N.M.R. INVESTIGATION OF DYNAMIC MOLECULES CONTAINING ELEMENTS OF GROUPS V OR VI.

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DOCTOR OF PHILOSOPHY

by

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To

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ABSTRACT

a) Chalcogen inversion in $(Et_2X)_2MHal_2$ complexes.

The objective of this work was to establish pyramidal chalcogen (S,Se and Te) inversion and to ascertain which factors might influence the inversion rate in a series of transition metal complexes. Monodentate chalcogen complexes of the type $(Et_2X)_2MHal_2$ (X = S,Se or Te; M = Pt or Pd) were examined by variable temperature n.m.r. spectroscopy —— the issues arising from this choice forming the basis of further research. Both sulphur and selenium invert when coordinated to platinum, this being the first ever report of pyramidal selenium inversion. The rate of sulphur inversion depends on the nature of the ligand trans to the inverting centre. The geometries of the complexes in solution were established by dipole-moment measurements, which revealed in almost every case a trans-configuration. Contrary to popular belief, the $(Et_2Te)_2MHal_2$ complexes are trans in solution. A cis arrangement of inverting centres was effected by the synthesis of $(EtSeC_2H_4SeEt)MHal_2$ complexes and the v.t. n.m.r. results showed that the rate of selenium inversion also depends on the nature of the trans-ligand. The retention of $^{195}\underline{Pt} - X - C - \underline{H}$ coupling (^{195}Pt, $I = \frac{1}{2}$, 33.7% abundant) after coalescence served to differentiate between a pyramidal inversion and a ligand exchange mechanism in the platinum monodentate complexes, but the absence of a suitable magnetic

isotope of palladium of sufficient abundance meant that pyramidal chalcogen inversion in palladium complexes alone could not be unequivocally established. Addition of excess ligand to these complexes showed that ligand exchange was not involved at these temperatures and unambiguous sulphur inversion in the $(Et_2S)_2PdHal_2$ complexes was demonstrated. The order of ease of ligand exchange was shown to be $Et_2Te \gg Et_2Se > Et_2S$.

The pronounced effect of traces of diethyltelluride on the spectra of the $(Et_2Te)_2PtHal_2$ complexes offered a rationalisation of the high temperature spectra of these complexes when no excess ligand had been added. $^{195}\underline{Pt}$ - Te - C - $\underline{H}$ coupling was never observed at temperatures above those of coalescence, almost certainly due to a ligand exchange-recombination mechanism as a result of the decomposition of these complexes at high temperatures. The question of whether or not tellurium inverts led to many attempts to produce a suitable tellurium-containing complex, culminating in the synthesis of *cis*-$(Et_2Te)_2Pt(p\text{-tolyl})_2$ which showed v.t. n.m.r. characteristics consistent with pyramidal tellurium inversion. This represents the first unambiguous proof of such a mechanism. The order of ease of inversion within the chalcogens is S > Se > Te, and palladium complexes have faster inversion rates than analogous platinum complexes.

Lastly, a series of benzyl complexes, *trans*-$(Bz_2S)_2PdHal_2$ was examined by v.t. n.m.r. with the intention of calculating Free Energies of Activation for the inversion process by computer methods. These were not obtained, since at low temperatures other signals and coalescences were observed. Rationalisations in terms of *cis*-isomers are presented.

b) Hindered rotation about P - N bonds.

A series of compounds of the type $Ph_2P-N(R)-P(Ph)Cl$ (I) was prepared, (R = Me, Et, Pr^n, Pr^i or Bu^t). ^{31}P and $^1H\{^{31}P\}$ n.m.r. spectra were obtained and from the coalescence temperatures it was established that the torsional barriers are dependent on the steric requirement of the R group on nitrogen — the order of ease of rotation being $R = Me > Et \approx Pr^n > Pr^i > Bu^t$. The variation in $\underline{P}-N-\underline{P}$ coupling constant with temperature is related to the two dihedral angles between the lone pairs on both phosphorus atoms and the P-N bonds of the other phosphorus atoms. This enabled low temperature conformational preferences to be assigned. For (I), (R = Me, Et, Pr^n), this is the (0,0) conformer (ie. two 0^o dihedral angles between the lone pairs and the P-N bonds). Molecular models suggest a low temperature conformation close to (0,180) for (I), (R = Pr^i, Bu^t), these being the first examples of negative $\underline{P}-N-\underline{P}$ coupling constants between trivalent phosphorus atoms. The mechanism of P-N rotation is depicted in a thermodynamic rather than in a kinetic sense, encompassing different conformer populations whose stabilities are determined by steric interactions.

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CHAPTER 1

HISTORICAL INTRODUCTION

INTRODUCTION

HISTORICAL BACKGROUND

Platinum and Palladium

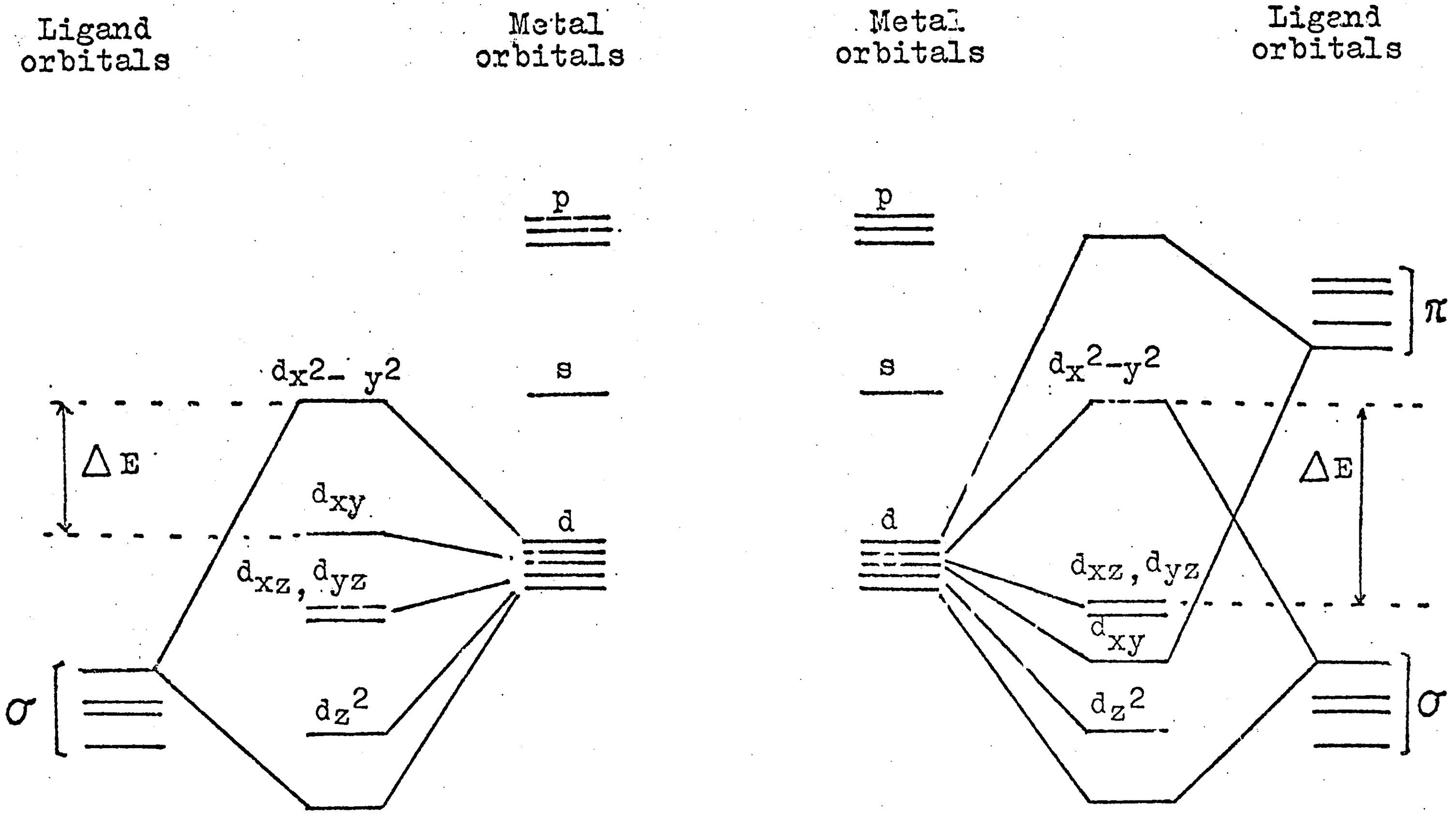
Platinum was discovered in the 16th century in Columbia, and was originally called 'PLATINA DEL PINTO', 'the little Silver of the PINTO river'. The metal was brought to Europe in 1741. It was not until 1803, however, that palladium was discovered(1), being named by its discoverer, W.H. Wollaston, after the recently discovered asteroid, 'PALLAS'. The systematic study of both metals was undertaken during the 19th century and gathered momentum in the 20th. During this time a large part was played in the development of the empirical facts and the theoretical significance of covalence. Many transition-metal complexes were synthesised in this period, but it was not till the discovery of ferrocene(2) in the 1950's that fresh impetus was given to organometallic research. More recently, the commercial availability of I.R. and N.M.R. spectrometers (^{195}Pt, 33.7% abundant has a spin quantum number of $\frac{1}{2}$) has led to even more interest in this area of chemistry. The discovery in 1969 of the anti-cancer activity(3) of some platinum complexes focused attention on the biological applications of the Gp.VIII transition-metal complexes. The high melting points and the corrosion resistant properties of the metals have found numerous applications in industry(4).

The most common oxidation state of platinum and palladium metal ions is +2. The zero and +4 states also exist, but are more common for platinum. The +1 and +3 oxidation states have not been unambiguously identified for either metal, but platinum shows both +5 (PtF_5) and +6 (PtF_6) states. Neither is known in oxidation states in excess of 6.

Chatt and coworkers(5) classified Pt (II) and Pd (II) as 'class b' metal ions, i.e., 'soft acids' according to Pearson's theory(6). Both are noted for the propensity with which they form 16-electron square-planar complexes. In these, the destabilisation of the $d_{x^2-y^2}$ orbital (Figure 1) is so great that the 8 d-electrons pair in the remaining four d-orbitals, making the complexes diamagnetic. It is interesting to note that Ni(II) complexes have the ability to adopt a variety of stereochemistries. Their tetrahedral, square-planar and octahedral geometries are a result of higher spin pairing energies and lower Crystal Field Stabilisation Energy(7).

In the 1950's, Chatt(8) and Orgel(9) independently proposed the concept of synergic bonding in transition-metal complexes. Chatt(8) described the R_3P-Pt bond, shown below, in terms of sigma- and pi-components. Phosphorus donates two electrons to platinum to form a sigma-bond, and accepts electrons from filled metal-orbitals to form a pi-bond.

Figure 1



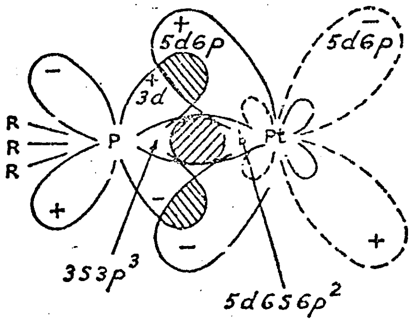
(a) only σ-bonding

(b) π-bonding in d_{xy} plane

Schematic energy level diagrams for square-planar complexes.

FIGURE 2

σ- AND π-BONDING AT PLATINUM[a]



a) Diagram taken from reference 8.

Of the nine orbitals available for forming bonds, namely the 5d, 6s and 6p, those used to form sigma-bonds are by symmetry requirements the $5d_{x^2-y^2}$, $6p_x$, $6p_y$, 6s and $5d_{z^2}$. This leaves metal orbitals of appropriate symmetry, namely the d_{xy}, d_{xz}, d_{yz} and $6p_z$ to form a system of π-molecular-orbitals by interaction with the appropriate ligand orbitals. A schematic energy level diagram showing only the d-orbitals of the metal is given in Figure (1). Symmetry alone does not determine the extent of bond-formation. There is also an energy criterion. Thus overlapping orbitals must be of similar energies in order to form strong bonds.

SELENIUM AND TELLURIUM

DISCOVERY(10)

Tellurium was discovered in 1782 by F.J. Müller von Reichenstein, an Austrian chemist. Sixteen years later, M.H. Klaproth established definite evidence that the element discovered by his fellow countryman had unique properties, and named it TELLURIUM, derived from the Latin tellus meaning 'earth'. In 1817, J.J. Berzelius and J.G. Gahn discovered selenium, and because of its similarity to tellurium, they named it SELENIUM, from the Greek SELENA, the Greek goddess of the moon.

ABUNDANCE AND OCCURRENCE

The abundance of selenium has been estimated(11) as approximately $6 \times 10^{-5}\%$ of the earth's crust, while that of tellurium (ca. $10^{-7}\%$) is generally considered to be comparable to that of gold. No significant quantities of either are recovered in Europe, although a limited amount is associated with the copper deposits mined in both Sweden and Finland. The U.S.S.R., Canada and the U.S.A. are the world's major producers of selenium and tellurium, but Peru, Australia and Japan all boast of significant deposits of these minerals.

USES(12)

The electrical properties of selenium have led to successful application in photocells, metal rectifiers and xerography. It is also used as a colouring agent for glass, and both the dialkyl selenides and tellurides are added to lubricating oils as oxidation inhibitors. Selenium sulphide is used commercially in 'SELSUN' shampoo as a dandruff inhibitor. The suggestion(13) that selenium may act as a carcinostatic has led to further intensified interest(14) in the chemistry of this element. Addition of selenium or tellurium to steel and copper improves the machinability of the metal. The semiconductor properties of bismuth and lead telluride aroused much interest in the late 1950's, and thermoelectric applications of these and similar compounds are still being investigated.

TOXICOLOGY(15)

Tellurium complexes are generally considered to be rather less toxic than those of selenium, probably because of their rapid reduction in the body to elementary tellurium, which is ultimately excreted in the form of unpleasant smelling organo-tellurium compounds. Both cause pronounced garlic odour of the breath and sweat, lasting for a considerable time after exposure. The recommended treatment for this garlic odour (Me_2Se or Me_2Te) is a daily intake of Vitamin C, but it has been found that the decrease in garlic breath is only temporary. As soon as the Vitamin C treatment is suspended, the odour appears again. Symptoms of tellurium intoxication which have been noted include:- transient headaches, somnolence, metallic taste and dryness of the mouth. Acute tellurium poisoning causes restlessness, tremor, diminished reflexes, paralysis, convulsions, somnolence, unconsciousness, cessation of respiration and finally, death!

Although none of the latter symptons have been experienced by us, the socially offensive nature of the selenides and tellurides caused us to be banned from the chemistry department, and the preparations of Et_2Se_2 and Et_2Te_2 had to be conducted in a fume-cupboard vented at the summit of a nine-storey building! Like every good story told in scientific journals, a precedent already existed. In his book(16) on 'Humour and Humanism in Chemistry', Reid describes the consequences of a roof-top preparation of MeSeEt. His work with Pope in Cambridge chanced to coincide with the Darwin Centenary celebrations of 1909, and 'THE SMELL' as he describes it, caused disruptions of open-air tea-parties and garden-parties. The headlines 'WHAT WAS IT? **SUSPECTED DRAINS EXONERATED**. SCIENCE THE SINNER' in the Cambridge Daily News, subsequently led to a continuation of his work from the comparitive isolation of an open field!

ORGANIC COMPOUNDS

The first organotellurium compound, Et_2Te, was synthesised by Wöhler(17) in 1840, 58 years after the discovery of the element. Subsequent work led to the synthesis of a series of organo-selenides and - tellurides, and as Table 1 shows, most of them have been established for at least a century. The alkyl selenides and tellurides are the best known of the organo compounds

TABLE 1

SOME ORGANO-SELENIUM AND -TELLURIUM COMPOUNDS

SELENIUM			TELLURIUM		
Compound	Date	Ref.	Compound	Date	Ref.
Se	1817	12	Te	1782	12
Me_2Se	1875	18	Me_2Te	1855	21
Et_2Se	1869	19	Et_2Te	1840	17
Bz_2Se	1875	18	Bz_2Te	1914	22
Me_2Se_2	1856	20	Me_2Te_2	1934	23
Et_2Se_2	1869	19	Et_2Te_2	1851	24

of these elements. They are evil-smelling liquids which are generally colourless when pure, but usually have a yellow tinge due to the presence of small amounts of the diselenide or ditelluride. Most are soluble in organic solvents but insoluble in water. Dialkyl- selenides tend to be bright yellow, whereas the tellurides are generally dark red, oils. Their exceedingly obnoxious odours have no doubt been the major reason for the relatively small amount of research on these compounds.

TRANSITION METAL COMPLEXES

Many diorgano-chalcogen transition metal complexes are known. Their preparations are usually very simple and generally involve shaking solutions of the ligands and the transition metal halides. Most of the complexes tend to be insoluble and precipitate as crystalline solids or amorphous powders. Table 2 shows some representative complexes. The following Tables(3 and 4)list all the known types of selenoether and telluroether, platinum (II) and palladium (II) complexes. The first of these to be prepared was, $(Et_2Se)_2PtCl_2$, which was synthesised in 1898 by Petrén(25).

TABLE 2

SOME REPRESENTATIVE TRANSITION-METAL SELENIDE[a] AND TELLURIDE[b] COMPLEXES

$(Ph_2Se)_2Mn(CO)_3Br$

$(Ph_2Se)Mo(CO)_3phen$

$\left[(R_2Se)Re(CO)_3Hal\right]_2$

$(Et_2Se)_2Re(CO)_3Hal$

$\left[(Ph_2Te)Mn(CO)_4\right]_2$

$(Ph_2Te)_2Mn(CO)_3Hal$

$(Ph_2Te)_2Mn(NO)_3$

$Ph_2TeFe(CO)_4$

$Ph_2TeFe(CO)_3Hal_2$

$Ph_2TeFe(NO)_2CO$

$RR'TeHgHal_2$

$(Me_2Te)(AgI)_2$

a) Taken from ref. 26

b) Taken from ref. 27

TABLE 3

SELENOETHER PLATINUM AND PALLADIUM COMPLEXES

	COMPLEX	Ref.
	$(R_2Se)_2PtHal_2$	28
trans-	$[(Et_2Se)pip.]\,PtCl_2$[a]	29
trans-	$(Et_2Se)_2PtRHal$	30
trans-	$(Et_2Se)_2Pt(mesityl)_2$[b]	30
trans-	$(Et_2Se)_2Pt(RSO_2)Cl$	31,32
trans-	$(Et_2Se)_2Pt(PhSO_2)_2$	32
	$(R_2Se)_2Pt_2Cl_4$	33
	$(RSeC_nH_{2n}SeR)PtHal_2$	34
trans-	$(R_2Se)_2PdHal_2$	35,41
trans-	$(Et_2Se)_2PdRHal$	36
	$(R_2Se)_2Pd_2Hal_4$	37
	$(RSeC_nH_{2n}SeR)PdHal_2$	34

a) pip. is 

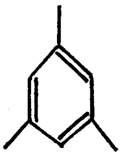
b) mesityl is 

TABLE 4

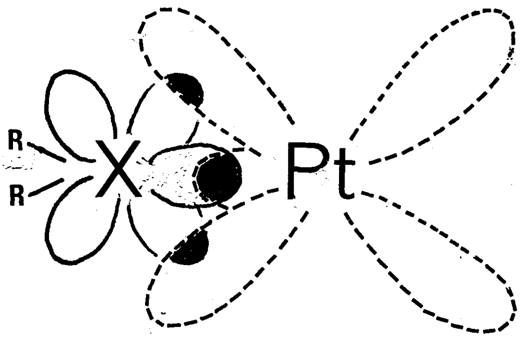
TELLUROETHER PLATINUM AND PALLADIUM COMPLEXES

Complex	Ref.
$(R_2Te)_2PtHal_2$	38,39
trans- $[(Et_2Te)pip.]PtCl_2$	29
trans- $(Et_2Te)_2PtRHal$	40
trans- $(Et_2Te)_2Pt(PhSO_2)Cl$	31
trans- $(Et_2Te)_2Pt(o\text{-}tolyl)_2$	40
$(R_2Te)_2Pt_2Cl_4$	33
$(R_2Te)_2PdHal_2$	41
trans- $(Et_2Te)_2PdRHal$	36
$(R_2Te)_2Pd_2Cl_4$	37

It is interesting to note that no such ether complexes have been reported. R_2X ligands (R = S, Se, Te) are generally considered to be two-electron donor ligands, as shown in the diagram below.

FIGURE 3

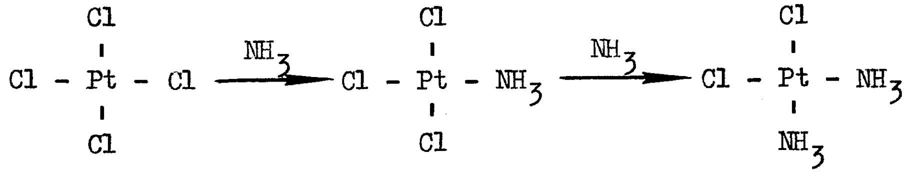
DESCRIPTION OF R_2X-Pt BOND



A σ-bond is formed between one lobe of an unfilled metal hybrid orbital and a filled sp ligand orbital. A π-bond can then be formed between filled metal d-orbitals of appropriate symmetry and energy, and empty ligand d-orbitals, as described previously. The relative contributions of both these bonds to the overall bond strength, and indeed the order of bond strength is still open to debate. The bond order reported by Allkins and Hendra(42), namely, M-S $>$ M-Se $<$ M-Te (M = Pt, Pd) may be doubtful, at least in the telluride case, due to the confusion which existed at that time as to the geometry of these complexes. In addition, Plusčec and Westland(43), on the basis of I.R. and molar conductivity data, suggested that selenium forms a stronger π-bond to palladium than does sulphur and proposed the bond strength order :- Pd-Se$>$Pd-S. They also concluded that the π-contribution to the platinum-selenium bond is abnormally slight and that this bond is unusually weak. The view that the strongest π-bond should be formed between elements of the same row in the periodic table is supported by the work of others. Hartley(44) concluded, from X-ray crystallographic data, that little or no π-bonding in the metal (II)-sulphur bond exists, a view shared by Cattalini and Edwards(45). Sergi and coworkers(36) suggested that overlap between the filled 4d orbitals of Pd (II) and the empty 4d and 5d orbitals of selenium and tellurium respectively is far more important, - the latter interaction being the greater. The relative π-acceptor capability of both sulphides and selenides is however reported on the basis of low frequency I.R. data, to be less effective than that of phosphines(46). Chatt and Venanzi(37) have suggested that the relative sizes of the orbitals used in forming the σ-bond is also important. Those of selenium are comparable with those of palladium and those of tellurium with platinum, resulting in an enhancement of the Pd-Se and Pt-Te bond strengths.

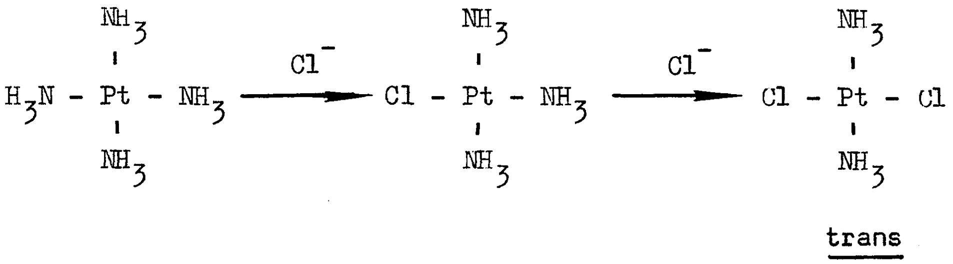
TRANS EFFECTS

In 1844, Peyrone(47) isolated α and β forms of $(NH_3)_2\ PtCl_2$, but it was only towards the end of the 19th century that Werner(48) introduced the concept of a square planar configuration rather than a tetrahedral one at platinum. He concluded that the α and β forms were in fact cis and trans isomers. This observation was not generally utilised until after 1926, when Chernaev(49) introduced the concept of TRANS EFFECT to correlate many of the reactions of Pt(II) complexes. He called attention to the general phenomenon that a negative ligand e.g. Cl^- has a greater labilising effect on a group trans to it than it does on groups in cis positions. Peyrone's original observations(47) could be explained in terms of the concept of the trans- effect. The cis-complex was synthesised by reaction of $PtCl_4^{2-}$ with ammonia:-



cis

Heating solid $\left[(NH_3)_4Pt\right]Cl_2$ to approximately 250°C was required to produce the trans- complex:-



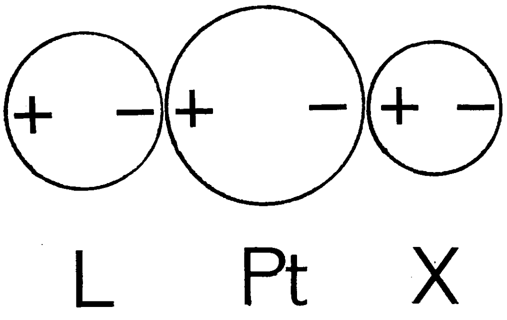
$$H_3N - \underset{NH_3}{\overset{NH_3}{Pt}} - NH_3 \xrightarrow{Cl^-} Cl - \underset{NH_3}{\overset{NH_3}{Pt}} - NH_3 \xrightarrow{Cl^-} Cl - \underset{NH_3}{\overset{NH_3}{Pt}} - Cl$$

Thus in both cases the trans- directing influence of the chloride ion dictates the course of the substitution.

The earliest theory, proposed in 1935, to account for trans-effects was the polarisation theory. Grinberg(50) suggested that in the molecule trans- PtA_2LX, the primary charge on the metal induces a dipole on the ligand L which in turn induces a dipole on the central metal. This negative charge repels the bonding electrons in the trans ligand X and produces a weaker bond.

FIGURE 4

GRINBERG'S POLARISATION THEORY.



Despite agreement with the experimental observation that effects were stronger with the more polarisable metal ions, such as Pt (II), this simple electrostatic approach had severe limitations and led, in many cases, to erroneous conclusions. Attention was duly focused in 1948 on the nature of hybridisation at the metal. Syrkin(51) discussed it, in square planar Pt(II) complexes, in terms of $5d_{x^2-y^2}$, 6s, $6p_x$ and $6p_y$ orbitals. Since the covalent bond to ligand L will tend to contain a larger proportion of the metal 5d and 6s orbitals (order of energies is $5d \approx 6s < 6p$), and the trans ligand X must share the same (s + d) hybrid, the resulting decreased availability of these orbitals will produce a weaker bond to X.

With the advent of new theory, this valence bond approach gave way in the 1950's and '60's to other explanations in terms of π-bonding and M.O. theory.

At that time, the stability of certain transition metal complexes was rationalised(52) in terms of overlap of the filled d_π metal orbitals with ligand orbitals of appropriate symmetry, to form a π-bond. This withdrawal of electrons from the metal was proposed independently by Chatt(8) et al. and Orgel(9) as an explanation of trans-effects. They postulated a resulting stabilisation of the transition state relative to the ground state in a substitution reaction. However, the high trans-effects of anions such as H^- and CH_3^- with no π-bonding properties remained unexplained, and it was necessary to invoke a σ- and π- trans-effect(53).

A ligand L which forms a stronger covalent bond takes on a larger part of the σ_X bonding orbital leaving a smaller share for X; the increased rate of substitution of X is a direct result of the weaker bond.

It was becoming increasingly obvious that a good trans-directing ligand could be the result of a bond weakening mechanism or one in which the transition state of the substitution was stabilised(8), and that both were not necessarily related. Consequently a new term, 'trans-influence' was adopted(8) and defined in terms of ground state energies as 'the extent to which the ligand weakens the bond trans to itself in the equilibrium state of that complex'. 'Trans-effect' remained, but only in the kinetic sense, and was defined(54) as 'the effect of the trans ligand on the rate of substitution of the substituent opposite to it'.

A recent review(55) outlines developments in trans- effect studies, but by far the most effort has gone into the theoretical(56) and experimental(57) investigation of trans-influence. Since the main area of disagreement in the former treatment has been in the particular type of metal orbital used in bonding, the tendency has been to turn towards a combination(58) of the three principal techniques used in the measurement of trans-influence. All three indicate that the trans-influence of a ligand increases as its σ-donor ability increases, and a brief description of each is now presented.

If the Pt-X bond in trans- PtA_2LX is found by X-ray crystallography to be 'unusually long' compared to the sum of the covalent radii, or longer than the bond lengths in related structures, a high trans-influence is assigned to L(57). One disadvantage of this technique is that it fails to take into account the variation in covalent radii with hybridisation or formal charge effects, but in general it has proved extremely useful, especially in the comparison of structures of closely related compounds.

This last feature applies to almost every spectroscopic technique and in particular to the infra-red detection of trans-influence(57). The high trans-influence of L gives rise to a corresponding decrease in the Pt-X stretching frequency - assuming that no vibrational coupling exists between this and other molecular vibrations. Ideally a comparison of the force constants for the particular stretching vibrations should be made, but these are generally not readily available.

Nuclear magnetic resonance coupling constants and chemical shift data have both been used in the detection of trans-influence. In particular, coupling constants - which are thought to be dominated by the Fermi contact term(57) - give an indication of the type of hybridisation used in bonding in a series of closely related compounds. A ligand with a high trans-influence will tend to take on a larger part of the s-electron density leaving a smaller share for the ligand in the trans-position. Coupling of the metal nucleus to nuclei in the trans position will therefore be reduced.

Perfect linear correlation between the various techniques used as a measure of trans-influence is not expected - and indeed is not found. Not only are different sensitivities to the hybridisation and electrostatic aspects of the metal-ligand bond shown, but also indicated is subjectivity to different approximations and simplifications. Consequently only a general order of trans-influence is called for, and any particular arrangement within this structure will require a definition of the technique and its limitations. The general order is as follows:-

C-donors > P-donors > As-donors > S-donors > N-donors > halides > O-donors.

a) HALOGENS

The π-bonding tendency of the halogens was reported in 1961(59) to fall in the order:-

$I^- > Br^- > Cl^-$

A few years later, Parshall,(60) by ^{19}F n.m.r. studies, attempted to assess the σ- and π- contributions to trans-effects and arrived at the following conclusions:-

σ-effect $Cl^- > Br^- > I^-$

π-effect $I^- > Br^- > Cl^-$

Although the method has been strongly criticised(55), recent X-ray photoelectron spectroscopy studies(61) have confirmed the σ-effect order, stressing the relative unimportance of the π-acceptor properties of the halogens. I.R. and Raman data(42) suggest the following bond strength order:-

$$M - Cl > M - Br > M - I$$

(where M = Pt, Pd)

b) CHALCOGENS

A *trans*-influence order based on N-H stretching frequencies in the infra-red has been suggested(8) as:-

$$Et_2Te > Et_2Se > Et_2S.$$

Other literature conclusions(39)(42)(43) on *trans*-phenomena and bond strengths are confusing and often conflicting, mainly due to the difficulties in assigning *cis*- and *trans*- configurations to the complexes.

INVERSION

In 1924 Meisenheimer and coworkers$^{(62)}$ suggested that the inability of trivalent nitrogen to sustain optical activity was due to fast inversion about nitrogen. Five years later, E.F. Barker$^{(63)}$ obtained the first direct experimental manifestation of an inversion process when he reported the doubling of infrared lines in the spectrum of ammonia. The subsequent effort undertaken concerning the determination of the magnitude of this inversion barrier initiated further experimental investigation, which has gathered momentum in the last two decades due to the commercial availability of n.m.r. spectrometers, and to the different time-scale of this method.

An atom bonded to three substituents in a pyramidal geometry and possessing an unshared pair of electrons may undergo an inversion of configuration. This 'pyramidal inversion' can be described$^{(64)}$ in terms of passage through a transition state in which the lone pair has pure p-character and the bonds from the central atom to the substituents are sp^2 hybridised.

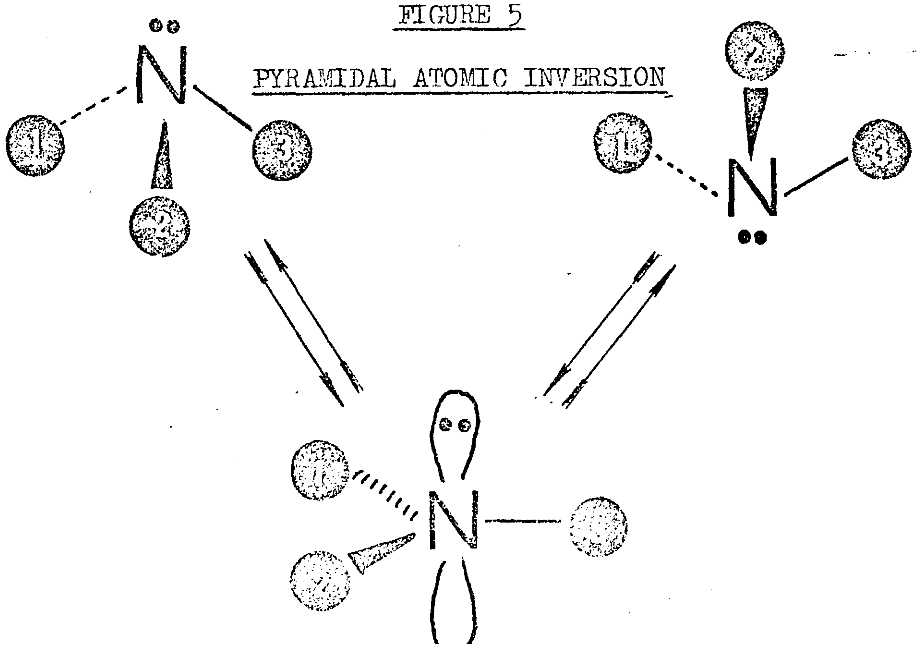


FIGURE 5

PYRAMIDAL ATOMIC INVERSION

Such a 'classical mechanism'(65) depicts a vibrational mode which leads to inversion through a coplanar or near coplanar arrangement of substituents round the central atom, with intra-group angles of about 120°. (A second 'non-classical' mode, 'quantum mechanical tunnelling'(66) can cause inversion, but is only thought to be important when one of the substituents on the inversion centre is hydrogen or deuterium and when the barrier to inversion is low(65)).

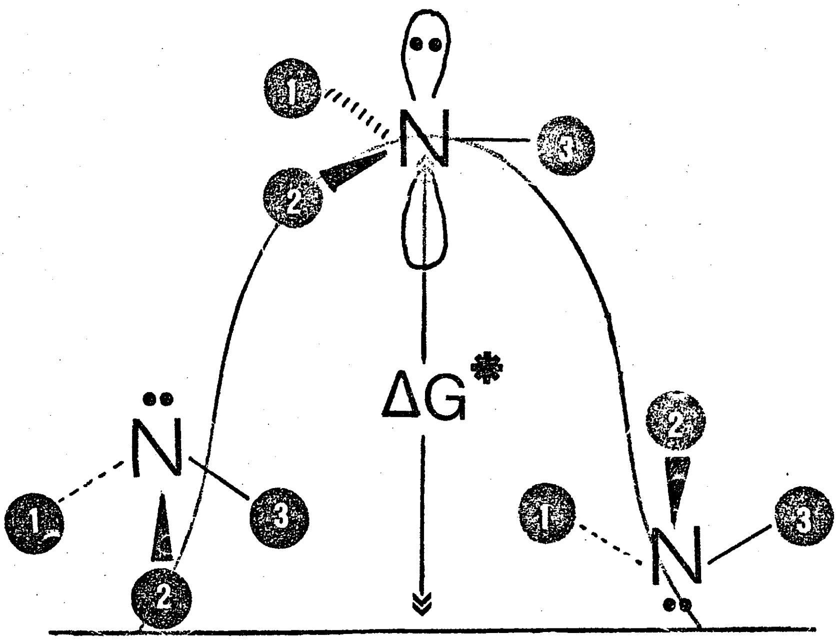
Pyramidal atomic inversion is one of the most subtle of molecular processes. A reversal of configuration takes place, but no bonds are broken and none are formed, except perhaps simultaneously(67). Problems arise therefore, when alternative mechanisms such as dissociation-recombination(68), bimolecular exchange(69), various inter-(68) and intra-(70) molecular interactions, bond rotations(71), and ring reversal(72) in cyclic compounds exist as ambiguous inversion pathways, and caution must be exercised when dealing with these systems and in interpreting the origin of the effects.

MEASUREMENT

A useful thermodynamic parameter in the description of inversion processes, and indeed of all fluxional processes, is $\Delta G^{\ddagger}$, the free energy of activation, a temperature dependent term. (Much preferable would be E_A, the activation energy, but this parameter is often difficult to obtain).

Figure 6

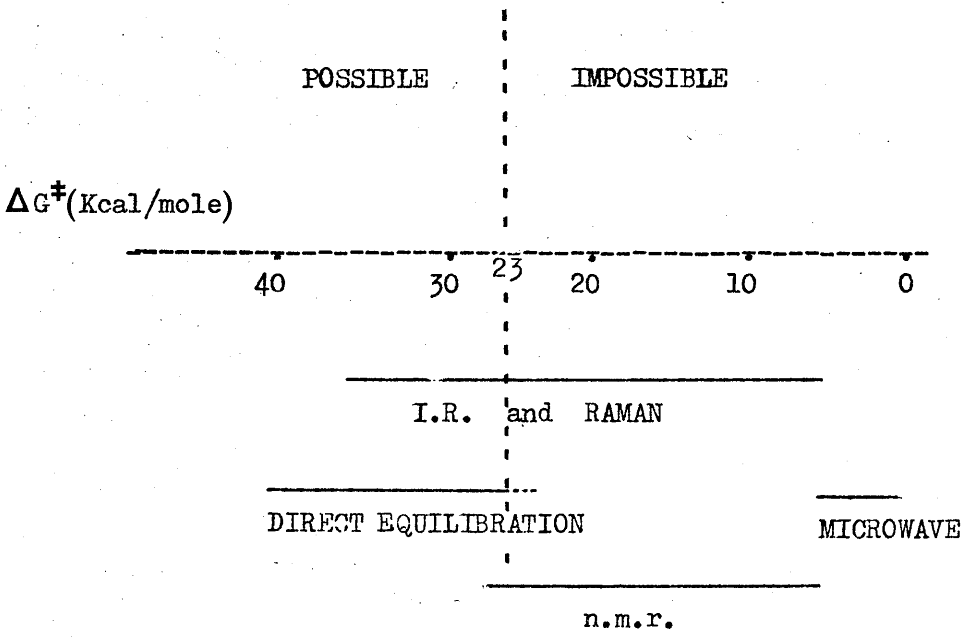
ILLUSTRATION OF $\Delta G^{\ddagger}$



Thus, as the next diagram shows, a particular experimental technique can only be used when $\Delta G^{\ddagger}$ falls within a certain range(73).

FIGURE 7

PHYSICAL SEPARATION AT ROOM TEMPERATURE



Classical kinetic methods can be used, for example when the isomers are separable at room temperature(74) ($\Delta G^{\ddagger} \gtrsim 23$ Kcal/mole), but below this other spectroscopic techniques must be employed. The most widely used is that of dynamic nuclear magnetic resonance(75), (d.n.m.r.), which is responsible for the solutions of many rate processes of fundamental importance in chemistry.

N.M.R.

As illustrated in Figure (7), characteristic changes in an n.m.r. spectrum on variation of a parameter, such as temperature, indicates the presence, and sometimes nature, of a rate process with an activation energy between 5 and 25 Kcal/mole.. (1 cal = 4.187 joule) Unfortunately this quantitative aspect of dynamic n.m.r. is fraught with difficulties and pitfalls. The values of 7 to 24 Kcal/mole which have been obtained for the barrier to rotation in N,N-dimethylformamide(77) highlight the errors involved in the use of approximate formulae. Methods of obtaining barriers using these approximations are nevertheless justifiable under certain circumstances and these, together with their limitations are now outlined.

The magnitude of the barrier to inversion is determined from an analysis of the observed temperature-dependent spectral changes due to the effective averaging of the environments of diastereotopic(78) groups in the molecule. This 'effective averaging' causes a coalescence of the signals due to the diastereotopic groups, and can be thought of as an exchange between two sites A and B in the molecule.

METHOD 1

The 'approximate coalescence temperature method' extracts a rate constant k, at the coalescence temperature, which is then related to $\Delta G^{\ddagger}$ the free energy of activation in accordance with the Eyring equation(79):-

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT}$$

where k_B = Boltzmann's constant

h = Planck's constant

R = Gas constant

T = Absolute temperature.

The simplest example of such an equation(82) is

$$k = \pi/\sqrt{2}\ \Delta v_{AB}$$

where Δv_{AB} is the chemical shift difference in Hz. between A and B in the absence of exchange.

A modification of this equation when A and B are coupled together (J, (Hz)) is given by(80)

$$k = \pi/\sqrt{2}\ \ (6J^2 + \Delta v_{AB}{}^2)^{\frac{1}{2}}$$

These equations only apply when the two sites A and B are equally populated and when the chemical shift difference Δv_{AB} is far greater than the linewidth of the signals in the absence of exchange(77).

Since only a small amount of the spectral information is actually used to calculate barriers in this way, a more general method involving as much of the spectrum as possible is desirable.

METHOD II

Equations relating the rate constant k, to chemical shift differences and line-widths at half-height are used to determine values of k at specific temperatures below, at, and above coalescence(77).

The activation energy E_A is obtained from the Arrhenius relationship:-

$$2.303 \log k = -E_{A/RT} + 2.303 \log A$$

where A is the pre-exponential factor. The formula:-

$$\Delta H^{\ddagger} = E_A - RT$$

is then used to derive the enthalpy of activation ($\Delta H^{\ddagger}$) which, used in conjunction with $\Delta G^{\ddagger}$ (as obtained from the Eyring equation) in

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

can then afford $\Delta S^{\ddagger}$, the entropy of activation of the process.

Although more spectral information is used, the formulae used to evaluate k are still approximate and large systematic errors in E_A, log A, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can result(77). Consequently a better method would be to use all the spectral data and treat it with more accurate formulae.

METHOD III

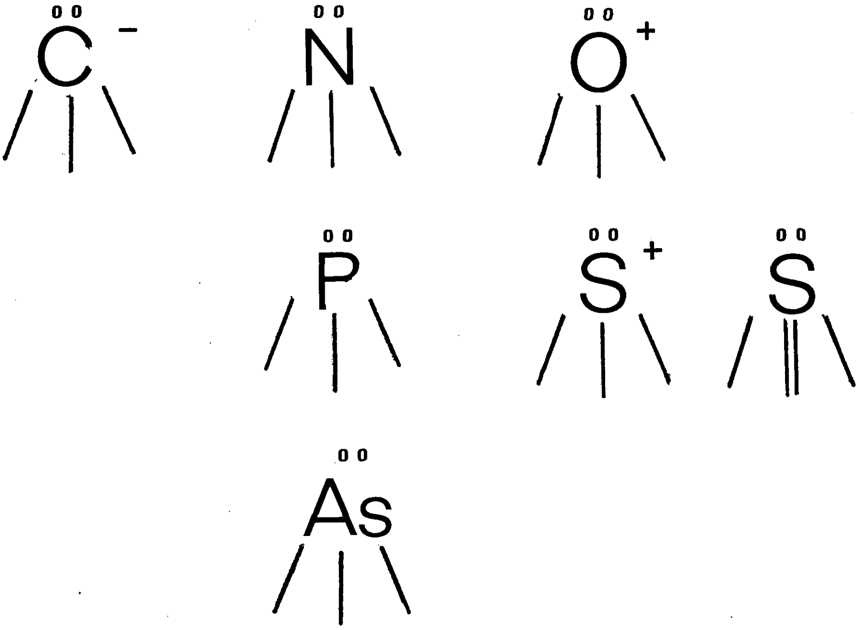
A complete line shape analysis is performed by computer(81), using exact equations. The input parameters are varied until perfect visual matching of the experimental and calculated spectra is obtained. This gives the rate at different temperatures. Obviously this is the most accurate method of obtaining rates and barriers to inversion, but the time factor in the investigation of a series of similar compounds can be prohibitive, and recourse is often made to one of the more approximate methods.

INVERSION CENTRES

Inversion barriers have been determined for the following pyramidal systems(73):-

FIGURE 8

SUMMARY OF INVERTING CENTRES



GROUP V

Nitrogen is by far the most thoroughly studied central atom(83), not only because of the stability and ease of synthesis of many of its compounds, but also because of the convenient range for measurement of its inversion barriers. The bulk of information on rate controlling factors, therefore, relates to nitrogen and may or may not apply to other atoms.

Factors which tend to raise inversion barriers are:-

a) Severe angular strain(84), when the inverting atom is incorporated into a small ring for example. This stabilises the pyramidal relative to the planar form.

b) Electronegative substituents(85) which increase the s-character(86) of the lone pair.

c) Lone-pair - lone-pair repulsion(87) which is greatest in the transition state.

d) Descending the periodic table(90).

A lowering of the inversion barrier can be caused by conjugation of the lone pair on the inverting centre(88). Steric strain, on the other hand, can either be relieved(84) or aggravated(89) in the transition state leading to lower or higher barriers.

GROUP VI

a) SULPHUR

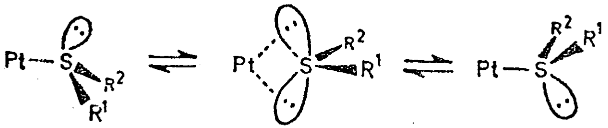
The pyramidal environment about sulphur(IV) is now well established(91)(92). When Harrison, Kenyan and Philips resolved sulphoxides for the first time in 1926(93) they demonstrated the configurational stability of sulphur to support optical activity. Both sulphoxides(74) and sulphonium ion(94) racemisation have since been shown in certain cases to proceed via 'pyramidal atomic inversion' with typical $\Delta G^{\ddagger}$ values of 35-43 Kcal/mole and 25-29 Kcal/mole respectively.

In 1966, Abel et al(95) noticed that coordination of a sulphur chelate ligand to platinum or palladium lowered the barrier to inversion sufficiently, compared to other tri-coordinate sulphur systems, to permit use of dynamic n.m.r. methods.

Subsequent work(96) on monodentate sulphur coordination complexes e.g. $\left[(PhCH_2)_2S\right]_2 PtCl_2$ served to throw some light on the inversion mechanism. Retention of Pt-S-C-H coupling above the coalescence temperature led the authors to postulate the following mechanism:-

FIGURE 9

INVERSION MECHANISM.



i.e. nucleophilic attack on platinum by the lone pair on sulphur with concomitant rupture of the 'existing' Pt-S bond. This postulate is hereafter referred to as 'Haake and Turley's' mechanism(96).

Inversion at sulphur has since been detected in iron(97) and gold(98) complexes and a correlation of inversion rates with trans effects has been made(96)(99). Table 5 lists the coalescence temperatures of all inverting sulphur ligands bonded to transition metals.

b) SELENIUM AND TELLURIUM

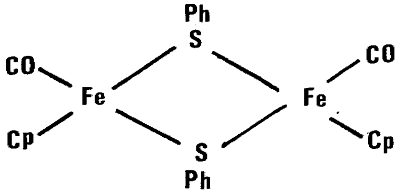
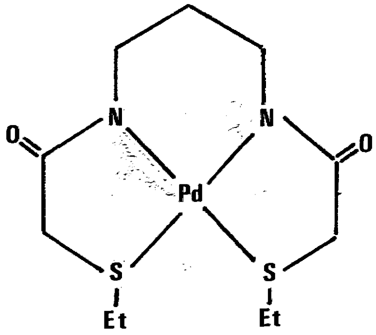
The pyramidal configuration at selenium in compounds of the type RR'Se = O has been known for a long time(100). After many unsuccessful attempts(102), optically active selenoxides were isolated for the first time in 1970(103), but their barriers to racemisation proved to be above the range of kinetic observation.

Telluronium ions were shown in 1929(104) to be sensitive to chemical racemisation.

Until this study, however, no systematic investigation of selenium or tellurium inversion has been carried out.

TABLE 5

COALESCENCE TEMPERATURES OF SULPHUR INVERSION IN TRANSITION METAL COMPLEXES

Compound	Solvent	T_c (°C)▲	Ref.
1. $(MeSC_2H_4SMe)PtCl_2$	$(CD_3)_2S{=}O$	95	95
2. $(MeSC_2H_4SMe)PdCl_2$	"	≈ 40	95
3. *cis*- $[(PhCH_2)_2S]_2PtCl_2$	$CDCl_3$	35(16.6)	96
4. *trans*- $[(PhCH_2)_2S]_2PtCl_2$	"	<27(<15)	96
5. *cis*-$(Et_2S)_2PtCl_2$	"	60 (16.8)	96
6. *trans*-$(Et_2S)_2PtCl_2$	"	1 (13.9)	96
7. *cis*-$(CH_3SCH_2Ph)_2PtCl_2$	CH_2Cl_2	36 (16.5)	96
8. *trans*-$(CH_3SCH_2Ph)_2PtCl_2$	$CDCl_3$	<-50(<12)	96
9. 	T.H.F.	(30.7)●	97
10. 	D_2O	≈75	105
11. $(PhCH_2)_2SAuCl_3$	$CDCl_3$	≈ 56(17)	98
12. $(PhCH_2)_2SAuCl$	$(CH_3)_2C{=}O$	<-95	98

●E_A by classical kinetic method. ▲Values in parentheses $\Delta G^{\ddagger}$ in Kcal/mole.

Compound				Solvent	T_c($^\circ$C)	Ref.
$(RSC_2H_4SR)PtX_2$						
		R	X			
13.	a	Me	Cl	$(CD_3)_2S{=}O$	100	99
	b	Me	I	"	87	"
	c	Et	Cl	$PhNO_2$	80	"
	d	Et	I	"	50	"
	e	Et	Ph	$CDCl_3$-CF_2Cl_2	-70	"
	f	Pr^n	Cl	$PhNO_2$	95	"
	g	Pr^n	Br	"	75	"
	h	Pr^n	I	"	50	"
	i	Pr^i	Cl	$(CD_3)_2S{=}O$	92	"
	j	Pr^i	Br	$PhNO_2$	71	"
	k	Pr^i	I	"	47	"
	l	Bu^n	Cl	"	92	"
	m	Bu^n	Br	$CDCl_3$	67	"
	n	Bu^n	I	$PhNO_2$	67	"
$(RSC_2H_4SR)PdX_2$						
		R	X			
14.	a	Pr^n	Cl	$CDCl_3$	50	99
	b	Pr^n	Br	"	20	"
	c	Pr^n	I	"	6	"
	d	Bu^n	Cl	"	50	"
	e	Bu^n	Br	"	34	"
	f	Bu^n	I	"	0	"

CHAPTER 2

CHARACTERISATION OF THE COMPLEXES

CHARACTERISATION OF COMPLEXES

All compounds of the type $[(RCH_2)_2X]_2MCl_2$ (R = CH_3, Ph; X = S, Se or Te; M = Pt or Pd) were prepared by standard methods(108). This generally involved addition of the chalcogen ligand to an aqueous solution of potassium chloroplatinite (or palladite), shaking, filtering, and recrystallisation from ethanol. The corresponding bromides and iodides were synthesised by treatment of an ethanolic solution of the chloride with an approximate ten-fold excess of LiBr or LiI, respectively.

A variety of techniques was used to establish the identity of the complexes. Elemental C and H analyses were obtained for all the complexes, and, where possible, melting points were compared with literature values. Geometric ambiguities in solution were resolved by dipole moment determinations. Further structural evidence was obtained by ^1H n.m.r. Infra-red and Raman spectra were also obtained but proved to be of limited application. Since a molecular ion was never observed in the Mass Spectra of these compounds, this technique was not pursued further.

A) DIPOLE MOMENTS

THEORY

Molecular dipole moments were conveniently determined by dielectric constant and refractive index measurements on solutions of the compounds in benzene. The Debye theory(109), outlined below, was used.

DEBYE THEORY

The dielectric constant, D, of a liquid is determined by measuring the capacity of a condenser first with air (C_A) and then the liquid (C_B) as its dielectric. Since the dielectric constant of air is very close to unity,

$$D_{\text{liquid}} = C_B/C_A$$

Let subscript 1 denote solvent and subscript 2 solute.

The total polarisation (P_{12}) of a solution is given by:-

$$\left[\frac{D-1}{D+2}\right]\frac{x_1M_1 + x_2M_2}{\rho} = P_{12}$$

where D is the dielectric constant of the solution

x_1 is the mole fraction of the solvent

x_2 is the mole fraction of the solute

ρ is the density of the solution

M_1 is molecular weight of the solvent

M_2 is molecular weight of the solute.

We may describe P_{12} in terms of its various electronic (P^E), atomic (P^A), and orientation (P^o) contributions. Thus:-

$$P_{12} = x_1(P_1{}^E + P_1{}^A + P_1{}^o) + x_2(P_2{}^E + P_2{}^A + P_2{}^o)$$

For a non-polar solvent, $P_1^{\,o} = 0$, and for pure solvent:-

$$P_1^{\,E} + P_1^{\,A} = \left[\frac{D_1 - 1}{D_1 + 2}\right] M_1/\rho_1$$

The electronic polarisation is connected to the refractive index (n) of the solution in the following way:-

$$\left[\frac{n^2 - 1}{n^2 + 2}\right]\frac{x_1M_1 + x_2M_2}{\rho} = x_1P_1^{\,E} + x_2P_2^{\,E}$$

and for pure solvent:-

$$\left[\frac{n_1^{\,2} - 1}{n_1^{\,2} + 2}\right]\frac{M_1}{\rho_1} = P_1^{\,E}$$

The contributions to the total polarisation from the atomic terms $P_1^{\,A}$ and $P_2^{\,A}$ are regarded as small and lead to the approximation:-

$$P_1^{\,A} = P_2^{\,A}$$

Hence:-

$$x_2P_2^{\,o} = \left[\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2}\right]\frac{x_1M_1 + x_2M_2}{\rho}$$

$$- \left[\frac{D_1 - 1}{D_1 + 2} - \frac{n_1^{\,2} - 1}{n_1^{\,2} + 2}\right] M_1/\rho_1$$

All the terms in this equation, with the exception of P_2^o, can be determined experimentally. According to Debye, P_2^o depends on the dipole moment (μ) of the solute and the absolute temperature ($T(^oK)$) in the following manner:-

$$P_2^o = \frac{4\pi N\mu^2}{9kT}$$

where N = Avogadro's number

and k = Boltzmann's constant.

Hence

$$\mu = \sqrt{\frac{9kTP_2^o}{4\pi N}}$$

ERRORS

Several methods were used in an attempt to estimate the errors in the dipole measurements.

The dipole moment of cis-$(Ph_3P)_2PtPh_2$(M.p. 151-154°C(d)) was determined (μ = 7.3 D) and found to be in good agreement with the literature value(110) of 7.2 D. Repetition of the measurements at four different concentrations of trans-$(Et_2Te)_2PtCl_2$ yielded values of 2.3 D, 2.4 D, 2.7 D and 2.6 D. Finally a calculation on the same complex showed the standard deviation to be of the order of 0.5 D, arising mainly from the capacity measurements in the experiments.

Thus, although the errors could be in the region of 25%, the dipole determinations are sufficiently accurate to enable a cis or trans geometry to be assigned to the complexes.

RESULTS AND DISCUSSION

Table 6 lists the dipoles of most of the compounds used in this study. The non-zero value of the trans complexes is generally taken to be a result of large atomic polarisations rather than permanent orientation dipoles(109)(110). The contribution of the atomic polarisation (P^A) to the total polarisation cannot be accurately assessed, and is either omitted or taken as an arbitrary percentage of the electronic polarisation (P^E). (Trans- $(Et_2Se)_2PdCl_2$ has been shown to have a centre of symmetry in the solid state(107), but its experimentally determined dipole is 2.2 D). The experimental results are presented in detail in table 7.

TABLE 6

DIPOLE MOMENTS OF $(Et_2X)_2MHal_2$ COMPLEXES IN BENZENE

Compound	μ(D)	T(°C)	Ref.
cis -$(Et_2S)_2PtCl_2$	9.5	20	a
trans-$(Et_2S)_2PtCl_2$	2.41	20	a
trans-$(Et_2S)_2PtBr_2$	2.26	20	a
trans-$(Et_2S)_2PtI_2$	2.41	20	a
trans-$(Et_2Se)_2PtCl_2$	2.41	20	a
trans-$(Et_2Te)_2PtCl_2$	2.3	20	b
trans-$(Et_2Te)_2PtBr_2$	1.9	21	b
trans-$(Et_2Te)_2PtI_2$	1.8	20	b
trans-$(Et_2S)_2PdCl_2$	2.19	20	a
trans-$(Et_2Se)_2PdCl_2$	2.2	25	b
trans-$(Et_2Se)_2PdBr_2$	1.9	20	b
trans-$(Et_2Se)_2PdI_2$	2.1	28	b
trans-$(Et_2Te)_2PdCl_2$	1.8	24	b
trans-$(Et_2Te)_2PdBr_2$	1.8	24	b
trans-$(Et_2Te)_2PdI_2$	1.9	29	b
trans-$[(PhCH_2)_2S]_2PdCl_2$	2.0	19	b
cis-$(Ph_3P)_2PtPh_2$	7.3	20	b

a) Ref. 111. b) This work.

TABLE 7

DIPOLE MOMENT MEASUREMENTS BY
DIELECTRIC-CONSTANT-REFRACTIVE INDEX METHOD.

Compound	Geom.	μ(D)	T^oC	X_1	X_2	ρ	ρ_1	D	D_1	n	n_1	P_2^o
$(Et_2Te)_2PtCl_2$	*trans*	2.3	20	0.99743	0.00257	0.8902	0.8771	2.2878	2.2622	1.5032	1.5010	107.90
$(Et_2Te)_2PtBr_2$	*trans*	1.9	21	0.99804	0.00196	0.8849	0.8768	2.2891	2.2743	1.5022	1.5005	73.039
$(Et_2Te)_2PtI_2$	*trans*	1.8	20	0.99817	0.00183	0.8881	0.8797	2.2861	2.2709	1.5033	1.5010	66.967
$(Et_2Se)_2PdCl_2$	*trans*	2.2	25	0.99768	0.00232	0.8792	0.8727	2.2747	2.2552	1.5002	1.4989	99.626
$(Et_2Se)_2PdBr_2$	*trans*	1.9	20	0.99586	0.00414	0.8920	0.8774	2.3051	2.2745	1.5051	1.5023	78.529
$(Et_2Se)_2PdI_2$	*trans*	2.1	28	0.99836	0.00164	0.8776	0.8699	2.2650	2.2482	1.4973	1.4951	92.950
$(Et_2Te)_2PdCl_2$	*trans*	1.8	24	0.99832	0.00168	0.8792	0.8738	2.2703	2.2579	1.4998	1.4981	64.426
$(Et_2Te)_2PdBr_2$	*trans*	1.8	24	0.99823	0.00177	0.8822	0.8731	2.2799	2.2661	1.5000	1.4980	65.051
$(Et_2Te)_2PdI_2$	*trans*	1.9	29	0.99863	0.00137	0.8759	0.8705	2.2637	2.2510	1.4953	1.4933	73.253
$(Bz_2S)_2PdCl_2$	*trans*	2.0	19	0.99708	0.00292	0.889	0.8781	2.2897	2.2608	1.5063	1.5023	83.928
$(Ph_3P)_2PtPh_2$	*cis*	7.3	20	0.99928	0.000719	0.878	0.8744	2.3304	2.2670	1.5027	1.5000	1116.1

The results for the sulphides and selenides show good agreement with literature configurations. In some cases, the published dipoles were accepted. This was not done, however, with the tellurides, where large discrepancies between Jensen's work(112) and this study were observed. In 1937, Jensen(112) assigned a '<u>cis</u>' configuration to $(Et_2Te)_2PtCl_2$ on the basis of his experimentally determined dipole of 6.0 D. He dissolved what he could of the complex in cold benzene, filtered, and carried out his measurements in a manner similar to this work. In this study, an approximate thirty-fold increase in concentration was effected by stirring the complex in benzene (in the dark) for a few days, and a value of 2.3 D was found. The method of preparation of the complex was identical in both cases. The melting point of our solid (126 - 129°C) matched that of Jensen's (126°C), and although this physical measurement did not appear in his original paper, it is reported in Gmelin(113) as a supplement to this paper by Jensen himself. (No reference given). The ^1H n.m.r. of our sample of $(Et_2Te)_2PtCl_2$ remained invariant before and after stirring, illustrating the presence of only one species in solution. Moreover there is no mention in the literature of more than one isomer of this complex, which leads us to the conclusion that Jensen was probably in error due to dilute solutions and that $(Et_2Te)_2PtCl_2$ has a '<u>trans</u>' geometry. Our errors have been estimated as being of the order of 25%, and it seems certain that instead of a reported ±8%, an error closer to 60% was incurred in Jensen's experiments. Our value of 2.3 D for <u>trans</u>- $(Et_2Te)_2PtCl_2$

is of the same order of magnitude as the 2.48 D dipole moment reported for trans- $(Et_2Te)_2Pt(o\text{-tolyl})_2$ by Sergi and coworkers(40). The synthesis of $(Et_2Te)_2PtBr_2$ (M.p. 125 - 127°C) was reported for the first time in 1964 by Chatt and coworkers(39). They assigned a '*cis*' configuration to this molecule, presumably on the basis of Jensen's work(112) on $(Et_2Te)_2PtCl_2$. Our sample of $(Et_2Te)_2PtBr_2$ has a similar melting point (127-128°C) but its experimentally determined dipole moment was found by us to be 1.9 D. We conclude that these complexes are *trans* in solution, but the possibility that a *cis* geometry exists in the solid state cannot be ignored. In fact a solution of $(Et_2Te)_2PtBr_2$ in $Cl_2CH\text{-}CHCl_2$ showed two sets of methyl signals in the n.m.r., the smaller one gradually disappearing when the temperature was raised. This sample was run about 30 secs. after dissolving the complex, and indicates that *cis* and *trans* isomers might in fact exist. Surprisingly, similar treatment of the chloride ($CDCl_3$ and $Cl_2CH\text{-}CHCl_2$ solutions) and the iodide ($CDCl_3$, PhCl and $Cl_2CH\text{-}CHCl_2$ solutions) failed to produce another set of methyl signals in the n.m.r. spectra. However, since the geometries of these complexes in the solid state have been inferred from erroneous work in solution, we postulate a *trans* configuration for both complexes in the *solid state* and in *solution*.

B) INFRA-RED AND RAMAN SPECTROSCOPY

Having confirmed the geometry of the transition-metal complexes by dipole-moment measurements in solution, it seemed worthwhile to attempt a comparison between this and I.R. and Raman techniques. In particular, a closer look at the telluride complexes was desirable, since I.R. spectroscopy(39) seemed to confirm the apparently erroneously assigned <u>cis</u>-configuration(112) of $(Et_2Te)_2PtCl_2$. A major problem lies in the fact that much of the spectroscopic work was done using nujol mulls or polythene discs and that under these conditions, different geometries might exist from those in solution. Nevertheless discrepancies do exist between solid state Raman and I.R. results(42), and there is general confusion about the relative bond strengths and <u>trans</u>-influences of the telluride ligand in transition-metal telluride complexes(8)(39)(42)(43). We believe that treating the tellurides as <u>trans</u> complexes removes, if not solves these ambiguities.

In theory, <u>cis</u> and <u>trans</u> isomers in square planar complexes of the type $L_2M(Hal)_2$ can be differentiated by the number of metal-halogen, ν(M-X), stretches in the infra-red(42). Allowed transitions are shown below.

TABLE 8

METAL-HALOGEN I.R. PEAKS OF CIS AND TRANS COMPLEXES

Compound	Symmetry Group	ν(M-X)
<u>trans</u>-L_2MX_2	D_{2h}	1 B_{3u}
<u>cis</u>- L_2MX_2	C_{2v}	1 A_1
		1 B_1

One metal-halogen stretching frequency should denote a trans- and two, a cis-isomer. The strongest peaks in the low frequency I.R. spectra were assigned to the metal-halogen stretches (Table 9). Below these are shown literature values(39)(114). In all complexes involving sulphur or selenide ligands, only one metal-halogen stretching frequency is observed, and a 'trans' assignment is therefore justified.

TABLE 9

I.R. METAL-HALOGEN STRETCHING FREQUENCIES OF TRANS-L_2MX_2 COMPOUNDS

	PLATINUM			PALLADIUM		
L	X=Cl	X=Br	X=I	X=Cl	X=Br	X=I
Et_2S[a]	343	239	190	361	271	-
Et_2Se	339	245	206 or 177	356	269	218
Et_2Te	310	218	200 or 135	298	259	?
	304	210		275		
	282					
Et_2S[b]	341.9	253.5	-	358[c]		
Et_2Se	337.2	240.7	-			
Et_2Te	302.2	217.0	-			
	282.2	208.2	-			

a) Pressed rigidex discs, this work. b) Nujol mulls on polythene discs taken from ref. (39). c) Ref.(114)

However, complications arise with the telluride complexes. The Table below shows the number of strong peaks in the ν(M-Hal) region (rigidex discs), and the dipole of the complex in benzene. Both measurements were made by us.

TABLE 10

I.R. AND DIPOLES OF TELLURIDE COMPLEXES

Complex	$\nu(M\text{-}X)^a$	$\mu(D)^a$
$(Et_2Te)_2PtCl_2$	3	2.3
$(Et_2Te)_2PtBr_2$	2	1.9
$(Et_2Te)_2PdCl_2$	2	2.2

a) This work.

This seems to suggest that different geometries might in fact, exist in different media, but it is highly unlikely that the palladium complex is also <u>cis</u> in the solid state. Indeed, a spectroscopic investigation of $(Me_2Te)_2PtBr_2$ revealed that infra-red bands were paralleled by Raman emissions at similar frequencies(42). The authors stated that although this could be taken as a clear indication that the molecule does not possess a centre of symmetry (i.e. it is a <u>cis</u>-complex), the chemical evidence clearly indicates a <u>trans</u>-structure. (The I.R. samples were run as nujol mulls on polythene discs, and the Raman samples as pressed-powder pellets). It would seem therefore that structural determinations from I.R. and Raman evidence alone is unjustified. Raman data (chlorobenzene solutions) are compared with I.R. results (polythene discs) for the diethyl chalcogen complexes in Table 11. The values shown were obtained by us, and are the metal-halogen stretching frequencies determined by both techniques. Those in red illustrate that a similar effect to that found in $(Me_2Te)_2PtBr_2$ could be operative here. The suggestion(42) that 'the bulky telluride ligands distort the system sufficiently for the 'mutual exclusion rule' to break down' highlights the pitfalls involved in studies of this nature.

TABLE 11

ν(M-Hal) OF TRANS - L_2MHal_2 COMPLEXES^a

L	Cl		Br		I	
	I.R.	RAMAN	I.R.	RAMAN	I.R.	RAMAN
M=Platinum						
Et_2S	343	330	239	204	190	148
Et_2Se	339	328	245	207	177	151
Et_2Te	310	-	218	203	135	153
	304		210			
	282					
M=Palladium						
Et_2S	361	305	271	189	-	-
Et_2Se	356	300	269	190	218	137
Et_2Te	298 275	300	259	190	-	160

a) This work.

Another telluride complex which has undergone a similar history is $(Me_2Te)_2PtCl_2$. The infra-red data(42) in the Table below show two metal-halogen stretching frequencies for this compound. Identical values for ν(M-Hal) for R=Me and Et, suggest a similar geometry for both complexes.

TABLE 12

ν(Pt-Cl) in $(R_2X)_2PtCl_2$ complexes

X	R=Me[a]	R=Et[b]
S	344	341.9
Se	340	337.2
Te	303	302.2
	283	282.2

a) Ref. 42 b) Ref. 39 (Both measurements were made on nujol mulls on pressed polythene sheets).

Unfortunately, even after stirring for two months, the solubility of $(Me_2Te)_2PtCl_2$ in benzene was only ca. 6 mg/ml., and its dipole moment could not be determined. However it seems certain that this is a trans-complex, at least in solution, by analogy with the diethyl derivative.

In summary, we believe that wrong structural assignments (i.e. cis instead of trans) have been made on the following tellurium complexes:-

TABLE 13

	COMPLEX	REF.
1.	$(Et_2Te)_2PtCl_2$	112
2.	$(Et_2Te)_2PtBr_2$	39
3.	$(Et_2Te)_2PdCl_2$	27
4.	$(Me_2Te)_2PtCl_2$	42

The geometries of 2), 3) and 4) were inferred from the wrongly determined dipole of 1) and seemed to be corroborated by I.R.

The implications of these misinterpretations are quite interesting. A vicious circle of wrong conclusions on the *trans*-influences and bond strengths has appeared in the literature, each author unknowingly basing his evidence on an extrapolation of the same false premises. This is presuming of course, that the same geometry exists in the solid state as we have found in solution, namely in all cases, *trans*. The historical sequence of events is now traced.

A) *1937*. Jensen(112) wrongly assigned a *cis*-configuration to $(Et_2Te)_2PtCl_2$.

B) 1964. Chatt and coworkers(39), in a far - infra-red study of *cis*- and *trans*- complexes of diethyl-chalcogen ligands drew up a *trans*-influence series as follows:- $Et_2Te > Et_2Se$, Et_2S.

However, their evidence is based on $(Et_2Te)_2PtCl_2$ being cis, and also on the corresponding cis-dibromide, this being the first report of the latter.

C) 1965. Plušček and Westland(43) calculated group moments for Pt-L in the series of compounds cis - L_2PtCl_2 where L = Et_2S, Et_2Se, Et_2Te. Their conclusion, namely that the trend:-

$Pt-SEt_2$	$Pt-SeEt_2$	$Pt-TeEt_2$
4.7 D	4.4 D	2.2 D

supports greater π-back bonding in the telluride complexes is based totally on result A.

D) 1967. Allkins and Hendra(42) examined the I.R. and Raman spectra of solid samples of platinum and palladium complexes of the type L_2MHal_2 where L = Me_2S, Me_2Se, Me_2Te. A crude calculation yielded the following force constants (mdyne $Å^{-1}$):-

k_{Pt-S}	k_{Pt-Se}	k_{Pt-Te}
2.2	1.4	2.1

Their evidence rests solely on the assignment of a cis-geometry to $(Me_2Te)_2PtCl_2$, a compound which appears for the first time in this reference. Support for their conclusions, namely that the order of bond strength of Group VI donor complexes is:-

$$M - S > M - Se < M - Te$$

is given as:-

a) Trans- $(Me_2Te)_2PtCl_2$ is difficult to prepare.

b) Pluščec and Westland's results(43) (C).

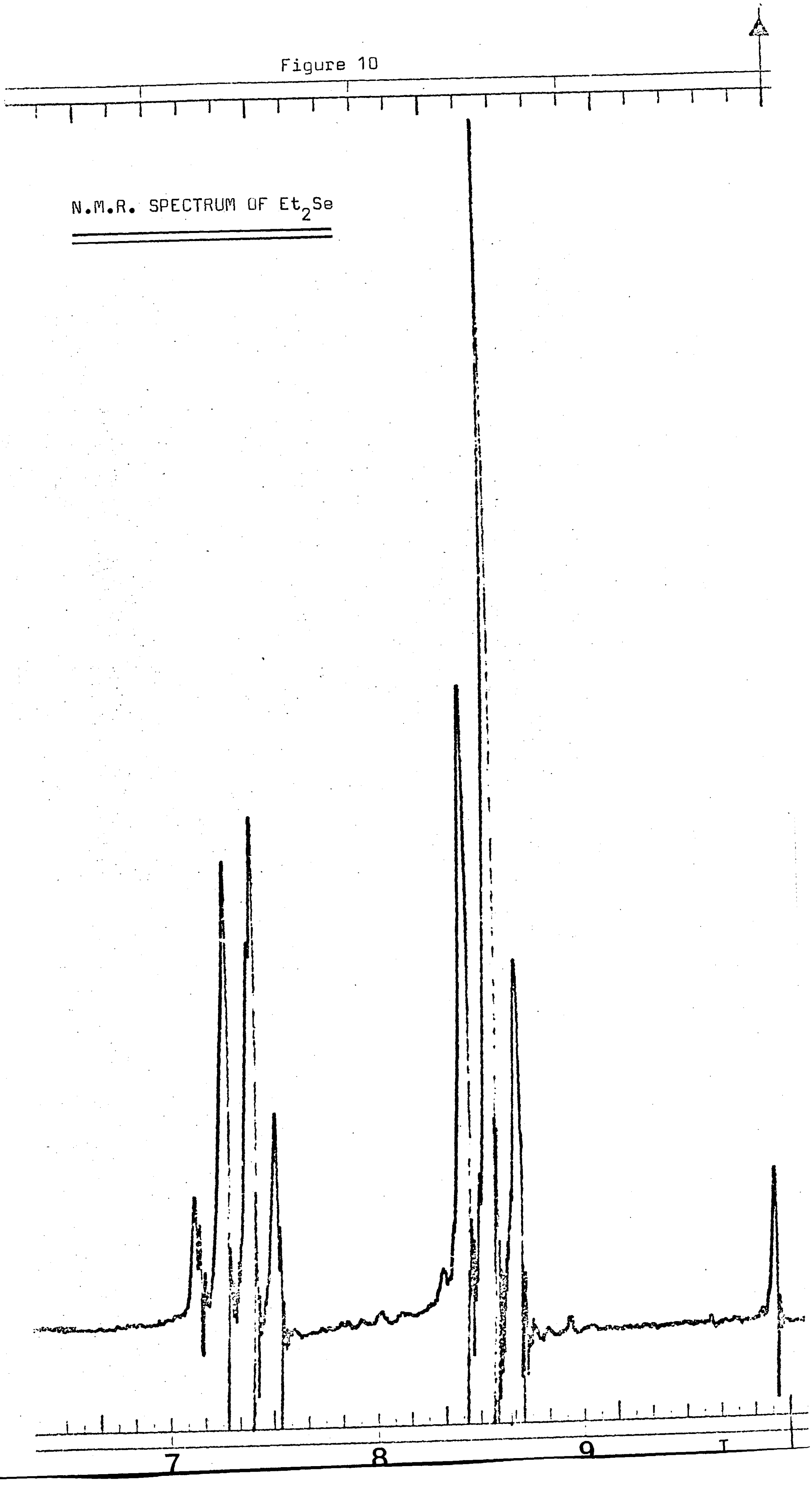
None of the conclusions on the behaviour of the tellurides in these complexes appears to be valid. Furthermore, until the anomalous I.R. and Raman spectra can be adequately explained, it would seem that these techniques are of doubtful value in ascertaining the exact nature and consequences of a transition-metal-tellurium bond.

C) NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

In the past, nuclear magnetic resonance (n.m.r.) spectroscopy has been used extensively to study transition-metal complexes. Not only have such compounds been characterised by n.m.r.(115), but the technique has also been used to follow the kinetics of some reactions(116). This study uses n.m.r. for both purposes.

The n.m.r. spectrum of diethyl selenide is shown in Figure 10. The upfield signal is the methyl proton resonance and is split by the methylene protons to a triplet. The coupling constant (J) is 7.7 Hz.

Figure 10



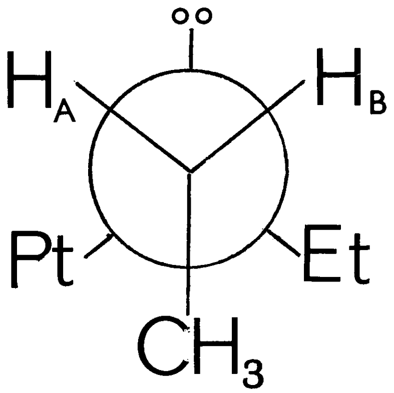
N.M.R. SPECTRUM OF Et_2Se

The methylene proton resonance consists of a quartet, due to interaction with the methyl protons. Such a spectrum can be described as an A_2M_3 system. However, when diethyl-selenide is complexed to platinum, as for example in trans-$(Et_2Se)_2PtI_2$, the spectrum changes. A triplet is still observed for the methyl resonance, but a more complicated methylene signal results. Reasons for this are illustrated in the Newman projection below:-

FIGURE 11

NEWMAN PROJECTION DOWN C-Se

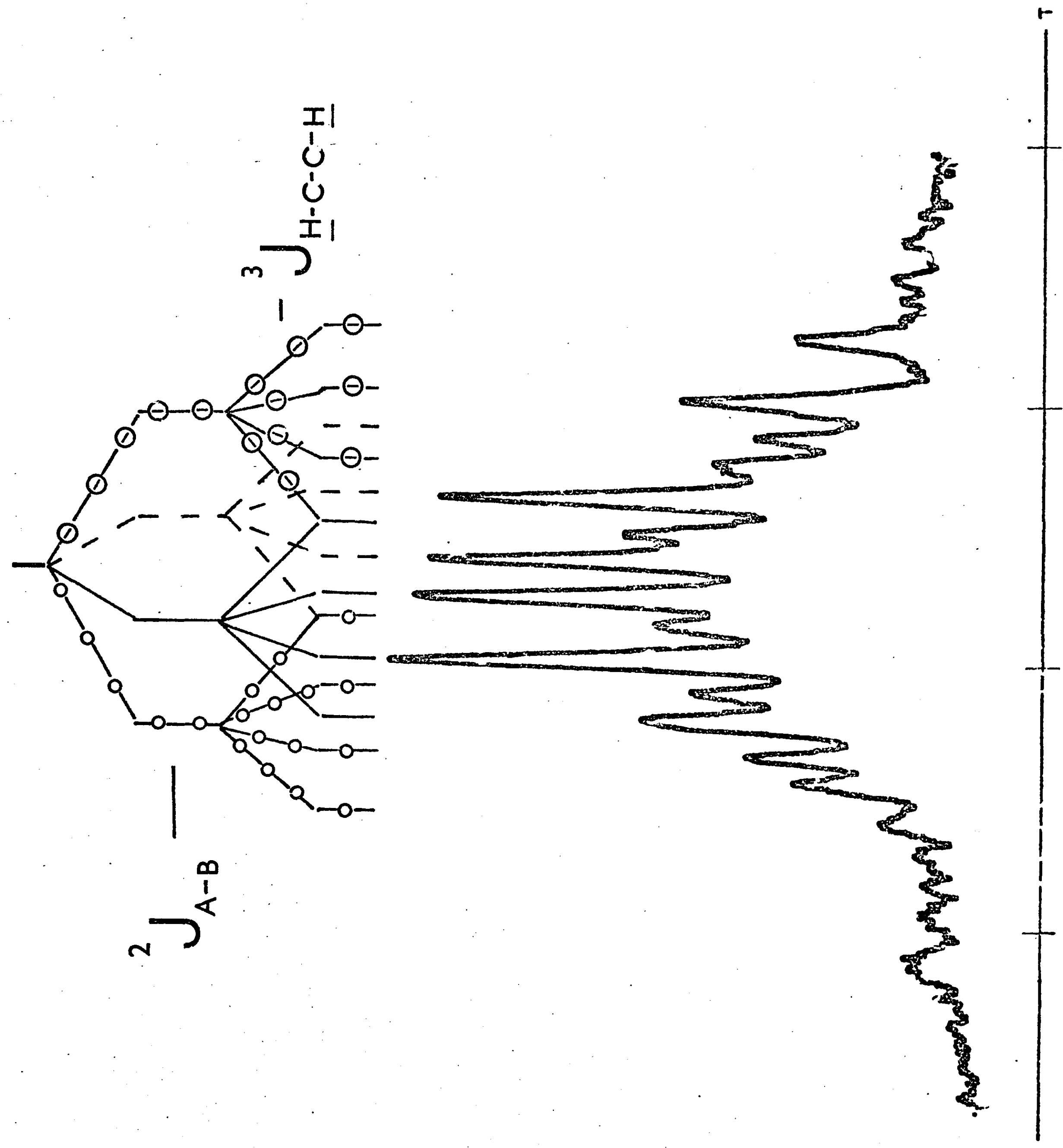
BOND IN $(Et_2Se)_2PtI_2$



The projection down the C-Se bond shows the methylene protons to be non-equivalent. Although the selenium atom in the complex is not strictly speaking asymmetrically substituted, the methylene protons effectively 'see' an asymmetric atom and this causes different electronic environments round both protons. These are now termed diastereotopic protons and if no further coupling is observed, give rise to a second order spectrum, an AB quartet. In trans- $(Et_2Se)_2PtI_2$ further coupling is observed and this is shown in Figure 12. (PhCl solvent.)

Figure 12

METHYLENE REGION OF SPECTRUM OF $(Et_2Se)_2PtI_2$ AT -40°C.



The AB quartet is split by the methyl signals to give 4 AB quartets, as illustrated in the figure. Peaks not accounted for in the diagram are those caused by interaction of the resonances with an isotope of platinum (^{195}Pt, which is 33.7% abundant, and has a spin quantum number (I) of $\frac{1}{2}$.) Every line in the spectrum will therefore be further split to a 1:4:1 triplet. (^{77}Se also has I=$\frac{1}{2}$, but the low abundance (7.5%) means that splitting due to this is not often detectable.) In practice accidental equivalence causes overlap of many of the signals and less lines are normally observed.

The n.m.r. parameters for the ligands and their corresponding complexes are given in Tables 14 and 15.

A slightly higher τ value is obtained for all the resonances when chlorobenzene solvent is used instead of deuterochloroform. This is a general phenomenon and is a consequence of the non-zero averaging of the anisotropy in the diamagnetic susceptibility of the aromatic solvent molecules(117).

TABLE 14

^{1}H N.M.R. PARAMETERS OF $(Et_2X)_2MHal_2$ COMPLEXES

Compound [a]	τ_{Methyl}	$\tau_{Methylene}$	$J_{CH_3-CH_2}$ [b] (Hz)
cis -$(Et_2S)_2PtCl_2$	8.88	7.28	7.4
trans-$(Et_2S)_2PtCl_2$	8.85	7.42	7.4
trans-$(Et_2S)_2PtBr_2$	8.84	7.27	7.4
trans-$(Et_2S)_2PtI_2$	8.86	7.09	7.4
trans-$(Et_2Se)_2PtCl_2$	8.76	7.33	7.4
trans-$(Et_2Se)_2PtBr_2$	8.78	7.26	7.4
trans-$(Et_2Se)_2PtI_2$	8.88	7.16	7.4
trans-$(Et_2Te)_2PtCl_2$	8.55	7.22	7.7
trans-$(Et_2Te)_2PtBr_2$	8.58	7.19	7.7
trans-$(Et_2Te)_2PtI_2$	8.67	7.17	7.5
trans-$(Et_2S)_2PdCl_2$	8.79	7.42	7.3
trans-$(Et_2S)_2PdBr_2$	8.79	7.22	7.3
trans-$(Et_2Se)_2PdCl_2$	8.76	7.38	7.8
trans-$(Et_2Se)_2PdBr_2$	8.77	7.24	7.3
trans-$(Et_2Se)_2PdI_2$	8.85	7.08	7.3
trans-$(Et_2Te)_2PdCl_2$	8.61	7.31	7.6
trans-$(Et_2Te)_2PdBr_2$	8.63	7.24	7.6
trans-$(Et_2Te)_2PdI_2$	8.63	7.06	7.5

a) Chlorobenzene solutions. b) Measured from methyl signals.

TABLE 14 (continued)

^1H N.M.R. PARAMETERS OF $(Et_2X)_2MHal_2$ COMPLEXES

Compound	$J_{CH_3-H_A}$	$J_{CH_3-H_B}$	J_{A-B}
cis -$(Et_2S)_2PtCl_2$	/	/	/
trans-$(Et_2S)_2PtCl_2$	/	/	/
trans-$(Et_2S)_2PtBr_2$	/	/	/
trans-$(Et_2S)_2PtI_2$	/	/	/
trans-$(Et_2Se)_2PtCl_2$	7.8	7.3	11.5
trans-$(Et_2Se)_2PtBr_2$	7.6	7.2	11.3
trans-$(Et_2Se)_2PtI_2$	7.6	7.2	11.3
trans-$(Et_2Te)_2PtCl_2$	7.8	7.3	/
trans-$(Et_2Te)_2PtBr_2$	/	/	/
trans-$(Et_2Te)_2PtI_2$	7.8	7.4	11.6
trans-$(Et_2S)_2PdCl_2$	/	/	/
trans-$(Et_2S)_2PdBr_2$	/	/	/
trans-$(Et_2Se)_2PdCl_2$	8.0	7.4	11.8
trans-$(Et_2Se)_2PdBr_2$	/	/	/
trans-$(Et_2Se)_2PdI_2$	/	/	/
trans-$(Et_2Te)_2PdCl_2$	8.0	7.2	/
trans-$(Et_2Te)_2PdBr_2$	7.8	7.2	/
trans-$(Et_2Te)_2PdI_2$	8.0	7.2	/

All J values measured in Hz.

TABLE 15

^{1}H N.M.R. PARAMETERS OF $(Et_2X)_2MHal_2$ COMPLEXES

Compound [a]	τ_{Methyl}	$\tau_{Methylene}$	$J_{CH_3-CH_2}$ (Hz)
<u>cis</u>- $(Et_2S)_2PtCl_2$	8.60	7.04	7.5
<u>trans</u>-$(Et_2S)_2PtCl_2$ [b]	8.55	7.12	7.3
<u>trans</u>-$(Et_2S)_2PtBr_2$ [b]	/	/	7.4
<u>trans</u>-$(Et_2S)_2PtI_2$	/	/	7.3
<u>trans</u>-$(Et_2S)_2PdCl_2$	8.47	7.04	7.2
<u>trans</u>-$(Et_2S)_2PdBr_2$	8.56	7.02	7.3
<u>trans</u>-$(Et_sSe)_2PdCl_2$	8.45	7.05	7.5
<u>trans</u>-$(Et_2Se)_2PdBr_2$	8.47	6.94	7.4
<u>trans</u>-$(Et_2Se)_2PdI_2$	8.50	6.80	7.4
<u>trans</u>-$(Et_2Te)_2PdCl_2$	8.33	7.03	/
<u>trans</u>-$(Et_2Te)_2PdBr_2$	8.50	7.20	7.5
<u>trans</u>-$(Et_2Te)_2PdI_2$	8.38	6.88	7.6

a) $CDCl_3$ solutions. b) 100 MHz.

TABLE 15 (continued)

^{1}H N.M.R. PARAMETERS OF $(Et_2X)_2MHal_2$ COMPLEXES

Compound[a]	$J_{CH_3-H_A}$	$J_{CH_3-H_B}$	J_{A-B}
cis- $(Et_2S)_2PtCl_2$	7.5	7.2	12.0
trans-$(Et_2S)_2PtCl_2$[b]	7.6	7.2	12.0
trans-$(Et_2S)_2PtBr_2$[b]	7.6	7.2	12.0
trans-$(Et_2S)_2PtI_2$	7.6	7.2	11.9
trans-$(Et_2S)_2PdCl_2$	7.5	7.3	12.7
trans-$(Et_2S)_2PdBr_2$	7.7	7.3	12.5
trans-$(Et_2Se)_2PdCl_2$	7.8	7.2	11.5
trans-$(Et_2Se)_2PdBr_2$	7.8	7.2	11.6
trans-$(Et_2Se)_2PdI_2$	7.9	7.2	/
trans-$(Et_2Te)_2PdCl_2$	/	/	/
trans-$(Et_2Te)_2PdBr_2$	7.6	7.4	/
trans-$(Et_2Te)_2PdI_2$	7.9	7.2	/

a) $CDCl_3$ solutions. b) 100 MHz.

All J values measured in Hz.

The methylene protons in the complexes resonate at lowest field when the halogen attached to the transition metal is iodine. A look at the Table below, which shows the variation in chemical shift with halogen substituent, illustrates this point.

TABLE 16

VARIATION IN METHYLENE PROTON CHEMICAL SHIFT WITH HALOGEN SUBSTITUENT

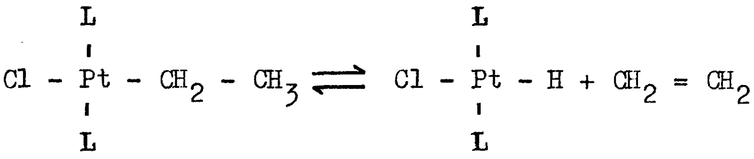
	Platinum					Palladium				
	Cl		Br		I	Cl		Br		I
S	●	-0.15	●	-0.18	●	●	-0.20	●		●
Se	●	-0.07	●	-0.10	●	●	-0.14	●	-0.16	●
Te	●	-0.03	●	-0.02	●	●	-0.07	●	-0.18	●

The methylene protons in $(Et_2Se)_2PdBr_2$, for instance, resonate in a position 0.14 p.p.m. lower than the methylene protons in the corresponding chloride derivative.

This effect has been interpreted previously as due to an increase in the π-bonding character of the metal-halogen bond, in the order $I^- > Br^- > Cl^-$. By removing more electron density (via π-bonding) from the central metal ion, iodine makes the metal more acidic, and effects a greater electron withdrawal from the C-H bond. The proton nucleus is then deshielded and resonates at lower field. It is also possible that this observation is an example of the well known β-interaction. Transition metal derivatives which have σ-bonded ligands containing β-hydrogens attached to saturated carbon, undergo metal hydride elimination fairly readily(118). An example of this is shown below.

FIGURE 13

EXAMPLE OF THE β-INTERACTION



$$\mathrm{Cl} - \overset{\mathrm{L}}{\underset{\mathrm{L}}{\mathrm{Pt}}} - \mathrm{CH_2} - \mathrm{CH_3} \rightleftharpoons \mathrm{Cl} - \overset{\mathrm{L}}{\underset{\mathrm{L}}{\mathrm{Pt}}} - \mathrm{H} + \mathrm{CH_2} = \mathrm{CH_2}$$

The nature of the halogen substituent would therefore dictate the extent of interaction of the orbitals on the metal with the β-hydrogens on the chalcogen ligands. A strong interaction would pull electron density away from the protons and have a deshielding effect. However, because of its greater electronegativity, $\mathrm{Cl^-}$ contracts these orbitals and causes less interaction and less deshielding. Higher τ values for these resonances would therefore be observed.

A similar look at the methyl proton resonances shows no definite order, but there seems to be in some cases a trend in the <u>opposite</u> direction. The chemical shift differences (in chlorobenzene) are illustrated in Table 17.

TABLE 17

VARIATION OF METHYL PROTON CHEMICAL SHIFT WITH HALOGEN SUBSTITUENT

	Platinum					Palladium				
	Cl		Br		I	Cl		Br		I
S	●	-0.01	●	+0.02	●	●	0	●		●
Se	●	+0.02	●	+0.10	●	●	+0.01	●	+0.08	●
Te	●	+0.03	●	+0.09	●	●	+0.03	●	0	●

It has been suggested(41) that halogen-proton non-bonded interactions are responsible. The greater the electronegativity of the halogen, the more it deshields the methyl protons and the chemical shifts of the protons follow the order $Cl^- < Br^- < I^-$.

Indeed, halogen-proton non-bonded interactions might well be in evidence in both the methyl and methylene resonances, since calculations(41) based on the crystal structure(107) of trans- $(Et_2Se)_2PdCl_2$ show that both sets of protons may come within 3 Å of the halogens.

A more likely explanation for both trends, is that while the methyl resonances are mainly a result of through-bond effects, non-bonded interactions are responsible for the chemical shifts of the methylene protons. This is based on the Table (page 77) of high temperature coupling constants which shows the iodides to have most s-electron density in the Pt-X-C-H (X=S or Se) bonds.

If these electrons make a large diamagnetic contribution to the shielding of the methylene proton nuclei, a net increase in chemical shift would be observed. In fact the opposite is found. This suggests that metal-proton non-bonded interactions are present. The lack of definite order, or - and in some cases, an increase in the observed τ values of the methyl protons of the iodides - make it likely that opposing non-bonded and through-bond interactions are in evidence, with a preponderance of the latter.

CHAPTER 3

VARIABLE TEMPERATURE N.M.R.

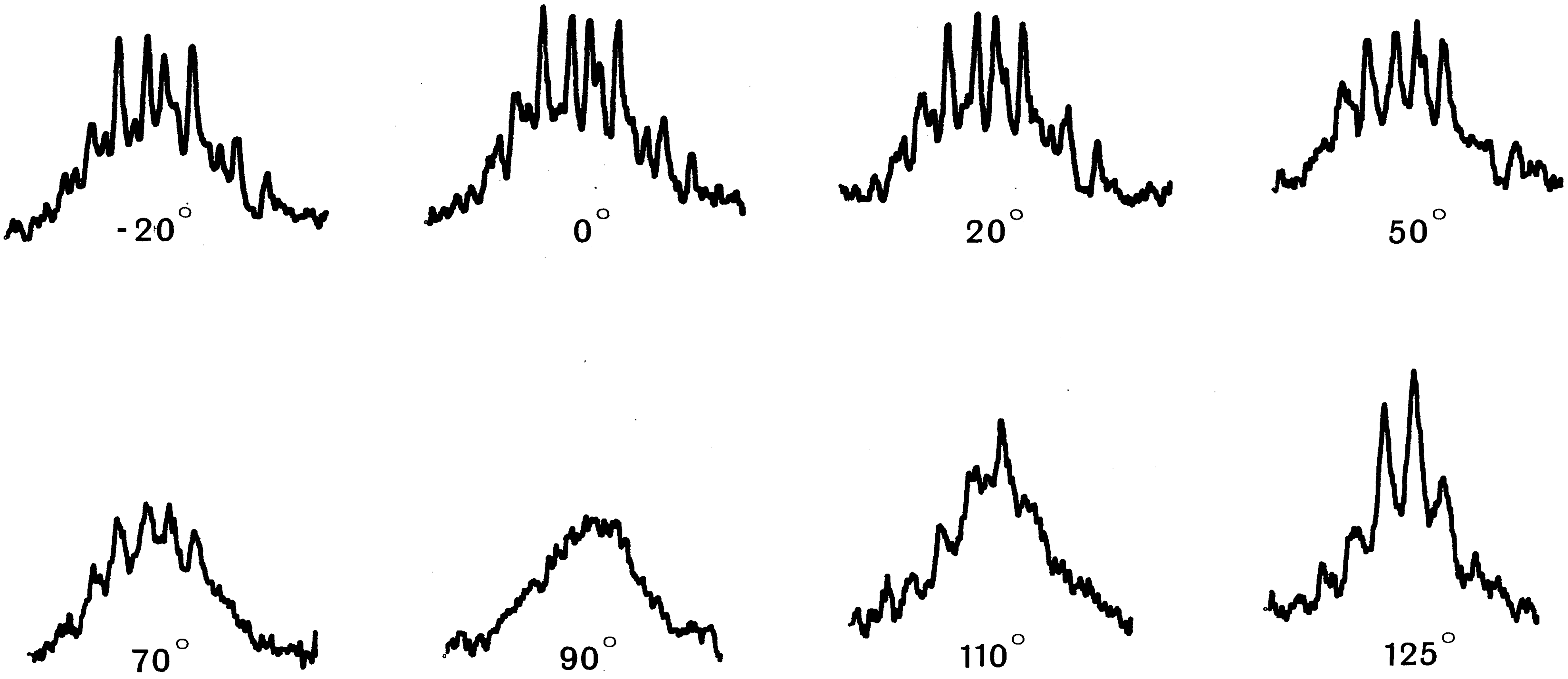
VARIABLE TEMPERATURE NUCLEAR MAGNETIC RESONANCE

A) MONODENTATE COMPLEXES

The temperature-dependent changes observed in the methylene region of the ^1H n.m.r. spectra of trans-$(Et_2Se)_2PtI_2$ gives an insight into the nature of the dynamic processes occurring in this and the related organo-chalcogen transition-metal complexes.

The spectrum of trans-$(Et_2Se)_2PtI_2$ at -40°C, already described, changes with increasing temperature as shown in Figure 14. Many of the signals begin to overlap and become less well defined, until at +90°C, 'coalescence' to a broad signal is observed. Raising the temperature above this coalescence point results in the emergence of fine-structure until at about 120°C, a much simpler, well-defined, spectrum is obtained. Careful analysis shows that the $(ABM_3 + ABM_3X)$ system at low temperatures (-40°C) has been converted to an $(A_2M_3 + A_2M_3X)$ spectrum at high temperatures (+125°C). In other words, the methylene protons are no longer diastereotopic and are now equivalent. Since fast rotation alone, about any of the bonds in the molecule is not sufficient to bring the methylene protons into identical electronic environments(96), reasons for these changes must be sought elsewhere.

Dissociation of the ligand followed by recombination via the original lone pair on selenium,

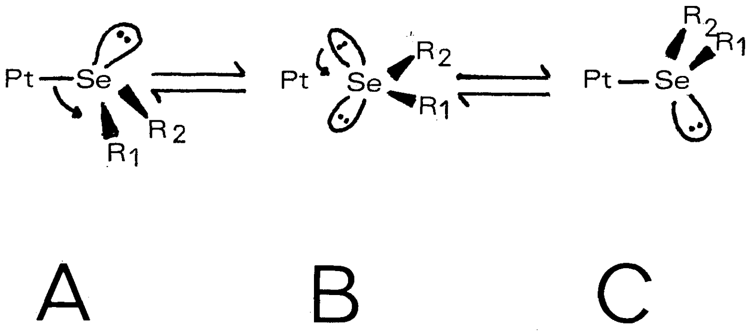


- Figure 14 -

TEMPERATURE DEPENDENCE (°C) OF METHYLENE REGION OF TRANS-$(Et_2Se)_2PtI_2$

FIGURE 15

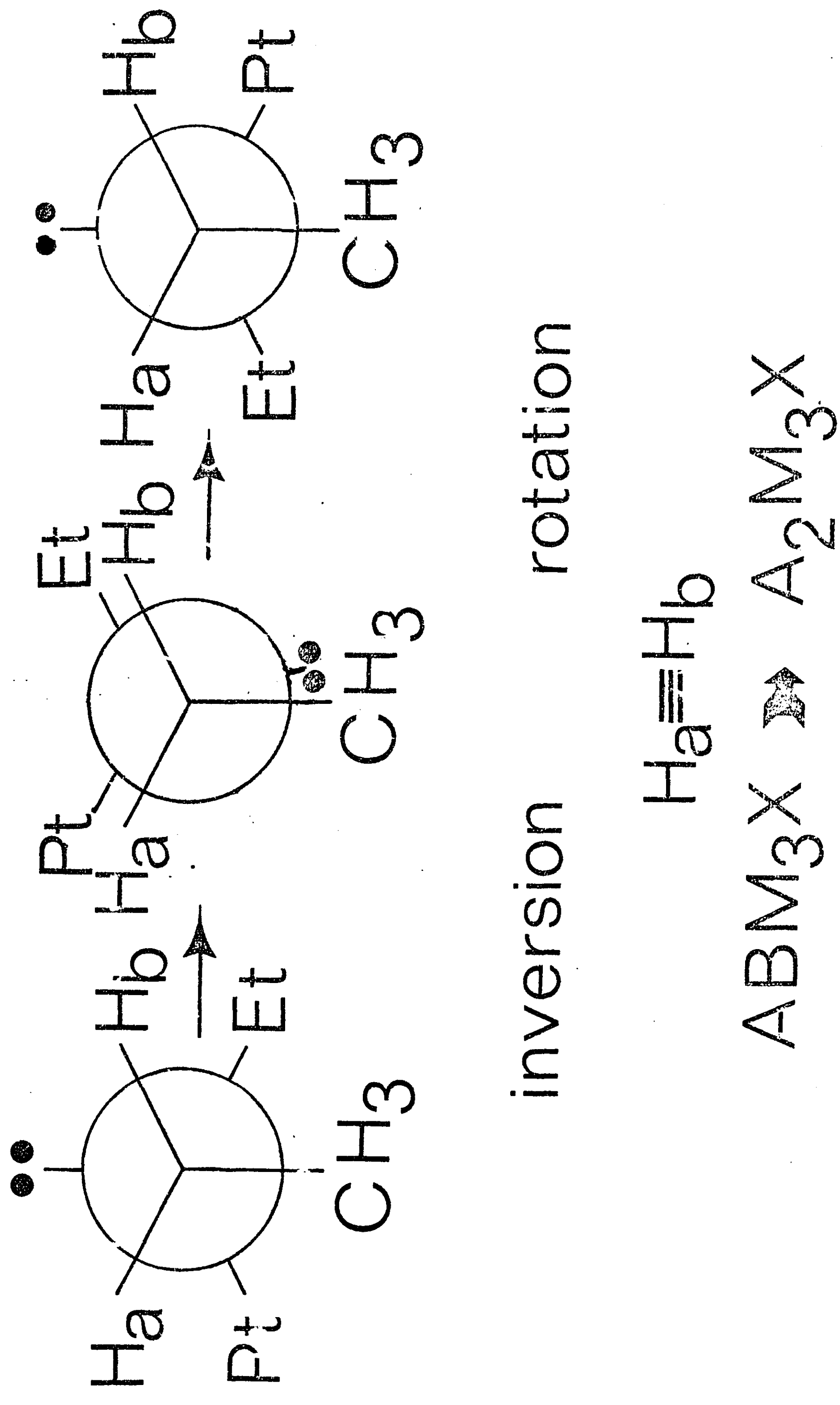
LIGAND DISSOCIATION AND RECOMBINATION



could explain the spectroscopic changes up to, but not after, coalescence. Retention of $^{195}\underline{Pt}$-Se-C-$\underline{H}$ coupling <u>above</u> the coalescence temperature rules out any mechanism involving breaking of the Pt-Se bond. A closer look at A and C in the diagram above (Figure 15) shows that the net result of this process is an inversion of configuration about selenium and suggests that, in fact, atomic pyramidal inversion at selenium could explain <u>all</u> the variable temperature spectral characteristics. The Pt-Se bond remains intact during the inversion process and is consistent with the observation of ^{195}Pt satellites at temperatures above coalescence. Examination of Newman projections along the C-Se bond (Figure 16) reveals that selenium inversion, followed by rotation about the C-Se bond, <u>does</u> confer equivalence on the diastereotopic methylene protons.

Figure 16

NEWMAN PROJECTIONS DOWN C-Se BOND IN TRANS-$(Et_2Se)_2PtI_2$



The fluxional behaviour of trans-$(Et_2Se)_2PtI_2$ as observed by dynamic nuclear magnetic resonance spectroscopy, is best explained then in the following terms. Although C-Se bond rotation is fast (C-S bond rotation in Et_2S has been estimated as ca. 1.75 Kcal/mole(127) (7.32 KJ/mole)), at ambient temperatures and below, inversion is slow on the n.m.r. time scale, and a 'frozen out' spectrum is obtained. This inversion process speeds up with increasing temperature until none of the signals from the proton nuclei can be discerned from one another. The coalescence temperature is a measure of the activation energy of the process. An averaged spectrum, which represents the weighted mean of the electronic environments of the protons during fast inversion is obtained at temperatures above coalescence. These observations conclusively demonstrate, for the first time, the fluxional process of pyramidal selenium inversion.

TABLE 18

COALESCENCE TEMPERATURES (^{o}C) OF DIETHYL-CHALCOGEN TRANSITION METAL COMPLEXES

Complex[a]	Cl	Br	I
trans-$(Et_2S)_2PtHal_2$	6(56)[b]	4	2
trans-$(Et_2S)_2PdHal_2$	-24	-28	-
trans-$(Et_2Se)_2PtHal_2$	90	90	90
trans-$(Et_2Se)_2PdHal_2$	50	43	28
trans-$(Et_2Te)_2PtHal_2$	107	110	105
trans-$(Et_2Te)_2PdHal_2$	30	51	18

a) chlorobenzene solvent. b) value in parentheses is that of cis-$(Et_2S)_2PtCl_2$.

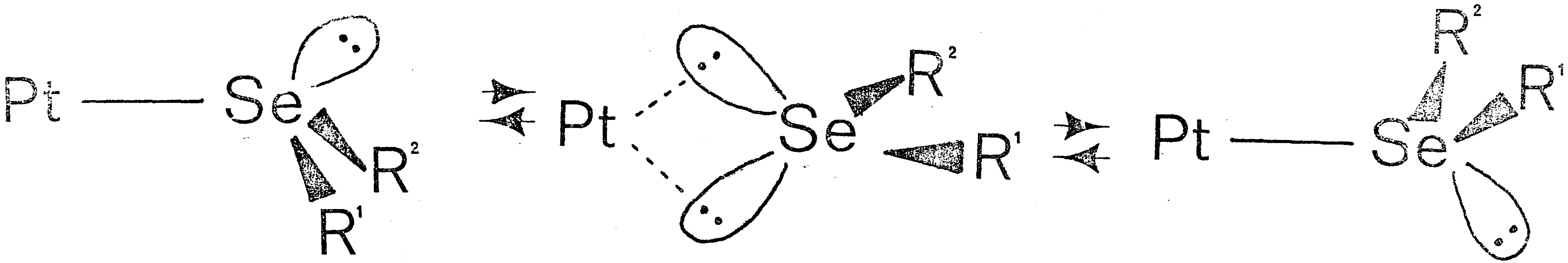
Table 18 shows the coalescence temperatures of a series of complexes consisting of diethyl-chalcogen ligands coordinated to a transition metal. (Platinum(II) and palladium(II) were chosen for historical reasons(119) and because of their predictable square planar geometries).

Is the fluxional behaviour of all of these complexes attributable to the same phenomenon, i.e. atomic pyramidal inversion, as has just been demonstrated for trans-$(Et_2Se)_2PtI_2$? In all cases, the spectra are similar to that described previously, but although ^{195}Pt-**S**-C-H and ^{195}Pt-**Se**-C-H coupling are observed at temperatures above coalescence, ^{195}Pt-Te·C·H coupling is not. Conclusive evidence, therefore, of both sulphur and selenium inversion is presented, but no definitive conclusions can be drawn about the origin of the coalescences in the diethyl-telluride complexes. This ambiguity also exists for all the palladium derivatives, since none of the isotopes of palladium has a spin quantum number of $\frac{1}{2}$. High temperature coupling, similar to that described previously, is precluded and an inversion mechanism cannot, on this evidence alone, be differentiated from one involving ligand-dissociation and recombination.

It is shown later, however, that the ambiguity in $(Et_2S)_2PdHal_2$ complexes can be removed, and that inversion at sulphur is, in fact, responsible for these spectroscopic changes.

MECHANISM OF INVERSION

At this stage it is necessary to recall the inversion mechanism as proposed by Haake and Turley(96) and reassess their reasons for such a mechanism. Their scheme for selenium inversion at platinum is shown in Figure 17. They rejected the mechanism normally invoked for nitrogen inversion (Figure 5) - it involves passage through a trigonal planar state - because it did not appear to be capable of explaining the 10^{18} - 10^{20} rate difference between sulphoxide and sulphide complex inversion. Their description showed inversion through a partially dissociated state with platinum in a distorted pentacoordinate geometry, bonding to both sulphur (or Se) unshared electron pairs. This is essentially delocalisation of inversion mechanism



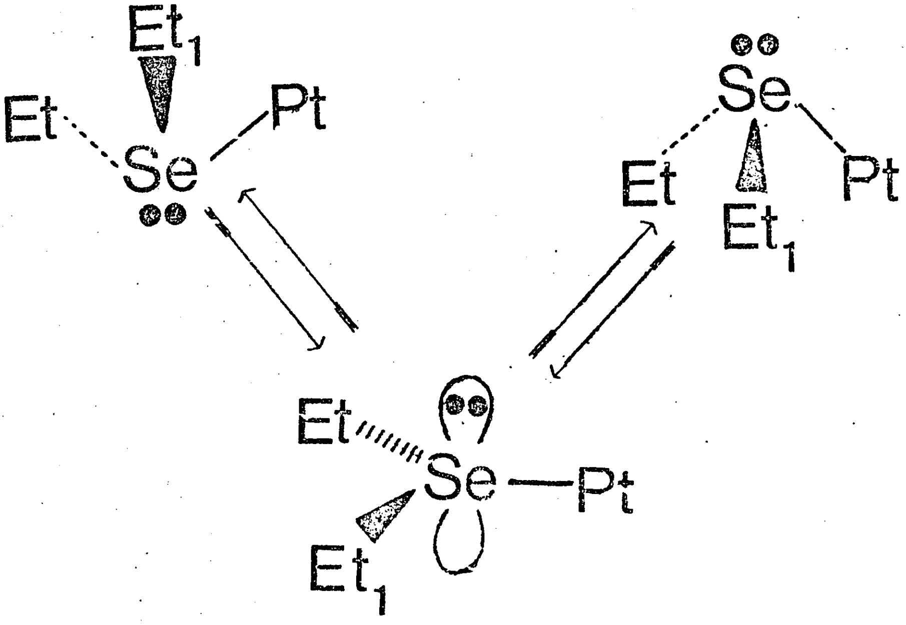
— Figure 17 —

the lone pair of electrons into vacant metal orbitals i.e. $(p\text{-}d)_{\pi}$ overlap - a concept of which theoretical treatments tend to be contradictory(120) - and suggests the following description of inversion:-

According to the Franck-Condon principle(121), electronic changes are rapid compared to bond vibrations. Therefore in the time taken to bend the bonds the lone pair will have automatically rearranged itself, according to the scheme shown in Figure 18. This strongly suggests that more consideration should be given to bond bending, and provides this description of the inversion process:-

FIGURE 18

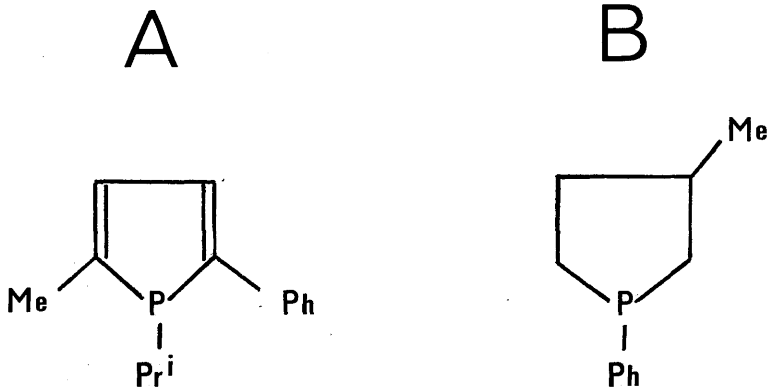
CLASSICAL INVERSION MECHANISM.



This is the mechanism normally invoked for pyramidal nitrogen inversion - the one rejected by Haake and Turley(96) - and involves a transition state in which the lone pair possesses pure p-character. It consists essentially of a bending mode which brings the substituents round selenium into a planar configuration. Obviously the weaker a bond is the easier it is bent, and this provides an explanation of the variation in inversion rate caused by ligands <u>trans</u> to the inverting centre, as will be discussed later. Furthermore, delocalisation of the lone pair into vacant metal orbitals will also lower the barrier to inversion by analogy with the two complexes shown below.

FIGURE 19

DELOCALISATION LEADING TO LOWER INVERSION BARRIERS.



$\Delta G^{\ddagger}$	16 Kcal/mole (66.9 KJ /mole)	38 Kcal/mole (159 KJ /mole)

$(3p-2p)_{\pi}$ conjugation in (A) lowers the barrier to phosphorus inversion considerably$^{(88)}$.

This mechanism and that described by Haake and Turley$^{(96)}$ are in fact different representations of essentially the same process. We believe, however, that the latter description is more in keeping with the mechanism normally invoked for all other inversion processes, and as such provides better explanations of our experimental results.

The coalescence temperatures in red in Table 18 are those caused by unambiguous pyramidal inversion at either sulphur or selenium. A number of conclusions can be drawn.

a) Sulphur inversion is faster in palladium complexes.

b) The barrier to inversion is dependent on the trans-ligand.

c) Selenium inversion requires more energy than sulphur inversion.

DISCUSSION OF CONCLUSIONS

a) SULPHUR INVERSION IS FASTER IN PALLADIUM COMPLEXES

The coalescence temperatures of trans-$(Et_2S)_2PtCl_2$ (+6°C) and trans-$(Et_2S)_2PdCl_2$ (-24°C) (illustrated in Figure 20) indicate that approximately 1.6 Kcal/mole less energy is required to effect sulphur inversion when the central metal is changed from platinum to palladium.

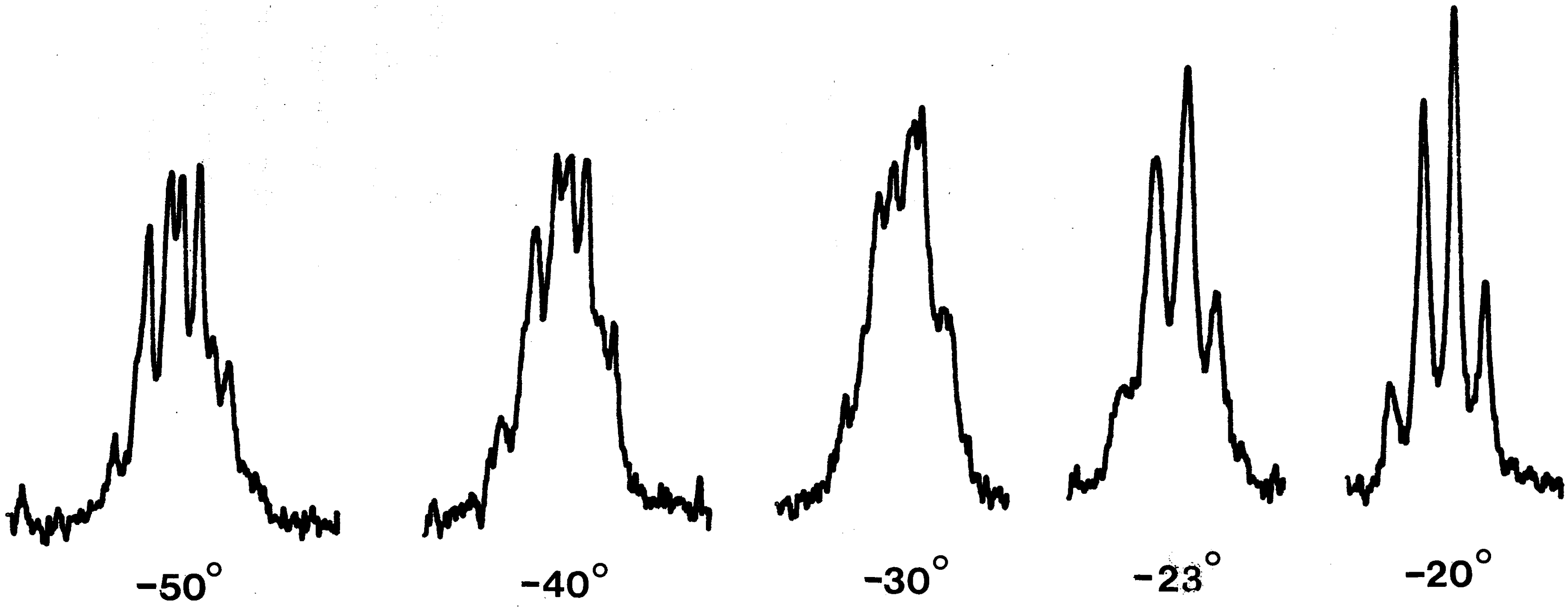


Figure 20

TEMPERATURE DEPENDENCE (^{0}C) OF METHYLENE REGION OF N.M.R. SPECTRUM OF TRANS-$(Et_2S)_2PdCl_2$

This could be a reflection of the weaker palladium-sulphur bond(46), since less energy will be required to bend it. If Haake and Turley's postulate(96) is invoked, one can imagine the metal-sulphur bond to be actually broken during the inversion process, even if another is formed simultaneously. Thus, if this were the rate determining step during inversion, palladium derivatives - by virtue of the weaker Pd-S bond - should have inversion barriers which are lower than those of the corresponding platinum complexes.

These observations could also be explained in terms of greater delocalisation (over that postulated for platinum) of the lone pair on sulphur into vacant palladium d-orbitals, leading to increased stabilisation of the transition state to inversion. Since most effective $(p\text{-}d)_\pi$ overlap might be produced by the conjugating elements coming from the same row of the periodic table(122), the proximity of palladium and sulphur might favour $S \rightarrow Pd\ (3p \rightarrow 4d)_\pi$ over $S \rightarrow Pt,\ (3p \rightarrow 5d)_\pi$ overlap, leading to lower inversion barriers at palladium.

b) BARRIER TO INVERSION IS DEPENDENT ON THE TRANS LIGAND

The different inversion rates of cis-$(Et_2S)_2PtCl_2$ ($T_c = 56^\circ C$) and the corresponding trans-isomer ($T_c = 6^\circ C$) can be explained by a consideration of two factors - the inversion mechanism and the role of the ligand trans to the inverting centre. The bending modes necessary to bring about inversion will be dependent on the strength of the bonds. Thus a ligand trans to the inverting centre with a strong trans-influence(57) will weaken the metal-sulphur bond, and cause a faster rate of inversion. However a ligand with a strong 'trans-effect'(55) might bring about greater delocalisation of the transition-state lone pair, since this delocalisation can be regarded as a type of nucleophilic attack by sulphur on the metal. For this reason 'trans-effects' are referred to when discussing inversion, since it is felt that 'influence' is a too specific term. Et_2S has a stronger trans-effect than Cl^- (123). This explains why trans-$(Et_2S)_2PtCl_2$ inverts more rapidly than the cis-isomer. Approximately 3 Kcal/mole (12.6 KJ/mole) extra energy is needed to bring about sulphur inversion in the cis-isomer and is a measure of the difference in the trans-effects of Et_2S and Cl^-.

c) RATE OF INVERSION IS S>Se

Inversion at selenium requires greater energy than inversion at sulphur. Similar observations with inverting elements in other parts of the periodic table have been explained(124) in terms of molecular geometries. Thus NH_3 inverts more rapidly than PH_3 because the H-N-H intragroup angles (107°) are closer to the ideal planar transition state angles of 120° than the H-P-H angles (94°). Equivalent to this argument is one based on lone pair hybridisation(124). The lone pair in ammonia ($\sim sp^3$) is much closer in energy to the transition-state lone pair (p) than is the lone pair in phosphine($\approx s$). By analogous reasoning, the higher inversion barriers of the selenide complexes are probably due to increased s-character of the selenium lone pair. Evidence for this can be found by looking at Table 19. The high temperature ^{195}Pt-$\underline{Se}$-C-H coupling constants are smaller than the ^{195}Pt-$\underline{S}$-C-H values and indicates less s-electron density in the bonds of the selenide complexes. More s-character is concentrated in the selenium lone pair, and the increased energy difference between this and the p-character of the lone pair in the transition state, leads to slower inversion at selenium than at sulphur. It might be expected too that delocalisation of the lone pair on the inverting centre would be enhanced as a function of its p-character, since these orbitals are more directional in character. This too would favour faster sulphur inversion.

The observation of sulphoxide inversion barriers(74), but not those of selenoxides, which are above the range of kinetic measurement(103), can be explained by arguments similar to those presented above.

TABLE 19

HIGH TEMPERATURE Pt-X-C-H COUPLING CONSTANTS

COMPOUND	$^3J_{Pt-H}$(Hz)	T_c(°C)[a]
cis- $(Et_2S)_2PtCl_2$	44	56
trans-$(Et_2S)_2PtCl_2$	38	6
trans-$(Et_2S)_2PtBr_2$	39	4
trans-$(Et_2S)_2PtI_2$	42	2
trans-$(Et_2Se)_2PtCl_2$	30	90
trans-$(Et_2Se)_2PtBr_2$	30	90
trans-$(Et_2Se)_2PtI_2$	32	90

a) Chlorobenzene solvent. (Error on J values is ±1 Hz.)

A closer look at the contributing factors to the ca. 5 Kcal/mole (20.9 KJ/mole) extra energy required to invert the selenium pyramid in the *trans*-L_2PtCl_2 complexes being discussed, is necessary. This difference is probably the sum of a number of opposing effects. The intrinsic ease of sulphur inversion relative to that of selenium(103) widens the energy gap, but this is counter-balanced by weaker selenium-platinum bonds(43), which lead to faster rates of inversion.

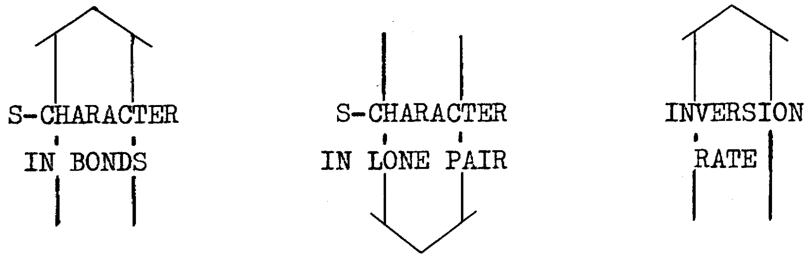
Because Et$_2$Se has a higher trans-effect$^{(8)}$ than Et$_2$S, the mutual weakening$^{(125)}$ of the selenium-platinum bonds is greater, and this causes faster inversion and hence a decrease in the energy gap. Although the relative magnitudes of these factors are not known, the dominating one is probably the intrinsic ease of inversion of the atom. A measure of the trans-effect difference between Et$_2$S and Cl$^-$ has been estimated at ca. 3 Kcal/mole and such a difference is probably considerably less for Et$_2$S and Et$_2$Se. Furthermore, when the trans-ligand is kept constant, as illustrated later by a study of chelate ligand platinum complexes, much the same energy difference (ca. 5 Kcal/mole, 20.9 KJ/mole) in the rates of sulphur and selenium inversion is found.

The Table (19) of high temperature ^{195}Pt-X-C-H (X=S, Se) coupling constants shows cis-(Et$_2$S)$_2$PtCl$_2$ to have the most s-character in the Pt-X-C-H bonds, but not the lowest coalescence temperature. It has already been argued that there is a correlation between inversion rate and s-character in the lone pair as shown below.

FIGURE 21

DEPENDENCE OF INVERSION RATE

ON S-CHARACTER



The reason for this apparent anomaly is that in the cis-isomer, the diethylsulphide ligand has a high s-demand and depletes the Pt-Cl bond of Pt(6s) character. Extrapolation to the s-electron content of the lone pair on sulphur is therefore invalid. The assumption made throughout is that cis-effects are negligible, and that large ^{195}Pt-X-C-H (X=S or Se) coupling constants in the trans-complexes indicate a depletion of s -character from the lone pair on X. The slightly larger values observed for the iodides suggest a possible cis-influence, albeit a small one, in these complexes.

SOLVENT DEPENDENCE

For reasons already discussed, the coalescence phenomena of some of the selenide and telluride complexes could not be unambiguously assigned to a pyramidal atomic inversion mechanism. It was therefore decided to consider the premise that such a process should occur independent of the nature of the solvent and then see what effect a change of solvent would have on the coalescence temperatures of the ambiguous cases. Table (20) shows the effects of a variety of solvents of different polarities on the coalescence temperature of trans-$(Et_2S)_2PdCl_2$. Inversion at sulphur is known to be the cause of the coalescence. The results in the Table are best quoted as $T_c = 28^{\circ}C \pm 4^{\circ}C$, and, as the exact coalescence point is not always easily recognisable, it is regarded as invarient. Pyramidal sulphur inversion, then, occurs independently of the nature of the solvent.

TABLE 20

COALESCENCE TEMPERATURES OF TRANS-$(Et_2S)_2PdCl_2$ IN DIFFERENT SOLVENTS

SOLVENT	T_c(°C)	ε_{20} (126)
PhCl	-24	5.7
$CDCl_3$	-29	4.8
CH_2Cl_2	-32	9.1
CCl_4/CH_2Cl_2[a]	-29	5.6[b]
CCl_4	< -16	2.2
CH_3OH	< R.T.	33.6

a) 1:1 mixture.   b) ε_{20} is average of two values.

Table (21) shows the variation in the coalescence temperatures of the series of complexes brought about by a change of solvent. No difference is found where unequivocal pyramidal atomic inversion has been established, and these values are shown in red. The trans-$(Et_2Se)_2Pd(Hal)_2$ series also shows no solvent dependent characteristics and this could be taken as indicative of the absence of a ligand dissociation-recombination mechanism. However, not only are the dielectric constants of the two solvents similar (PhCl: $\varepsilon_{20} = 5.7$; $CHCl_3$: $\varepsilon_{20} = 4.8$(126)), but also the magnitude of the solvent dependence of such a mechanism is unknown. The tellurides show unusual solvent effects and will be discussed at a later stage.

TABLE 21

SOLVENT DEPENDENCE OF COALESCENCE TEMPERATURE

COMPLEX	T_A	T_B
cis- $(\mathrm{Et_2S})_2\mathrm{PtCl_2}$	56	60[a]
trans-$(\mathrm{Et_2S})_2\mathrm{PtCl_2}$	6	6[a]
trans-$(\mathrm{Et_2S})_2\mathrm{PtBr_2}$	4	2[a]
trans-$(\mathrm{Et_2S})_2\mathrm{PtI_2}$	2	1
trans-$(\mathrm{Et_2Te})_2\mathrm{PtCl_2}$	107	129[b]
trans-$(\mathrm{Et_2Te})_2\mathrm{PtBr_2}$	110	115[b]
trans-$(\mathrm{Et_2Te})_2\mathrm{PtI_2}$	105	118[b]
trans-$(\mathrm{Et_2S})_2\mathrm{PdCl_2}$	-24	-29
trans-$(\mathrm{Et_2S})_2\mathrm{PdBr_2}$	-28	-31
trans-$(\mathrm{Et_2Se})_2\mathrm{PdCl_2}$	50	46
trans-$(\mathrm{Et_2Se})_2\mathrm{PdBr_2}$	43	40
trans-$(\mathrm{Et_2Se})_2\mathrm{PdI_2}$	28	26
trans-$(\mathrm{Et_2Te})_2\mathrm{PdCl_2}$	30	None
trans-$(\mathrm{Et_2Te})_2\mathrm{PdBr_2}$	51	47
trans-$(\mathrm{Et_2Te})_2\mathrm{PdI_2}$	18	19

T_A is the coalescence temperature ($^\circ$C) in chlorobenzene, and

T_B in deuterochloroform.

a) 100 MHz.

b) 1, 1, 2, 2 - tetrachloroethane.

CONCENTRATION DEPENDENCE

A systematic study of the concentration dependence of the inversion process was not undertaken. However, not only do our values agree (within experimental error) with literature values(96), but also we have never found any variation in the inversion coalescence temperature using the same solvent. This indicates that, as expected, pyramidal atomic inversion is a concentration-independent process.

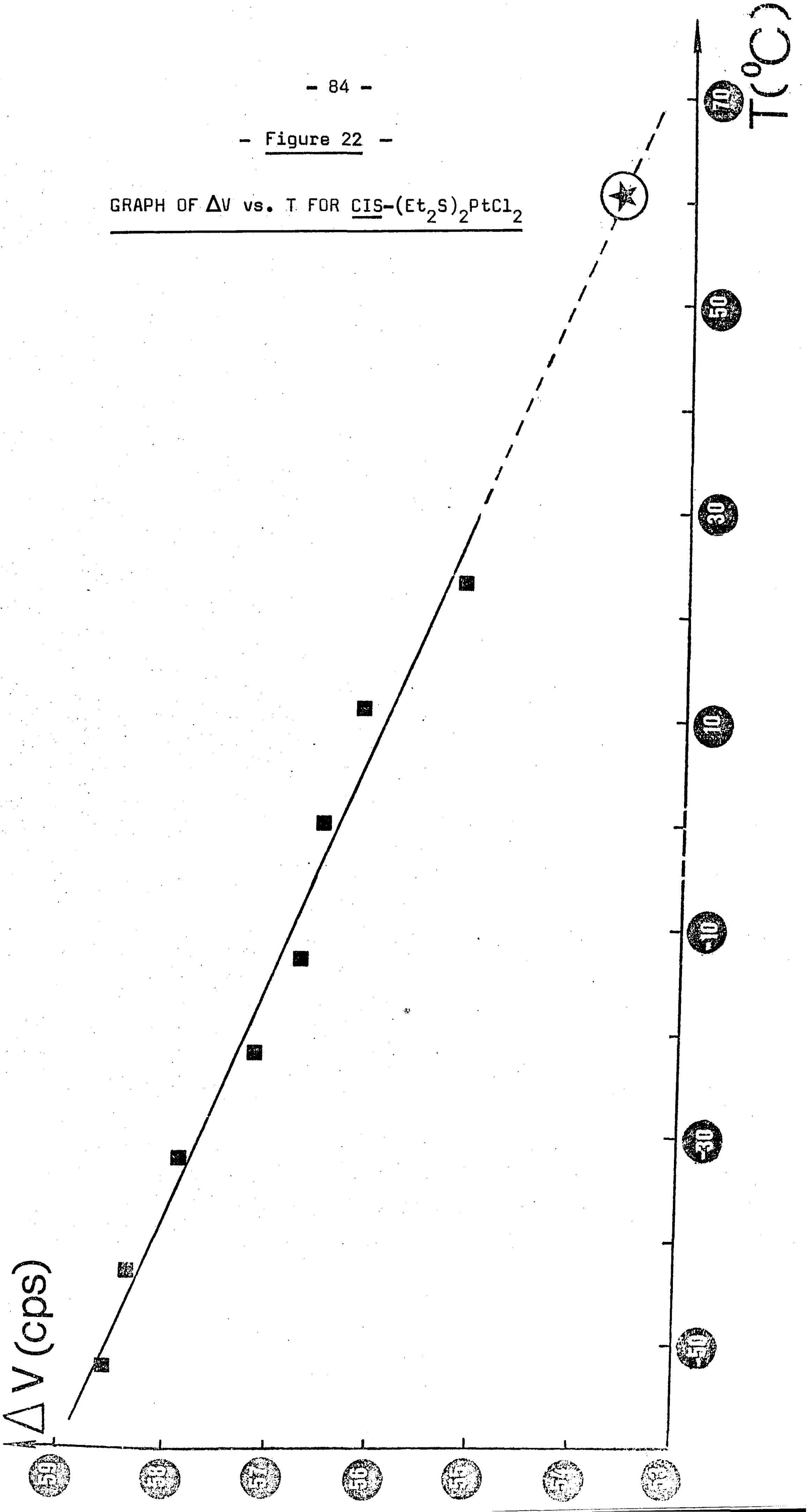
B) FREE ENERGIES OF ACTIVATION

Due to the similarity of the compounds being investigated, it was decided to use Method I, (page 26), to evaluate $\Delta G^{\ddagger}$, the free energy of activation. In some cases, because of the complexity of the spectra, sufficient data below the coalescence temperature was not obtained, and $\Delta G^{\ddagger}$ values could not be calculated. The procedure adopted is described in detail for cis-$(Et_2S)_2PtCl_2$, and the results for all of the complexes summarised in Table 22.

At as many different temperatures as possible, up to about 40°C below the coalescence temperature, the chemical shifts of the 4 peaks of the AB quartet are measured and both J_{AB}(Hz), and ΔV_{AB}(Hz) evaluated. By extrapolation from the graph of ΔV vs. T, as shown in Figure 22, the chemical shift difference of the A and B signals in the absence of exchange is found, and a rate constant k for the process obtained by use of the equation on page 26. Substitution of both this rate constant and the coalescence temperature into the Eyring equation provides a value of $\Delta G^{\ddagger}$, the free energy of activation of the system (Table 22).

- Figure 22 -

GRAPH OF ΔV vs. T FOR CIS-$(Et_2S)_2PtCl_2$



COMPOUND	SOLVENT	ΔV_{AB}(Hz)	J_{AB}(Hz)	k(sec^{-1})	$\Delta G^{\ddagger}$(Kcal/mole)	$\Delta G^{\ddagger}$(KJ/mole)	T_c(°C)
cis- $(Et_2S)_2PtCl_2$	$CDCl_3$	53.64	12.0	135.9	16.3	68.2	60
trans-$(Et_2S)_2PtBr_2$	$CDCl_3$	30.95	12.0	94.85	13.6	56.9	2
trans-$(Et_2S)_2PtI_2$	$CDCl_3$	25.47	11.9	86.02	13.6	56.9	1
trans-$(Et_2Se)_2PtCl_2$	PhCl	25.30	11.5	84.14	18.2	76.2	90
trans-$(Et_2Se)_2PtBr_2$	PhCl	25.60	11.3	83.78	18.2	76.2	90
trans-$(Et_2Se)_2PtI_2$	PhCl	23.15	11.3	80.19	18.2	76.2	90
trans-$(Et_2Se)_2PdCl_2$	PhCl	17.24	11.8	74.79	16.2	67.8	50
trans-$(Et_2Se)_2PdBr_2$	$CDCl_3$	15.00	11.5	70.91	16.0	66.9	46
trans-$(Et_2Se)_2PdI_2$	$CDCl_3$	16.50	11.6	73.02	15.7	65.7	40

TABLE 22

THERMODYNAMIC PARAMETERS FOR T.M. CHALCOGEN COMPLEXES

ERRORS

In some cases, relatively large errors (ca. 30%) were incurred in the determination of ΔV_{AB}, the chemical shift difference in the absence of exchange. However, the magnitude of $\Delta G^{\ddagger}$, as calculated from the Eyring equation, is largely dependent on T_c, the coalescence temperature. Since coalescence is reasonably well-defined for the complexes in Table 22, and the temperatures of the coalescences checked in the usual manner, the error on $\Delta G^{\ddagger}$, as measured by this method, is considered small. Systematic errors, of course, cannot be reliably assessed. These may arise when the A and B protons are coupled to another spin system(77). Not only is this true in this study, but in many of the complexes, still further coupling is present. However such errors only affect the rate constant k, which, as already discussed, is only of minor importance in the determination of $\Delta G^{\ddagger}$ by the Eyring equation.

It is tempting to try and obtain by approximate methods, a value of $\Delta S^{\ddagger}$, the entropy of activation, and use it to decide between a dissociation-recombination mechanism (large positive entropy values) and one involving pyramidal atomic inversion (ca. zero). Large systematic errors, however, would render such a determination meaningless. Computer line shape methods are the only reliable way of obtaining such information.

C) CHELATE COMPLEXES

The importance of the ligand trans to the inversion centre has already been considered. Due to the fact that in most cases only one isomer i.e., the trans-isomer could be prepared, it was decided to extend the series of complexes to include chelate chalcogen transition metal complexes of the type $(EtXC_2H_4XEt)MHal_2$, where X = Se and Te. The variable temperature n.m.r. characteristics of the analogous sulphur compounds had already been investigated(99), and it was hoped to include these other group VI derivatives. Unfortunately only the selenide complexes could be prepared by the standard method(34c). Attempts to isolate $EtTeC_2H_4TeEt$ were unsuccessful.

A look at the n.m.r. spectrum of 1,2-bisethylselenoethane in $CDCl_3$ (Figure 23) shows three different sets of signals which are assigned as follows:-

a) Bridge protons (4H):- singlet at 7.17 τ
b) Terminal $-CH_2-$protons (4H):- quartet at 7.32 τ
c) Terminal $-CH_3$ protons (6H):- triplet at 8.57 τ
$(J_{CH_3-CH_2} = 8\ Hz)$

At this stage it is necessary to examine in detail the reasons for such a spectrum and then to compare it with that of the complexed ligand. The Newman projection down the carbon-selenium bond, as shown overleaf, (Figure 24) indicates that free rotation about this bond results in identical electronic

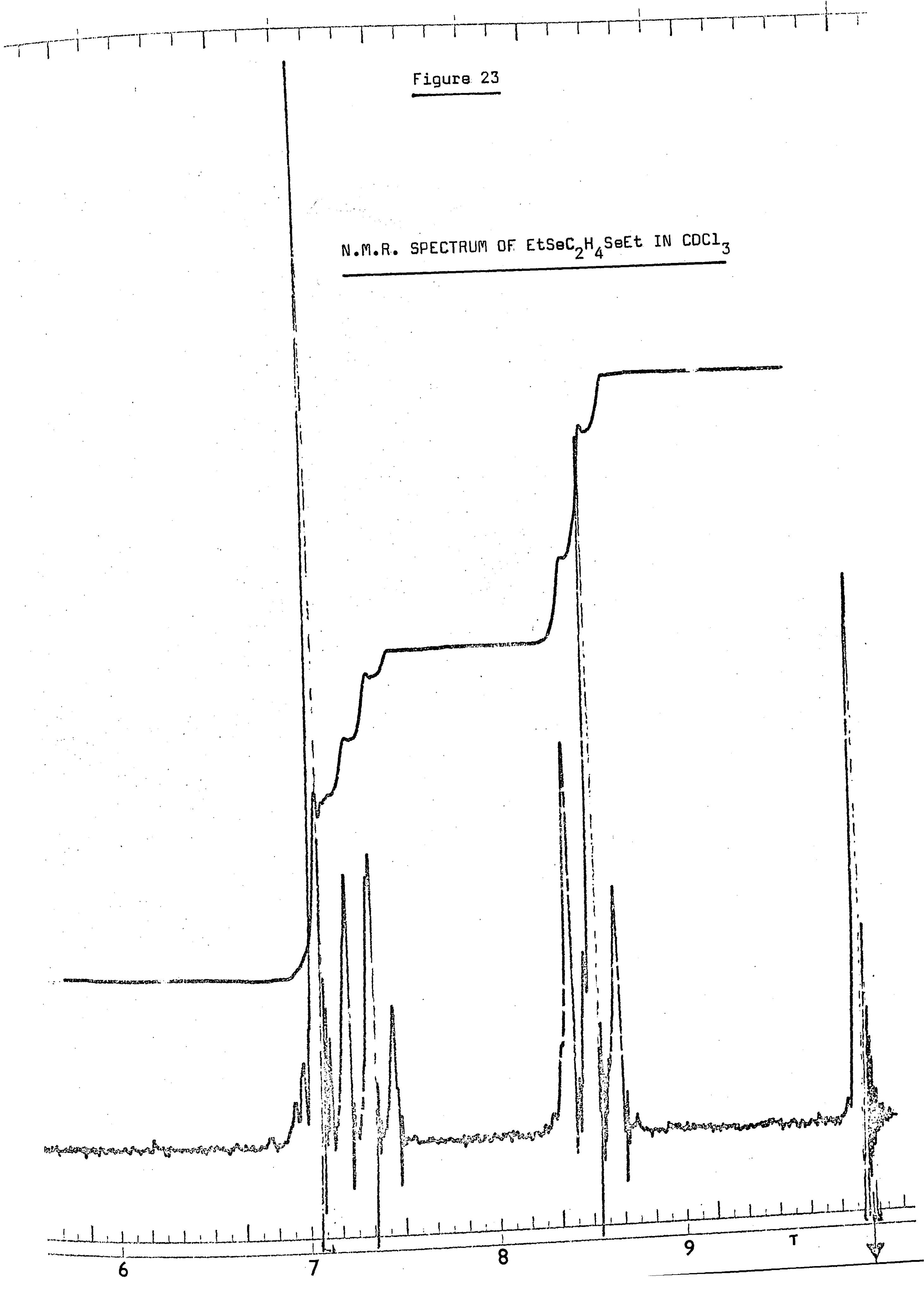


Figure 23

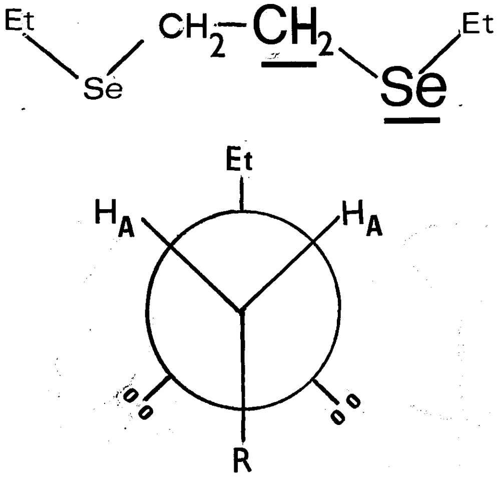
N.M.R. SPECTRUM OF $EtSeC_2H_4SeEt$ IN $CDCl_3$

environments for any one set of $-CH_2-$ bridging protons, and hence they exhibit chemical shift equivalence.

FIGURE 24

NEWMAN PROJECTION DOWN C-Se BOND

IN $EtSeC_2H_4SeEt$



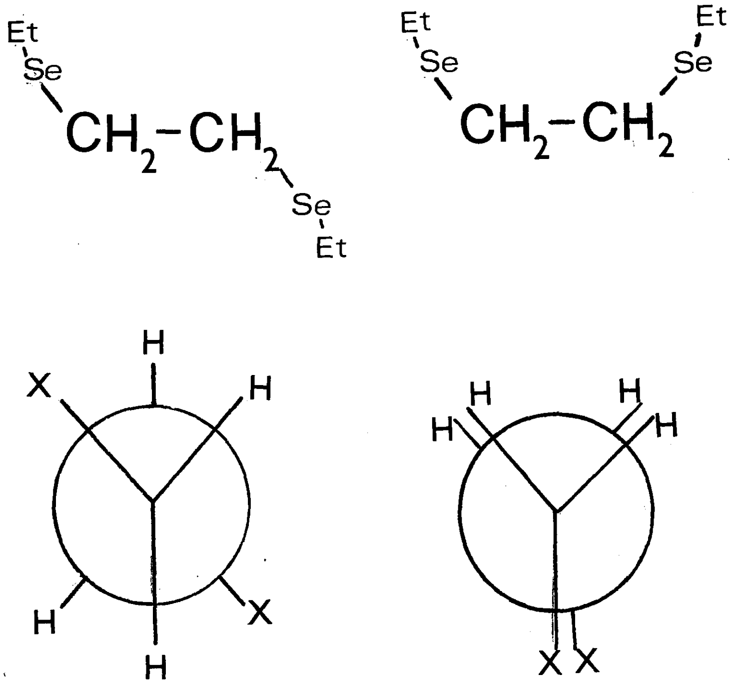
These isochronous(128) protons absorb at the same r.f./field values in achiral solvents and a singlet is observed.

Similar projections down the carbon-carbon bridging bond, i.e.,

FIGURE 25

NEWMAN PROJECTION DOWN C-C BOND

IN $EtSeC_2H_4SeEt$



show both sets of methylene protons to be equivalent to each other. Fast rotation about the carbon-carbon bond results in an averaged spectrum which represents the weighted mean of the individual conformers. This confers equivalence on the two sets of protons, and consequently a singlet, representing an A_4 resonance, is observed for the bridge protons. Figure 24 could well represent (with minor modification) a projection down the terminal carbon-selenium bond. The terminal methylene protons are therefore isochronous. Furthermore, unrestricted bridging carbon-selenium rotation allows both terminal ethyl groups to 'see' the same electronic environment, and only one signal, best described as A_2M_3, results.

In summary, in the free ligand, $EtSeC_2H_4SeEt$, unhindered rotation about all the bonds, and the absence of chiral(129) centres in the molecule produce a simple, easily interpretable n.m.r. spectrum. This is not the case, however, when the ligand is chelated to a transition metal, as in $(EtSeC_2H_4SeEt)PdI_2$. (Figure 27). Two sets of methyl signals and much more complicated bridging and terminal methylene proton resonances are observed at low temperatures. Reasons for this lie in the following areas.

The diagrams below show possible products when one of the lone pairs of electrons on each of the selenium atoms is coordinated to palladium.

FIGURE 26

POSSIBLE ISOMERS OF $(EtSeC_2H_4SeEt)PdHal_2$

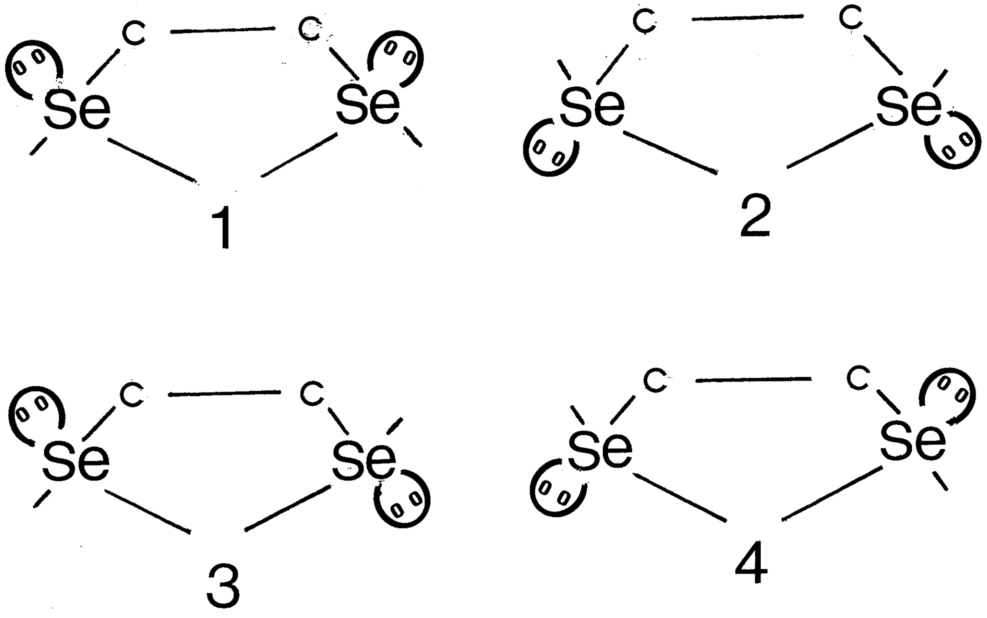


Figure 27

Temperature dependence (^{o}C) of n.m.r. spectrum of

$(EtSeC_2H_4SeEt)PdI_2$

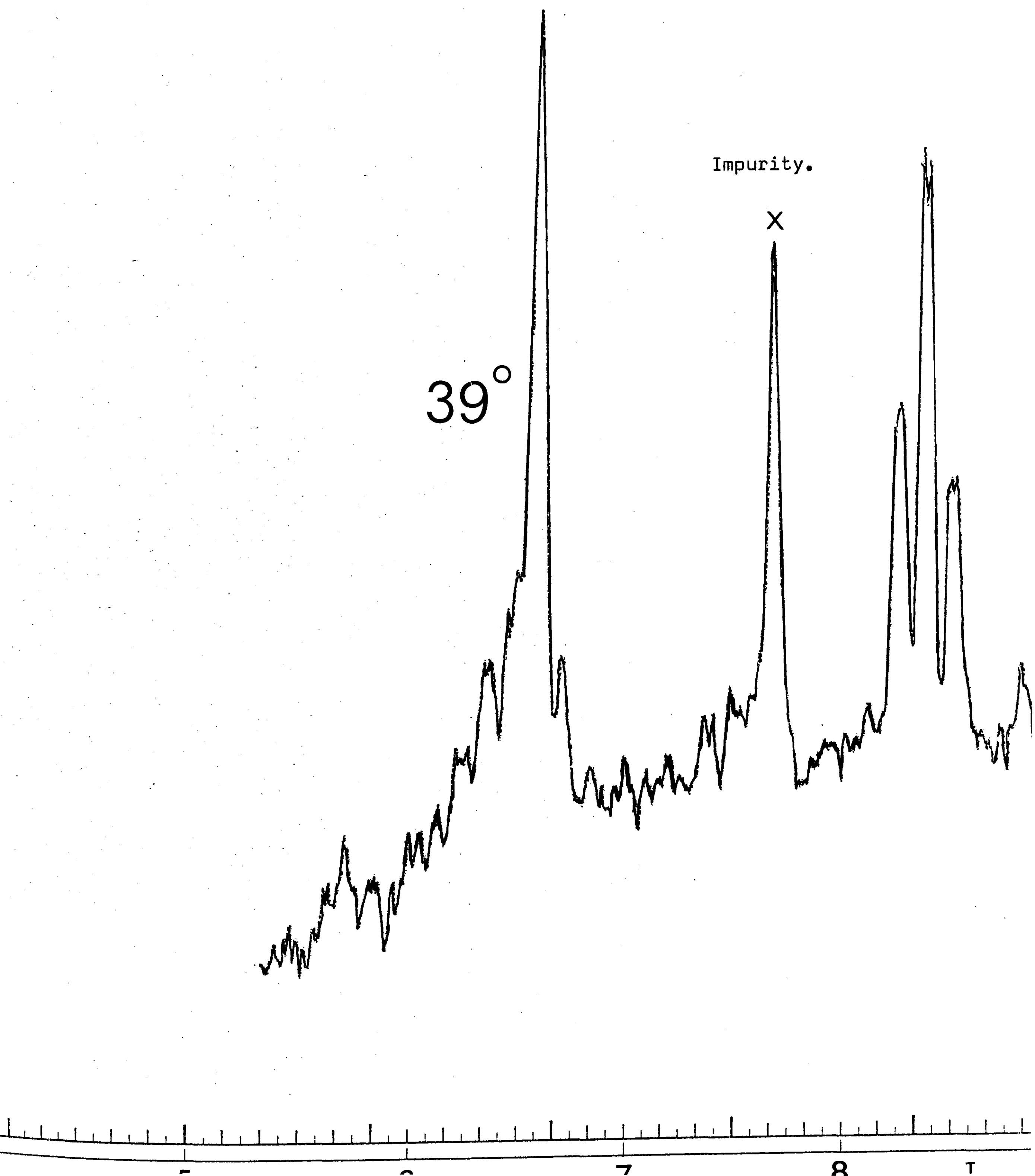


Figure 27

Temperature dependence (^{o}C) of n.m.r. spectrum of

($EtSeC_2H_4SeEt$)PdI_2

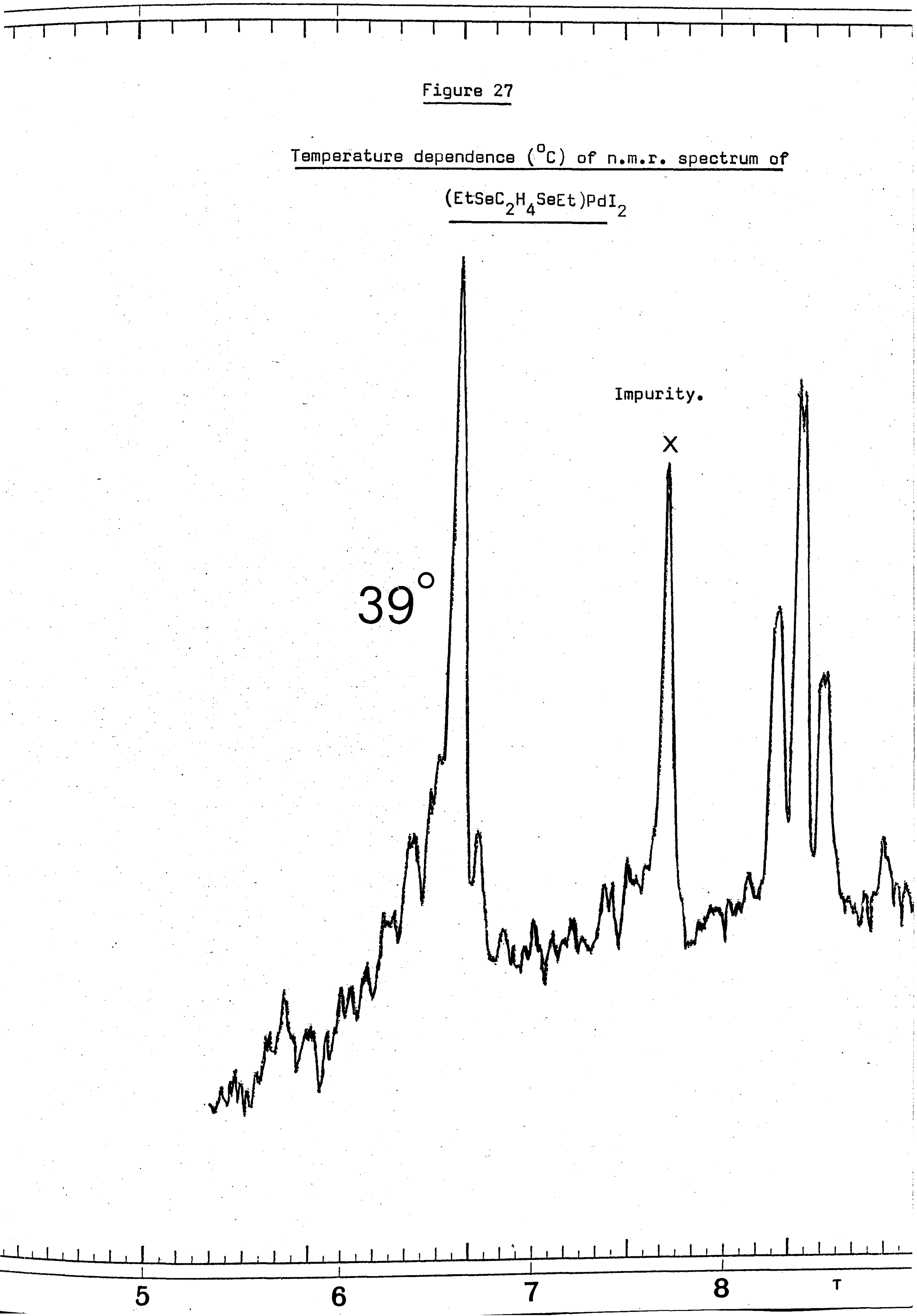


Figure 27 (cont.)

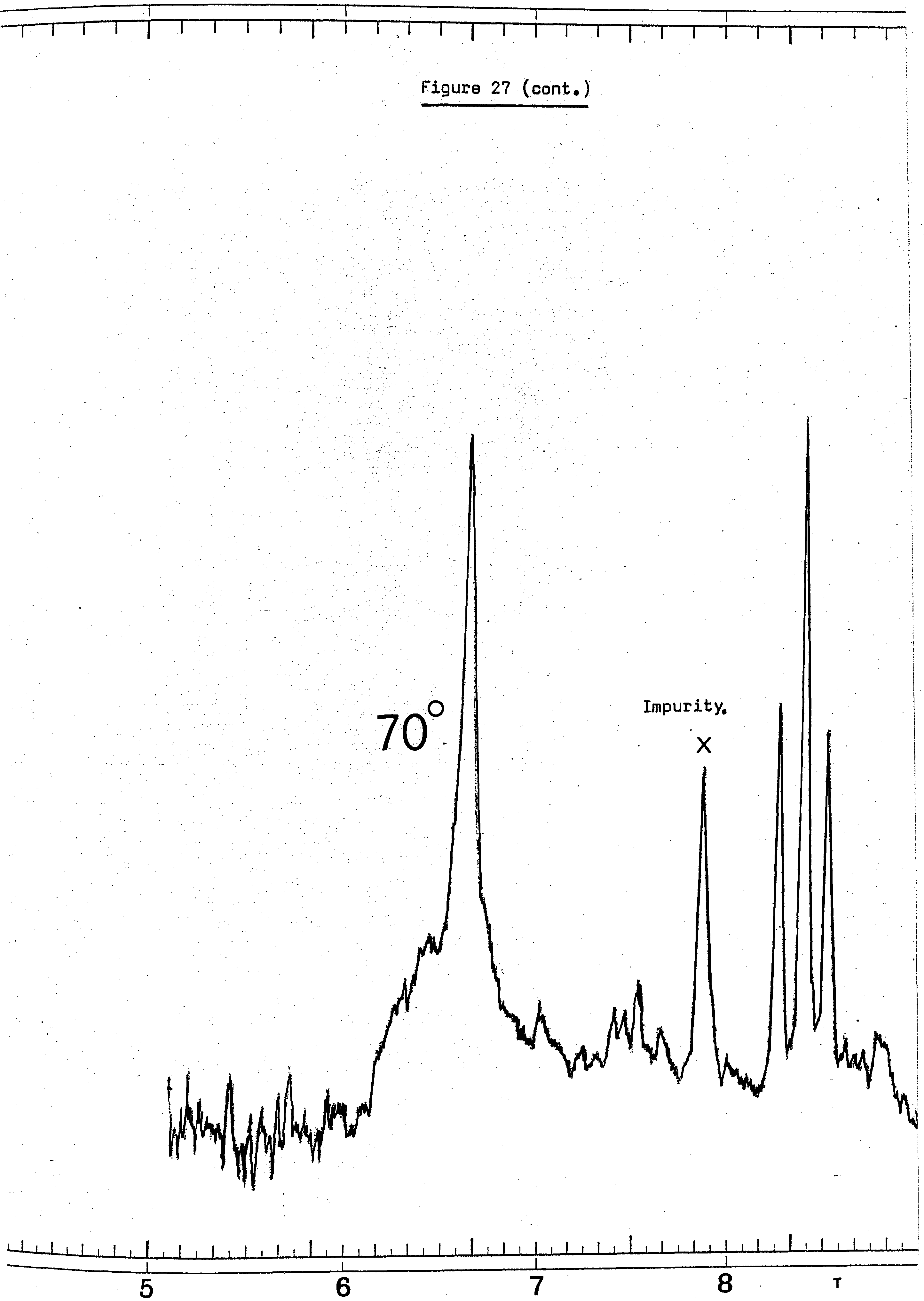
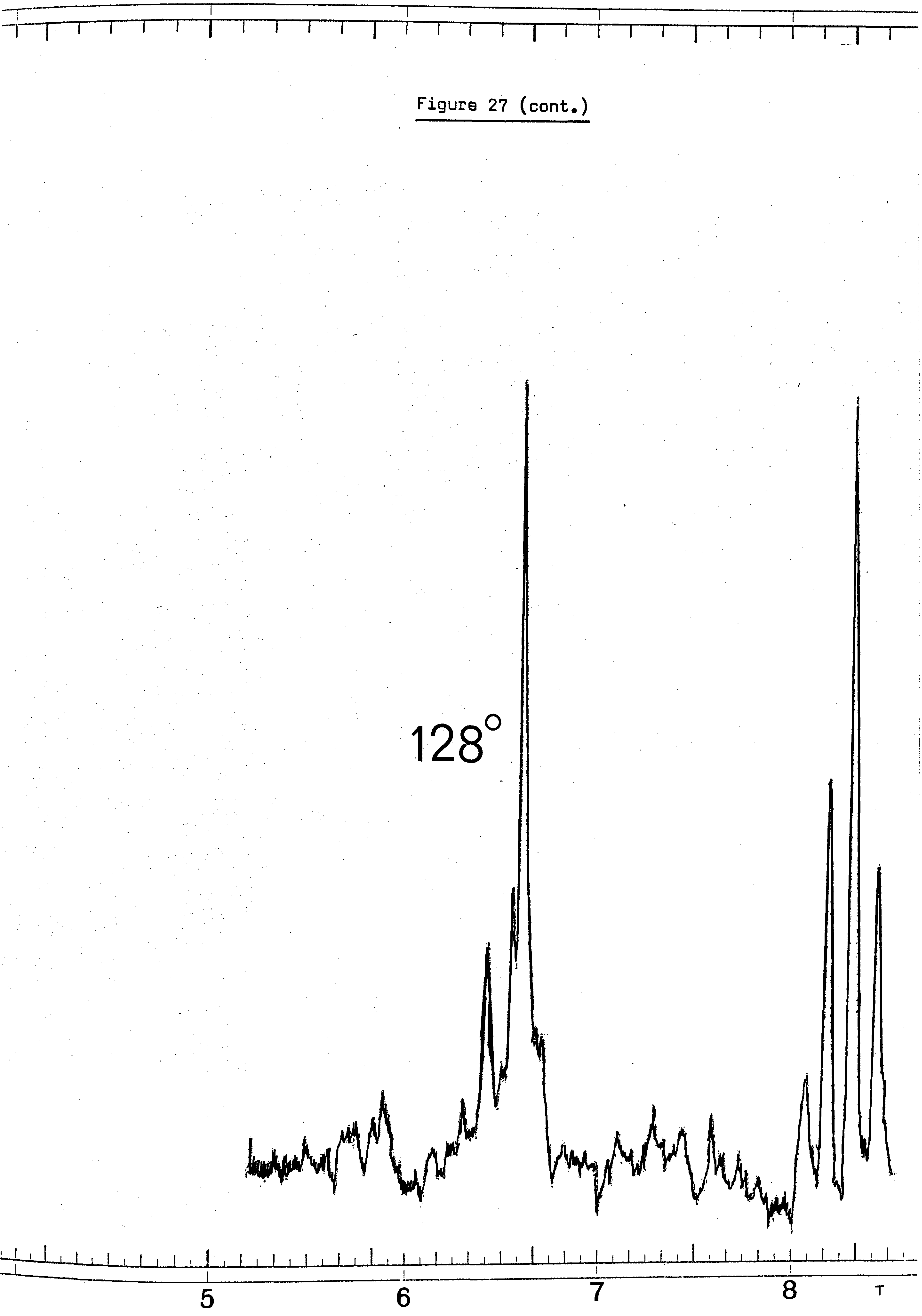


Figure 27 (cont.)



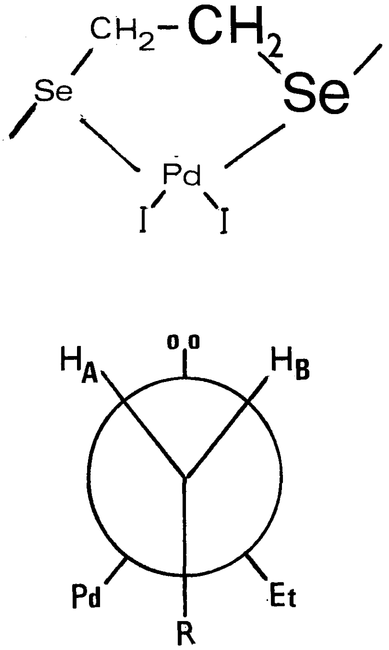
(1) and (2) are equivalent, and because of a plane of symmetry bisecting the C-C bridge and the palladium atom, this isomer is termed 'meso'. (3) and (4) are related as mirror images of one another and are therefore 'd and l' enantiomers. Thus the presence of two chiral centres (the selenium atoms) in the complex gives rise to 'meso' and 'd,l' diastereoisomers(129), and from each of these isomers different sets of signals in the n.m.r. should be observed. The terminal groups in the meso-isomer are in identical electronic environments, as also are those in the d-, and in the l-isomers. Although d- and l- are similar to each other, they both differ from the meso-diastereoisomer and two separate terminal group resonances are expected. Reports of more than two signals(130) mean that the possibility of puckering of the five-membered ring to give pseudo-axial and pseudo-equatorial R groups for each isomer, (i.e. a total of four signals) cannot be dismissed. In this study, however, only two sets of triplets for the terminal methyl groups are ever observed, and these are assigned to the two diastereoisomers, (Figure 26), of approximately equal proportions.

The complexity of the terminal methylene proton resonance can be understood by consideration of the same arguments as have been presented for trans-$(Et_2Se)_2PtI_2$. The two methylene protons of any one terminal group are diastereotopic due to the effective asymmetry of the selenium atom and give rise to an AB quartet. Two such quartets are possible (one from each isomer) and further splitting by the methyl protons can result in two ABM_3 resonances or 8 AB quartets. By the same reasoning, the bridging methylene protons are also diastereotopic,

FIGURE 28

NEWMAN PROJECTION DOWN C-Se BOND

IN $(EtSeC_2H_4SeEt)PdI_2$



as shown above (Figure 28) by the Newman projection down the bridging-carbon-selenium bond. Furthermore, each of the four methylene protons in the bridge couples differently to each other, and this magnetic non-equivalence produces an AA'BB' pattern. Static configurations of the bridge protons will form three different AA'BB' patterns. (See figure 32 on page 106.)

A summary of the expected low temperature n.m.r. characteristics of $EtSeC_2H_4SeEtPdI_2$ is given in the Table below.

TABLE 23

EXPECTED LOW TEMP.SIGNALS IN N.M.R. OF $(EtSeC_2H_4SeEt)PdI_2$

Protons	Signals
Methyl	2 or more Triplets
Terminal Methylene	8 AB Quartets
Bridging Methylene	3 AA'BB' Patterns

Unfortunately both the terminal and bridging methylene protons resonate within the same, very small range, (0.7 ppm) and make interpretation of this part of the spectrum impossible. However, an insight into the possible fluxional processes occurring within this molecule, may still be gained by consideration of the variable temperature n.m.r. spectra.

The two methyl triplets merge at 52°C. Only one triplet is observed at higher temperatures, (Figure 27) and indicates interconversion of the meso- and d,l,-diastereoisomers.. Molecular models show that no combination of bending and/or rotational modes of the five-membered $-\overline{\mathrm{C{-}Se{-}Pd{-}Se{-}C}}-$ ring can possibly lead to this interconversion, but that the two mechanisms discussed previously can. These are pyramidal selenium inversion (I) and dissociation of the Pd-Se bond, followed by recombination (II). Both (I) and (II) lead to the loss of the asymmetric centres at the selenium atoms, and further evidence for this is found in the methylene region of the spectrum. At about 70°C, the signals from the terminal methylene protons coalesce, as shown in Figure 27. At 128°C, these signals appear to be much simpler than the corresponding ones at temperatures below coalescence, and although complicated by other resonances, a quartet with the same coupling constant as the methyl signal (J=7.6 Hz) can be discerned. From the appearance, then, of one A_2M_3 signal at high temperatures, two conclusions can be drawn:-

a) An averaging of the environments of the terminal ethyl groups has taken place to produce a resultant apparent planar configuration at selenium such that these groups now appear parallel to the plane of the ring.

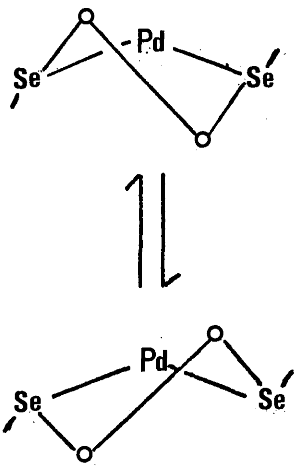
b) The two asymmetric centres at the selenium atoms are no longer apparent from the n.m.r. spectra.

Bridging Protons

The singlet due to the protons on the bridge does not appear to change with increasing temperature, apart from getting sharper. Considerations on what is happening at the bridge must therefore be speculative. Oscillations of the bridge at room temperature between the staggered conformations shown below

FIGURE 29

BRIDGE CONFORMATION IN $(EtSeC_2H_4SeEt)PdI_2$



could possibly reduce the 3 AA'BB' patterns to two - one for the meso - and one for the d,l-isomer mixture. Taking away the asymmetric centres at high temperatures would still not remove the magnetic non-equivalence of these protons, since free carbon-carbon bond rotation is not possible in the five-membered ring. It appears though, that even when attached to centres of asymmetry, only a small intrinsic non-equivalence of the bridging protons exists. This results in small values of $\Delta V/J$ and hence an apparent singlet is observed at all temperatures. The singlet above the coalescence temperature is sharper, since less intrinsic non-equivalence is present.

The results of a variable temperature n.m.r. study on a series of chelate selenium transition metal complexes are shown in Tables 24 and 25. In all cases, the methylene region of the spectrum was of similar complexity to that described for $(EtSeC_2H_4SeEt)PdI_2$, and coalescence temperatures could only be quoted to ±10°C. For the same reasons, and also because of the high temperatures involved, neither $^{195}\underline{Pt}$-Se-C-$\underline{H}$ coupling after coalescence, nor the ambiguity over the mechanism of the fluxional processes within the molecule were resolved. Nevertheless, interesting patterns do emerge.

TABLE 24

N.M.R. PARAMETERS OF CHELATE SELENIDE COMPLEXES IN $PhNO_2$

COMPLEX	τ_{Methyl}	τ_{bridge}	$J_{CH_3-CH_2}$ (Hz.)
$EtSeC_2H_4SeEt$[a]	8.57	7.17	≈8
$EtSeC_2H_4SeEtPtCl_2$	8.32	6.70	7.9
$EtSeC_2H_4SeEtPtBr_2$	8.34	6.71	7.9
$EtSeC_2H_4SeEtPtI_2$	8.33	6.74	7.9
$EtSeC_2H_4SeEtPdCl_2$	8.29	6.47	7.5
$EtSeC_2H_4SeEtPdBr_2$	8.28	6.43	7.6
$EtSeC_2H_4SeEtPdI_2$	8.28	6.59	7.6

a) τ_{CH_2} (term.)is 7.32 when complexed, τ_{CH_2} (term.) is too close to τ_{bridge} to be measured accurately.

TABLE 25

COALESCENCE TEMPERATURES OF CHELATE SELENIDE COMPLEXES

$EtSeC_2H_4SeEtMHal_2$[a]		T_c^1(°C)	T_c^2(°C)
M	Hal		
Pt	Cl	>180	180
	Br	150	140
	I	140	125
Pd	Cl	95	85
	Br	85	75
	I	70	52

a) $PhNO_2$ solvent.

T_c^1 is the coalescence temperature of the terminal methylene protons (±10°C) and T_c^2 is the coalescence temperature of the methyl protons (±5°C).

MECHANISM

The question of a dissociation - recombination mechanism versus one involving pyramidal selenium inversion can only be solved in the context of previous work. The coalescence temperatures of two pairs of sulphur and selenium complexes is given below, and in all but the last one, is pyramidal chalcogen inversion known to cause the coalescences.

TABLE 26

COALESCENCE TEMPERATURES OF SULPHUR AND SELENIDE COMPLEXES

	COMPOUND	T_c(°C)	Ref.
A	trans-$(Et_2\underline{S})_2PtI_2$	2	a
	trans-$(Et_2\underline{Se})_2PtI_2$	90	a
B	$(Et\underline{S}C_2H_4\underline{S}Et)PtI_2$	50	b
	$(Et\underline{Se}C_2H_4\underline{Se}Et)PtI_2$	140	a

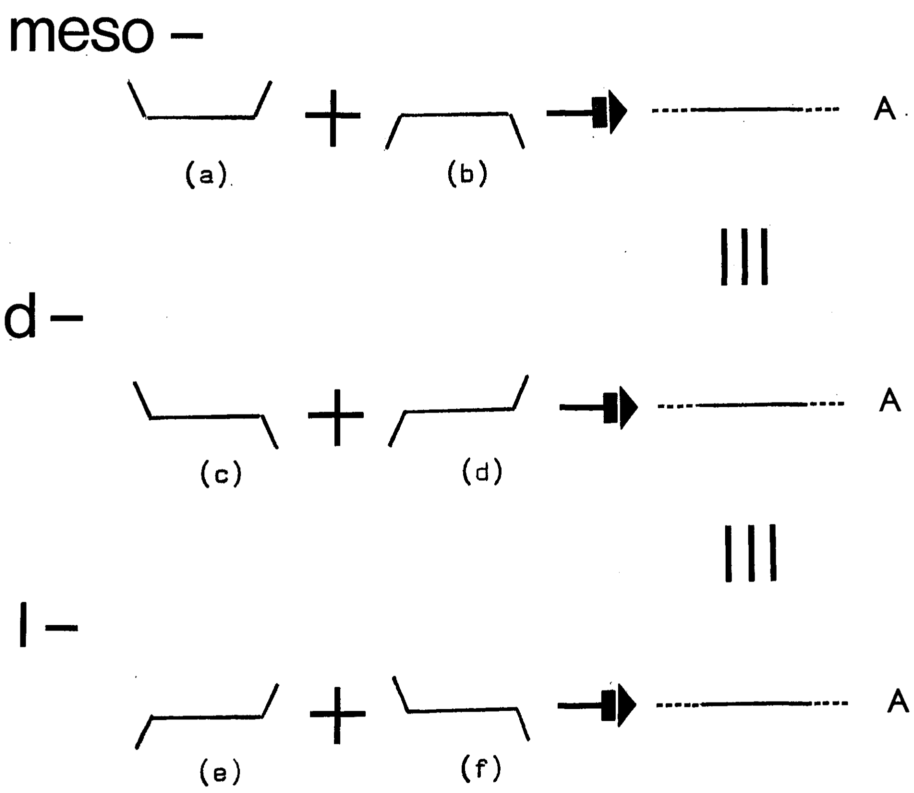
a) This work. b) Ref.99

If the assumption that the *trans* effects of Et_2S and Et_2Se are very similar(39) is valid, then set A indicates that the intrinsic inversion ease of sulphur is ca. 3 Kcal/mole (12.6 KJ/mole) greater than that of selenium. This same difference is found in set B and suggests a similar mechanism for both members of the set.

Simultaneous inversion at both selenium atoms would interconvert d- and l- but not meso, - and d,l - isomers. Such a mechanism however, would seem to lead to an averaged planar conformation at the selenium atoms for all the isomers and as a consequence of this it might be expected that all the terminal group resonances would be identical. This is illustrated below.

FIGURE 30

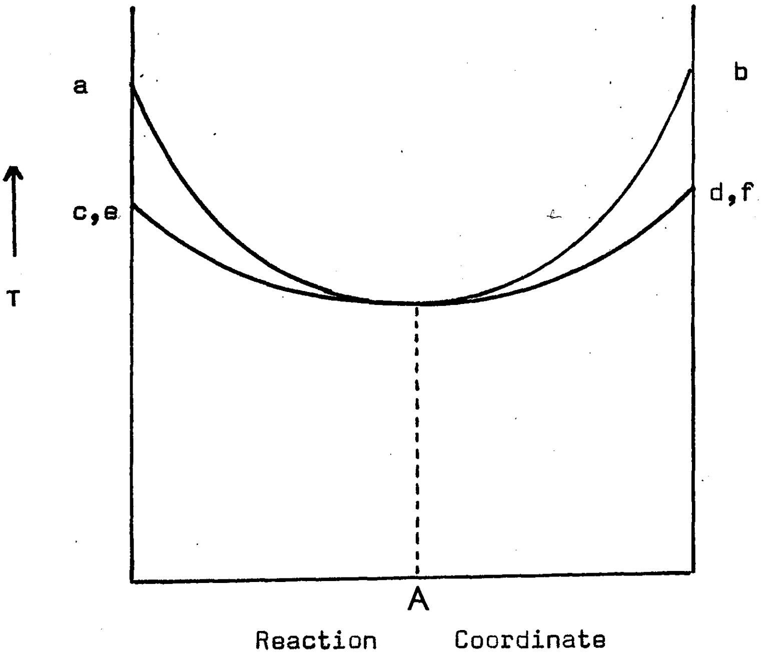
SIMULTANEOUS INVERSION AT BOTH SELENIUM ATOMS



However, the resultant chemical shift of any two interconnecting isomers by simultaneous inversion is not equal to that of an 'isomer' with planar conformations at the selenium atoms, as shown in Figure 31.

FIGURE 31

CONFORMER CHEMICAL SHIFTS OF CHELATE COMPLEXES



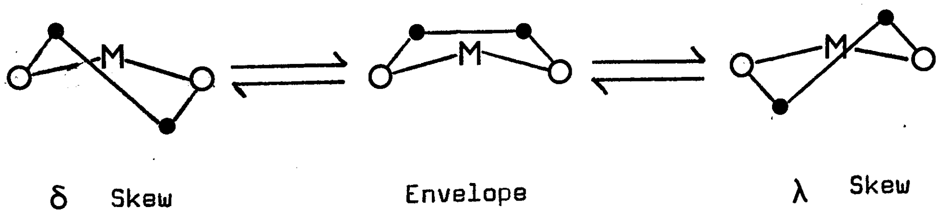
The relative positions of a and c,e are arbitrary.

Simultaneous inversion at both selenium atoms will not lead to one A_2M_3 resonance for the terminal ethyl groups on selenium unless of course, accidental chemical shift equivalence occurs in <u>all</u> the complexes under examination. The predominant process therefore is more likely to be inversion at single selenium centres.

In the course of this work several papers have been published by Hunter et al(130)(131) which are not in accord with our explanations of the coalescence-phenomena exhibited by chelate selenium transition metal complexes. In the first of these(130), the temperature-dependent n.m.r. spectrum of $(Pr^iSeC_2H_4SePr^i)PdCl_2$ was rationalised in terms of "total chelate ring inversion", rather than pyramidal selenium inversion. The solid state molecular structure of this compound had been determined previously(106), and showed only a 'syn' conformation of the terminal isopropyl groups. The three isopropyl signals at low temperatures (intensity ratios 1:1.8:1) were therefore attributed to the two skew and one envelope conformation of this one isomer, as shown below:-

FIGURE 32

CONFORMATIONS OF $(Pr^iSeC_2H_4SePr^i)PdCl_2$



C = ●
Se = ○
Pd = M

The methylene part of the spectrum consisted of two partially superimposed AA'BB' multiplets and coalesced at ca.107°C ($\Delta G^{\ddagger} \approx 19.1$ Kcal/mole, (80 KJ/mole)) to a broad singlet. Interconversion of the skew conformations via the intermediate envelope conformation was stated as the explanation of these observations.

We believe this interpretation to be misleading on a number of points. Extrapolation from the solid state to behaviour in solution is of doubtful validity, and we therefore question the postulated existence of only the meso-isomer in solution. (A single crystal would likely contain only one isomer, anyway). The authors$^{(130)}$ state that their explanations are more plausible than those based on pyramidal atomic inversion, but do not compare or contrast the two approaches. In fact, all their observations are consistent with inversion of configuration at selenium. The three terminal group resonances at low temperatures in the ratio 1:1.8:1 are readily explained in terms of meso- and d,l-isomers. The centre signal is due to the meso-isomer and the outer signals are the pseudo-axial or pseudo-equatorial d,l, proton resonances. The two AA'BB' multiplets arise from gauche conformations of the bridge protons of these two isomers. Furthermore, the coalescence temperature of $(Pr^iSeC_2H_4SePr^i)PdCl_2$ (107°C)$^{(130)}$ is very similar to that obtained for $(EtSeC_2H_4SeEt)PdCl_2$ (95°C ±10°C) in this study, and strongly suggests that identical processes are being monitored.

Finally, the same authors have examined the variable temperature n.m.r. parameters of $(BzSC_2H_4SBz)Mo(CO)_4$ and recently communicated (private communication), that lone pair inversion best accounts for the high temperature singlet obtained for the benzyl methylene resonance of this compound.

Table 25 shows the dependence of the coalescence temperature on the ligand trans to the inverting centre. It drops significantly along the series $Cl > Br > I$, and is in agreement both with the trans-effect order(132) $I^- > Br^- > Cl^-$ and with previous results obtained for corresponding sulphur chelate transition metal complexes(99). The lowering of the coalescence temperatures when the central metal ion is changed from platinum to palladium is also in agreement not only with these results(99) but also with similar observations on the monodentate series of compounds already discussed.

The two sets of protons on the terminal ethyl groups of the ligand coalesce at different temperatures. In all cases, the coalescences of the methyl groups are ca. 10-20°C lower than those of the methylene signals, and could be a direct result of the smaller chemical shift differences of the former. This is readily understood by recalling the equation(82) which extracts a rate constant (k) at the coalescence temperature, if coupling is ignored (See page 26). A look at the equation,

$$k = \pi/\sqrt{2}\,\Delta V_{AB}$$

shows that the number of inversions per second at selenium which are required to cause coalescence of the methyl signals is a function of the chemical shift difference (Δv_{AB}) of these signals in the absence of exchange. At low temperatures the chemical shift difference between the sites of the methyl protons is approximately 0.05 Hz, and although not measurable in these chelating complexes, a value of the order of 0.3 Hz is found for the methylene protons in similar monodentate complexes. A smaller number of inversions per second at selenium are therefore required to cause merging of the methyl signals. The observation of two coalescence temperatures caused by the same process can be described, then, in the following terms. As inversion at selenium proceeds, a specific rate is reached which is sufficient to cause the methyl, but not the methylene protons, to interchange such that one signal is observed. A faster rate of inversion, and hence a higher temperature, is required in order to effect exchange between the non-equivalent sites of the diastereotopic methylene protons, such that only one resonance from these protons is recorded.

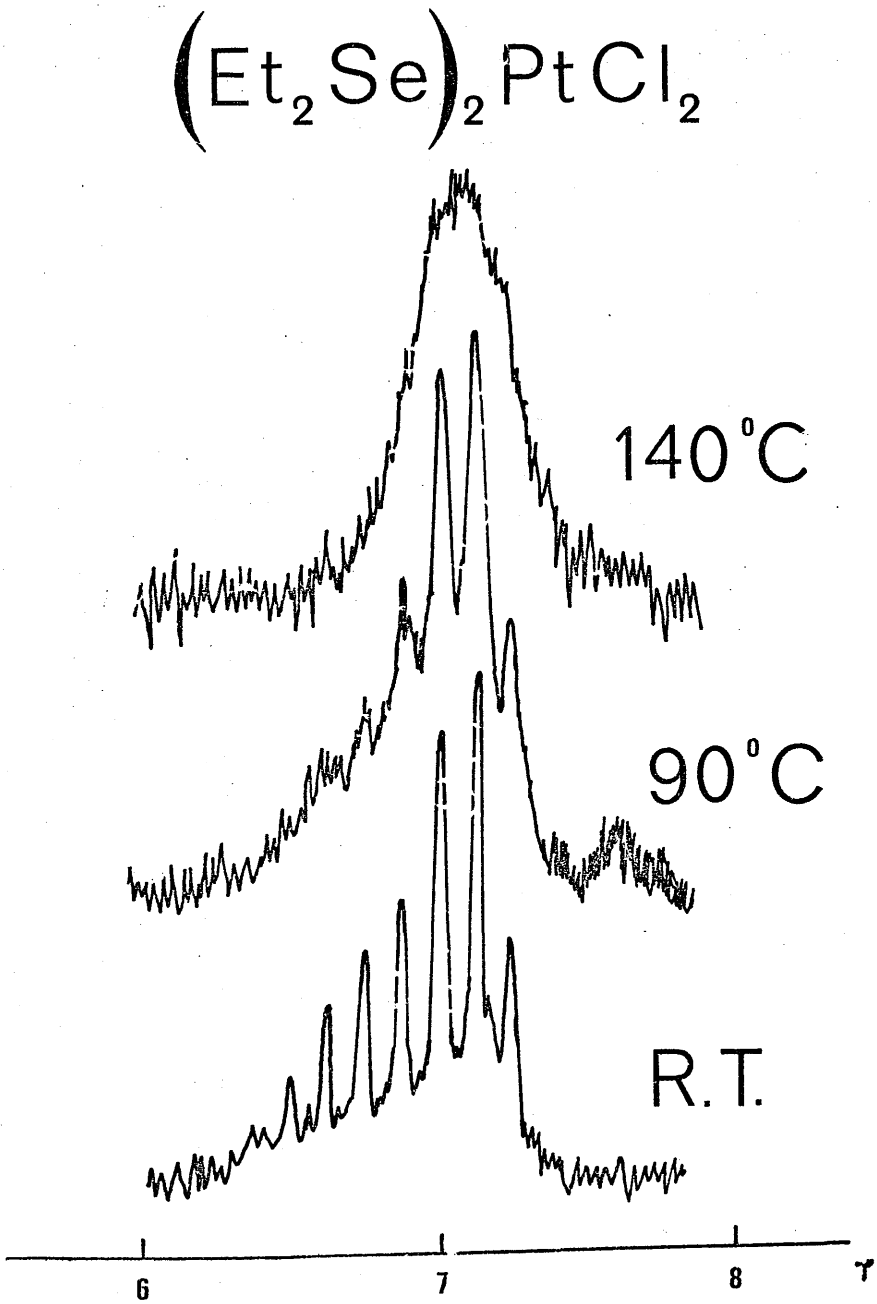
Therefore the argument that the coalescence temperatures of a similar series of compounds can be compared in a meaningful way, is only valid when the detector nuclei (i.e., those causing the coalescences) are in comparable sites relative to that part of the molecule which is fluxional.

D) LIGAND EXCHANGE

On the basis of the data already presented, there still existed some ambiguity as to the cause of some of the coalescences listed in Table 18. In order to ascertain whether pyramidal atomic inversion (I) or ligand dissociation-recombination (II) were in fact operative, it was decided to vary those parameters which would result in different coalescence temperatures, depending on the mechanism. Since unsatisfactory conclusions from both the solvent and the concentration dependences of the coalescences could only be drawn, a new approach was sought. The effect of excess ligand on coalescence temperature was explored.

Figure 33 shows the room temperature n.m.r. spectrum (methylene region) obtained when 20 μl. Et_2Se was added to an 0.121 M solution of trans-$(Et_2Se)_2PtCl_2$ in sym.-tetrachloroethane. The methylene region of the spectrum shows two different sets of overlapping resonances. The downfield portion is that due to the diastereotopic methylene (AB) protons of the complex, and in fact only four lines of the ABM_3X system can be discerned. (M = methyl protons, X = ^{195}Pt nuclei in 33.7% abundance). The upfield signal, centred at 7.01τ , is the A_2M_3 quartet of the free ligand, Et_2Se. As the temperature is raised, two different coalescences of these signals are observed. At +90°C, the ABM_3X system coalesces to a broad signal as shown in the figure. This is the same coalescence temperature obtained in previous experiments when no excess ligand was present, and its cause then was unambiguously assigned to mechanism I, pyramidal inversion

Figure 33



Adding excess ligand to $(Et_2Se)_2PtCl_2$

at the selenium atoms. Between 125°C-140°C coalescence of the remaining signals occurs, and we interpret this as a result of fast ligand exchange in the molecule.

The following sequence of events, then, best describe the above observations. At ambient temperatures, in the presence of excess ligand, no fluxional process is occurring sufficiently fast to affect the appearance of the n.m.r. spectrum. As the temperature is raised, the rates of both inversion at selenium and Et_2Se exchange are increased, but only the former is fast enough at 90°C to cause the signals from the complex to coalesce. Further heating (ca.130°C) provides sufficient energy for fast ligand dissociation-recombination. At, and above, the second coalescence temperature both processes are probably occurring, such that rapid atomic inversion is taking place in the time intervals between exchanges.

RESULTS

a) SULPHUR

The results of addition of excess Et_2S to some platinum and palladium complexes are shown in Table 27. A conductometric titration carried out by previous workers(133) provided evidence that halide ion exchange was not responsible for the changes in the n.m.r. spectra. No sharp increase in conductivity was observed when Et_2S was added to a methanolic solution of trans-$(Et_2S)_2PdCl_2$ indicating the absence of a long lived $(Et_2S)_3PdCl^+Cl^-$ species. Furthermore, never more than two triplets (trans-complex and free ligand) were found in the methyl regions in the spectra of either the platinum or the palladium complexes, indicating that no trans ⇄ cis isomerisation had taken place. The second coalescence was therefore not the result of pyramidal sulphur inversion of a cis-isomer. An additional check was the absence of a coalescence near 56°C (inversion T_c of cis-$(Et_2S)_2PtCl_2$) when Et_2S was added to trans-$(Et_2S)_2PtCl_2$.

The results of the $Et_2S/(Et_2S)_2MHal_2$ system, taken from reference 133 are shown in Table 27. In all cases the first coalescence temperature (T_c^1) reached was very close to that obtained in separate experiments without addition of excess ligand. The apparent variation in T_c^1 is well within experimental error. Overlapping of the signals causes difficulties in assessing the exact coalescence temperature. T_c^2, the ligand exchange coalescence, is dependent (M = Pd) on both the concentration of the complex and of free ligand. This dependence suggests an associative mechanism and is consistent with previous observations(134). Because of the ill-defined nature of these coalescences, which were generally spread over a 20-25°C range, and because of the complexity of the signals, no attempt was made to investigate further the kinetics of ligand exchange. In the course of this work, the kinetics of the $Me_2S/(Me_2S)_2PdCl_2$ system were investigated(134), and it was shown that the rate of ligand exchange was first order in both complex and free ligand. The usual associative mechanism was assumed to apply.

TABLE 27

INVERSION AND LIGAND EXCHANGE IN

$(Et_2S)_2MHal_2$ COMPLEXES

COMPLEX	M_1	M_2	T_c^1	T_c^2	Range of T_c^2
trans-$(Et_2S)_2PtCl_2$	0.495	0.517	+3 (6)	>90	-
	0.202	0.051	-3 (6)	>90	-
	0.202	0.101	0 (6)	-	-
	0.202	0.404	0 (6)	>90	-
trans-$(Et_2S)_2PdCl_2$	0.045	0.011	-34(-24)	>90	-
	0.045	0.022	-38(-24)	-	-
	0.045	0.089	-34(-24)	70	(70-90)
	0.129	0.089	-26(-24)	60	-
	0.129	0.180	? (-24)	57	(48-65)
trans-$(Et_2S)_2PdBr_2$	0.128	0.090	-34(-28)	+80	(70-90)
	0.128	0.180	? (-28)	+66	(60-80)

M_1 is the molarity of the complex.

M_2 is the molarity of the ligand.

$T_c^1(^\circ C)$ is the inversion coalescence temperature and the values in parentheses are these obtained in separate experiments without addition of excess ligand.

$T_c^2(^\circ C)$ is the ligand-exchange coalescence temperature.

The platinum complexes showed only one coalescence (T_c^1), due to sulphur inversion, when excess ligand was added. Attempts to observe a ligand exchange coalescence by increasing both complex and Et_2S concentrations, were unsuccessful.

b) SELENIUM

The results in Table 28 of inversion and ligand exchange in selenide complexes have already been partially discussed. Conductivity experiments, undertaken more than 50 years ago(135), indicate, as with the corresponding sulphur analogues(133), the absence of long lived ionic species. In addition to the two triplets, (complex and free ligand) expected in the methyl region of the spectrum of trans-$(Et_2Se)_2PtCl_2$, a third of lesser intensity was observed at room temperature. Although this signal was not apparent at higher temperatures, the possibility of trans ⇌ cis isomerisation, with coalescence of the cis-isomer (due to selenium inversion) cannot be definitively discussed, especially since spectra well above the second coalescence temperature ($\approx 130^\circ C$) were not obtained. Cis-$(Et_2Se)_2PtCl_2$ is known(136), but difficult to synthesise, and trans ⇌ cis isomerisations, although rare, are also known(137-139). Moreover there is a 50°C difference in the inversion coalescence temperatures of cis- and trans-$(Et_2S)_2PtCl_2$, and cis-$(Et_2Se)_2PtCl_2$ might well be expected to coalesce (inversion at selenium) at about 140°C. However, the similar T_c^2 values of the corresponding dibromide where no cis-isomer is known, and the absence of such an isomerisation in both the sulphide and telluride complexes make it almost certain that exchange of Et_2Se is responsible for the coalescences (T_c^2).

TABLE 28

INVERSION AND LIGAND EXCHANGE IN $(Et_2Se)_2MHal_2$ COMPLEXES

COMPLEX	M_1	M_2	T_c^1	T_c^2	Range of T_c^2
trans-$(Et_2Se)_2PtCl_2$[a]	0.121	0.366	90(90)	130	(125-140)
	0.121	0.549	>78(90)	125	(120-140)
trans-$(Et_2Se)_2PtBr_2$[a]	0.145	0.544	>78(90)	140	-
	0.145	0.816	≈90(90)	125	(120-140)
trans-$(Et_2Se)_2PdBr_2$[b]	0.138	0.103	/ (43)	20	(3-30)
	0.138	0.206	/ (43)	13	(-19-25)
	0.138	0.309	/ (43)	9	(3-16)

a) Sym-tetrachloroethane solvent.

b) Chlorobenzene solvent.

The notation is the same as in Table 27.

Only one coalescence occurred with the palladium complexes, at least 20°C below that observed with no excess ligand present. The dependence of this coalescence temperature on the concentration of $[Et_2Se][M_2]$ is consistent with an associative mechanism, as discussed previously.

c) TELLURIUM

The results in Table 29 show that in all cases but one, no coalescences of the methylene signals were observed, and that these resonances were typical of the 'high-temperature' type of spectra. Conclusive evidence for facile Et_2Te exchange in these transition metal complexes, suspected by these negative results, was obtained by adding <1 µl Et_2Te to a 0.136 M solution of <u>trans</u>-$(Et_2Te)_2PtI_2$ in sym.-tetrachloroethane, and examining the methylene region of the spectrum immediately. At -30°C a complicated spectrum indicated no Et_2Te exchange, but heating to 2°C resulted in a coalescence of the signals. After leaving for approximately one hour, the n.m.r. spectra above room-temperature were run, and surprisingly, coalescence began again about 48°C. Further heating resulted in coalescences at 57°C, 70°C and then 90°C. They were however, not reversible, illustrated by cooling to 2°C and observing, instead of coalescence, a complicated spectrum in the methylene region. Heating again saw the signals coalesce about 100°C, and at 160°C, an A_2M_3 quartet ($J \approx 8$ Hz) (no ^{195}Pt satellites) was observed.

TABLE 29

FAST LIGAND EXCHANGE IN TELLURIDE COMPLEXES

COMPLEX	M_1	M_2	T_c^1	T_c^2	Range of T_c^2
trans-$(Et_2Te)_2PtI_2$[a]	0.181	0.359	/ (119)	<-30	/
	0.163	0.060	/ (119)	<-28	/
	0.136	<0.012	/ (119)	2	0-4
trans-$(Et_2Te)_2PdBr_2$[b]	0.160	<0.019	/ (18)	<-28	/

a) Sym.-tetrachloroethane solvent.

b) Chlorobenzene solvent.

The notation is the same as in Table 27.

These variable irreversible coalescences demonstrate the pronounced effect of even a trace of free ligand on the behaviour of $(Et_2Te)_2MHal_2$ complexes in solution. Presumably slight decomposition of Et_2Te in the solvent, or even evaporation by heating occurred during the n.m.r. experiment. This appeared to cause sufficient depletion in the small amount of free ligand present to effect a coalescence temperature rise of about $100^{o}C$.

DISCUSSION

(1) LIGAND EXCHANGE

The data in Table 30 attempt to quantify the relative ease of ligand exchange down Gp.VI.

TABLE 30

LIGAND EXCHANGE COALESCENCE TEMPERATURES

OF TRANS-$(Et_2X)_2MHal_2$ COMPLEXES

M	X	$[M_1][M_2]$	T_c^2 (°C)
Pt	S	0.0816	>90
	Se	0.0664	125
	Te	<0.00156	2
Pd	S	0.0230	66
	Se	0.0285	13
	Te	<0.0030	<-28

The product of the complex (M_1) and free ligand (M_2) concentrations is compared with the coalescence temperature for ligand exchange (T_c^2), since the latter is dependent on both M_1 and M_2. For the platinum derivatives, the ease of ligand exchange falls in the order:-

$$Et_2Te \gg Et_2Se,\ Et_2S,$$

and a similar trend, namely

$$Et_2Te \gg Et_2Se > Et_2S$$

is found for the palladium complexes. Also, exchange at Pd is faster than exchange at Pt.

The two main considerations in the process:-

$$\underline{trans}\text{-}(Et_2X)_2MHal_2 \ + \ Et_2X^*$$
$$\rightleftharpoons$$
$$\underline{trans}\text{-}(Et_2X)(Et_2X)^* \ MHal_2 \ + \ Et_2X$$

are those of bond-making and bond-breaking. In their study of the kinetics of thioether nucleophilic displacement of various ligands in Pt(II)complexes, Cattalini and coworkers(140) observed that bond making was of prime importance. The rate of displacement was more sensitive to the nature of the entering group than it was to that of the leaving group. It might be expected therefore, since the bimolecular reactivity of different nucleophiles is mainly related to their polarisability(141), that the softest base Et_2Te should react fastest with the soft acid Pt(II). This is in fact found here, and suggests that bond-making is important. On the other hand, the antisymbiotic(142) effect of two trans Et_2Te ligands in trans-$(Et_2Te)_2PtI_2$ should weaken the Pt-Te bond (relative to the Pt-S bond in the corresponding sulphur analogue) since 'two soft ligands in mutual *trans* positions will have a destabilising effect on each other when attached to class-b metal atoms(125).' An increase in the rate of displacement of Et_2Te will result. However, the relative efficiencies of Et_2S, Et_2Se and Et_2Te as leaving groups is not known, and the contribution of bond breaking to the overall rate cannot be reliably assessed.

The increased rate of substitution at palladium is in accord with the relative ease of palladium (over platinum)(II) to increase its coordination number from 4 to 6(143).

(2) INVERSION

The results obtained by these studies present a convenient method of discriminating between coalescences caused by pyramidal atomic inversion (I) and exchange of ligand (II). The first coalescence temperature reached ($T_c^{\,1}$ in Table 27) when Et_2S was added to a solution of *trans*-$(Et_2S)_2PdCl_2$ was identical (within experimental error) to that obtained in the absence of free ligand, and represents the first unambiguous proof of *pyramidal sulphur inversion at palladium.* However, a definitive mechanism cannot be assigned to the coalescences of the *trans*-$(Et_2Se)_2PdHal_2$ complexes in the absence of free Et_2Se, since the coalescence temperatures observed in these experiments ($T_c^{\,2}$, Table 28) were always at least 20°C lower.

The implications of the Et_2Te results are far-reaching. Not only must there be no trace of Et_2Te present initially when examining for an inversion coalescence in the v.t.n.m.r. of the telluride complexes, but also any thermal or photochemical decomposition in the course of the experiment, to produce free ligand, would unquestionably lead to erroneous conclusions.

F) TELLURIUM COMPLEXES

No attempt has been made so far to explain the results obtained in the v.t.n.m.r. of $(Et_2Te)_2PtHal_2$ and $(Et_2Te)_2PdHal_2$ complexes when no excess ligand was added. In particular, the question of whether or not any of the coalescences might be explained unambiguously in terms of pyramidal tellurium inversion was of interest, since, although suggested(102b),(104), this mechanism had never been unequivocally established. The marked effect on the spectra of small amounts of Et_2Te should allow us to clarify some of the apparent anomalies.

(1) PLATINUM

The n.m.r. spectra of the trans-$(Et_2Te)_2PtHal_2$ complexes all showed variable temperature characteristics, similar to those described previously for the sulphur and selenium analogues. At low temperatures, complicated (presumably ABM_3X) resonances were found in the methylene regions of the spectra, and reproducible coalescence occurred at the temperatures shown overleaf.

TABLE 31

COAL.TEMPS. OF TRANS-$(Et_2Te)_2PtHal_2$ COMPLEXES IN CHLOROBENZENE

HAL	T_c(°C)
Cl	107
Br	110
I	105

The values obtained suggested that a similar mechanism might be responsible for the coalescences of all the complexes and that this mechanism might well be pyramidal tellurium inversion, since it had already been established for sulphur and selenium platinum compounds, that cis ligands have no effect on the rate of inversion. The proximity of the boiling point of chlorobenzene (132°C) to these coalescence temperatures did not allow the recording of 'high temperature' spectra, and other higher boiling solvents had to be used. The temperatures in Table 32 are those at which the signals of the telluride complexes coalesced using $Cl_2CH-CHCl_2$ solvent (B.p.146°C).

TABLE 32

COAL. TEMPS. OF *TRANS*-$(Et_2Te)_2PtHal_2$ COMPLEXES IN Cl_2CH-$CHCl_2$

Hal	T_c(°C)	Range(°C)
Cl	125	(122-128)
Br	115	(103-115)
I	119	(119-128)
	118	(118-123)

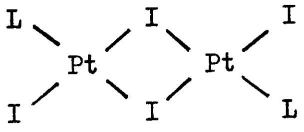
Above this an A_2M_3 spectrum in the methylene region was observed. No ^{195}Pt-Te-C-H coupling was apparent and indicated that tellurium inversion could not explain the total sequence of events. More plausible was the process of Et_2Te dissociation and then recombination. However, although there were no visible signs of it at the coalescence temperature, a considerable amount of decomposition was caused by further heating.
This suggested the possibility that free ligand was produced in the thermal decomposition of the complexes, and that fast ligand exchange was then promoted. If this occurred *after* coalescence, pyramidal tellurium inversion would still be responsible for the coalescences. On the other hand, the

higher T_c values with $Cl_2CH-CHCl_2$ solvent (compare Tables 31 and 32) could imply that the coalescences were only a function of the thermal stability of the complexes in solution. A ligand exchange coalescence would accompany decomposition if even small amounts of Et_2Te were produced. A number of experiments were performed in an attempt to throw some light on the situation.

a) Some of the variable temperature determinations were repeated with degassed solutions in nitrogen-filled n.m.r. tubes in order to eliminate the possibility of oxygen reacting with the complexes at high temperatures to produce free ligand. However no $^{195}\underline{Pt}$-Te-C-$\underline{H}$ coupling after coalescence was observed.

b) A test on the reversibility of the coalescences showed that the coalescence temperatures did not vary outside experimental error. Et_2Te was therefore not a primary product of the thermal decomposition of these complexes.

c) Since the concentration of free ligand required to cause an exchange coalescence was estimated at $\ll$ 0.012 M, a complex which would react with traces of ligand was desirable. Accordingly the bridging iodide complex(144) (0.0038 M in $Cl_2CH-CHCl_2$)



(L = $PhMe_2P$)

was added to a solution of trans-$(Et_2Te)_2PtI_2$ (0.12 M) since it is well established that these bridging complexes readily react with free ligand to split the iodide bridge(8). ^{195}Pt satellites were still not found at temperatures above that of coalescence.

d) Heating $(Et_2Te)_2PtCl_2$ in $PhNO_2$ (Expt.1) directly to 150°C for almost an hour resulted in a silvery mirror being formed round the inside of the n.m.r. tube, and other ethyl peaks were observed (Table 33) in the n.m.r. Since similar inexplicable peaks had also been obtained by heating the same compound in Cl_2CH-$CHCl_2$ to 148°C for a shorter period, (Expt. 2) it was decided to investigate the thermal decomposition of these complexes further.

TABLE 33

THERMAL DECOMPOSITION OF TRANS-$(Et_2Te)_2PtCl_2$

EXPERIMENT	SOLVENT	PEAKS
1	$PhNO_2$	6.5τ, quartet. 8.6τ, triplet. $J \approx 8$ Hz.
2	Cl_2CH-$CHCl_2$	6.53τ, quartet. 8.19τ, triplet. $J \approx 8$ Hz.

Trans-$(Et_2Te)_2PtI_2$ (0.073g) ($Cl_2CH-CHCl_2$ solvent) was heated to 120°C for two weeks, during which time considerable decomposition took place. The black powder obtained was shown by X-ray powder photography to contain elemental tellurium but not platinum metal. Although the former appeared to be produced quantitively (22 mg. obtained, 22.7 mg. expected), the supernatant liquid still contained $(Et_2Te)_2PtI_2$, which showed v.t. n.m.r. characteristics similar to those described previously. The black powder which was filtered off could well have been a mixture of Te and PtI_2.

The failure to observe ^{195}Pt satellites in the high temperature n.m.r. spectra of the telluride complexes led to other approaches in an attempt to detect and establish tellurium inversion. Five different avenues were explored. All but the first involved synthesising complexes, which for various reasons were expected to show coalescence phenomena at temperatures below those shown by the $(Et_2Te)_2PtHal_2$ complexes, and hence surmount the problem of thermal decomposition. None of the five complexes had been previously reported in the literature.

1) $(EtTeC_2H_4TeEt)PtHal_2$

Synthesis of the complexes shown above were undertaken as an extension of the work on the analogous sulphur(99) and selenium complexes. The table overleaf (34) shows coalescence temperatures of some of these complexes, already interpreted by us and other workers(95)(99) in terms of pyramidal chalcogen inversion.

TABLE 34

COALESCENCE TEMPERATURES OF $(EtXC_2H_4XEt)PtHal_2$ COMPLEXES

X	Hal	T_c(°C)
S	Cl	80
S	I	50
Se	Cl	>180
Se	Br	150
Se	I	140

Of course the problem might not be completely solved if the trend shown in the Table below continued and coalescence occurred at very high temperatures. Nevertheless, the project was undertaken, but attempts to prepare 1,2-bis(ethyl<u>telluro</u>)ethane by the route shown below were unsuccessful.

$$Et_2Te_2 \not\xrightarrow[\text{THF}]{\text{Li}} 2\ EtTe^-$$

$$2\ EtTe^- + ClC_2H_4Cl \not\longrightarrow EtTeC_2H_4TeEt$$

Although 1,2-bis(ethylseleno)ethane had been successfully synthesised by this method, lithiation apparently did not split the Te-Te bond, since ca. 56% of the diethylditelluride was recovered. Other workers have made similar observations. Pluščec and Westland(43) reported an unsuccessful attempt at the synthesis of the chelate telluride ligand, $PhTeC_3H_6TePh$, by reaction of NaTePh with 1,3-dibromopropane, in spite of the fact that the method proved suitable for the corresponding sulphur and selenium analogues.

2) $(PhCH_2TeMe)_2PtHal_2$

Table 35 records the effect of the substituents on sulphur on its rate of inversion.

TABLE 35

EFFECT OF R GROUPS ON RATE OF SULPHUR INVERSION

COMPLEX $(RR'S)_2PtCl_2$ GEOM.	R	R'	$T_c(^\circ C)^a$
cis	Et	Et	60
cis	Bz	Me	36
trans	Et	Et	1
trans	Bz	Me	<-50

a) Taken from Ref.96.

For either steric or electronic reasons, sulphur, in the benzylmethylsulphide complexes, appears to invert faster than the same atom in equivalent diethylsulphide complexes. Accordingly an attempt was made to synthesise complexes of benzylmethyl telluride. As a class, the unsymmetrical aliphatic tellurides are virtually unknown(145), and the method used was similar to that employed in the synthesis of mixed aromatic aliphatic tellurides(146). Treatment of a mixture of BzMgBr and elemental tellurium with MeI in ether failed to produce BzTeMe. The only produce isolated was bibenzyl, illustrating that symmetrisation at one of the stages in the synthesis had occurred.

3) $(PhTeEt)_2PtHal_2$

It was thought that additional delocalisation of the lone pair on tellurium might cause faster inversion(147). Sulphur and selenium inversion rates are greatly accelerated by coordination to transition metals(95-100), probably because of lone pair delocalisation into vacant d-orbitals on the metal. Although it had been noted that $(p\text{-}2p)_\pi$ overlap is less effective when the central atom is from the second row of the periodic table or beyond(147), we decided to synthesise platinum complexes of PhTeEt, a known ligand(146). Even slight $(5p\text{-}2p)_\pi$ delocalisation of the lone pair on tellurium into the p orbitals of the benzene ring might be sufficient to cause a lowering of the inversion coalescence temperature. The method used was the same as that employed by Bowden and Braude(146).

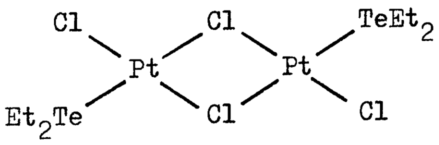
The liquid obtained from the reaction was reacted immediately with aqueous K_2PtCl_4, since the disproportionation reaction,

$$2\ \mathrm{PhTeEt} \rightleftharpoons \mathrm{Ph_2Te} + \mathrm{Et_2Te}$$

was thought to occur rapidly(146). However a mixture of products was obtained. The similar solubilities precluded separation of this mixture, thought to consist of $(Ph_2Te)_2PtCl_2$, $(Et_2Te)_2PtCl_2$, $(PhTeEt)_2PtCl_2$, and possibly $(PhTeEt)(Et_2Te)PtCl_2$ $(PhTeEt)(Ph_2Te)PtCl_2$ and $(Et_2Te)(Ph_2Te)PtCl_2$ as a result of very fast symmetrisation of the aromatic aliphatic telluride.

4) Di-μ-iodo-diiodo-trans-bis(diethyltelluride)diplatinum(II).

The lack of success with the various telluride ligands (1-3) led to the idea of changing other aspects of the molecule in the attempt to detect tellurium inversion. In particular, the dependence of the inversion rate on the *trans* ligand(96)(99) led to the idea of varying the nature of the ligand *trans* to the inverting centre. Because the dimeric platinum complexes $Pt_2Cl_4(Et_2Te)_2$ had been previously synthesised(33) and assigned a structure with bridging halogens, *viz*:-



it was decided to investigate the analogous iodide complexes for a number of reasons:-

a) Iodides are known to have higher trans effects than chlorides(132).

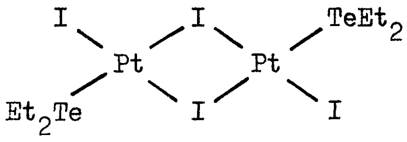
b) A recent paper by Goggin, Goodfellow and Reed(148) showed that in complexes of the type $Pt_2X_4(Et_2S)_2$, bridging sulphide ligands were possible, but only where X = Cl or Br. When X = I, the complexes are generally thought to consist of terminal chalcogen ligands.

At the time this experiment was attempted, it was thought that the telluride complex $(Et_2Te)_2PtI_2$ which had been studied previously, might possibly have a cis-geometry in solution, by analogy with the corresponding chloride complex, to which a cis-structure had been erroneously assigned(112). The relative trans effects of bridging and terminal iodides had been little explored, and it was felt that even a minor difference in this trans-effect order could allow a 10-20°C reduction in the tellurium inversion coalescence temperature, sufficient to avoid complications from thermal decomposition. Unfortunately, however, $(Et_2Te)_2PtI_2$ was discovered in the course of this work to have a trans geometry. Furthermore, Goggin, Goodfellow and Reed(148) reported bridging Me_2S to have a lower trans- influence than terminal Me_2S.

Stirring a 1:1 molar ratio of aqueous K_2PtI_4 and Et_2Te for nine days in the dark produced a brown complex which analysed as $Pt_2I_4(Et_2Te)_2$. Its solubility in a variety of organic solvents (MeOH, EtOH, Cl_2CH-$CHCl_2$, $CDCl_3$) was so low that n.m.r. spectroscopic parameters could not be obtained by continuous wave techniques. An attempted soxhlet extraction in EtOH led to decomposition, and indicated that even if solubility had not been a limiting factor, high temperature n.m.r. spectra could not have been obtained. A Fourier Transform spectrum in $CDCl_3$ (14 hours, 10,000 scans) showed the following resonances:-

Triplet - 8.40τ
Multiplet - 7.14τ
$J_{CH_3-CH_2}$ = 8 Hz.

11 lines of the multiplet could be discerned and were taken as part of 3 of the 4 overlapping AB quartets in



Absence of fast tellurium inversion or Et_2Te exchange causes non-equivalence of the diastereotopic methylene protons and an ABM_3X spectrum (further coupling to the ^{195}Pt nuclei is expected) results. The observation of only one triplet in the methyl region rules out the possibility of bridging and terminal Et_2Te ligands, unless of course accidental chemical shift equivalence causes the simplification. The complexity of the methylene region is consistent with terminal chalcogen ligands, and we have, following the work of others, assigned a '*trans*-structure' to the molecule.

Establishing the identity of the title complex, however, has not brought us further forward in our search for proof of pyramidal tellurium inversion.

5) cis-$(Et_2Te)_2Pt(p\text{-tolyl})_2$

In their studies of sulphur inversion in chelate compounds of the type $(EtSC_2H_4SEt)PtX_2$, Cross and coworkers(99) noticed that a 120°C drop in coalescence temperature was obtained when X was changed from I to Ph. Since the following trans-effect order was suggested:-

$$Ph^- > R_2S > I^-,$$

it was thought that complexes of the type cis-$(Et_2Te)_2Pt(aryl)_2$ might also show a drop in the inversion coalescence temperature. The aryl complex $(Et_2Te)_2Pt(o\text{-tolyl})_2$ had already been synthesised, but its geometry established as trans(40). Since the high trans-effects of aryl groups should normally favour cis-isomers(149), it was thought that steric interactions of the methyl groups could have been responsible, and accordingly, p-tolyl groups were chosen. $(Et_2Te)_2Pt(p\text{-tolyl})_2$ was synthesised by stirring a ca. 2.4:1 molar ratio of p-tolyllithium and trans-$(Et_2Te)_2PtI_2$ in ether at room temperature in the dark for 95 hours. The pale-yellow solid obtained after work up was not recrystallised lest cis $\rightleftharpoons$ trans isomerisation should occur. The ^1H n.m.r. (CD_2Cl_2) showed sets of resonances at the following values:-

triplet : $8.54\,\tau$

singlet : $7.73\,\tau$

multiplet : $7.43\,\tau$

multiplet : ca. $3.2\,\tau$

The ratio of the intensities of the signals, shown in the table below,

TABLE 36

N.M.R. INTENSITY RATIOS OF $(Et_2Te)_2Pt(p\text{-tolyl})_2$

	ETHYL				p-TOLYL
	CH_3 —	CH_2			$-CH_3$
Calculated	2	:	1.3	:	1
Observed	< 2.6	:	< 1.7	:	1

matches, within experimental limitations, that expected for $(Et_2Te)_2Pt(p\text{-tolyl})_2$. The multiplet in the methylene region requires further examination. The appearance of the spectrum (Figure 34) at room temperature is exactly that expected for an $(A_2M_3 + A_2M_3X)$signal with

$$J_{CH_2-CH_3} = 7.5\ \text{Hz}$$

$$J_{\underline{Pt}-Te-C-\underline{H}} = 29\ \text{Hz}$$

(The p-tolyl methyl resonance shows slight ortho-coupling). The relative intensities show good agreement with the expected values.

Figure 34

N.M.R. Spectrum (CD_2Cl_2) of cis-$(Et_2Te)_2Pt(p\text{-tolyl})_2$

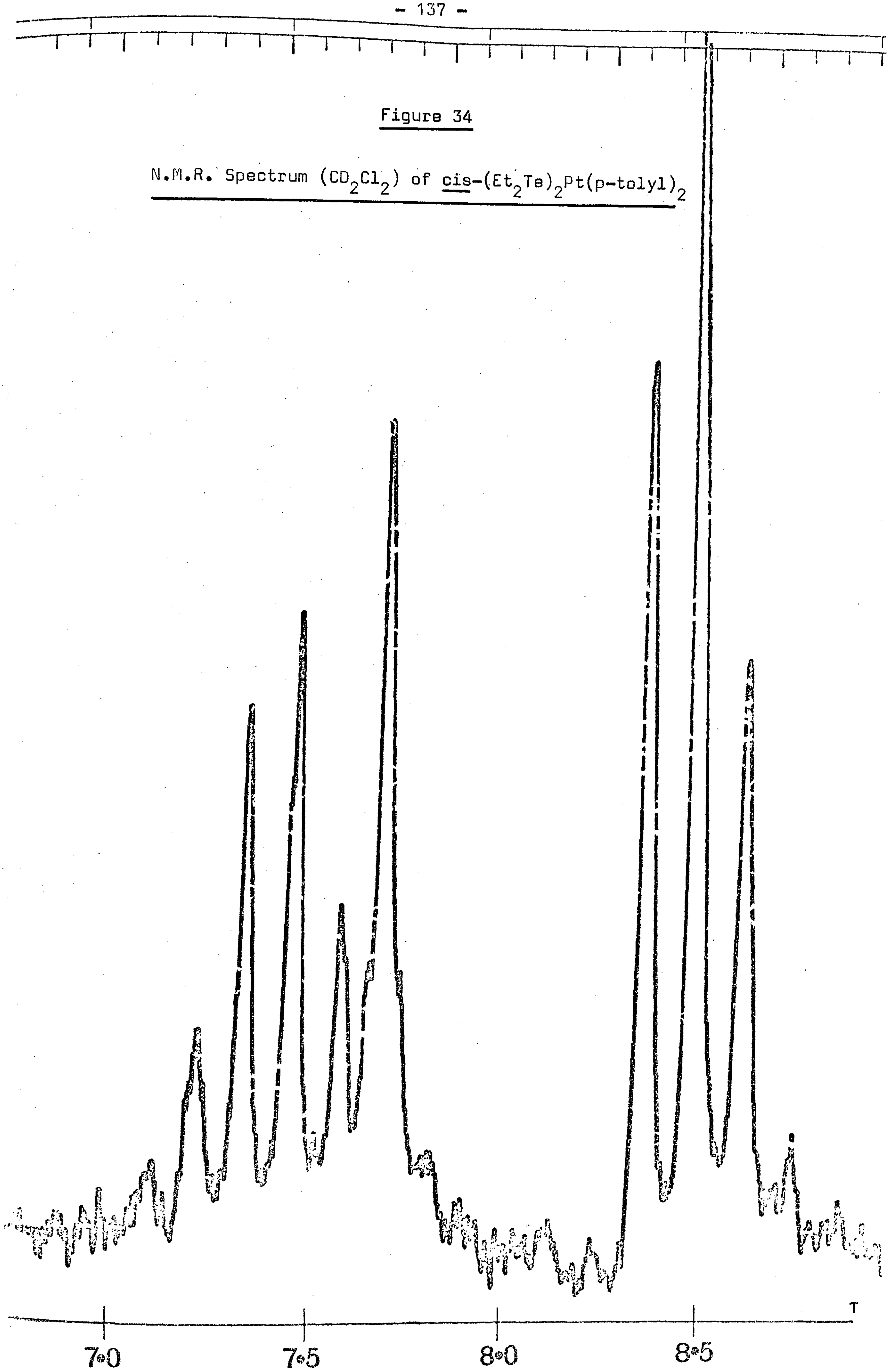


Figure 34a

Expansion of methylene region in figure 34.

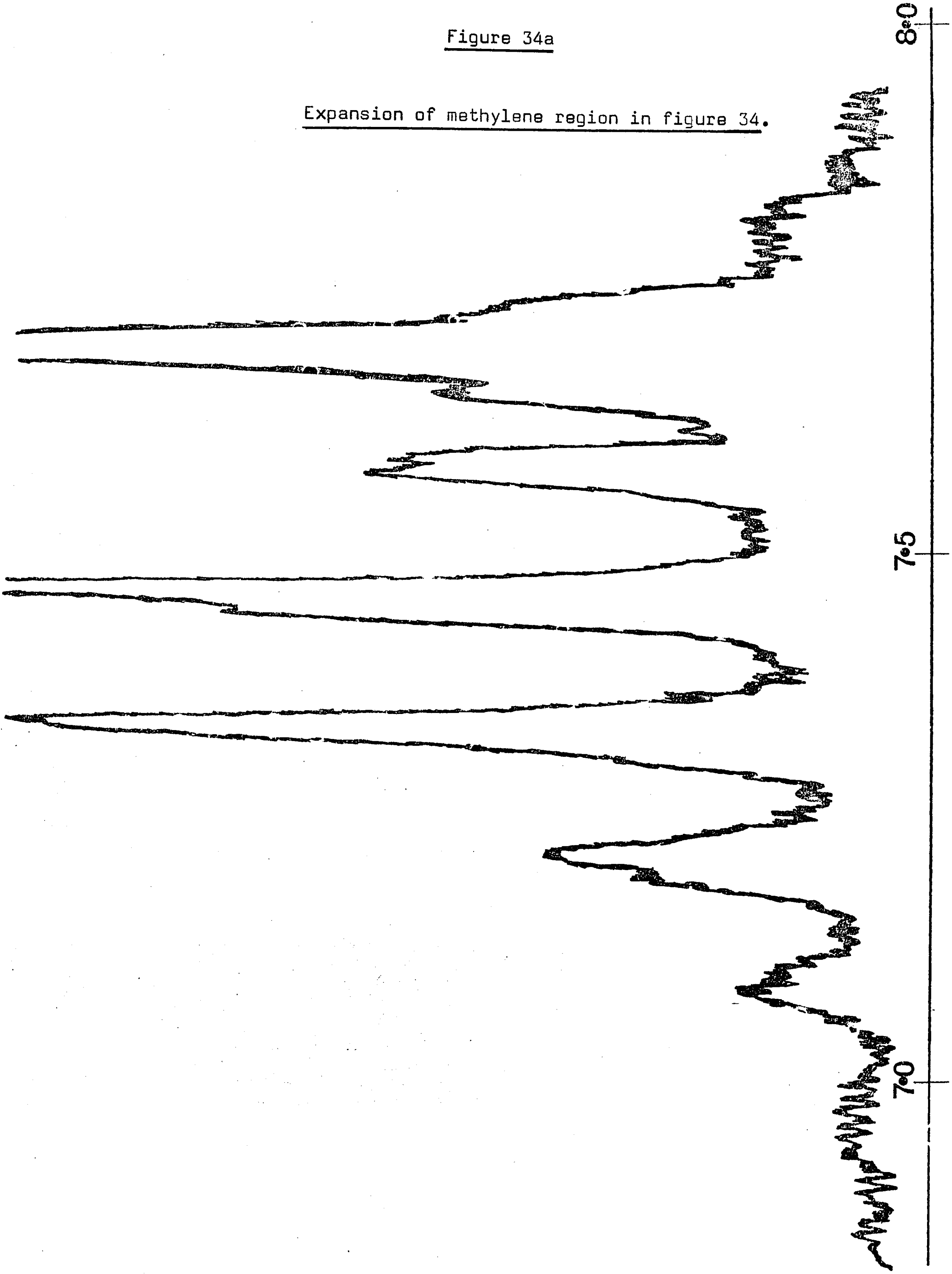


TABLE 37

N.M.R. INTENSITY RATIOS IN FIGURE 34a

Calculated	1 :	3 :	7 :	13 :	13 :	7 :	39 :	1
Observed	1 :	2.4 :	6.8 :	14.4 :	17 :	9.3 :	31 :	1.2

Excessive noise prevented determination of platinum chemical shifts, and ^{195}Pt decoupling was therefore not possible. The chemical shift of free Et_2Te was too close to the coordinated ligand in this complex to monitor the effect of free ligand on the shape of the n.m.r. spectrum. Nevertheless, the retention of ^{195}Pt coupling at room temperature means that pyramidal tellurium inversion is responsible for the simple A_2 pattern of the methylene protons in $(Et_2Te)_2Pt(p\text{-tolyl})_2$. Tellurium, just like sulphur and selenium, inverts! Cooling the spectrum down to -60°C does not alter its appearance, setting an upper limit on the rate of tellurium inversion.

ISOMERISATION

The intensity ratios given in Table 36 show that $(Et_2Te)_2Pt(p\text{-tolyl})_2$ was being examined, and the simplicity of the methyl region indicates that only one isomer was present. The upper limit placed on the rate of tellurium inversion suggests that the inverting centre is trans to a high trans-effect ligand, namely $p\text{-PhCH}_3$, and that this is in fact the cis-isomer. Its sharp melting point was taken as an indication of its purity. A solution of this isomer in CH_2Cl_2, kept for 6 weeks in the dark, showed an invarient n.m.r. spectrum, illustrating the stability of the cis-isomer in solution. Recrystallisation, however led to isomerisation. The yellow solid was dissolved in MeOH, filtered and H_2O added to precipitate the complex. A brown solid came out of solution. Its analysis was consistent with $(Et_2Te)_2Pt(p\text{-tolyl})_2$ and was therefore taken to be the trans-isomer. It melted between 64-65°C to a yellow solid, which then melted in the range ca. 95-100°C, just below the region at which the original solid melted. This is indicative of trans $\rightleftharpoons$ cis isomerisation. The yellow liquid remaining from the recrystallisation still contained the cis-complex, demonstrated by evaporating off the solvent and recovering a yellow solid which melted in the range 105-113°C. This sample rapidly turned brown on exposure to air and light.

The isolation of the original pale yellow solid from an ether solution and its subsequent behaviour in $MeOH/H_2O$ and CH_2Cl_2 solutions are consistent with the cis-complex being more stable in polar solvents, presumably because of large dipole-dipole interactions. Table 38 below shows the dielectric constants for these solvents.

TABLE 38

DIELECTRIC CONSTANTS OF VARIOUS SOLVENTS(126)

SOLVENT	ε_{20}
MeOH	33.6
H_2O	80.4
Et_2O	4.3
CH_2Cl_2	9.1

cis-$(Et_2Te)_2Pt(p\text{-tolyl})_2$ stayed in solution in the highly polar solvents, but came out of solution when Et_2O was used as solvent. In addition, the observation that trans- complexes are normally more strongly coloured than cis-complexes and generally have lower melting points(150), leave little doubt that we are dealing with the cis- and trans-isomers of $(Et_2Te)_2Pt(p\text{-tolyl})_2$. The ^1H n.m.r. spectrum of the brown solid however, showed, in addition to these peaks obtained for the yellow solid, other resonances, most of which could not be identified. Since the spectrum was obtained about 3 hours after dissolving the solid in CD_2Cl_2, it would seem that not only had trans $\rightleftharpoons$ cis isomerisation taken place, but that rapid decomposition in solution to produce among other things, toluene or bitoluene had occurred. Black particles were deposited at the bottom of the n.m.r. tube and could have been either tellurium or platinum or both.

(2) PALLADIUM

Table 39 shows a list of the coalescence temperatures of trans-$(Et_2Te)_2PdHal_2$ complexes in a variety of solvents. The variation is readily explained in terms of the dramatic effect of even small amounts of Et_2Te on the appearance of the spectra. Presumably in these cases where no coalescence was observed, small amounts of free ligand were present, and the process of ligand exchange - recombination catalysed. Extreme caution must therefore be exercised when examining such compounds for inversion coalescences. Not only must no free Et_2Te be present initially when examining for inversion coalescences, but also decomposition to produce free ligand must also be avoided, otherwise the process of ligand exchange-recombination will be catalysed. Because of this it might never be possible, by these and similar methods, to establish tellurium inversion at palladium definitively. Even reproducibility and solvent independence do not necessarily prove tellurium inversion. In fact, the general absence of both these factors, and the lack of any specific order within the halogen series indicates that tellurium inversion is probably not responsible for these observations and strongly suggests that, as in the case of the corresponding platinum complexes, the coalescences are a function of their thermal and/or photochemical stabilities.

TABLE 39

COALESCENCE TEMPERATURES OF TRANS-$(Et_2Te)_2PdX_2$ COMPLEXES IN VARIOUS SOLVENTS

X	T_A	T_B	T_C
Cl	30	<-60	/
Br	51,39	47	<-30
I	18	19	/

T_A is the coalescence temperature (°C) in chlorobenzene,

T_B in deuterochloroform and

T_C in 1,1,2,2 - tetrachloroethane.

G) BENZYL COMPLEXES

The use of the approximate equation

$$k = \pi/\sqrt{2}\ (\Delta v_{AB}{}^{2} + 6\ J^{2})^{\frac{1}{2}}$$

in the determination of Free Energies of Activation is thought to give rise to large systematic errors if the A and B protons couple not only to each other, but also to other nuclei in the molecule(77). Since this is the case with the diethyl-chalcogen complexes already studied, it was decided to examine the coalescence phenomena of a series of benzyl complexes of the type trans- $[(PhCH_2)_2S]_2PdHal_2$ with the intention of comparing the above approach (Method I) with the computer simulated procedure (Method III) (see pages 25-28) of obtaining $\Delta G^{\ddagger}$ values. In addition, the effect of the variation of the organic group on the coalescence temperature was of interest in itself, since in all previous experiments only ethyl groups were attached to sulphur. Moreover, the v.t.n.m.r. behaviour of both cis- and trans-$(Bz_2S)_2PtCl_2$ had already been examined(96) and comparison with a palladium analogue seemed desirable. Unfortunately, the coalescence temperatures of our complexes were considered too low to enable rate constant determinations by the approximate method (I) and because of this and other complications, computer simulated spectra were not obtained. Nevertheless, interesting results emerged from this study.

CHARACTERISATION OF COMPLEXES

The four complexes involved in this study, namely $(Bz_2S)_2PdHal_2$ (Hal = Cl, Br or I) and $(MeSBz)_2PdCl_2$ were all synthesised by standard techniques(151). A trans-configuration in solution was assumed for all structures, and verified for $(Bz_2S)_2PdCl_2$ by dipole-moment measurement (μ = 2.0 D in benzene solution at 19°C). Their ^1H n.m.r. spectra at room temperature (Table 48) were all consistent with the structures shown above.

VARIABLE TEMPERATURE N.M.R.

The n.m.r. spectrum of trans-$(Bz_2S)_2PdCl_2$ in $CDCl_3$ at -47°C (Figure 35) consists not of the expected single quartet, but of two, in the methylene region. Both have similar coupling constants, but coalesced to singlets at different temperatures (Figures 35-38). As the temperature was raised, the intensity ratio of the signals altered. (Table 42). The same behaviour was also found when CD_2Cl_2 was used as solvent, but in both cases the coalescence temperatures of the low field quartet were identical. Vastly different coalescence temperatures were found for the high field quartet. A summary of these results is contained in Table 40.

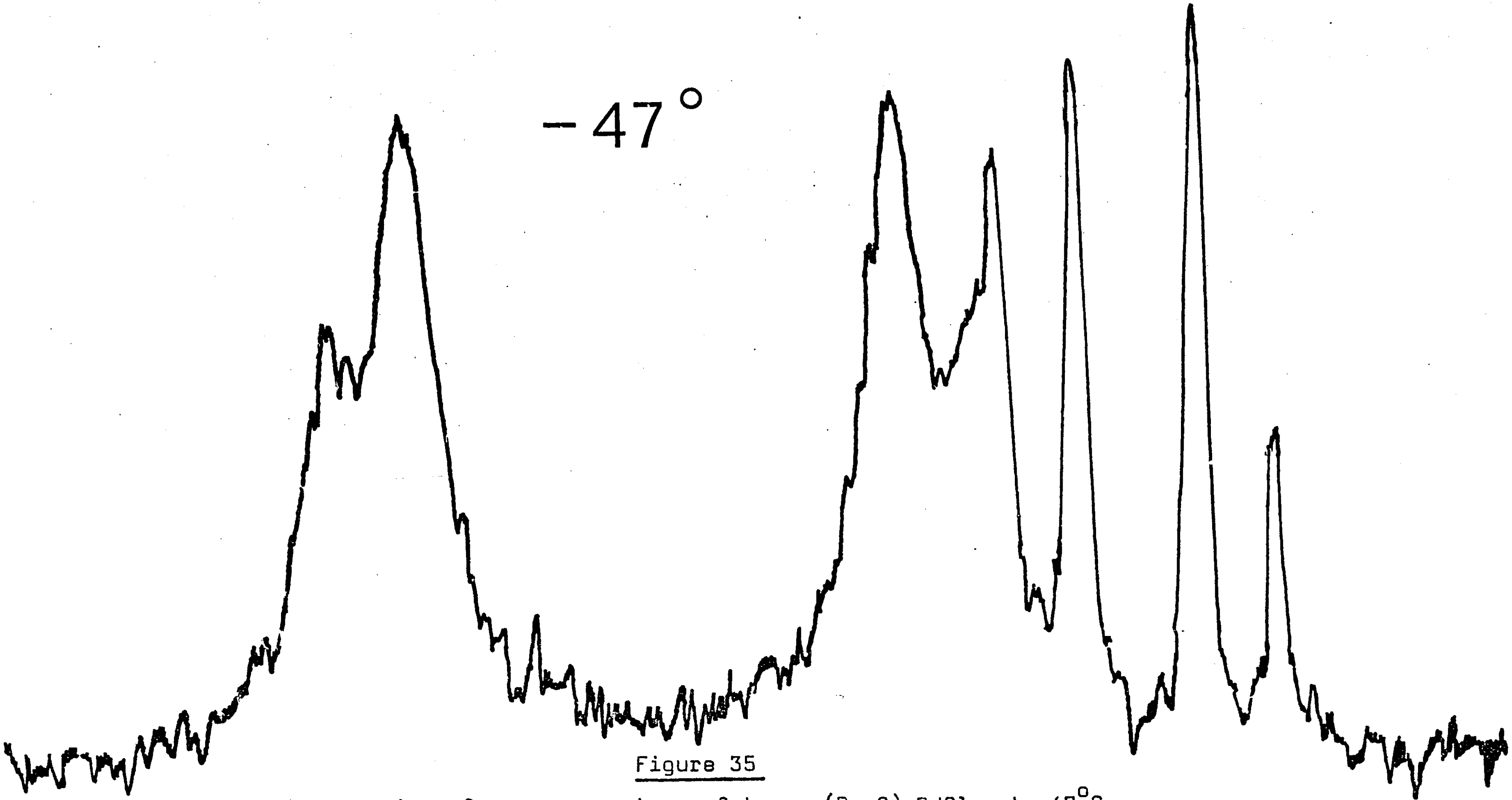


Figure 35

Methylene region of n.m.r. spectrum of trans-$(Bz_2S)_2PdCl_2$ at -47°C.

Figure 36

Methylene region of n.m.r. spectrum of trans-$(Bz_2S)_2PdCl_2$ at -30°C.

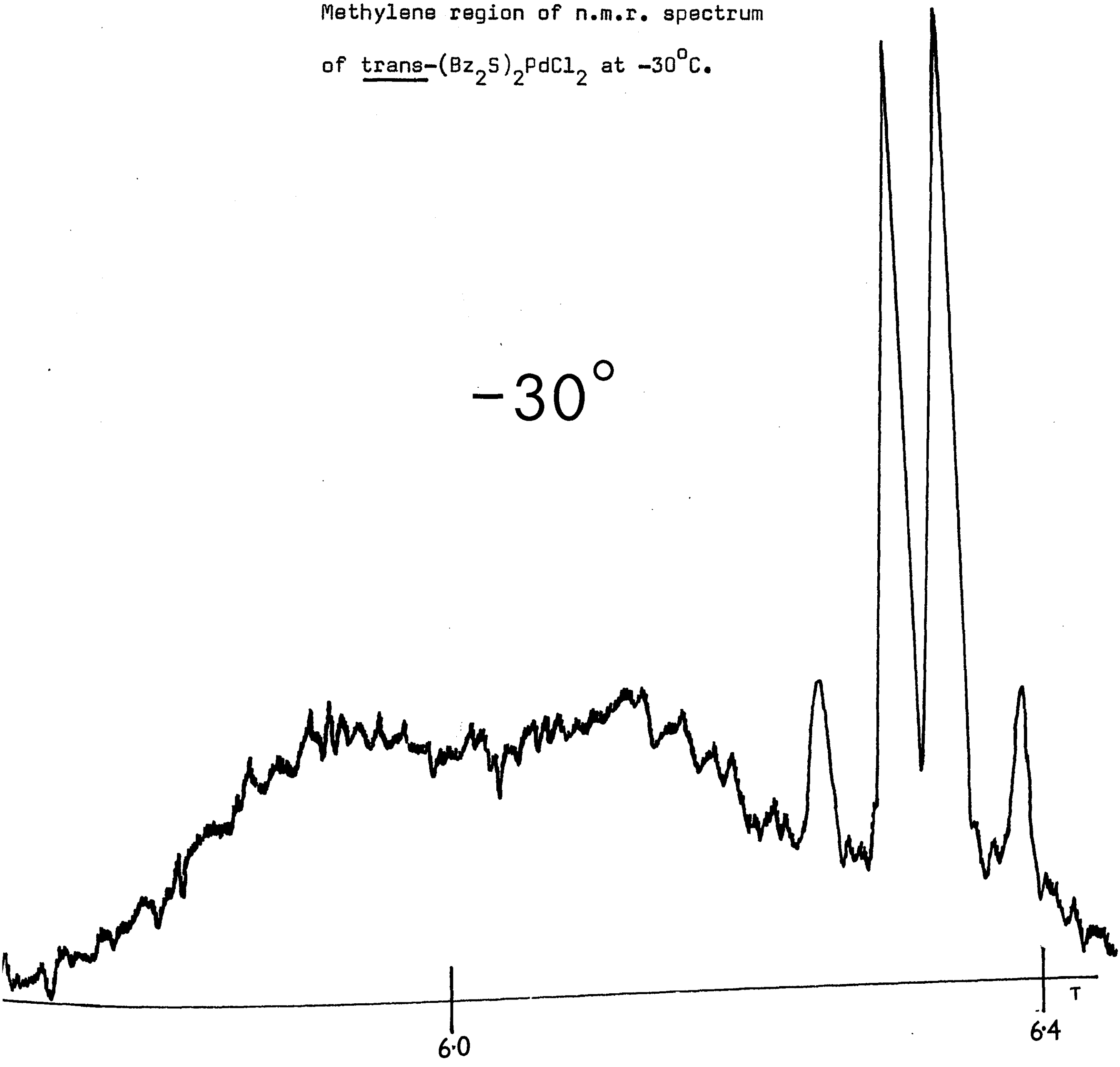


Figure 37

Methylene region of n.m.r. spectrum of trans-$(Bz_2S)_2PdCl_2$ at -24^oC.

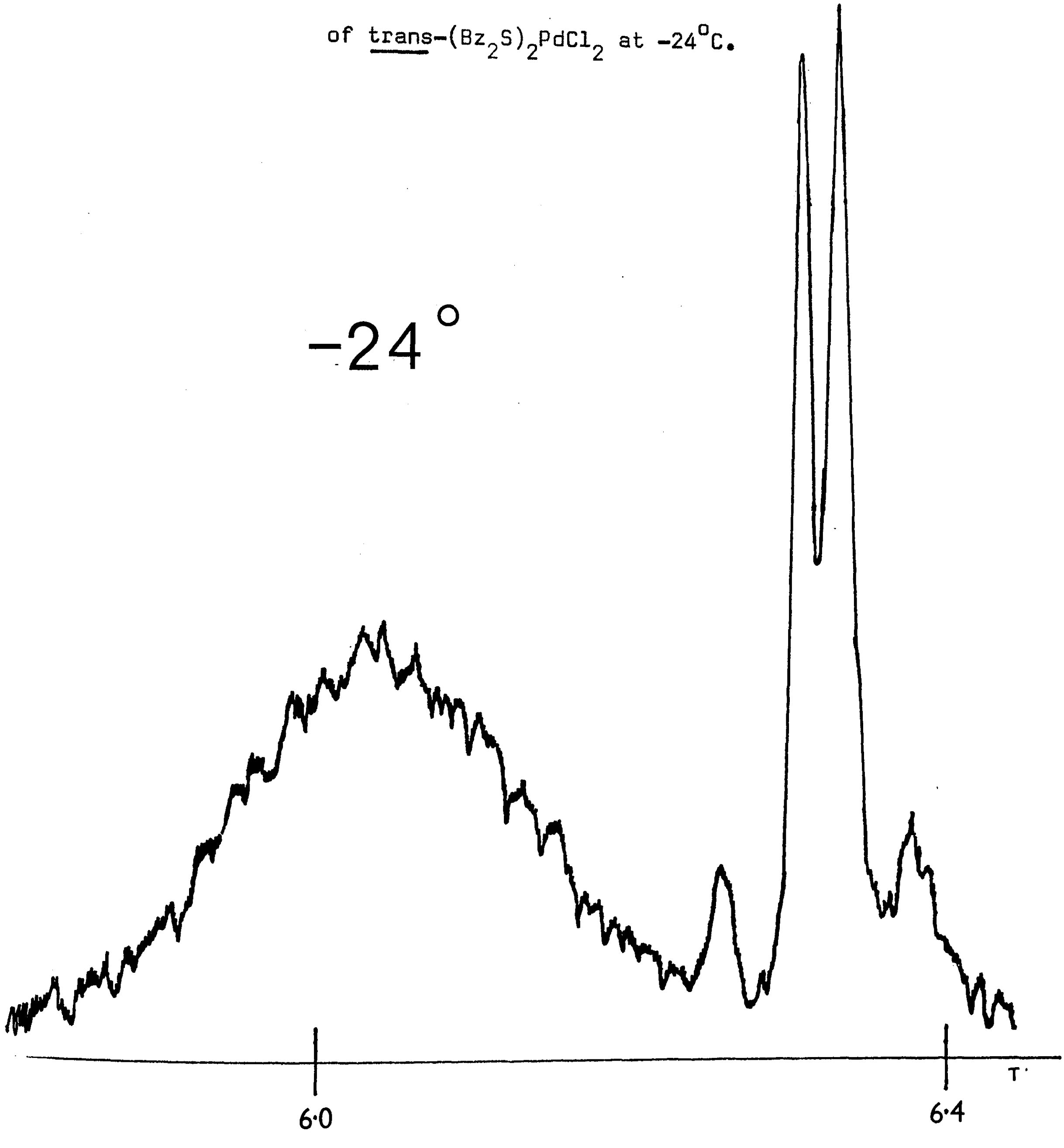


Figure 38

Methylene region of n.m.r. spectrum of trans-$(Bz_2S)_2PdCl_2$ at $-10^{\circ}C$.

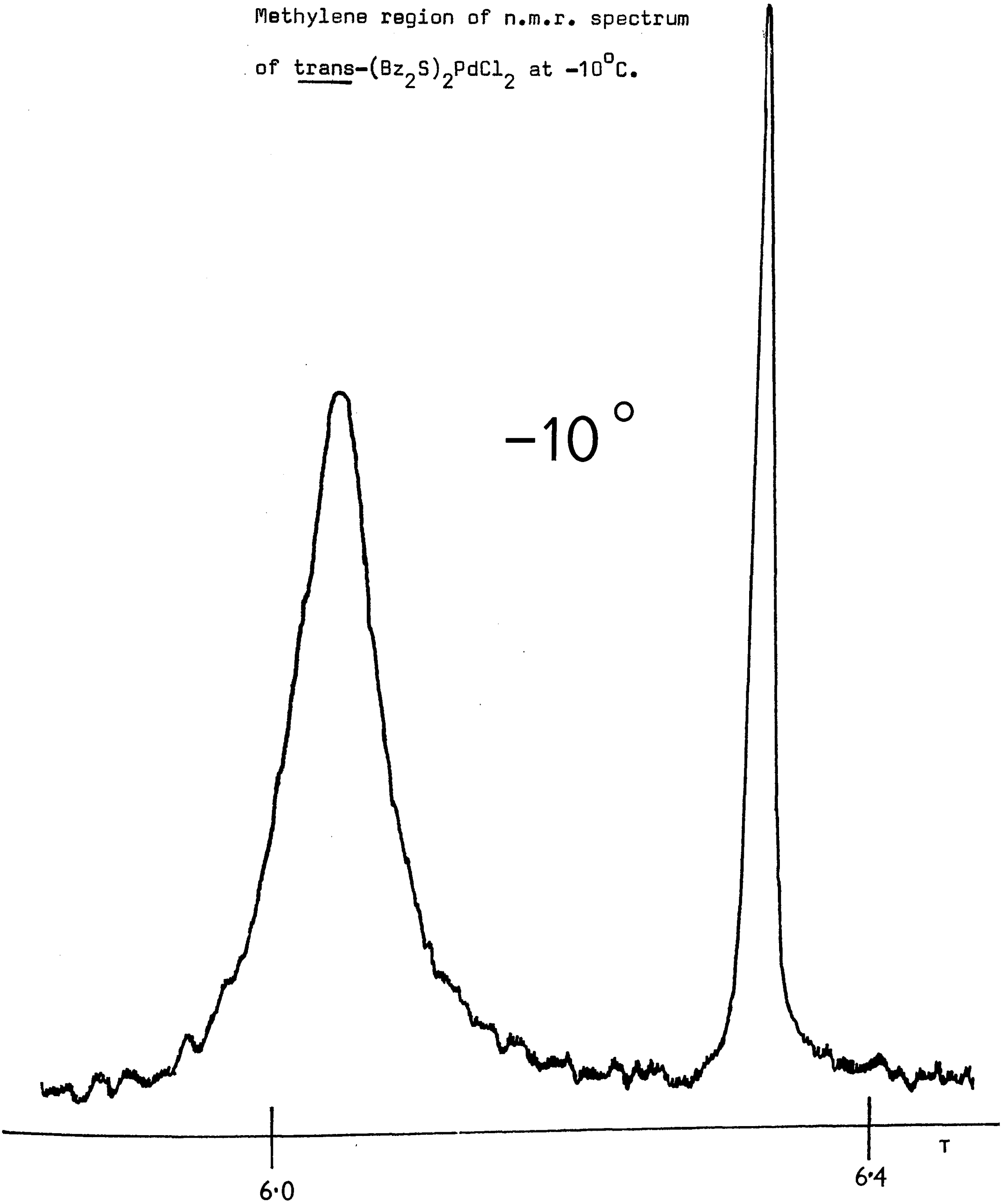


TABLE 40

COALESCENCE TEMPERATURES OF TRANS-$(Bz_2S)_2PdCl_2$

Solvent	Signal	T_c (°C)
$CDCl_3$	low field	-28
CD_2Cl_2	low field	-28
$CDCl_3$	high field	-20
CD_2Cl_2	high field	-55

LOW FIELD SIGNAL

The invariance of the coalescence temperature of the signal to low field, and its similarity to that of *trans*-$(Et_2S)_2PdCl_2$ (T_c = -29°C) suggests that a similar dynamic process is occurring in both molecules, namely pyramidal sulphur inversion. Thus, at temperatures below that of coalescence, the prochiral(78) centre at sulphur causes non-equivalence of the benzyl methylene protons, and an AB quartet (J ≈ 12 Hz) is observed. As the temperature is raised, inversion at sulphur confers equivalence on these protons and a concentration— and solvent— independent coalescence to a singlet results. The ambiguity between this and a ligand exchange mechanism was resolved by addition of excess dibenzylsulphide and observing reversible inversion (T_c^1) and exchange (T_c^2) coalescences. (Figures 39 and 40).

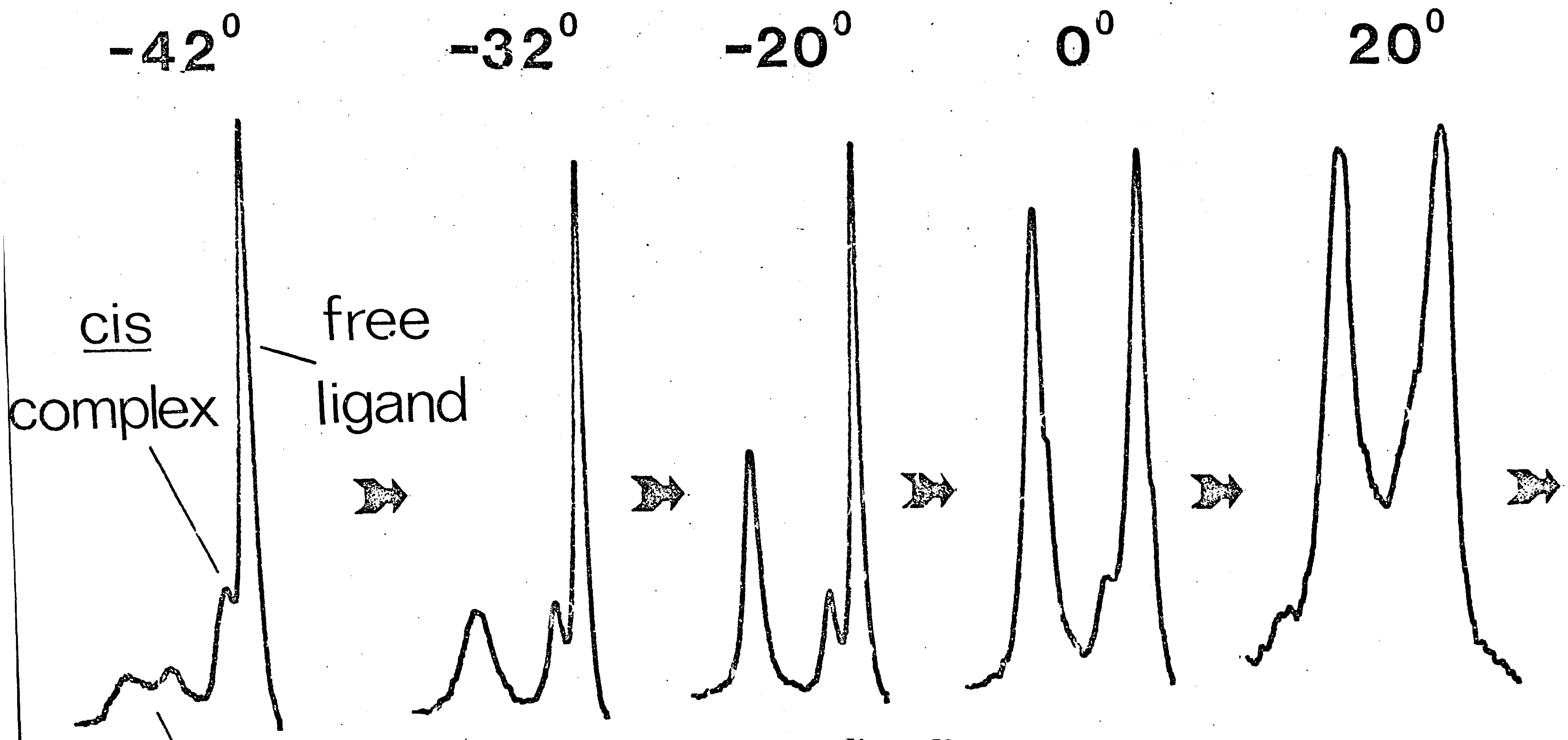


Figure 39

Temperature dependence (°C) of n.m.r. spectrum of trans-$(Bz_2S)_2FeCl_2$ in $CDCl_3$.

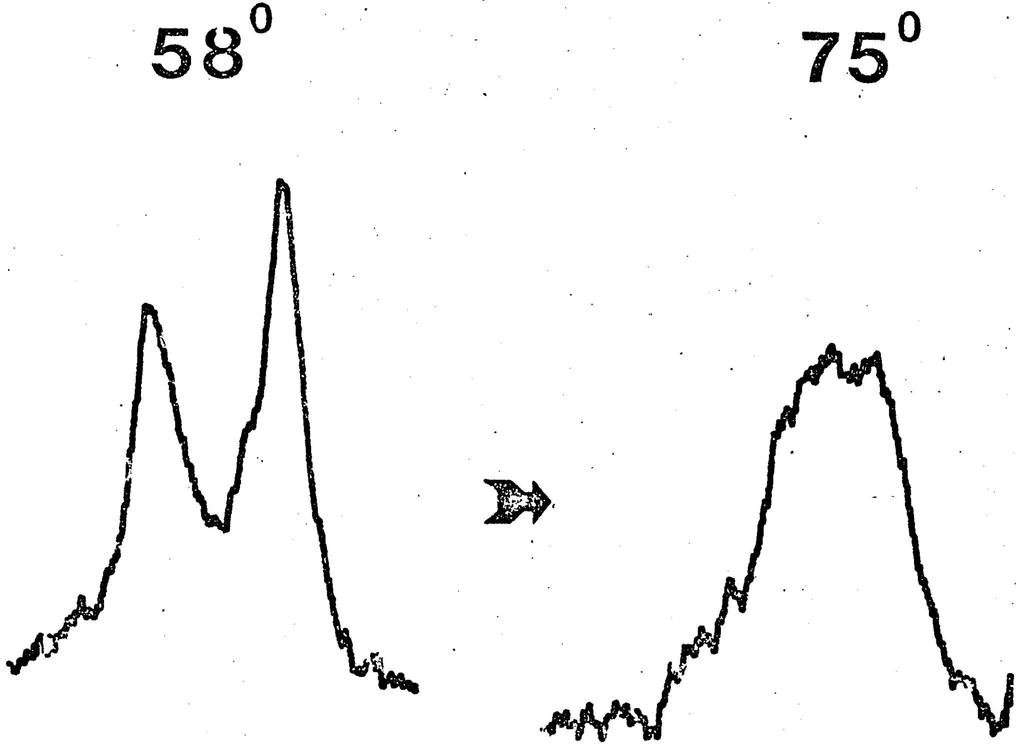


Figure 39 (continued)

Figure 40

Temperature dependence of n.m.r. spectrum of trans-$(Bz_2S)_2PdCl_2$ in $Cl_2CH-CHCl_2$

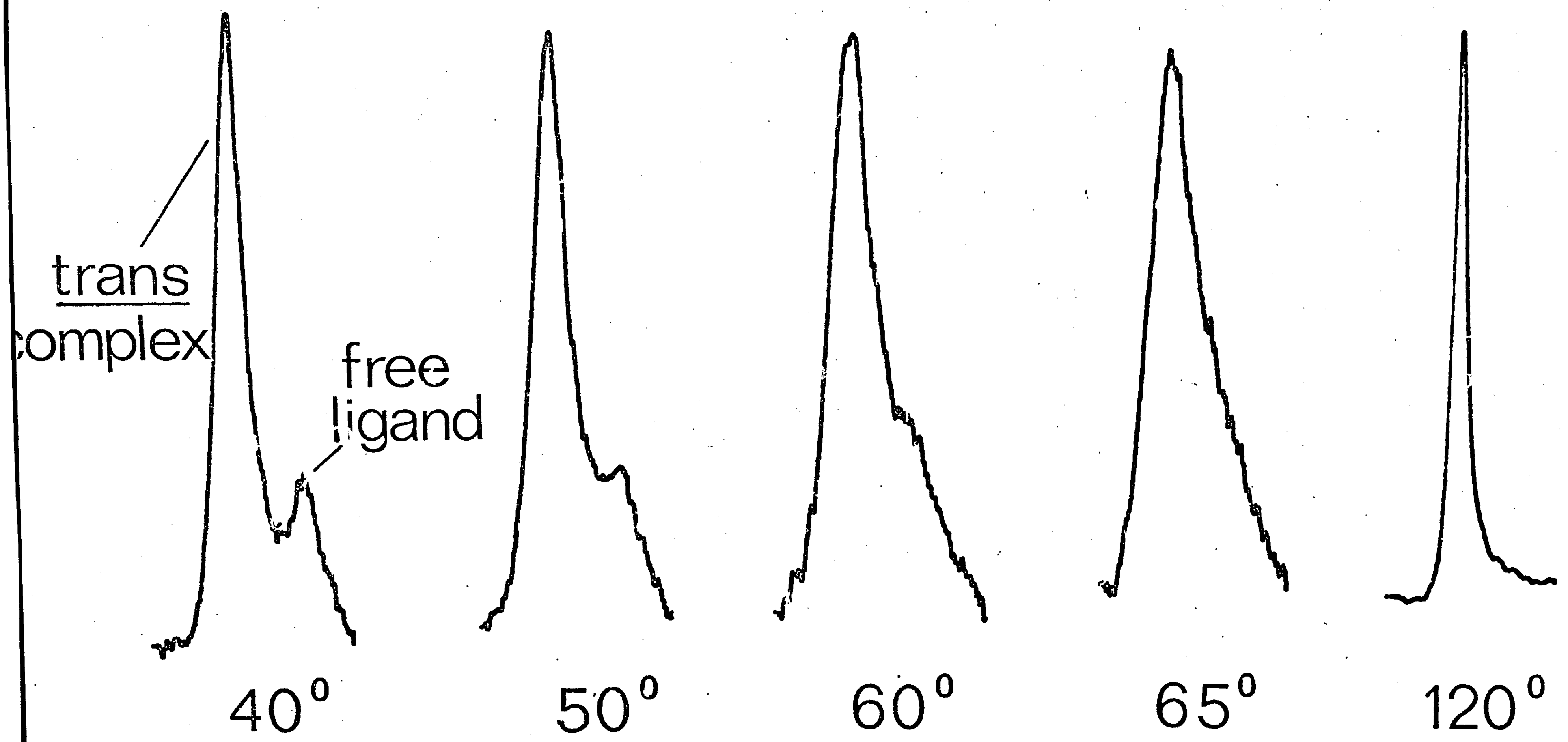


TABLE 41

COALESCENCE TEMPERATURES OF LOW FIELD SIGNAL OF TRANS-$(Bz_2S)_2PdCl_2$

Solvent	T_c^1 (°C)	T_c^2 (°C)
$CDCl_3$	-32	≈ 80
Cl_2CH-$CHCl_2$	-25	≈ 65

This behaviour too, is similar to that shown by the trans-$(Et_2S)_2PdHal_2$ complexes.

HIGH FIELD SIGNAL

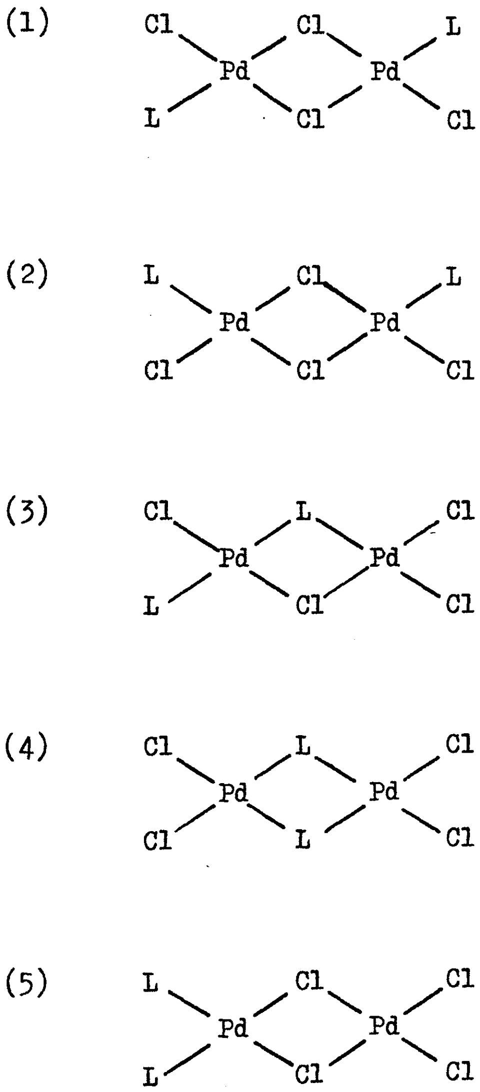
A ORIGIN

The origin of the second quartet is not particularly well understood. The chemical shift separation from the main signal is never more than ca. 0.4 ppm. and suggests a similar species to trans-$(Bz_2S)_2PdCl_2$. Furthermore the (AB) coupling constant is also ca. 12 Hz. Some considerations of the possible sources of this high field signal are therefore necessary.

a) Restricted Pd-S rotation could in theory produce up to 4 AB quartets at low temperatures. These should either coalesce on heating to one AB quartet and then to a singlet, or to four singlets and then the one singlet, depending on the relative energies of Pd-S rotation and the dynamic process causing collapse of the quartet to the singlet. However, coalescence of the separate signals is never observed, even in $PhNO_2$ solution up to 170°C. In fact the high field singlet disappeared at ca. 80°C in this experiment. Furthermore, we have never found any evidence for either restricted Pd-S or Pt-S rotation in our studies of other similar complexes, and Haake and Turley(96) have also made similar observations about restricted Pt-S rotation. The high field signal is therefore not due to restricted Pd-S rotation in trans-$(Bz_2S)_2PdCl_2$.

b) Dimerisation to form bridging species of the type depicted below, (L = Bz_2S),

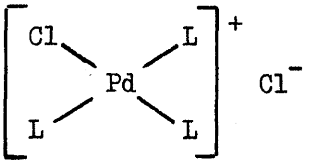
FIGURE 41



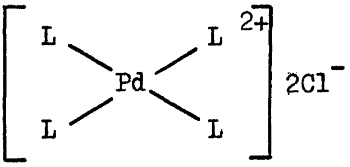
would result in resonances with similar chemical shifts and coupling constants to that exhibited by <u>trans</u>-$(Bz_2S)_2PdCl_2$.

These dimers are prone to facile bridge-cleavage in the presence of excess ligand$^{(33)}$, but the high field signal remained even when excess Bz_2S was added. Dimers are therefore not responsible for the high field signal.

c) Ionic species such as



and



would only be expected in the presence of excess L (L = Bz_2S), but coalescences occurred when no excess ligand was present. The singly charged species above can also be ruled out on the grounds that L is <u>trans</u> to two different types of substituent on the metal with differing <u>trans</u>-influences, and if no accidental chemical shift equivalence occurs, two different sets of resonances would be expected.

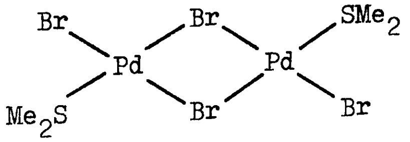
d) The sulphonium ion $\underline{Bz_3S^+Cl^-}$ is ruled out since there is no non-equivalence of the benzyl methylene protons in this species, and anyway, the inversion barriers for sulphonium ions generally lie in the range 25-29 Kcal/mole$^{(152)}$, (104-121 KJ/mole) which is just outside the range of n.m.r. measurement.

e) Cis-$(Bz_2S)_2PdCl_2$ could be stable enough at low temperatures to account for the similar n.m.r. parameters. Although many cis and trans platinum complexes have been prepared, not many pairs of isomers of palladium have been isolated. Nevertheless studies using infrared and n.m.r. methods in the last 12 years have shown that cis complexes of palladium are indeed more common than originally believed(153-158). A closer look at the relative stabilities and formation of cis- and trans-isomers in solution is required.

The Free Energy change (ΔG) for cis $\rightleftharpoons$ trans isomerisation depends on both enthalpy (ΔH) and entropy (ΔS) terms, according to the equation:-

$$\Delta G = \Delta H - T\Delta S.$$

The major contributions to ΔH are the change in internal bond energy (ΔH_E) and the change in the enthalpy of solvation (ΔH_S). If the relative bond strength order is Pd-S > Pd-Cl, this means that the total bond strength depends more on the Pd-S bonds than on the Pd-Cl bonds, and it is more important that the metal-sulphur bonds be as strong as possible. As a consequence of the greater trans-influence of the R_2S ligands, (the bond trans to R_2S in



is longer than the bond trans to the halogen(159)), ΔH_E should favour formation of cis-$(Bz_2S)_2PdCl_2$ rather than the corresponding trans-isomer. Also, because of the much larger dipole of the cis-complexes (generally of the order of 9 D in Pt complexes)$^{(160)}$, dipole-dipole interactions with polar solvents are greater, and the ΔH_S term favours the cis-isomer. However, a higher degree of solvation is expected for a cis-complex and a large positive ΔS value (favouring the trans-isomer) should accompany a cis to trans conversion. (Chatt and Wilkins$^{(161)}$ have previously argued that ΔS involves release of two molecules of solvent during the course of the isomerisation process of cis-platinum complexes). Thus ΔH favours the cis geometry and ΔS the trans. Conditions which promote trans $\rightleftharpoons$ cis isomerisation are, we believe, met by cooling a solution of the trans-complex in a polar solvent. By restricting the movement of solvent at low temperatures, the entropy factor is diminished, and, assuming that $T\Delta S$ is of comparable magnitude to ΔH, the Free Energy of Isomerisation approaches zero. At low temperatures therefore the trans $\rightleftharpoons$ cis equilibrium is shifted to the cis- side. In the course of this work, Cooper and Powell reported$^{(162)}$ a temperature dependent cis:trans isomer ratio found for $(Me_2(o\text{-tolyl})P)_2PdCl_2$. This was >95% cis at -20°C in $CDCl_3$. We postulate therefore, that the second signal (6.34τ) in Figures 35-38 is due to cis-$(Bz_2S)_2PdCl_2$. Our hypothesis was tested in a number of ways.

1) The *trans*:*cis* ratio was compared over a ca. 50°C temperature range with that of the corresponding bromide. The higher *trans*-influence of Br^- reduces the contribution from the ΔH_E term to the stabilisation of the *cis*-isomer, and less is formed(163).

TABLE 42

TRANS : CIS ISOMER RATIOS OF $(Bz_2S)_2PdHal_2$ COMPLEXES IN $CDCl_3$

Chloride		Bromide	
T°C	*trans*:*cis* ratio	T°C	*trans*:*cis* ratio
-28	1.6 : 1	-25	4 : 1
-20	2.4 : 1	-16	6 : 1
-10	3 : 1	-7	8 : 1
-1	4.7 : 1	+1	9 : 1
+19	8 : 1	+21	19 : 1

The ratios shown were not reproducible, but generally remained within the order shown.

2) The polarity of the solvent was varied in the manner shown in Table 43.

TABLE 43

TRANS : CIS ISOMER RATIOS OF $(Bz_2S)_2PdCl_2$ AS A FUNCTION OF SOLVENT AT -23°C

Solvent	Diel. Const.(126)	trans:cis ratio
CD_2Cl_2	9.1	2.5 : 1
$CDCl_3$	4.8	1.5 : 1
$PhCH_3$	2.4	2.4 : 1

It was hoped that the more polar solvents would favour *cis*-formation, but the figures shown were again non-reproducible. This last feature, apparent in investigations (1) and (2), indicates that *trans* $\rightleftharpoons$ *cis* equilibration had not taken place in the time interval of the measurements. We suggest therefore, as an extension of this work, that carefully controlled studies on this system could be carried out and equilibrium constants leading to Free Energies of Isomerisation be determined.

3) The variable temperature n.m.r. of trans-$(MeSBz)_2PdCl_2$ was investigated for the following reasons. In the course of this work, thermodynamic parameters for cis$\rightleftharpoons$trans equilibria of platinum complexes of the type $(RR'S)_2PtHal_2$ were published(134). The relevant free energy changes, ($CHCl_3$ solvent) are summarised in the table below.

TABLE 44

CIS-TRANS EQUILIBRIA OF $(RR'S)_2PtHal_2$ COMPLEXES[a]

Complex	ΔG (cis $\rightleftharpoons$ trans) (Kcal/mole)
a) $(Bz_2S)_2PtCl_2$	+1.15
b) $(Bz_2S)_2PtBr_2$	+0.45
c) $(MeSBz)_2PtCl_2$	-0.16

a) Taken from Ref.134.

On the assumption that a similar trend holds for the corresponding palladium derivatives, less cis-isomer might be formed on cooling a solution of trans-$(MeSBz)_2PdCl_2$ than had been found for either the dibenzyl chloride or bromide complexes. Accordingly, trans-$(MeSBz)_2PdCl_2$ was synthesised, and its ^1H n.m.r. spectrum at room temperature obtained. The methylene region consisted of a sharp singlet, but virtually nothing in a similar position to that described previously for the dibenzylsulphide complexes. On lowering the temperature, however, another signal did appear to high field of the singlet, and at -35°C, it integrated as 1/9th of the original singlet (A reversible coalescence (singlet → quartet) at -34°C was recorded for the main signal, and this was rationalised, as in previous cases, in terms of pyramidal inversion at sulphur in _trans_-$(MeSBz)_2PdCl_2$). A _trans_ : _cis_ ratio of ca. 9 : 1 was observed then at the following temperatures for the three complexes:-

TABLE 45

TEMPERATURE OF TRANS:CIS RATIOS OF CA. 9 : 1 IN $(RR'S)_2PdHal_2$ COMPLEXES

Complex	Temp.(°C)
$(Bz_2S)_2PdCl_2$	$> +19$
$(Bz_2S)_2PdBr_2$	+1
$(MeSBz)_2PdCl_2$	-35

Going from dibenzyl-to methylbenzyl-sulphide increases the basicity of the ligand but diminishes its ability to accept π-electron density. A reduction in the contribution of the ΔH_E term to the stabilisation of cis-$(MeSBz)_2PdCl_2$ would explain the virtual absence of this isomer at ambient temperatures.

B BEHAVIOUR OF HIGH FIELD SIGNAL

The range of coalescence temperatures exhibited by what we postulate as cis-palladium complexes, adds more mystery to an already complicated story. Figures 37 and 38 show spectra either side of the coalescence temperature of cis-$(Bz_2S)_2PdCl_2$ in $CDCl_3$. As discussed previously, the proportion of this isomer decreased with increasing temperature, until at -10°C, a ratio of ca. 3:1 (trans:cis) was obtained. Table 46 shows the coalescence temperatures of mainly unknown concentrations of the complexes in different solvents. All the coalescences shown were obtained with undetermined concentrations, and attempts to reproduce them were unsuccessful. As a consequence of this, the reversibility, as well as the effect of concentration and solvent on the coalescences were never tested, but it would appear that they are in fact concentration and probably also solvent dependent.

An inversion coalescence of cis-$(Bz_2S)_2PdCl_2$ by analogy with the corresponding platinum derivative, would be expected to occur at a somewhat higher temperature than -28°C, the coalescence temperature of trans-$(Bz_2S)_2PdCl_2$.

TABLE 46

COALESCENCE TEMPERATURES OF

CIS-$(Bz_2S)_2PdHal_2$ COMPLEXES

Complex	Solvent	T_c(°C)
$(Bz_2S)_2PdCl_2$	CD_2Cl_2[a]	-55
"	CD_2Cl_2	≈ -80
"	CH_2Cl_2[b]	≈ -80
"	$CDCl_3$[c]	-20
"	$C_6D_5CD_3/CDCl_3$	NONE[d]
$(Bz_2S)_2PdBr_2$	CD_2Cl_2[a]	-25
	$PhCH_3$	NONE
	$CDCl_3$	NONE[d]
$(Bz_2S)_2PdI_2$	$PhCH_3$	NONE

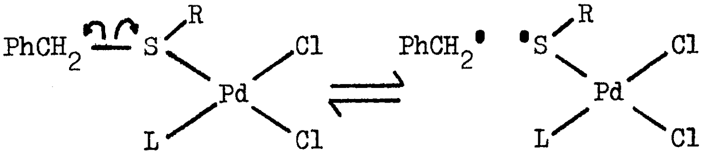
a) 100 MHz

b) known concentration (0.11M)

c) 220 MHz

d) small temperature independent peaks observed, probably due to impurities.

In some cases, however, a lower value is observed. This, together with its irreproducibility, and concentration and solvent dependences, make it certain that pyramidal sulphur inversion is not responsible for the temperature dependent behaviour of this species. Indeed, neither is fast exchange of ligand, since addition of free ligand (Figure 39) does not cause coalescence of the two signals, even at temperatures well above that of coalescence. A plausible explanation is one involving benzyl radicals. A possibility is homolytic scission of the sulphur-carbon bonds, followed by cage recombination:-



The two radicals are generated in close proximity to each other within a solvent cage. Before diffusing out of the cage they undergo collision with each other and combine to regenerate the initial complex. Such a process will lead to equivalent benzyl protons since the prochiral centre at sulphur is destroyed. It will also be dependent on the ability of the solvent to cage the radicals and be susceptible to radical scavengers in the solvent.

However, we have no direct evidence for radical formation. Our postulate is based on the irreproducibility of the coalescences and by failure to account for them by other, better understood, mechanisms. The observations of Mislow and coworkers(164) are nevertheless consistent with the above approach, albeit in a different system. They found that optically active benzyl-p-tolyl-sulphoxide racemised thermally in benzene at a rate 10^3 to 10^4 faster than either phenyl-p-tolyl-sulphoxide or methyl-p-tolyl-sulphoxide. The latter two had been shown previously(165) to racemise by a pyramidal inversion mechanism. They postulated, and in fact proved, that sulphoxide racemisation in $PhCH_2$-S(O)Ar occurred by a dissociative radical process. The greater stability of the benzyl radicals promoted dissociation into $PhCH_2^{\bullet}$ and $ArSO^{\bullet}$ radicals which then recombined to give the racemic mixture.

CONCLUSIONS

The Table overleaf summarises the inversion coalescence temperatures of the trans-benzylsulphide-palladium complexes in a variety of solvents.

TABLE 47

SULPHUR INVERSION IN PALLADIUM COMPLEXES

Complex	Solvent	T_c(°C)
1) $(Bz_2S)_2PdCl_2$	CD_2Cl_2[a]	-28
"	CH_2Cl_2[b]	-30
"	$CDCl_3$[c]	-28
"	$C_6D_5CD_3/CDCl_3$[d]	-29
2) $(Bz_2S)_2PdBr_2$	CD_2Cl_2	-35
"	$C_6H_5CH_3$	-40
"	$CDCl_3$	-38
3) $(Bz_2S)_2PdI_2$	$C_6H_5CH_3$	-46
"	CD_2Cl_2	-44
4) $(MeSBz)_2PdCl_2$	CD_2Cl_2	-34

a) 100 MHz.

b) 0.11 M. solution.

c) 220 MHz.

d) only a trace of $CDCl_3$ added.

CIS-EFFECT

There seems to be a *cis*-effect operative in the inversion rates of the dibenzyl-sulphide-palladium complexes. Iodide causes the greatest acceleration in the rate of inversion, and the order of ease is:-

$$I^- > Br^- > Cl^-$$

This suggests either extensive Pd-S bond weakening by the *cis*-iodide anion or better removal of electron density from the central metal ion which would facilitate sulphur lone-pair — metal overlap. The latter proposal is consistent with the proximity of palladium and iodine in the periodic table, leading to a stronger π-effect(165) and also with the results shown in Table 48. The chemical shift of the benzyl methylene protons is less in the iodide complexes (the order is $Cl^- > Br^- > I^-$) and indicates a drift of electron density from the ligand to the metal and then to the halogen. It is interesting to note that this *cis*-effect (or influence), contrary to observations in the past(166)(167), varies in the same direction as the *trans*-effect. It should be noted, however that its magnitude is less than that exhibited by the same ligands in *trans* positions. (Compare results in Table 25). A similar effect was noted in the coalescence temperatures of *trans*-$(Et_2Se)_2PdHal_2$ complexes (Table 18), but the cause of these coalescences was never unequivocally established.

TABLE 48

N.M.R. PARAMETERS OF $(RR'S)_2PdHal_2$ COMPLEXES

			CH$_2$ Protons			
Complex	Solvent	τ_{Ph}	τ_{trans}	τ_{cis}	J^{trans}_{A-B}	J^{cis}_{A-B}
$(Bz_2S)_2PdCl_2$	CD_2Cl_2^{a}	2.62	6.02	6.4	12.3	≈12
	$CDCl_3$^{b}	2.63	6.03	6.34	≈12	12.3
$(Bz_2S)_2PdBr_2$	CD_2Cl_2^{a}	2.66	5.91	≈ 6.3	≈ 12	≈ 12
	$CDCl_3$	/	5.90	/	≈ 12	/
$(Bz_2S)_2PdI_2$	CD_2Cl_2	2.63	5.72	/	≈ 12	/
	$CDCl_3$	/	5.80	/	/	/
$(MeSBz)_2PdCl_2$	CD_2Cl_2	2.58	5.83	≈6.2	≈13	/

a) 100 MHz

b) 220 MHz.

Coupling Constants in Hz.

R-GROUP

Comparison of the diethylsulphide, dibenzylsulphide and methylbenzylsulphide results below, suggests that steric and electronegativity effects are not important in determining the rate of sulphur inversion.

TABLE 49

INVERSION COALESCENCE TEMPERATURES OF $(RR'S)_2PdCl_2$ COMPLEXES

R	R'	T_c(°C)	Solvent
Et	Et	-24	PhCl
Bz	Bz	-28	CD_2Cl_2
Me	Bz	-34	CD_2Cl_2

Considering the ±5°C error on these coalescence temperatures, it would seem that altering the basicity or steric requirements of the sulphide ligand do not substantially alter the rate of sulphur inversion. The order of basicity of the ligands is $Et_2S > MeSBz > Bz_2S$, and that of steric requirement is $Bz_2S > MeSBz > Et_2S$.

The more electronegative substituents on sulphur in Bz_2S should lead to slower inversion rates, but steric relief on going to the transition state should result in faster sulphur inversion. The order of ease of inversion,

$$MeSBz > Bz_2S > Et_2S$$

indicates that neither effect dominates.

It is interesting to note that these effects are much more important when sulphur is coordinated to platinum. The Table below (50) shows the coalescence temperatures of a series of platinum complexes coordinated to the same sulphide ligands shown in Table 49.

TABLE 50

INVERSION COALESCENCE TEMPERATURES[a] OF

CIS-$(RR'S)_2PtCl_2$ COMPLEXES

R	R'	$T_c(^oC)$	Solvent
Et	Et	60 (1)[b]	$CDCl_3$
Bz	Bz	34 (<27)	$CDCl_3$
Me	Bz	36 (<-50)	CH_2Cl_2

a) Taken from Ref. 96

b) The values in parentheses are the coal. temps. of the corresponding *trans*-complexes.

Steric relief in the transition-state to inversion of the benzyl-containing complexes would seem to lead to faster inversion rates, but the role played by the basicity of the ligands is not clear.

H GENERAL SUMMARY

A) INVERSION

The fluxional process of pyramidal atomic inversion has been demonstrated for sulphur, selenium and tellurium, as summarised in Table 51. These are the first unequivocal demonstrations of both selenium and tellurium inversion. Some doubt exists as to the cause of the coalescences in L_2PtHal_2 complexes, where L = Et_2Te, but the relative order of the coalescence temperatures in this type of complex when L = Et_2S, Et_2Se, and the fact that tellurium can invert, suggests an order on the ease of pyramidal chalcogen inversion as:-

$$S > Se > Te$$

Similar observations have been made with inverting atoms in group V of the periodic table(168).

Inversion is solvent and concentration independent and is accelerated by coordinating the inverting centre to a transition metal. Palladium is more effective at increasing the inversion rate than platinum. The nature of the R groups plays little part in the rate of inversion in $(RR'S)_2PdHal_2$ complexes, but seems to be important in the corresponding platinum derivatives(96).

TABLE 51

SUMMARY OF INVERTING CHALCOGEN COMPLEXES

Complex	Solvent	T_c(°C)
SULPHUR		
cis- $(Et_2S)_2PtCl_2$	a	56
trans-$(Et_2S)_2PtCl_2$	a	6
trans-$(Et_2S)_2PtBr_2$	a	4
trans-$(Et_2S)_2PtI_2$	a	2
trans-$(Et_2S)_2PdCl_2$	a	-24
trans-$(Et_2S)_2PdBr_2$	a	-28
trans-$(Bz_2S)_2PdCl_2$	b	-30
trans-$(Bz_2S)_2PdBr_2$	b	-35
trans-$(Bz_2S)_2PdI_2$	b	-44
trans-$(MeSBz)_2PdCl_2$	b	-34
SELENIUM		
trans-$(Et_2Se)_2PtCl_2$	a	90
trans-$(Et_2Se)_2PtBr_2$	a	90
trans-$(Et_2Te)_2PtI_2$	a	90
$(EtSeC_2H_4SeEt)PtCl_2$	c	>180
$(EtSeC_2H_4SeEt)PtBr_2$	c	150
$(EtSeC_2H_4SeEt)PtI_2$	c	140
$(EtSeC_2H_4SeEt)PdCl_2$	c	95
$(EtSeC_2H_4SeEt)PdBr_2$	c	85
$(EtSeC_2H_4SeEt)PdI_2$	c	70
TELLURIUM		
cis- $(Et_2Te)_2Pt(p\text{-tolyl})_2$	b	<-60

a) PhCl b) CD_2Cl_2 c) $PhNO_2$

(1) TRANS EFFECTS

A strong trans-effect ligand increases the rate of inversion, and the trans-effect order of

$$I^- > Br^- > Cl^-$$

has been confirmed(149) in our study of chelate complexes. Although we can say nothing about the relative trans-effect order within the chalcogens, other orders such as

$$p\text{-tolyl} > Et_2Te$$

and

$$Et_2S > Cl^-$$

have been determined.

(2) CIS EFFECTS

We have found no evidence for cis-effects in the platinum complexes. However cis-ligands in benzyl palladium complexes cause an acceleration in the rate of inversion in the order

$$I^- > Br^- > Cl^-$$

This is the same order found for trans-effects(99), but the magnitude of the rate accelerations is not so great.

(3) MECHANISM

We have suggested that the classical mechanism of inversion (i.e., through a planar transition state, as outlined in Figure 18) offers a better description of inversion than Haake and Turley's postulate(96). We invoke delocalisation of the lone pair on the inverting centre into empty metal orbitals of correct symmetry and energy to explain the rate accelerations caused by coordination to transition-metals. Effects such as these summarised here are better explained by this mechanism.

B) LIGAND EXCHANGE

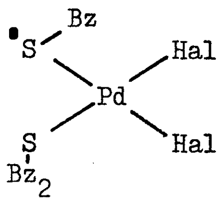
The effect of excess ligand on the coalescences of the L_2MHal_2 complexes offers a novel way of establishing pyramidal atomic inversion when M is a metal (e.g. Pd) with no magnetic isotope of natural abundance. Using this technique, sulphur inversion has been established for the first time in $(Et_2S)_2PdHal_2$ complexes. The ease of ligand exchange has been found to vary in the order:-

Pt :- $Et_2Te \gg Et_2Se, Et_2S$

Pd :- $Et_2Te \gg Et_2Se > Et_2S$

The more polarisable ligand, Et_2Te exchanges fastest with the two soft acids Pt(II) and Pd(II) and accounts for the unusual behaviour of the $(Et_2Te)_2MHal_2$ complexes when heated.

C) BENZYL COMPLEXES

Additional peaks in the v.t. n.m.r. spectra of *trans*-$(Bz_2S)_2PdHal_2$ complexes lead us to postulate the existence of *cis*-isomers at low temperatures. We suggest that the coalescence phenomena exhibited by the *cis*-$(Bz_2S)_2PdHal_2$ complexes are due to homolytic scission of the sulphur-carbon bonds leading to $PhCH_2^\bullet$ and  radicals.

These radicals are generated and recombine at low temperatures in solution.

D) DIPOLES

Contrary to popular belief(112)(39), $(R_2Te)_2MHal_2$ complexes are *trans* in solution. This casts serious doubt on conclusions in the literature about the relative bond strengths and ligand *trans*-effects of transition-metal chalcogen complexes. In the absence of crystal structure data, we have assumed similar geometries in the solid state, and attempted to reassess if not reinterpret these conclusions. Finally, the suggestion that the finite dipole moment of *trans*-$(Et_2S)_2PtCl_2$ is due to the resultant moment of the four ethyl groups on the same side of the plane of the molecule containing the Pt, Cl and S atoms(169) is refuted, since this molecule undergoes fast pyramidal sulphur inversion (more than 36 inversions per second)(96) at the temperature of the dipole-moment measurements. The corresponding dibenzylsulphide and diethylsulphide palladium complexes also have similar dipole moments, and even faster rates of inversion.

I) EXPERIMENTAL

I.R. Spectra were recorded on Perkin-Elmer 225 (4000 - 200 cm^{-1}) and Intek F.T.C. (400 - 40 cm^{-1}) spectrometers. Raman spectra were obtained using a Spex Ramalog spectrometer, with Kr and Ar lasers. N.m.r. spectra were recorded on Varian HA 220 (220 MHz., by courtesy of P.C.M.U. Harwell), Varian HA 100 (100 MHz), Varian T60 (60 MHz) and Jeol C-60HL (60 MHz) spectrometers. Integrations were obtained directly from the machine or by the method of cutting and weighing. The variable temperature unit was calibrated by the standard methanol and ethylene glycol techniques(170).

Melting points (uncorrected) were obtained on a Reichert-Kofler hot-stage apparatus. Where necessary, solvents were dried by adding sodium wire. Some of the reactions were carried out in an atmosphere of dry nitrogen, and the complexes obtained were vacuum dried before analysis. Et_2Se and Et_2Te were obtained commercially from Alfa Products Ltd. (Mass., U.S.A.) and used without further purification. Preparations involving Et_2Se_2 and Et_2Te_2 were performed in a fume cupboard, venting well away from inhabited areas.

a) DIPOLE MOMENTS

A universal bridge TF 2700 and a variable condenser were used to measure capacitance and an Abbe refractometer to measure the refractive index.

The variable condenser cell had two resettable positions - (1) with the rotating vanes fully out of the stationary vanes and (2) with the rotating vanes fully in. The capacity of the cell with air as the dielectric was measured in the two positions and then with the vanes totally immersed in pure solvent (benzene). The refractive index of the solvent was determined using the Abbe refractometer, and its density measured by accurate weighing of 10 ml. of liquid. The solution temperatures were carefully noted.

These measurements were then repeated on a solution of the compound in benzene of accurately known composition, and P_2^{o} (and hence μ) calculated from the results.

The benzene solutions generally consisted of 1 - 2 gm. of the transition metal complex dissolved in either 50 ml. or 100 ml. benzene. Where solubility appeared to be low, as in the case of the tellurides, stirring for a day or two in benzene (under nitrogen and in the dark) was sufficient to bring the complexes into solution. Where necessary, filtration was carried out prior to determination of the dipole moment.

b) COMPLEXES

All compounds of the type $[(RCH_2)_2X]_2MCl_2$ (R = Me, Ph; X = S, Se or Te; M = Pt or Pd) were prepared by similar methods, as outlined below. The corresponding bromides and iodides were synthesised by treatment of an ethanolic solution of the chloride with an approximate ten-fold excess of LiBr or LiI respectively, and recrystallisation from hot ethanol. Et_2Te reacted faster than Et_2Se or Et_2S with the platinum or palladium salts. The tellurides were heat and light sensitive in solution.

1) *cis*-$(Et_2S)_2PtCl_2$(169)

To a solution of K_2PtCl_4 (4.15g., 0.01 mole) in water (50 ml.) in a 250 ml. round-bottomed flask was added diethyl sulphide (4.31 ml., 3.6g., 0.04 mole) from a syringe, and the mixture shaken vigorously until the deep red supernatant liquid had become colourless. The mixture was allowed to remain in the stoppered flask for about 24 hours, whereupon the yellow precipitate of the *trans* isomer, initially formed above, dissolved. The resulting clear yellow solution was filtered and allowed to evaporate to dryness in an evaporating dish in the fume cupboard. The *cis* isomer was extracted from the residue by treatment with the minimum amount of hot benzene (ca. 50 ml.) and hot filtration. The benzene solution was evaporated to half volume and cooled in an ice-bath, whereupon fine yellow crystals of the *cis* isomer formed. After filtration and washing with several 5 ml. portions of petroleum ether (to remove any trans isomer) the crystals were then dissolved in a minimum amount (ca.5 ml.) of hot acetone. Cold pet. ether (ca. 3 ml.) was added slowly to the hot acetone solution until the mixture just became cloudy and cooling again in an ice-salt bath yielded pale yellow flakes of cis-$(Et_2S)_2PtCl_2$ which were filtered off and vacuum dried.

M.p. 100 - 107°C [lit. 107 - 108°C]

Analysis:- Found, C = 21.30%, H = 4.38%. $C_8H_{20}Cl_2PtS_2$ requires C = 21.52%, H = 4.48%.

2) trans-$(Et_2S)_2PtCl_2$ (169)

To a solution of K_2PtCl_4 (4.15 g. 0.01 mole) in water (50 ml.) in a 250 ml. round-bottomed flask was added Et_2S (2.16 ml., 1.8g., 0.02 mole) in small amounts, the mixture being shaken vigorously after each addition to ensure complete reaction. The bright yellow precipitate was immediately filtered, washed with several 5-ml. portions of ice-cold alcohol and then with several 5-ml. portions of water (to remove the KCl). Recrystallisation from the minimum amount of hot ethanol (ca. 6 ml.) yielded bright yellow needles of trans-$(Et_2S)_2PtCl_2$.

M.p. 93 - 100°C [lit. 107 - 108°C]

Analysis:- Found, C = 21.70%, H = 4.64%. $C_8H_{20}Cl_2PtS_2$ requires C = 21.52%, H = 4.48%.

3) trans-$(Et_2S)_2PtBr_2$ (171)

Orange-yellow. M.p. 125 - 127°C [lit. 128 - 129°C] Analysis:- Found, C = 17.92%, H = 3.58%. $C_8H_{20}Br_2PtS_2$ requires C = 17.95%, H = 3.74%.

4) trans-$(Et_2S)_2PtI_2$ (171)

Brown. M.p. 130 - 134°C. [lit. 139 - 140°C] (A small amount melted below 120°C).
Analysis:- Found, C = 15.18%, H = 3.30%. $C_8H_{20}I_2PtS_2$ requires C = 15.27%, H = 3.18%.

5) ATTEMPTED PREPARATION OF CIS-$(Et_2Se)_2PtCl_2$ (172)

K_2PtCl_4 (1.20 g., 0.00290 mole) in 100 ml. water was shaken for two days with a four-fold excess of Et_2Se (1.29 cc, 0.0116 mole). No precipitate was formed. After removal of the water on the rotary evaporator, the residue was recrystallised from hot ethanol. Yellow and red crystals were obtained, but the latter turned yellow on exposure to air. The melting point however (ca. 60°C) indicated that the *trans*-isomer had been produced [lit. 55-60°C](172). Nothing melted above 70°C, the expected melting point of *cis*-$(Et_2Se)_2PtCl_2$ [lit. 73 - 75°C .]

6) trans-$(Et_2Se)_2PtCl_2$ (172)

A solution of K_2PtCl_4 (1.01 g., 0.00244 mole.,) in 100 ml. water was shaken with Et_2Se (0.67 g., 0.545 ml., 0.00489 mole) for 30 minutes. The crude product was filtered, washed with ice-cold ethanol and then water, and subsequently recrystallised from the minimum amount of hot ethanol to give orange-yellow crystals of <u>trans</u>-$(Et_2Se)_2PtCl_2$.

M.p. 55 - 59°C. [lit. 55 - 60°C]

Analysis:- Found, C = 17.85%, H = 3.80%. $C_8H_{20}Cl_2PtSe_2$ requires C = 17.78%, H = 3.71%.

7) <u>trans</u>-$(Et_2Se)_2PtBr_2$ (172)

Orange-yellow. M.p. 77 - 79°C. [lit. 75°C]

Analysis:- Found, C = 15.00%, H = 3.05%. $C_8H_{20}Br_2PtSe_2$ requires C = 15.27%, H = 3.18%.

8) <u>trans</u>-$(Et_2Se)_2PtI_2$ (172)

Red. M.p. 91 - 94°C.

Analysis:- C = 13.35%, H = 2.67%. $C_8H_{20}I_2PtSe_2$ requires C = 13.28%, H = 2.77%.

9) <u>trans</u>-$(Et_2Te)_2PtCl_2$ (113)

A solution of K_2PtCl_4 (4.2 g., 0.01 mole) in 50 ml. water was shaken with Et_2Te (3.7 g., 2.3 ml., 0.02 mole) and the yellow precipitate immediately filtered and washed with cold ethanol and water. Recrystallisation from the minimum amount of hot ethanol resulted in brown-yellow crystals of <u>trans</u>-$(Et_2Te)_2PtCl_2$. (This compound was originally reported <u>cis</u>,

but dipole studies show it to be trans in solution.)
M.p. 126 - 129°C. [lit. 126 - 127°C .]
Analysis:- Found, C = 15.00%, H = 3.04%. $C_8H_{20}Cl_2PtTe_2$ requires C = 15.06%, H = 3.14%.

10) trans-$(Et_2Te)_2PtBr_2$ (39)

(This compound has also been shown to be trans, and not cis, as has been previously reported(39)).
Brown-yellow. M.p. 127 - 128°C. [lit. 125 - 127°C]
Analysis:- Found, C = 13.16%, H = 2.75%, $C_8H_{20}Br_2PtTe_2$ requires C = 13.22%, H = 2.75%.

11) trans-$(Et_2Te)_2PtI_2$

Maroon. (Red and yellow crystals were seen under the microscope.) M.p. 87 - 89°C. Analysis:- Found, C = 11.60%, H = 2.52%. $C_8H_{20}I_2PtTe_2$ requires C = 11.71%, H = 2.45%.

12) trans-$(Et_2S)_2PdCl_2$ (151)

To a solution of K_2PdCl_4(3.26 g., 0.01 mole) in water (50 ml.) was added Et_2S (2.16 ml., 1.8 g., 0.02 mole) and the mixture shaken for 2½ hours. The crude product was filtered, washed with cold ethanol and water, and recrystallised from the minimum amount of hot ethanol to yield orange crystals

of trans-$(Et_2S)_2PdCl_2$. M.p. 79 - 81°C. [lit. 81°C.]
Analysis:- Found, C = 27.09%, H = 5.56%. $C_8H_{20}Cl_2PdS_2$ requires C = 26.87%, H = 5.60%.

13) trans-$(Et_2S)_2PdBr_2$(151)

Brown. M.p. 98 - 103°C. [lit. 98 - 103°C .]
Analysis:- Found, C = 21.49%, H = 4.44%. $C_8H_{20}Br_2PdS_2$ requires C = 21.52%, H = 4.48%.

14) ATTEMPTED PREPARATION OF trans-$(Et_2S)_2PdI_2$(151)

The metathetical reaction of LiI and $(Et_2S)_2PdCl_2$ produced a black powder only a small part of which was soluble in ethanol. Its melting point was greater than 300°C (some melted below 180°C [lit. 110°C]) and was probably either Pd, or PdI_2 from the thermal decomposition of $(Et_2S)_2PdI_2$.

15) trans-$(Et_2Se)_2PdCl_2$(151)

The precipitate formed on addition of Et_2Se (1.43 ml., 1.76 g., 0.0129 mole) to an aqueous solution of K_2PdCl_4 (2.1 g., 0.00643 mole) was filtered immediately, and after washing with cold alcohol and water, was recrystallised from ethanol to give orange-brown crystals of $(Et_2Se)_2PdCl_2$.
M.p. 43 - 44°C. [lit. 45°C.]
Analysis:- Found, C = 21.45%, H = 4.57%. $C_8H_{20}Cl_2PdSe_2$ requires C = 21.28%, H = 4.43%.

16) trans-$(Et_2Se)_2PdBr_2$(151)

Brown. M.p. 65 - 67°C. [lit. 167°C .]

Analysis:- Found, C = 17.72%, H = 3.74%. $C_8H_{20}Br_2PdSe_2$ requires C = 17.78%, H = 3.70%.

17) trans-$(Et_2Se)_2PdI_2$(151)

Brown. M.p. 57 - 61°C. [lit. 60°C.]

Analysis:- Found, C = 15.17%, H = 3.10%. $C_8H_{20}I_2PdSe_2$ requires C = 15.14%, H = 3.16%.

18) trans-$(Et_2Te)_2PdCl_2$

Immediate filtration and the usual work up produced maroon crystals of trans-$(Et_2Te)_2PdCl_2$. M.p. 97 - 99°C. (There were traces of black particles in the liquid melt).

Analysis:- Found, C = 17.73%, H = 3.82%. $C_8H_{20}Cl_2PdTe_2$ requires C = 17.50%, H = 3.65%.

19) trans-$(Et_2Te)_2PdBr_2$

Maroon. M.p. 110 - 112°C.

Analysis:- Found, C = 14.88%, H = 3.18%. $C_8H_{20}Br_2PdTe_2$ requires C = 15.06%, H = 3.14%.

20) trans-$(Et_2Te)_2PdI_2$

Black. M.p. 87 - 89°C.

Analysis:- Found, C = 13.05%, H = 2.57%. $C_8H_{20}I_2PdTe_2$ requires C = 13.13%, H = 2.73%.

21) trans- $[(PhCH_2)_2S]_2PdCl_2$ (151)

To a solution of K_2PdCl_4 (3.1 g., 0.0095 mole) in water (100 ml.) was added an ethanol solution (100 ml.) of $(PhCH_2)_2S$ (4.07 g., 0.019 mole). A precipitate was immediately produced, which, after filtration and washing with cold ethanol and then water, was recrystallised from hot ethanol to give orange-yellow crystals of trans- $[(PhCH_2)_2S]_2PdCl_2$.

M.p. 150 - 152°C. [lit. 154°C .]

Analysis:- Found, C = 55.66%, H = 4.75%. $C_{28}H_{28}Cl_2PdS_2$ requires C = 55.50%, H = 4.63%.

22) trans- $[(PhCH_2)_2S]_2PdBr_2$

Orange. M.p. 133 - 136°C.

Analysis:- Found, C = 50.28%, H = 4.64%. $C_{28}H_{28}Br_2PdS_2$ requires C = 48.40%, H = 4.03%.

23) trans-$[(PhCH_2)_2S]_2PdI_2$

Dark maroon. M.p. 123 - 125°C.

Analysis:- Found, C = 43.55%, H = 3.99%. $C_{28}H_{28}I_2PdS_2$ requires C = 42.63%, H = 3.55%.

24) $PhCH_2SCH_3$ (173)

Benzylmercaptan, $PhCH_2SH$ (12.4 g., 11.7 cc, 0.1 mole) was added over a period of 5 minutes to an ice-cooled solution of sodium (2.3 g., 0.1 mole) in 200 ml. ethanol under an atmosphere of dry nitrogen. Methyl chloride gas was passed through the solution for about 20 minutes, and a white precipitate (NaCl) was formed. After refluxing for 1 hour at a temperature just above 90°C, the solution was filtered (5.8 g., ca. 0.1 mole NaCl obtained) and the ethanol removed on the rotary evaporator. Subsequent distillation (130°C, unknown pressure) yielded $PhCH_2SCH_3$ [Lit. 94 - 96°C/18 mm.Hg (173)]

N.M.R. (neat)

singlet	8.14 τ (3H)	-	—S — CH_3
singlet	6.47 τ (2H)	-	—S — CH_2
singlet	2.80 τ (5H)	-	Ph.

25) trans-$(PhCH_2SCH_3)_2PdCl_2$

Red brown. M.p. 146 - 148°C.

Analysis:- Found, C = 42.95%, H = 4.66%. $C_{16}H_{20}Cl_2PdS_2$ requires C = 42.35%, H = 4.41%.

26) Et_2Se_2 (174)

Selenium (16 g., 0.202 mole) was added to a mixture of sodium hydroxide (8 g., 0.2 mole), rongalite (sodium formaldehyde sulphoxylate, 12.5 g., 0.081 mole) and water (125 cc.), and stirred for 20 mins. Et_2SO_4 (15.25 cc., 17.95 g., 0.117 mole) was slowly added and the mixture heated and stirred for 1 hour. A heavy red-black oil separated out and this was extracted with chloroform. After drying overnight over anhydrous magnesium sulphate, evaporation of the chloroform and vacuum distillation (ca. 100°C/1 mm. Hg.) yielded 6.15 g. of the red-orange product (28% yield based on selenium). When the reaction was repeated on a larger scale (using double the quantities above) 16.48 g. Et_2Se_2 was obtained. (38% yield based on selenium).

n.m.r.

triplet (8.57 τ) - CH_3.
quartet (7.07 τ) - CH_2.
$J_{CH_3 - CH_2} = 7.5$ Hz.

27) $EtSe(C_2H_4)SeEt$

T.H.F. was dried by refluxing over sodium (using benzophenone as indicator) under dry nitrogen, and 100 ml. distilled into a 3-necked 250 ml. round-bottomed flask. Lithium (0.95 g., 0.138 mole, ca. three-fold excess) was cut up as quickly as possible in the nitrogen stream and added to the T.H.F. After stirring for a few hours Et_2Se_2 (8.93 g., 0.0414 mole) was added and the reaction allowed to stir for three days. To the now brown-yellow solution was added $ClCH_2-CH_2Cl$ (50 cc., 61.75 g., 0.624 mole) and refluxing continued for another day, during which time a black-brown colour developed. After addition of methanol (to destroy the excess lithium) both it, the T.H.F., and the excess $Cl_2C_2H_4Cl$ were distilled off. Vacuum distillation (54°C/0.1 mm. Hg.) yielded 1,2 - bis(ethylseleno)ethane, (2.12 g., 21% yield based on Et_2Se_2). (This compound was not analysed for C and H due to its pungent smell).

n.m.r.

singlet (7.17 τ) - $CH_2 - CH_2$ bridge
quartet (7.32 τ) - CH_2 terminal
triplet (8.57 τ) - CH_3
$J_{CH_3-CH_2}$ = 8 Hz.

(The above method is analogous to that used by Greenwood and Hunter$^{(34c)}$ in the preparation of $Pr^iSeC_2H_4SePr^i$)

28) $(EtSeC_2H_4SeEt)PtCl_2$

K_2PtCl_4(1.69 g., 0.004 mole), was dissolved in water (75 ml.) and $EtSeC_2H_4SeEt$ (0.975 g., 0.004 mole) was added. The mixture was shaken for 3½ hours and an orange brown precipitate was formed. This precipitate was filtered and washed with cold water (to remove KCl) but was found to be very insoluble. It analysed correctly without further recrystallisation. The crystals appear to decompose at around 145°C, gradually melting (ca. 170 - 180°C) to a wine-red liquid which was covered by a black film.

Analysis:- Found, C = 14.16%, H = 2.70%. $C_6H_{14}Cl_2PtSe_2$ requires C = 14.12%, H = 2.75%.

29) $(EtSeC_2H_4SeEt)PtBr_2$

The insoluble nature of the chloride necessitated large amounts of ethanol for the metathetical reaction with LiBr. This was carried out in the usual manner and yellow-brown crystals of 1,2-bis(ethylseleno)ethaneplatinum(II)dibromide were obtained. Solubility reasonable. M.p. 144 - 146°C. Analysis:- Found, C = 12.25%, H = 2.82%. $C_6H_{14}Br_2PtSe_2$ requires C = 12.03%, H = 2.34%.

30) $(EtSeC_2H_4SeEt)PtI_2$

Dark brown. M.p. 179 - 180°C. Solubility good. Analysis:- Found, C = 10.19%, H = 2.20%. $C_6H_{14}I_2PtSe_2$ requires C = 10.39%, H = 2.02%.

31) $(EtSeC_2H_4SeEt)PdCl_2$

$EtSeC_2H_4SeEt$ (1.597 g., 0.00655 mole) was added to an aqueous solution of K_2PdCl_4 (2.14 g., 0.00655 mole) and an orange-yellow precipitate resulted. After shaking for 4 hours and refluxing for 30 minutes, the solution was filtered hot, and a precipitate formed on cooling. This was washed with water and recrystallised from hot ethanol to yield orange crystals of 1,2 - bis(ethylseleno)ethanepalladium(II)dichloride.
M.p. 187 - 189°C. Solubility poor.
Analysis:- Found, C = 17.39%, H = 3.37%. $C_6H_{14}Cl_2PdSe_2$ requires C = 17.09%, H = 3.32%.

32) $(EtSeC_2H_4SeEt)PdBr_2$

Red-orange. Reasonable solubility. M.p. 152 - 154°C. Analysis:- Found, C = 14.23%, H = 2.91%. $C_6H_{14}Br_2PdSe_2$ requires C = 14.18%, H = 2.75%.

33) $(EtSeC_2H_4SeEt)PdI_2$

Red-brown. Very soluble. M.p. 148 - 150°C. Analysis:- Found, C = 11.54%, H = 2.49%. $C_6H_{14}I_2PdSe_2$ requires C = 11.92%, H = 2.32%.

34) Et_2Te_2

Clean sodium metal (9.6 g., 0.417 mole) was added to 300 ml. of anhydrous ammonia at -78°C in a 500 ml. flask equipped with a reflux condenser, stirrer and dropping funnel. After stirring for 1 hour, high purity finely ground tellurium (54.6 g., 0.428 mole) was added in small portions, each addition causing a violent exothermic reaction. Ethyl iodide (80.09 g., 0.514 mole) was then added dropwise with stirring over a 30 minute period. Stirring was continued for a further 30 minutes after which the ammonia was allowed to evaporate off. Water was added to the residue and the mixture extracted with ether. A deep red extract was obtained. After drying overnight over anhydrous calcium chloride, distillation of the ether and subsequent vacuum distillation (70°C/0.15 mm. Hg.) yielded

32.26 g. (48% yield based on tellurium) of diethylditelluride. This dark red liquid did not have the same sickly smell as the corresponding selenide, and had a tendency to stick to the sides of the flask. C and H analyses were not carried out and the compound was characterised by n.m.r. Slight traces of Et_2Te were observed.

n.m.r.

triplet (8.38 τ) - CH_3

quartet (6.92 τ) - CH_2

$J_{CH_3 - CH_2}$ = 8 Hz.

(This preparation is analogous to that used by Chen and George(175) in the preparation of Me_2Te_2).

35) Attempted preparation of $EtTeC_2H_4TeEt$

The method followed was identical to that used in the preparation of the corresponding selenide chelate(34c). Lithium (1.32 g., 0.191 mole., ca. three-fold excess) was cut up in a stream of dry nitrogen and added to 100 ml. of T.H.F. which had been refluxed over sodium (using benzophenone as indicator) before being distilled into the reaction vessel. After stirring for 30 minutes, Et_2Te_2 (17.95 g., 0.0573 mole was added. The wine-red colour of the selenide changed to dark green after a few minutes. ClC_2H_4Cl (3.15 g., 0.0318 mole) was added dropwise and the reaction mixture stirred for 3 hours. The excess lithium was carefully removed and stirring continued for a further 20 hours. After heating for 45 minutes, methanol was added to destroy any traces of lithium still present, and this and the T.H.F. were distilled off. Vacuum distillation (ca. 65°C/0.15 mm. Hg.) however produced the starting material, diethylditelluride (ca. 10 g. (56%)) as shown by n.m.r. Even removal of the excess lithium before addition of ClC_2H_4Cl and a 20 hour reflux, also failed to produce the desired product, 1,2-bis(ethyltelluro)ethane.

36) Et_2Te

To a warmed solution of tellurium (40 g. 0.314 mole.,) sodium formaldehyde sulphoxylate (rongalite) (90 g., 0.584 mole), and sodium hydroxide (70 g., 1.75 mole) in water (400 cc.), was slowly added ethyl iodide (102.5 g., 0.657 mole.) in ethanol (350 cc.) with stirring over a period of 1½ hours. Bluish-green crystals were formed on the sides of the flask. After refluxing for 2 hours and filtering, the mixture was extracted with ether and stored overnight over anhydrous magnesium sulphate. Distillation at normal atmospheric pressure first of all produced the ether, but at about 80°C a red solution containing an approximately 10:1 ratio of EtOH : Et_2Te (calculated from n.m.r.) was obtained.

This was reacted directly with K_2PdCl_4/K_2PtCl_4 without any further purification.

(The method used was the same as that employed by Balfe, Chaplin and Phillips(176), in the preparation of $Bu^{\underline{n}}_2Te$.)

37) ATTEMPTED PREPARATION OF $PhCH_2TeMe$

Magnesium turnings (4.8 g., 0.198 mole) were stirred in ether (150 ml.) in a 500 ml. flame-dried flask. After adding a couple of drops of 1,2-dibromoethane to catalyse the reaction, benzyl bromide (31.617 g., 21.99 cc., 0.185 mole.,) in 100 ml. ether was added dropwise to the stirred solution, which was cooled using an ice-bath. A suspension of tellurium (25.6 g., 0.201 mole.) in 200 ml. ether was added and the mixture stirred (with difficulty) for about 30 minutes. After heating under reflux for 3 hours, during which time the solution turned black, methyl iodide (24.47 g., 0.201 mole.) in 50 ml. ether was added dropwise. The mixture turned pale green and refluxing was continued for another hour. After cooling, excess ice-cold HCl was added and the solution turned yellow. A yellow powder (A) was extracted from the aqueous layer. The ethereal layer was separated, washed with 30% aqueous NaOH and then dried over anhydrous calcium chloride for two days. Once the ether had been distilled from the now orange solution, vacuum distillation (83°C/0.3 mm. Hg.) yielded 2.46 g. of a product (B).

PRODUCT B

n.m.r.

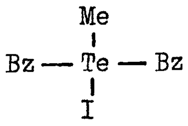
singlet (2H) - 7.17 τ

singlet (6H) - 2.85 τ

The absence of resonances in the methyl region of the spectrum indicated that $PhCH_2TeMe$ had not been formed, and the integration and chemical shifts suggested either $(PhCH_2)_2Te$ or $Ph\text{-}CH_2\text{-}CH_2\text{-}Ph$. (Expected integration for both = 2:5).

PRODUCT A

Greenish and a whitish powders were obtained when the yellow powder was washed with acetone. The white powder did not melt below 270°C ($MgBr_2$?) but the other melted at 65°C and then at ca. 140°C a black solid was produced (Te ?) which did not melt below 250°C. It was thought that the green solid might be a Te (IV) complex, possibly



$$Bz - \overset{\displaystyle Me}{\underset{\displaystyle I}{Te}} - Bz$$

formed by oxidative addition of MeI to Bz_2Te. Many coloured Te (IV) complexes (e.g. Me_3TeI, $MeTeI_3$, Me_2TeI_2) are known(177). However the identity of the green solid was not established, mainly due to its nasty smell.

38) FURTHER REACTION OF PRODUCT B

An attempt was made to react this product with K_2PtCl_4, in the hope of isolating a telluride complex, possibly $(Bz_2Te)_2PtCl_2$.

Product B was dissolved in a $CHCl_3$/MeOH mixture and reacted with an aqueous solution of K_2PtCl_4 (1.64 g.). After shaking for ca. 15 minutes, a dark brown precipitate was filtered off, and this was recrystallised from a 50:50 $CHCl_3$/MeOH mixture. An n.m.r. of the crude product in $Cl_2CH\text{-}CHCl_2$ showed aromaticity. However a white precipitate (C) was formed from the recrystallising mixture and this was shown by melting point comparison and analysis to be bibenzyl.

Product C

M.p. 52 - 53°C (bibenzyl melts at 52°C)$^{(178)}$

Analysis:- Found, C = 90.46%, H = 7.55%. $(PhCH_2)_2$ requires C = 92.3%, H = 7.69%.

No transition-metal telluride complex was obtained.

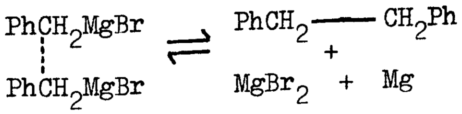
Instead of the following simplified reaction scheme:-

1) $Mg + BzBr \rightleftharpoons BzMgBr$

2) $'Bz^-' + Te \rightleftharpoons 'BzTe^-'$

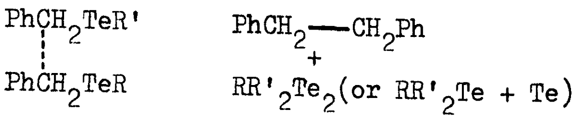
3) $BzTe^- + MeI \rightleftharpoons \underline{\underline{BzTeMe}} + I^-$

it would appear that either at the Grignard stage (4), or later (5)

4) 

$$\begin{array}{c} PhCH_2MgBr \\ \vdots \\ PhCH_2MgBr \end{array} \rightleftharpoons \begin{array}{c} PhCH_2 — CH_2Ph \\ + \\ MgBr_2 + Mg \end{array}$$

5)



$$\begin{array}{l} \mathrm{PhCH_2TeR'} \\ \vdots \\ \mathrm{PhCH_2TeR} \end{array} \qquad \begin{array}{c} \mathrm{PhCH_2{-}CH_2Ph} \\ + \\ \mathrm{RR'_2Te_2(or\ RR'_2Te + Te)} \end{array}$$

(R = Me, Bz).

condensation to product bibenzyl had occurred.

39) PREPARATION OF Ph - Te - Et(146)

a) A few drops of 1,2-dibromoethane were added to magnesium turnings (2.43 g. 0.1 mole) stirring (mechanical stirrer) in 100 ml. ether, and phenylbromide (15.69 g., 10.46 cc., 0.1 mole) in 50 ml. ether was added dropwise. The flask was ice-cooled during the addition. A suspension of tellurium (12.8 g. 0.1 mole.) in ether (100 ml.) was then added and the mixture refluxed for 3 hours. The dark green solution turned black for a while and then back to its original colour. Ethyl iodide (15.5 g., 0.1 mole.) in ether (50 ml.) was very slowly allowed into the cooled solution, and refluxing commenced for an hour. Ice-cold HCl was added to the cooled solution, which immediately turned orange-yellow. The ethereal layer was separated, washed with 30% aqueous NaOH and with water, and dried overnight over anhydrous calcium chloride. After distilling off the ether, a vacuum distillation yielded small amounts of two products.

D) 28°C/ca. 5mm.Hg

E) 64°C/ca. 2mm.Hg.

40) FURTHER REACTION OF PRODUCT E

Neither of the products was properly identified, but E showed a quartet in the ethyl region ($CDCl_3$ soln., $\tau \approx 7.1$), and it was decided to try and complex it. Accordingly aqueous K_2PtCl_4 was shaken with the crude oil, a solid filtered off, and a chloroform solution showed the following n.m.r. signals.

Triplet	(3H)	- 8.1 τ
Quartet	(2H)	- 5.7 τ
J ≈ 7 Hz.	(ext. T.M.S.).	

However, no ^{195}Pt satellites were apparent in the methylene region of the spectrum, even at -32°C. The purpose in making a complex of PhTeEt was to (hopefully) increase the rate of tellurium inversion such that detection of ^{195}Pt-Te-C-H coupling might be possible at amenable temperatures. The absence of ^{195}Pt satellites in the spectrum described above either indicated traces of free ligand still present in the solution (leading to ligand dissociation-recombination) or in fact that the required platinum complex had not been made. It was decided to repeat the experiment using a better method.

41) PREPARATION OF Ph-Te-Et BY ANOTHER METHOD

(This method is analogous to that used by Okamoto and Yano(179) in the preparation of Pr^iTePh).

b) To a solution of Et_2Te_2 (3.173 g., 0.01 mole.) in 20 ml. dioxane (distilled over molecular sieves) was added slowly with stirring a suspension of Ph_2Hg (3.592 g. 0.01 mole.) in 40 ml. dioxane over a period of 40 minutes. Refluxing was commenced for 3 hours, during which time the mixture turned brown-black. (Okamoto and Yano(179) observed metallic mercury at this stage in similar reactions, but we found a black powder (Te ?), with a small amount of white powder, (Ph_2Hg ?) at the bottom of the flask). After distilling off the solvent, a vacuum distillation yielded product (F) at 65°C/0.7 mm.Hg.

N.M.R. of Product F.

2 triplets - ca. 8.5 τ

2 overlapping quartets - ca. 7.4 and 7.1 τ

2 multiplets - ca. 2.3 and 2.8 τ

$J_{CH_3-CH_2}$ = ca. 8 Hz.

Integration revealed an approximately 2:1 ratio of the Et:Ph signals. This spectrum was obtained about an hour after the distillation, but even the symmetrisation:-

$$2PhTeEt \rightleftharpoons Ph_2Te + Et_2Te$$

would not explain the intensity ratio. Presumably some unreacted Et_2Te_2 (Bp.70°C/0.15 mm. Hg) was present. Since the above symmetrisation is thought to occur rapidly, product F was reacted immediately with a stoichiometric amount of K_2PtCl_4 in the usual way. The black brown tar and brown precipitate which were produced were recrystallised from MeOH/$CHCl_3$, but the n.m.r. showed a mixture of products, (G) presumably $(Ph_2Te)_2PtCl_2$, $(Et_2Te)_2PtCl_2$, $(PhTeEt)_2PtCl_2$ and cross-products. It appeared that PhTeEt had either symmetrised before or during complexing.

N.M.R. of Product G.

Multiplets at 9.2τ, 8.6τ, 6.8τ, 5.8τ, 2.7τ and 2.4τ

42) Di-μ-iodo-diiodo-trans-bis(diethyltelluride)diplatinum(II).

To an aqueous solution of K_2PtCl_4 (1.483 g., 0.00358 mole.) was added LiI (5.8 g., 0.0433 mole., ca 12-fold excess) under nitrogen and after stirring for 10 minutes, Et_2Te (0.665 g., 0.00358 mole.) was added and the mixture stirred in the dark for nine days. The brown precipitate which formed immediately was still there after the nine days. This was filtered (crude weight = 2.15 g.) and washed a few times with cold water. Some was dissolved in ca. 500 ml. Cl_2CH-$CHCl_2$ in the cold, filtered, and reduced in volume to about 40 ml. Addition of n-heptane precipitated a dark brown product. Crude yield = 47%.

M.p. 160 - 163°C.

Analysis:- Found, C = 7.51%, H = 1.73%. $C_8H_{20}I_4Pt_2Te_2$ requires C = 7.56%, H = 1.58%.

43) p-tolyllithium

A solution of 4-bromotoluene (15.69 g., 0.0917 mole.) in anhydrous diethyl ether (30 ml.) was added dropwise to a stirred dispersion of finely chopped lithium metal (1.6 g., 0.232 g. atom.) in ether (250 ml.) under an atmosphere of dried nitrogen. The mixture was stirred at gentle reflux for 5 hours, until a bright metallic lustre was exposed on the surface of the lithium pellets. Gilman I test indicated the presence of organolithium. After being allowed sufficient time at ambient temperature for sedimentation of suspended solids, the solution was decanted through dried glass wool into a nitrogen filled, pressure-equilibrating reservoir funnel for determination, storage and subsequent use. Unreacted metallic lithium was destroyed by rapid addition of a large volume of methanol.

44) Determination of p-tolyllithium solution

A modification of the Gilman double-titration technique(180) was used to obtain an accurate determination of the effective concentration of p-tolyllithium in its ether solution. Into one 25 ml. conical flask was placed ca. 10 ml. distilled water, while into another was placed ca. 5 ml. dried 1,2 dibromoethane. Both flasks were fitted with rubber septum caps and thoroughly purged with dried nitrogen (via hypodermic needles). Meanwhile a 2 ml. hypodermic syringe was flushed with nitrogen, and used to accurately extract 1 ml. of the p-tolyllithium solution, which was injected directly into the distilled water, and the mixture vigorously shaken. The resultant solution was then carefully titrated against 0.1 M HCl using bromothymol blue as indicator, to determine the overall hydroxide ion concentration after hydrolysis of the organolithium. A further 1 ml. aliquot of the aryllithium solution was then accurately withdrawn and injected directly into the dibromoethane, thus effectively quenching the organolithium without the production of free hydroxide. After thorough mixing, ca. 10 ml. of distilled water was introduced, and the whole shaken vigorously for 5 minutes, to ensure efficient transfer of all residual base to the aqueous phase. This was now similarly titrated to determine the 'background' concentration of base in the diethyl-ether solvent. Subtraction of this latter residual base determination from the former, total base determination yielded the free hydroxide concentration arising from organolithium hydrolysis alone, and hence the concentration of aryllithium itself. Our preparation yielded a 0.281 M solution of p-tolyllithium in ether.

45) $(Et_2Te)_2Pt(p\text{-tolyl})_2$

$(Et_2Te)_2PtI_2$ (0.81 g., 0.000988 mole.) was dissolved in ether (200 ml.) under dry nitrogen. p-tolyllithium (8.4 ml. of an 0.281 M solution in ether; 0.00236 mole., ca. 2.4 : 1 molar ratio with complex) was added to the maroon solution, and a dull yellow mixture resulted. After stirring for 95 hours at room temperature and in the dark, 30 ml. H_2O was added and the solution filtered into a separating funnel. The yellow-orange ether layer was removed and a yellow-white solid formed as the ether was being taken off on the vacuum line. This precipitate was washed with cold water (to remove LiI) and since it melted within a 2°C temperature range (114-116°C) and only gave one set of n.m.r. signals, it was considered to consist of only one isomer, namely cis-$(Et_2Te)_2Pt(p\text{-tolyl})_2$.

N.M.R. (CD_2Cl_2 solvent)

triplet (12H) :- 8.54 τ
singlet (6H) :- 7.73 τ
multiplet (8H) :- 7.43 τ
multiplet :- ca. 2.2 τ

Attempted recrystallisation from $MeOH/H_2O$ produced a brown solid which melted at 64-65°C to a yellow solid, which in turn melted at ca. 95-100°C. This brown solid was taken as trans-$(Et_2Te)_2Pt(p\text{-tolyl})_2$, and was consistent with the following elemental analysis figures:-

Analysis:- Found, C = 35.80%, H = 5.09%. $C_{18}H_{24}PtTe_2$ requires C = 35.28%, H = 4.54%.

N.M.R.

An n.m.r. spectrum in CD_2Cl_2, run a few hours after dissolving the solid, indicated that trans $\rightleftharpoons$ cis isomerisation had taken place and that considerable decomposition had occurred.

Although light was excluded, black particles were deposited at the bottom of the n.m.r. tube and the solution itself turned cloudy. In addition to those peaks already listed for <u>cis</u>-$(Et_2Te)_2Pt(p\text{-tolyl})_2$, other resonances at the following values were found:-

multiplet - $9.2\,\tau$
strong singlet - $8.8\,\tau$
strong singlet - $8.6\,\tau$
weak singlet - $8.4\,\tau$
strong singlet - $7.7\,\tau$
multiplet - $2.7\,\tau$

The strong singlet at $7.7\,\tau$ could have been due to toluene or bitolyl.

CHAPTER 4

PHOSPHORUS-NITROGEN TORSIONAL BARRIERS

(1) HISTORICAL INTRODUCTION

A PHOSPHORUS(181)(182)

Phosphorus may have been discovered as early as the 12th century(183) by one Alchid Bechil, an Arabian alchemist. However the first preparation of relatively pure elemental white phosphorus is generally attributed to Hennig Brandt in 1669(184). In an attempt to convert base metals into gold, he had cause to distil large volumes of human urine and one of the final products of this distillation was a liquid which 'emitted a strange light! The element phosphorus was consequently later named after the two Greek works φψs , (light) and φερω (I bear).

In the late 18th century phosphorus played an important part in Lavoisier's theory of combustion, since it provided the experimental evidence of increase of weight on burning. The element 'fire', as Brandt and his contemporaries thought of it, gave way to the chemical element of phosphorus. White phosphorus was prepared on a relatively large scale in the early 19th century and its pyrophoric properties made it an ideal product for use in the match industry, until it was gradually replaced by the less toxic red allotrope. By the second half of the same century, the first organophosphorus chemistry was carried out and within 40 or 50 years a considerable amount of work was done in this area, notably in Germany by Michaelis and coworkers(185).

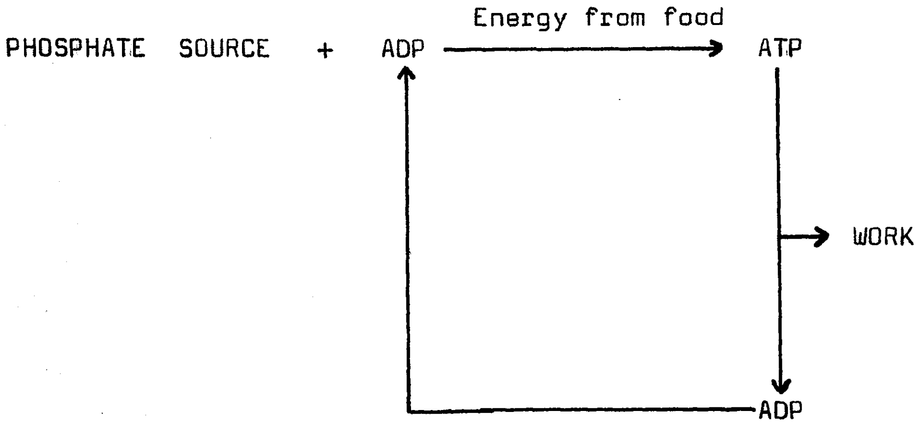
It was not however till the 1920's that organophosphorus compounds had any commercial value. The real expansion in their use came in the 1940's as additives in plastics, where they act as antioxidants and stabilisers. In fact the great majority of phosphorus compounds used commercially are inorganic, and cover a wide range of applications. Fertilisers, detergents, animal feedstuffs, pharmaceuticals, insecticides, flameproofing agents and nerve gases are some of the uses of phosphorus-containing compounds.

The development and application of spectroscopic techniques over the last 20 years has led to many advances in chemistry in general, but it is really only in recent years that they have been applied profitably to phosphorus chemistry. In particular, I.R., n.m.r., and mass spectroscopy have offered and in fact shown the greatest potential source of structural information in this branch of chemistry.

Undoubtedly the most important aspect of phosphorus chemistry is its role in biological processes(186). The ultimate energy source in all organisms is the intracellular breakdown of food molecules. This energy is conserved in adenosine triphosphate (ATP) by the synthesis of this compound from adenosine diphosphate (ADP) and phosphate, according to the scheme shown overleaf.

FIGURE 42

ROLE OF PHOSPHATE IN ENERGY CYCLE



An important source of phosphate is creatine phosphate which is present in high concentrations in both the muscle and nerve cells. It acts as a reserve store of energy by phosphorylating ADP (formed by muscular action) back to ATP. The latter then acts as the central energy-transfer agent in the body.

The outer-shell electronic configuration of phosphorus is $3s^2 3p^3$, and the element can use all five electrons to form bonds which are normally covalent in character. Compounds with phosphorus bonding to 3,4,5 and 6 other atoms are known, with phosphorus either in the tri- or pentavalent state. The hybridisation at P(III) is a subject of some controversy. The observed bond angles in PH_3(187) for example are close to 90°, implying that the lone pair of electrons on phosphorus is in an almost pure 3s orbital. This has been invoked(124) to explain the slower rate of pyramidal phosphorus inversion in PH_3 over that of nitrogen inversion in NH_3. The lone pair on nitrogen is considered to be in an sp^3 hybrid, which is closer to the p-orbital transition state (see Figure 5) of pyramidal inversion than the lone pair on phosphorus. However, lack of sp hybridisation at phosphorus implies no directional character of the lone pair(188), but its angular dependence in a variety of phosphorus compounds is now well documented(189). In addition <u>ab initio</u> SCF LCAO-MO calculations on PH_3(190) indicate a considerable p-character in the lone pair. P (III) compounds can thus act as nucleophiles, and it is interesting to note that phosphines are generally regarded as weaker bases but stronger nucleophiles than amines due to the polarisability of the lone pair(191). They also show electrophilic character. Because of low lying empty d-orbitals, P (III) can stabilise transition states or intermediates when reacting with nucleophiles. In fact without a doubt the most controversial feature of phosphorus chemistry in recent years has been the role of d-orbitals in bonding. π-bonding in P (V) compounds has been described both in terms of(192) and without(193) d-orbital participation, but the generally acceptable hybridisation schemes involve the use of d-orbitals. The stereochemistry of pentacoordinate phosphorus compounds is trigonal bipyramidal(194), but is often complicated by the process of pseudorotation(66).

Phosphorus forms bonds to many other elements. In particular the chemistry of organic compounds with phosphorus-nitrogen bonds has been studied since the latter part of the 19th century, notably by Michaelis and his school(185), and continues to be studied to the present day.

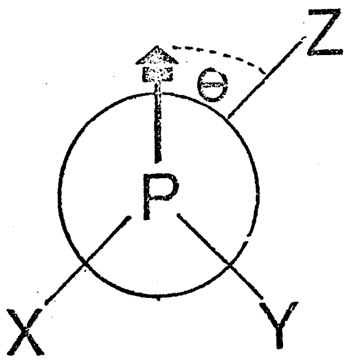
B COUPLING CONSTANTS

If a pair of nuclei, each possessing an inherent spin, are placed in proximity to one another, they may interact so that different combinations of the allowed spin states differ in total energy(195). There are several mechanisms by which these nuclear spins may be coupled, the most important generally being the Fermi Contact(196) description of coupling. The coupling constants of tricoordinated phosphorus compounds are complicated by the presence of the lone pair. As soon as it was realised that vicinal(197) and geminal(198) coupling constants were influenced by a lone pair of electrons, its angular dependence to bonds in the molecule was also explored.

Although it had been argued that the very high s-character of the lone pair on phosphines would give these electrons little or no directional properties(188), evidence was soon provided(199)(200) to show that the coupling constants in P (III) compounds are strongly dependent on the dihedral angle subtended by the bond and the lone pair on phosphorus. (Figure 43).

FIGURE 43

ILLUSTRATION OF DIHEDRAL ANGLE



The angular dependences of various P (III) coupling constants has been examined, and the results of a number of these studies are summarised in Table 52.

TABLE 52

ANGULAR DEPENDENCE OF COUPLING CONSTANTS

Coupling	Dihedral Angle		Ref.
	0°	180°	
$\underline{P}$-C-$\underline{H}$	large positive	zero[a]	199,200
$\underline{P}$-C-$\underline{H}$	"	smaller negative	201
$\underline{P}$-C-$\underline{F}$	"	smaller positive	201
$\underline{P}$-N-$\underline{C}$	"	small negative	202
$\underline{P}$-N-C-$\underline{H}$	"	" "	203

a) A minimum was obtained at 120°, corresponding to a small negative coupling constant.

In general, a 0° dihedral angle (Figure 43) gives rise to a large positive coupling constant, and small (negative or positive) values are associated with 180° angles. The relationship is similar to that described by Karplus(204), the difference being that he discussed the variation in coupling constant in terms of the dihedral angle between bonds in the molecule. (In fact it has recently been discovered that $^3J_{\underline{P}-\underline{H}}$ coupling depends on both dihedral angles.(205)) The effect of the orientation of the phosphorus lone pair on coupling constants is normally regarded as a 'through space' interaction.(206)(207)

In recent years an understanding of this type of relationship has become increasingly important in the attempt to explain the geometries of cyclic phosphorus compounds$^{(205)(208)}$ and also the preferred conformations round P-N bonds$^{(202)(207)}$.

C PHOSPHORUS-NITROGEN ROTATION BARRIERS

The magnitudes of torsional barriers about a variety of single bonds are known$^{(209)}$. It was only in 1967, however, that Simmonin and coworkers$^{(210)}$, using variable temperature n.m.r. methods, detected restricted rotation about a formally single P-N bond. At -52°C, the methyl signals of $PhP(Cl)-NMe_2$ coalesced, and the authors discussed this and subsequent temperature dependence in terms of hindered rotation about the P-N bond. On the basis of their results it was not possible to exclude the process of pyramidal nitrogen inversion as the rate-determining process. The origin of the hypothesised P-N rotation barrier was postulated to be a result of phosphorus lone-pair-nitrogen lone-pair repulsions and/or the partial double bond character of this bond. The authors reported a private communication from Friebolin, who, along with Imbery published$^{(211)}$ the following year, the results of a similar study on the same compound. In addition, by the use of other groups rather than methyl on nitrogen, they were able to demonstrate that pyramidal nitrogen inversion was not rate-determining, and their results indicated a large steric contribution to the P-N torsional barrier. Almost simultaneously, Cowley, Dewar and Jackson(71) published their results of a v.t. n.m.r. investigation, again on the same compound (PhP(Cl)-NMe_2). These authors claimed the first measurement of a rotational barrier round a P-N bond, although Simmonin's manuscript(210) had actually appeared before theirs was submitted. Their conclusions were similar to those of Friebolin and Imbery, except that they rejected explanations in terms of $(p-d)_\pi$ bonding on the basis of work done 8 years earlier by one of them (Dewar)(212) which indicated that π-bonding does not lead to hindered P-N rotation in phosphonitrilic chlorides. In 1969, Goldwhite and Rowsell(213), by varying the nature of the groups attached to phosphorus, obtained strong evidence in favour of a $(p-d)_\pi$ contribution to the P-N rotational barrier. The following year Cowley and coworkers(203) rejected some of Imbery and Friebolin's conclusions on the symmetrically substituted compound Cl_2P-NMe_2. They also showed, in accord with previous ideas on coupling to trivalent phosphorus (See Table 52), that the coupling constant was a function of the dihedral angle between the bond in question and the phosphorus lone pair. Their evidence suggested that the largest coupling constant was obtained when the bond was cis to the lone pair, corresponding to a 0° dihedral angle (See Figure 43). They concluded that steric, lone-pair - lone-pair repulsions, and somewhat reluctantly, $(p-d)_\pi$ bonding effects all contributed to the torsional barriers. Symmetrical compounds have far lower barriers than unsymmetrical ones (Table 53), and this suggested that in the latter, the $(p\text{-}d)_{\pi}$ contribution to the torsional barrier is enhanced by an asymmetry induced in the P(3d) orbitals by virtue of the differing substituents on phosphorus. (A recent study on a series of phosphorus imides(214)(215) revealed torsional barriers about P = N to be less than 7 Kcal/mole (29 KJ/mole). The consequences of changing the oxidation state at phosphorus are not understood in sufficient depth to allow direct comparison of both sets of results).

Subsequent papers by others(216-220) have served to confirm the origins of the coalescence phenomena of these and similar compounds in terms of restricted rotation about a phosphorus-nitrogen bond. Table 53 lists all the known barriers to rotation about a formally single P(III)-N bond, contained in these papers.

TABLE 53

TORSIONAL P-N BARRIERS IN AMINOPHOSPHINES OF THE TYPE XYP-NRR'

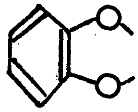
Compound					Solvent	T_c(°C)	$\Delta G^\ddagger$ (Kcal/mole)	Ref.
No.	X	Y	R	R'				
1	Me	Cl	Me	Me	a	-40	11.8	220
2	$ClCH_2$	Cl	"	"	b	-44	11.3	220
3	Ph	Cl	"	"	c	-50	10.8	i
4	Et	Cl	"	"	a	-56	10.8	220
5	Cl_2CHCF_2	Cl	"	"	/	-50→-60	/	213
6	Pr^i	Cl	"	"	a	-67	9.7	220
7	CF_3	Cl	"	"	b	-70	10.5	203
8	Ph	F	"	"	d	-71	9.9	219
9	Bu^t	Cl	"	"	a	-85	9.4	220
10	Ph	MeO	"	"	b/e	-99	8.4	219
11	CF_3	CF_3	"	"	e	-105	8.7	203
12			"	"	b/e	-112	7.8	219
13	Cl	Cl	"	"	f	-113	8.4	203
14	Ph	$C{\equiv}C{-}CH_3$	"	"	c	<-80	/	210
15	Ph	Pr^i	"	"	c	<-80	/	210
16	$ClCH_2$	F	"	"	/	<-100	/	213
17	F	F	"	"	f	<-120	/	203
18	Ph	Ph	"	"	f	<-130	/	203
19	Me_2N	Cl	"	"	f	<-140	/	203
20	MeO	MeO	"	"	b/e	<-152	/	203
21	CF_3	CF_3	H	Me	e	-101	9.0	71

TABLE 53 (continued)

No.	X	Y	R	R'	Solv.	T_c(°C)	$\Delta G^{\ddagger}$ (Kcal/mole)	Ref.
22	MeONMe	Cl	OMe	Me	e	-109	8.3	218
23	MeONMe	Br	OMe	Me	e	-127	/	218
24	MeONMe	F	OMe	Me	e	<-130	/	218
25	F	F	OMe	Me	e	<-130	/	218
26	Cl	Cl	OMe	Me	e	<-130	/	218
27	Br	Br	OMe	Me	e	<-130	/	218
28	F	F	MeN-PF_2	Me	b	-120	/	218
29	Ph	Cl	Et	Et	c	-50	10.0	j
30	Cl	Cl	"	"	c	<-80	/	203
31	Ph	Ph	"	"	f	<-120	/	203
32	Ph	Cl	Pr^n	Pr^n	c	-55	-10.8	211
33	Ph	Cl	Pr^i	Pr^i	b	-15	12.8	k
34	Me	Cl	"	"	a	-20	13.4	220
35	Me	F	"	"	a	-60	10.9	220
36	Ph	Cl	Bu^n	Bu^n	c	-60	10.7	211
37	Ph	Cl	Bu^s	Bu^s	c	+15	14.6	211
38	Me	Cl	"	"	g	-5	13.5	220
39	Me	F	"	"	h	-50	10.8	220
40	Ph	Cl	H	Bu^t	c	<-80	/	210
41	Ph	Cl	Me	Bz	c	-48	11.1	211
42	Ph	Cl	Bz	Bz	g	-46	/	203
43	Cl	Cl	Me	Bz	c	<-80	/	211

TABLE 53 (continued)

No.	X	Y	R	R'	Solv.	T_c (^oC)	$\Delta G^\ddagger$ (Kcal/mole)	Ref.
44	Ph	Ph	Me	Bz	c	<-80	/	211
45	Ph	Cl	Pr^i	Bz	c	<-80	/	211
46	Ph	Cl	Me	Ph	c	<-80	/	210
47	$C\equiv C-CH_3$	$C\equiv C-CH_3$	Me	Ph	c	<-80	/	210
48	Ph	Cl	Et	Ph	c	<-80	/	210

a) $CHCl = CH_2$; b) $CFCl_3$; c) CS_2; d) nC_6H_{14} e) $CHFCl_2$; g) $CDCl_3$; h) $CHClF_2$; i) Refs. 203, 210, 211 and 219; j) Refs. 203 and 211; k) Refs. 203, 211 and 219.

(2) CHARACTERISATION

A GENERAL

Compounds of the type $Ph_2P\text{-}N(R)\text{-}P(Ph)Cl$ (I) (R = Me, Et, Pr^n, Pr^i, Bu^t) were synthesised using a variety of methods. The first involved reaction of $Ph_2P\text{-}N(H)R$ with $PhPCl_2$ and adding Et_3N to produce (I) and the amine hydrochloride. Where R = Me, a large amount of the phosphine oxide was produced, and another method was explored. $Ph_2P\text{-}N(Me)\text{-}SiMe_3$ was reacted with $PhPCl_2$ when product (I) (R = Me) was obtained and Me_3SiCl given off. Although this was successful (R = Me, Et), a quicker route to (I) was established by lithiation of $Ph_2P\text{-}N(H)R$ with Bu^nLi and addition of $PhPCl_2$. Products (I) (R = Et, Pr^n, Pr^i and Bu^t) were synthesised by this method.

DIPHOSPHINOAMINES

The diphosphinoamines were characterised by elemental (Table 54), mass spectroscopic and ^{31}P and ^{1}H n.m.r. spectroscopic analyses. The procedure generally adopted was to use crude samples for the variable temperature n.m.r. investigations and then purify for C, H and N, and mass spectral analyses. This allowed the preparations to be carried out on a smaller scale than usual.

N.M.R.

In order to understand the resonances obtained in the ^1H n.m.r. spectrum a brief description of the symmetry properties of the compounds is required.

FIGURE 44

PHOSPHORUS ATOM NOTATION

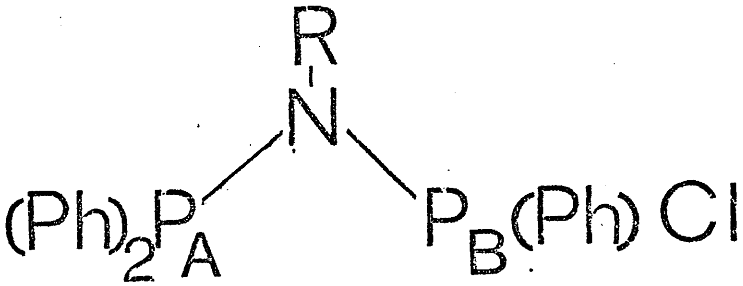


TABLE 54

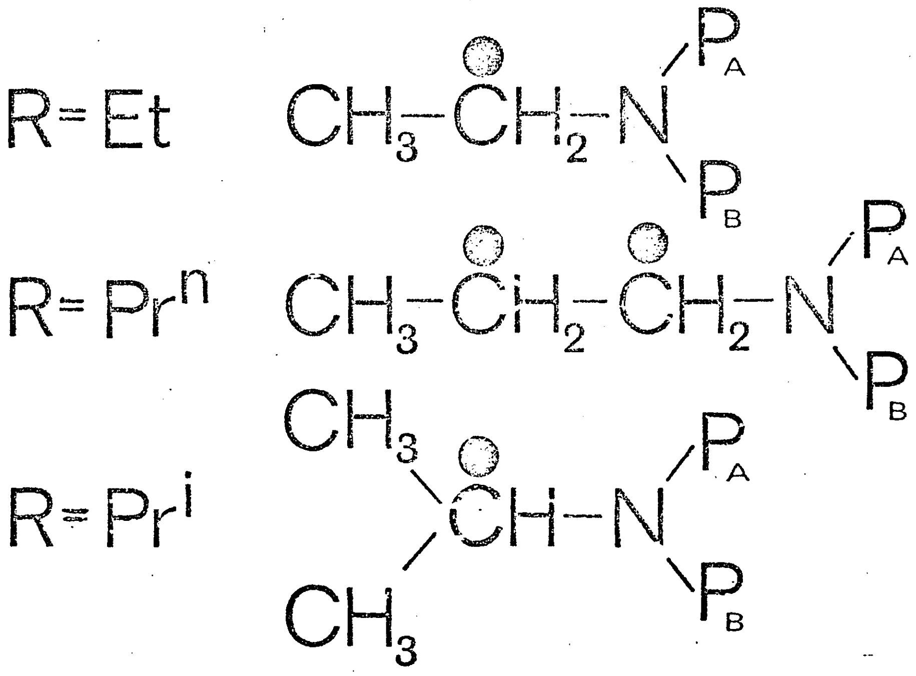
ELEMENTAL ANALYSES ON $Ph_2P-N(R)-P(Ph)Cl$

R	% Found			% Required		
	C	H	N	C	H	N
Me	64.02	5.64	3.02	63.78	5.03	3.92
Et	64.64	6.54	5.10	64.60	5.38	3.77
Pr^n	63.47	5.93	3.04	65.37	5.71	3.63
Pr^i	64.92	5.91	2.26	65.37	5.71	3.63
Bu^t	62.32	5.94	2.66	66.08	6.01	3.50

Trivalent phosphorus is normally configurationally stable on the n.m.r. time scale(221) at ambient temperatures. P_B in Figure 44 is therefore a CHIRAL(78), and P_A a PROCHIRAL centre(222). The phenyl groups on P_A can in theory show chemical shift non-equivalence in chiral or achiral solvents, but this effect is generally not readily detectable due to the complicated resonances often found in the aromatic region of such spectra. However, in (I) (R = Et, Pr^n or Pr^i) other prochiral centres exist in the molecule (Figure 45) and these anisochronous resonances are generally easier to identify.

FIGURE 45

PROCHIRAL CENTRES IN Ph$_2$P-N(R)-P(Ph)Cl COMPOUNDS



Prochiral centres are labelled ●

Table 55 shows the ^1H n.m.r. parameters of all the compounds under investigation. The resonances obtained are consistent with the structure shown in Figure 44. In the methyl derivative (I , R = Me), the two phosphorus nuclei couple differently to the methyl proton nuclei, the largest $\underline{P}$-N-C-$\underline{H}$ coupling being to the chlorophenylphosphino-moeity (P_B). This is based on $^1H\{^{31}P\}$ selective irradiation experiments. (See Table 59). These also show that P_A couples more strongly to the methyl signal of the ethyl derivative (I, R = Et), although this coupling is not in fact resolved. A similar result was obtained with the methylene protons (-N-$\underline{CH_2}$-) of the n-propyl compound (I, R = Pr^n). The methylene resonance of the ethyl derivative (I, R = Et) shows only a small degree of chemical shift non-equivalence of these prochiral protons, but a much larger effect is found for methyl protons of the i-propyl compound (I, R = Pr^i). Two doublets ($J_{\underline{H}-C-C-\underline{H}}$ = 6.7 Hz) are found, 16.5 Hz apart. (Four strong peaks were observed in the methyl region of the t-butyl spectrum (I, R = Bu^t), illustrating that some decomposition had probably occurred).

TABLE 55

^{1}H n.m.r. PARAMETERS OF $Ph_2P-N(R)-P(Ph)Cl$ COMPOUNDS

R	Solvent	τ_{Ph}	τ_{CH_3}	τ_{CH_2}	τ
Me	CH_2Cl_2	2.5(m)	7.54^a(2d)	/	/
Et	CH_2Cl_2	2.5(m)	9.3^b(t)	6.9(q)	/
Pr^n	PhCl	2.8(m)	9.7(m)	8.6^d(m)	7.1^e(m)
Pr^i	CH_2Cl_2	2.6(m)	8.8^c(2d)	/	6.3^f(m)

(m = multiplet, q = quartet, t = triplet, d = doublet)

a) $^3J_{P-H}(Ph_2P-)$ = 2.4 Hz; $^3J_{P-H}(PhPCl)$ = 4.8 Hz.

b) $J_{\underline{H}-C-C-\underline{H}}$ = 7.3 Hz;

c) Two doublets ($J_{\underline{H}-C-C-\underline{H}}$ = 6.7 Hz) 16.5 Hz apart.

d) $N-CH_2-\underline{CH_2}-$

e) $N-\underline{CH_2}-$

f) Methine proton.

Shifts quoted to one decimal place are approximate because of the complex nature of the signals involved.

^{31}P chemical shifts and P-N-P coupling constants were obtained by ^{31}P n.m.r. and $^{1}H\{^{31}P\}$ selective irradiation experiments. These results are shown in Table 56.

TABLE 56

^{31}P CHEMICAL SHIFTS AND COUPLING CONSTANTS OF Ph_2P-N(R)-P(Ph)Cl COMPOUNDS[a]

	Chemical Shift[b]				Coupling Constant	
	PhPCl		Ph_2P		$2J_{P-N-P}$ (Hz)	
R	^{1}H	^{31}P	^{1}H	^{31}P	^{1}H	^{31}P
Me	-141.8	/	-67.4	/	+333	/
Et	-139.9	-138	-65.1	-63.5	+165	158
Pr^n	/	-124.4	-64.8	-63.5	+139	145
Pr^i	-134.6	-132	-44.1	-42.1	-26	29
Bu^t	/	-128.7	/	-59	/	35

a) Measured at room temperature.

b) Relative to external 85% H_3Po_4. Negative values to low field.

The ^{31}P spectra generally consisted of two signals separated by at least 70 p.p.m. Each signal was split into a doublet (P-N-P coupling). The lowest field resonances were assigned to the phenylchlorophosphino-phosphorus nucleus (P_B) on the basis of the data presented in Table 57.

TABLE 57

EFFECT OF HALOGEN SUBSTITUENT ON ^{31}P CHEMICAL SHIFT[a]

Compound	^{31}P Chem. Shift (p.p.m.)
Ph_3P	+7
Ph_2PCl	-80
$PhPCl_2$	-162
PCl_3	-219

a) Values taken from Ref. 223 and relative to external 85% H_3PO_4

Increasing the number of chlorine substituents causes a ^{31}P chemical shift to low field.

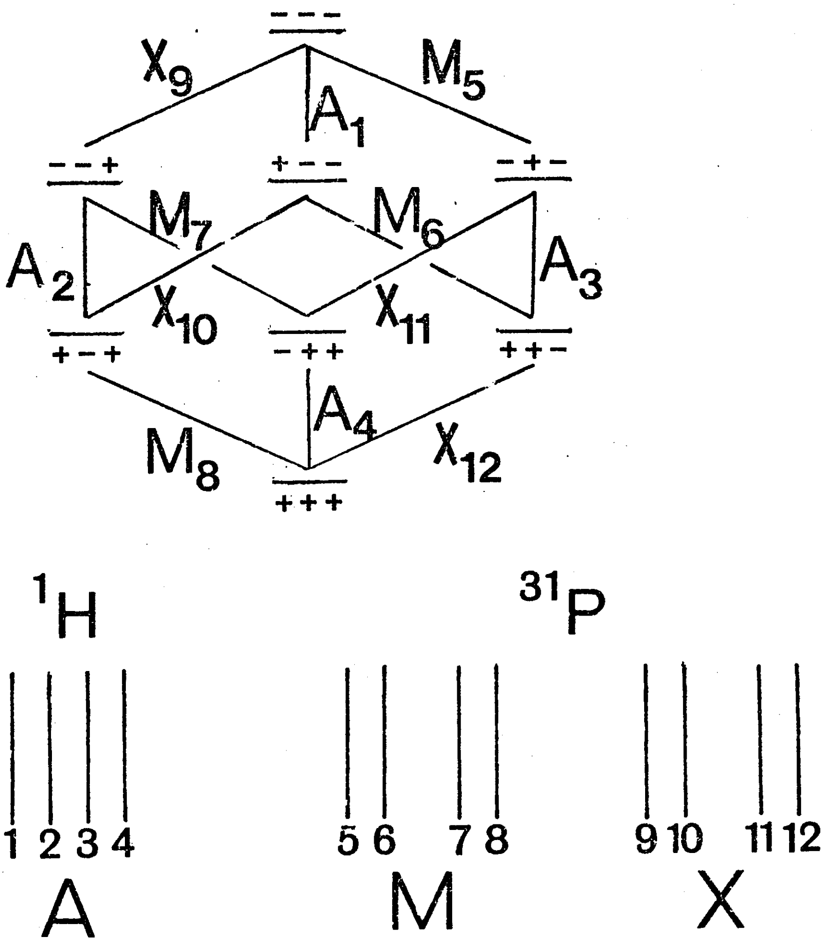
B SIGNS OF COUPLING CONSTANTS

Correlations between coupling constants and some other physical measurement (e.g. electronegativity) are generally only valid when the relative sign of the coupling constant is known. In this study, conformer populations about a P-N-P framework are related to the P-N-P coupling constant. Before describing in more detail the results of a determination of the signs of these coupling constants, it is worthwhile giving a simplified account of the theory behind the method. (See reference 224 for a fuller discussion of the theory).

Coupling (J) between nuclei may be either positive or negative. If the energetically more stable orientation of the coupled nuclear spins is antiparallel, J is said to be positive. A parallel arrangement denotes a negative J. Figure 46 shows a simplified diagram of the transitions responsible for the lines produced in both the ^{1}H and ^{31}P spectra of $Ph_2P\text{-}N(Me)\text{-}P(Ph)Cl$. The methyl group is treated as a one-spin system, and coupling to the aryl protons is ignored. As discussed previously, the ^{1}H spectrum consists of two doublets due to coupling with the two different phosphorus atoms, and two sets of doublets are also observed in the ^{31}P spectrum due to $\underline{P}$-N-$\underline{P}$ coupling. The closely spaced lines in the ^{31}P spectra, ($M_{5,6}$, $M_{7,8}$, $X_{9,10}$ and $X_{11,12}$) were not resolved. A_1 denotes the lowest energy transition in the ^{1}H spectrum and is represented in the figure by a transition starting from an antiparallel arrangement of spins. Similarly M_5 and X_9 are the lowest energy transitions in the doublets obtained in the ^{31}P spectra. A positive $\underline{P}$-N-C-$\underline{H}$ coupling constant is assumed based on the work of Verkade and coworkers(225) ——— the $\underline{P}$-N-$\underline{P}$ coupling constant is assumed to have the same sign as $^{3}J_{P-H}$, namely positive. Selective irradiation of the ^{31}P resonance frequencies, while observing the ^{1}H spectrum will produce the following results. Irradiation of X_{11} and X_{12} will perturb A_3 and A_4, since all are connected in the energy level diagram.

FIGURE 46

ENERGY LEVEL DIAGRAM FOR $Ph_2P\text{-}N(R)\text{-}P(Ph)Cl$



(+) = spin moments are parallel to H_o.

(-) = spin moments are antiparallel to H_o.

Similarly the following perturbations will be observed.

TABLE 58

$^{1}H\{^{31}P\}$ CORRELATIONS FOR POSITIVE COUPLING CONSTANTS

	M		X	
Irradiating Freq.	5,6	7,8	9,10	11,12.
Perturbed Signals	$A_1 A_3$,	$A_2 A_4$,	$A_1 A_2$,	$A_3 A_4$.

In general the high field part of the ^{31}P doublet will affect the high field part of the ^{1}H spectrum, and there is also a low-field - low-field perturbation correlation. The results shown in the Table below were those obtained for the methyl derivative.

TABLE 59

$^{1}H\{^{31}P\}$ RESULTS FOR $Ph_2P-N(Me)-P(Ph)Cl$

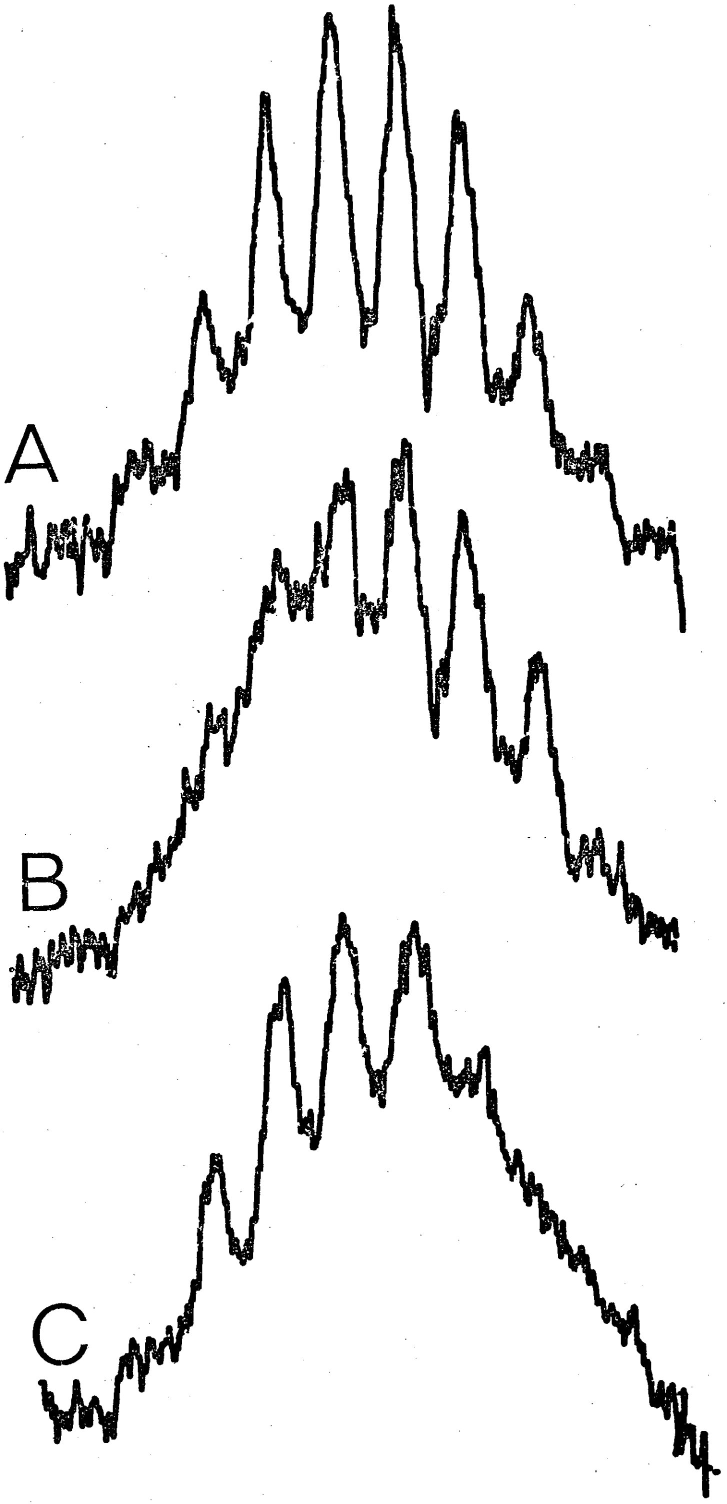
^{1}H n.m.r. Lines	^{31}P Irradiating Frequencies (MHz) [a]
A_1	24.290324, 24.288516
A_2	24.289991, 24.288516
A_3	24.290324, 24.288183
A_4	24.289991, 24.288183

a) ±2 Hz.

These results correspond to the representations given in Table 58 and demonstrate that $\underline{P}$-N-$\underline{P}$ coupling in Ph_2P-N(Me)-P(Ph)Cl is positive, assuming of course that the $\underline{P}$-N-C-$\underline{H}$ coupling is also positive. Similar investigations of the sign of $J_{\underline{P}-N-\underline{P}}$ in (I, R = Et, Pr^n) revealed positive coupling constants. However an inverse correlation between the high field parts of the ^1H and ^{31}P n.m.r. spectra were found in the i-propyl compound. This is illustrated in Figure 47, and represents the first example of a negative $\underline{P}$-N-$\underline{P}$ coupling constant between trivalent phosphorus nuclei. $J_{\underline{P}-N-\underline{P}}$ for (I,R = Bu^t) could not be measured by this method, but was assumed to be negative on the basis of the similar coupling and also the similar v.t. n.m.r. behaviour to the i-propyl compound (I, R = Pr^i). (See figure 57, page 252.)

FIGURE 47

^{1}H-METHINE RESONANCE OF $Ph_2P-N(Pr^i)-P(Ph)Cl$



A : No irradiation

B : High field ^{31}P irradiation (24.289923 MHz)

C : Low field ^{31}P irradiation (24.289951 MHz)

3 VARIABLE TEMPERATURE N.M.R.

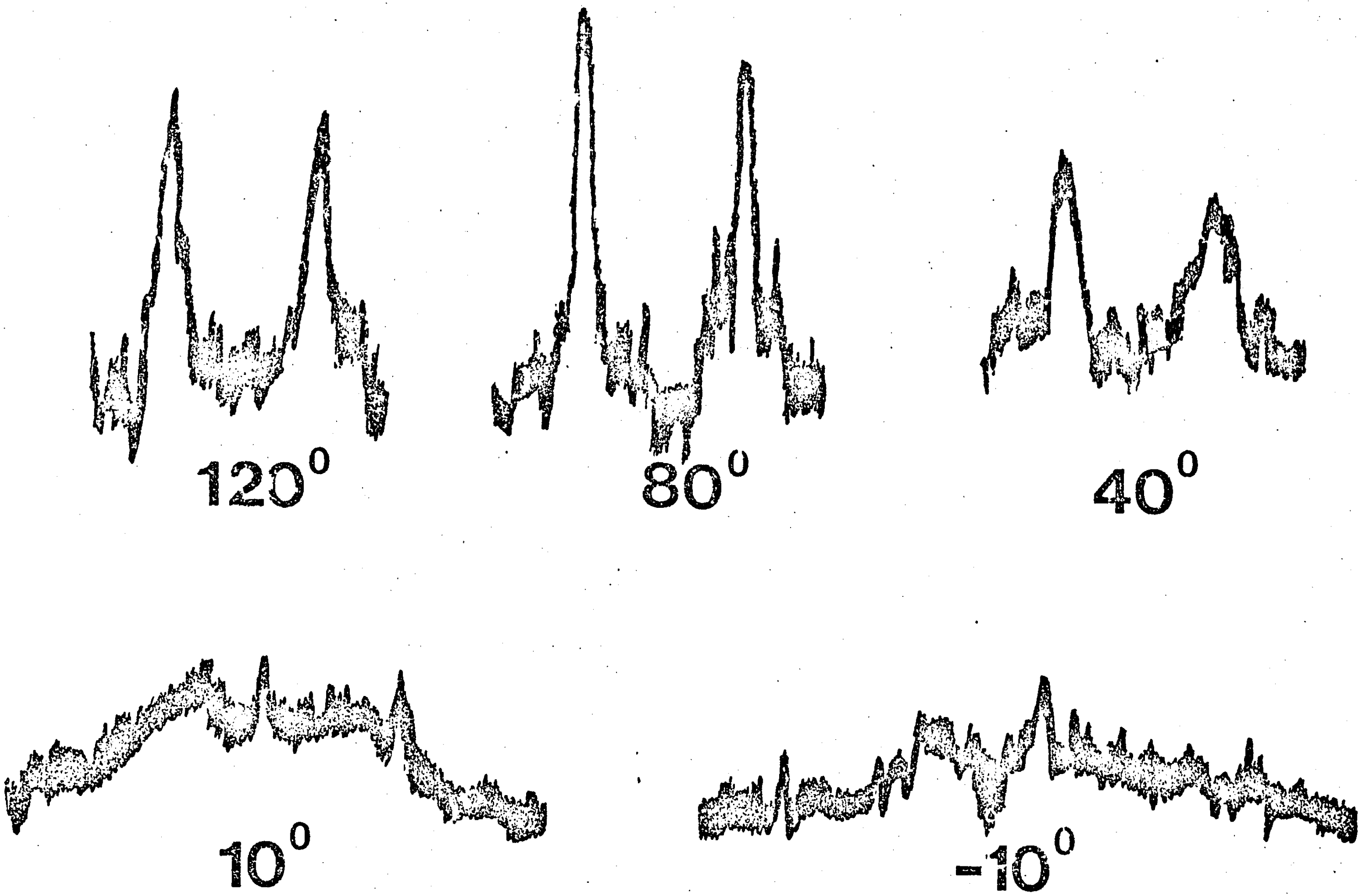
All the compounds discussed in the previous section were examined by variable temperature n.m.r. Figure 48 shows the results of such a study on (I) ($R = Pr^i$) (CH_2Cl_2 and PhCl solutions), and illustrates the behaviour of the high field doublet (Ph_2P signal) over a $-40 \rightarrow +120^\circ C$ temperature range. A number of features emerge. Firstly, a dynamic process is occurring in the molecule causing coalescence of the signals ($T_c \approx -25^\circ C$), and secondly there is a variation in the $\underline{P}$-N-$\underline{P}$ coupling constant with temperature. Coalescences generally occurred in (I) (R = Et, Pr^n, Pr^i and Bu^t) (Table 60) over a 20 - 30°C range, and in some cases (e.g. low field signal of I, ($R = Bu^t$)) only one signal coalesced. In addition much larger variations in the $\underline{P}$-N-$\underline{P}$ coupling constants were found for the ethyl and n-propyl derivatives. The causes, significance and possible origins of these observations are now discussed.

TABLE 60

COALESCENCE TEMPERATURES OF Ph_2P-N(R)-P(Ph)Cl

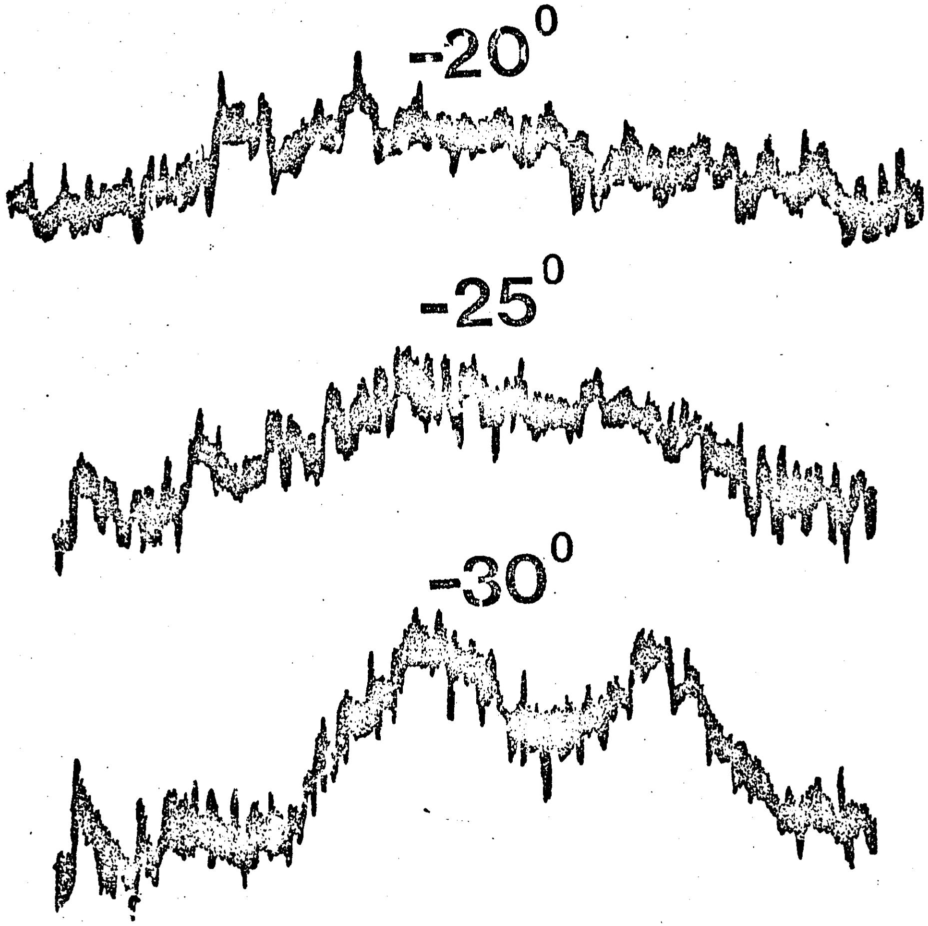
R	T_c(°C)
Me	< -100
Et	-75
Pr^n	-80
Pr^i	-25
Bu^t	+20

FIGURE 48



TEMPERATURE DEPENDENCE OF Ph_2P SIGNAL (^{31}P) OF $Ph_2P-N-(Pr^i)-P(Ph)Cl$

FIGURE 48 (continued)



(A) Identification of the rate-determining dynamic process.

The most likely configurational and conformational changes giving rise to the v.t. n.m.r. behaviour in molecules of the type $Ph_2P-N(R)-P(Ph)Cl$ are:-

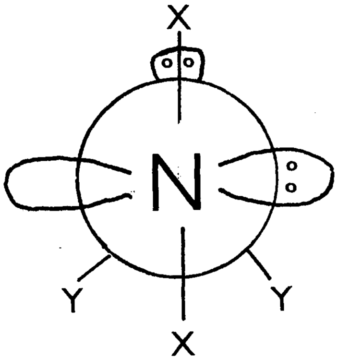
a) Pyramidal phosphorus inversion
b) Chloride ion exchange
c) Pyramidal nitrogen inversion
d) Phosphorus-nitrogen bond rotation.

The presence of two signals (16.5 Hz. apart) from the prochiral methyl groups of the i-propyl compound at room temperature has already been discussed. These signals indicate that $-\underline{P}(Ph)Cl$ constitutes a configurationally stable pyramidal centre on the n.m.r. time scale and therefore that pyramidal phosphorus inversion or chloride ion exchange (leading to phosphorus inversion) are not responsible for the coalescence phenomena exhibited by these compounds. Indeed, the Free Energy of Activation of pyramidal phosphorus inversion is generally greater than 25 Kcal/mole (105 KJ/mole), just outside the range of dynamic n.m.r. measurement, although values less than this have been found(226). Furthermore, no variation in the coalescence temperature was found in (I) (R = Me, Et) in the presence of either amine hydrochloride or lithium chloride, both of which might be expected to promote halide ion exchange. Fontal and Goldwhite(227) observed such a process in a study of tri-coordinate phosphorus compounds, but the coalescences were strongly concentration dependent. (A variation with concentration of more than 100°C was found). Neither of processes a) or b) is therefore responsible for the temperature dependent spectra.

The coalescence temperatures of these compounds are shown in Table 60. Increasing the bulk of the substituent on nitrogen causes a decrease in the rate of the process causing the coalescences. Since bulky substituents on nitrogen generally lead to steric relief in the transition state of pyramidal inversion(228) and hence to a rate increase, we assume that this process is not rate-determining in our studies. (In fact the low barriers to pyramidal nitrogen inversion in acyclic molecules with no strongly electron-withdrawing substituents nearly always preclude the use of d.n.m.r. methods, although the presence of a heteroatom with a lone pair can serve to increase the barrier(229)). Cowley and coworkers have suggested(203) that given this rapid inversion rate on the n.m.r. time scale, even at low temperatures, the best representation of the ground state geometry of nitrogen is that of an sp^2 hybrid (Figure 49) and strong π-overlap of the remaining p-orbitals with d-orbitals on phosphorus.

FIGURE 49

ILLUSTRATION OF PLANAR GEOMETRY OF NITROGEN



This is consistent with the planar or near planar geometry of nitrogen found in aminophosphines of the type:- F_2P-NMe_2 (X-ray(230) and microwave(231)), F_2P-NH_2 (microwave)(232) $Ph_2P-N(Me)-P(S)Ph_2$ (X-ray)(233), Cl_2P-NMe_2 (electron-diffraction)(234) and $F_2P-N(Me)-PF_2$ (electron-diffraction)(235). The short P-N bonds found in these compounds indicates considerable π-overlap of the lone pair on nitrogen with vacant (d) orbitals on phosphorus. We believe then that hindered P-N rotation best explains our v.t. n.m.r. results. Steric congestion is normally increased in the transition state to rotation, leading to rate decelerations, and Table 60 shows that the highest coalescence temperatures associated with the compounds with the bulkiest R groups. This same effect has been observed in other studies of hindered rotation about formally single P-N (Table 53), S-N(236) and N-O(237) bonds. The large variations (-38 → + 343 Hz) in the P-N-P coupling constants can be rationalised in terms of preferred conformations about the phosphorus-nitrogen bonds.

B CONFORMATIONAL PREFERENCES AT LOW TEMPERATURES AND COUPLING CONSTANTS

Table 61 records the variation in P-N-P coupling constant with temperature. The range of values obtained can be understood in terms of the steric requirement of the R group, leading to different dihedral angles between the lone pairs and the P-N bonds. (Nixon(238) also found large $^2J_{P-P}$

TABLE 61

VARIATION IN J_{P-N-P} IN $Ph_2P-N(R)-P(Ph)Cl$ AS A FUNCTION OF TEMPERATURE

R = Me[a]		R = Et		R = Pr[n]		R = Pr[i]		R = Bu[t]	
T	J(Hz)	T	J(Hz)	T	J(Hz)	T	J(Hz)	T	J(Hz)
-30	343	-97	343	-100	332	-60	-35	-30	-38
-5	339	-93	317	-95	313	-50	-34	-20	-38
+26	335	-86	302	-90	295	-40	-33	+10	-35
+51	327	-36	214	-60	218	-10	-29	+30	-35
+80	318	-32	200	-50	202	0	-30	+40	-35
+105	309	-23	196	-40	195	+10	-29	+50	-35
+135	304	-12	185	-30	175	+40	-26	+70	-35
		+10	172	-20	166	+60	-24	+80	-34
		+40	156	-10	161	+80	-26	+100	-34
		+60	148	0	157	+100	-27	+124	-34
		+80	139	+10	155	+120	-25		
		+100	133	+40	139				
		+130	127	+60	129				
				+80	122				
				+100	116				
				+120	110				

a) Although temperatures as low as -100°C were obtained in search of coalescence phenomena, $^2J_{P-P}$ determinations did not continue past -30°C.

coupling constants (Table 62) in a series of $F_2P-N(R)-PF_2$ compounds which varied according to the size of the substituent on nitrogen).

TABLE 62

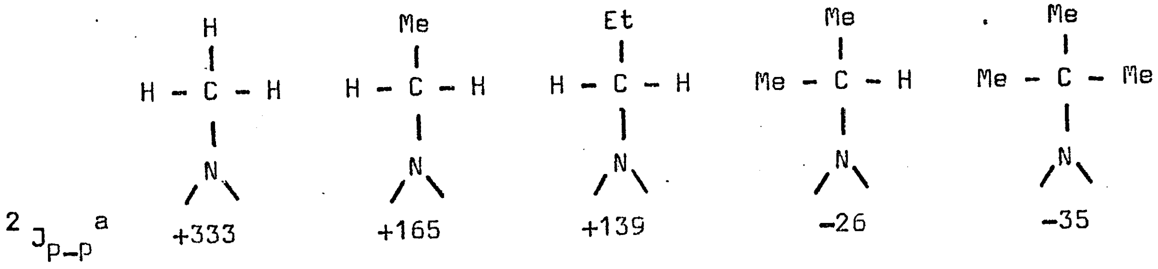
P-N-P COUPLING CONSTANTS IN $F_2P-N(R)-PF_2$

R	$^2J_{P-P}$(Hz)
Me	437
Et	446
Ph	371
m -ClC_6H_4	372

Because of the correlation which exists between the steric bulk of the substituent on nitrogen and the P-N-P coupling constant at room temperature (Figure 50), a detailed examination, by molecular models, of the steric requirements of all the compounds is necessary.

FIGURE 50

P-N-P COUPLING CONSTANTS AT R.T.



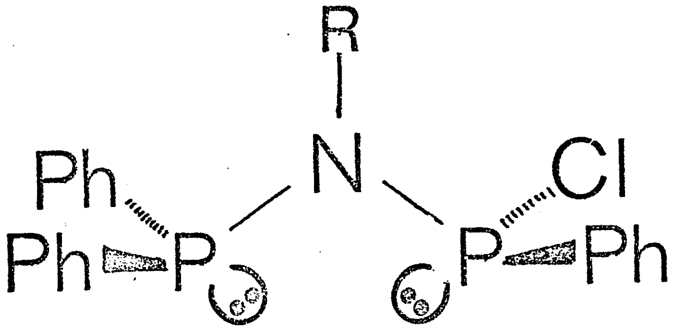
a) Hz., at room temperature. Error on measurements is ±2 Hz.

This is related to the dihedral angle between the lone pair on one phosphorus atom and the P-N bond involving the other phosphorus atom. Two sets of lone pairs and P-N bonds give rise to two dihedral angles, and the results are shown in Table 63.

a) I, (R = Me). The most stable conformer is the (0,0) case, corresponding to two 0^o dihedral angles between both P-N bonds and phosphorus lone pairs. This is illustrated below.

FIGURE 51

(0,0) CONFORMATION



This allows all the phenyl rings in the molecule to be furthest apart. The (0,180) conformer (Figure 52) also appears to be sterically favourable.

TABLE 63

ALLOWED CONFORMATIONS IN Ph_2P-N(R)-P(Ph)Cl COMPOUNDS

Conformer	R=Me	R=Et	R=Pr^n	R=Pr^i	R=Bu^t
(0, 0)	+	+	+	-	-
(0, 90)	?	-	-	-	-
(0, 180)	+	+	+	+	+
(0, 270)	-	-	-	-	-
(90, 0)	+	+	+	-	-
(90, 90)	-	-	-	-	-
(90, 180)	-	-	-	-	-
(90, 270)	+	+	+	?	-
(180, 0)	?	-	-	-	-
(180, 90)	-	-	-	-	-
(180, 180)	-	-	-	-	-
(180, 270)	-	-	-	-	-
(270, 0)	+	+	+	?	-
(270, 90)	-	-	-	-	-
(270, 180)	-	-	-	-	-
(270, 270)	-	-	-	-	-

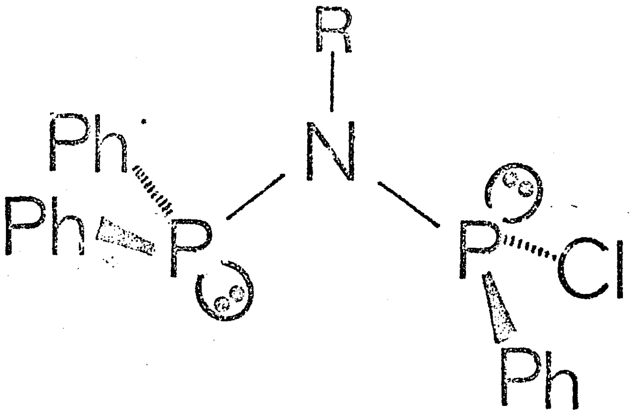
\+ = Sterically favourable conformer

\- = Sterically congested conformer

? = Possible conformer.

FIGURE 52

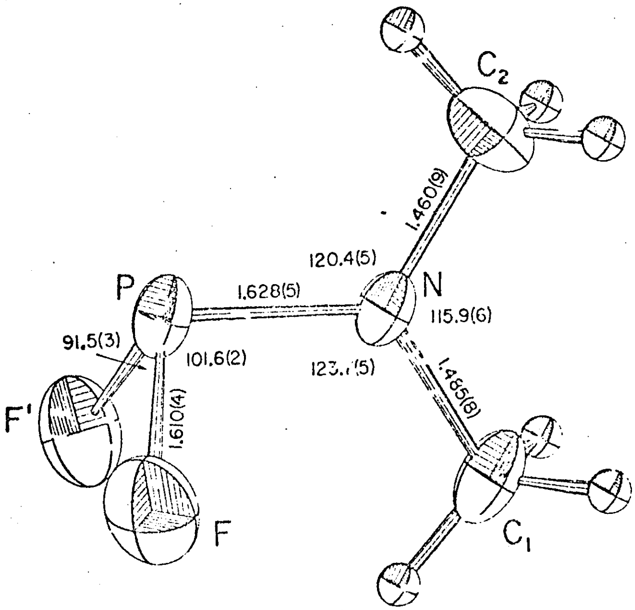
(0,180) CONFORMER



Morris and Nordman(230) reported 0° and 180° dihedral angles between the lone pair on phosphorus and C-N bonds, as shown below.

FIGURE 53

ORTEP DRAWING OF F_2P-NMe_2 (ELECTRON DIFFRACTION) [a]



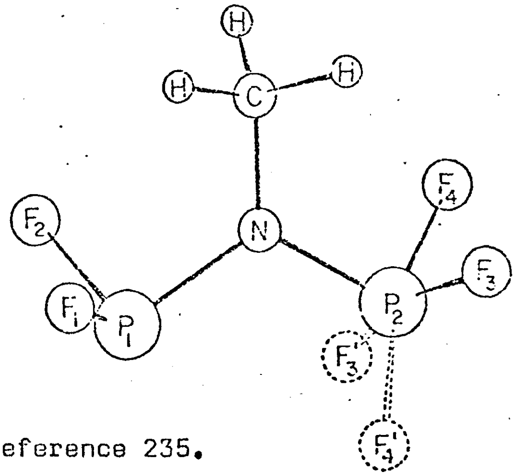
(Bond lengths in Å, angles in degrees)

a) Taken from reference 230.

It is interesting to note too that Hedberg and coworkers(235) also observed the (0,0) conformer in their electron diffraction investigation of $F_2P-N(Me)-PF_2$ (Figure 54),

FIGURE 54

STRUCTURE OF $F_2P-N(Me)-PF_2$ [a]



a) Taken from reference 235.

and that they could not rule out the presence of a small amount of another conformer, postulated as the (0,180) rotamer.

(b) I, (R = Et). The steric requirement of the ethyl group is similar to that of methyl, except that slight interactions with all three benzene rings are now possible. Again, the (0,0) conformer is predominant.

(c) I, (R = Pr^n). The longer chain does not have a greater steric demand, except that now slight steric interactions with all the groups attached to both phosphorus atoms exist. The (0,0) rotamer is still the most sterically favourable.

d) I, ($R = Pr^i$). Conformation (0,0) is the most sterically hindered due to strong methyl-phenyl and methyl-chlorine interactions. The most stable arrangement is the (0,180) conformation.

e) I, ($R = Bu^t$). A similar situation to I ($R = Pr^i$) is found except that (0,180) seems to be the only conformer that can exist. The magnitude and temperature variation of the P-N-P coupling can be rationalised on the assumption that 0° dihedral angles lead to large positive coupling constants and 180° angles to small negative values. Both are reasonable assumptions in the light of previous work (see Table 52) although the latter might be open to some doubt. At low temperatures the methyl, ethyl and n-propyl compounds exist predominantly in the (0,0) conformation (Figure 51) and show large positive P-N-P coupling constants. On raising the temperature P-N bond rotation occurs such that other conformers are relatively more populated, and since all of these necessarily have smaller $^2J_{P-P}$ values than the (0,0) conformer (see Figure 51), a net reduction in the P-N-P coupling is found. A concomitant increase in the P-N-C-H coupling constant is also expected and indeed found (Table 64) although the smaller values make the effect less obvious.

TABLE 64

CORRELATION BETWEEN $^{2}J_{P-P}$ AND $^{3}J_{P-H}$ IN $Ph_2P-N(Me)-P(Ph)Cl$

J(Hz)	-30°C	+105°C	Change
$\underline{P}-N-\underline{P}$	343	309	-10%
$\underline{P}_B-N-C-\underline{H}$	4.5	4.9	+9%
$\underline{P}_A-N-C-\underline{H}$	2.2	2.5	+14%

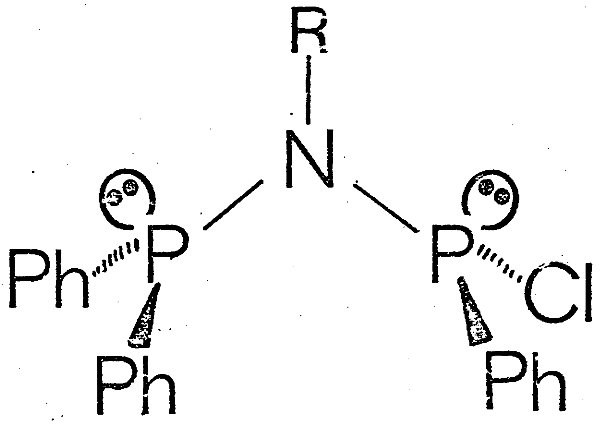
Because the methyl derivative has more allowed conformers with 0° dihedral angles (Table 63), its $\underline{P}-N-\underline{P}$ coupling constants are greater at every temperature than those of the ethyl or n-propyl compounds. Furthermore the fact that a steady coupling constant is never observed, even at temperatures as low as -100°C, implies that slow P-N bond rotation is still taking place at these temperatures and that although the (0,0) conformer is predominant, other sterically favourable conformations exist.

Not so easily explained are the small negative coupling constants of the i-propyl and t-butyl compounds. Table 63 shows that the (0,180) conformer (see Figure 52) is the most favoured, but such a combination of dihedral angles is expected to give rise to at least a medium sized positive $\underline{P}-N-\underline{P}$ coupling constant. A re-examination of some of our assumptions and premises is therefore necessary.

a) If phosphorus lone-pair - nitrogen lone-pair repulsions say, dominate the stereochemistry of these compounds, our steric model might be invalid and conformers such as (180,180) (Figure 55) which are expected to show small negative $^2J_{P-P}$ coupling might be predominant.

FIGURE 55

(180,180) CONFORMATION



This is however unlikely, and it is interesting to note that Hedberg and coworkers(235) also rejected the (180,180) rotamer as the other possible conformer of $F_2P-N(Me)-PF_2$.

b) A 180° dihedral angle between the phosphorus lone pair and the P-N bond could result in a large negative P-N-P coupling constant. Mavel(201) has tentatively suggested that a 180° dihedral angle relating to P-C-H coupling results in negative coupling constants of magnitude ca.70% of those corresponding to the 0° situation, but apart from this there is no precedent to substantiate this suggestion.

c) Both phosphorus lone pairs might contribute unequally to the overall coupling constant. The fact that P-N-C-H coupling in I(R = Me) (see Table 55) is greater for the chlorophenylphosphorus nucleus could indicate that, if the Fermi Contact coupling mechanism(196) is predominant, that the lone pair on this phosphorus has more p-character and hence stronger directional properties. Its contribution to the overall coupling constant would therefore be greater and the 0° dihedral angle in the (0,180) conformer would be less important.

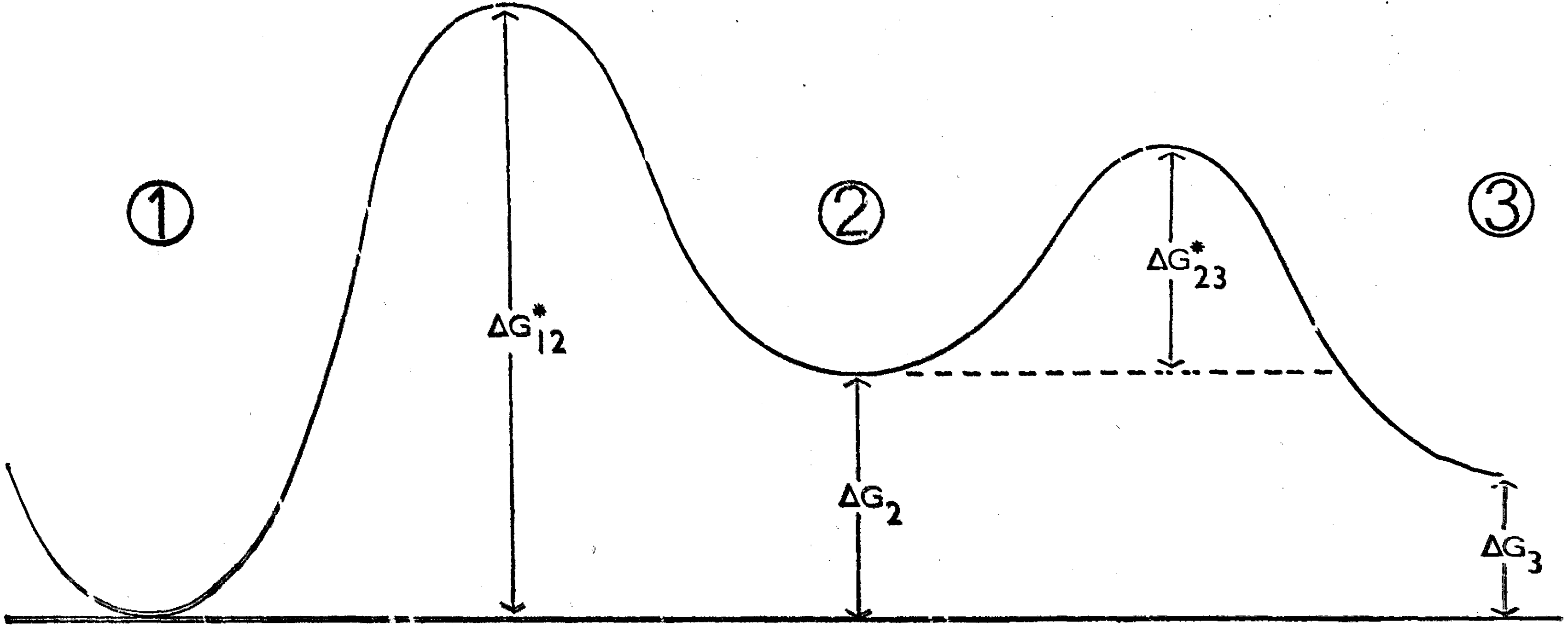
The small variation of both the i-propyl and t-butyl derivatives (Table 62) indicates that these molecules exist predominantly in one conformation, presumably (0,180) (see Figure 52) or close to it, even at high temperatures. Thus although P-N bond rotation might be fast at these temperatures, maximum residence time is spent in the one, sterically favourable conformation.

C COALESCENCE TEMPERATURES AND MECHANISM

A typical diagrammatic representation of rotation about a P-N bond is shown in Figure 56. Since the ground state energies of the various conformers are different, exchange takes place between unequally populated sites and the activation

FIGURE 56

TYPICAL FREE ENERGY PROFILE FOR ROTATION ABOUT A P-N BOND



(1) (2) and (3) represent different rotamers.

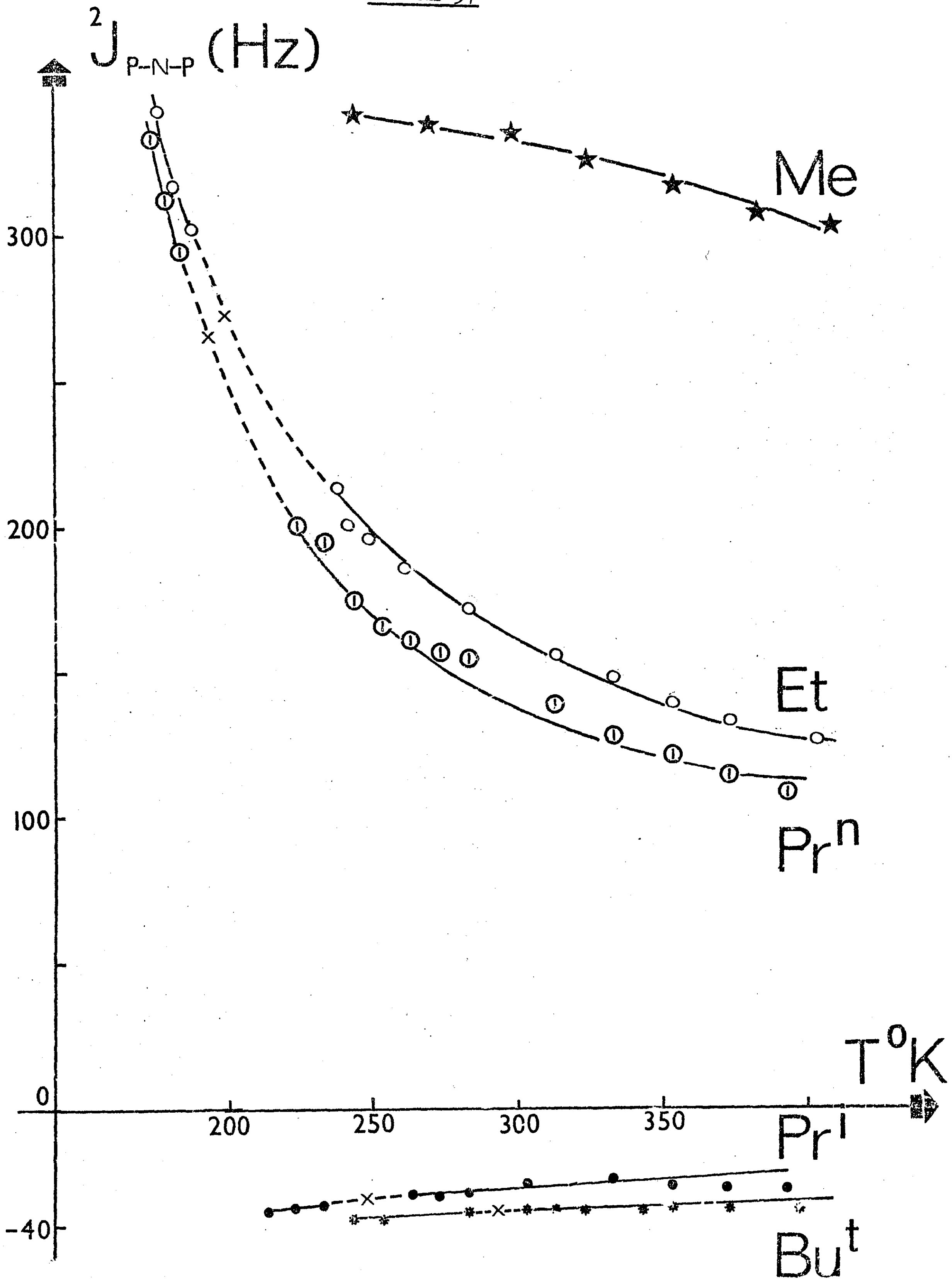
parameters of the forward and reverse reaction pathways are also different. Interconversions between conformers do not necessarily change the magnetic environments of the nuclei, therefore the corresponding barriers will not affect the appearance of the n.m.r. spectrum. (Small barriers are evident in the variation of P-N-P coupling constant with temperature (Figure 57)). The fact that coalescence of the high field signal of I (R = Bu^t) is not observed can be explained in these terms. No alteration in the chemical shift of this signal (±1 p.p.m. experimental error) is found throughout the coalescence temperature range of the low field signal.

The exchange broadened parts of the spectra do not then respond to the rate processes with equal sensitivity, so that all the activation energy barriers cannot be reliably assessed. This lack of response explains why only one coalescence temperature in each compound is generally observed. It corresponds presumably to the highest torsional barrier in each molecule.

Because phosphorus-nitrogen bond rotation can occur at two sites in the molecule (I), a number of descriptions of the dynamic nature of these compounds are possible.

a) Completely uncorrelated rotation about both P-N bonds is in theory possible. This mechanism is thought to be operative in $F_3P(NH_2)_2$, (239) but the unsymmetrical nature of the two P-N bonds in (I) make this an unlikely process. More plausible would be preferential hindered rotation about one of the P-N bonds. This is most likely to be the PhP(Cl)-N bond,

FIGURE 57



VARIATION OF P-N-P COUPLING CONSTANTS IN Ph_2P-N(R)-P(Ph)Cl WITH TEMPERATURE.

(Dotted regions refer to coalescence temperature range).

since barriers to rotation about totally symmetrically substituted phosphorus compounds (see Table 53) are generally lower than unsymmetrical ones.

b) A 'cogwheel' effect could be operative. As the temperature is raised, rotation about both P-N bonds occurs, not so much in a kinetic but more in a thermodynamic sense, involving different conformer populations whose stabilities are determined by steric interactions. Since rotation of one P-N bond is dependent on the rotation of the other, this is named a 'cogwheel effect'.

There is no way of differentiating, from the data obtained in this study, between the two mechanisms. The cogwheel mechanism implies that steric, and hindered PhP(Cl)-N rotation could imply that $(p\text{-}d)_{\pi}$ bonding considerations are responsible for the torsional barriers. However, since the lone pair on nitrogen can overlap with two sets of 3d (phosphorus) orbitals leading to diminished $(p\text{-}d)_{\pi}$ bonding to any one phosphorus atom, mechanism a) is thought to be less important and the 'cogwheel' mechanism is favoured.

D SUMMARY

Hindered P-N bond rotation occurs in $Ph_2P\text{-}N(R)\text{-}P(Ph)Cl$ (R = Me, Et, Pr^n, Pr^i, Bu^t). The variation in the $\underline{P}\text{-}N\text{-}\underline{P}$ coupling constant has allowed conformational assignments at low temperatures, and the order of ease of rotation about the

P-N bonds is Me > Et ≈ Pr^n > Pr^i > Bu^t (Table 65). This is consistent with other reports.

TABLE 65

SUMMARY OF RESULTS AND CONCLUSIONS ON $Ph_2P-N(R)-P(Ph)Cl$

R	$^2J_{P-P}$ (a)	Low Temp. Conformation (b)	T_c (°C)
Me	+343 (-30)	(0,0)	< -100
Et	+343 (-97)	(0,0)	-75
Pr^n	+332 (-100)	(0,0)	-80
Pr^i	-35 (-60)	(0,180)[b]	-25
Bu^t	-38 (-30)	(0,180)[b]	+20

a) Values in parentheses are the temperatures (°C) of the measurements.

b) Approximations. Evidence for the (0,180) conformers is based on molecular models only.

The origin of these barriers is mainly steric, although other contributions (e.g. lone-pair - lone pair repulsions, $(p\text{-}d)_{\pi}$ back bonding) cannot be reliably assessed on this study alone. A 'cogwheel' mechanism of rotation is suggested involving interdependent rotations about both P-N bonds. The first examples of a negative coupling constant between trivalent phosphorus atoms (I, R = Pr^i, Bu^t) are recorded and rationalised in terms of the conformation dictated by the steric effects of the substituent on nitrogen. Figure 57 summarises these results.

4 EXPERIMENTAL

Reactions were carried out in an atmosphere of dry nitrogen, and the apparatus flame-dried prior to use. Solvents were dried by conventional means. Variable temperature n.m.r. determinations were generally on crude samples of the compounds, and the amine hydrochloride or lithium chloride were usually centrifuged off. ^{1}H and ^{31}P spectra were obtained on a Jeol C60-HL spectrometer at 60 and 24.3 MHz respectively. Selective $^{1}H\{^{31}P\}$ decoupling experiments were performed using a Schomandl ND 100M frequency synthesiser and T.M.S. or PhCl were used to activate the internal lock in the frequency sweep mode. ^{31}P chemical shifts were recorded relative to external 85% H_3PO_4. Mass spectra were obtained on an A.E.I. MS12 instrument.

(1) DIPHENYLPHOSPHINOMETHYLAMINE

$$Ph_2PCl + 2\,MeNH_2 \rightarrow \underline{Ph_2P\text{-}N(H)Me} + MeNH_3^+Cl^-$$

$MeNH_2$ was passed through Ph_2PCl (28.59 g., 0.130 mole.) in 40-60 pet. ether for four hours at room temperature, during which time a dense white precipitate formed. ($MeNH_3^+Cl^-$. Crude weight = 8.93 g.; 8.75 g. expected). After distilling off the ether, a vacuum distillation (ca. 104°C/0.25 mm.Hg.) yielded $Ph_2P\text{-}N(H)Me$. (6.82 g., 24.5% yield). (Lit.Bp.(240) is 93 - 102°C/0.1 mm. Hg.) The low yield was due to further reaction of the phosphine-amine with diphenylphosphinochloride, i.e.

$$Ph_2P\text{-}N(H)Me + Ph_2PCl + MeNH_2 \longrightarrow \begin{array}{c}\underline{Ph_2P\text{-}N\text{-}PPh_2}\\ +\\ MeNH_3^+Cl^-\end{array}$$

(The diphosphinoamine was recovered from the residue in the flask after vacuum distillation).

The purity of the product was demonstrated by n.m.r.

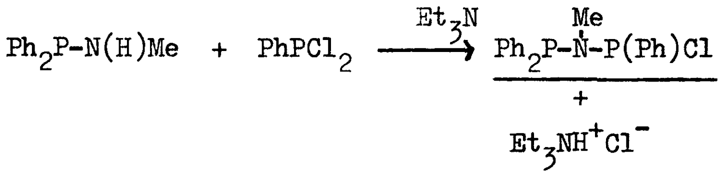
^{1}H N.M.R. of $Ph_2P\text{-}N(H)Me$. (neat)

ca. 2.8 τ (multiplet) - phenyl protons

7.63 τ (2 doublets) - methyl protons

ca. 8.1 τ (multiplet) - N-<u>H</u> proton.

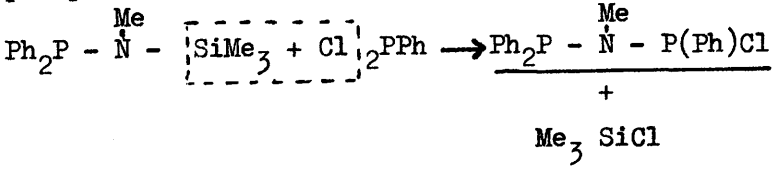
(2) FIRST PREPARATION OF DIPHENYLPHOSPHINO(PHENYLCHLOROPHOSPHINO)METHYLAMINE



$$Ph_2P\text{-}N(H)Me \;+\; PhPCl_2 \xrightarrow{Et_3N} \underline{Ph_2P\text{-}\overset{Me}{N}\text{-}P(Ph)Cl} \;+\; Et_3NH^+Cl^-$$

To $Ph_2P\text{-}N(H)Me$ (3.636 g., 0.0169 mole.) in ether (150 ml.) was added with stirring, $PhPCl_2$ (3.035 g., 0.0169 mole.) and the flask cooled to 0°C with ice. Et_3N (2.6 ml., 1.893 g., 0.0187 mole., slight excess) was then slowly added from a dropping funnel. After refluxing for about an hour, attempts were made to filter off the amine hydrochloride, but a precipitate still remained. The ether was distilled off and a vacuum distillation (74 - 100°C/0.07 mm.Hg) yielded a white product. Its n.m.r. however, revealed strong signals approximately 0.3 p.p.m. downfield from those due to the methyl protons, and it was concluded that these were due to the oxide of the title compound. A better preparative method was therefore sought.

The procedure adopted was to first of all synthesise the trimethylsilyl derivative and react it with dichlorophenylphosphine.



$$Ph_2P - \overset{Me}{N} - \boxed{SiMe_3 + Cl}_2PPh \longrightarrow \underline{Ph_2P - \overset{Me}{N} - P(Ph)Cl} \;+\; Me_3\,SiCl$$

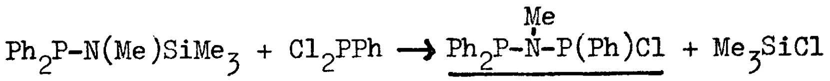
(3) DIPHENYLPHOSPHINO(TRIMETHYLSILYL)METHYLAMINE

$Ph_2P\text{-}N(H)Me$ (1.954 g., 0.00909 mole.) in benzene (50 ml.) was added with stirring to Bu^nLi (2.35 M solution in hexane, 4.2 cc., 0.00987 mole., slight excess) in 25 ml. benzene. The reaction did not appear to be exothermic. 30 minutes later, Me_3SiCl (0.987 g., 0.00911 mole.) was added and refluxing commenced for one hour. Most of the benzene was then distilled off and the solution filtered to remove the LiCl. (Some precipitate remained). A vacuum distillation (100°C/0.1 mm. Hg, lit. = 106 - 109°C/0.03)(241) yielded 1.1 g. $Ph_2P\text{-}N(Me)SiMe_3$. (42% yield).

^{31}P n.m.r. (CH_2Cl_2 solvent):- Singlet at -46 p.p.m. (H_3PO_4 standard).

Mass Spectrum:- Found, M^+ = 287 (s). $C_{16}H_{22}NPSi$ requires 287.

(4) SECOND PREPARATION OF DIPHENYLPHOSPHINO-(PHENYLCHLOROPHOSPHINO)METHYLAMINE



$$Ph_2P\text{-}N(Me)SiMe_3 + Cl_2PPh \longrightarrow \underline{Ph_2P\text{-}\overset{Me}{N}\text{-}P(Ph)Cl} + Me_3SiCl$$

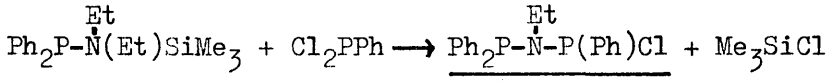
$Ph_2P\text{-}N(Me)SiMe_3$ (1.075 g., 0.00374 mole.) was added to $PhPCl_2$ (0.670 g., 0.00374 mole.) and the mixture heated (115°C - 120°C) for one hour. The colourless mixture gradually turned yellow and bubbles (Me_3SiCl) were given off. Vacuum distillation (60 — 78°C/0.08 mm. Hg.) yielded a small amount of a white product.

Analysis:- Found, C = 64.02%, H = 5.64%, N = 3.02%

$C_{19}H_{18}ClNP_2$ requires C = 63.78%, H = 5.03%, N = 3.92%.

Mass Spectrum:- Found, M^+ = 357(m). $C_{19}H_{18}{}^{35}ClNP_2$ requires 357.

(5) FIRST PREPARATION OF DIPHENYLPHOSPHINO-(PHENYLCHLOROPHOSPHINO)ETHYLAMINE



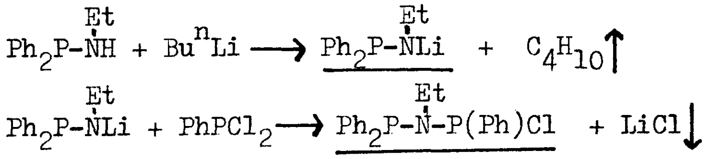
$$Ph_2P\text{-}\overset{Et}{N}(Et)SiMe_3 + Cl_2PPh \longrightarrow \underline{Ph_2P\text{-}\overset{Et}{N}\text{-}P(Ph)Cl} + Me_3SiCl$$

$Ph_2P\text{-}N(Et)SiMe_3$ (1.135 g., 0.00377 mole.) was added to $PhPCl_2$ (0.674 g., 0.00377 mole.) and the mixture heated (115°C) for 1½ hours. During this time a yellow colour developed and bubbles (Me_3SiCl) were given off. Vacuum distillation resulted in two products:-

a) 86 - 96°C/0.08 mm. Hg.
b) 130 - 154°C/0.08 mm. Hg.

The ^1H n.m.r. and mass spectrum of b) were both consistent with the title compound. (see next experiment for details). At this stage, however, it was decided to explore another method of preparation. Instead of a two-stage synthesis involving the Me_3Si derivative, direct addition of dichloro-phenylphosphine to the lithiated phosphinoamine was used.

(6) SECOND PREPARATION OF DIPHENYLPHOSPHINO-(PHENYLCHLOROPHOSPHINO)ETHYLAMINE



$$Ph_2P\text{-}\overset{Et}{N}H + Bu^nLi \longrightarrow \underline{Ph_2P\text{-}\overset{Et}{N}Li} + C_4H_{10}\uparrow$$

$$Ph_2P\text{-}\overset{Et}{N}Li + PhPCl_2 \longrightarrow \underline{Ph_2P\text{-}\overset{Et}{N}\text{-}P(Ph)Cl} + LiCl\downarrow$$

To $Ph_2P\text{-}N(H)Et$ (3.289 g., 0.01436 mole.) in 50 ml. benzene at room temperature was added Bu^nLi (2.35 M solution in hexane, 6.6 ml., 0.0155 mole., ca. 10% excess) and the mixture stirred for 2½ hours. $PhPCl_2$ (2.570 g., 0.01436 mole.) was added and a white precipitate (LiCl) formed immediately. After refluxing for 2 hours, the LiCl was centrifuged off and the solvent removed by distillation. Vacuum distillation (140°C/0.15 mm. Hg.) resulted in a colourless liquid which solidified to a whitish solid when cooled.

Analysis:- C = 64.64%, H = 6.54%, N = 5.10%. $C_{20}H_{20}ClNP_2$ requires C = 64.60%, H = 5.38%, N = 3.77%.

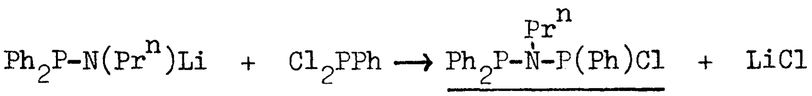
Mass Spectrum:- Found:- $M^+ = 371(s)$. $C_{20}H_{20}{}^{35}ClNP_2$ requires 371.

(7) DIPHENYLPHOSPHINO-n-PROPYLAMINE

$$Ph_2PCl + 2\,Pr^nNH_2 \longrightarrow \underline{Ph_2P\text{-}N(H)Pr^n} + Pr^nNH_3{}^+Cl^-$$

A solution of Pr^nNH_2 (11.5 ml., 8.22 g., 0.139 mole., excess) in 40-60 pet. ether (100 ml.) was cooled to 0°C (ice-bath) and Ph_2PCl (14.95 g., 0.0678 mole.) was slowly added over a period of 20 minutes. A white precipitate formed immediately. After refluxing for 30 minutes, the amine hydrochloride precipitate was filtered off and the solvent removed. Vacuum distillation (128°C/0.35 mm. Hg.) (lit. 106°C/0.1 mm. Hg.)(240) yielded $Ph_2P\text{-}N(H)Pr^n$ (11.1 g., 67% yield) ^{31}P n.m.r. (neat):- Singlet at -41.2 p.p.m. (H_3PO_4 standard).

(8) DIPHENYLPHOSPHINO(PHENYLCHLOROPHOSPHINO)n-PROPYLAMINE



$$Ph_2P\text{-}N(Pr^n)Li \ + \ Cl_2PPh \longrightarrow \underline{Ph_2P\text{-}\overset{Pr^n}{N}\text{-}P(Ph)Cl} \ + \ LiCl$$

To $Ph_2P\text{-}N(H)Pr^n$ (2.268 g., 0.00933 mole.) in 50 ml. benzene at room temperature was added Bu^nLi (2.35 M solution in hexane, 4.4 ml., 0.0103 mole., ca 10% excess) and the mixture stirred for ½ hour. $PhPCl_2$ (2.057 g., 0.00933 mole.) was added and a white precipitate (LiCl) formed immediately. After refluxing for 1 hour, centrifuging and distilling off the solvent, a yellow oil was left which was vacuum distilled. At about 80°C/0.35 mm. Hg., a white solid sublimed out on the walls of the condenser. This was washed down with methylene chloride and the solvent removed on the vacuum line.

Analysis:- Found, C = 63.47%, H = 5.93%, N = 3.04%.

$C_{21}H_{22}ClNP_2$ requires C = 65.37%, H = 5.71%, N = 3.63%.

The method used in the production of the corresponding Pr^i, Bu^t and Ph derivatives were the same as those outlined for $Ph_2P\text{-}N(Pr^n)P(Ph)Cl$.

(9) DIPHENYLPHOSPHINO(-i-PROPYL)AMINE

Vacuum distillation (110°C/0.45 mm. Hg.) yielded ca. 2 g. (26% yield) $Ph_2P\text{-}N(H)Pr^i$.

^{31}P n.m.r. (neat) singlet at -33.4 p.p.m. (H_3PO_4 reference).

^{1}H n.m.r. (neat)

ca. 2.8 τ (multiplet) - phenyl protons

6.85 τ (septet) - methine proton

8.05 τ (2 doublets) - N-$\underline{H}$

9.0 τ (doublet) - methyl protons.

$$J_{CH_3\text{-}CH} = 6.8 \text{ Hz.}$$

(10) DIPHENYLPHOSPHINO(PHENYLCHLOROPHOSPHINO)i-PROPYLAMINE

162°C/0.1 mm.Hg.

Analysis:- C = 64.92%, H = 5.91%, N = 2.26%. $C_{21}H_{22}ClNP_2$ requires C = 65.37%, H = 5.71%, N = 3.63%.

Mass Spectrum:- Found, M^+ = 385(W). $C_{21}H_{22}{}^{35}ClNP_2$ requires 385.

(11) DIPHENYLPHOSPHINO(PHENYLCHLOROPHOSPHINO)-t-BUTYLAMINE

50-66°C/0.1 mm. Hg.

Analysis:- C = 62.32%, H = 5.94%, N = 2.66%.

$C_{22}H_{24}ClNP_2$ requires C = 66.08%, H = 6.01%, N = 3.50%.

Mass Spectrum:- Found M^+ = 399(s). $C_{22}H_{24}{}^{35}ClNP_2$ requires 399.

The residue in the flask was dissolved in benzene, filtered and evaporated to dryness. It analysed as follows:- C = 63.20%, H = 5.81%, N = 2.70%. It melted in the range 84 - 104°C., and its general appearance suggested that polymerisation had taken place during the vacuum distillation and that this product was in fact a polymer of the title compound. This was confirmed by the fact that both the residue and the distillate had identical ^1H n.m.r. spectra.

(12) DIPHENYLPHOSPHINOANILINE

The crude product was recrystallised from hot MeOH to yield a white solid (M.p. 55 - 60°C). 21% yield.

Analysis:- C = 76.48%, H = 5.97%, N = 5.19%.
$C_{18}H_{16}NP$ requires 77.98%, H = 5.78%, N = 5.05%.

(13) ATTEMPTED PREPARATION OF DIPHENYLPHOSPHINO-(PHENYLCHLOROPHOSPHINO)ANILINE

The crude product was obtained as a yellow solid after the LiCl had been centrifuged off and solvent removed. It melted over a long range starting at 95°C. Washing with benzene produced a white solid which also melted very gradually this time starting at ca. 130°C. It did not analyse satisfactorily.

Analysis:- C = 55.48%, H = 5.66%, N = 6.21. $C_{24}H_{20}ClNP_2$ requires C = 68.65%, H = 4.77%, N = 3.34%.

No molecular ion was obtained in the mass spectrum.

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