.983(12)
P1 - C11	1.95 (4)
P1 - C13	1.82 (3)
P2 - C21	1.86 (4)
P2 - C23	1.86 (3)
P3 - C31	1.87 (4)
P3 - C32	1.86 (3)
P3 - C33	1.77 (3)
P4 - C41	1.83 (3)
P4 - C42	1.87 (3)
P4 - C43	1.81 (3)
S1 - Ru - S4	77.4 (3)
S2 - Ru - S3	77.6 (3)
P1 - S1 - Ru	89.5 (4)
P1 - S4 - Ru	84.6 (4)
P2 - S2 - Ru	88.7 (4)
P2 - S3 - Ru	84.5 (4)
S1 - P1 - S4	104.0 (5)
S2 - P2 - S3	105.1 (5)
Mean C-C(phenyl)	1.43(6)
Mean C-C(ethyl)	1.42(12)

Erratum

The compound formulated as $K[RhCl_2(S_2CO)(PMe_2Ph)_2]$ (see Chapter 3) has been shown by X-ray crystallography[370] to be $K[Rh(S_2CO)_2(PMe_2Ph)_2]\cdot 3H_2O$ with the anion having the trans configuration. Our assignment of the structure of this compound was based on analytical figures for carbon and hydrogen which are close for each formulation. Our failure to detect water in the ^1H n.m.r. spectrum arises from the fact that the spectrum was run in $(CD_3)_2CO$ which already contains some HDO thus masking the water of crystallisation of the molecule.

We appreciated that the analytical and spectroscopic properties could equally well be explained by either formulation but opted for the chloro containing species since chlorine was detected qualitatively in the X-ray fluorescence spectrum of the sample. Finally, the assignment of the peak at 320 cm^{-1} in the i.r. spectrum of the complex to Rh-Cl shows the great care that must be taken in interpreting the far infra-red spectra of complex molecules.

The complex is presumably formed by attack of excess KS_2COEt on trans - $Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2$.

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