Studies in the co-ordination chemistry of germanium and neighbouring elements

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STUDIES IN THE CO-ORDINATION CHEMISTRY OF GERMANIUM AND NEIGHBOURING ELEMENTS

by

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St Mary's College

A thesis submitted to the University of Durham for the degree of Doctor of Philosophy.

August 1973

To my Father.

' "The time has come," the Walrus said,
"To talk of many things:" '

LEWIS CARROLL
'The Walrus and the Carpenter' from
'Through the Looking Glass'.

CONTENTS

PART ONE Studies on Germyl- and Stannyl-Platinum Complexes

PART TWO Azomethine Derivatives of Some Main Group Elements.

CHAPTER I Some Azomethine Derivatives of Silicon and Germanium.

ACKNOWLEDGEMENTS

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I also wish to thank Drs. H.R. Keable and R. Snaith for their helpful discussions and for checking the original manuscript, and Mr B. Hall for valuable technical assistance during the course of the work.

Finally, I am indebted to the Science Research Council for a maintenance grant.

J. Spencer
Durham 1973

MEMORANDUM

The work described in this thesis was carried out in The Queen's University of Belfast between October 1970 and September 1971 and in the University of Durham between October 1971 and July 1973. It has not been submitted for any other degree and is the original work of the author except when acknowledged by reference.

Part of the work in this thesis has formed the subject matter of the following publication:

Imino derivatives of boron, silicon and phosphorus.
by E.A. Forman, J. Spencer and K. Wade. Abstr. 24th International Union of Pure and Applied Chemistry Congress, Hamburg, September 1973, 53.

Abstract

In the first part of this thesis, the preparation of the known compounds trans-$(Et_3P)_2Pt(X)mC_6H_4F$, and trans-$(Et_3P)_2Pt(X)pC_6H_4F$ where X = Cl, $SnCl_3$ and of the new compounds trans-$(Et_3P)_2Pt(GeCl_3)mC_6H_4F$ and trans-$(Et_3P)_2Pt(GeCl_3)pC_6H_4F$ is described. Attempts to prepare further such compounds where X = $SiMe_3$, $GeBr_3$ were unsuccessful.

The mass, infra-red, proton, magnetic resonance, fluorine magnetic resonance and X-ray photoelectron spectra of these compounds were recorded and the ^{19}F n.m.r. and X-ray photoelectron spectra were used to investigate the trans-effect of the group IVb ligands, in these platinum-group IVb element complexes.

In the first chapter the trans-effect theory is discussed. The second chapter is concerned with the experimental details and spectral data. The results obtained are discussed in the light of other evidence for the high trans-effect in platinum(II)-group IVb compounds in Chapter 2.

In Part II, the preparation of some methyleneamino derivatives containing groups $R_2C{:}N-$ attached to silicon, germanium and phosphorus (R = t-butyl, p-tolyl, phenyl) is described. The new compounds prepared are $[R_2C{:}N]_4Ge$, (R = phenyl, p-tolyl), $[Bu^t_2C{:}N]_xGeX_{4-x}$ (x = 1,2,3; X = Br, Cl), and $Me_xSi[N{:}C(p\text{-tolyl})_2]_{4-x}$ (x = 1,2) (Chapter 1) and $P[N{:}CR_2]_3$ (R = p-tolyl, phenyl), $X_2P[N{:}CR_2]$ (X = Cl, Ph; R = t-butyl, phenyl, p-tolyl) and $OPCl_x(N{:}CR_2)_{3-x}$, (R = t-butyl, p-tolyl, phenyl; x = 0,1,2) (Chapter 2). The mass, infrared and ^1H nuclear magnetic resonance spectra were recorded and, for the phosphorus compounds the ^{31}P n.m.r. spectra were recorded. These compounds were prepared with the

object of finding model systems for the study of dative $N \overset{\rightharpoonup}{-} M$ π-bonding nitrogen and silicon, germanium and phosphorus.

The shape (linear or bent) of the M-N-C skeletons (M = silicon, germanium and phosphorus) in these moisture sensitive methyleneamino compounds could not be unambiguously determined from the n.m.r. and infrared spectral data obtained. The mass spectral data and molecular weight determination indicated the compounds to be in a monomeric state of association. ^{31}P n.m.r. data are discussed with reference to analogous isocyanate, isothiocyanate and amino derivatives of phosphorus, (Chapter 2).

Attempts to prepare $Bu^t_2C:NMe$ are described in Appendix 1 and experimental techniques, instrumentation and analytical methods are described in Appendices 2,3 and 4.

NOTES ON NOMENCLATURE

The Chemical Society have requested the name 'methyleneamine' be used for the (unknown) compound $CH_2{:}NH$ and that derivatives be named accordingly. Hence, $CH_2{:}NMX_n$ is a methyleneamino derivative of the metal M, $RCH{:}NMX_n$ is an alkyl- or aryl-methyleneamino derivative (or "aldimino" derivative) depending on the nature of the group R, and $R_2C{:}NMX_n$ is a dialkyl- or diarylmethyleneamino derivative (or "ketimino" derivative) depending on the nature of group R.

In this thesis, however, the older and clearer terms "aldimino" and "ketimino" will be used partly for the sake of brevity and partly because such terminology clearly distinguishes "imino" from "amino" derivatives.

PART ONE

STUDIES ON GERMYL- AND STANNYL-PLATINUM COMPLEXES.

CHAPTER 1

INTRODUCTION

Over the last ten to fifteen years there has been a great interest shown in compounds containing metal-metal bonds. Complexes containing silicon, germanium, tin or lead bonded to a d-block transition element have been isolated for most of the metals. Features of this interest in metal-metal bonded complexes include their possible catalytic applications and the opportunity for detailed spectroscopic studies of metal-metal interactions. Compounds containing Group IVb elements bonded to other metals were the subject of a recent review.[1]

The aim of the work to be described in Part One of this thesis, was to make a series of platinum complexes, of the type shown in Fig. 1.1, in which X is a group attached to platinum via a Group IVb element namely silicon, germanium or tin and to investigate the electronic and <u>trans</u> effects of the ligand X in these compounds by recording the ^{19}F nuclear magnetic resonance spectra of these compounds. This is a continuation of work initiated by Parshall[2] which will be discussed later.

(i) (ii)

Fig. 1.1

The Trans-Effect and Trans-Influence.

This is a particular feature of ligand replacement reactions in square planar complexes and to a lesser extent in octahedral complexes.

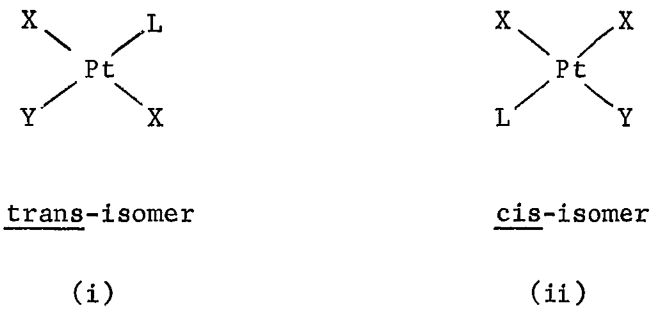
Most of the work done on the trans-effect has been done with Pt^{II} complexes since these are numerous and varied and have fairly convenient rates of reaction.

Consider the general reaction shown in scheme A.

$$[PtLX_3]^- + Y^- \rightarrow [PtLX_2Y]^- + X^-$$

Scheme A.

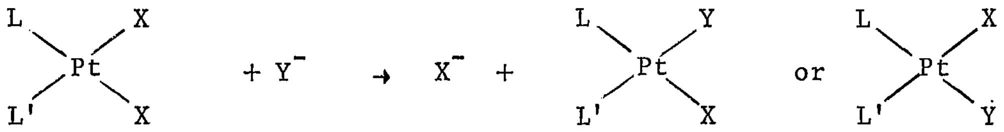
Sterically there are two possible reaction products as in Fig. 1.2.


trans-isomer (i)

cis-isomer (ii)

Fig. 1.2

The relative proportions obtained of (i) and (ii) are found to vary appreciably with the ligand L. A similar reaction is generalised by scheme B.



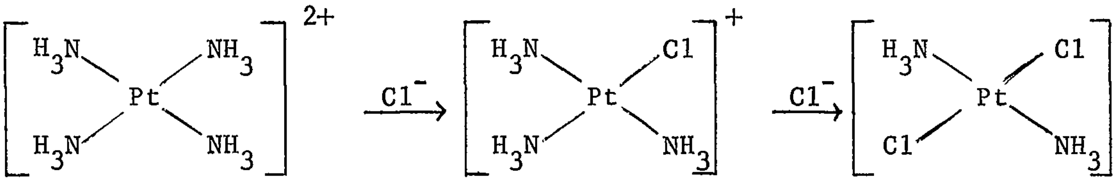
Scheme B.

For both reaction schemes, A and B, a wide range of ligands can be arranged in the same order with respect to their ability to facilitate substitution in the position trans to themselves.[3,4,5] Part of this series is,

$$H_2O < OH^- < NH_3 < Cl^- < Br^- < I^- \sim NO_2^- \sim PR_3 \ll CO \sim C_2H_4 \sim CN^- < CH_3^- < H^-$$

the ligands being in order of increasing trans-directing ability. This phenomenon is known as the Trans-Effect. Reference 5 provides a useful lead into early literature on this subject.†

The classic example of the trans-effect is the preparation of the cis-[6] and trans-[7] isomers of $[PtCl_2(NH_3)_2]$. The trans-isomer is made by the reaction of chloride ions with $[Pt(NH_3)_4]^{2+}$ (scheme C).



Scheme C.

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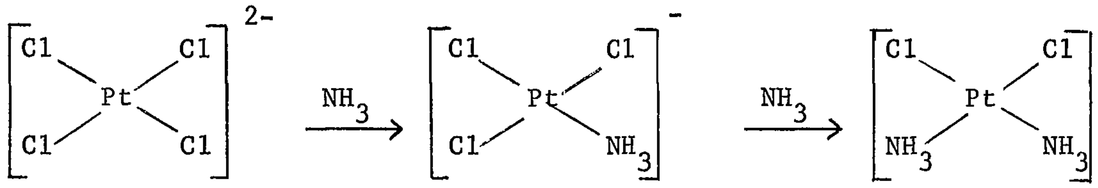
† A further review was published after Part I of this thesis had been written and typed.
Reference: F.R Hartley, Chem. Revs. 1973, 2, 163.

However, the cis-isomer is formed when $[PtCl_4]^{2-}$ is treated with ammonia (scheme D).



Scheme D.

Substitution always occurs trans to the chloride ion indicating that chloride ion has a greater labilising effect on the group opposite than does ammonia i.e. chloride ion has a greater trans-effect than does ammonia. The above trans-effect series was compiled by studies of a number of similar reactions.

The way in which a ligand exerts a trans-effect is unknown but it was originally thought that groups of high trans-directing effect weaken the bond in the position trans to themselves i.e. increase the tendency of the bond to heterolytic fission. This led to the definition of the trans-effect by Quagliano and Schubert[8] as:

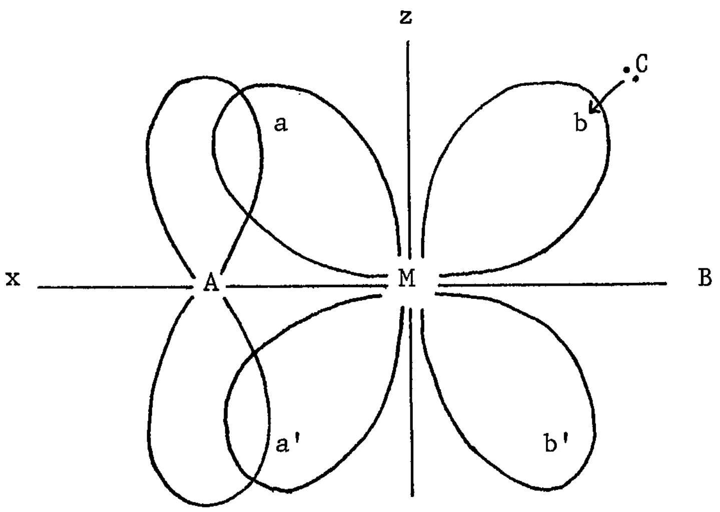
"The trans-effect stipulates that the bond holding a group trans to an electronegative or labilising group is weakened".

However, Chatt et al[9] found evidence to suggest that in some cases, the bond holding a group trans to a labilising group was strengthened, and this gave rise to their definition of the *trans*-effect as:

"The *trans*-effect or *trans*-influence of a group (A) co-ordinated to a metal ion is the tendency of that group to direct an incoming substituent group into the position *trans* to itself (A)".

They believed the amount of double-bonding between a metal and a ligand through inductive and mesomeric effects to be the main cause of the *trans*-effect. A mechanism by which a ligand exerts a *trans*-effect, put forward by Chatt *et al*,[9] fits observed facts far better than that involving bond-weakening.

It has been pointed out[10] that ligands showing the largest *trans*-effect are those with vacant orbitals suitable for π-bonding. (For a discussion of methyl and hydride ligands, see later). If all groups attached to a metal atom have a low *trans*-effect, then the withdrawal of d-electrons to form dative π-bonds will be small and the electron density in the metal d-orbitals will be high, thus ~~en~~discouraging nucleophilic attack at the metal d-orbitals. (All substituting reagents in complex chemistry are nucleophilic). The slow displacement reaction may therefore occur by a slow SN1 dissociative or SN2 associative mechanism. However, if one of the ligands is replaced by a ligand of high multiple-bonding capacity, the withdrawal of d-electrons from the metal will facilitate nucleophilic attack, thus accelerating an SN2 reaction. Fig. 1.3 shows electron withdrawal by the ligand A from a d-orbital of metal M on forming a dative π-bond and the proposed mechanism of substitution of B by a donor C in the presence of a ligand A of high trans-effect.



A = ligand of high trans-effect; B = ligand displaced by C; C = donor.

Fig. 1.3

Since electron withdrawal occurs from the regions bb', it facilitates the introduction of groups to the side of the molecule remote from group A and near to the trans-group B, which may then be eliminated and replaced by the substituting group C. The greater the double bonding properties of A, the greater the electron affinity of metal atom M especially in the regions bb' and the faster the rate of substitution. Examples of this increased electron affinity in platinous complexes are the resistance to oxidation shown by platinous complexes containing ligands of high trans-effect.

eg. $K[(C_2H_4)Pt^{II}Cl_3]$ shows the same resistance to oxidation as $K[(NH_3)Pt^{IV}Cl_5]$[11] and $[(CO)_2PtCl_2]$ can be prepared in the presence of chlorine.

The double bonding hypothesis therefore predicts that slow substitutions, characteristic of cis substitution, may be SN1 or SN2 but that fast substitutions occurring in compounds containing a group of high trans-effect should be an SN2 type reaction and the greater rate of trans substitution would be due to a lowering of the activation energy of formation of the transition state rather than to weakening of the trans bond.

In order to establish the mechanism of substitution in reactions of the type shown in scheme E, kinetic studies have been carried out.[12,13]

$$[PtA_3X] + Y \rightarrow [PtA_3Y] + X$$

Scheme E.

The rate law for such a reaction is given by,

$$\text{Rate} = k_1[PtA_3X] + k_2[PtA_3X][Y]$$

where k_1 is a first order rate constant for a solvent controlled reaction and k_2 a second order rate constant for reaction with Y. Pseudo- first-order rate constants $k_{obs.}$ are obtained by having Y in large excess so that

$$k_{obs.} = k_1 + k_2[Y]$$

Plots of $k_{obs.}$ against [Y] are necessarily linear in this case and for any one solvent, the intercept k_1 is constant and the reaction is said to be solvent controlled. The gradient k_2 is a measure of the reactivity of Y and it is found that for various ligands the order is,

$$PR_3 \sim SCN^- \sim I^- > N_3^- \sim NO_2^- > py \sim NH_3 \sim Br^- > Cl^- > OH^- > H_2O.$$

which is very similar to the trans-effect series, suggesting that a good trans-labilising group is also a good substituting ligand. This is consistent with an SN2 mechanism in which the activated complex contains the entering group Y. The two term rate law requires a two path reaction mechanism shown in Fig. 1.4.[14]

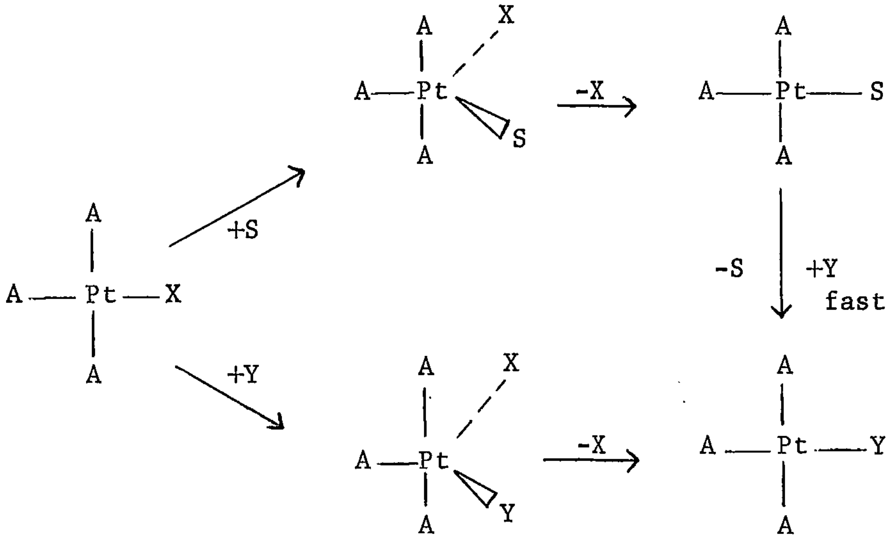


Fig. 1.4. Two path mechanism proposed for reaction of a square planar complex PtA_3X with Y to yield PtA_3Y. The upper path is the solvent path and the lower one is the direct path, represented by k_1 and k_2 respectively in the equation $k_{obs.} = k_1 + k_2[Y]$.

That the substitutions are mainly second order is supported by the fact that fairly rapid equilibrium between cis and trans isomers otherwise expected, does not occur.

$$\underset{\underline{cis}}{PtA_2BC} \rightleftharpoons PtABC + A \rightleftharpoons \underset{\underline{trans}}{PtA_2BC}$$

If the reactions are second order, then the intermediate must involve five-co-ordinate platinum. In the substitution reactions of platinous compounds of the type considered (<u>ie</u> square planar complexes) the stereochemical configuration is maintained, <u>ie</u> in the reaction

$$Pt^{II}ABCD + E \rightarrow Pt^{II}ABCE + D$$

the replacement of D by E takes place without any change in the relative positions of A, B and C. The only configuration having the required properties is a distorted bipyramid structure[15] as shown in Fig. 1.5.

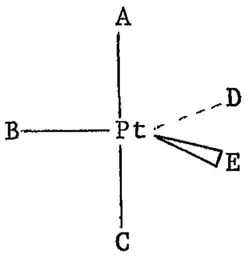


Fig. 1.5

In the proposed reaction path, the entering group E approaches the complex ion from one side of the plane and in the critical stage of the reaction moves over the group to be replaced, D, and then moves downward until the transition state is reached. The replaced group is then eliminated by a similar process. Orgel proposed[15] that the transition state is stabilised by reduction of d-electron density along the Pt-D and Pt-E directions by the π-bonding of ligand B with the metal.

The theory of Chatt et al[9] that ligands of high trans influence have little effect on the σ bonds but modify the molecular π-bonding system involving the d-orbitals of the metal can be used to explain why, in trans-$[Pt(C_2H_4)NH(CH_3)_2Cl_2]$[16] although the ethylene has a strong trans labilising effect, there is no lengthening of the Pt-N bond ie high trans-effect but little trans-influence. [Using the definition of trans-influence of a ligand as the extent to which that ligand weakens the bond trans to itself in the equilibrium state of the substrate.[17]] The high trans-effect is due to stabilisation of the transition state and not due to some ground state effect.[15]

Wunderlich et al[18] in the structure determination of Zeise's salt $K[Pt(C_2H_4)Cl_3]H_2O$ found a lengthening of the Pt-Cl bond trans to ethylene. The difference between this and the lack of bond lengthening in the Pt-N bond of trans$[Pt(C_2H_4)NHMe_2Cl_2]$[16] can be attributed to the fact that the Pt-Cl bond in Zeise's salt may have some π-bonding character and removal of some π-electron density from the platinum by the ethylene will reduce the π-bonding in the Pt-Cl bond thereby causing bond lengthening. On the other hand, nitrogen has no vacant orbitals of suitable energy with which to π-bond to the platinum and is therefore unaffected by the ethylene.

The *trans*-effect was first noticed in platinous complexes because electronic conditions in such compounds are especially favourable to the development of directing effects by the mechanism outlined above. These conditions are

1. Double bonding is facilitated in the third transition series where the 5d orbitals have energy levels close to the 6s and 6p orbitals (as distinct from nickel and palladium).

2. The vacant $6p_z$ orbital of the platinum atom, by hybridisation with the $5d_{xz}$ orbital, produces π-type orbitals especially favourable for dative π-bond formation,[19] as shown in Fig. 1.6.

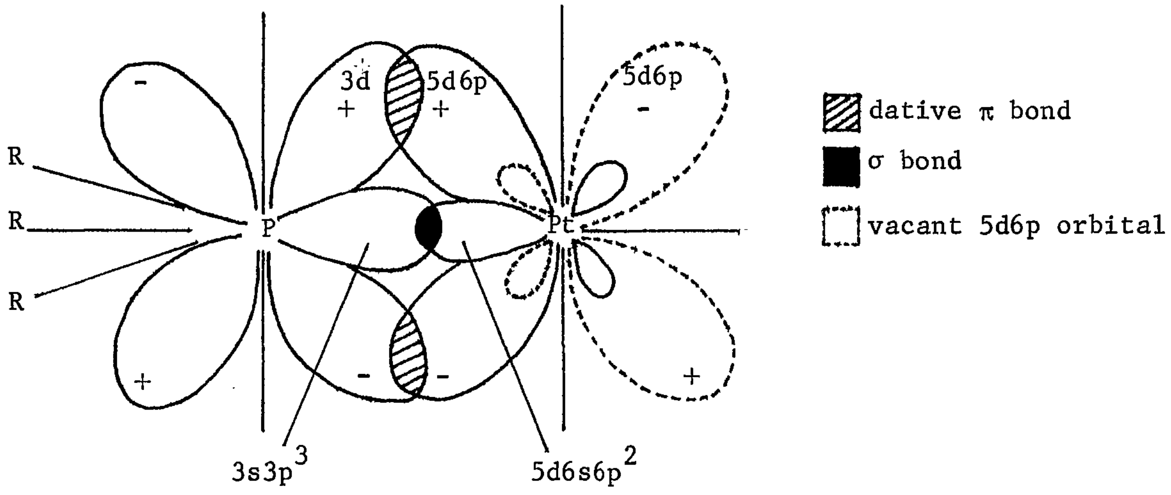


Fig. 1.6 Representation of the R_3P = Pt bond.

When one of these is involved in dative π-bond formation, the other, in much the same place as the antinodes bb' of the pure d-orbital (Fig. 1.3) is available to receive the lone pair of electrons of the attacking nucleophile.

3. Platinum(II) forms a unique series of configurationally stable complexes with a greater variety of ligands than any other acceptor atom.

4. The square planar dsp^2 arrangement of bonds brings the substituting ligand entering in the regions b or b' (Fig. 1.3) uniquely close to the trans ligand B, causing 100% trans substitution when A has a high trans effect.

There is a possibility that gold (III) would also show the trans-effect as strongly as platinum(II) but it is doubtful whether any other metal in a common valency state would.[9]

The π-bonding theory of the trans-effect, while explaining most known facts, does not account for the very high trans-effect of the methyl and hydride ligands since in these cases, π-bonding between ligand and metal cannot take place. This can, however, be explained if a polarisation theory is invoked.[20] In a square planar platinum compound $[PtX_4]^{=}$ where X = halide ion, there is a positive centre surrounded by four monovalent, negatively charged ions. Mutual polarisability results in induced dipoles in the anions and in the central ion. Because of the symmetrical distribution of charge around the central atom Fig. 1.7(i), the induced dipoles in the central metal ion are compensated and the resultant dipole is zero.

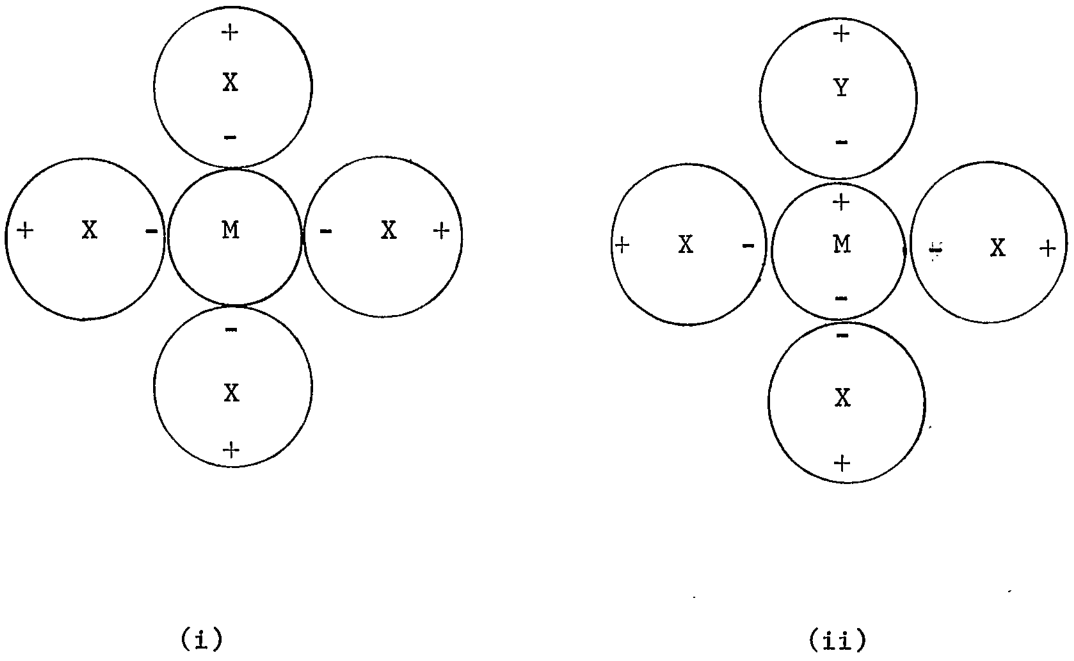


Fig. 1.7 Distribution of induced charges by a ligand Y of greater polarisability than ligand X.

However, if a group Y of different polarisability is introduced Fig. 1.7(ii) there is no mutual compensation resulting in a dipole in the central ion as well as in the structure as a whole. If Y is a strongly electronegative or an electron-rich group, the <u>trans</u> Pt-X bond is weakened due to repulsion between the induced dipoles. This theory accounts for the high <u>trans</u>-effect of hydride and methyl ligands.[21] The hydride ion, with its large electrostatic effect, would be expected to cause large ligand field splittings. This has been confirmed,[22] in fact both hydride and methide ions cause large ligand field splittings of the d-energy levels in ruthenium II complexes. The development of negative charge on the side of the platinous ion trans to the hydride ion should also lead to long bonds of considerable ionic character between the metal and the trans ligand. This has been observed in trans-$(Et_3P)_2Pt(H)Br$ where the Pt-Br distance is 2.56Å as compared with the sum of the covalent radii, 2.43Å.[23]

Since the trans-effect is primarily a kinetic effect, the influence of a ligand on various ground state observations is frequently described as the trans-influence to distinguish it from the kinetic trans-effect. Several methods have been used to correlate ground state observations with the trans-influence of ligands and these will be briefly reviewed below.

A. X-Ray Crystallography.

Many compounds of Platinum(II) have been studied using X-ray diffraction techniques and evidence for the trans-influence of various ligands has been obtained from the results. In complexes of the type trans- PtA_2LX, if a change in the trans-influence of ligand L produces a change in the Pt-X bond strength then a measure of the Pt-X bond length by X-ray studies should give a measure of the trans-influence of L. It is found that there are trends in the Pt-X bond length as L changes. In Table I, the Pt-Cl bond lengths in a series of compounds with various trans ligands are given. From the order of Pt-Cl bond lengths it can be seen that the order of the trans-influence is,

$$Si > H > P > C = C \sim Cl > O.$$

which agrees approximately with the order of the trans-effect of the ligands.

Table 1

Variation of the Pt-Cl bond length with trans ligand in some platinum(II) compounds.

Complex	Trans ligand	Pt-Cl bond length(Å)
trans-$(PPhMe_2)_2Pt(SiMePh_2)Cl$	Si	2.45 ± 0.01 [24]
trans-$(PPh_2Et)_2PtHCl$	H	2.42 ± 0.01 [25]
cis-$(PMe_3)_2PtCl_2$	P	2.37 ± 0.01 [26]
$^*(C_{12}H_{17})_2Pt_2Cl_2$	C = C	2.31 ± 0.01 [27]
trans-$(Et_3P)_2PtCl_2$	Cl	2.30 ± 0.01 [28]
$[Pt(acac)_2Cl]^-$	O	2.28 ± 0.01 [29]

$^*C_{12}H_{17}$ = dehydrohexamethyldewar-benzene which is bonded in this complex by a σ-bond from the methylene group to one platinum atom, and by donation of two electrons from each olefin bond to the other platinum atom.

The data in Table 1 show that the trans-influence of the ligand, L, increases smoothly with decreasing electronegativity (the effective electronegativity of C = C is that of trigonal carbon).[30] Chatt et al[31] reached a similar conclusion from infra-red data [to be described in the next section]. Evidence for the high trans influence of the hydride[23,28] and arsine[32] ligands has also been obtained by X-ray studies.

Gray and Langford[33] based a theory of the trans-effect on the magnitude of the M-L and M-X σ-overlap integrals in compounds of the type trans-LMA_2X. This theory proposes that if the σ-donor orbital of the ligand L has a greater overlap with the metal pσ-orbital than does the ligand X σ-orbital, then the M-L bond is strengthened at the expense of the M-X bond. For Pt(II), the σ-overlap integrals have the order

$$\mathrm{Si} \sim \mathrm{H, C, P} > \mathrm{Cl} > \mathrm{N} > \mathrm{O} > \mathrm{F}.$$

which is in general qualitative agreement with the trends in bondlengths obtained from X-ray data.

Other X-ray diffraction structure determinations[34] support the suggestion,[21] that there is no single explanation for the trans-effect and that only some trans-directing ligands produce a significant lengthening of the trans-bond. Evidence for the trans effect in d^6-octahedral complexes has been discussed[35] and the conclusions arrived at were similar to those for planar complexes namely that the trans-influence of a ligand arises principally from its inductive σ-donor ability transmitted to the trans-ligand by the appropriate metal pσ-orbital. The magnitude of the effect exerted in this way is modified firstly, if the "influencing" ligand has π-acceptor properties and secondly, if the cis ligands are capable of π-bonding.[36]

In the latter case, this appears to be of importance only if one or both of the trans ligands themselves possess π-bonding properties.

B. Infra-Red Spectroscopy.

As mentioned earlier, Chatt *et al*[31] using infra-red data, reached conclusions about the *trans*-effect similar to those obtained from X-ray studies. Chatt *et al* examined a series of compounds of the type *trans*-$[L,amPtCl_2]$ where "am" is a primary or secondary amine and L a series of uncharged ligands having as great a variety of donor atoms as possible. By measuring the N-H stretching frequencies in the infra-red spectra of the above series of compounds in dilute carbon tetrachloride, the change in electron distribution in the Pt-N bond from one compound to another in the series could be assessed. As the electron-withdrawing power of the ligand L increases, there is movement of electrons as shown in Fig. 1.8, causing the proton to be

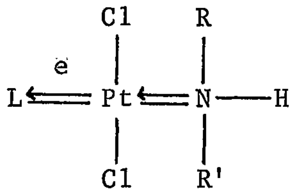


Fig. 1.8

less strongly bonded to the nitrogen and hence a decrease in ν(N-H). In order of decreasing N-H frequency, the ligands studied were

$PR_3 > SbR_3 > P(OR)_3 > AsR_3 > R_2Te > C_2H_4 > R_2Se > R_2S >$ piperidine

This order must be close to that of increasing Pt-N bond strength and of decreasing tendency of L to donate electrons to platinum. With the exception of ethylene, the order roughly parallels the trans-effect order. Ethylene is in an anomalous position here since if earlier work be correct,[9] a complex in which ethylene is trans to an amine would have the weakest Pt-N bond and hence the greatest N-H frequency. Olefin complexes certainly do not contain the weakest Pt-N bonds.[31]

A further study of the measure of the trans-influence was obtained by an investigation of the effect of ligands on the Pt-H stretching frequency in a series of complex hydrides of platinum(II). It has been shown that the hydrogen atom has a high trans effect in platinum complexes[21] and that the stretching frequency of the Pt-H bond, ν(Pt-H), is very sensitive to the nature of the group in the position trans to the hydrogen, decreasing with increasing trans-effect of that group.[37] Values of ν(Pt-H) for various X in compounds trans (L_2PtHX) where L is triethylphsophine or triethylarsine and X is a univalent anionic ligand are given in Table 2.[38]

Table 2

Stretching frequencies in cm^{-1} of the Pt-H bond in the compounds trans-[L_2PtHX] in hexane at 20^oC.

X	NO_3	Cl	Br	I	NO_2	SCN	CN
ν(Pt-H) L = PEt_3	2242	2183	2178	2156	2150	2112	2041
ν(Pt-H) L = $AsEt_3$	-	2174	2167	2139	-	2108	-

The values in Table 2 are in order of decreasing Pt-H frequency and therefore of decreasing Pt-H bond strength. Again, the order parallels that of increasing trans-effect. Values of ν(Pt-H) for a hydride ligand trans to a tertiary phosphine suggest that tertiary phosphines have a trans-effect comparable to that of cyanide ion.[39,40] In $[Ph_2PCH_2CH_2PPh_2Pt(PEt_3)H]Cl$, ν(Pt-H) is at $2043cm.^{-1}$ [40]

The far infra-red ($170-460cm^{-1}$) spectra of many complexes of the type cis- and trans-$[PtX_2L_2]$ (X = Cl, Br and L = a neutral ligand) and trans-$[PtXR(PEt_3)_2]$ (X = Cl, Br and R = H, Me, Ph) have been recorded[41] and the metal-halogen stretching frequency ν(Pt-Cl) and ν(Pt-Br) assigned. A wide range of values was obtained indicating a considerable dependence of the platinum-halogen bond strength on L. This was found only in cis complexes where L is in the position trans to the halogen; in the trans complexes, ν(Pt-X) is almost insensitive to L. The results obtained gave the lowest values of ν(Pt-X) for the complexes trans-$[(Et_3P)_2PtXR]$ and the highest for the complexes trans-$[L_2PtX_2]$, thus comparing well with results from the platinum hydride complexes mentioned earlier. The results also showed that hydride, methyl and phenyl ligands have a high trans-influence.

C. Nuclear Magnetic Resonance Studies.

(i) Proton n.m.r. studies.

The ^1H n.m.r. spectra have been recorded for a series of compounds of the type trans-$[PtHX(PEt_3)_2]$ where X = NO_3^-, Cl^-, Br^-,

I^-, NO_2^-, SCN^-, CN^-, $SnCl_3^-$.[42,43] The proton resonance of the hydridic proton shows a large chemical shift to high field due to the paramagnetic shielding of the proton by the d-electrons of the platinum metal.[44] The hydridic shifts for various ligands are given in Table 3.

Table 3.

Chemical shifts (τ) for compounds of the type trans-[$PtHX(PEt_3)_2$]

X	Solvent	τ^*
NO_3	C_6H_6	33.8
Cl	C_6H_6	26.9
Br	C_6H_6	25.6
I	C_6H_6	22.7
NO_2	C_6H_6	29.7
SCN	C_6H_6	23.2
	C_6H_6	27.9
$SnCl_3$	C_6H_6	19.2
CN	C_6H_6	17.8

* relative to C_6H_6 as internal reference (τ = 2.7).

The ligands X in the above table are arranged in order of increasing trans-effect which is also approximately the order of decreasing τ value indicating some correlation between the trans-effect and the chemical shift, τ. The compounds having X = NO_2 or SCN as ligand, show anomalous τ values. The possibility of isomerisation from -NO_2 to -ONO which would explain the observed τ values is not consistent with infra-red evidence.[42] The anomalies in the thiocyanate spectrum would be explained if the complex in the strong solution used for measuring the spectrum were a mixture of thiocyanate and isothiocyanate. Again, infra-red evidence is not consistent with this explanation.[42]

(ii) ^{19}F n.m.r. studies.

The ^{19}F n.m.r. shielding parameters of substituted fluorobenzenes are found to be a sensitive probe for electronic effects in aromatic compounds.[45] Parshall *et al*[2,43,46,47] applied this to an investigation of *trans*-effects in platinum complexes of the type shown in Fig. 1.1 (page 1) and redrawn below for the sake of clarity.

(i) (ii)

Fig. 1.1

The ^{19}F shielding parameters, Δm, for the meta-substituted compounds, Fig. 1.1(i), vary with the σ-donor character of X as transmitted by the platinum atom, while the ^{19}F shielding parameters for the para-substituted compounds, Δp, Fig. 1.1(ii) vary with the π-acceptor nature of X, since the metal $5d_{xy}$ orbital overlaps not only with the p_{π} orbital of the carbon bound to platinum but also with the trans ligand X.

The fluorophenyl platinum compounds Fig. 1.1(i) and (ii) generally show strongly positive shielding parameters which implies that the $-Pt(X)(PEt_3)_2$ group when bound to fluorobenzene is an electron donor in both the inductive and resonance senses. The shielding parameters depend strongly on the nature of the trans group X. A set of shielding parameters for various trans groups X is given in Table 4.[47]

The shielding parameter sequence of the meta-fluorophenyl compounds, Δm, parallels the basicity sequence of X,[48] as measured in a non-polar solvent* eg.

$$CH_3 > C_6H_5 > C_6H_5C \equiv C \quad \text{and} \quad CN > Cl > Br > I$$

This is to be expected since the inductive enhancement of the ^{19}F shielding parameter should be proportional to the electron density injected by ligand X into the σ-bond system of the complex.

---

* Basicity as measured by the equilibrium constant for the reaction $N_{aq} + H^+_{aq} \rightleftharpoons NH^+_{(aq)}$ N = a base.

Table 4

^{19}F Shielding Parameters for compounds (i) (Δm) and (ii) (Δp) for various ligands X.

Ligand X	Δm ppm	Δp ppm	π-acceptor parameter
CH_3	3.93	11.7	0
C_6H_5	3.46	10.9	0.3
pFC_6H_4	3.30	10.8	0.3
$C_6H_5C{\equiv}C$	3.21	10.4	0.6
mFC_6H_4	3.07	10.6	0.3
OCN(or NCO)	2.30	10.1	0
CN	2.27	9.32	0.7
Cl	2.11	10.1	-0.2
Br	1.97	9.86	-0.1
SCN(or NCS)	1.75	9.29	0.2
I	1.56	9.54	-0.2
$SnCl_3$	-0.23	6.96	0.6

Shifts Δm and Δp are measured in acetone solution with fluorobenzene as internal reference. Temperature ~ 40°C.

The $SnCl_3^-$ ligand is a very weak σ-donor as indicated by the above figures.

For the para-fluorophenyl compounds, the shielding parameters, Δp, are much larger. This can be explained by the contributions of the resonance structures shown in Fig. 1.9 which enhance the electron density at the ortho and para positions.

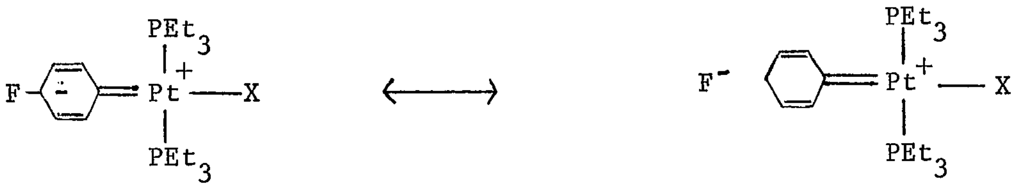


Fig. 1.9

This resonance effect is superimposed on the inductive effect measured by the shielding parameters for the meta-substituted compounds. Hence, a measure of the inductive effect of a ligand is obtained from the magnitude of Δm, and that of the π-bonding ability of a ligand by observing the difference (Δp-Δm) <u>ie</u> Δp gives a measure of the π-bonding ability of the ligand after the inductive contribution as measured by Δm has been subtracted.

The shielding parameters for the parafluorophenyl compounds, Δp, follow the same sequence as for the metafluorophenyl compounds, except for the positions of the potential π-acceptor ligands,

$C_6H_5C{\equiv}C^-$, CN^-, SCN^-. For these ligands, the chemical shifts are smaller because a π-acceptor ligand on platinum will compete with the fluorophenyl ring for the electron density in the π-orbitals of the complex.

The π-acceptor parameters were obtained from the expression

$$\pi\text{-acceptor parameter} = (\Delta p - \Delta m)_{CH_3} - (\Delta p - \Delta m)_X$$

This compares the π-acceptor parameter of a ligand X with that of a ligand with no accessible π-orbitals, the methyl group.

The results so obtained show $C_6H_5C{\equiv}C^-$, CN^- and $SnCl_3^-$ to be strong π-acceptors, the aryl and thiocyanate ligands to be modest π-acceptors, and the cyanate group to have no π-acceptor tendencies. The halide ions gave negative π-acceptor parameters indicating that in the platinum(II) complexes studied, halide ions are π-donors. As predicted by Orgel,[49] the donor p_π action is probably stronger than the acceptor d_π action in halide complexes.

Hence these results give data supporting the idea that trans-effect ligands are of two types:[5]

a) Strong σ-donors of low electronegativity eg H^- and CH_3^-.

b) Strong π-bonding ligands such as PR_3 and CN^-.

The case of $SnCl_3^-$ will be discussed later.

The strongly positive ^{19}F shielding parameters for the para-fluorophenyl platinum complexes suggest extensive interaction between the π-orbitals of the benzene ring and those of the platinum atom; that is, large contributions from the resonance structures shown in Fig. 1.9. The orbital interactions believed to be responsible for this effect are pictured in Fig. 1.10.

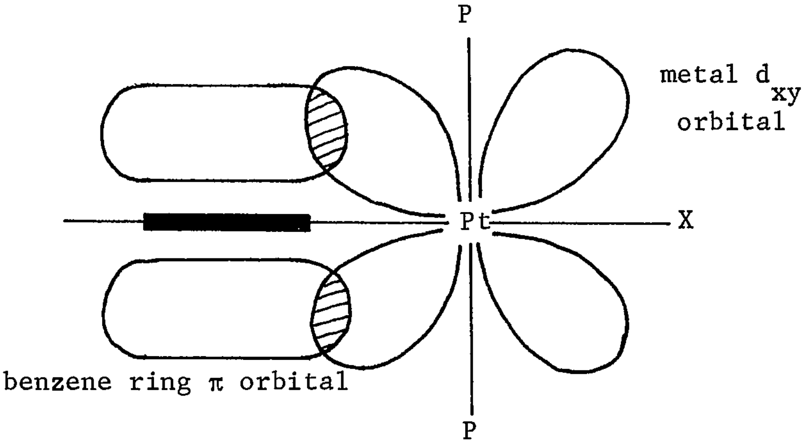


Fig. 1.10

The most favourable orientation of the benzene ring is probably perpendicular to the plane defined by the other three ligands, although there is almost certainly free rotation. If the ligands are placed on the x and y axes, the $5d_{xy}$ orbital of platinum will overlap with the π-orbitals of the aromatic ring. Similarly, the $5d_{xy}$ orbital will overlap with any π-orbitals on the <u>trans</u> ligand X. Hence, if X has filled p orbitals, as in the halide ions, electron density is displaced in the direction of the ring and the shielding of the p-fluorine nucleus is enhanced. Vacant orbitals such as the π^* orbitals of the cyanide ion withdraw electrons from the aromatic ring and cause deshielding.

Parshall *et al*[47] also included in this study, an investigation into *cis*-compounds of the type shown in Fig. 1.11 in order to compare the electronic effects of the *trans*-triethylphsophine ligand with those of the anionic ligands.

(i) (ii)

Fig. 1.11

If the *cis*-ligand, X, in compounds (i) and (ii) in Fig. 1.11 had similar properties to triethylphosphine, a valid comparison should be possible. Triethylphosphine could then be used as a standard to match sequences of anionic ligands against sequences of neutral ligands. Results obtained for five ligands are given below in Table 5. Taking the average value for Δm as 3.35 ppm. it indicates PEt_3 to be a σ-donor ligand comparable in strength with an aryl group. For compound (ii) the shielding parameters, Δp, are

Table 5.

^{19}F Shielding Parameters in ppm. for compounds (i) and (ii) in Fig. 1.11.

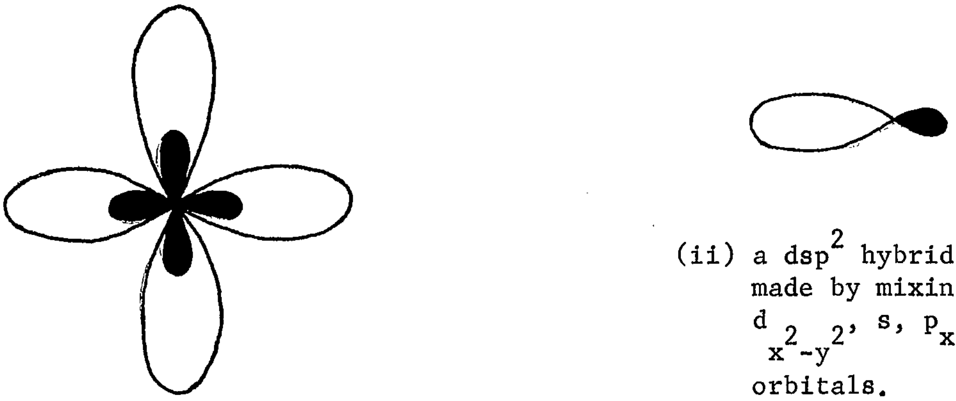
X	Δm	Δp
C_6H_5	3.55	11.6
pFC_6H_4	3.55	11.4
mFC_6H_4	3.44	11.2
CN	2.85	9.48
Cl	3.37	9.75

All measured in 2-5% solutions in acetone with reference to fluorobenzene as internal reference. Temperature $\sim 40^oC$.

larger than the corresponding values for the trans compound Fig. 1.1(ii). Values of (Δp - Δm) are so large that meaningful values of the π-acceptor character of Et_3P cannot be made. It can, however, be concluded that π-interactions in cis compounds are much larger than σ-interactions. π-donor and π-acceptor ligands in the cis- position to the fluorophenyl ring can interact, through the $5d_{xy}$ orbital, with the benzene ring in the same way as in trans compounds, which implies that π-acceptor ligands should affect the detector ligand whether in a cis or trans position. The large ^{19}F shielding parameters for the two compounds Fig. 1.1(ii) and Fig. 1.11(ii) are in agreement with this concept.

Chatt et al,[41] proposed that strong donor ligands weakened the transition metal-ligand bond by polarisation of the platinum atom, while π-acceptor ligands stabilise the transition state of the reaction, thus facilitating substitution. The polarisation aspect of this proposal can be rationalised by considering the orbital interactions in Fig. 1.12.

Introduction of a strong σ-donor ligand such as R_3P or $C_6H_5^-$ into a σ-orbital will displace electron-density into the trans-orbital and weaken the metal-ligand bond. Even a strong donor ligand will have little effect on the cis ligands via the σ-orbitals, as demonstrated by the ^{19}F shielding parameters. The contrast between the magnitudes of cis and trans σ effects is probably due to the differences in effective overlap of cis and trans σ-orbitals in square planar complexes.



(ii) a dsp^2 hybrid orbital made by mixing the $d_{x^2-y^2}$, s, p_x and p_y orbitals.

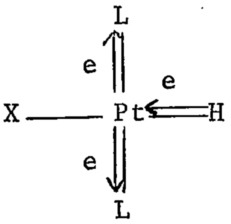
Fig. 1.12

As in Fig. 1.12(i) the "tail" of each directed dsp^2 hybrid bond overlaps the trans orbital. There is little overlap between cis orbitals and hence little electronic interaction is expected.

In conclusion, the trans effect can be considered to be transmitted by a mesomeric effect, an inductive effect or a combination of both. The inductive effect is transmitted through σ-bonds and usually involves weakening of the *trans* bond. This influence on ground state phenomena such as bond length and infra-red stretching frequencies is normally referred to as the *trans*-influence. The mesomeric effect is transmitted through d-orbitals of the platinum and ligand orbitals which can be either d-orbitals or vacant π-orbitals. This π-bonding mechanism operates by stabilisation of the transition state for a 5-coordinate intermediate although weakening of the *trans* bond can occur if the *trans* ligand is able to π-bond to the platinum.

The Cis-Effect

The effect of *cis* ligands on Pt(II) systems is considered to be small. It has been found that the effect of *cis* phosphines on the Pt-H stretching frequency is to cause ν(Pt-H) to rise as the electron-withdrawing ability of the *cis* ligands increases.[38] (Table 6).



X = Cl

Table 6.

Variation of ν(Pt-H) with cis ligands L.

L	$AsEt_3$	PMe_3	PEt_3	PPr^n_3	PPh_2Et	PPh_3	
ν(Pt-H)	2174	2182	2183	2183	2210	2224	cm^{-1}

The infra-red shift differences are very small and this has prevented a satisfactory characterisation of the cis-influence of ligands,[41] but a measure of the cis-influence of ligands can be obtained by observing the ^{35}Cl nuclear quadrupole resonance frequency of a co-ordinated chlorine which is sensitive to changes in the cis-ligands.[50]

From the observed frequencies for a series of compounds trans-L_2MCl_2, M = Pt and Pd, the M - Cl bond is weakened as the cis ligand L is changed from left to right in the following order:

M = Pd^{II} L = PhCN, EtCN, nBu_3P, nBu_3As, pyridine, piperidine.

M = Pt^{II} L = nBu_3P, pyridine, $(CH_3)_2NH$, NH_3.

Thus the cis-influence of these ligands ~~de~~increases from left to right.

This weakening of the M-Cl bond in the ground state appears to assist nucleophilic substitution reactions of the chlorine, because the rate of replacement of chlorine in trans- L_2PtCl_2 by weak nucleophiles increases in a similar order.[51]

$$L = Et_3P < Et_3As < \text{pyridine} < \text{piperidine}$$

As can be seen, the cis-influence order is virtually the reverse of the trans-influence order. A possible explanation for this is that the π-acceptor abilities of the ligands in the trans-influence series

$$NH_3 \sim RNH_2 < \text{pyridine} < R_3As < R_3P$$

increase from left to right, resulting in an increased trans-effect in the same order, whereas the total charge donated by ligands (σ-donation less π withdrawal) increases from left to right in the cis-influence series, allowing the cis M-Cl bond to become increasingly polarised and therefore weakened.

CHAPTER 2.

RESULTS AND DISCUSSION

In the work to be described in this chapter, the intention was to make a series of compounds of the types shown in Fig. 2.1(i) and (ii) in which X was a ligand attached to platinum by a group IVb element, namely silicon, germanium and tin and then, by using Parshall's method,(see Chapter 1, page 21) to investigate the electronic and trans- effects of the ligands X by observing the ^{19}F n.m.r spectra of these compounds. This method has also been used to investigate substituent effects in copper,[52] gold[53] and manganese[54] complexes.

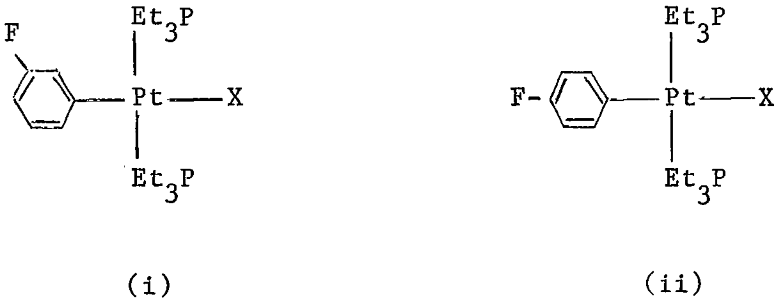


Fig. 2.1

Church and Mays,[55] however, expressed a doubt as to the validity of deducing relative π-acceptor strengths of ligands by observation of ^{19}F n.m.r. shielding parameters (page 21). In Parshall's work it was assumed that the measured changes in (Δp - Δm) (Δp = shielding parameter for parafluorophenyl compounds, Δm that for the metafluorophenyl compounds) reflect the change in the amount of π-electron density accepted by the aryl group. [As previously explained, Δm represents the inductive effect of the ligand, ie the σ-donor character of X as transmitted by the platinum atom, while the shielding parameter Δp varies with the π-acceptor nature of X since the metal $5d_{xy}$ orbital overlaps not only with the p_{π} orbital of the carbon bound to platinum but also with the trans-ligand X].

Church and Mays point out that the trans ligand X will affect the π-electron density in two ways:-

a) An increase in the π-acceptor ability of X reduces the amount of π-electron density available to the aryl group.

b) A change in the σ-donor strength of X affects the ability of the aryl group to accept π-electrons in the following manner:

(i) An increase in the σ-donor strength of X will decrease the effective nuclear charge on the metal and cause an expansion of the metal d-orbitals, changing the degree of π-overlap of these orbitals with the aryl group and all other ligands.

(ii) An increase in the trans-influence of X will weaken the trans metal-carbon bond,[56] and this weakening is likely to be associated with an increase in bond length. Any such changes in the M-C bond length will alter the interaction between the metal and the aryl group.

Hence, they suggest that the σ-effects cannot be assessed from Δm alone. Since the degree to which they affect the value of Δp-Δm in the fluorophenyl complexes is not known, caution is necessary in interpreting results obtained in this manner.

Experimental.

Compounds of the type in Fig. 2.1 in which X = $SnCl_3$ were prepared by insertion of $SnCl_2$ into the Pt-Cl bond in the compounds in which X = Cl,[47] and those of $GeCl_3$ from the reaction of (i) and (ii) (Fig. 2.1) (X = Cl) with $Me_3NHGeCl_3$ or $CsGeCl_3$. Similar reactions with $CsGeBr_3$ failed. It was intended to prepare MMe_3 derivatives by preparation of trans-$(Et_3P)_2Pt(SiMe_3)(C_6H_4F)$ from $(Me_3Si)_2Hg$ and trans-$(Et_3P)_2Pt(Cl)(C_6H_4F)$ and then to obtain $GeMe_3$ and $SnMe_3$ derivatives by exchange reactions with Me_3MH (M = Ge,Sn),[57] but the attempted preparation of the trimethyl-silicon compound $(Et_3P)_2Pt(SiMe_3)m\text{-}C_6H_4F$ was unsuccessful. The compounds trans-$(Et_3P)_2Pt(Cl)pC_6H_4F$ and trans-$(Et_3P)_2Pt(Cl)mC_6H_4F$ were not prepared as described in reference 49 but by the more straightforward procedure of reacting $(mC_6H_4F)_2Hg$ or $(pC_6H_4F)_2Hg$ with cis-$(Et_3P)_2PtCl_2$. Similar work was later published by Cross and Wardle.[58] Full experimental details of the compounds prepared are given below.

1. Preparation of trans-$(Et_3P)_2Pt(Cl)m\text{-}C_6H_4F$ (new route).

cis-$(Et_3P)_2PtCl_2$ (1gm; 1.79 mmoles) was dissolved in refluxing ethanol (100ml) and a suspension of $(m\text{-}C_6H_4F)_2Hg$ (0.76g; 1.94 mmoles) in ethanol (20ml) was added. The mixture was refluxed for about three hours to give a clear solution. The ethanol was removed *in vacuo* to leave a white solid. This was extracted with hexane to leave a white solid identified as $(m\text{-}C_6H_4F)HgCl$. The hexane extract was evaporated in vacuo to small volume and left at $-20^{\circ}C$ when white crystals of trans-$(m\text{-}C_6H_4F)ClPt(Et_3P)_2$ separated out.

M.Pt = 89°-$91^{\circ}C$. Literature Value = 90°-$91^{\circ}C$.[46]

2. Preparation of trans-$(Et_3P)_2Pt(Cl)p\text{-}C_6H_4F$ (new route).

This was prepared in a similar way to the m-fluorophenyl analogue, using $(p\text{-}C_6H_4F)_2Hg$. The product was trans-$(p\text{-}C_6H_4F)ClPt(Et_3P)_2$.

M.Pt = 102-$104^{\circ}C$. Literature Value = 103-$104^{\circ}C$.[146]

3. Preparation of trans$(Et_3P)_2Pt(SnCl_3)m\text{-}C_6H_4F$ and trans-$(Et_3P)_2Pt(SnCl_3)p\text{-}C_6H_4F$.

The compounds were prepared by the method described by Parshall.[47] Products were trans-$(Et_3P)_2Pt(SnCl_3)m\text{-}C_6H_4F$, M.Pt = 147-$149^{\circ}C$. Literature Value = 147-149°dec.[47] and trans-$(Et_3P)_2Pt(SnCl_3)p\text{-}C_6H_4F$, M.Pt. = 168-$171^{\circ}$dec. Literature Value = 169-$171^{\circ}C$ dec.[47]

4. Preparation of the new compound trans-$(Et_3P)_2Pt(GeCl_3)m\text{-}C_6H_4F$.

Caesium trichlorogermanite (0.25g) and trans-$(Et_3P)_2Pt(Cl)m\text{-}C_6H_4F$ (0.4g), were refluxed together in dry diethyl ether (30ml). A white precipitate of caesium chloride was deposited after refluxing for three days. The solvent was removed in vacuo and the solid residue extracted with benzene. The product was recrystallised from a benzene/

hexane mixture to give very pale yellow crystals, of trans-$(Et_3P)_2Pt(GeCl_3)m\text{-}C_6H_4F$.

M.Pt. = 155-157°C.

The same compound was obtained in better yield by the use of $Me_3NHGeCl_3$ instead of $CsGeCl_3$.

Analysis: Found C: 30.2; H:4.8; Cl: 15.3; P: 9.2%.

$C_{18}H_{34}Cl_3FGeP_2Pt$ requires: C: 30.6; H: 4.8; Cl: 15.1; P: 8.8%.

^{31}P n.m.r. run in acetone gave J_{P-Pt} = 2552 Hz indicating that the trans-isomer had been formed in the reaction. [The values of $J_{(Pt-P)}$ in cis and trans platinum diphosphine complexes are in general in the ranges 3200-6000cps for cis compounds and 2200-2800cps for trans compounds.[17]]

5. Preparation of the new compound trans-$(Et_3P)_2Pt(GeCl_3)p\text{-}C_6H_4F$.

This was prepared in a similar way to the metafluorophenyl compound described above, using trans-$(Et_3P)_2Pt(Cl)p\text{-}C_6H_4F$ and $Me_3NHGeCl_3$. Yellow crystals of trans-$(Et_3P)_2Pt(GeCl_3)p\text{-}C_6H_4F$ were obtained.

M.Pt = 141- 143°C.

Analysis: Found C: 30.9; H: 4.9; P: 8.0; Cl: 15.3%.

$C_{18}H_{34}Cl_3FGeP_2Pt$ requires: C: 30.6; H: 4.8; Cl: 15.1; P: 8.8%.

^{31}P n.m.r. run in acetone gave J_{P-Pt} = 2576 Hz indicative of trans-$(Et_3P)_2Pt(GeCl_3)p\text{-}C_6H_4F$.

6. Reaction between $(Me_3Si)_2Hg$ and trans m-$C_6H_4F(Cl)Pt(Et_3P)_2$ [59]

Trans-$(Et_3P)_2Pt(Cl)$m-C_6H_4F (0.4g) was dissolved in dry refluxing benzene (20ml). $(Me_3Si)_2Hg$ (0.23g) in dry benzene (10 ml) was added dropwise under nitrogen. An immediate reaction occurred, mercury was deposited and the solution turned blue-green. The solution was allowed to reflux overnight to form a brown solution. The reaction mixture was cooled under nitrogen, filtered and the solvent removed *in vacuo* to leave a brown waxy residue. This was washed with hexane to leave a brown intractable residue. On evaporation of the hexane washings some starting material was recovered.

7. Reaction between $CsGeBr_3$ and trans-(p-$C_6H_4F)ClPt(Et_3P)_2$

Trans-$(Et_3P)_2Pt(Cl)$p-C_6H_4F (0.4g) and $CsGeBr_3$ (0.56g) were refluxed in dry ether (80ml) for three days. The solvent was removed *in vacuo*, the residue extracted, with benzene and the solution filtered to remove CsCl. Slow evaporation of solvent under a stream of nitrogen resulted in a yellow intractable oil being obtained. A thin-film infra-red spectrum revealed a Pt-Cl stretch at 273cm^{-1} and a possible $GeBr_3$ doublet at 390 and 415cm^{-1}. Attempted isolation of a pure solid failed.

Spectral Data

1. Mass Spectra

The mass spectra of the following compounds were recorded.

trans-$(Et_3P)_2Pt(Cl)$m-C_6H_4F
trans-$(Et_3P)_2Pt(Cl)$p-C_6H_4F
trans-$(Et_3P)_2Pt(SnCl_3)$m-C_6H_4F
trans-$(Et_3P)_2Pt(SnCl_3)$p-C_6H_4F
trans-$(Et_3P)_2Pt(GeCl_3)$m-C_6H_4F
trans-$(Et_3P)_2Pt(GeCl_3)$p-C_6H_4F.

Table 7.

Mass Spectral data for trans-$(Et_3P)_2Pt(Cl)C_6H_4F$.

$^m/e$	Ion*	Fragment Lost.
562	$(Et_3P)_2Pt(Cl)C_6H_4F$	
543	$(Et_3P)_2Pt(Cl)C_6H_4$	562 - F
526	$(Et_3P)_2PtC_6H_4F$	562 - Cl
467	$(Et_3P)_2PtCl$	562 - C_6H_4F 526 - C_6H_4F
431	$(Et_3P)_2Pt$	467 - Cl
403	$(Et_3P)(PEt_2H)Pt$	431 - C_2H_4
375	$(Et_2PH)_2Pt$	403 - C_2H_4 431 - $2C_2H_4$
347	$(Et_2PH)(EtPH_2)Pt$	375 - C_2H_4
313	$Pt(PEt_3)$	431 - PEt_3
284	$PtPEt_2$	
255	PtPEt	
227	PtPH	
195	Pt	

* positive charges omitted

Metastable confirmed transitions:-

$$\underset{431}{\overset{+}{Pt(Et_3P)_2}} \xrightarrow[m^* = 376.8]{-C_2H_4} \underset{403}{\overset{+}{(Et_3P)(PEt_2H)Pt}}$$

$$\underset{403}{\overset{+}{Pt(Et_3P)(PEt_2H)}} \xrightarrow[m^* = 348.9]{-C_2H_4} \underset{375}{\overset{+}{Pt(Et_2PH)_2}}$$

$$\underset{431}{\overset{+}{\mathrm{Pt}}(\mathrm{Et_3P})_2} \xrightarrow[m^* = 326.3]{-2C_2H_4} \underset{375}{(\mathrm{Et_2PH})_2\overset{+}{\mathrm{Pt}}}$$

$$\underset{375}{\overset{+}{\mathrm{Pt}}(\mathrm{Et_2PH})_2} \xrightarrow[m^* = 321.1]{-C_2H_4} \underset{347}{(\mathrm{Et_2PH})(\mathrm{EtPH_2})\overset{+}{\mathrm{Pt}}}$$

$$\underset{403}{\overset{+}{\mathrm{Pt}}(\mathrm{Et_3P})(\mathrm{PEt_2H})} \xrightarrow[m^* = 298.8]{-2C_2H_4} \underset{347}{(\mathrm{Et_2PH})(\mathrm{EtPH_2})\overset{+}{\mathrm{Pt}}}$$

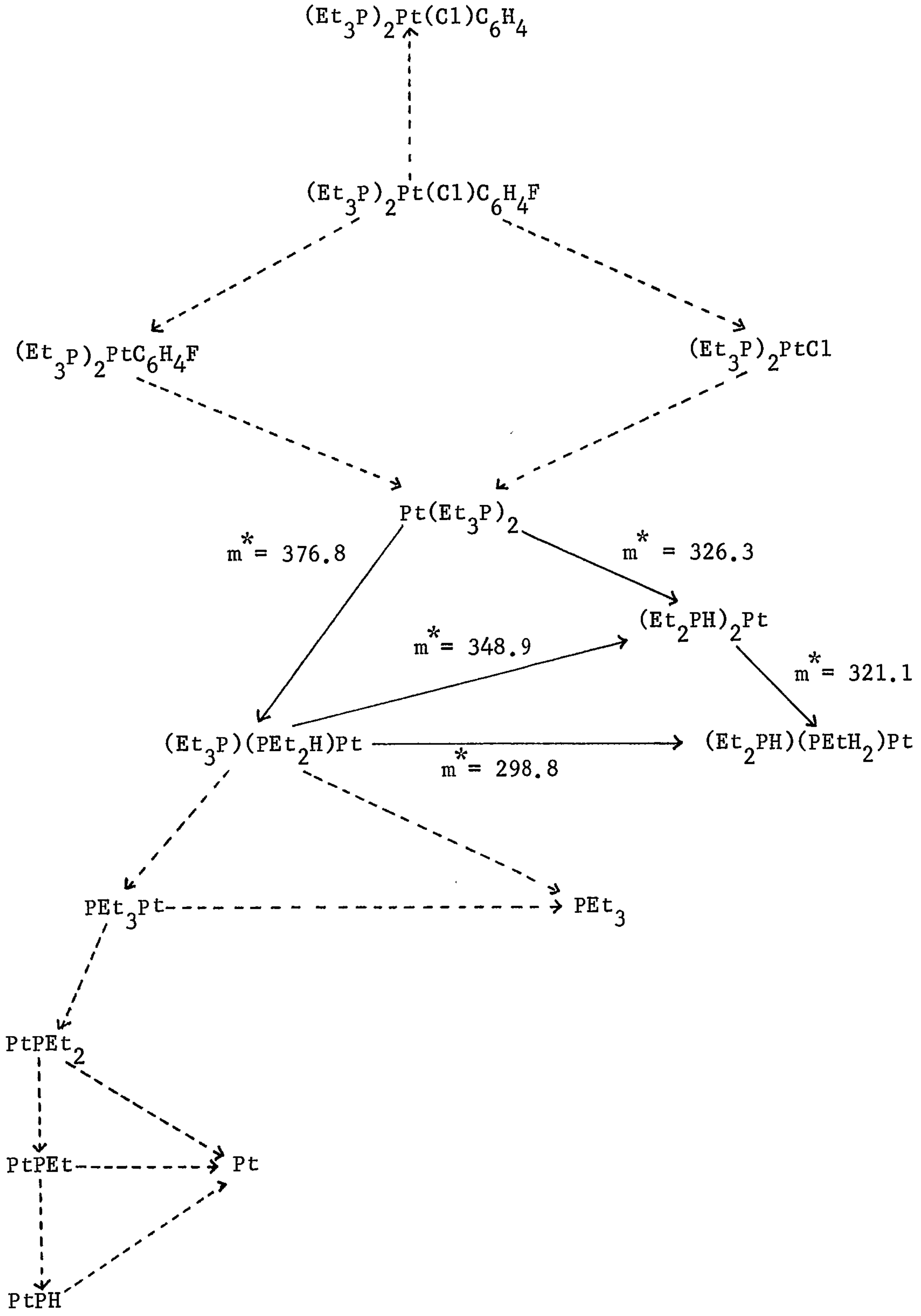


Fig. 2.2(i) Fragmentation pattern of trans-$(Et_3P)_2Pt(Cl)C_6H_4F$.

(positive charges omitted)

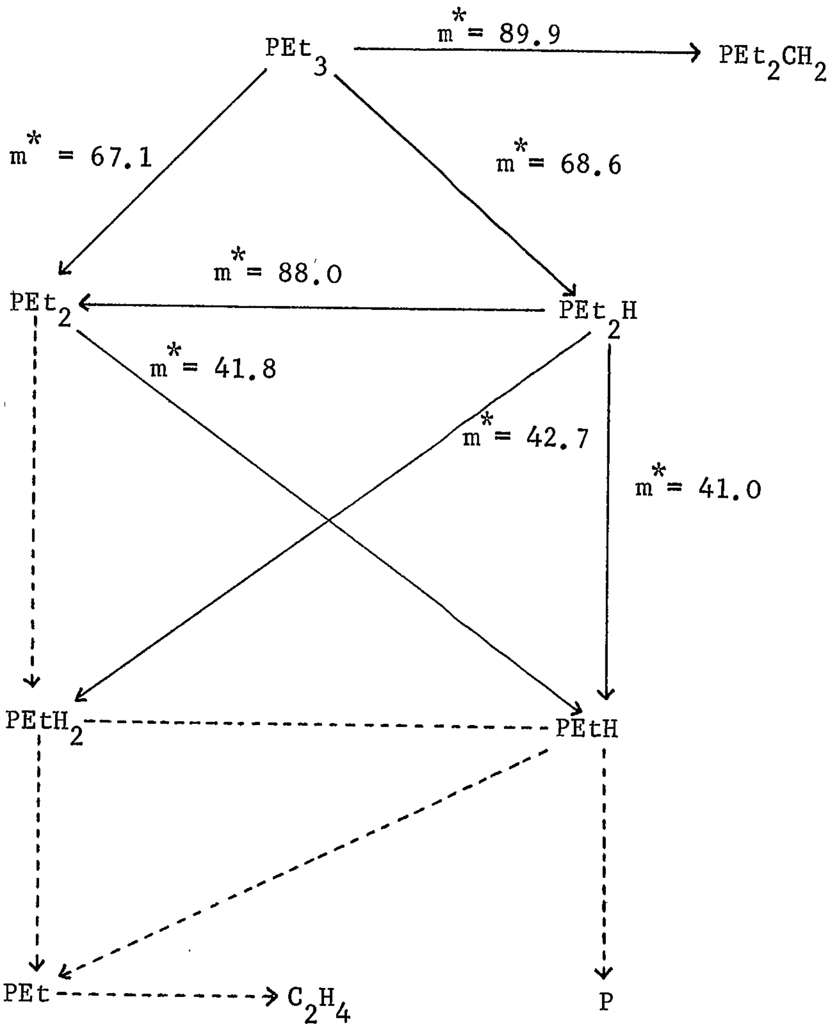


Fig. 2.2(ii) Fragmentation pattern of PEt_3.

(positive charges omitted)

All compounds gave a peak at $^{m}/e$ 562 due to $(Et_3P)_2\overset{+}{Pt}(Cl)C_6H_4F$ and hence, except for additional peaks due to the $SnCl_3$ and $GeCl_3$ ligands, the fragmentation patterns were all similar, ie that of trans-$(Et_3P)_2Pt(C_6H_4F)Cl$ which is shown in Fig. 2.2(i) and (ii) with details of platinum containing fragments in Table 7.

The additional peaks in the spectra of the tin and germanium containing ligands and their assignment are given below in Tables 8 and 9. No apparent difference was observed between the spectra of the meta- and para-fluorophenyl compounds.

Table 8.

Mass Spectral Data for trans-$(Et_3P)_2Pt(SnCl_3)C_6H_4F$.

$^{m}/e$	Ion.*
† 652	$(C_6H_4F)Pt(PEt_2)(PEt_3)SnCl$.
605	$(PEt_3)(PEtH_2)Pt(SnCl)C_6H_4$.
587	$H(SnCl)Pt(Et_3P)_2$.
225	$SnCl_3$
190	$SnCl_2$
155	SnCl
120	Sn

† Peak at highest $^{m}/e$ observed.

* Positive charges omitted.

Metastable confirmed transitions:

$$\underset{225}{\overset{+}{Sn}Cl_3} \xrightarrow{-Cl} \underset{190}{\overset{+}{Sn}Cl_2}$$

$$m^* = 160.$$

Table 9.

Mass Spectral Data for trans-$(Et_3P)_2Pt(GeCl_3)C_6H_4F$.

$^m/e$	Ion*
† 671	$(Et_3P)_2Pt(GeCl_2)C_6H_4F$
652	$(Et_3P)_2Pt(GeCl_2)C_6H_4$
179	$GeCl_3$
144	$GeCl_2$
109	GeCl

† Peak at highest $^m/e$ observed.

* Positive charges omitted

No metastable ions from fragmentations involving germanium were observed.

Isotope distribution patterns for all compounds were calculated by computer and the fragments in Tables 7,8,9 were all confirmed by this method.

Fragments above $^m/e$ 562 which necessarily contain tin or germanium were of low abundance implying that the platinum-metal bond is the weakest platinum-ligand bond in the compounds and that cleavage of the Pt-M bond (M = Sn,Ge) to form $(Et_3P)_2Pt(Cl)C_6H_4F$ by loss of MCl_2 takes place readily.

2. Infra-Red Spectra.

The stretching frequencies in the infra-red spectra of particular interest are given below in Table 10. The spectra were run as pressed CsI discs.

Table 10.

Infra-red data for the compounds trans-$(Et_3P)_2PtX(C_6H_4F)$.

Compound		
trans-$(Et_3P)_2Pt(Cl)p\text{-}C_6H_4F$	ν(Pt-Cl)	278 cm^{-1}
trans-$(Et_3P)_2Pt(Cl)m\text{-}C_6H_4F$	ν(Pt-Cl)	281 cm^{-1}
trans-$(Et_3P)_2Pt(SnCl_3)p\text{-}C_6H_4F$	ν(Sn-Cl)	333, 312 cm^{-1}
trans-$(Et_3P)_2Pt(SnCl_3)m\text{-}C_6H_4F$	ν(Sn-Cl)	328, 304 cm^{-1}
trans-$(Et_3P)_2Pt(GeCl_3)p\text{-}C_6H_4F$	ν(Ge-Cl)	364, 338 cm^{-1}
trans-$(Et_3P)_2Pt(GeCl_3)m\text{-}C_6H_4F$	ν(Ge-Cl)	369, 339 cm^{-1}

These compounds are in agreement with values quoted in the literature, for $SnCl_3^-$ and $GeCl_3^-$ compounds.[60,61]

3. ESCA* Studies.

The X-ray photoelectron spectra were obtained for the six compounds prepared and the data are given below in Table 11. Changes in the binding energy of core electrons tend to reflect changes in electron density at that particular atom - a decrease in binding energy

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* ESCA = Electron Spectroscopy for Chemical Analysis.

implies an increase in electron density.

The fluorine F(1s) binding energy does not vary significantly from compound to compound having a value of 689.7 ± 0.2 eV, which is within experimental error. Similarly the binding energies of phosphorus $P(2p_{3/2})$ and $Pt(4f_{7/2})$ respectively 131.9 ± 0.1 eV and 7.33 ± 0.1 eV are not significantly different in the different compounds. The binding energies of the chlorine atoms in the $Pt\text{-}SnCl_3$ and the $Pt\text{-}GeCl_3$ compounds are also very similar. In the Pt-Cl compounds the binding energy of the chlorine core electrons is lower by ~ 1eV compared with that of the chlorine core electrons in the tin and germanium compounds, reflecting greater competition for the negative charge when there are three chlorine atoms on one metal ie. $Pt\text{-}Cl^{\delta-}$ and $SnCl_3^{\delta-/3}$, $GeCl_3^{\delta-/3}$.

It has been found that within complexes of the type $(R_3P)_2Pt^{II}XY$, the phosphorus $P(2p_{3/2})$ binding energy changes very little and that the platinum atom acts mainly as a centre for electron distribution between ligands.[62,63] The platinum $Pt(4f_{7/2})$ binding energy changes markedly only when the oxidation state of platinum changes.[64] The figures in Table 12,[64] show that the binding energies of $Pt(4f_{7/2})$ within Pt^{II} complexes are within a range of about 1.2eV ie they change slightly with varying ligands.

Normalising the results in Table 11 to give $P(2p_{3/2})$ = 130.7eV, the values of the binding energies in trans-$(p\text{-}C_6H_4F)ClPt(Et_3P)_2$ are

$Cl(2p_{3/2})$ = 197.7 eV
$Pt(4f_{7/2})$ = 72.0 eV
$P(2p_{3/2})$ = 130.7 eV.

Table 11.

Binding Energies of some atoms in fluorophenyl-platinum Complexes.

Compound	Binding Energy in eV.				
	$Cl(2p_{3/2})$	C(1s)	F(1s)	$Pt(4f_{7/2})$	$P(2p_{3/2})$
trans-$(pC_6H_4F)Pt(PEt_3)_2SnCl_3$	199.8	286.1	689.8	73.4	131.9
trans-$(mC_6H_4F)Pt(PEt_3)_2SnCl_3$	199.9	286.1	689.5	73.2	131.9
trans-$(pC_6H_4F)Pt(PEt_3)_2Cl$	198.9	286.1	689.7	73.2	131.8
trans-$(mC_6H_4F)Pt(PEt_3)_2Cl$	198.9	286.1	689.9	73.2	131.9
trans-$(pC_6H_4F)Pt(PEt_3)_2GeCl_3$	200.1	286.1	689.7	73.4	132.0
trans-$(mC_6H_4F)Pt(PEt_3)_2GeCl_3$	broad	286.1	689.6	73.2	131.9

Notes.

1. Carbon C(1s) binding energies are taken from the centroid of relatively broad peaks. Under these conditions, the $Au(4f_{7/2})$ peak has a binding energy of 84eV. All lines are calibrated to this value.

2. The underlined values are used as internal reference peaks to correct for charging effects. Binding energies are correct to ± 0.2eV.

3. Samples were studied as thin films on a gold backing from evaporation of an acetone solution of the compound.

This shows a slightly lower binding energy for Pt($4f_{7/2}$) and Cl($2p_{3/2}$) than in trans-($^{n}Bu_3P)_2PtCl_2$ indicating that the C_6H_4F ligand is less electron attracting (ie has a lower electronegativity) than Cl^-.

Table 12

Compound	Binding Energy in eV			
	C(1s)	Cl($2p_{3/2}$)	Pt($4f_{7/2}$)	P($2p_{3/2}$)
trans-($PPh_3)_2PtMe_2$	285.0	-	71.6	130.6
trans-($^{n}Bu_3P)_2PtCl_2$	285.0	198.1	72.3	130.7
trans-($PMe_3)_2Pt(CN)_2$	285.0	-	72.8	130.7

Although the results obtained are consistent within themselves, it is not possible to deduce any information from them to strengthen the n.m.r. results to be discussed in a following section. This is not unreasonable because

a) ESCA shifts are small and are subjected to much greater errors in measurement than are n.m.r. shifts.

b) Since shifts in core level binding energies are primarily due to valence shell changes, a qualitative correlation between ESCA shifts and n.m.r. chemical shifts might be expected. Such a correlation has been claimed for P(2p) shifts and ^{31}P n.m.r. shifts in quaternary phosphonium complexes.[65] Although limited results from halomethanes seemed to indicate a correlation between C(1s) shifts and ^{13}C n.m.r. shifts,[66,67] data from the full series now show that no correlation holds.[68]

4. ^{1}H n.m.r. Spectra.

The compounds, with the exception of trans-$(mC_6H_4F)ClPt(Et_3P)_2$ and trans-$(pC_6H_4F)ClPt(Et_3P)_2$,were only very slightly soluble in common organic solvents suitable for n.m.r. spectra, such as benzene, chloroform and acetone. Carbon disulphide was inappropriate in view of the possibility of insertion reactions into the platinum-metal bonds. Acidic solvents could not be used in case cleavage of the platinum-metal bond occurred. Owing to their low solubility in acetone and chloroform, poor quality spectra were obtained. All signals were complex multiplets due to coupling between ^{1}H, ^{19}F, ^{31}P and ^{195}Pt. The details of the spectra obtained are presented below in Table 13.

In the spectra of the tin and germanium compounds, the phenyl protons were not observable except in one case where the signal was very weak and broad. The shifts of the ethyl group protons vary only slightly with X(X = Cl, $SnCl_3$, $GeCl_3$) indicating that the cis ligands are relatively unaffected by X. In the case of trans-$(Et_3P)_2Pt(SnCl_3)pC_6H_4F$, the difference is almost certainly due to a solvent effect.

Table 13.

^{1}H n.m.r. Spectral Data

Compound	Protons	Signal*	Solvent
trans-$(Et_3P)_2Pt(Cl)pC_6H_4F$	phenyl (4)	2.98τ 3.42τ	$CDCl_3$
	ethyl CH_2 (12)	8.44τ	
	ethyl CH_3 (18)	8.94τ	
trans-$(Et_3P)_2Pt(Cl)mC_6H_4F$	phenyl (4)	3.01τ 3.47τ	$CDCl_3$
	ethyl CH_2 (12)	8.40τ	
	ethyl CH_3 (18)	8.93τ	
trans-$(Et_3P)_2Pt(SnCl_3)pC_6H_4F$	phenyl (4)	2.82τ	$(CD_3)_2CO$
	ethyl CH_2 (12)	7.93τ	
	ethyl CH_3 (18)	8.88τ	
trans-$(Et_3P)_2Pt(SnCl_3)mC_6H_4F$	phenyl	not observable	$CDCl_3$
	ethyl CH_2	8.07τ	
	ethyl CH_3	8.92τ	
trans-$(Et_3P)_2Pt(GeCl_3)pC_6H_4F$	phenyl	not observable	$CDCl_3$
	ethyl CH_2	8.22τ	
	ethyl CH_3	8.95τ	
trans-$(Et_3P)_2Pt(GeCl_3)mC_6H_4F$	phenyl	not observable	$CDCl_3$
	ethyl CH_2	8.22τ	
	ethyl CH_3	8.94τ	

* Shifts are given relative to tetramethylsilane as internal reference.

Table 14.

^{19}F Chemical Shifts in ppm. at 40°C.

Compound	Chemical Shift (in acetone solution *)	Chemical Shift (in chloroform solution *)	Chemical Shift (in acetone solution†)
trans-$(Et_3P)_2Pt(Cl)mC_6H_4F$	-47.50	-46.04	+ 2.55
trans-$(Et_3P)_2Pt(Cl)pC_6H_4F$	-39.70	-38.41	10.35
trans-$(Et_3P)_2Pt(SnCl_3)mC_6H_4F$	-49.93	-48.66	0.12
trans-$(Et_3P)_2Pt(SnCl_3)pC_6H_4F$	-42.96	-41.93	7.29
trans-$(Et_3P)_2Pt(GeCl_3mC_6H_4F$	-49.38	-47.99	0.67
trans-$(Et_3P)_2GeCl_3)pC_6H_4F$	-42.78	-41.40	7.27

* Shifts relative to C_6F_6

† Shifts relative to C_6H_5F

≠ The ^{19}F Chemical Shifts were determined using a Dupont 310 Curve Resolver (Analogue Computer).

5. ^{19}F n.m.r. Spectra

The solutions of the germanium and tin compounds were very dilute due to their low solubility, so only poor quality spectra were obtained. Again, the solvents used were acetone and chloroform, in which the compounds appeared to be most soluble. Hexafluorobenzene was used as internal reference, and the shifts relative to monofluorobenzene were calculated in order that a direct comparison with Parshall's values could be obtained. Where X = Cl the compounds were readily soluble. Signals, in general, were very broad and complex due to coupling of ^{19}F with ^{195}Pt, ^{31}P, ^{1}H. For two cases, trans-$(Et_3P)_2PtCl(pC_6H_4F)$ and trans-$(Et_3P)_2Pt(GeCl_3)mC_6H_4F$, spectra were run with an attempt to decouple the protons. The spectra of the compounds in acetone solution and the two spectra with protons decoupled are shown in Figs. 2.3, 2.4 and 2.5, and the chemical shifts observed given in Table 14. An attempt was made to measure coupling constants from the spectra, but this proved impossible due to their complexity.

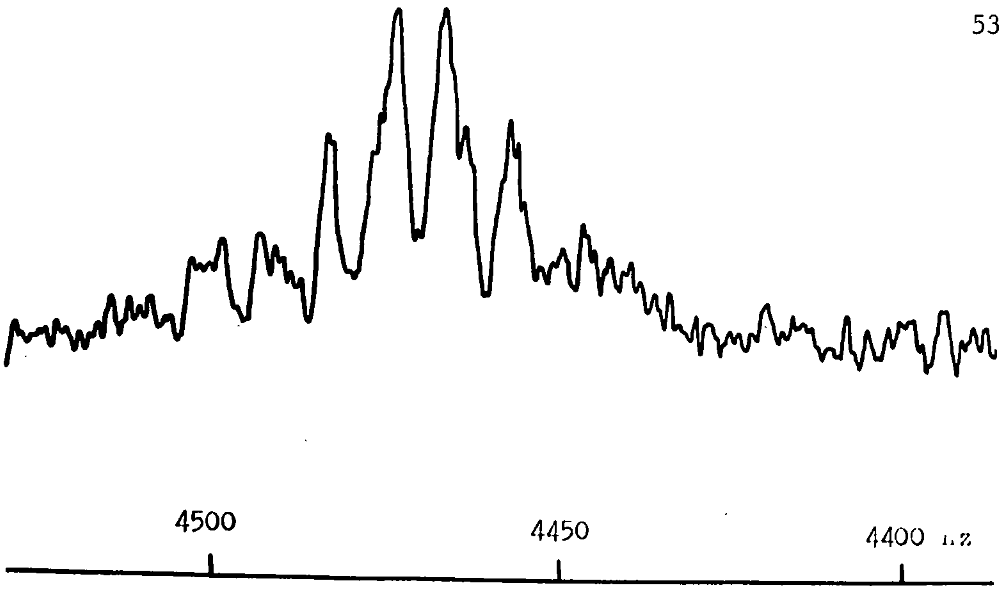
Discussion.

Parshall[2] obtained the ^{19}F n.m.r. spectra of a series of compounds of the type in Fig. 2.1(i) and (ii) where X was a variety of ligands. The ^{19}F shielding parameter Δm as measured by the chemical shift of the compounds of type Fig. 2.1(i) and Δp as measured by the chemical shift of the compounds of type Fig. 2.1(ii) were obtained and are recorded below in Table 15.

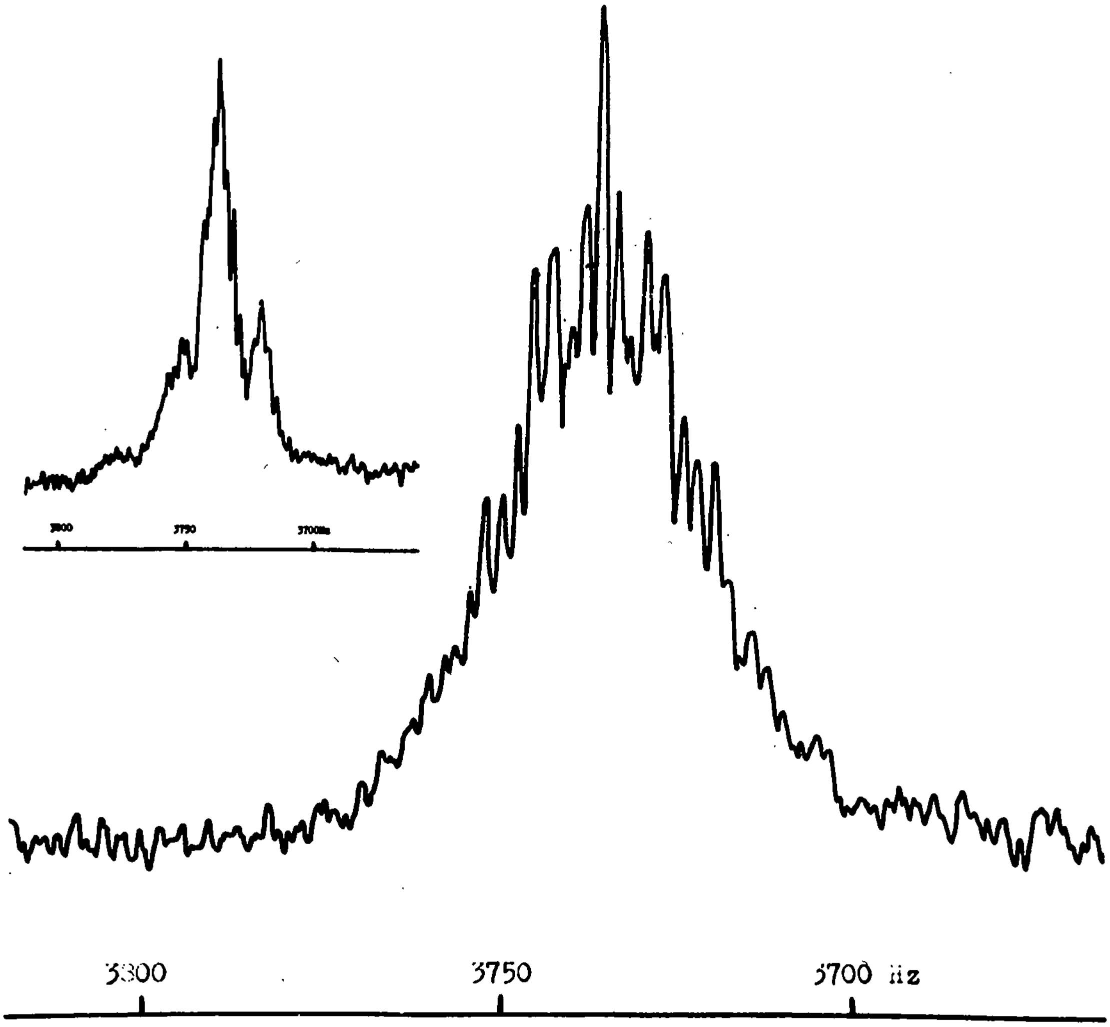
Parshall[2] defined a π-bond criterion, Z, as

$$Z = \Delta p - \Delta m$$

which corrects Δp for inductive effects (measured by Δm) and

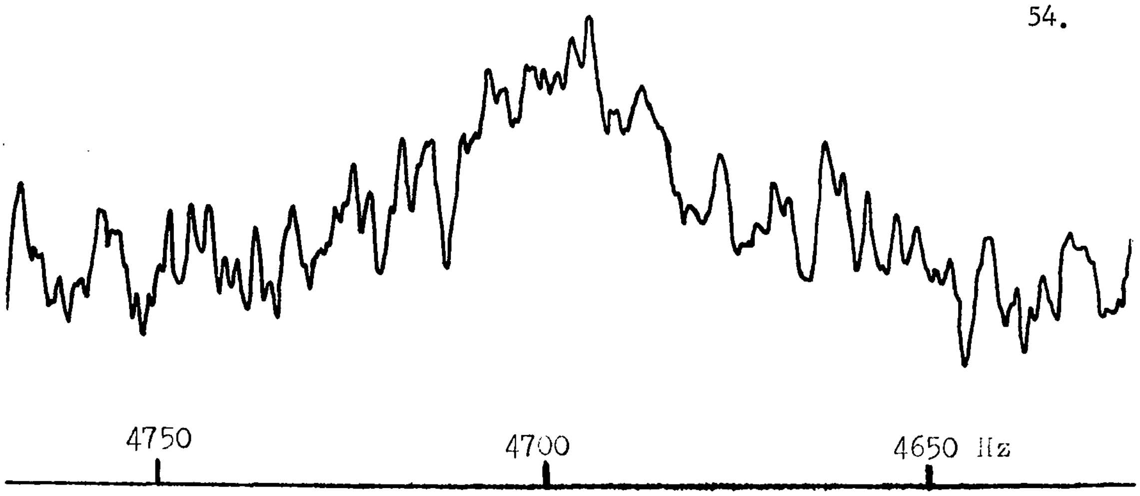


^{19}F spectrum of trans-(Et$_3$P)$_2$Pt(Cl)mC$_6$H$_4$F run in acetone at 40°C with C$_6$F$_6$ as internal reference.

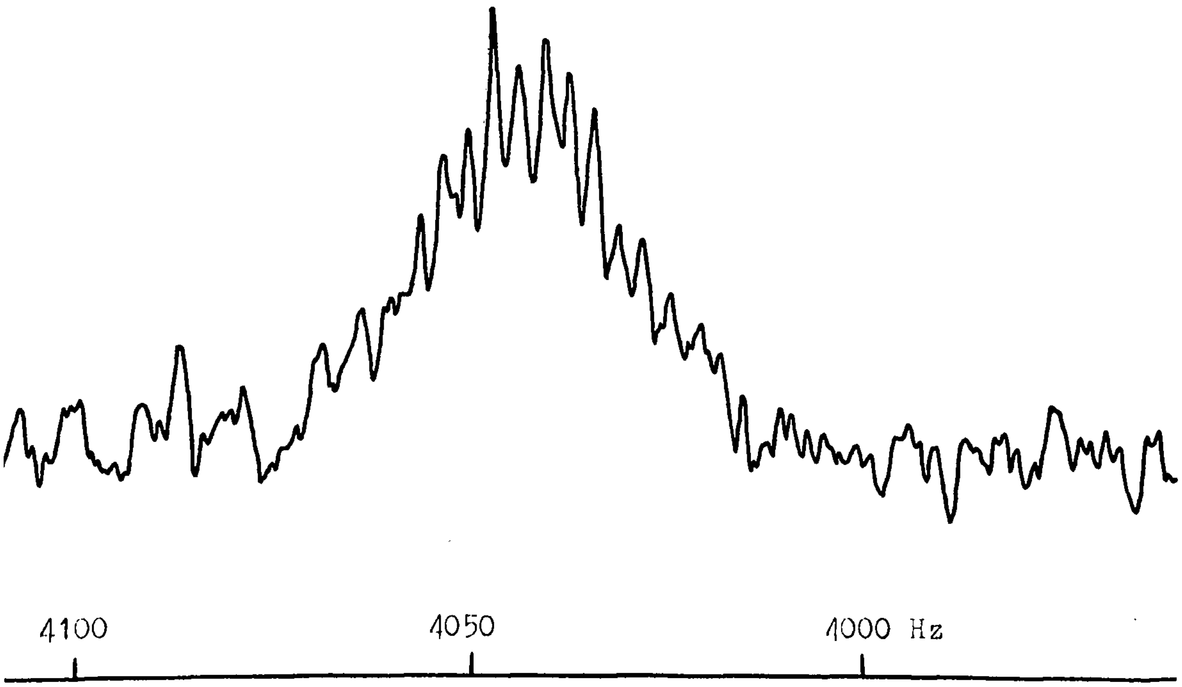


^{19}F spectrum of trans-(Et$_3$P)$_2$Pt(Cl)pC$_6$H$_4$F, insert, spectrum obtained by decoupling the protons. Both spectra were run in acetone at 40°C with C$_6$F$_6$as internal reference.

FIG. 2.3

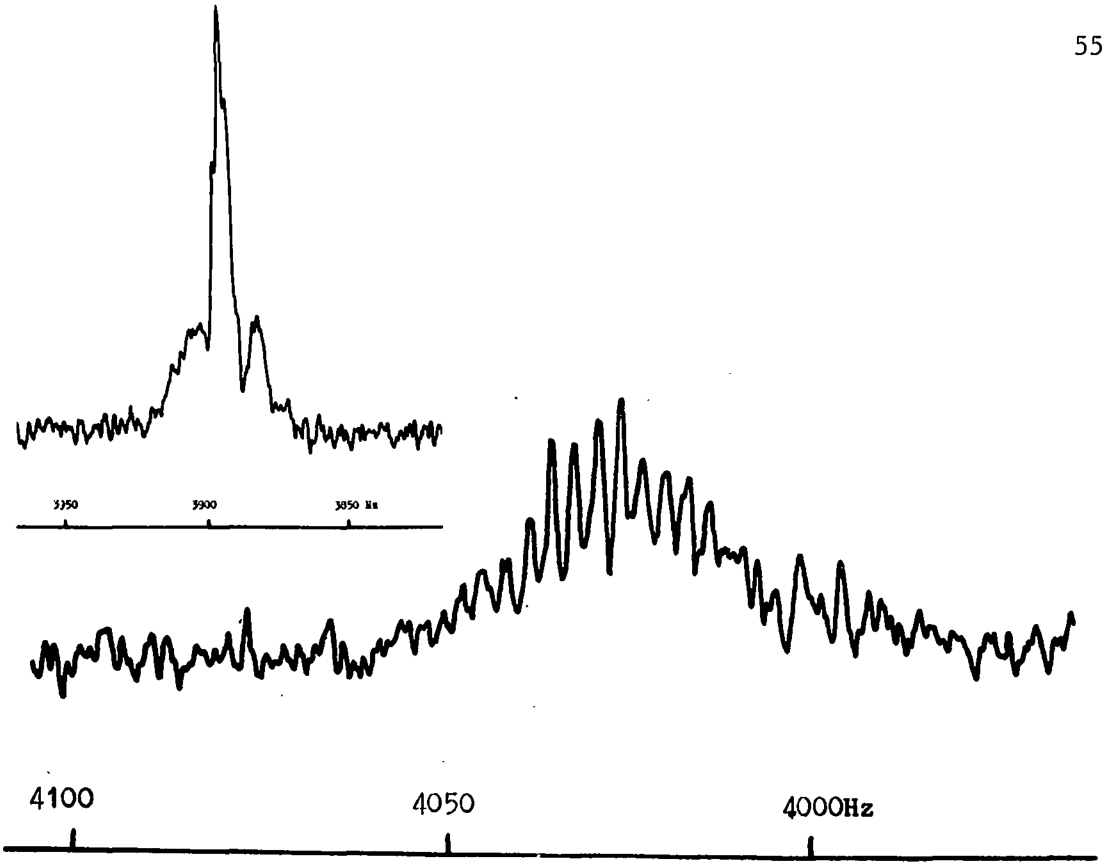


^{19}F n.m.r. spectrum of trans-$(Et_3P)_2Pt(SnCl_3)$ mC_6H_4F run in acetone at 40°C with C_6F_6 as internal reference.

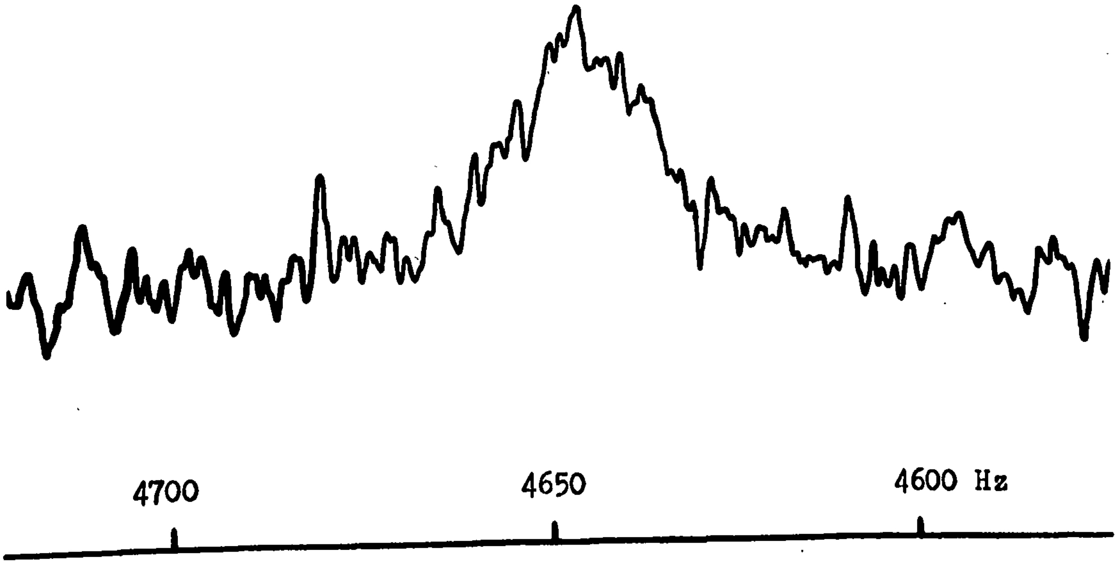


^{19}F n.m.r. spectrum of trans-$(Et_3P)_2Pt(SnCl_3)pC_6H_4F$ run in acetone at 40°C with C_6F_6 as internal reference.

FIG. 2.4



^{19}F n.m.r. spectrum of <u>trans</u>-$(Et_3P)_2Pt(GeCl_3)pC_6H_4F$ run in acetone
Insert, spectrum obtained by decoupling the protons, run in chloroform
Both spectra were run at 40°C with C_6F_6 as internal reference.



^{19}F n.m.r. spectrum of <u>trans</u>-$(Et_3P)_2Pt(GeCl_3)$ in C_6H_4F run in acetone at 40°C with C_6F_6 as internal refcrence.

FIG. 2.5

Table 15.

^{19}F Chemical Shifts for compound (i) and (ii) in Fig. 2.1 for varying ligand X.

Ligand X	Δm	Δp	Z = Δp-Δm
CH_3	+4.06	11.70	7.64
C_6H_5	3.50	10.92	7.42
mFC_6H_4	3.42	10.65	7.23
pFC_6H_4	3.30	10.79	7.49
CN	2.27	9.32	7.05
Cl	2.13	10.11	7.98
Br	1.97	9.86	7.89
NCS	1.75	9.29	7.54
I	1.56	9.54	7.98
$SnCl_3$	-0.23	6.96	7.19

Shifts are measured in p.p.m. relative to fluorobenzene as internal standard in an 8-10% solution of the complex in acetone-d_6.

hence provides a criterion of ability of X to compete with the p-fluorophenyl ring for electron density in the platinum d_{xy} orbital. As can be seen, Z takes values ranging from 7.05 for the strongly π-bonding cyanide ligand to almost 8 for the halide ligands, which have little or no π-acceptor capacity.[69] The halide ligands have higher Z values than does the methyl ligand which is expected to be a non-π-bonding ligand, suggesting that halides may actually be weak π-donors.[69]

In Table 16 the Z values of the ligands in this study are calculated.

Table 16.

Calculation of Z values for various ligands X.

X	Δp	Δm	Z
Cl	+ 10.35	+ 2.55	+ 7.80
$GeCl_3$	+ 7.27	+ 0.67	+ 6.60
$SnCl_3$	+ 7.29	+ 0.12	+ 7.17

The significance of the results obtained can be discussed under three headings:

1. σ-donor effects (Δm values)
2. π-bonding effects (Δp-Δm values)
3. Effect on Δp.

1. σ-donor effects

From the above values of Δm, the ligands can be arranged in order of their σ-donor properties, this order being

$$Cl \gg GeCl_3 > SnCl_3.$$

Chloride is by far the strongest σ-donor of the three ligands and $SnCl_3$ is shown to be a very weak σ-donor. This result was also found by Parshall.[47] $GeCl_3$ is shown to be a considerably weaker σ-donor than chloride but significantly stronger than $SnCl_3$.

That germanium has a large inductive effect was deduced from the infra-red stretching frequency of trans Pt-Cl bonds in trans-$PtCl(GeMePh_2)(PMe_2Ph)_2$.[70,71,72] The value of ν(Pt-Cl) was low indicating the strong inductive effect of the germanium ligand. A similar result was also observed for the silicon analogue. Germanium has also been shown to have a strong inductive effect, although less than silicon which has the greatest trans effect of inductive origin ever observed, judging by the magnitude of the $^{31}P - {}^{195}Pt$ coupling constants in some platinum(II) complexes of the type trans $PtXY(PhMe_2P)_2$ X = Cl, Br and Y = $SiMePh_2$, $GeMePh_2$, $SiPh_3$ and $GePh_3$.[73]

2. π-bonding effects

The values of Z calculated, places the ligands in order of their π-bonding capacity as

$$GeCl_3 > SnCl_3 > Cl.$$

The results imply that $GeCl_3$ has a very strong π-bonding capacity and from Parshall's value of Z for CN in Table 14 it appears that $GeCl_3$ has a stronger π-bonding capacity than the strongly π-bonding cyanide ion. Parshall found that $SnCl_3$ was a strong π-acceptor ligand[47] this property being considered responsible for its powerful trans activating ability.

If one considers which orbitals are available for π-bonding on platinum, germanium and tin, viz. 5d and 5p on platinum, 4d on germanium and 5d on tin, it might appear that conditions most favourable for π-bonding are to be found in the platinum-tin system, since then all the orbitals involved are in the same quantum shell. However, the results indicate that germanium has a greater π-bonding capacity than tin in these compounds. This can be rationalised in the following way.

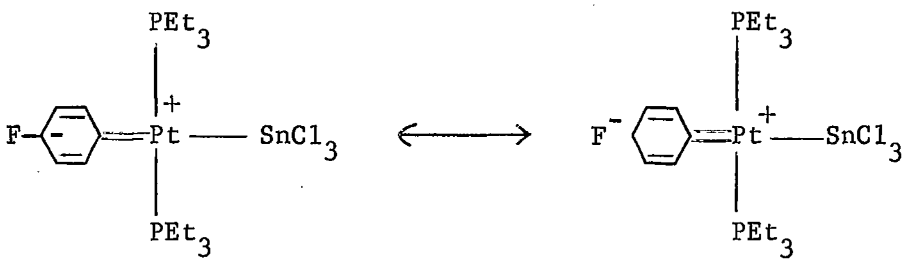
Germanium is more electronegative than tin (Allred Rochow values Ge 2.02, Sn 1.72[74,75]) which would tend to induce a greater positive charge on the platinum atom. This would have the effect of shrinking the orbitals on platinum to a size more favourable for overlap with germanium 4d orbitals. (Since the other ligands on tin and germanium ie Cl are the same, this argument can be applied). However, the greater the positive charge on platinum, the less likely it is to donate into the vacant group IVb metal orbitals. Hence, this works against the electropositivity factor since donation into germanium orbitals becomes less likely as the positive charge on platinum is increased.

Also relevant are the relative energies of the bonding orbitals of the platinum and of the group IVb element, since the more similar the energies of the bonding orbitals the greater the overlap. The platinum and germanium orbital energies may be more compatible than the platinum and tin orbital energies thus accounting for the apparent stronger π-bonding in the germanium compound.

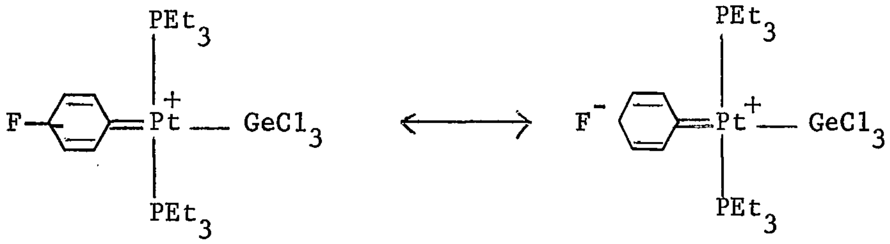
However, as was pointed out by Church and Mays,[55] an increase in the σ-donor strength of a ligand decreases the effective nuclear charge on platinum and hence causes an expansion of the metal d-orbitals changing the degree of π-overlap of these orbitals with the fluorophenyl group. Germanium has been shown to have a higher σ-donor effect than tin and this almost certainly affects the value of Z.

3. Effect on Δp.

The results imply that the overall effect of the $SnCl_3$ and $GeCl_3$ ligands on the shielding parameter Δp is very much the same since the chemical shifts are so close, Δp = 7.29 and 7.27 respectively. Hence the shielding of the p-fluorophenyl ring fluorine in both the tin and germanium compounds is the same. However, in the case of $SnCl_3^-$, the shifts observed ($\Delta m = 0.12 \quad \Delta p = 7.29$) imply that the greater part of this shielding is due to contributions from the resonance structures



with only a very small contribution from inductive effects. In the case of the $GeCl_3$ compound for which $\Delta m = 0.67$ and $\Delta p = 7.27$, the inductive effect is much larger with a smaller contribution from the resonance structures

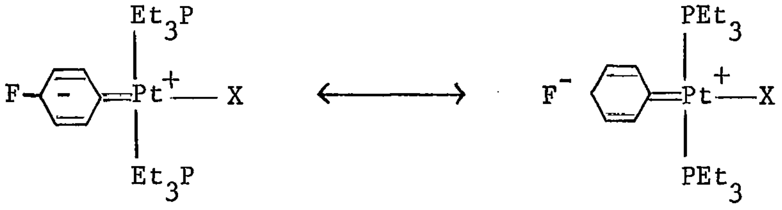


The smaller chemical shifts of the $SnCl_3$ and $GeCl_3$ complexes relative to those containing Cl is to be expected because, being π-acceptor ligands, they will compete with the fluorophenyl ring for electron density in the π-orbitals of the complex and hence cause a reduction in shielding of the fluorine atom.

The metafluorophenyl complexes have been found to be more stable thermally than the p-isomers or the unsubstituted phenyl compounds.[75a] This is not unexpected since the metafluorophenyl group is more electronegative than the p-fluorophenyl or phenyl groups and hence the Pt-C bond is less susceptible to cleavage in the m-substituted compounds. This is also consistent with Parshall's findings (see Table 15) that the electron accepting ability increases in the order

$$m\text{-}C_6H_4F > C_6H_5 > p\text{-}C_6H_4F.$$

Although the mesomeric effect in the p-fluorophenyl group is greater than in the meta-substituted compounds due to the contribution of resonance structures



the repulsion between the ring electron density and lone pair on the fluorine, works adversely, reducing its effective electronegativity

Other evidence for the trans-effect of Group IVb elements.

Apart from the work already mentioned (references 2, 47, 70, 71, 72, 73), there is other evidence supporting the high trans-effect of Group IVb elements.

(i) Germanium

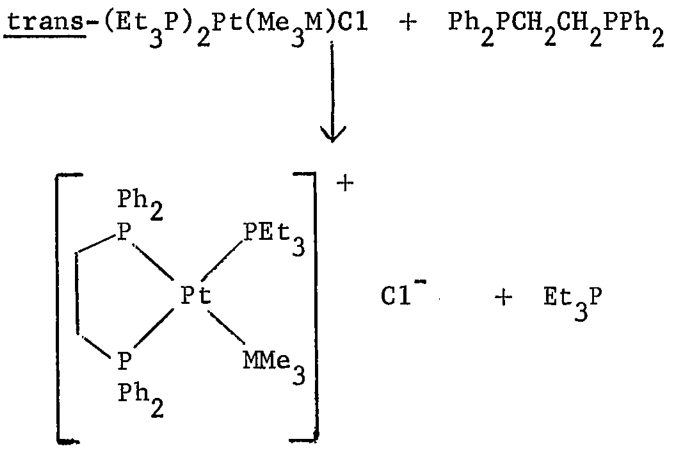
The high trans-effect of the Me_3Ge group is illustrated by the ease of the reaction[59]

$$\text{trans-}(Et_3P)_2Pt(Cl)GeMe_3 + MX \rightarrow \text{trans}(Et_3P)_2Pt(X)GeMe_3 + MCl$$

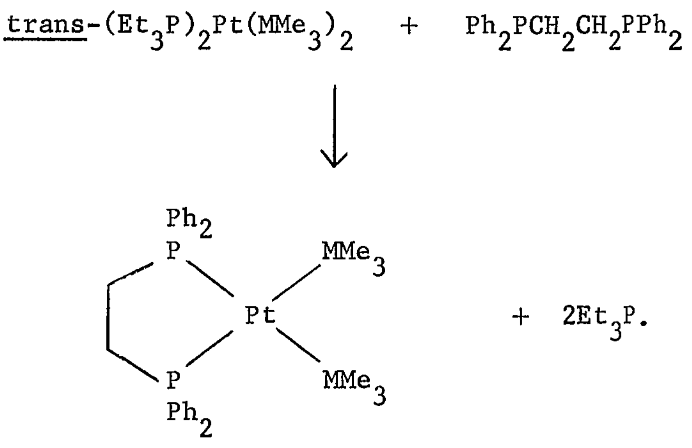
$$M = Li, Na, K. \quad X = Br, I, SCN.$$

Glockling and Hooton[40] found that on treating complexes of the type $(Et_3P)_2Pt(Cl)MMe_3$ (M = Si, Ge) with a ditertiary phosphine $Ph_2PCH_2CH_2PPh_2$ in benzene only one Et_3P molecule is replaced, chloride ion is expelled and benzene-insoluble ionic complexes are formed in high yield (Reaction 1).

Why this reaction occurs rather than one similar to reaction 2 is not clear but it could well be a result of the extremely high



Reaction 1



Reaction 2

trans-effect of Me_3Si and Me_3Ge groups weakening the Pt-Cl bond and producing a stable anion, which is not possible in reaction 2.

It is likely that the ligand GeH_3^- has a high trans-effect, this property being the probable cause of the failure to produce anything but a black tar from the reaction[39]

$$H_3GeLi + (Et_3P)_2PtCl_2 \longrightarrow (Et_3P)_2Pt(GeH_3)Cl + LiCl$$

although hydrogen or hydrogen chloride elimination is also possible with this group.

(ii) Tin.

Infra-red evidence has indicated a high trans influence for tin[76] which is also consistent with n.m.r. work done by Parshall.[2] The compounds trans-$PtCl(SnPh_3)(PPh_3)_2$ and trans-$PtCl(PbPh_3)(PPh_3)_2$ give ν(Pt-Cl) at 298 and 286 cm^{-1} respectively showing the high trans influence of both $SnPh_3$ and $PbPh_3$ ligands.

(iii) Silicon and Lead.

As well as evidence discussed above, the ligand $PbPh_3$ has been shown to have a similar trans influence to that of the phenyl group[77] by an X-ray structure determination on cis $(Ph_3P)_2(\sigma Ph)Pt(PbPh_3)$ in which the bond lengths of Pt-P were found to be the same within experimental error.

Conclusions.

There is evidence, therefore, that all Group IVb ligands exert a high trans-effect and trans-influence. The conclusions drawn from the ^{19}F n.m.r. data are consistent with the conclusion drawn from the other studies described in the preceding pages. Heaton and Pidcock[73] attributed the high trans-effect of germanium ligands to their very high inductive effect but the ^{19}F n.m.r. results suggest that germanium is a strong π-acceptor and only a weak σ-donor. One can only conclude that the trans-effect of $GeCl_3^-$ is due partly to its σ-donor ability weakening the trans metal-ligand bond by polarisation of the platinum atom and partly to its high π-acceptor ability facilitating substitution by stabilisation of the transition state during the reaction.

In the case of tin, however, it would seem that its high trans-effect is attributable to its high π-acceptor capacity. Despite the reservations of Church and Mays,[55] results obtained in this way for these compounds are consistent with other findings.

Problems encountered.

The problems met with in this attempted study of the trans-effect of ligands containing Group IVb elements were of two types:

a) Difficulty in the preparation of compounds.

b) The insolubility of the compounds prepared.

a) A reason for the failure of the attempted preparation of a complex containing $SiMe_3$ ie trans-$(Et_3P)_2Pt(SiMe_3)C_6H_4F$ could well be the high trans effect of the ligand $SiMe_3$ resulting in a very unstable product being formed decomposing to a brown intractable tar. Had time permitted, the preparation of $GeBr_3$ complexes could have been attempted using $Me_3NHGeBr_3$ rather than $CsGeBr_3$, since in the analogous $GeCl_3$ reaction the expected product was obtained in greater yield, than in the reaction using $CsGeCl_3$. An attempt could also be made to obtain $GeMe_3$ compounds using the reaction

$$(Et_3P)_2PtCl(C_6H_4F) + (GeMe_3)_2Hg \rightarrow Me_3GeCl + Hg + (Et_3P)_2Pt(GeMe_3)C_6H_4F.$$

$SnMe_3$ compounds could then be obtained by an exchange reaction with $SnMe_3H$.[57]

b) As previously mentioned, the compounds where X = $SnCl_3$ and $GeCl_3$ were barely soluble in the solvents used, although they were most soluble in acetone and chloroform. They were insoluble in benzene, toluene and hexane. Diethyl ether was found to be a no better solvent than acetone or chloroform.

Carbon tetrachloride and carbon disulphide were not used because of the likelihood of cleavage of the platinum-metal bond occurring. Acidic or alkaline solvents were unsuitable because cleavage of the platinum-metal bond is likely to occur in such solvents. To a certain extent, the solubility problem might have been anticipated as Baird[76] found that solutions of <u>trans</u>-$Pt(H)SiPh_3(PEt_3)_2$ and its germanium analogue were too weak (because of their insolubility) for proton n.m.r. spectra to be obtained.

The spectra of the compounds prepared were so complex as to make interpretation very difficult,and so it is likely that even if other related compounds could have been prepared as would have been desired, further information would have been equally difficult to obtain. It is hard to understand how Parshall could assign ^{19}F shifts with such apparent certainty since his spectra of the $SnCl_3^-$ and Cl^- compounds would be reasonably expected to be as complex as ours of these compounds and in the case of the Cl^- compound even more so since we obtained the spectrum with the protons decoupled. Fig. 2.3.

CHAPTER 3

THE PREPARATION OF STARTING MATERIALS

1. Triethylphosphine.[78,79]

This was prepared from ethyl magnesium bromide and phosphorus trichloride using magnesium (100g.; 4.25 moles), ethyl bromide (436gms; 4 moles) and phosphorus trichloride (180g; 1.33 moles), diethyl ether (2000ml.).

The magnesium turnings were stirred in a 5-litre, 3-necked flask to roughen the surface of the turnings. Enough dry diethyl ether was added to cover the magnesium and neat ethyl bromide was added from a dropping funnel until the reaction to produce ethyl magnesium bromide was well under way as indicated by the ether refluxing. The remainder of the ethyl bromide was added slowly as a 50:50 mixture with diethyl ether so as to maintain steady refluxing of the ether. When the addition of ethyl bromide was complete, the reaction mixture was allowed to reflux for thirty minutes. After cooling under a stream of nitrogen, the reaction flask was surrounded by an acetone/CO_2 bath to maintain a temperature of about -40°C and phosphorus trichloride in diethyl ether (500 mls) was added over $1\frac{1}{2}$-2 hrs. The reaction mixture was allowed to reach room temperature to complete the reaction. The ether layer was then decanted from the solid residue which was extracted with ether to remove any remaining phosphine. The ether solution was hydrolysed by first adding degassed, distilled water (200ccs) followed by a degassed solution of concentrated hydrochloric acid (180ccs) in distilled water (320ccs) to destroy excess Grignard reagent. The aqueous layer which contained the phosphine was made alkaline using ammonia solution so that the phosphine passed into the ether layer. The aqueous layer was separated and extracted with ether as far as possible under nitrogen, and the combined ether extracts dried over anhydrous sodium sulphate. The dried solution was decanted off the solid and distilled. After the ether had distilled over, the phosphine distilled over at 128°C. Yield: 72gms.

2. Germanium tetrabromide.[80]

Germanium dioxide (50g) was suspended in 48% aqueous hydrobromic acid (500ccs). The mixture was heated to a temperature somewhat short of the boiling point of HBr, and then HBr gas, which was made by the dehydration of 60% HBr by P_2O_5, was passed in until the concentration reached constant boiling mixture proportions. [It is possible to tell when sufficient HBr has been passed in since, up to that point, germanium tetrabromide and water condense together and the tetrabromide is hydrolysed to germanium dioxide which is deposited on the condenser tube. When the reaction is complete, there is disappearance of practically all germanium dioxide in the reaction mixture and there occurs the appearance of two liquid layers in the flask]. The mixture was allowed to cool and the lower layer of germanium tetrabromide separated using a separating funnel. The crude product was redistilled when colourless germanium tetrabromide came over. This was distilled *in vacuo* at ~40°C and dried over anhydrous sodium carbonate. Pure germanium tetrabromide was then obtained by further distillation. Melting point 26.1°C.

3. Tribromogermylcaesium.[81]

Hypophosphorous acid (30g. 0.4 mole) and hydrobromic acid (20ml. 48% ~ 0.2 mole.) were warmed in a beaker equipped with watch glass, thermometer and magnetic stirrer. Germanium tetrabromide (20g. 0.05 mole) was added and the temperature taken up to 85°C. The mixture was mixed vigorously for four hours and then cooled to about 60°C. A five percent molar excess of caesium bromide (11.8g.) was added giving an immediate yellow precipitate of caesium tribromogermanite which was filtered off, and dried under vacuum.

4. Caesium trichlorogermanite.[81]

Hypophosphorous acid (70g. 0.53 moles *ie* slightly more than a four to one excess), and hydrochloric acid (80 ml of 3 molar HCl) were warmed in a one-litre beaker equipped with a watch glass and magnetic stirrer. Germanium tetrachloride (28.19g. 0.13 moles) was added and the temperature raised to 85°-90°C. The solution was vigorously mixed for five hours and then cooled to 50°C. The addition of a five percent molar excess of caesium chloride (9.3g) produced a fluffy white precipitate upon further cooling to room temperature. The solid was filtered off and dried at 25°C for eight hours.

5. Trimethylammonium trichlorogermanite.[82]

Germanium tetrachloride (14g. 0.06 mole) was reduced by hypophosphorous acid (35g. 0.46 mole) in hydrochloric acid (50ml. 3 Molar HCl) and the complex precipitated by addition of trimethylammonium chloride (6g.). The complex was filtered off and dried *in vacuo*. This compound is more soluble in benzene and tetrahydrofuran than the caesium analogue.

6. bis-(p-fluorophenyl)mercury.[83]

A sodium amalgam was made from sodium (23g.) and enough mercury for the amalgam to be liquid. Dry xylene (500ml) containing ~ 1ml. ethyl acetate was added. The ethyl acetate acts as a catalyst and without it, the reaction is very slow. The reaction vessel was stirred and heated to reflux temperature and p-fluorophenylbromide (100mls. 150g.) was added dropwise. After the addition was completed, the reaction was allowed to reflux for three days. At this stage, the mixture was orangey-brown. The solution was allowed to cool under nitrogen and the solids allowed to settle. The solid residue was filtered off and washed thoroughly with xylene. The solvent was removed using a rotary evaporator, to leave a brownish-yellow solid. The product was sublimed *in vacuo* and recrystallised from ethanol to obtain white needles. Melting Point 151°C.

7. bis-(m-fluorophenyl)mercury.[83]

This was prepared in a similar manner to the above preparation, using meta fluorophenyl bromide. The product was a crystalline solid, the needles melting at 116°-117°. Both products turn yellow on prolonged exposure to air and turn grey if exposed to strong light.

8. bis-(trimethylsilyl)mercury.[59]

Sodium amalgam, prepared from mercury (200g.) and sodium (2g.) was shaken in a flask fitted with two 'rotaflo' taps with cyclohexane (20ml.) and chlorotrimethyl silane (10ml.) under an atmosphere of argon, until an intense green coloration was formed (about five weeks). (The reaction was shaken in the dark). The product was extracted with cyclohexane and evaporated in a schlenk to give greeny-yellow crystals. These were sublimed in vacuo at about 100°C.

9. cis-(bistriethylphosphine)platinum dichloride.[84]

Platinum dichloride (10g. 0.038mole) was dissolved in dry ethanol (60ccs) and triethylphosphine (13ccs. 0.09 moles) was added against a counter-current of nitrogen. An excess of phosphine was used so that the equilibrium,

$$\text{cis-}(Et_3P)_2PtCl_2 \rightleftharpoons \text{trans-}(Et_3P)_2PtCl_2$$

was well over to the left. The reaction was refluxed overnight and allowed to cool under nitrogen. White crystals of cis-$(Et_3P)_2PtCl_2$ were deposited as well as some metallic platinum. The solid was filtered off, washed with ethanol to remove excess phosphine, and the platinum removed by Soxhlet extraction with ethanol. On cooling, crystals of cis-$(Et_3P)_2PtCl_2$ were deposited, which were filtered off, washed with cold ethanol and dried. M.Pt. = 191-192°C. Literature Value = 191-192°C.[84] This product can also be prepared from potassium tetrachloroplatinate.[85]

APPENDIX

Isotopic Masses and their natural abundances for the constituent elements of some platinum complexes.

Tin

Isotopic Mass	111.905	113.903	114.904	115.902	
Natural Abundance (%)	0.950	0.650	0.340	14.240	
Isotopic Mass	116.903	117.902	118.903	119.902	121.903
Natural Abundance (%)	7.570	24.010	8.580	32.970	4.710
Isotopic Mass	123.905				
Natural Abundance (%)	5.980				

Platinum

Isotopic Mass	189.960	191.961	193.963	194.965	195.965
Natural Abundance (%)	0.012	0.780	32.900	33.800	25.300
Isotopic Mass	197.968				
Natural Abundance(%)	7.210				

Germanium

Isotopic Mass	69.924	71.922	72.923	73.921	75.921
Natural Abundance (%)	20.560	27.420	7.790	36.470	7.760

Carbon

Isotopic Mass	12.000	13.003
Natural Abundance (%)	98.980	1.110

Hydrogen

Isotopic Mass	1.008	2.014
Natural Abundance (%)	99.985	0.015

Fluorine

Isotopic Mass	18.998
Natural Abundance(%)	100.000

Chlorine

Isotopic Mass	34.969	36.966
Natural Abundance(%)	75.530	24.470

Phosphorus

Isotopic Mass	30.974
Natural Abundance(%)	100.000

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PART TWO

AZOMETHINE DERIVATIVES OF SOME MAIN GROUP ELEMENTS

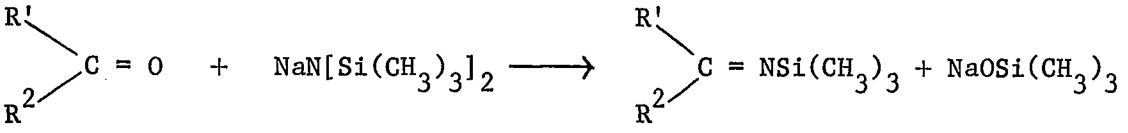
CHAPTER I

SOME AZOMETHINE DERIVATIVES OF SILICON AND GERMANIUM.

GENERAL CONSIDERATIONS

Introduction.

In 1963, Krüger *et al* synthesised the first N-organosilyl ketimines by the following reaction:[1]



$$R^1R^2C=O + NaN[Si(CH_3)_3]_2 \longrightarrow R^1R^2C=NSi(CH_3)_3 + NaOSi(CH_3)_3$$

Chan and Rochow[2] later found an alternative method for synthesising these derivatives which involved the action of the lithium derivative of the ketimine, $>C=NLi$ on organo-silanes. Lithio-ketimines were prepared by the addition of an organolithium reagent to the $C\equiv N$ group in nitriles or by elimination of the N-hydrogen of a ketimine by reaction with an organo-lithium reagent, as in the reaction scheme below:

$$R'C\equiv N + R''Li \longrightarrow R'R''C=NLi \xrightarrow{R_3'''SiCl} R'R''C=NSiR_3''' + LiCl$$

$$R_2'C=NH + RLi \xrightarrow{-RH} R_2'C=NLi \xrightarrow{R_3'''SiCl} R'_2C=NSiR_3''' + LiCl$$

By this method, several ketimino complexes of silicon, germanium and tin were prepared. Details are in reference 2. The reaction was found to proceed readily when R' and R'' were aryl groups e.g. Ph, o-,m-,p-$CH_3C_6H_4$ but when either R' or R'' were alkyl groups with α-hydrogen atoms, a hydrogen in the α-position in the ketimine entered into enamine tautomerism,[3] resulting in an equilibrium mixture of ketimine and enamine as in Fig. 1.1.

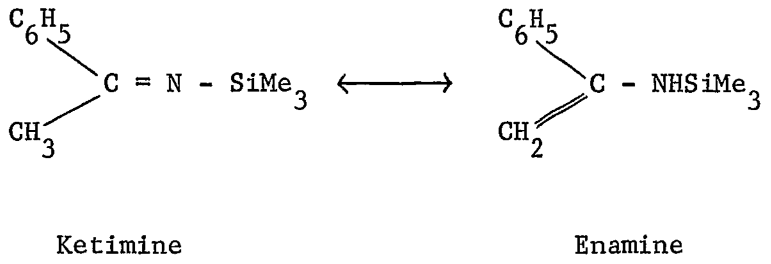


Fig. 1.1

Further N-organosilyl-ketimine complexes have been described by Wade _et al_,[4,5] and Lappert and Palmer[6,7] reported some alkylideneamido and perfluoroalkylideneamido derivatives of silicon, germanium and tin.

In the work to be described in this chapter, further N-organosilyl- and -germyl ketimines are described and the nature of the metal-nitrogen bond discussed in the light of i.r. and ^1H n.m.r. spectral evidence. Di-phenyl-, di-p-tolyl-, and di-t-butyl-ketimino derivatives were prepared. Di-phenylketimine derivatives are convenient for working out preparative methods and frequently give crystalline products whereas di-p-tolyl- and di-t-butyl-ketimine derivatives are more convenient for spectroscopic study. In the case of di-phenylketimino compounds, proton n.m.r. spectra do not provide structural information since the resonances due to their aryl protons are too broad to allow the positions and number of these signals to be used as a guide as to whether they contain only one or two magnetically distinct types of phenyl group. However, the p-tolylketimino compounds are not subject to the same difficulties since the p-tolyl methyl groups produce either a singlet for two magnetically equivalent methyl groups or a doublet if the groups are in magnetically different environments. This also applies to the methyl groups of a t-butyl group in di-t-butylketimino derivatives. Hence, in general, as far as proton n.m.r. spectroscopy is concerned, di-p-tolyl- and di-t-butyl-ketimino compounds provide more information on the shape of the C=N-M link and, by implication, on the nature of the metal-nitrogen bond in such compounds as in Fig. 1.2 (M = metal, X = ketimine, aryl, halide etc.). Di-t-butylketimine has no α-hydrogen atoms and therefore does not undergo ketimine-enamine tautomerism.

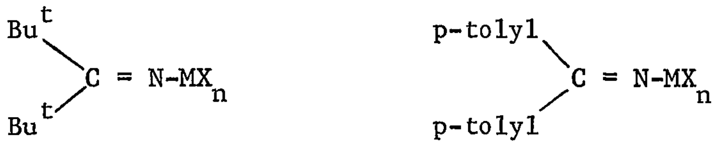


Fig. 1.2

Bonding in metal-ketimine derivatives

As a ligand, the group $R_2C{=}N-$ can act as either a one or three electron donor depending on the involvement of the nitrogen lone pair in the bonding. For maximum overlap between the orbitals of the metal M and of the $R_2C{=}N-$ group, the M-N-C skeleton should be linear.

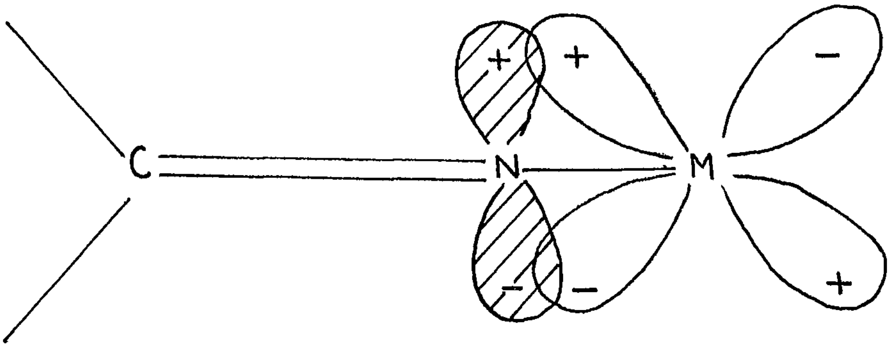


Fig. 1.3(i) p_π-d_π bonding involving a linear C=N-M skeleton.

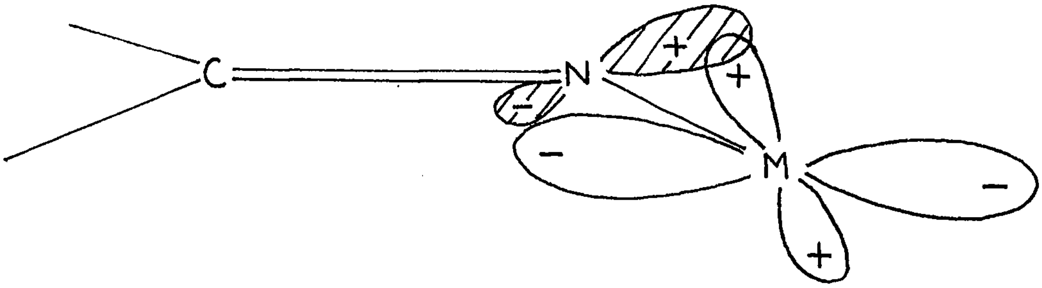


Fig. 1.3(ii) π-bonding involving a bent C=N-M skeleton.

In this situation, the nitrogen would be sp hybridised and the lone pair in a pure p orbital of the correct symmetry for overlap with the metal d-orbitals. Bonding would then involve electron donation via σ and $p_\pi \rightarrow d_\pi$ bonding (Fig. 1.3(i)). Ebsworth[8] has calculated overlap integrals for nitrogen bonded to silicon and concluded that substantial p_π-d_π bonding from a nitrogen lone pair to vacant silicon d-orbitals, while possible in a non-linear skeleton (Fig. 1.3(ii)), is not expected to be as extensive as in a linear system (Fig. 1.3(i)).

Spectral Studies on Linear and Non-Linear Systems

a) N.M.R. Spectroscopy.

When R in R_2CN- is a t-butyl or p-tolyl group, if a linear M-N-C skeleton is present in a metal-ketimino compound, then the signals due to the methyl groups, in both cases would be expected to be singlets since the t-butyl or p-tolyl groups would be in magnetically equivalent environments (Fig. 1.4(a)), provided X_n is symmetrical with respect to R. If the skeleton is bent, however, then doublets would be expected since then the two groups would be magnetically inequivalent. (Fig. 1.4(b)).

Fig. 1.4

However, as explained below, a bent C=N-M unit will not necessarily produce doublets in the n.m.r. spectra of the methyl groups of di-p-tolyl- and di-t-butyl-ketimine complexes.

Many compounds of the type RR'C=NX (R,R',X = alkyl, aryl, hydrogen, halogen) have been synthesised and studied mainly by n.m.r. techniques. When R $\neq$ R' and the C=N-X angle $\neq 180^{\circ}$, then two isomers can arise as in Fig. 1.5.

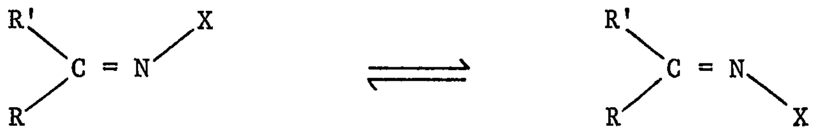


Fig. 1.5

This syn-anti isomerism at the C=N bond has been extensively investigated in the past few years. The topic has recently been reviewed[9] and studies on the mechanism have been carried out.[10] Generally, crystalline derivatives are obtained as single stereoisomers, although recently Cl(CN)C=NF has been isolated in essentially equimolar amounts of the cis and trans isomers.[11] The evidence available, however, suggests that such species rapidly establish an equilibrium mixture of the two isomers on being dissolved in solvents.

X-ray diffraction studies on various oximes have established the non-linearity of the C=N-O group (CNO = 113 ± 2°)[12-16] which gives rise to the isomerism in these compounds. N.m.r. studies have also been carried out on these oximes. The n.m.r. spectra of aldoximes,[17,18] RCH = NOH show two multiplets separated by 0.6 p.p.m., due to the aldehydic protons and this is attributed to the simultaneous existence of syn and anti isomers in solution. N-aryl-ketimines derived from unsymmetrically substituted benzophenones e.g. $Ph(p\text{-}CH_3OC_6H_4)C = NC_6H_4Me$ and $Ph(p\text{-}CH_3OC_6H_4)C = NC_6H_4NMe_2$,[19,20] also exhibit this isomerism. The signals of the methoxy protons appear as a doublet with a separation of 0.06 p.p.m. at room temperature.

In compounds where R = R', <u>i.e.</u> in $R_2C = NX$ and in which the C=N-X bond angle ≠ 180°, then again, in solution, isomerism can result from inversion of the group X about the nitrogen atom, (Fig. 1.6).

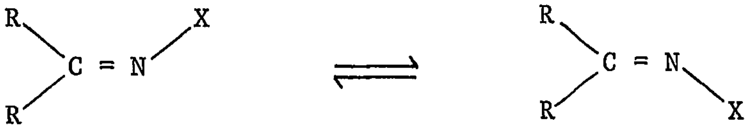


Fig. 1.6

In this case, the groups R will be magnetically inequivalent as determined by n.m.r. spectroscopy, only if the activation energy of inversion of X about N is large enough, at a given temperature, for isomerism to be slow on the n.m.r. time scale, in which case the resonances of the protons on R will appear in the ^1H n.m.r. spectrum twice with equal intensity. The N-cyano-ketimines, $X_2C = N - C \equiv N$, (X = SMe, OMe, NMe_2)[21] thus show singlet methyl resonances in the proton n.m.r. spectra at room temperature, but on cooling, the resonance is split into doublets. However, if X = Me, two singlets are apparent at room temperature, coalescing only at 85°. These inversion processes have activation energies of from 10 to 19 kcal. mole.$^{-1}$

N-perfluoroalkyl-ketimines also show a similar temperature dependence of their n.m.r. spectra. In the fluoroketimine $(CF_3)_2CF - N = C(CF_3)_2$,[22] the two signals due to the $CF_3C=$ groups are separated by more than 5 p.p.m. at temperatures below their coalescence temperature of 32°. The activation energy for this inversion process was calculated as 13 ± 3 kcal. $mole.^{-1}$

b) Infra-Red Spectroscopy.

The azomethine stretching frequencies ν(C=N) in the parent ketimines are given below:

$Ph_2C{=}NH$ ν(C=N) = $1603cm^{-1}$ [23]
$(p\text{-}CH_3C_6H_4)_2C{=}NH$ ν(C=N) = $1597cm^{-1}$ [24]
$Bu^t_2C{=}NH$ ν(C=N) = $1610cm^{-1}$ [23]

The change in the position of the stretching vibration ν(C=N) on replacement of the N- attached hydrogen by various groups has been used as an indication of the shape (linear or bent) of the C=N-M unit in ketimino compounds.

The variation in ν(C=N) depends on the shape of the C=N-M unit in compounds such as $R_2C{=}N\text{-}MX_n$ (R = alkyl or aryl groups; M = metal; X = alkyl, aryl, halide etc.). In general, if the C=N-M linkage is linear, an increase in ν(C=N) is expected relative to the free ketimine. A linear C=N-M unit will be expected to absorb at a higher frequency than a bent C=N-M unit since coupling will be greatest when the C=N and N-H bonds are co-linear. If the skeleton is bent, there may still be an increase in ν(C=N) relative to that in the free ketimine (1590-1670cm^{-1}),[25] since π-bonding between nitrogen and the metal is still possible,[8] but the increase will be smaller than that found in compounds with linear skeletons. To illustrate this point, some data for compounds of boron, aluminium and silicon are given below in Table 1.

Table 1

Some azomethine stretching vibrations in some boron, aluminium and silicon compounds.

Compound	ν(C=N)cm^{-1}	Ref.
$Ph_2C=NBPh_2$	1786	26
$(p\text{-tolyl})_2C=NBPh_2$	1793	26
$PhCH=NB(mesityl)_2$	1818	26
$Al(N=CBu^t_2)_3$	1690	27
$Ph_2C=NSiMe_3$	1667	4
$(Ph_2C=N)_4Si$	1646	4

The first four compounds in Table 1 are believed to have linear C=N-M links [as proved by X-ray diffraction studies on $Ph_2C=NB(mesityl)_2$,[28] $[Be(N=CBu^t_2)_2]_2$,[29] and $LiAl(N=CBu^t_2)_4$[30]] and show strong absorptions,due to the asymmetric stretching vibration of these units,at a much higher frequency than ν(C=N) in the free ketimine. In the silicon compounds, the relatively low values of ν(C=N) may mean these have bent structures.

The variation of ν(C=N) with the groups, R, attached to silicon does not appear to follow any easily identifiable trend.[2] From the data in Table 2, it can be seen that ν(C=N) decreases in the series

Table 2

Some azomethine stretching vibrations in some analogous ketimine Complexes of Group IVb elements.[2]

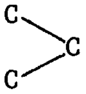
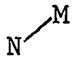
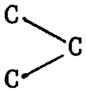
Compound	ν(C=N)cm^{-1}
$Ph_2C=NSiMe_3$	1642
$Ph_2C=NSiPh_3$	1662
$Ph_2C=NGeMe_3$	1630
$Ph_2C=NGePh_3$	1633
$Ph_2C=NSnMe_3$	1613
$Ph_2C=NSnPh_3$	1613

Si $>$ Ge $>$ Sn for analogous ketimine derivatives, the increase in atomic weight of the metal on going from silicon to tin, probably being partly responsible for this decrease in ν(C=N).

There appear to be three major factors affecting ν(C=N) in azomethine compounds:

1. Mechanical coupling.
2. The electronegativity of the metal.
3. Nitrogen-to-metal multiple bonding.

1. Mechanical Coupling.

Since the C=N bond is embedded in the skeleton of the molecule, its stretching will be affected by the rigidity of both the  and the  units. There is no reason to expect the rigidity of the  skeleton to vary significantly with changing M because of the distance between them, but ν(C=N) will be affected significantly by the M-N force constant and by the C-N-M bond angle, the greatest effect being observed when the C-N-M skeleton is linear since mechanical coupling will be greatest in this situation. This mechanical coupling, which will have the effect of increasing ν(C=N), will increase as the force constant increases on going from tin to silicon; the observed increase in ν(C=N) is consistent with this interpretation.

2. The electronegativity of the metal.

The less electronegative the metal, the greater should be the electron density in the $>$C=N- link and the higher the azomethine stretching frequency. The electronegativities of the group IVb elements in the M^{IV} state are in the order[31]

$$C > Ge > Si \simeq Sn$$

and hence the observed trend in ν(C=N) in group IVb-ketimine derivatives does not parallel the trend in electronegativity of the elements.

3. Nitrogen-to-metal multiple bonding.

The involvement of the nitrogen lone pair in p_π-d_π interaction might be expected to reduce the electron density in the azomethine link. However, it has been found that adducts $RR'C:NR^2.MX_n$ of ketimines $RR'C:NR^2$ with Lewis acids, MX_n, exhibit higher azomethine stretching frequencies than do the free ketimines, as shown in Table 3.[32,33]

The carbonyl stretching frequencies of many benzophenone derivatives $(XC_6H_4)_2C{=}O$ have been recorded and related to the electronic effect of the substituents X.[34] In particular, ν(C=O) decreases in the sequence

$$(p\text{-}ClC_6H_4)_2C{=}O > Ph_2C{=}O > (p\text{-tolyl})_2C{=}O.$$

However, from the data in Table 3 a different substituent effect on ν(C=N) for related imines is observed <u>ie</u> ν(C=N) increases in the sequence

$$(p\text{-}ClC_6H_4)_2C{=}NH < (p\text{-tolyl})_2C{=}NH < Ph_2C{=}NH$$

The effect of R^2 on ν(C=N) of $RR'C{=}NR^2$ is illustrated by comparing the figures for $Ph_2C{=}NMe$ and $Ph_2C{=}NPh$ (respectively 1634 and 1616cm^{-1}) or for PhCH = NMe and PhCH = NPh (respectively 1658 and 1634cm^{-1}). The greater π-delocalisation and the subsequently lower C=N bond order may well contribute to the lower value of ν(C=N) when R^2 = Ph.

Table 3

Azomethine stretching frequencies ν(C=N) of the imines, their hydrochloride and boron trifluoride adducts[33]

$RR'C{:}NR^2$	$\nu(C{=}N)(cm^{-1})$			$\Delta\nu^{\ddagger}\ (cm^{-1})$		$\nu(C{=}O)cm^{-1}$
	Imine	Imine HCl	Imine BF_3	Imine HCl	Imine BF_3	RR'C=O
$Ph_2C{:}NH$	1607	1653	1628	46	21	1664
$p\text{-}BrC_6H_4(Ph)C{:}NH$	1607	1652	1629	45	22	1665[a]
$(p\text{-}ClC_6H_4)_2C{:}NH$	1590	1654	1633	64	43	1670[a]
$(p\text{-tolyl})_2C{:}NH$	1597[24]	1643	1626	46	29	1659[a]
$p\text{-tolyl}(^tBu)C{:}NH$	1617	1656	1666	39	49	-
$^tBu_2C{:}NH$	1610	1670	1672	60	62	1687[b]
$Ph_2C{:}NMe$	1634	1669	1661	35	27	1664[a]
$Ph_2C{:}NPh$	1616	1623	1621	7	5	1664[a]
$PhCH{:}NMe$	1658	1695	1712	37	54	1708[a]
$PhCH{:}NPh$	1634	1672	1673	38	39	1708[a]

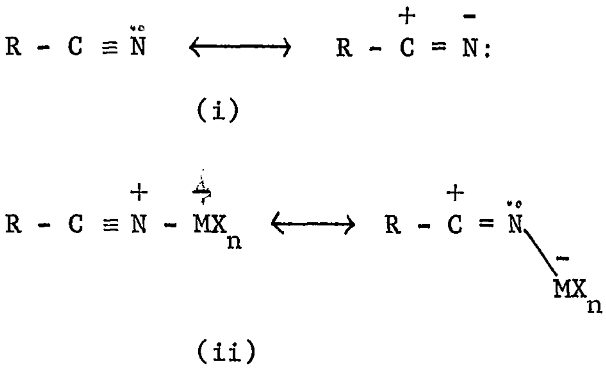
Except where otherwise stated, figures for solid compounds are for Nujol mulls and those for liquid compounds are for Nujol solutions
a = CCl_4 soln. b = C_2Cl_4 soln.

$$\Delta\nu^{\ddagger} = \nu(C{=}N)_{adduct} - \nu(C{=}N)_{parent\ imine}$$

The above figures relate to ca 10wt. % solutions in Nujol.
$Ph_2C{:}NH$ and $p\text{-}BrC_6H_4(Ph)C{:}NH$ absorbed at $1603cm^{-1}$ as neat liquids.
$Bu^t{}_2CNH$ absorbed at $1610cm^{-1}$ as the neat liquid or in Nujol or CCl_4.

Co-ordination of the imines was found to cause little change in the intensity of the $>$C=N stretching band but invariably caused an increase, $\Delta\nu$, in ν(C=N). The magnitude of $\Delta\nu$ varied from *ca* 5 cm^{-1} in the case of $Ph_2C{=}NPh$ (the imine with the most extensive delocalised π-electronic system) to about 60cm^{-1} in the cases of $Bu^t_2C{=}NH$, $(p\text{-}ClC_6H_4)_2C{=}NH$, and PhCH=NMe. As expected, these include $Bu^t_2C{=}NH$, the imine with no aryl substituents conjugated with the azomethine group. The results for imines are in contrast to those for ketones which exhibit a decrease of about 80-120cm^{-1} in ν(C=O) on co-ordination, explained in terms of a weakening of the C=O bond by electron flow to the co-ordinate link; for example, ν(C=O) of benzophenone decreases by 112cm^{-1} on co-ordination with boron trifluoride.[35-38]

The general increase in ν(C=N) of imines on co-ordination may be compared with the increase in ν(C≡N) of nitriles that invariably occurs on formation of adducts, $RC \equiv N.MX_n$.[39] This increase is believed to arise in part from the mechanical constraint applied to the nitrogen of the co-ordinated nitrile,[40-42] although there is also X-ray crystallographic evidence[43,44] that co-ordination is accompanied by a shortening of the C ≡ N bond, *ie* by a fractional increase in its bond order, an effect which apparently reflects slight modification of the hybridisation at nitrogen.[45-47] It was originally argued that, whereas in the free nitrile, the carbon-nitrogen link is approximately intermediate between a double and a triple bond, Fig. 1.7(i), such mesomerism would not be possible in the adduct because of the very different geometry of the two structures, Fig. 1.7(ii).[45] The structures of the boron trihalide adducts of nitriles have linear $C \equiv N \rightarrow B$ co-ordinate links[27] (sp hybridised



$$R-C\equiv\overset{\cdot\cdot}{N} \longleftrightarrow R-\overset{+}{C}=\overset{-}{N}:$$

(i)

$$R-C\equiv\overset{+}{N}-\overset{-}{M}X_n \longleftrightarrow R-\overset{+}{C}=\overset{\cdot\cdot}{N}-\overset{-}{M}X_n$$

(ii)

Fig. 1.7

nitrogen). A shorter $C \equiv N$ bond length and an increase in the $C \equiv N$ order in the adduct as compared with the free nitrile is thus expected, and has been observed in the case of $MeCN.BF_3$[44] in which the CN bond length was found to be 1.122Å compared with the CN bond length of 1.157Å in MeCN.[48]

By analogy, therefore with ketimine adducts, it is not unreasonable to expect ν(C=N) in metal-substituted ketimine derivatives to increase with increasing p_π-d_π interaction. Increasing p_π-d_π overlap would also be likely to result in an increase in s-character of the nitrogen orbitals (as $C\hat{N}M$ approaches 180°) and a subsequent shortening of the $C = N$ bond resulting in an increase in ν(C=N). On this argument, the observed increase in ν(C=N) on going from tin to silicon agrees with the expected increase in p_π-d_π interaction.[49]

It is concluded, therefore, that the electronegativity and mass of the central metal M have a role in determining ν(C=N) and that electronic effects may be transmitted through M although whether this involves π as well as σ mechanisms remains an open question.

NEW KETIMINO DERIVATIVES OF SILICON AND GERMANIUM

I. Experimental.

A. Ketimino Derivatives of Germanium.

1. Reaction between germanium tetrabromide and diphenylketimino-lithium (1:4).

Di-phenylketimine (2.1ml, 12 mmole) was dissolved in dry diethyl ether (40ml) and cooled to -196° using liquid nitrogen. n-Butyllithium (4.2ml of a 2.87M solution in pentane, 12 mmole) was added by syringe and the solution allowed to reach room temperature with stirring. The red solution of di-phenylketiminolithium so formed was cooled to -196° and germanium tetrabromide (1.17g, 3 mmole) dissolved in ether (10 ml) was added. As the solution reached room temperature, the red coloration changed to pale orange. Because of its solubility in ether, no lithium bromide was precipitated. After stirring for 30 min. at room temperature, the solvent was removed *in vacuo*, a pale yellow solid precipitating out when most of the ether had been removed. Dry toluene (10 ml) was added and the solution heated. Filtration gave a brown solution and a white insoluble solid identified as lithium bromide. Addition of hexane to the toluene solution produced yellow crystals, identified as *tetrakis-(di-phenylketimino)-germanium*, $(Ph_2C{:}N)_4Ge$, m.pt. 188°C (slight decomposition and sublimation). (Found: C, 77.5; H, 5.0; N, 7.1%; *M* (by cryoscopy in benzene) 754. $C_{52}H_{40}GeN_4$ requires C, 78.9; H, 5.1; N, 7.1%; *M* 793)

ν_{max} (KBr disc) 3080w, 3058w, 3028w, 1661s, 1611sh, 1603ms, 1600sh, 1597sh, 1570ms, 1491m, 1449ms, 1365s, 1320w, 1312w, 1301w, 1280w, 1260w, 1198ms, 1179m, 1160sh, 1154w, 1072w, 1031m, 1002w, 942m, 932m, 892ms, 850w, 790ms, 764m, 722m, 696vs, 671m, 641w, 624s, 576w, 445w, 350w cm^{-1}.

2. Reaction between germanium tetrabromide and di-p-tolylketiminolithium (1:4)

Di-p-tolylketimine (2.5g, 12 mmole) was dissolved in ether (40ml) and n-butyllithium (4.2ml of a 2.87M solution in pentane) added at -196°. On warming to room temperature with stirring, the solution became the characteristic bright red colour of di-p-tolylketiminolithium. Germanium tetrabromide (1.17g, 3 mmole) dissolved in ether (10 ml) was added to the frozen iminolithium solution (-196°). After reaching room temperature and stirring for 30 min, the solution was a deep red. Ether was removed in vacuo and replaced by 40-60° petroleum ether (20ml) and the insoluble lithium bromide removed by filtration. Pale yellow crystals formed which were recrystallised from 40-60° pet. ether and identified as tetrakis-(di-p-tolylketimino)-germanium, (p-tolyl$_2$C:N)$_4$Ge, m.pt. 60°C (dec.).

(Found: C, 79.5; H, 6.3; N, 6.0%; *M* (by cryoscopy in benzene) 869. $C_{60}H_{56}GeN_4$ requires C, 79.6; H, 6.2; N, 6.2%; *M* 905).

ν_{max} (CsI disc) 3038w, 2924w, 2870w, 1651ms, 1610s, 1593s, 1563sh, 1554ms, 1517m, 1511sh, 1445w,br, 1411ms, 1382m, 1358s, 1317m, 1311sh, 1298w, 1280ms, 1220m, 1198m, 1192m,1186sh, 1180vs, 1150s, 1120m, 1041w, 1023m, 1019m, 982w, 973w, 953w, 929m, 890vs, 838vs, 818s, 804w, 781m, 752ms, 738vs, 619m, 682m, 666ms, 637m, 585m, 570ms, 556w, 470s, 382w, 858w, 269w cm^{-1}.

3. Reaction between germanium tetrachloride and di-t-butylketiminolithium (1:4).

t-Butyl cyanide (1.66g, 20 mmole) was dissolved in hexane (120ml) and cooled to -196^{o}. t-Butyllithium (10.1 ml of a solution 1.98M in hexane) was added. On warming to room temperature with stirring, a lemon yellow solution was formed characteristic of di-t-butylketiminolithium. Germanium tetrachloride (0.58ml, 5 mmole) was added to the solution at -196^{o} and the reaction allowed to reach room temperature when a white solid was precipitated and the solution turned a more intense yellow. After heating under reflux overnight, the solvent was removed in vacuo and the sticky residue partially dissolved in hexane (10 ml), the undissolved solid, lithium chloride, being separated by filtration. After cooling the hexane solution to -20^{o}, no solid was deposited and so the solvent was removed in vacuo to leave a clear yellow oil identified as tris-(di-t-butylketimino)-germanium chloride, $(Bu^{t}_{2}C{=}N)_{3}GeCl$.

(Found: C, 61.9; H, 10.7; Cl, 6.8; N, 7.6%; M (by cryoscopy in benzene) 473.

$C_{27}H_{54}ClGeN_{3}$ requires C, 61.4; H, 10.2; Cl, 6.7; N, 8.0%; M 528).

ν_{max}(thin film). 2954vs, 2918sh, 2872s, 1652vs, 1608w, 1498ms, 1487s, 1478sh, 1412s, 1392s, 1368s, 1324w, 1264m, 1244ms, 1203m, 1100sh, 1083w, 1042ms, 1032m, 1018w, 958s, 932m, 880vw, 818w, 796sh, 731s, 697ms, 582m, 550m, 469m, 400ms cm^{-1}.

4. Reaction between germanium tetrabromide and di-p-tolylketiminolithium (1:2)

Di-p-tolylketimine (2.5g, 12 mmole) was dissolved in ether (200ml) and n-butyllithium (4.5 ml of a solution 2.68M in pentane, 12 mmole) added to the solution at -196^{o}. On reaching room temperature with stirring, the solution was bright red, characteristic of di-p-tolyliminolithium solutions in ether. After 30 min, germanium tetrabromide (2.3g, 6 mmole) in ether (40 ml) was added to the frozen solution (-196°). A brown solution with a pale brown precipitate was formed after stirring for 2hr. at room temperature. Removal of solvent *in vacuo* and extraction with toluene produced a yellow solution and a precipitate of lithium bromide on filtration. Attempts to isolate a solid with consistent analyses from the solution failed.

5. Reaction between germanium tetrachloride and di-t-butylketiminolithium (1:2)

t-Butyl cyanide (1.66g, 20 mmole) was dissolved in hexane (80 ml) and t-butyllithium (10.1 ml of a 1.98M solution in hexane, 20 mmole) was added to the frozen solution (-196°). After reaching room temperature, a pale yellow solution was formed which was again cooled to -196° and germanium tetrachloride (1.2 ml, 10 mmole) in hexane (40 ml) was added. Within 30 min. of reaching room temperature, the solution had paled considerably and a white precipitate had formed. After stirring overnight, the solvent was removed *in vacuo* and the sticky residue extracted with hexane (10 ml) and filtered to produce a pale yellow solution and a white solid identified as lithium chloride. Removal of the hexane *in vacuo* gave a pale yellow oil which was distilled under vacuum (120°C, 0.5 mmHg) and identified as bis-(di-t-butylketimino)-germanium dichloride, $(Bu^t_2C{:}N)_2GeCl_2$.

(Found:C, 50.1; H, 8.7; Cl, 17.1; N, 6.6%; M (by cryoscopy in benzene), 398.

$C_{18}H_{36}Cl_2GeN_2$ requires C, 51.0; H, 8.5; Cl, 16.8; N, 6.6% M, 424).

ν_{max} (thin film). 2960vs, 2920sh, 2870s, 1645vs, 1482s, 1460s, 1392s, 1368s, 1223ms, 1203m, 1042ms, 1018w, 959s,936w, 818w, 793w, 741m, 582w, 550w, 474w, 423ms, 400s, 380sh cm^{-1}.

6. Reaction between germanium tetrabromide and di-t-butylketimino-lithium (1:2)

A similar reaction to that described above (5) was carried out using germanium tetrabromide (3.9g, 10 mmole). A lemon yellow oil was again obtained on distillation into the bucket apparatus described on p 168 . The oil was identified as bis-(di-t-butylketimino)-germanium dibromide, $(Bu^t_2C{=}N)_2GeBr_2$.

(Found: C, 41.3; H, 7.4; Br, 31.2; N, 5.5%; M (by cryoscopy in benzene) 483.

$C_{18}H_{36}Br_2GeN_2$ requires, C. 42.1; H, 7.0; Br, 31.2; N, 5.5%; M, 513.

ν_{max} (thin film) 2960vs, 2928sh, 2868s, 1646vs, 1480s, 1475sh, 1458s, 1390s, 1367vs, 1222s, 1202m, 1189m, 1041ms, 1013m, 960s, 930m, 806w, 736ms, 581m, 550m, 473w, 398m cm^{-1}

7. Reaction between germanium tetrabromide and di-t-butylketiminolithium (1:1)

t-Butyl cyanide (0.83g, 10 mmole) was dissolved in hexane (80 ml) and t-butyllithium (5.1 ml. of a 1.98M solution in pentane, 10 mmole) added to the frozen solution (-196°). After reaching room temperature, a pale yellow solution was formed which was cooled to -196° and germanium tetrabromide (3.9g, 10 mmole) in ether (10 ml) was added.

On reaching room temperature a precipitate formed in a yellow solution. The solvent was removed in vacuo and the residue extracted with 40-60° petroleum ether/toluene mixture. Yellow-orange crystals were formed which were filtered off and identified as di-t-butylketiminogermanium tribromide, $Bu^t{}_2C{:}NGeBr_3$, m.pt. 48°C.

(Found: C, 23.5; H, 3.7; Br, 53.8; N, 2.9%; M (by cryoscopy in benzene) 428.

$C_9H_{18}Br_3GeN$ requires C, 23.9; H, 4.0; Br, 53.0; N, 3.1% M 453).

ν_{max}(thin film) 2970vs, 2914sh, 2869s, 1693vw, 1624vs, 1478vs, 1460sh, 1392s, 1368vs, 1327w, 1220s, 1200m, 1168w, 1042m, 963s, 933m, 902vw, 879w, 848vw, 794w, 731m, 582w, 550m, 482m, 400m, 312vs.

8. Reaction between bis-(di-t-butylketimino)-germanium dibromide and methyllithium (1:2)

Bis-(di-t-butylketimino)germanium dibromide (1.23g, 4.2 mmole) was dissolved in ether (50 ml) and the solution cooled to -196°. Methyllithium (2.5ml of a solution 2M in ether, 8.4 mmole) was added by syringe and the reaction allowed to reach room temperature. A pale yellow solution formed after stirring overnight. The ether was removed in vacuo to leave a small amount of white powder which was redissolved in benzene to give a solution from which no solid could be isolated except a fine white powder which gave no distinct, sharp, absorption bands except those due to solvent, nujol.

B. Ketimino derivatives of Silicon

1. Reaction between silicon tetrachloride and di-p-tolylketiminolithium (1:4)

Di-p-tolylketimine (4.18g, 20 mmole) was dissolved in ether (80 ml) and cooled to -196°. n-Butyllithium (6.96 ml of a 2.87M solution in hexane, 20 mmole) was added and the reaction allowed to reach room temperature with stirring. Silicon tetrachloride (0.57ml, 5 mmole) was added by syringe to the frozen iminolithium solution (-196°). On warming up to room temperature, a lemon yellow solution was formed and a white precipitate was deposited. After stirring overnight, the solvent was removed *in vacuo* and the solid residue extracted with hexane to leave a white deposit of lithium chloride on filtration. Attempted recrystallisation failed and distillation produced an intractable, tarry residue.

2. Reaction between methyltrichlorosilane and di-p-tolylketiminolithium (1:3)

Di-p-tolylketimine (3.14g, 15 mmole) was dissolved in ether (50 ml) and n-butyllithium (5.60 ml of a solution 2.68M in hexane, 15 mmole) added by syringe to the frozen solution (-196). After reaching room temperature with stirring, the solution was again cooled to -196° and methyltrichlorosilane (0.68ml, 5 mmole) in ether (20 ml) added. As the solution reached room temperature, it turned to a lemon yellow colour and a white precipitate was deposited. After stirring overnight the solvent was removed *in vacuo* and the residue extracted with benzene. No solid could be obtained from the solution but on removal of solvent, a yellow oil was obtained and identified as methyl-tris-(di-p-tolylketimino)silane, $MeSi(N{:}Cp\text{-}tolyl_2)_3$. (Found: C, 80.4; H, 7.0; N, 6.5%; M (by cryoscopy in benzene) 613. $C_{46}H_{45}N_3Si$ requires C, 82.8; H, 6.8; N, 6.3%; M 667).

ν_{max}(thin film) 3084sh, 3048sh, 3015m, 2959ms, 2923ms, 2868m, 1642vs, 1606vs, 1582m, 1564sh, 1509m, 1482w, 1450m, 1408ms, 1378w, 1360m, 1309s, 1292sh, 1264s, 1212w, 1195sh, 1180s, 1152w, 1112ms, 1083br,ms, 1036ms, 1021s, 950w, 922vs, 888sh, 864sh, 857vs, 832vs, 800s, 781sh, 740s, 726w, 678ms, 641w, 632m, 618m, 586m, 576sh, 527ms, 478m, 458w, 410sh, 390w,cm^{-1}.

3. Reaction between methyltrichlorosilane and di-p-tolylketiminolithium (1:2)

Di-p-tolylketimine (4.18g, 20 mmole) was dissolved in ether (120ml) and n-butyllithium (7.46ml of a solution 2.68M in hexane, 20 mmole) was added to the frozen solution (-196°). The solution was allowed to reach room temperature with stirring and then methyltrichlorosilane (1.36ml, 10 mmole) was added to the solution at -196°. After stirring for three days, the solvent was removed *in vacuo* and replaced by 40-60° petroleum ether and toluene and filtered to remove lithium chloride. Attempts to isolate a solid or workable liquid failed and produced only a yellow intractable oil.

4. Reaction of dimethyldichlorosilane with di-p-tolylketiminolithium (1:2)

Di-p-tolylketimine (3.14g, 15 mmole) was dissolved in ether (100ml) and cooled to -196°. n-Butyllithium (5.60 ml of a solution 2.68M in hexane, 15 mmole) was added. When the solution had been stirred at room temperature for 30 min, it was again cooled and dimethyldichlorosilane (0.90ml, 7.5 mmole) was added. After stirring overnight, the solution was yellow and a white precipitate was formed. The solvent was removed *in vacuo* and the residue extracted with benzene. As no solid could be isolated, the solvent was removed *in vacuo* to leave a yellow oil identified as *dimethylbis(di-p-tolylketimino)-silane*, $Me_2Si(N:C\ p\text{-}tolyl_2)_2$.

(Found: C, 79.9; H, 7.4; N, 5.8%; *M* (by cryoscopy in benzene) 453. $C_{32}H_{34}N_2Si$ requires C, 81.0; H, 7.2; N, 5.9% *M*, 474.

ν_{max}(thin film). 3082w, 3052sh, 3025m, 2960m, 2914m, 2868w, 1643s, 1608s, 1573w, 1565sh, 1507w, 1451w, 1408w, 1380w, 1360w, 1309m, 1291sh, 1263s, 1250sh, 1212w, 1180s, 1153w, 1112m, 1088br,w, 1038m, 1032m, 949w, 924s, 888sh, 860vs,832s, 804s, 788s, 739s, 720w, 678w, 658w, 632w, 618w, 584w, 573sh, 523w, 510sh, 480w, 452w, 380sh cm^{-1}.

5. Reaction between silicon tetrachloride and di-p-tolylketimino-lithium (1:2)

Di-p-tolylketimine (4.18g; 20 mmole) was dissolved in ether (120ml) and n-butyllithium (7.46ml. of a solution 2.68M in hexane, 20 mmole) was added to the solution at -196°. After the reaction had reached room temperature and stirred at that temperature for 30 min, it was again cooled and silicon tetrachloride (1.14ml, 10 mmole) was added. As the solution warmed up to room temperature, it changed from red to yellow and a precipitate was deposited. After stirring overnight, the solvent was removed in vacuo and the residue extracted with pentane. Attempts to isolate a solid or liquid resulted in the formation of a thick intractable oil.

II. Discussion.

The compounds prepared are presented in Table 4.

Table 4.

$Ge[N:CPh_2]_4$	yellow crystals
$Ge[N:C(p\text{-}tolyl)_2]_4$	yellow crystals
$Ge[N:CBu^t_2]_3Cl$	yellow oil
$Ge[N:CBu^t_2]_2Cl_2$	pale yellow oil
$Ge[N:CBu^t_2]_2Br_2$	pale yellow oil
$Ge[N:CBu^t_2]Br_3$	yellow-orange crystals
$MeSi[N:C(p\text{-}tolyl)_2]_3$	yellow oil
$Me_2Si[N:C(p\text{-}tolyl)_2]_2$	yellow oil

The new tetrakis(ketimino)-germanium complexes, $Ge[N:CPh_2]_4$ and $Ge[N:C(p\text{-}tolyl)_2]_4$ were both crystalline solids, stable for a few hours to air and moisture, but on prolonged exposure to air, a white residue (GeO_2) formed.

$$Ge[N{:}CAr_2]_4 \quad + \quad 2H_2O \quad \longrightarrow \quad GeO_2 \quad + \quad 4Ar_2C{:}NH$$

Ar = p-tolyl, Ph.

This stability to air is in marked contrast with $Si[N{:}CPh_2]_4$[4] which is hydrolysed rapidly on exposure to atmospheric moisture. The mono-substituted compound, $Br_3GeN{:}CBu^t{}_2$, was a crystalline solid less stable to air and moisture than the tetrakis-derivatives but more stable than the bis- and tris-substituted compounds, $ClGe[N{:}CBu^t{}_2]_3$, $Cl_2Ge[N{:}CBu^t{}_2]_3$, $Br_2Ge[N{:}CBu^t{}_2]_2$ which were all pale yellow oils which fumed immediately on exposure to air.

The two new silicon compounds prepared, decomposed rapidly on exposure to air, the hydrolysis reaction being represented by the following equation:

$$Me_2Si[N{:}C(p\text{-tolyl})_2]_2 \quad + \quad H_2O \quad \longrightarrow \quad 2(p\text{-tolyl})_2C{:}NH \quad + \quad \frac{1}{n}(Me_2Si\text{-}O)_n$$

The behaviour of these compounds towards hydrolysis is in line with that of the group IVb - ketimine derivatives prepared by Chan and Rochow,[2] Wade and co-workers[4,5] and Lappert et. al.[7] Sensitivity towards hydrolysis in ketimine complexes has been found to increase in the series M = Si < Ge < Sn and n = 1 < 2 < 3 < 4.[7] However, of the germanium compounds described here, tetrakis-(diphenylketimino)-germanium was found to be less sensitive to hydrolysis than the analogous silicon compound.[4] Di-t-butylketimino-germanium tribromide was more stable to hydrolysis than either the bis- or tris-substituted derivatives, as expected.

It is interesting to note that whereas attempts to prepare bis-, tris- and tetrakis-(di-t-butylketimino)-silanes $[Bu^t_2C{:}N]_xSiMe_nCl_{4-n-x}$ (x = 2,3,4) by use of correspondingly greater proportions of di-t-butylketiminolithium, and by use of more vigorous reaction conditions, failed to place more than one di-t-butylketimine group onto silicon,

$$xBu^t_2C{:}NLi + MenSiCl_{4-n} \not\longrightarrow (Bu^t_2C{:}N)_xSiMe_nCl_{4-n-x} + xLiCl$$

$$x = 2,3,4.$$

two such groups were readily placed onto germanium and a third after refluxing for twenty-four hours, the tris-(di-t-butylketimino)-germanium chloride being the product of a 1:4 reaction of di-t-butylketiminolithium and germanium tetrachloride, indicating that germanium is affected less by steric effects than is silicon, an observation which is not unexpected in view of the covalent radii of tetrahedral silicon and germanium, respectively 1.17 and 1.22Å.[50]

Mass Spectral Data.

The two new silicon compounds prepared failed to show anything but di-p-tolylketimine and products of its breakdown in their mass spectra. The germanium-containing fragments that were identified in the mass spectra of the germanium compounds are given in Table 5.

Table 5

Germanium containing fragments in the mass spectra of $Bu^t{}_2CNGeBr_3$, $[Bu^t{}_2C{:}N]_2GeBr_2$, $[Bu^t{}_2C{:}N]_2GeCl_2$ and $Ge[N{:}C(p\text{-tolyl})_2]_4$.

$Ge[N{:}C(p\text{-tolyl})_2]_4$

Fragment	m/e
$Ge[N{:}C(p\text{-tolyl})_2]_3$	698
$Ge[N{:}C(p\text{-tolyl})_2]_2p\text{-tolyl}$	581
$Ge[N{:}C(p\text{-tolyl})_2]_2$	486
Ge(p-tolyl)	165

$Bu^t{}_2C{:}NGeBr_3$

Fragment	m/e
$(C_4H_9)_2C{:}NGeBr_2$	372
$C_6H_4C{:}NGeBr_2$	344
$C_4H_{10}C{:}NGeBr_2$	316
$GeBr_3$	313
$C_4H_9C{:}NGeBr$	236
$GeBr_2$	232
$(C_4H_9)_2C{:}NGe$	214
$C_4H_9C{:}NGe$	157
GeBr	153

$[Bu^t{}_2C{:}N]_2GeBr_2$

	m/e
$Bu^t{}_2C{:}N(HCN)GeBr_2$	399
$(C_4H_9)_2C{:}NGeBr_2$	372
$C_6H_{14}C{:}NGeBr_2$	344
$C_4H_{10}C{:}NGeBr_2$	316
$C_4H_9C{:}NGeBr$	236
$GeBr_2$	232
$(C_4H_9)_2C{:}NGe$	214
$C_4H_9C{:}NGe$	157
GeBr	153

$[Bu^t{}_2C{:}N]_2GeCl_2$

Fragment	m/e
$(C_4H_9)_2C{:}NGeCl_2$	284
$(C_4H_9)_2C{:}NGe$	214
$(C_4H_9C{:}NGe$	157
$GeCl_2$	144
GeCl	109

The compounds $\mathrm{Ge[N{:}CPh_2]_4}$ and $\mathrm{[Bu^t{}_2C{:}N]_3GeCl}$ showed only peaks due to the parent ketimines and their breakdown fragments. The assignments of the m/e numbers to the fragments listed in Table 5 were supported by computer calculation of the m/e numbers for the fragments from the isotopic masses of the constituent elements. The isotopes and their respective natural abundances are given in Table 6.

All compounds were found, by cryoscopy in benzene, to have a monomeric state of association. This cannot be unambiguously confirmed from the mass spectral data, since a parent peak was not observed in the mass spectrum of any of the compounds prepared, though no fragments of mass higher than the monomer were observed.

Table 6.

Isotopic masses and their natural abundances for the constituent elements of some germanium-ketimine compounds.

Germanium

Mass	69.924	71.922	72.923	73.921	75.921
Natural Abundance(%)	20.560	27.420	7.790	36.470	7.760

Chlorine

Mass	34.969	36.966
Natural Abundance(%)	75.530	24.470

Bromine

Mass	78.918	80.916
Nat.Abund. %	50.540	49.460

Nitrogen

Mass	14.003	15.000
Natural Abundance(%)	99.630	0.370

Hydrogen

Mass	1.008	2.014
Natural Abund. %	99.985	0.015

Carbon

Mass	12.000	13.003
Natural Abundance(%)	98.890	1.110

Infra-Red Spectral Data

The infra-red spectra of all the compounds prepared were recorded and the frequencies of some characteristic bands are shown in Table 7. Although $Bu^t_2CNGeBr_3$ was isolated as a solid, it melted below room temperature, and hence its infra-red spectrum was obtained as a thin liquid film. For $MeSi[N:C(p\text{-}tolyl)_2]_3$ and $Me_2Si[N:C(p\text{-}tolyl)_2]_2$ ν(Si-N) was assigned as $922cm^{-1}$ and $924cm^{-1}$ respectively by analogy

Table 7.

I.r. Spectroscopic Data for some Silicon and Germanium ketimino-derivatives.

Compound	Phase	$\nu(C{=}N)cm^{-1}$
$Ge[N:CPh_2]_4$	KBr disc	1661
$Ge[N:C(p\text{-}tolyl)_2]_4$	CsI disc	1651
$ClGe[N:CBu^t_2]_3$	thin film	1652
$Cl_2Ge[N:CBu^t_2]_2$	thin film	1645
$Br_2Ge[N:CBu^t_2]_2$	thin film	1646
$Br_3Ge[N:CBu^t_2]$	thin film	1624
$MeSi[N:C(p\text{-}tolyl)_2]_3$	thin film	1642
$Me_2Si[N:C(p\text{-}tolyl)_2]_2$	thin film	1643

with values of ν(Si-N) for previously reported di-phenylketiminosilanes which were found in the region $905\text{-}913cm^{-1}$.[2] In $Me_3SiN:C(p\text{-}tolyl)_2$, the Si-N stretching mode was given as $923cm^{-1}$ so that values of 922 and 924cm^{-1} are not unreasonable for the compounds described here. [There are no other bands that could be assigned as ν(Si-N) in the region 900-950cm^{-1}].

In a series of bis-(trifluoromethyl)-ketimino derivatives, $Me_{4-n}M[N:C(CF_3)_2]_n$ (M = Si, Ge, Sn) the values of ν(M-N) are given in Table 8.[7]

Table 8.

ν(M-N)cm^{-1} for a series of bis-(trifluoromethyl)ketimino- complexes

$Me_{4-n}M[N:C(CF_3)_2]_n$

Compound	ν(M-N)cm^{-1}		
	M = Si	M = Ge	M = Sn
$Me_3MN:C(CF_3)_2$	955	955	948
$Me_2M[N:C(CF_3)_2]_2$	957	957	949
$MeM[N:C(CF_3)_2]_3$	959	961	956
$M[N:C(CF_3)_2]_4$	959	961	957

All measured as liquid films.

As can be seen, there is little change in ν(M-N) as M changes from silicon to germanium to tin, nor on increasing the number of ketimine groups on the same metal. ν(Si-N) for $Si[N:CPh_2]_4$ has been reported as 913cm^{-1} [4] and so it would not seem unreasonable to expect a band to appear in a similar region in the two germanium compounds, $Ge[N:CPh_2]_4$ and $Ge[N:C(p\text{-tolyl})_2]_4$. For the former compound, a medium strong absorption occurs at $892cm^{-1}$ with weak bands at 932 and $942cm^{-1}$, and in the latter, a strong absorption is found at $890cm^{-1}$ with weak bands at 929 and $953cm^{-1}$. The (Ge-N) stretching frequencies in $Ge[N:CPh_2]_4$ and $Ge[N:C(p\text{-}tolyl)_2]_4$ can be tentatively assigned as 892 and $890cm^{-1}$ respectively.

The following (Si-N) stretching vibrations have been reported for some di-t-butylketimino derivatives of silicon.[5] (Table 9). Following the same considerations as above, one might expect to find a band due to ν(Ge-N) in the region $950\text{-}970cm^{-1}$ in the spectra of the new di-t-butylketimino derivatives of germanium. The only bands appearing in the region $800\text{-}1000cm^{-1}$ in the spectra of these compounds are listed in Table 10 with their relative intensities. From these values, the value of ν(Ge-N) can be tentatively assigned as in Table 11 which gives the probable values of ν(Ge-N) in all the new germanium compounds described here.

Table 9

Silicon-nitrogen stretching frequencies for some di-t-butylketimino-silicon compounds

Compound	$\nu(Si\text{-}N)cm^{-1}$
$Bu^t_2C:NSiMe_3$	959
$Bu^t_2C:NSiMe_2Cl$	965
$Bu^t_2C:NMeCl_2$	966
$Bu^t_2C:NSiCl_3$	967

All measured as liquid films.

Table 10.

Absorption bands in the region 800-1000cm^{-1} in some new di-t-butylketimino-germanium compounds.

Compound	Absorption bands in the region 800-1000cm^{-1} in cm^{-1}.
$ClGe[N{:}CBu^t{}_2]_3$	818w, 880vw, 932m, 958s
$Cl_2Ge[N{:}CBu^t{}_2]_2$	818w, 936w, 959s
$Br_2Ge[N{:}CBu^t{}_2]_2$	806w, 930m, 960s
$Br_3Ge[N{:}CBu^t{}_2]$	848vw, 879w, 902vw, 933m, 963s

All measured as thin films.

Table 11.

Tentative Assignments of ν(Ge-N) (cm^{-1}) for some new ketiminogermanium compounds.

Compound	ν(Ge-N)cm^{-1}
$Ge[N{:}CPh_2]_4$	892
$Ge[N{:}C(p\text{-tolyl})_2]_4$	890
$ClGe[N{:}CBu^t{}_2]_3$	958
$Cl_2Ge[N{:}CBu^t{}_2]_2$	959
$Br_2Ge[N{:}CBu^t{}_2]_2$	960
$Br_3GeN{:}CBu^t{}_2$	963

The eight compounds prepared all show a strong absorption characteristic of the azomethine stretching vibration $\nu(C{=}N)$ in the region 1620-1670cm^{-1} (Table 7). The positions of the bands do not show whether the M-N-C skeletons are linear or bent. The two tetrakis-ketimine complexes $Ge[N{:}CPh_2]_4$ and $Ge[N{:}C(p\text{-}tolyl)_2]_4$ have $\nu(C{=}N)$ at 1661 and 1651cm^{-1} respectively. In $Si[N{:}CPh_2]_4$, $\nu(C{=}N)$ was found at 1646cm^{-1} which was regarded as consistent with angular C=N-Si units.[4] Comparing the masses of silicon and germanium, respectively 28 and 74 a.m.u., it would be expected that in analogous compounds, if the M-N=C skeletons are the same shape, the germanium compound would have the lower $\nu(C{=}N)$. This, in fact, was found by Lappert <u>et al</u> for some perfluoroalkylketimine compounds.[7] (See Table 12).

The higher value of $\nu(C{=}N)$ in $Ge[N{:}CPh_2]_4$ compared with that of

Table 12.

Azomethine stretching vibrations in some perfluoroalkylketimine compounds of silicon, germanium and tin.

Compound	$\nu(C{=}N)cm^{-1}$		
	m = Si	M = Ge	M = Sn
$Me_3MN{:}C(CF_3)_2$	1765	1730	1720
$Me_2M[N{:}C(CF_3)_2]_2$	1770	1730	1719
$MeM[N{:}C(CF_3)_2]_3$	1774	1733	1717
$M[N{:}C(CF_3)_2]_4$	1786	1730	1717

the analogous silicon compound may mean that the skeletons are considerably different and that perhaps the tetrakis-germanium-compounds have linear C=N-M units. At present, X-ray diffraction studies are being carried out on $Si(N:CPh_2)_4$, $Ge(N:CPh_2)_4$ and $Ge[N:C(p\text{-tolyl})_2]_4$ which should reveal the shapes of their C=N-M units.

Similar comparisons cannot be drawn between silicon and germanium di-t-butylketimino complexes, except in the case of $Bu^t{}_2CNGeBr_3$ since for silicon only one such group could be attached and the C=N-Si skeleton was found in this case to give an i.r. absorption at <u>ca.</u> 1730cm^{-1}, high enough to be consistent with a linear C=N-Si skeleton. Addition of more than one ketimine group to a metal would be expected to lower the value of ν(C=N) relative to that of a mono-substituted derivative, and the heavier germanium metal should also cause a decrease. Hence, the values of ν(C=N) in the bis- and tris-substituted germanium compounds reported here do not exclude the possibility that they have linear skeletons, which would seem reasonable since the silicon compounds probably have linear Si-N-C units and also, since germanium is a larger atom and would be expected to accommodate the groups better than silicon. Chan and Rochow[2] found that the two compounds $Ph_2C:NGeMe_3$ and $Ph_2C:NGePh_3$ had ν(C=N) at 1630 and 1633cm^{-1} respectively which, together with u.v. data, they interpreted in terms of bent skeletons for these molecules. The corresponding silicon compounds showed azomethine stretching vibrations at 1642 and 1662cm^{-1} respectively which again were interpreted in terms of bent Si-N=C units. Hence in these compounds a decrease in ν(C=N) on going from silicon to germanium is observed, of 12cm^{-1} in the MMe_3 compounds and of 29cm^{-1} in the MPh_3 compounds. In the case of $Bu^t{}_2CNGeBr_3$, ν(C=N) was found at 1624cm^{-1}. In $Bu^t{}_2C:NSiCl_3$, ν(C=N) was found at 1729cm^{-1}, and thought to be consistent with a linear Si-N=C skeleton. It is interesting that in the germanium compound $Bu^t{}_2CNGeBr_3$, ν(C=N) should be so low especially since it is lower than in the bis-substituted compound. It is unlikely that the low value is due to the bromine atoms since in the cases of $Cl_2Ge[N:CBu^t{}_2]_2$ and $Br_2Ge[N:CBu^t{}_2]_2$ no appreciable change in ν(C=N) was observed. It is possible that in $Bu^t{}_2CNGeBr_3$ the C=N-Ge unit is bent this being responsible for the relatively low value of ν(C=N). The two new silicon compounds described here, having ν(C=N) at 1642 and 1643cm^{-1} respectively for $MeSi[N:C(p\text{-tolyl})_2]_3$ and $Me_2Si[N:C(p\text{-tolyl})_2]_2$,by comparison with Chan and Rochow's results[2],would also be expected to have bent skeletons.

The absorption at ca. 1650cm^{-1} in some diphenylketiminosilanes has been found to be peculiarly insensitive to the number of ketimino group attached to the metal,[2,4,5] ν(C=N) hardly changing in the series $(Ph_2C:N)_nSiMe_{4-n}$ (n = 1 → 4), a result in itself suggesting little or no (p → d)π bonding in the N → Si links in these compounds. The silicon compounds described here likewise have ν(C=N) insensitive to the number of imino groups.

However, it has also been found that in the linear di-t-butylketimine derivatives of silicon,[5] $\nu(C=N)$ is surprisingly insensitive to the nature of the other groups attached to silicon, the change of methyl to chlorine having no significant effect, an unexpected result since chlorine has been shown to be capable of π-bonding with silicon.[51, 52] The compound $Bu^t_2C:NSi(vinyl)Cl_2$[5] shows $\nu(C=N \dashrightarrow Si)$ in a similar position to other di-t-butyl-ketimine derivatives of silicon, although a significant change in N → Si π-bond order might have been expected due to a competitive electron back-bonding $Si \leftarrow C$ π-interaction similar to that thought to be present in silylbutadienes[53] and silylethylenes.[54] In the bis-(di-t-butyl-ketimino)-germanium compounds, no appreciable change was observed on going from chlorine to bromine. However, the addition of a second ketimine group raised $\nu(C=N)$ by 22cm^{-1} relative to the mono-substituted compound and addition of a third ketimine group caused an increase in 6cm^{-1} relative to the bis-substituted compound, these increases possibly being due to an increase in mechanical constraint on the C=N-Ge link on increasing the number of ketimine groups in the molecule.

N.M.R. Spectral Data

The n.m.r. spectra of the compounds prepared were all measured and their characteristic signals presented in Table 13.

The fact that singlets were obtained for the tolyl methyl groups of di-p-tolylketimino compounds and for the protons of the di-t-butyl groups of di-t-butylketimino compounds is not diagnostic of a linear C=N-M unit, since, as mentioned earlier (p. 84), inversion of the group R can occur about the carbon-nitrogen bond thus making the R' groups magnetically equivalent if the inversion process is fast on the n.m.r. time scale. (Fig. 1.6). Cooling to -60°C produced no splitting of the signals.

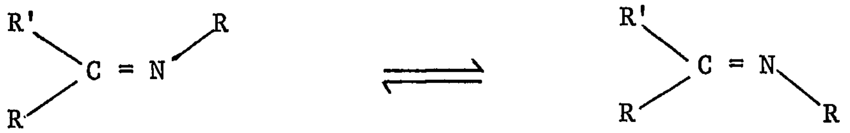
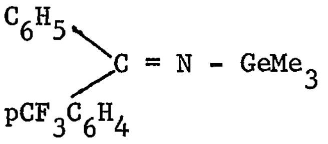


Fig. 1.6

The protons on R' will appear at different chemical shifts only if this inversion process is slow (ie the activation energy of the inversion process is large) on the n.m.r. time scale, at a given temperature, for the protons on the two R' groups to be in magnetically different environments.

The trimethylgermyl proton n.m.r. spectrum of the compound



$(C_6H_5)(pCF_3C_6H_4)C = N - GeMe_3$

was found to have two overlapping singlets ($\Delta\nu_{AB}$ = 1.1Hz at 60MHz) attributed to the syn and anti forms of the imine, on cooling to -110°, coalescence occurring at -108° and becoming a sharp singlet at -70° and above.[55] The first order rate constant of this inversion reaction was calculated to be $k_{-108} = 2.4\text{sec}^{-1}$ and $\Delta G_{-108} = 9.2\text{kcal.mole.}^{-1}$

Table 13.

N.M.R. Spectral Data for some new azomethine derivatives of silicon and germanium.

Compound	τ values
$Ge[N:CPh_2]_4$	(Ar) multiplets at 2.61(16) and 2.57(24)
$Ge[N:C(p\text{-}tolyl)_2]_4$	(Ar-Me) 8.43
$ClGe[N:CBu^t_2]_3$	8.73
$Cl_2Ge[N:CBu^t_2]_3$	8.75
$Br_2Ge[N:CBu^t_2]_2$	8.70
$Br_3GeN:CBu^t_2$	8.81
$MeSi[N:C(p\text{-}tolyl)_2]_2$	(Ar-Me) 7.83
$Me_2Si[N:C(p\text{-}tolyl)_2]_2$	(Ar-Me) 7.83

All compounds were run in C_6H_6 (except $Ge[N:CPh_2]_4$ which was run in C_6D_6) and were referenced to C_6H_6 at 2.76τ. Aryl protons were obliterated by solvent in all spectra of the diarylketimino compounds except $Ge[N:CPh_2]_4$, and the Si-Me protons were obliterated by TMS.

This value is remarkably low when compared with typical inversion barriers of N-alkyl- and N-aryl-imines (similarly substituted at the imino-carbon) which range from 17 to 27 kcal. $mole.^{-1}$ [56-58] The only conclusion that can be drawn from the n.m.r. spectra of the new compounds described here, is that the M-N=C skeletons are either linear or even at -60° the rate of inversion of the group attached to the nitrogen in a bent C=N-M link is too fast compared with the n.m.r. time scale, to be detected.

Other Organo-Nitrogen Derivatives of Silicon and Germanium

The question of N → Si (p_π-d_π) multiple bonding has been extensively studied over the last few years and several reviews have recently appeared on N → Group IVb elements p_π-d_π multiple bonding.[59,60] Several electron diffraction studies have been made, the compounds reported including $(SiH_3)_3N$,[61,62] which has been shown to have an effectively planar silicon-nitrogen skeleton (Si-N-Si = 119.6 ± 4°). Data consistent with planar Si_2NN groups has been found for $(H_3Si)_4N_2$,[63] and for $(Me_3Si)_2NH$,[64] $ClSi(NMe_2)_3$[65] $(SiH_3)_2NH$,[61] and $(SiH_3)_2N.BF_2$,[64,66] the evidence implies a planar arrangement of ligands about the central nitrogen atom, the BF_2 compound having planar Si_2NB and NBF_2 groups which are slightly twisted with respect to each other. The Si-N bond length determined for H_3SiNMe_2[67] supports some degree of (p → d)π bonding but the $SiNC_2$ skeleton is non-planar, a result which is in agreement with the high basicity of nitrogen in this compound. Other X-ray studies have been carried out on compounds such as $[(Me_3Si)_2N]_2$,[68] $[(Me_3Si)_2N]_3Al$[69] and $[Me_3SiNSiMe_2]_2$,[70] all of which show marked stereochemical inactivity of the nitrogen lone pairs together with relatively short Si-N bond lengths (1.72 - 1.75Å), evidence consistent with substantial N → Si (p → d)π-bonding which is maximised if the lone pair is in a pure p orbital.

The pseudo-halide derivatives $Si(NCS)_4$,[71] $Si(NCO)_4$,[72] H_3SiNCS,[73] Me_3SnNCS,[74] $Me_2Sn(NCS)_2$[75,76] and $[(Me_2SnNCS)_2O]_2$[77] have all been shown to have the shape for optimum N → M π-bonding, ie have near linear M-N-C units, (bond angles $M\hat{N}C$ varying from 168-176°) in the crystal structure although in the gaseous state there is evidence that angular M-N-C units ($M\hat{N}C$ ca 154°) exist for Me_3SiNCS and Me_3SiNCO.[78] It is thought that $Ge(NCO)_4$ is approximately tetrahedral but the Raman spectrum indicates some deviation from pure tetrahedral symmetry possibly in the form of a slight kinking of the Ge-N=C=O unit.[72]

Some degree of N → M (p-d)π-bonding has been found in compounds having pyramidal or angular units which Ebsworth predicted from his calculations on non-linear silicon compounds,[8] even though planar or linear configurations maximise conditions for such bonding. In some N-organo-silyl- and -germyl-ketimines the presence of non-linear M-N-C units was inferred from u.v. studies but a small degree of N → M π-bonding was also evident.[2]

Other evidence of (p-d) π overlap in Group IVb metal-nitrogen compounds is apparent from studies on the basicities of compounds such as $R_3MNR'_2$ and $M[NR'_2]_4$ for M = Si, Ge, Sn and R and R' = Et, Me.[79,80] The relative basicities are in the order Si $>$ Ge $>$ Sn for the $R_3MNR'_2$ series and Si $>$ Ge $\geq$ Sn for the tetrakis series. This is explained in terms of a decrease in the p_π-d_π bonding in the order Si $>$ Ge $>$ Sn.

An ^1H n.m.r. study on chloroaminosilanes has also given results consistent with nitrogen → silicon p_π-d_π bonding.[81] Two investigations carried out on the tetrahalides of group IVb elements have shown, by photoelectron spectroscopy, that the halides are capable of and, indeed, do take part in $(p\text{-}d)\pi$-bonding to germanium and tin and, in particular, to silicon.[51,52] Hence, chloroaminosilanes are of special interest since, in theory, both chloride and amino groups are capable of $(p\text{-}d)\pi$ bonding to silicon.

CHAPTER 2

AZOMETHINE DERIVATIVES OF PHOSPHORUS

Introduction.

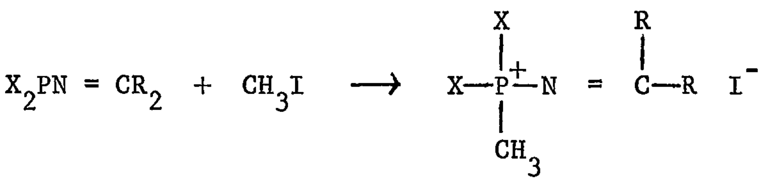
Previous to the work to be described in this chapter, the ketimino-phosphorus compounds in Table 14 had been prepared.[27,82]

Table 14

Some methyleneaminophosphines

Compound	Ref.
$Ph_2C:NPCl_2$	82
$Ph_2C:NP(Ph)Cl$	82
$Ph_2C:NPPh_2$	82
$Ph_2C:NPMe_2$	82
$Ph(OMe)C:NPPh_2$	82
$Ph(OEt)C:NPPh_2$	82
$(OEt)_2C:NPPh_2$	82
$Ph_2C:NP(OMe)_2$	82
$Ph_2C:NP(Ph)OMe$	82
$Bu^tC:NPPh_2$	27

These studies were mainly concerned with the reactions of these compounds and it was found that these methyleneaminophosphines, $X_2PN = CR_2$, are nucleophilic at the phosphorus and electrophilic at the carbon; $X_2PN = CR_2$ will react with methyl iodide to give a crystalline methyleneamino-phosphonium iodide:

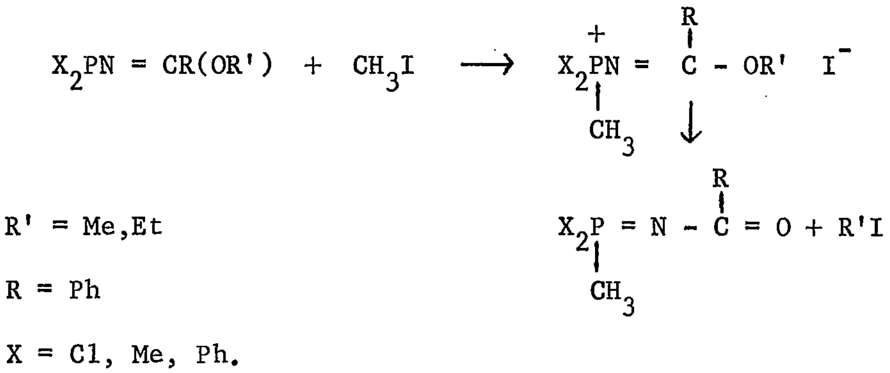


$$X_2PN = CR_2 + CH_3I \longrightarrow X\text{—}\underset{\displaystyle CH_3}{\overset{\displaystyle X}{\overset{+}{P}}}\text{—}N = \overset{\displaystyle R}{C}\text{—}R \quad I^-$$

X = Cl, Me, Ph

R = Ph, OMe, OEt.

(Alkoxymethyleneamino)phosphines (R = OAlkyl) were found to resemble alkoxyphosphines as they rearrange with methyl iodide to form acylphosphinimines in a Michael-Arbusov type reaction:



$$X_2PN = CR(OR') + CH_3I \longrightarrow \underset{\displaystyle CH_3}{\overset{+}{X_2PN}} = \overset{\displaystyle R}{C} - OR' \quad I^- \;\downarrow\; \underset{\displaystyle CH_3}{X_2P} = N - \overset{\displaystyle R}{C} = O + R'I$$

R' = Me,Et

R = Ph

X = Cl, Me, Ph.

It was of interest to us, to prepare some similar compounds and to obtain infra-red, phosphorus and proton n.m.r. spectral data and if possible deduce from those data, the shape (linear or bent) of the C-N-P skeletons in these compounds.

Further ketimino-derivatives were therefore prepared to compare their shape and degree of P-N interaction with that in amino derivatives and isocyanate and isothiocyanate derivatives of phosphorus.

Phosphorus-nitrogen multiple bonding.

d_π-p_π bonding between phosphorus and 2p orbitals of nitrogen has been the subject of considerable interest in recent years and has been extensively reviewed.[83-88]

The electronic configuration of phosphorus in the ground state is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^3$. The 3d orbitals, although unoccupied in the free atom, are energetically not too far above the valence shell so that they can be of considerable chemical significance. Involvement of d orbitals can occur in the formation of single (σ) bonds, as in PCl_5,[89] or multiple bonds as in P_4O_{10}.[90,91] Conditions for π-bonding in phosphorus compounds are optimised when the phosphorus without multiple bonding would be positively charged. When the phosphorus would be neutral or negatively charged without π-bonding, then although possible, π-bonding is generally insignificant.[89,92]

In a molecule in which the central phosphorus atom is bonded to a series of other atoms or groups, ie ligands, L, which have filled orbitals having π-symmetry with respect to the P-L bond, such as oxygen, chlorine or an unsaturated group, the valence-shell electrons may be divided into two types; σ, and π electrons. The σ-electrons (ie those which form σ-bonds) are believed to make the predominant contribution to the binding energy of the molecule and hence determine its geometry.[93] Phosphorus has no π electrons but the atoms or groups L do. Phosphorus, however, has d-orbitals of the correct π symmetry with respect to some or all of the σ bonds. Hence, the formation of a π bond between phosphorus and L, and thus valence-shell expansion of phosphorus, can occur only by donation of π electrons by L to phosphorus. In the case of compounds containing uncharged phosphorus, the 3d orbitals of phosphorus are too diffuse and hence can participate very little, if at all, in chemical bonding. However, a positive charge on phosphorus contracts its d-orbitals for more effective 3d-2p orbital overlap _ie_ enables valence shell expansion to take place.[89,94.]

d_π-p_π Bonding in phosphorus(v) nitrogen compounds is evident in cyclic phosphazenes,[83,87,95] and linear phosphonitrile polymers[96] as well as in monomeric phosphorus-nitrogen compounds such as phosphinimines, $R_3P = NR'$.[84] There is plenty of physical evidence in favour of the presence of p_π-d_π bonding in phosphorus compounds such as high bond energies of phosphorus-oxygen and phosphorus-nitrogen bonds respectively in tertiary phosphine oxides such as $Me_3P = O$ (P - O bond energy = 139.3 ± 3 kcal/mole) and phosphinimines such as $Me_3P = NEt$ (P-N bond energy = 97 kcal/mole),[97,98] and a very significant difference in the stretching frequencies of P = N and P-N bonds, ν(P-N) being commonly in the region 680-820cm^{-1} [25,99,100] and ν(P=N) in the region 1200-1500cm^{-1}.[25,101,102] (See Table 15). The stability of phosphoryl substituted carbanions such as $(EtO)_2\text{-}\overset{O}{\overset{\|}{P}}\overset{-}{C}HCO_2Et$ is considered to be due to d_π-p_π bonding involving 3d orbitals of phosphorus and 2p orbitals of the adjacent carbanionic carbon atom.[103]

Phosphine imines of the type $R_3P = NEt$ can be regarded like the phosphoryl compounds as $R_3\overset{+}{P} - \overset{-}{N}Et$, the charge distribution being modified by back coordination from 2p orbitals of the NEt group to the vacant $3d_\pi$ orbitals of $\overset{+}{P}$ thus giving the P-N bond double-bond character, with the additional possibility of back co-ordination from the R groups, if these have donor electrons.[97]

Table 15

Some typical P = N and P - N stretching frequencies.

Compound	ν(P-N)cm^{-1}	Ref.
$PCH_2(Ph)_2P{:}N^tBu$	1300	104
$Ph_3P{:}NPh$	1348	105
$Ph_3P{:}NCOPh$	1340	106
$Ph_3P{:}NSiPh_3$	1260	107
$Ph_3P{:}NGePh_3$	1270	107
$PO(NH_2)_3$	725	108
$(Me_2N)_3P$	673, 645	109
$(Me_2N)_2PO$	744	109
Me_2NPCl_2	690	110
$(Me_2N)_2POMe$	704	110

Van Wazer and Letcher have calculated ^{31}P n.m.r. shifts for compounds of general formula PZ_3, POZ_3 and PSZ_3 and interpreted the difference between calculated and observed values in terms of σ and π bonding.[111]

The σ-bonding contribution for molecules of the type PZ_2T is calculated taking into account the electronegativities of Z and T and ZPZ and ZPT bond angles. Their experimental data for PR_3 type compounds led to the results in Table 16.

Data similarly obtained for POR_3 type molecules are given in Table 17.

Table 16.

Estimated number of π electrons per phosphorus atom for symmetrically substituted phosphines

Molecule	Estimated no of π electrons per P atom.
PH_3	0.00
$P(CN)_3$	0.01
$P(CH_3)_3$	0.00
PF_3	0.01
PPh_3	0.00
PCl_3	0.30
PBr_3	0.34
PI_3	0.42
$P(NMe_2)_3$	0.02
$P(OMe)_3$	0.15

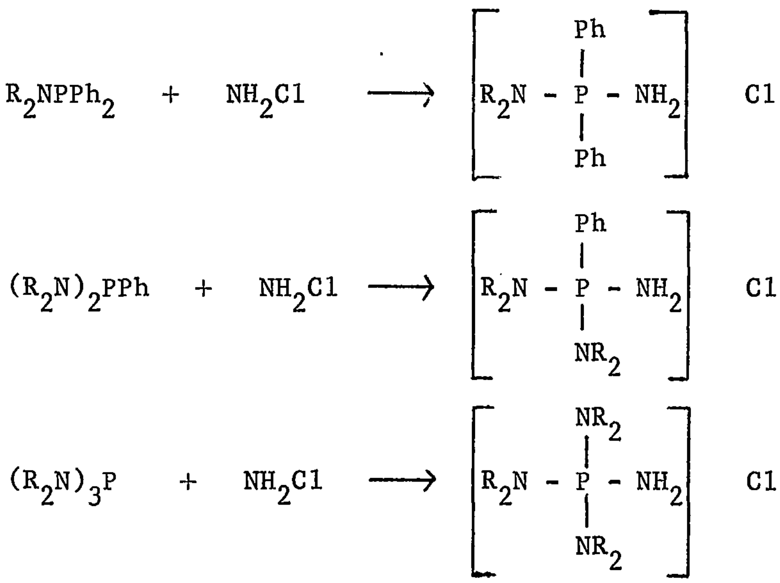
Van Wazers' results show that amines of the type - NR_2 form π-bonds through the nitrogen with phosphorus to a very small extent in P^{III} compounds and possibly to a slightly larger extent in P^V compounds

Table 17

Estimated number of π bonds per phosphorus atom for OPZ_3 type molecules

Molecule	π bonds/P estimated
$PO(NPh_2)_3$	0.96
$PO(NH_2)_3$	1.06
$PO(NR_2)_3$	1.04
$PO(N[CH_3]_2)_3$	1.03
$POCl_3$	0.86

although the figures in Table 17 refer to the total number of π-bonds per phosphorus atom and hence the contribution from the π-bond between phosphorus and oxygen is included in the figure. That there is some π-bonding between phsophorus and nitrogen in P^{III} and P^{V} compounds is borne out by the fact that in the chloroamination of aminophosphines, chloroamination takes place only on the phosphorus atom, indicating that the basicity of nitrogen in aminophosphines is low. Deactivation of the nitrogen lone pair may be brought about by partial donation into phosphorus d-orbitals.



$$R_2NPPh_2 + NH_2Cl \longrightarrow \left[R_2N - \overset{Ph}{\underset{Ph}{P}} - NH_2 \right] Cl$$

$$(R_2N)_2PPh + NH_2Cl \longrightarrow \left[R_2N - \overset{Ph}{\underset{NR_2}{P}} - NH_2 \right] Cl$$

$$(R_2N)_3P + NH_2Cl \longrightarrow \left[R_2N - \overset{NR_2}{\underset{NR_2}{P}} - NH_2 \right] Cl$$

The fact that diethylaminodiphenylphosphineoxide is inert to chloroamination yields additional evidence that deactivation of the unshared electron pair on nitrogen has taken place.[112]

P-N d_{π}-p_{π} bonding in P^{III} compounds is expected to be less than in P^{V} compounds because in phosphorus-III compounds, phosphorus has a lone pair which would give rise to a degree of repulsion between itself and the lone pair on nitrogen.

There is little evidence of P-N π bonding in $P(NCO)_3$, $P(NCS)_3$, $OP(NCO)_3$ and $OP(NCS)_3$. Infra-red studies have given values of ν(P-N) as in Table 18 which according to the ranges quoted earlier would indicate little or no π-bonding[113,114] *i.e.* a predominantly single P-N bond. Although the molecules have been shown to possess C_{3v} symmetry, studies have not yet shown whether the P-N=C=S and P-N=C=O linkages are linear or bent (Fig. 2.1). Conditions would be optimised for π-bonding in a linear P-N-C-O skeleton.

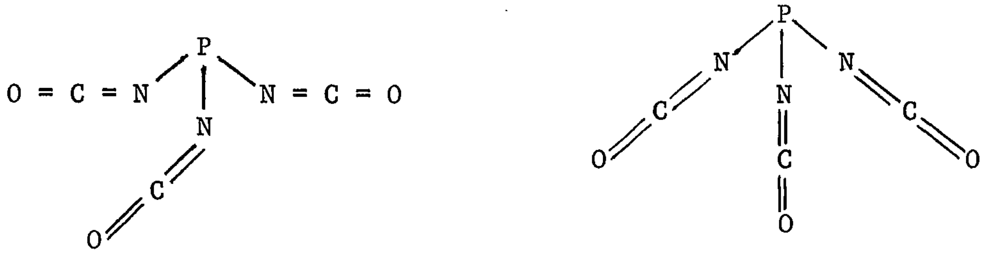


Fig. 2.1

Table 18

Compound	ν(P-N)cm^{-1}
$P(NCO)_3$	699
$P(NCS)_3$	620
$OP(NCO)_3$	704
$OP(NCS)_3$	640

Experimental

New Ketimino Derivatives of Phosphorus.

General method of preparation of di-arylketimino compounds.

The di-arylketimine $Ph_2C{:}NH$ or $(p\text{-tolyl})_2C{:}NH$ was dissolved in dry di-ethyl ether and cooled to $-196^\circ C$. The appropriate quantity of n-BuLi was added as a standard solution in hexane and the reaction mixture allowed to reach room temperature. After stirring for 30 mins., the reaction mixture was again cooled to $-196^\circ C$ and the phosphorus compound, $POCl_3$, PCl_3 or Ph_2PCl added. Work up procedure for all reactions was similar, in that solvent was removed *in vacuo* and the residue extracted with a suitable solvent (hot) (*e.g.* pet. ether 40-60°, toluene, benzene) and filtered to remove lithium chloride. Apart from two isolated cases, crystals were not, in general, obtained but a solid was isolated by removal of solvent *in vacuo*.

Preparation of di-t-butylketimino compounds.

^tBuCN was dissolved in hexane and cooled to $-196^\circ C$ and ^tBuLi, as a standard solution in pentane, was added, the reaction mixture then being allowed to reach room temperature with stirring. After 30 mins., the solution was again cooled to $-196^\circ C$ and the phosphorus compound added. Work up procedures were similar to those for di-arylketimino compounds.

A. Ketimino Derivatives of Phosphorus(III)

Reactions to prepare $[(p\text{-tolyl})_2C{:}N]_2PCl$, $[Ph_2C{:}N]_2PCl$ and $[Bu^t{}_2C{:}N]_2PCl$ by the methods described above, resulted in the mono-substituted compound being formed in each case. The attempted preparation of $[Ph_2C{:}N]_2PCl$ and $[(p\text{-tolyl})_2C{:}N]_2PCl$ by a different route as well as that by the general method is described in full below.

Reaction of $(Ph_2C{:}N)_3P$ and $Ph_2C{:}NPCl_2$ (1:1)

$(Ph_2C{:}N)_3P$ (10 mmole) in benzene (60 ml) and $Ph_2C{:}NPCl_2$ (10 mmole) in benzene (60 ml) were stirred together at room temperature for 2h. A ^{31}P n.m.r. spectrum of the reaction solution at this stage was obtained (see later). Removal of the solvent, benzene, in vacuo and extraction of the red residue with benzene/pet. ether 40-60° gave a solution from which only an intractable, sticky residue could be isolated.

Reaction of $[(p\text{-tolyl})_2C{:}N]_3P$ and $(p\text{-tolyl})_2C{:}NPCl_2$ (1:1)

A similar reaction to that above was carried out using 10 mmole of each reactant in benzene (60 ml). Exactly the same procedure was followed and, again, an intractable, sticky residue was obtained.

Reaction between di-phenylketiminolithium and phosphorus trichloride (2:1)

Di-phenylketiminolithium was prepared in the manner described generally above, from di-phenylketimine (3.45ml, 20 mmole) and n-butyllithium (7.76ml of a solution 2.58M in pentane; 20 mmole) in ether (120 ml). The iminolithium solution was cooled to -196°C and phosphorus trichloride (0.87ml, 10 mmole) was added. On reaching room temperature a yellow solution was formed, together with a precipitate. After 2h at room temperature, the solvent was removed in vacuo to leave a yellow residue which was extracted with pentane and filtered. Slow evaporation of solvent under a stream of nitrogen, produced yellow crystals identified as di-phenylketiminodi-chlorophosphine, $Ph_2C{:}NPCl_2$. M.Pt. 39-40°C.

A similar reaction using di-p-tolylketimine and phosphorus trichloride (2:1) produced di-p-tolylketimino-di-chlorophosphine, $(p\text{-tolyl})_2C{:}NPCl_2$, M.Pt. 43-45°C. Reaction of $^tBu_2C{:}NLi$ and PCl_3 in the ratio 2:1 resulted in the formation of $Bu^t{}_2C{:}NPCl_2$. B.pt. 80°C/ 0.5mm. Hg.

The phosphorus(III) compounds prepared are tabulated in Table 19 with reaction conditions, solvent details and reactants. Analytical data is presented in Table 20.

Infra-Red Data.

$P(N{:}CPh_2)_3$ (KBr disc).

ν_{max} 3084vw, 3060m, 3039w, 1662w, 1607s, 1590s, 1571s, 1491m, 1448ms, 1313m, 1285ms, 1273sh, 1181w, 1162sh, 1160w, 1155sh, 1072m, 1028m, 1001w, 979vw, 972vw, 949m, 948sh, 940sh, 909m, 861w, 850w, 820m, 795ms, 790ms, 787s, 760br,w, 714s, 701vs, 698sh, 639ms, 630w, 627w, 617vw, 578w, 562m, 541m, 512vw, 492w, 464w, 453w, 445w, 350w, cm^{-1}.

$P[N{:}C(p\text{-tolyl})_2]_3$ (KBr disc)

ν_{max} 3048w, 3024w, 2920w, 2868w, 1912br,vw, 1805br,vw, 1655vw, 1638w, 1612sh, 1588s, 1552s, 1510sh, 1507m, 1469sh, 1460sh, 1449w, 1440sh, 1434sh, 1409w, 1380w, 1365vw, 1359sh, 1310ms, 1282s, 1268s, 1212w, 1181s, 1153w, 1113m, 1037w, 1021m, 986sh, 952m, 931ms, 894w, 868vw, 828s, 804sh, 788ms, 752w, 737ms, 719w, 680m, 648m, 632m, 584w, 527m, 476m. cm^{-1}.

$Ph_2C:NPCl_2$(KBr disc) (not reported in reference 82).

ν_{max} 3078vw, 2892w, 2768vw, 1650ms, 1593m, 1449ms, 1443sh, 1373s, 1227vw, 1200vw, 1178vw, 1190w, 1160m, 1137m, 1019br,w, 998m, 910m, 870w, 850w, 829w, 797ms, 760w, 727m, 702vs, 697sh, 613ms, 517ms, 524br,w, 450w, 439vw, 410w,cm^{-1}.

(p-tolyl)$_2$C:NPCl$_2$ (KBr disc)

ν_{max} 330-2400vbr, indistinct C-H absorptions, 1630s, 1600vs, 1444m, 1418m, 1370sh, 1363ms, 1317w, 1288m, 1191s, 1158s, 1140w, 1145w, 1030sh, 1025br,m, 912w, 874m, 832vs, 803w, 782w, 772m, 738vs, 709m, 688m, 660m, 630m, 561m, 548ms, 526sh, 478m, 470sh, 409m, 387m, 368w, 302w cm^{-1}.

$Bu^t{}_2C:NPCl_2$ (thin film)

ν_{max} 2960vs, 2917sh, 2868s, 1678vs, 1535w, 1480vs, 1460s, 1393vs, 1368vs, 1232s, 1198m, 1043s, 970vs, 936sh, 910ms, 841w, 810vs, 732w, 643w, 589m, 542ms, 497s, 460br,vs, 412br,vs, 372vs,cm^{-1}.

Table 19

Ketimino Derivatives of Phosphorus III

Reactants			Experimental Details	Solvent for Extraction	Product	Phase
$Ph_2C:NH$ + 5.2 ml. 30 mmole	^nBuLi + 30 mmole in 11.2 ml. hexane	PCl_3 0.87 ml. 10 mmole	Initial red solution characteristic of $Ph_2C:NLi$ turned an intense orange with formation of a precipitate. Stirred at room temperature overnight.	Toluene/pet. ether 40-60°	$P(N:CPh_2)_3$	Red crystals
(p-tolyl)$_2$C:NH + 6.28 g. 30 mmole	^nBuLi + 30 mmole in 11.2 ml. hexane	PCl_3 0.87 ml. 10 mmole	Initial red colour of iminolithium solution changed to brownish-orange with formation of a precipitate, then to very dark brown, to dark green and finally to bottle green after 2 h at room temperature. Solvent removed after 3h.	Toluene/pet. ether 40-60°	P[N:C(p-tolyl)$_2$]$_3$	Dark green amorphous solid
^tBuCN + 2.49 g. 30 mmole	^tBuLi + 30 mmole in 13.3 ml. pentane	PCl_3 0.87 ml. 10 mmole	The lemon-yellow iminolithium solution turned orange and a precipitate was deposited. Refluxed for 4 days.	Hexane/benzene	No product of consistent analyses could be obtained	
$Ph_2C:NH$ + 3.45 ml. 20 mmole	^nBuLi + 20 mmole in 7.76 ml. hexane	PCl_3 1.74 ml. 20 mmole	The initially red solution turned yellow immediately on addition of PCl_3 and a precipitate formed. Stirred at room temperature for 2h.	Pentane/benzene	$Ph_2C:NPCl_2$	Yellow crystals
(p-tolyl)$_2$C:NH + 4.18 g. 20 mmole	^nBuLi + 20 mmole in 7.76 ml. hexane	PCl_3 1.74 ml. 20 mmole	The initially red solution turned yellow and a precipitate formed. Stirred overnight at room temperature.	Pet. ether 60-80°/benzene Recrystallised from pet. ether 60-80° and toluene.	(p-tolyl)$_2$C:NPCl$_2$	Yellow crystals
^tBuCN + 1.66 g. 20 mmole	^tBuLi + 20 mmole in 9.9 ml. pentane	PCl_3 1.74 ml. 20 mmole	The lemon-yellow solution of $Bu^t{}_2CNLi$ turned to an intense yellow solution on addition of PCl_3 and a precipitate formed. Stirred overnight at room temperature. Product distilled.	Pentane	$Bu^t{}_2C:NPCl_2$	Lemon yellow oil
$Ph_2C:NH$ + 2.6 ml. 15 mmole	^nBuLi + 15 mmole in 5.82 ml. hexane	Ph_2PCl 2.6 ml. 15 mmole	Red solution turned orangey-yellow on addition of Ph_2PCl and a precipitate was deposited. Stirred at room temperature for 2h.	Pentane/benzene	$Ph_2C:NPPh_2$	Yellow needles
(p-tolyl)$_2$C:NH + 2.09 g. 10 mmole	^nBuLi + 10 mmole in 3.88 ml. hexane	Ph_2PCl 1.79 ml. 10 mmole	On addition of Ph_2PCl, the red solution turned yellowy-orange and a precipitate formed. Stirred at room temperature for 2h.	Pentane/benzene	(p-tolyl)$_2$C:NPPh$_2$	Yellow needles
^tBuCN + 0.83 g. 10 mmole	^tBuLi + 10 mmole in 5.0 ml. pentane	Ph_2PCl 1.79 ml. 10 mmole	Lemon-yellow solution darkened on addition of Ph_2PCl and warming to room temperature. A precipitate was deposited. Stirred at room temperature for 2h.	Pentane	$Bu^t{}_2C:NPPh_2$	Yellow needles

Table 20

Analytical Data for Ketimine Derivatives of Phosphorus III

Derivative	M.Pt.	%C	%H	%N	%P	%Cl	M.Wt.
$P(N:CPh_2)_3$	118-120°	78.2 (82.0)	5.7 (5.3)	7.1 (7.4)	5.4 (5.4)	0 (0)	577 (571)
$P[N:C(p\text{-tolyl})_2]_3$	50-52°	80.5 (82.5)	6.4 (6.4)	6.2 (6.4)	4.8 (4.7)	0 (0)	678 (655)
$Ph_2C:NPCl_2$	39-40°	54.1 (55.3)	3.9 (3.6)	5.3 (5.0)	11.4 (11.0)	26.3 (25.2)	253 (282)
$(p\text{-tolyl})_2C:NPCl_2$	43-45°	56.9 (58.1)	4.4 (4.5)	4.2 (4.5)	9.9 (10.0)	24.9 (23.0)	302 (310)
$Bu^t{}_2C:NPCl_2$	B.Pt. 80°C/0.5 mm.Hg	44.6 (44.6)	8.4 (7.4)	5.7 (5.8)	12.7 (12.8)	29.4 (29.3)	264 (242)
$Ph_2PN:CPh_2$	105-107°	83.4 (82.2)	5.4 (5.5)	3.8 (3.8)	8.3 (8.5)	0 (0)	380 (365)
$Ph_2PN:C(p\text{-tolyl})_2$	84°(dec)	84.4 (82.4)	6.5 (6.1)	3.6 (3.6)	8.1 (7.9)	0 (0)	367 (393)
$Ph_2PN:CBu^t{}_2$	41°	76.6 (77.4)	8.8 (8.7)	4.5 (4.3)	9.3 (9.5)	0 (0)	340 (325)

Figures in parenthesis are calculated analytical data.

$Ph_2C:NPPh_2$ (KBr disc) (not reported in reference 32).

ν_{max} 3060w, 3020vw, 2999vw, 1608sh, 1602ms, 1588ms, 1570sh, 1563ms, 1488ms, 1476ms, 1443ms, 1439ms, 1430s, 1380br,vw, 1323w, 1309ms, 1282ms, 1274sh, 1267sh, 1241sh, 1219w, 1178m, 1172m, 1160vw, 1149w, 1120vw, 1090m, 1070m, 1062m, 1027ms, 998m, 964w, 941ms, 922m, 906ms, 847ms, 839m, 798s, 781s, 749s, 736s, 692s, 632ms, 560m, 539m, 518s, 493s, 464s, 419m, 410m, 404m, 378m, 300vw, cm^{-1}.

$Ph_2PN:C(P\text{-}tolyl)_2$ (KBr disc).

ν_{max} 3062w, 3044vw, 3022vw, 3000vw, 1910vw, 1658w, 1612ms, 1591s, 1568m, 1559m, 1505m, 1478ms, 1434sh, 1432s, 1403m, 1374w, 1309m, 1290m, 1282ms, 1272m, 1261sh, 1242w, 1212m, 1182sh, 1179ms, 1156m, 1114m, 1110sh, 1107sh, 1090m, 1064m, 1026m, 1020m, 998vw, 994sh, 961w, 955vw, 950w, 928s, 913vw, 860vw, 849vw, 836s, 826s, 807m, 786s, 749s, 740s, 736s, 730s, 721m, 695s, 690sh, 684sh, 641w, 632w, 624ms, 620m, 590m, 539m, 527m, 513m, 500ms, 479s, 468m, 428sh, 419m, 410sh, 380w, cm^{-1}.

B. Ketimino Derivatives of Phosphorus(V)

The general procedures described in the previous section was adopted. Details of the compounds prepared are given in Tables 21 and 22.

Infra-Red Data.

$PO(N:CPh_2)_3$ (Benzene solution)

(Absorptions of the compound not masked by solvent, only are given).

ν_{max} 2968sh, 2385vw, 1990sh, 1878vw,br, 1619s, 1598m, 1578m, 1449m, 1368w, 1317m, 1271m, 1250m, 1229m, 1180m, 1168sh, 1152sh, 1075w, 1012sh, 1002sh, 992sh, 975sh, 943m, 916m, 790w, 760vw, 731sh, 624sh, 619sh, 612sh, 570m, 513sh, 497m, cm^{-1}.

$PO[N{:}C(p\text{-}tolyl)_2]_3$ (KBr disc)

ν_{max} 3028w, 2960w, 2925w, 2875w, 1620ms, 1599s, 1567m, 1510m, 1504sh, 1450br,w, 1409m, 1380w, 1364br,sh, 1311ms, 1294ms, 1270ms, 1225br,w, 1216sh, 1182ms, 1160w, 1116w, 1038sh, 1022w, 978br,w, 955w, 950w, 930s, 870s, 832m, 800m, 788sh, 753w, 741s, 720m, 680m, 648ms, 634ms, 598w, 586w, 550sh, 544ms, 529sh, 495sh, 477m, cm^{-1}.

$PO[N{:}CBu^t_2]_3$ (Hexane solution)

Absorptions due to the compound only are given except where masked by solvent peaks.

ν_{max} 2654sh, 2612w, 2588w, 1670vs, 1293sh, 1370ms, 1265vw, 1230m, 1204m, 1170vw, 1046m, 1039sh, 932w, 886sh, 878sh, 870sh, 825sh, 807s, 794sh, 777w, 677w, 601m, 560m, 529m, cm^{-1}.

$ClOP[N{:}CPh_2]_2$ (KBr disc)

ν_{max} v.broad absorption between 3500 and 2600cm^{-1} due to C-H stretching. 1660vs, 1599ms, 1579m, 1448s, 1405m, 1378m, 1319s, 1278vs, 1079m, 1067sh, 1049m, 1102m,br, 1077m, 1030w, 1000m, 942m, 920m, 811m, 799m, 767ms, 729m, 701vs, 640vs, 619m, 572m, 510br,m, 450w, 403vw, 380vw, cm^{-1}.

$ClOP[N:C(p\text{-}tolyl)_2]_2$ (Nujol Mull)

ν_{max} (Nujol) 1618sh, 1590s,br, 1565s, 1508w, (Nujol), 1408w, 1310m, 1290m, 1270m, 1242m, 1212w, 1182m, 1160w, 1118m, 1038m, 1020m, 930m, 880m, 830m, 800w, 783m, 741ms, 718m, 678ms, 642ms, 630ms, 596ms, 544ms, 510sh, 470w, 440w,cm^{-1}.

$ClPO[N:CBu^t_2]_2$ (Nujol Mull)

ν_{max} (Nujol) 1675sh, 1667s, 1550w, 1535m, 1486m, (Nujol), 1404w, 1292sh, 1288s, 1238w, 1200vw, 1168w, 1113s, 1092m, 1000br,m, 910w, 846w, 812w,br, 740w, 649m, 586s, 538s, 450br,w.cm^{-1}.

$Cl_2OPN:CPh_2$(Nujol Mull)

ν_{max} (Nujol) 1650m, 1590m, 1570w, (Nujol), 1364m, 1362m, 1289w, 1260w, 1165m, 1130m, 1093m, 999m, 971m, 938w, 918w, 890sh, 876w, 845w, 796m, 785m, 765w, 742m, 724m, 702s, 686s, 629w, 618m, 598w, 589w, 570m, 549sh, 530m,cm^{-1}.

$Cl_2OPN:C(p\text{-}tolyl)_2$ (thin film)

ν_{max} 3028m, 2954w, 2920m, 2865w, 1607sh, 1588vs, 1556s, 1508ms, 1450m, 1410ms, 1380m, 1318vs, 1300vs, 1270vs, 1249sh, 1217m, 1183vs, 1166m, 1120ms, 1040m, 1022m, 968m, 932s, 878vs, 834s, 801w, 788m, 744vs, 732m, 720m, 699m, 682m, 643m, 630ms, 598s, 546vs, 502m, 480m, 470m, 446w, 392m cm^{-1}.

$Cl_2OPN:CBu^t_2$(KBr disc)

ν_{max} 3004m, 2964m, 2928sh, 2876m, 1730ms, 1672sh, 1655s, 1472ms, 1395m, 1368m, 1290w, 1248ms, 1230m, 1200w, 1110w, 1044m, 973m, 947w, 918m, 877m, 812m, 800m, 790m, 838w, 595m, 530s, 518sh, 480m,cm^{-1}.

Table 21

Ketimino Derivatives of Phosphorus V

Reactants			Experimental Details	Solvent for Extraction	Product	Phase
Ph$_2$C:NH 30 mmole 5.2 ml.	+ n-BuLi 30 mmole in 11.2 ml. hexane	+ POCl$_3$ 10 mmole 0.91 ml.	On addition of POCl$_3$ and warming to room temperature the initially red solution turned pale yellow and a precipitate formed. Stirred overnight at room temperature. Solid isolated only by removal of solvent after extraction.	Toluene/pet. ether 40-60^o	OP[N:CPh$_2$]$_3$	Yellow amorphous solid
(p-tolyl)$_2$C:NH 30 mmole 6.28 g.	+ n-BuLi 30 mmole in 11.2 ml. hexane	+ POCl$_3$ 10 mmole 0.91 ml.	After the addition of POCl$_3$ and warming to room temperature, a precipitate formed and the solution turned orange, then brown, then dark greeny-blue. Stirred at room temperature for 30h. Solid isolated only by removal of solvent after extraction.	Benzene/pet.ether 40-60^o	OP[N:C(p-tolyl)$_2$]$_3$	Dark greeny-blue amorphous solid
^{t}BuCN 30 mmole 2.49 g.	+ t-BuLi 30 mmole in 13.3 ml. pentane	+ POCl$_3$ 10 mmole 0.91 ml.	Refluxed for 5 days, during which time a precipitate formed and the solution became orangey-yellow.	Benzene/hexane	OP[N:CBu$^t{}_2$]$_3$	Yellow crystals
Ph$_2$C:NH 20 mmole 3.34 ml.	+ n-BuLi 20 mmole in 7.7 ml. hexane	+ POCl$_3$ 10 mmole 0.91 ml.	After addition of POCl$_3$, the red solution paled to a cream colour and a precipitate formed. Stirred overnight at room temperature.	Benzene	OPCl[N:CPh$_2$]$_2$	White crystals
(p-tolyl)$_2$C:NH 20 mmole 4.2 g.	+ n-BuLi 20 mmole in 7.7 ml. hexane	+ POCl$_3$ 10 mmole 0.91 ml.	After addition of POCl$_3$, the solution changed from red, to orange, to green. Overnight stirring produced a precipitate and a browny-yellow solution.	Benzene	OPCl[N:C(p-tolyl)$_2$]$_2$	Brown, flakey solid
^{t}Bu$_2$C:NH 20 mmole 3.6 ml.	+ n-BuLi 20 mmole in 7.7 ml. hexane	+ POCl$_3$ 10 mmole 0.91 ml.	Lemon-yellow iminolithium solution paled on addition of POCl$_3$ and a precipitate formed. Stirred for 2h. at room temperature. Hexane solution was yellow.	Hexane	OPCl[N:CBu$^t{}_2$]$_2$	White powder
Ph$_2$C:NH 20 mmole 3.34 ml.	+ n-BuLi 20 mmole in 7.7 ml. hexane	+ POCl$_3$ 20 mmole 1.8 ml.	Red iminolithium solution turned yellow after addition of POCl$_3$ and stirring at room temperature for 2h. A precipitate formed. Benzene/pet. ether solution was brown.	Benzene/pet.ether 100-120^o	OPCl$_2$[N:CPh$_2$]	Off-white crystals
(p-tolyl)$_2$C:NH 15 mmole 3.1 g.	+ n-BuLi 15 mmole in 5.8 ml. hexane	+ POCl$_3$ 15 mmole 1.3 ml.	Red solution turned yellowy-brown after addition of POCl$_3$ and a precipitate formed. Stirred at room temperature overnight. Toluene solution was brown.	Toluene	OPCl$_2$[N:C(p-tolyl)$_2$]	Yellowy-orange amorphous solid
^{t}BuCN 20 mmole 1.66 g.	+ ^{t}BuLi 20 mmole 8.96 ml. pentane	+ POCl$_3$ 20 mmole 1.8 ml.	After addition of POCl$_3$, the lemon yellow solution turned very pale and a precipitate formed. Stirring overnight produced an off-white solution.	Hexane/pet.ether 40-60^o	OPCl$_2$[N:CBu$^t{}_2$[	White crystals

Table 22

Analytical Data for Ketimine Derivatives of Phosphorus V

Derivative	M.Pt.	%C	%H	%N	%P	%Cl	M.Wt.
$OP(N:CPh_2)_3$	46-48°	79.9 (79.7)	5.4 (5.1)	7.1 (7.2)	5.5 (5.3)	0 (0)	620 (587)
$OP[N:C(p\text{-tolyl})_2]_3$	72-73°	77.8 (80.5)	5.9 (6.3)	6.1 (6.3)	4.6 (4.6)	0 (0)	694 (671)
$OP[N:CBu^t{}_2]_3$	60-61°	67.4 (69.4)	11.7 (11.6)	8.7 (9.0)	6.9 (6.7)	0 (0)	477 (467)
$OP[N:CPh_2]_2Cl$	50°	69.3 (70.5)	4.7 (4.5)	6.1 (6.3)	7.3 (7.0)	8.2 (8.0)	417 (442)
$OP[N:C(p\text{-tolyl})_2]_2Cl$	65°	70.9 (72.2)	5.8 (5.6)	5.5 (5.6)	6.3 (6.2)	6.9 (7.1)	518 (498)
$OP[N:CBu^t{}_2]_2Cl$	49-51°	58.3 (59.6)	9.7 (9.9)	7.6 (7.7)	8.8 (8.6)	10.0 (9.8)	386 (362)
$OP(N:CPh_2)Cl_2$	47-49°	51.4 (52.3)	3.4 (3.4)	4.8 (4.7)	10.2 (10.4)	24.2 (23.8)	313 (298)
$OP[N:C(p\text{-tolyl})_2]Cl_2$	75-76°	53.9 (55.2)	4.3 (4.3)	4.1 (4.3)	9.8 (9.5)	22.3 (21.8)	338 (326)
$OP(N:CBu^t{}_2)Cl_2$	53-54°	43.2 (41.9)	6.7 (7.0)	5.4 (5.4)	11.9 (12.0)	27.7 (27.5)	275 (258)

Figures in parentheses are calculated analytical data

Results and Discussion.

The compounds prepared in the present work are listed in Table 23, below.

Table 23.

Phosphorus-Ketimino Compounds

Phosphorus(V) Compounds

$OP[N:CPh_2]_3$	$OP[N:C(p\text{-tolyl})_2]_3$	$OP[N:CBu^t_2]_3$
$OP[N:CPh_2]_2Cl$	$OP[N:C(p\text{-tolyl})_2]_2Cl$	$OP[N:CBu^t_2]_2Cl$
$OP[N:CPh_2]Cl_2$	$OP[N:C(p\text{-tolyl})_2]Cl_2$	$OP[N:CBu^t_2]Cl_2$

Phosphorus(III)Compounds

$P[N:CPh_2]_3$	$P[N:C(p\text{-tolyl})_2]_3$	$Ph_2PN:CBu^t_2$
$P[N:CPh_2]Cl_2$	$P[N:C(p\text{-tolyl})_2]Cl_2$	$P[N:CBu^t_2]Cl_2$
$Ph_2PN:CPh_2$	$Ph_2P[N:C(p\text{-tolyl})_2]$	

The fully substituted compounds of general formula POL_3 and PL_3 (L = ketimino group) decomposed slowly in moist air. After 48 hours, the solids became sticky and lost colour, due to the hydrolysis reaction:

$$POL_3 + 3H_2O \rightarrow 3LH + H_3PO_4$$

The partially substituted compounds decomposed rapidly in air, giving off a pungent smelling gas.

$$POLCl_2 + 3H_2O \rightarrow LH + H_3PO_4 + 2HCl$$

It is interesting to note that $P[N:CPh_2]_3$, $P[N:C(p\text{-tolyl})_2]_3$ and $PO[N:C(p\text{-tolyl})_2]_3$ were intensely coloured, the p-tolyl derivatives being green solids and $P[N:CPh_2]_3$ red. The remaining compounds were lemon yellow, off-white or brown, several of these giving brown solutions in toluene or benzene. It is interesting that $P(N:CBu^t{}_2)_3$ could not be obtained by reaction of PCl_3 and $Bu^t{}_2C:NLi$ (1:3) but that $PO(N:CBu^t{}_2)_3$ could readily be prepared by a 1:3 reaction of $POCl_3$ and $Bu^t{}_2C:NLi$.

The bis-substituted derivatives PL_2Cl were not preparable by the usual reaction of PCl_3 with iminolithium, the mono-substituted compound being the product in each reaction tried. However, a reaction in which PL_3 and $PLCl_2$ (L = the same ketimine in PL_3 and $PLCl_2$) in the ratio 1:1 gave a peak in the ^{31}P n.m.r. in the expected region for PL_2Cl (see later). Attempts to isolate the product failed.

In some cases, the initially isolated product was a sticky semi-solid e.g. $POCl_2N:C(p\text{-tolyl})_2$ which became an amorphous solid under a slow stream of nitrogen. The infra-red spectra of the semi-solid and of the amorphous solid were identical.

1. Mass Spectral Data.

The mass spectra of all compounds in Table 23 were obtained, as well as that of $Ph_2C:NPPh_2$. Several compounds produced mass spectra in which only fragments of the parent ketimine and products of its breakdown were observed. Data from the other compounds are listed in Table 24. Very few phosphorus containing fragments could be assigned, the assignments being confirmed by computer calculation of the isotope distribution pattern (isotope numbers and then natural abundances are listed in Table 25).

Table 24

Phosphorus containing fragments in the mass spectra of some phosphorus-ketimino compounds

$P[N{:}CBu^t_2]Cl_2$

Fragment	m/e
$Cl_2PC{:}NBu^t_2$	241
$ClPN{:}CBu^t_2$	206
$Cl_2PN{:}CBu^t$	184
$PNCBu^t_2$	171
$ClPN{:}CBu^t$	149
PNC_6H_{11}	128
$PNCBu^t$	114
PCl_2	101
PCl	66

$Ph_2PN{:}C(p\text{-tolyl})_2$

Fragment	m/e
$Ph_2PNC(p\text{-tolyl})_2$	393
$PhPNC(p\text{-tolyl})_2$	316
$Ph_2P(p\text{-tolyl})_2$	276
PNC	57

$OP[N{:}CPh_2]_3$

Fragment	m/e
$[Ph_2CN]_2PO$	407
Ph_2CNPHO	228
Ph_2CNPO	227
PCNH	58
PCN	57
H_3POH	51
H_3PO	50

$Ph_2PN{:}CPh_2$

Fragment	m/e
$Ph_2PN{:}CPh_2$	365
$PhPPh_2$	262
Ph_2PH	186

$P(N{:}CPh_2)_3$

Fragment	m/e
PC_4H_6	85
PC_3H_7	74
PNC	57

Table 25

Isotope numbers and their natural abundances of the constituent elements of phosphorus ketimines

Phosphorus

Mass Number	30.974		
Natural Abundance	100.000		

Chlorine

Mass Number	34.969	36.966	
Natural Abundance	75.530	24.470	

Hydrogen

Mass Number	1.008	2.014	
Natural Abundance	99.985	0.015	

Carbon

Mass Number	12.000	13.003	
Natural Abundance	98.890	1.110	

Nitrogen

Mass Number	14.003	15.000	
Natural Abundance	99.630	0.370	

Oxygen

Mass Number	15.995	16.999	17.999
Natural Abundance	99.759	0.037	0.204

All compounds were found by cryoscopy in benzene to have a monomeric state of association. This is confirmed by the mass spectral data in the cases of $P[N:CBu^t_2]Cl_2$, $Ph_2PN:C(p\text{-tolyl})_2$ and $Ph_2PN:CPh_2$ all of which showed parent peaks in their mass spectrum, and no fragments at higher $^m/e$. This is consistent with the findings of Snaith and Wade[27] who found $Ph_2PNCBu^t_2$ to have a monomeric state of association in the vapour phase, and in benzene solution. In the mass spectrum of $OP[N:CPh_2]_3$, the peak corresponding to $(Ph_2C:N)_2P{=}O$ was the highest $^m/e$ number that could be unequivocably assigned. A few relatively less intense peaks above 407 but below that expected for the parent peak were observed but could not be assigned. In other cases, since ketimine fragments only were observed no indication of the state of association of the compounds in the vapour phase was obtained.

2. Infra-Red Data.

Infra-spectra of the phosphorus-ketimine compounds were obtained as KBr discs, nujol mulls, thin films or hexane or benzene solutions. The values of $\nu(C{=}N)$ are given in Table 26.

a) P^{III} compounds.

In the two compounds $PL_3[L = Ph_2C:N$ and $(p\text{-tolyl})_2C:N)]$ the values of $\nu(C{=}N)$ are very little higher than $\nu(C{=}N)$ in the free ketimine (for $Ph_2C:NH$, $\nu_{C=N} = 1603cm^{-1}$,[23] for Bu^t_2CNH, $\nu_{C=N} = 1610cm^{-1}$,[23] and for $(p\text{-tolyl})_2CNH$ $\nu_{C=N} = 1597cm^{-1}$,[24]) and so the implication is that the P-N-C skeleton is bent (as explained in

Table 26

ν(C=N) for phosphorus-ketimino compounds

Compound	ν(C=N) cm^{-1}	Phase
$P[N:CPh_2]_3$	1607	KBr disc
$P[N:C(p\text{-}tolyl)_2]_3$	1612	KBr disc
$Cl_2PN:CPh_2$	1650	KBr disc
$Cl_2PN:C(p\text{-}tolyl)_2$	1630	KBr disc
$Cl_2PN:CBu^t{}_2$	1678	KBr disc
$Ph_2C:NPPh_2$	1608	KBr disc
$(p\text{-}tolyl)_2C:NPPh_2$	1612	KBr disc
$Bu^t{}_2C:NPPh_2$	1647	Nujol mull[27]
$OP[N:CPh_2]_3$	1619	Benzene solution
$OP[N:C(p\text{-}tolyl)_2]_3$	1620	KBr disc
$OP[N:CBu^t{}_2]_3$	1670	Hexane solution
$ClOP[N:CPh_2]_2$	1660	KBr disc
$ClOP[N:C(p\text{-}tolyl)_2]_2$	1618	Nujol mull
$ClOP[N:CBu^t{}_2]_2$	1667	Nujol mull
$Cl_2OPN:CPh_2$	1650	Nujol mull
$Cl_2OP[N:C(p\text{-}tolyl)_2]$	1607	Thin film
$Cl_2OPN:CBu^t{}_2$	1655	KBr disc

Chapter 1). In the mono-substituted compounds the increases $\Delta\nu$ $(\nu(C{=}N)_{(derivative)} - \nu(C{=}N)_{(parent\ ketimine)}$ especially in the t-butylketimine compounds, are considerably larger but as was discussed in the previous chapter, similar sized increases were found for some silicon compounds[2] for which other evidence suggested bent Si-N-C skeletons. Since the difference between the atomic masses of silicon and phosphorus is only 3 a.m.u., one might reasonably expect the change in ν(C=N) to be relatively unaffected by the slight increase in mass of phosphorus compared with silicon. Hence it seems that the infra-red evidence found for phosphorus compounds suggests that they too have bent skeletons. In the two mono-substituted compounds Cl_2PNCPh_2 and $Cl_2PNC(p\text{-}tolyl)_2$ the values of ν(C=N) are $43cm^{-1}$ and $18cm^{-1}$ higher than in the tris-substituted compounds. If there were any p_π-d_π, N → P bonding, then an increase would be expected since competition between ketimine residues for the P dπ bonds would be reduced in the mono substituted compounds. However, it has been found that Cl can and does π bond with phosphorus.[111] Hence the observed increase may be a result of one, or both factors:

1. The P-N-C bond angle in Cl_2PL compounds is significantly nearer 180^o than that in PL_3 compounds.

2. If there is π-bonding between the Ar_2CN nitrogen and phosphorus, then one would expect ν(C=N) in PL_3 to be lower than in $PLCl_2$ if the π-bonding ability of $Ar_2C{:}N$ is greater than that of Cl.

ν(C=N) for $Cl_2PN{:}CBu^t_2$ was found at $1678cm^{-1}$ which may be sufficiently high to be consistent with a linear P-N-C skeleton.

In the compounds Ph_2PL (L = diphenyl-, di-t-butyl- or di-p-tolyl-ketimine) the values of ν(C=N) are sufficiently low to be consistent with angular P-N-C units. The phenyl group was found not to π bond with phosphorus[111] and so if there be any π-bonding in the molecule it can only take place between nitrogen and phosphorus. In the phosphorus III compounds prepared, ν(C=N) is highest in the di-t-butylketimino-derivatives which is to be expected since there are no aryl substituents conjugated with the azomethine group.

b) P^V compounds.

In the three di-p-tolylketimino derivatives of P^V, and $PO[N:CPh_2]_3$, $\Delta\nu$ is very small. [$\Delta\nu = \nu_{C=N}$(compound) - $\nu_{C=N}$(free ketimine)]. In the remaining compounds, $\Delta\nu$ is much larger, the greatest $\Delta\nu$ value in each analogous set being the di-t-butylketimino derivatives. It is possible that these $\Delta\nu$ values are consistent with bent skeletons though in $ClOP[N:CPh_2]_2$, $OP[N:CBu^t_2]_3$ and $ClOP[N:CBu^t_2]_2$ the values of ν(C=N) may be high enough for the compounds to have near linear or linear P-N-C skeletons. Chan and Rochow[2] found that ν(C=N) in $(Ph_2C:N)_3SiPh$ was at $1670cm^{-1}$ and their u.v. spectral investigations led them to the conclusion that in this compound, the C-N-Si skeleton is bent. Hence by comparison, it would seem that the phosphorus compound described here are also likely to have bent skeletons.

As mentioned earlier (p. 124), in general, for formally single P-N bonds, ν(P-N) is found in the region $680-820cm^{-1}$ [25,99,100] and for double bonds, in the region 1200-1560cm^{-1} [25,101,102]. Since in the ketimino compounds the P-N bond is likely to be in between a single and a double bond, one would expect ν(P-N) to be in the region 680-1560cm^{-1}. However due to the complexity of the spectra in this region the P-N symmetric vibration cannot be unequivocably assigned from the spectra obtained.

3. N.M.R. Spectral Data.

(i) ^{31}P n.m.r. Spectra.

The chemical shifts of the ^{31}P nucleus in the compounds prepared are given in Tables 27 and 29. Where necessary, the spectrum was scanned several times and printed out after a sufficient number of scans had accumulated. All spectra were run at ~ 34 ^{o}C.

The chemical shifts listed in Table 27 are in the regions expected for three co-ordinate phosphorus with N=C substituents by comparison with isocyanate and isothiocyanate compounds (Table 28). Values of ^{31}P n.m.r. shifts for some related P-N species are quoted in Table 28.

The values for $P(NCO)_3$, $P(NCO)_2Cl$, $P(NCO)Cl_2$ and PCl_3 are spread over a range of 123ppm, loss of each successive chlorine causing a decrease in shift of between 30-50ppm. The same spread is observed in the new ketimine compounds described here. The shift for $Cl_2PN{:}CBu^t{}_2$ is anomalously high compared with the shifts of $Cl_2PN{:}CPh_2$ and $Cl_2PN{:}C(p\text{-tolyl})_2$.

In the reaction of PL_3 and $PLCl_2$ (L = $Ph_2C{:}N$- and $(p\text{-tolyl})_2C{:}N$-) the solutions gave peaks at -115.2 and -117.2ppm. respectively.

Table 27.

^{31}P Chemical Shifts for Phosphorus(III) Ketimino Compounds

Compound	δ ppm*	Solvent
$Ph_2C:NPPh_2$	-36.5	benzene
$(p\text{-tolyl})_2C:NPPh_2$	-37.3	benzene
$Bu^t{}_2C:NPPh_2$	-29.1	pentane
$(Ph_2C:N)_3P$	-85.5	toluene
$[(p\text{-tolyl})_2C:N]_3P$	-86.3	benzene
$Cl_2PN:CPh_2$	-157.2	benzene
$Cl_2PN:C(p\text{-tolyl})_2$	-159.0	Toluene/pet.ether
$Cl_2PN:CBu^t{}_2$	-85.3	Toluene
$ClP[N:CPh_2]_2$	-115.2	benzene
$ClP[N:C(p\text{-tolyl})_2]_2$	-117.3	benzene

* Measured relative to P_4O_6[115] external reference but quoted with reference to 85% aqueous H_3PO_4.

These peaks are in positions consistent with the presence in solution of a PL_2Cl species since the shifts for the corresponding isothiocyanate and isocyanate solutions were -114.0 ppm and -128ppm respectively. In order to confirm that these peaks were due to the bis-substituted species and not to an average shift of PL_3 and $PLCl_2$, samples were run containing an excess of one constituent.

Table 28

^{31}P n.m.r. chemical shifts for some related P-N species

Compound	δ ppm*	Ref
$P(NCO)_3$	-97.0	116
$P(NCS)_3$	-85.6	116
$PCl(NCS)_2$	-114.0	116
$PCl(NCO)_2$	-128.0	116
$PCl_2(NCS)$	-155.3	116
$PCl_2(NCO)$	-165.7	116
PCl_3	-220.0	116
$Ph_2C{:}NPCl_2$	-159.5	82
$Ph_2C{:}NPPh_2$	-28.8	82
$Ph_2C{:}NPMe_2$	-26.5	82
$Ph_2C{:}NPPh(Cl)$	-89.6	82
$P[NMe_2]_2Cl$	-158.7	117,118
$P[NMe_2]Cl_2$	-166.0	117,118
$P[NMe_2]_3$	-123.0	119

* Relative to 85% aqueous H_3PO_4 as external reference.

In each case, two peaks were seen, the one at $\delta = -114$ ppm remaining stationary and the second due to whichever constituent (*ie* PL_3 and $PLCl_2$) was in excess.

Table 29.

^{31}P Chemical Shifts in ppm for P^V Ketimino compounds.

Compound	δ ppm*	Solvent
$OP(N{:}CPh_2)_3$	+ 2.3	Benzene
$OP[N{:}C(p\text{-tolyl})_2]_3$	+ 1.5	Benzene
$OP(N{:}CBu^t{}_2)_3$	+17.7	Benzene
$ClOP(N{:}CPh_2)_2$	- 7.8	Benzene
$ClOP[N{:}C(p\text{-tolyl})_2]_2$	- 7.8	Benzene
$ClOP[N{:}CBu^t{}_2]_2$	$+\underline{17.0}$, + 4.1	Benzene
$Cl_2OPN{:}CPh_2$	$-\ \underline{7.9}$, + 2.0	Benzene
$Cl_2OP[N{:}C(p\text{-tolyl})_2]$	$-\ \underline{7.9}$, + 2.0	Benzene
$Cl_2OPN{:}CBu^t{}_2$	$+\underline{17.3}$, + 2.7	Benzene

* Measured relative to P_4O_6[115] as external reference but quoted with reference to 85% aqueous H_3PO_4.

The shifts for related isocyanate and isothiocyanate species are given in Table 30.

Table 30[116].

Compound	δ ppm*
$OPCl_3$	- 2.2
$OPCl_2(NCO)$	9.2
$OPCl(NCO)_2$	26.6
$OP(NCO)_3$	40.9
$OPCl_2(NCS)$	21.0
$OPCl(NCS)_2$	41.5
$OP(NCS)_3$	61.0

* Measured relative to 85% aqueous H_3PO_4 as external reference.

The values obtained for the P^V ketimino compounds are all in a range consistent with the phosphorus atom in each case being four co-ordinate. The spread of chemical shifts is much smaller than in the P^{III} compounds, which is expected since the chemical shifts of four co-ordinate phosphorus are less susceptible to changes in ligands than are those of three coordinate phosphorus.

At first sight, the chemical shifts for the P^V-ketimino compounds appear anomalous especially by comparison with the chemical shifts for isocyanate and isothiocyanate complexes in Table 30.

For the isocyanates and isothiocyanates, the chemical shifts are in the order

$$OP(NCO)_3 > OPCl(NCO)_2 < OPCl_2(NCO) < OPCl_3$$

ie the values for the bis- and mono-substituted compounds lie between the values for the tris-substituted compound and $OPCl_3$. Values for amine compounds are given in Table 31.

Table 31[111]

^{31}P n.m.r. data for some P^V - amine compounds.

Compound	δ ppm
$OPCl_3$	- 2.2
$OPCl_2(NMe_2)$	-18.1, -16.1
$OPCl(NMe_2)_2$	-30.3, -29.6
$OP(NMe_2)_3$	-23.4

Linear interpolation of the chemical shifts of $POCl_3$ and $PO(NMe_2)_3$ gives values for $OPCl_2(NMe_2)$ and $OPCl(NMe_2)_3$ as -9.1 ppm and -16.3ppm respectively (Fig. 2.2(i)). However, the observed values were -17.1 and -30.0ppm (taking the mean values of the chemical shifts) respectively for $OPCl_2(NMe_2)$ and $OPCl(NMe_2)_2$. The differences between the interpolated and observed values are represented in Fig. 2.2(i) by Δ_1 and Δ_2 for $OPCl_2(NMe_2)$ and $OPCl(NMe_2)_2$. Van Wazer[111] attributed these deviations, Δ_1 and Δ_2 to σ and π effects in the molecules. For the amine compounds in Table 31, he calculated the σ contribution to Δ_1 and Δ_2 to be zero and hence

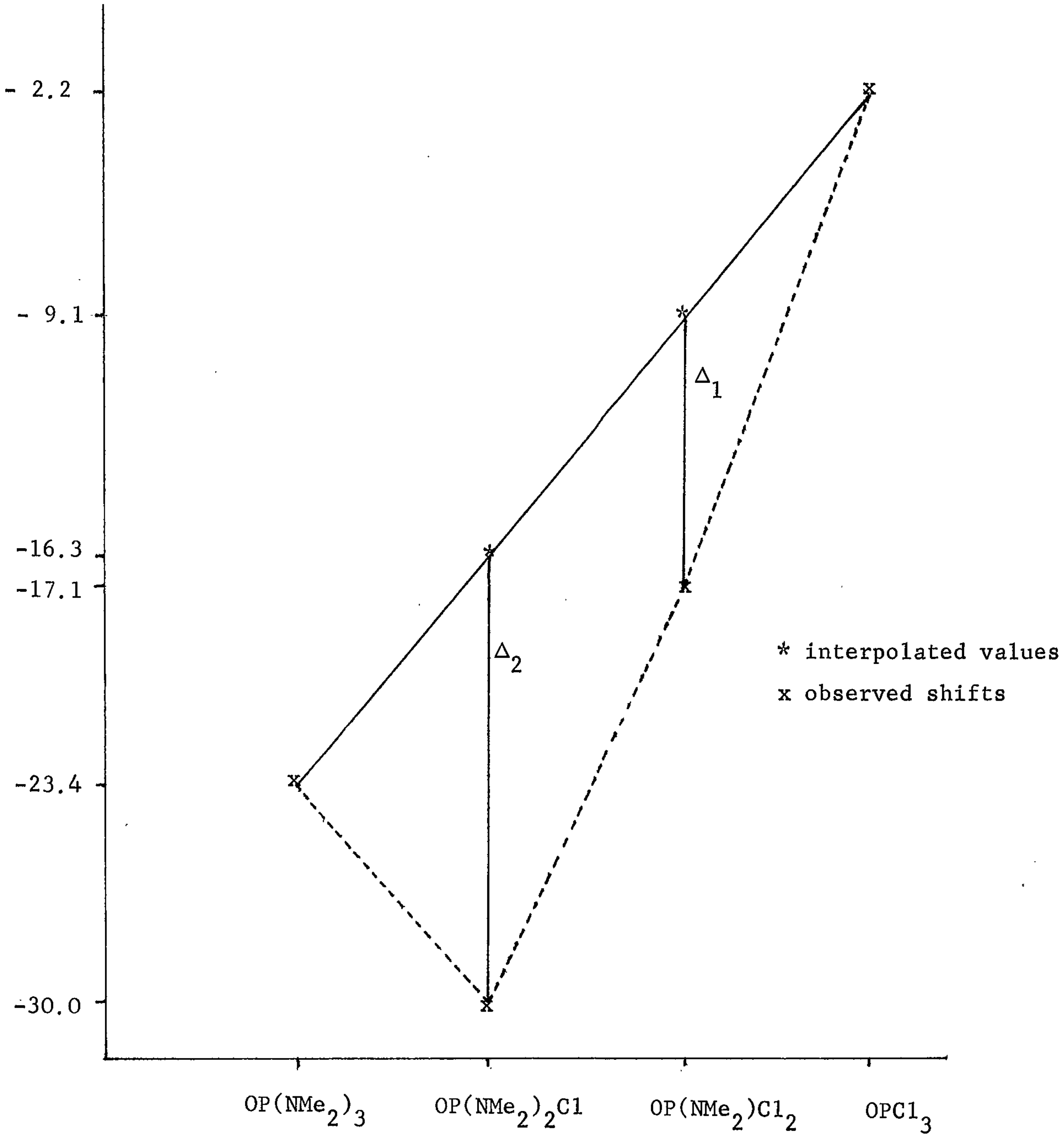

- 2.2
- 9.1
-16.3
-17.1
-23.4
-30.0
Δ1
Δ2
* interpolated values
x observed shifts
OP(NMe2)3
OP(NMe2)2Cl
OP(NMe2)Cl2
OPCl3

Fig. 2.2(i)

assumed that Δ_1 and Δ_2 were due to π interactions and were respectively -8.0 ppm and -13.7ppm.[111] Taking the chemical shifts of $PO(N{:}CPh_2)_3$ as 2.3ppm and that of $POCl_3$ as -2.2, then the interpolated chemical shifts for $POCl(N{:}CPh_2)_2$ and $POCl_2(N{:}CPh_2)$ are 0.8ppm and -0.7ppm respectively. The differences between the interpolated and observed chemical shifts for the di-phenylketimino phosphorus compounds are shown in Fig. 2.2(ii). The interpolated values are very close together because of the small difference between

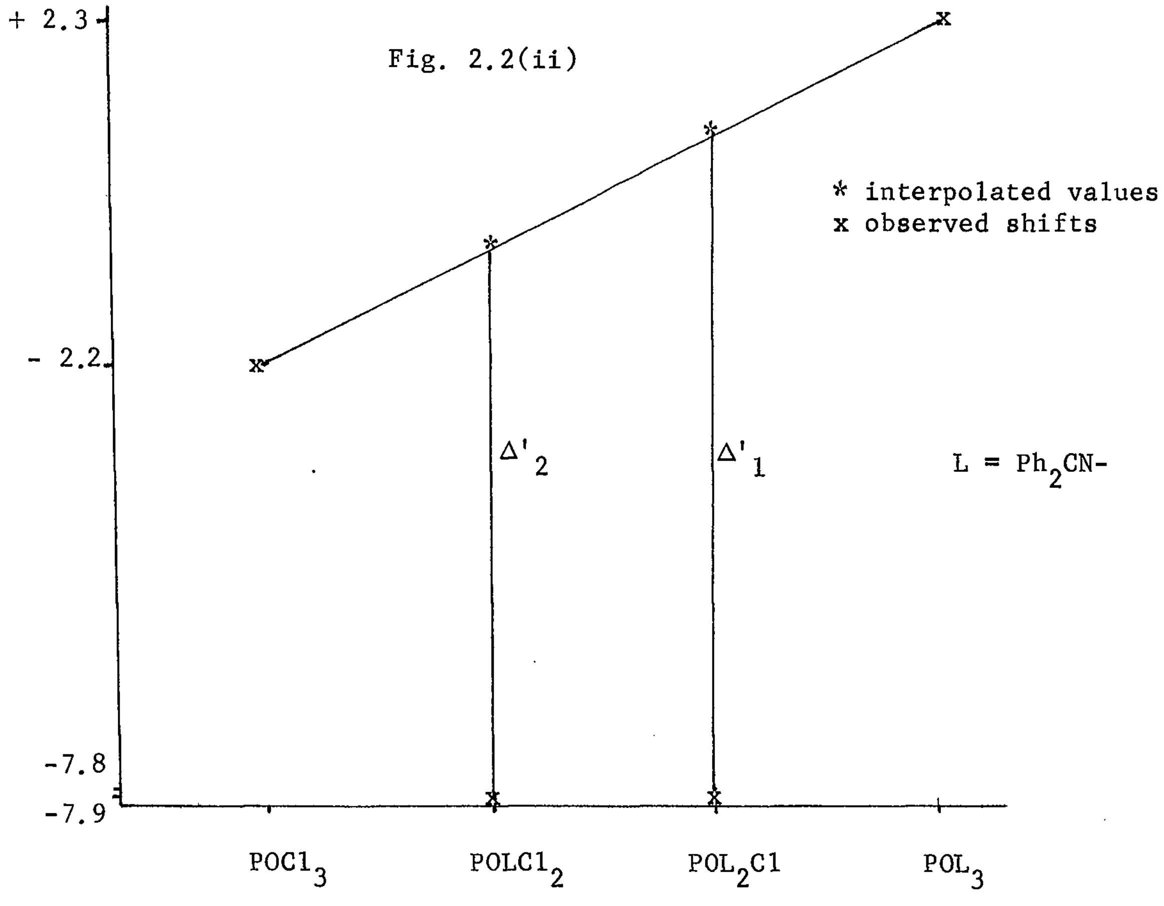


Fig. 2.2(ii)

the shifts of $POCl_3$ and POL_3. Defining the differences between the interpolated and observed values for POL_2Cl and $POLCl_2$ as Δ'_1 and Δ'_2 respectively, if the sum of the σ and π contributions to Δ'_1 and Δ'_2 were similar, then the observed chemical shifts would be very close. This is in fact observed. It is likely that the NMe_2 group will form stronger π-bonds with phosphorus than will the ketimino residue.[119a] Hence, if the deviation for $OPCl_2(NMe_2)$, <u>ie</u> Δ_1 be taken as the limiting deviation, then the chemical shifts for OPL_2Cl and $OPLCl_2$ would be at about -8.7ppm or higher. Again, this is found, (<u>ie</u> if the maximum values of Δ'_2 and Δ'_1 be taken as -8.0ppm).

Considering the spectra of the di-t-butylketimino-phosphorus(V) compounds, the similarity of the chemical shifts imply that in every case, $PO(N:CBu^t_2)_3$ is present. This implies that disproportionation may be taking place according to the equations:

$$3POLCl_2 \rightarrow 2POCl_3 + POL_3 \qquad L = Bu^t_2C:N-$$

$$2POL_2Cl \rightarrow POL_3 + POLCl_2.$$

Although the spectra showed two peaks, the shift underlined in Table 29 was due to by far the most intense peak. If $POCl_3$ were being formed in the case of $POCl_2(N:CBu^t_2)$, it is possible that it was so broad as to be unobservable at low concentration. If disproportionation were taking place two peaks of equal intensity would be expected only if the products formed were stable. In the case of $PO(N:CBu^t_2)_2Cl$, if disproportionation be taking place to $PO(N:CBu^t_2)Cl_2$ which in turn be disproportionating to $POCl_3$ and $PO(N:CBu^t_2)_3$, then overall the effect would be to produce twice as much $PO(N:CBu^t_2)_3$ as $POCl_3$.

$$3PO(N:CBu^t_2)_2Cl \rightarrow 2PO(N:CBu^t_2)_3 + POCl_3.$$

If $POCl_3$ is present, it may be undergoing exchange with $PO(N{:}CBu^t_2)Cl_2$ or $PO(N{:}CBu^t_2)_2Cl$ so that the smaller peak could well be an average peak of the chlorinated species in solution. The chemical shifts of $PO(N{:}CBu^t_2)_2Cl$, $PO(N{:}CBu^t_2)Cl_2$ and $POCl_3$, by similar arguments to those used above for the diphenylketimino derivatives, may well be so close together that the peak of lower intensity could represent all of these species. The lower intensity peak was very broad possibly due to exchange broadening of $POCl_3$. The peak at $\sim$+ 17.0ppm may be sufficiently separated from the peaks due to chlorinated species as to be unaffected by the averaging of the shifts. The results obtained for the di-t-butylketimino compounds are consistent with this averaging theory since if disproportionation be taking place as suggested above, then more $POCl_3$ would be expected in the case of $PO(N{:}CBu^t_2)Cl_2$ as compared with $PO(N{:}CBu^t_2)_2Cl$ and hence the average shift position would be lower, as is observed. Similar arguments to those used for di-t-butyl-ketimino compounds can be used to explain the appearance of two peaks in the spectra of $PO(N{:}CPh_2)Cl_2$ and $PO[N{:}C(p\text{-tolyl})_2]Cl_2$.

The Pairwise Additive Effect.

Kidd and Traux[120] measured ^{27}Al chemical shifts of a series of tetrahaloaluminate ions and observed that each halogen does not contribute a fixed increment to the aluminium shielding but rather, the contribution of each halogen is dependent on the other substituents bonded to aluminium. In a later paper, Malinowski[121] reported that the ^{27}Al shifts of the tetrahaloaluminate ions are pairwise additive.

This means that for a compound AlX_2YZ, the chemical shift δ is calculated as

$$\delta = 2\eta_{x,z} + 2\eta_{z,y} + \eta_{yz} + \eta_{x,x}$$

where η_{xy} is an empirical parameter associated with substituents X and Y but independent of Z. Pairwise contributions arise because the wave function of each substituent group suffers a linear correction due to the presence of each neighbouring substituent group.[122] In Table 32, values for ^{27}Al tetrahaloaluminate ions are presented.[121]

Table 32.

Comparison between Calculated and Observed ^{27}Al Shifts of Some Tetrahaloaluminate ions.

Anion	Pairwise Additivity	Calc. δ^{*}	Obs. $^{d}\delta^{*}$
AlI_4^-	$6\eta_{I,I}$	+27.0	+27.0
AlI_3Cl^-	$3\eta_{I,I} + 3\eta_{Cl,I}$	-21.3	-21.7
$AlI_2Cl_2^-$	$\eta_{I,I} + 4\eta_{Cl,I} + \eta_{Cl,Cl}$	-59.0	-59.4
$AlCl_2Br_2^-$	$\eta_{Cl,Cl,} + \eta_{Br,Br} + 4\eta_{Cl,Br}$	-93.2	-94.0
$AlCl_2IBr^-$	$2\eta_{Cl,Br} + 2\eta_{Cl,I} + \eta_{Br,I} + \eta_{Cl,Cl}$	-78.5	~ -79
$AlClBr_2I^-$	$2\eta_{Cl,Br} + \eta_{Cl,I} + 2\eta_{Br,I} + \eta_{Br,Br}$	-69.9	-69.3

* in ppm with reference to external aqueous acidic $Al(H_2O)_6^{3+}$.

The pairwise parameters for the tetrahaloaluminate ions are given in Table 33. The method of calculation of these parameters is given in reference 122.

Table 33.

Pairwise parameters for ^{27}Al Shifts of some tetrahaloaluminate Ions.

Substituents i,j	Pairwise parameters, ppm. η_{ij}
I,I	+ 4.5
Br,I	- 6.8
Cl,I	-11.6
Br,Br	-13.3
Cl,Br	-15.7
Cl,Cl	-17.1

All values of δ obtained from pairwise additivity agree with the experimental values well within the experimental error.

This effect is also observed for carbon-13,[123] fluorine-19,[122] boron-11,[122] and proton-1.[122] It was therefore of interest to see if P^{III}-ketimino compounds also showed pairwise additivity.

Consider the series of compounds

$$PL_3 \qquad PL_2Cl \qquad PLCl_2 \qquad PCl_3$$

where L = ketimino group, and let the pairwise parameters be

$$x = \eta_{L,L}, \qquad y = \eta_{L,Cl} \qquad z = \eta_{Cl,Cl}.$$

then the chemical shift δ, is given by

$$\begin{array}{llll} \text{For } PL_3 & \delta_1 & = & 3x \\ \phantom{\text{For }} PL_2Cl & \delta_2 & = & x + 2y \\ \phantom{\text{For }} PLCl & \delta_3 & = & 2y + z \\ \phantom{\text{For }} PCl_3 & \delta_4 & = & 3z \end{array}$$

x, y, and z can be calculated from the observed values of δ from three of these equations and the calculated δ from the fourth equation can then be compared with the observed value.

For $L = Ph_2CN$

Compound	PL_3	PL_2Cl	$PLCl_2$	PCl_3
Observed δppm	-85.6	-114.6	-157.4	-219[116]

Hence

$$\begin{aligned} -85.6 &= 3x \\ \underline{x} &\underline{= -28.53\text{ppm.}} \end{aligned}$$

$$\begin{aligned} -219 &= 3z \\ \underline{z} &\underline{= -73\text{ppm}} \end{aligned}$$

$$\begin{aligned} x + 2y &= -114.6 \\ -28.53 + 114.6 &= -2y \\ 2y &= -86.07 \\ \underline{y} &\underline{= -43.04 \text{ ppm}} \end{aligned}$$

Substituting

$$\begin{aligned} \delta_3 &= z + 2y \\ &= -86.07 - 73 \\ \underline{\delta_3} &\underline{= -159.07 \text{ ppm}} \end{aligned}$$

Observed value = -157.4ppm.

If ^{31}P n.m.r. shifts in P^{III} compounds exhibit the pairwise - additive effect, this deviation of ~ 2ppm is probably due to the fact that there is bound to be interaction between the substituents on phosphorus and the lone pair. The data available do not allow this interaction to be evaluated. It is quite possible, since the values calculated and observed are close, that ^{31}P n.m.r. shifts for P^{III} compounds are pairwise additive.

From our ^{31}P chemical shifts for P^{V} compounds it is impossible to investigate pairwise additivity since chemical shifts are available for

$POCl_3$, POL_2Cl, $POLCl_2$, POL_3 (L = ketimino-group)

but there are 5 pairwise parameters

$\eta_{L,O}$, $\eta_{L,L}$, $\eta_{L,Cl}$ $\eta_{Cl,Cl}$, $\eta_{Cl,O}$.

which means that the pairwise parameters cannot be calculated from experimental data.

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

Values of ^{1}H chemical shifts for both P^{III} and P^{V}-ketimino derivatives are presented in Tables 34 and 35 respectively.

In both tables, the shifts due to aromatic protons in di-t-butyl and di-p-tolylketimino derivatives are omitted since aromatic solvents

Table 34

^{1}H n.m.r. data for P^{III}-ketimino compounds

Compound	τ^{*}	Solvent
$P[N:CPh_2]_3$	2.37 (multiplet) 2.79 (multiplet)	Benzene-d_6
$P[N:C(p\text{-tolyl})_2]_3$	methyl protons: 7.84 (singlet)	Benzene
$Ph_2C:NPCl_2$	2.51 (multiplet) 2.77 (multiplet)	Benzene-d_6
$(p\text{-tolyl})_2C:NPCl_2$	methyl protons: 7.83 (singlet)	Benzene
$Bu^tC:NPCl_2$	methyl protons: 8.66 (singlet)	Toluene
$Ph_2C:NPPh_2$	2.42 (multiplet) 2.88 (multiplet)	Benzene-d_6
$(p\text{-tolyl})_2C:NPPh_2$	methyl protons: 7.89 (singlet)	Benzene
$Bu^t{}_2C:NPPh_2$	methyl protons: 8.68 (singlet)	Toluene
$(p\text{-tolyl})_2C:NPPh_2$	methyl protons: 7.82 (singlet)	Benzene

* Relative to C_6H_6 at 2.76τ with respect to TMS at τ = 10

were used since they proved the most suitable solvents for the spectra in view of the solubility of the compounds.

As mentioned in the previous chapter, diphenylketimino compounds in general show signals too broad to enable any conclusions to be drawn as to whether the phenyl groups are equivalent. In all cases of di-t-butylketimino derivatives, singlet resonances for the methyl protons were obtained, which remained as singlets on running the spectra on toluene solutions at -60°C. This implies that either the P-N-C skeletons are linear or that, if bent, inversion of the

Table 35.

^{1}H n.m.r. data for P^V Ketimino Compounds.

Compound	τ^*	Solvent
$OP[N:CPh_2]_3$	2.34(multiplet),2.79(multiplet)	Benzene-d_6
$OP[N:C(p\text{-tolyl})_2]_3$	methyl protons:7.87(singlet)	Benzene
$OP[N:CBu^t_2]_3$	methyl protons:8.59(singlet)	Benzene
$OP[N:CPh_2]_2Cl$	2.31(multiplet),2.77multiplet	Benzene-d_6
$OP[N:C(p\text{-tolyl})_2]_2Cl$	methyl protons:7.83 (singlet)	Benzene
$OP[N:CBu^t_2]_2Cl$	methyl protons:8.67 (singlet)	Benzene
$OP[N:CPh_2]Cl_2$	2.78(multiplet)	Benzene-d_6
$OP[N:C(p\text{-tolyl})_2]Cl_2$	methyl protons 7.89(singlet)	Benzene
$OP[N:CBu^t_2]Cl_2$	methyl protons 8.67(singlet)	Benzene

* Relative to C_6H_6 at 2.76 τ with respect to the TMS at τ = 10.

phosphorus residue about nitrogen is so rapid even at -60°C that the two ^{t}butyl groups appear equivalent (fig. 2.3).

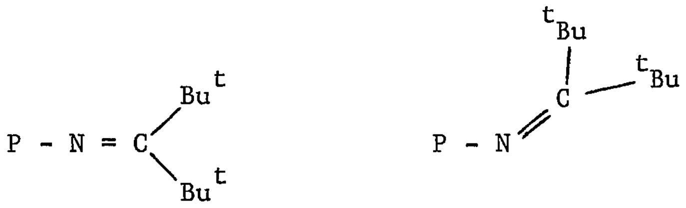


Fig. 2.3

Similar conclusions can be drawn from the methyl resonances of di-p-tolylketimino derivatives since in each case the aryl methyl protons gave a singlet which again remained as a singlet on cooling a toluene-d_8 solution of the compound to -60°C.

Hence, little information as to the shape of the phosphorus-ketimine molecules can be gained from their proton n.m.r. Infrared evidence suggests that the P-N-C skeletons may be bent in which case the proton n.m.r. spectra would imply that inversion about the N atom of the phosphorus residue is sufficiently rapid for the R groups on the ketimine residue to appear equivalent.

In conclusion, as with the isocyanates and isothiocyanates, the shape of the P-N-C skeleton is still undetermined in the ketiminoderivatives although the evidence described here suggests that the ketiminoderivatives may have bent structures.

APPENDICES

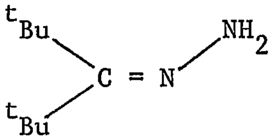
Appendix 1

Attempted preparation of $Bu^t{}_2C:NMe$.

Introduction

N-alkyl and N-aryl derivatives of ketimines and aldimines such as $Ph_2C:NMe$,[124] $Ph_2C:NPh$,[125] $CH_2:N^tBu$,[126] $MeCH:N^tBu$,[126] $PhCH:NMe$[127] and $PhCH:NPh$[128] have been prepared but similar derivatives of $Bu^t{}_2C:NH$ have not as yet been reported. Derivatives of the type $Bu^t{}_2C:NNH_2$[129] and $Bu^t{}_2C:NNMe_2$,[130] however, have been prepared.

The infra-red spectra of the two hydrazine derivatives of $^tBu_2C:NH$ have ν(C=N) at 1639 and 1603cm^{-1} respectively for $Bu^t{}_2C:NNH_2$ and $Bu^t{}_2C:NNMe_2$, positions low enough to be consistent with bent C=N-N skeletons. This non-linearity of the skeletons is confirmed by their n.m.r. spectra. For $Bu^t{}_2C:NNH_2$, the ^tBu groups show singlets at 8.80τ and 8.61τ at room temperature indicating that the groups are non-equivalent (Fig. 1) and this situation remains even at 136°.



$^tBu_2C:NNMe_2$, the t-butyl groups are again non-equivalent at room temperature, their resonances being at 8.77τ and 8.93τ.

Hence it was of interest to prepare an N-alkyl derivative to see if a similar situation was present.

Reaction of dimethyl sulphate with di-t-butylketiminolithium.

Bu^tCN (1.66g; 20 mmole) was added to hexane (120 ml) and cooled to -196^o. ^tBuLi (8.86ml of a 2.26M solution in pentane; 20 mmole) was added and the reaction allowed to reach room temperature with stirring. The reaction mixture was cooled to -196^o and dimethyl sulphate (1.26g; 10 mmole) was added. A white precipitate was formed after the solution had been stirred at room temperature for 2hr. After stirring overnight, the reaction mixture was filtered to give a white solid and a pale yellow solution. The white solid was soluble in absolute alcohol and was identified as $LiMeSO_4$ indicating incomplete reaction (Li_2SO_4 is insoluble in absolute alcohol). The only solid insolable from the yellow solution was di-t-butylketiminolithium $^tBu^t{}_2CNLi$ which crystallised out and remained after removal of solvent *in vacuo*.

A similar reaction was attempted using methylbromide as a methylating agent. Again only di-t-butylketiminolithium was isolated.

Appendix 2

Experimental Details and Starting Materials

All reactions described were carried out in an atmosphere of pure, dry nitrogen in two-necked flasks. Air sensitive materials were handled in a glove box or, if in solution, were transferred from one vessel to another by syringe against a counter current of nitrogen.

Nitrogen Supply

'White spot' nitrogen direct from the cylinder was dried by passage through two traps maintained at -196^{o}, through a tower at 400^{o} containing copper wire to remove traces of oxygen and delivered to a multiple outlet system. Or, nitrogen was drawn off from a tank containing liquid nitrogen, dried by passage through two wash bottles containing conc. H_2SO_4 followed by passage through a wash bottle containing glass wool, and delivered to a multiple outlet system. A constant pressure of nitrogen was maintained in the system by connecting one outlet to an oil bubbler.

Glove Box.

The nitrogen atmosphere in the Glove Box was purified by continuously recycling it through two traps at -196^{o}, through two towers at 400^{o} containing copper wire and back to the box. Nitrogen, described above, was used to flush out the transfer tube, after passage through this system. All external tubing was of copper where possible, and the gloves used were made of 'Butasol' rubber. An oxygen level of less than 50 p.p.m. was maintained by this system.

Solvents.

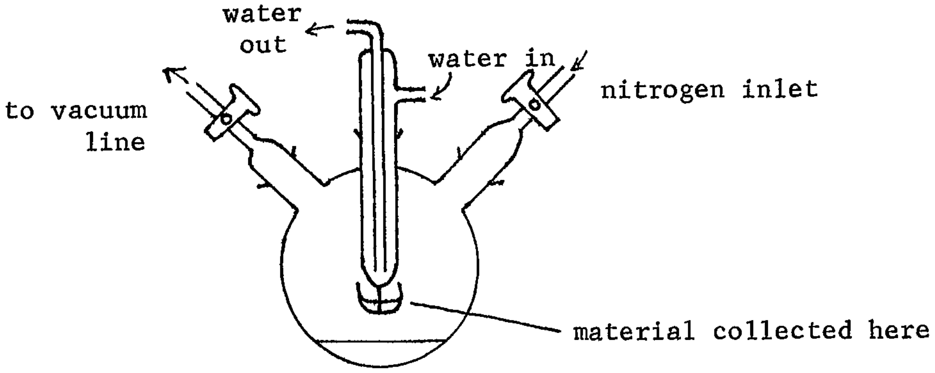
Hydrocarbon solvents and di-ethyl ether were dried over sodium wire. Chloroform and acetone were dried over molecular sieve.

Starting Materials.

The purity of the phosphorus compounds used was checked by observing their ^{31}P n.m.r. The ketimines used were prepared according to literature methods.

Distillation Apparatus.

The distillation of small quantities of liquids was carried out *in vacuo* using a bucket apparatus drawn below.



Material distilled into the bucket was syringed out against a counter current of nitrogen.

Appendix 3

Instrumentation

Infra-Red Spectra

Infra-red spectra in the range 4000-250cm^{-1} were recorded on a Perkin-Elmer 457 instrument. Spectra of solid samples were recorded in the form of nujol mulls between KBr plates or as pressed KBr or CsI discs. Solution spectra were recorded using a solution cell with KBr windows (separation 0.1 mm) which was filled by syringe.

Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance spectra were recorded using a Varian A56/60D spectrometer operating at 60MHz/sec. (^{1}H) or 56.4 MHz/sec (^{19}F) or a Perkin-Elmer R10 instrument operating at 24.29MHz/sec (^{31}P). Sample tubes were filled by syringe against a counter-current of nitrogen and, where necessary, sealed under nitrogen. Internal reference standards were tetramethylsilane or benzene (^{1}H) or $CFCl_3/C_6F_6$ mixture (^{19}F). P_4O_6 was used as external reference for ^{31}P n.m.r. spectra.

Mass Spectra.

Mass Spectra were recorded on an A.E.I. MS 9 mass spectrometer at 70 eV and an accelerating potential of 8 kv with a source temperature between 80° and 220° (depending on sample), and electromagnetic scanning. Compounds were introduced by direct insertion into the ion source.

Isotopic distribution patterns were computed using a programme kindly supplied to us by Dr E.H. Brooks.

X-ray Photoelectron Spectra.

X-ray photoelectron spectra were measured on an AEI ES100 electron spectrometer. Samples were studied in powder form evaporated from an acetone solution of the compound on a gold backing, using MgK$\alpha_{1,2}$ radiation. Deconvolutions of overlapping peaks were carried out with a Dupont 310 curve resolver. All levels were calibrated with respect to Au($4f_{7/2}$) 84 eV binding energy.

Appendix 4

Analytical Methods

Carbon, Hydrogen and Nitrogen

Carbon, hydrogen and nitrogen were determined by a Perkin-Elmer 240 Elemental Analyser; nitrogen was also determined by the Kjeldhal method.

Halogens.

Analyses for chlorine and bromine content were carried out by the departmental microanalyst by conventional potassium-fusion and titration methods.

Phosphorus.

Analysis for phosphorus content was carried out by the departmental microanalyst by Peroxide Bomb Fusion followed by colorimetric determination of the phosphorus in the form of the Vanadomolybdophosphate.

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