Hydrido and group-ivb derivatives of platinum

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HYDRIDO and GROUP-IVB
DERIVATIVES OF PLATINUM.

A.F. CLEMMIT.

HYDRIDO AND GROUP-IVb
DERIVATIVES OF PLATINUM

by

A.F. Clemmit, B.Sc.
(Hatfield College)

A Thesis submitted for the Degree of Doctor
of Philosophy in the University of Durham.

September 1970

A.F. Clemmit

SUMMARY

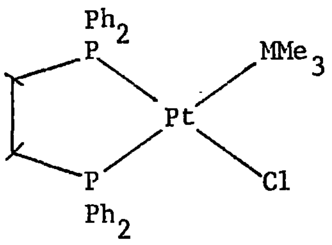
The work described in this Thesis can be divided into two parts.

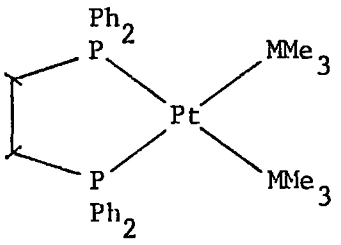
PART A Hydride Complexes of Platinum

The hydrogenation of the silyl complex $(Ph_2PCH_2CH_2PPh_2)PtCl(SiMe_3)$ yielded the cis-hydridochloride, $(Ph_2PCH_2CH_2PPh_2)PtHCl$. The preparation of this cis-hydride led to a reinvestigation of the reported cis and trans hydrides, $(Ph_3P)_2PtHCl$. From a study of their 'H n.m.r. and infra-red spectra it was concluded that the reported cis-$(Ph_3P)_2PtHCl$ was in fact the trans complex, the differences in Pt-H stretching frequencies between the two complexes being due to different crystallographic forms. The structure of the cis-hydride, $(Ph_2PCH_2CH_2PPh_2)PtH(GePh_3)$ was confirmed by its reaction with 1,2-dibromoethane and the preparation of the deuterium analogue $(Ph_2PCH_2CH_2PPh_2)PtD(GePh_3)$.

PART B Group-IVb Derivatives of Platinum

The complexes





M = Si or Ge

have been prepared by reacting $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ with 1 and 2 molar amounts of the mercury reagent $(Me_3M)_2Hg$ respectively. The analogous platinum-tin derivatives have also been obtained by the reactions of $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ and $(Ph_2PCH_2CH_2PPh_2)_2Pt(o)$ with trimethylstannane.

The reactions of some of these complexes with hydrogen and hydrogen chloride have been studied. With hydrogen, cleavage of the platinum-silicon bond in $(Ph_2PCH_2CH_2PPh_2)PtCl(SiMe_3)$ resulted in the cis-

hydridochloride, $(Ph_2PCH_2CH_2PPh_2)PtHCl$. The disubstituted silyl complex at different temperatures with hydrogen yielded $(Ph_2PCH_2CH_2PPh_2)PtH(SiMe_3)$ and at a higher temperature $\left[(Ph_2PCH_2CH_2PPh_2)_3Pt_4\right]$. Hydrogen chloride also cleaved the Pt–M bond, selectively eliminating the hydride Me_3MH and giving the platinum chloride product.

An interesting series of reactions carried out were silyl- germyl- and stannyl-exchange reactions:

$$(chelate)PtCl(SiMe_3) \xrightleftharpoons[Me_3SiH]{Me_3GeH} (chelate)PtCl(GeMe_3) \xrightarrow{Me_3SnH} (chelate)PtCl(SnMe_3)$$

$$(chelate)Pt(SiMe_3)_2 \xrightleftharpoons[Me_3SiH]{2Me_3GeH} (chelate)Pt(GeMe_3)_2 \xrightarrow{Me_3SnH} (chelate)Pt(SnMe_3)_2$$

The complexes $(chelate)PtCl(MMe_3)$ M = Si or Ge, with excess Me_3SnH gave the octahedral complex $(chelate)PtH(SnMe_3)_3$ which was also prepared by the addition of Me_3SnH to $(chelate)Pt(SnMe_3)_2$. The octahedral complex $(chelate)PtHCl(SnMe_3)_2$ was also obtained by the reaction of $(chelate)PtCl(SnMe_3)$ with Me_3SnH, both these additions being reversible.

The kinetics of the hydrogenation of $(chelate)Pt(SiMe_3)_2$ were shown to be first order with respect to hydrogen and first order with respect to the platinum complex. The equilibrium constant of the reaction

$$\underline{trans}\text{-}(Et_3P)_2PtHCl + Me_3SiH \rightleftharpoons \underline{trans}\text{-}(Et_3P)_2PtCl(SiMe_3) + H_2$$

was also determined.

The ^1H n.m.r. and mass spectra of the platinum-group-IVb complexes are also reported.

ACKNOWLEDGEMENT

I would like to express my sincere thanks to Professor F. Glockling for his help and encouragement throughout the work described in this Thesis.

I also wish to thank Dr. J. Walker of the Polymer and Petrochemical Laboratories, I.C.I., Runcorn, for the 220 M Hz. 'H n.m.r. spectra and the Science Research Council for a maintenance grant.

MEMORANDUM

The work described in this Thesis was carried out in the University of Durham between September 1967 and August 1969 and in The Queen's University of Belfast between August 1969 and September 1970. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

PUBLICATIONS

The work described in this Thesis has been the subject of the following publications with F. Glockling:

'*Cis* Hydridohalides of Platinum', J. Chem. Soc.(A), 2163, 1969.

'Silyl-, germyl- and stannyl-exchange reactions of Platinum(II) Complexes', Chem. Comm., 705, 1970.

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Reactions of $(Ph_2PCH_2CH_2PPh_2)_2Pt(o)$

Reactions of $(Ph_2PCH_2CH_2PPh_2)Pt(SiMe_3)_2$

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Contents (contd.)

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Section B Platinum Hydride Complexes

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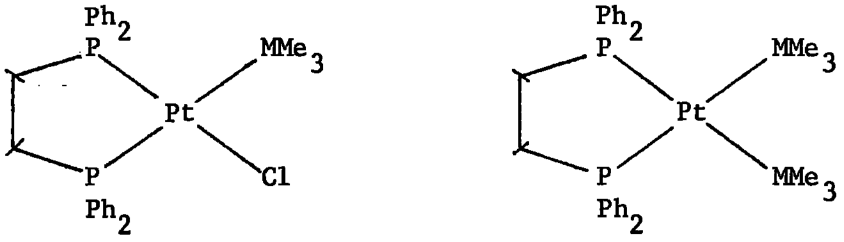
The complexes



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CHAPTER 1

GENERAL CHEMISTRY

THE CHEMISTRY OF PLATINUM

Platinum Metal

Atomic number 78. Atomic weight 195.09. Electronic configuration $5d^8\ 6s^2$.

Most abundant stable isotopes 194 (32.9%)
195 (33.8%)
196 (25.3%)
198 (7.21%).

The introduction to this thesis is concerned essentially with the chemistry of platinum, but at times it will be necessary to compare its chemistry with that of nickel and palladium. Particular emphasis will be placed on the +2 oxidation state though the 0, +4, +5 and +6 oxidation states are known.

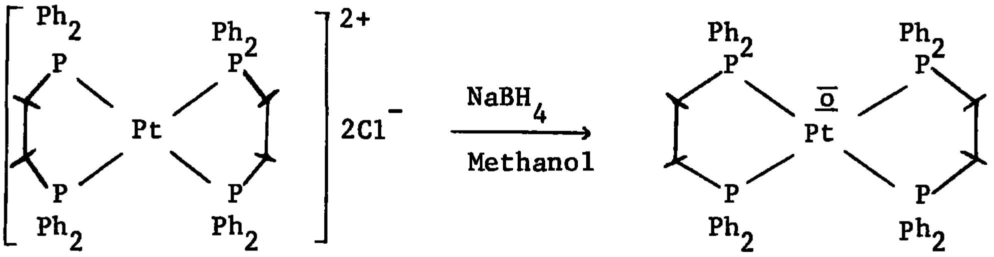
1. Zerovalent Complexes

The three metals all form complexes in the zerovalent oxidation state, but strongly π-bonding ligands are required for stability of these complexes, e.g. $(Ph_3P)_4Pt$, $(PF_3)_4Pt$, $Ni(CO)_4$. Pd(o) and Pt(o) complexes with phosphine, phosphite and isonitrile ligands may be prepared by reduction of Pd^{II} and Pt^{II} complexes in alkaline media[1,2].

$$(Ph_3P)_2PtI_2 + PPh_3\ (\text{excess}) \xrightarrow{N_2H_4} (Ph_3P)_4Pt$$

$$(Ph_3P)_2PtI_2 \xrightarrow{N_2H_4} (Ph_3P)_3Pt$$

The reduction of chelating diarsine and diphosphine Pd(II) and Pt(II) salts using sodium borohydride or naphthalenide gave complexes of the type $(Chelate)_2Pt$ [3,4].



Cluster compounds of Pt(o) containing PR_3 and CO as ligands have been reported but not all, as yet, have been fully characterised,[5,6,7] however, recently some mixed tertiary phosphine carbonyl tri- and tetra-nuclear cluster compounds have been prepared and characterised[8]. The complexes of the type $[Pt_3(CO)_3L_4]$ (L = PPh_3, PPh_2Me and PPh_2Et) and $[Pt_3(CO)_3L_3]$ (L = Ph_2PCH_2Ph), were prepared from alkali tetrachloroplatinite and hydrazine in the presence of carbon monoxide.

$$K_2PtCl_4 + 2L \longrightarrow [Pt(Cl_2L_2)] + 2KCl$$

$$[Pt(Cl_2L_2)] + 2N_2H_4 \longrightarrow [PtHClL_2]$$

$$[PtHClL_2] + KOH \xrightarrow{CO} [Pt(CO)_2L_2]$$

$$5[Pt(CO)_2L_2] \rightleftharpoons \underset{A}{[Pt_3(CO)_3L_4]} + 2PtL_3 + 7CO$$

The above equilibrium is shifted to the right when a solution of the $[Pt(CO)_2L_2]$ derivative is boiled, and due to the low solubility in the reaction medium (ethanol) of (A), a complete transformation to a mixture of $[Pt_3(CO)_3L_4]$ and PtL_3 is obtained.

The tetranuclear complexes were formed by further reaction of the trinuclear species:

$$2[Pt_3(CO)_3L_4] + 3CO \xrightarrow[1\ atm.]{25^{o}} [Pt_4(CO)_5L_4] + 2PtL_2(CO)_2.$$

The X-ray study of $[Pt_4(PPhMe_2)_4(CO)_5]$ has been reported[9] and is based on a distorted tetrahedral arrangement of the four platinum atoms with one non-bonding and five bonding metal-metal distances. The four phosphine ligands are each bonded to a different platinum atom and the five carbon monoxide bridging ligands span the five bonding edges of the distorted tetrametal tetrahedron. The structure, therefore, has two different kinds of platinum atoms: two seven coordinated, which each form bonds to the other three platinum atoms, to one phosphine and to three carbon monoxide ligands, and two five coordinated which are linked to the two seven coordinated metal atoms, one phosphine and two carbon monoxide ligands, (fig. 1). (For the purposes of clarity the phenyl and methyl groups of the phosphine ligands have been omitted from the diagram). In tris(triphenylphosphine)platinum(o) (fig. 2), the three phosphorus atoms are in a near trigonal arrangement around the platinum atom, the platinum and the three phosphorus atoms are approximately planar[9b], the distortion from planarity can be seen from the P-Pt-P bond angles; $<P_1-Pt-P_2 = <P_1-Pt-P_3 = 122^o$ and $<P_2-Pt-P_3 = 115^o$. In the crystal lattice, the molecules are packed in nearly hexagonal layers, the shortest Pt-Pt distance being about 8Å.

Direct interaction of platinous dichloride and trifluorophosphines has resulted in zerovalent platinum complexes[10].

$$PtCl_2 + 4L \xrightarrow{60^o} PtL_4. \quad L = PF_3, PF_2CF_3, PF(CF_3)_2.$$

These Pt(o) complexes are unreactive compared with the triphenylphosphine analogues, giving no reaction with hydrogen chloride, methylchloride, methyl iodide, ethylene or carbon disulphide at 60°. This behaviour contrasts markedly with that of triphenylphosphine complexes of zerovalent nickel, palladium and platinum[11]. The high reactivity of the triphenylphosphine complexes in solution is attributed to their ready dissociation and the following equilibria have been established[12,13] in which the trico-ordinated complex is the main species:

$$Pt(PPh_3)_4 \xrightleftharpoons{-PPh_3} Pt(PPh_3)_3 \xrightleftharpoons{-PPh_3} Pt(PPh_3)_2$$

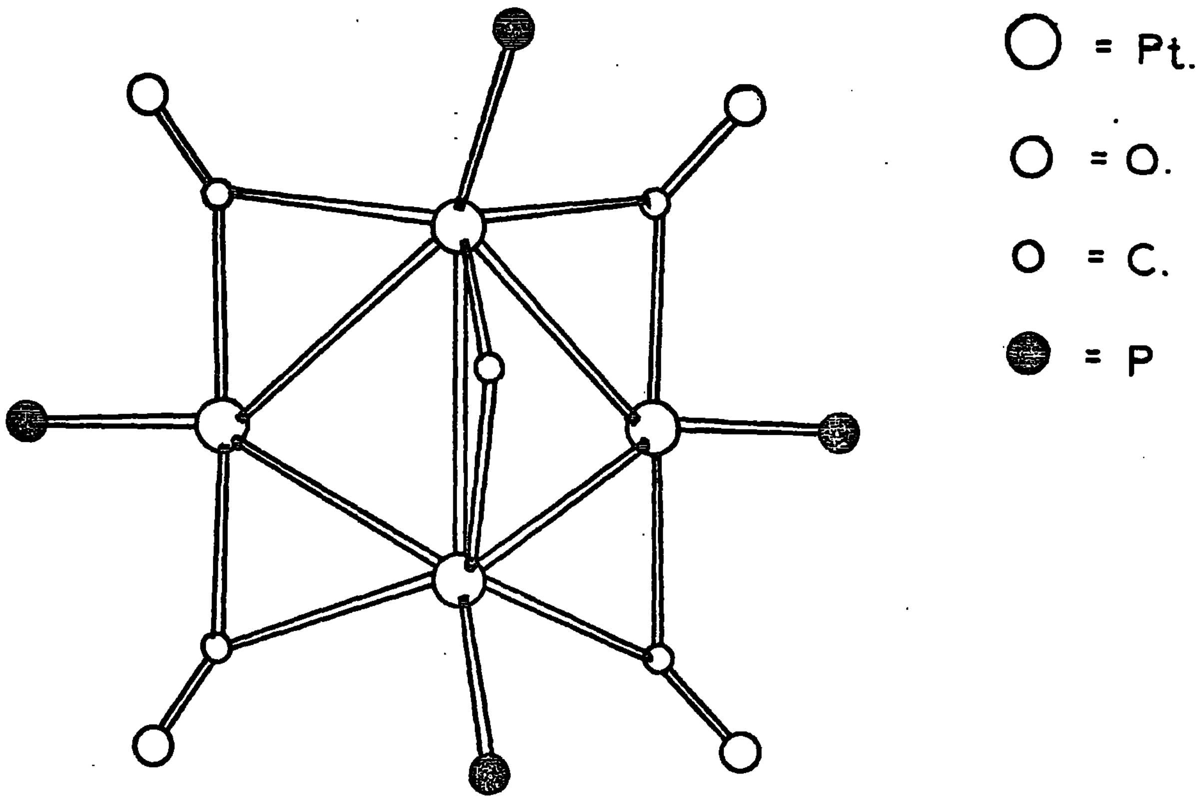


Fig. 1 X-ray crystal structure of $\left[Pt_4(PhMe_2P)_4(CO)_5\right]$

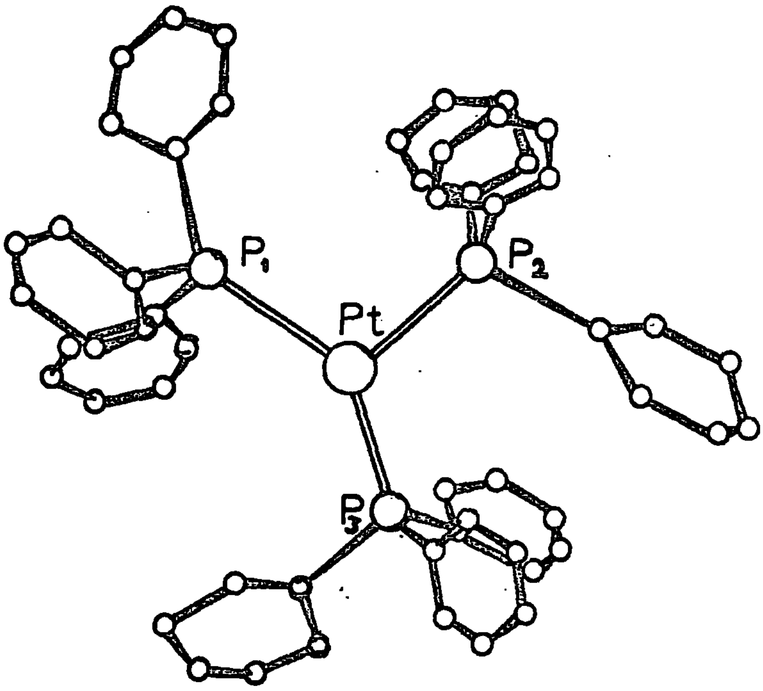


Fig. 2 X-ray crystal structure of $(Ph_3P)_3Pt$

No evidence for similar equilibria has been obtained for the trifluorophosphine complexes, the difference probably arises from the different donor-acceptor properties of the ligands, the triphenylphosphine, being a stronger σ-donor but a weaker π-acceptor than the trifluorophosphine ligands, on coordination leads to a build up of electron density on the platinum which facilitates dissociation to a coordinately unsaturated species which can then undergo further reaction.

The tertiary phosphine zerovalent platinum complexes have been used in the preparation of platinum hydrides[14] and platinum-silicon complexes[15] but these reaction will be treated in later sections.

2. Quadrivalent Oxidation State

The +4 oxidation state becomes increasingly stable down the group, for nickel there are relatively few compounds in this oxidation state whereas for platinum the +4 oxidation state is easily accessible and many compounds are known   Palladium(IV) complexes are of two types[16], halogen complexes M_2PdX_6 (M is an alkali metal, $X^\ominus = F^\ominus$, $Cl^\ominus$, $Br^\ominus$) and diammines of the type $PdAm_2X_4$ ($X = Cl^\ominus$, $Br^\ominus$).

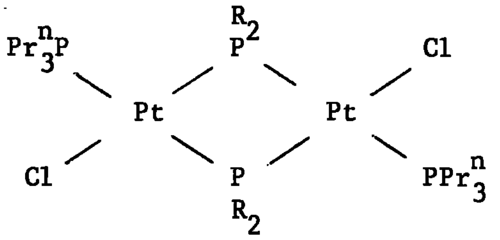
Platinum forms a large number of stable 4-valent compounds which are 6-coordinate and octahedral, however, novel bonding is sometimes required to achieve this. The trimethylplatinum halides are tetrameric with three-way halogen bridges. The complexes in the series ranging from hexahalo complexes to the hexammines, e.g. K_2PtCl_6, $[Pt(NH_3)_2Cl_4]$, $[Pt(NH_3)_5Cl]Cl_3$, form a typical and extensive series of platinum(IV) complexes. Many combinations of various amines, ammonia, hydrazine, hydroxylamine, halogens and pseudohalogens are known to occur in this type of complex.

3. Other Oxidation States

Oxidation states other than 0, +2 and +4 are relatively unimportant in the chemistry of nickel, palladium and platinum. No palladium or platinum^{I} complexes are known and compounds of nickel^{I} are very rare but include $[Ni_2(CO)_6]^{2-}$ and $[Ni_2(CN)_6]^{4-}$. Tervalent compounds of nickel are also known, oxidation of $(PEt_3)_2NiCl_2$ by nitrosyl chloride gave a compound with the composition $[(Et_3P)_2NiCl_3]$[17]. Although tervalent compounds of palladium and platinum have been claimed none has been characterised and some, shown stoichiometrically to contain the metal in the +3 oxidation state, were in fact compounds with the metal in mixed oxidation levels +2 and +4. Compounds with the metal in an oxidation state higher than +4 are few but include PtF_5 and PtF_6.

4. The Divalent State

In the divalent state, the chemistry of palladium and platinum is similar though the platinum complexes are thermodynamically and kinetically more stable than their palladium analogues. Nickel however, exhibits distinct differences being 4 or 6-coordinate and square planar, tetrahedral or octahedral whereas palladium and platinum compounds are usually 4-coordinate and square planar[16]. All types of mononuclear complexes of palladium and platinum, $[ML_4]^{2+}$, $[ML_3X]^{+}$, $[ML_2X_2]$, $[MLX_3]^{-}$ and $[MX_4]^{2-}$ are known (L = neutral ligand, e.g. PEt_3, $AsPh_3$; X = anionic ligand, e.g. halide). Bridged binuclear complexes also exist[18], having halogen, thiocyanate, RS and PR_2 bridging groups .

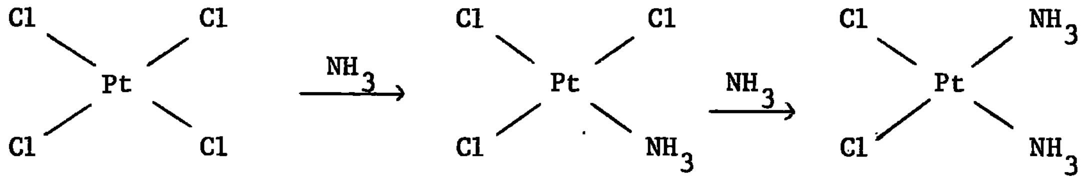


R = alkyl or aryl group.

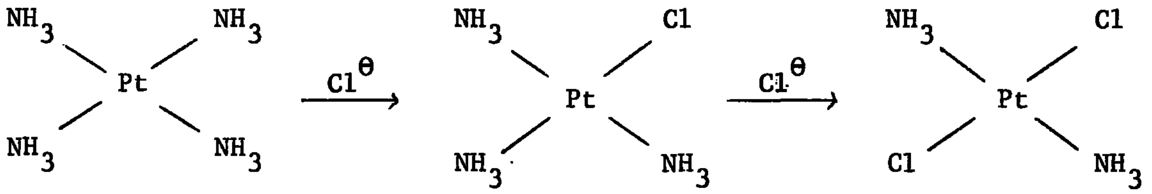
Although four is the usual coordination number for palladium and platinum(II) complexes there are some well-established cases of 5-coordination, the ions $[Pt(SnCl_3)_5]^{3-}$ and $[HPt(SnCl_3)_4]^{3-}$ being prime examples[19]. More recently[20] 'H n.m.r. evidence suggests 5-coordinate intermediates in ligand replacement reactions between palladium(II) and platinum(II) xanthates and thiocarbamates with methyldiphenylphosphine, when a phosphine adduct is formed as an intermediate prior to ligand substitution.

5. The Trans-Effect and Trans-Influence

The classification of ligands according to their trans-directing properties, i.e., their relative tendency to direct an incoming ligand into a position trans to themselves, for substitution in square planar platinum(II) complexes, has been established for some time[21]. This classification has been extended and the trans-effect defined as the tendency of "a group coordinated to a metal to direct an incoming group into a position trans to itself"[22]. The classic example of the trans-effect is the preparation of cis[23] and trans[24] isomers of the ion $[PtCl_2(NH_3)_2]^{2-}$. The cis isomer can be made by the action of ammonia on $[PtCl_4]^{2-}$:



However, if $[Pt(NH_3)_4]^{2+}$ is treated with chloride ions the trans isomer results:



It can be seen that substitution always occurs trans to a chloride ion, this can be rationalised by saying that chloride ion has a greater labilising effect on the group opposite than ammonia, i.e. Cl^- has a greater trans-effect than NH_3. By studies of similar substitution reactions, a series based on the effectiveness of a ligand to direct a substituent into a position trans to itself has been built up[25].

$$H_2O<OH<NH_3<\text{pyridine}<RNH_2<Cl^{\ominus}<Br^{\ominus}<I^{\ominus}<R_3P<CN^{-}\sim C_2H_4<CH_3<H$$

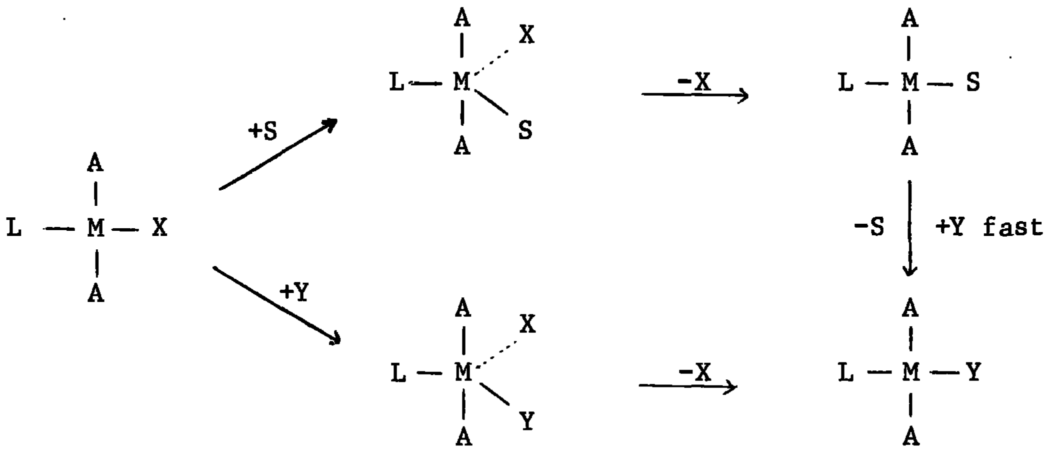
In order to obtain quantitative data on the trans-effect and to establish a mechanism of substitution reactions much work has been done on the kinetics of substitution reactions. The rate of substitution reactions of the type

$$Pt(A)_2LX + Y \longrightarrow Pt(A)_2LY + X$$

is given by the expression:

$$\text{Rate} = k_1[Pt(A)_2LX] + k_2[Pt(A)_2LX][Y].$$

k_1 is a first order rate constant for a solvent controlled reaction and k_2 is the second order rate constant for direct substitution by Y[26]. For an excess of Y the experimental first-order rate constant, k_{obs}, is given by $k_{obs} = k_1 + k_2[Y]$. This would require a plot of k_{obs} versus [Y] to be linear and for many substitution reactions of square planar complexes this is observed. This two-term rate law requires a two-path reaction mechanism which can be represented as follows:



S = solvent

That substitutions are bimolecular is supported by other experimental evidence:

1. Substitution occurs with retention of configuration.
2. Isolation of five and six coordinated systems.
3. Dependence of the rate of reaction on the entering reagent.
4. Steric effects on rates.

As the trans-effect is primarily kinetic, the influence of a group on various ground state observations is often described as the trans-influence to distinguish it from the kinetic trans-effect. How various ground state observations can be correlated to the trans-influence of groups will now be discussed.

(a) X-ray crystallography

If in complexes of the type PtA_2LX a change in the trans-influence of L gives a change in the Pt-X bond strength then a measure of the Pt-X bond strength should give a measure of the trans-influence of L. The determination of the Pt-X bond length by X-ray studies would thus give a measure of the Pt-X bond strength for changing L. X-ray studies have generally been used to establish structures of Pt(II) complexes, however, from the various systems studied there is some evidence to suggest that trends occur as L changes. For example, the compounds in Table 1, have been examined and the Pt-Cl bond length measured. From this, the order of trans-influence is $Si>H>P>C{=}C,\sim Cl>O$, roughly agreeing with the order of trans-effect of ligands. This data shows that the trans-influence of the ligand increases with decreasing electronegativity, this was also concluded by Chatt et al from infra-red data[22].

Table 1

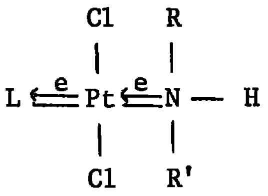
Molecule	Trans ligand	Pt-Cl bond length (Å)
$[Pt(acac)_2Cl]^-$	O	2.28 ± 0.01[27]
trans-$(PEt_3)_2PtCl_2$	Cl	2.30 ± 0.01[28]
$(C_{12}H_{17})_2Pt_2Cl_2$	C = C	2.31 ± 0.01[29]
cis-$(PMe_3)_2PtCl_2$	P	2.37 ± 0.01[30]
trans-$(PPh_2Et)_2PtHCl$	H	2.42 ± 0.01[31]
trans-$(PPhMe_2)_2Pt(SiPh_2Me)Cl$	Si	2.45 ± 0.01[29]

The crystal structure of trans-$(PEt_3)_2Pt(H)Br$ has been determined[32] and shows that the ligands are in a distorted square-planar arrangement. The Pt-Br distance, 2.56A, is longer than the sum of the atomic radii and also longer than the reported Pt-Br distance in trans-$(PEt_3)_2PtBr_2$[28] of 2.43A. This shows an increase in Pt-Br bond length for hydrogen trans to bromine compared with bromine trans to bromine, attributable to the high trans-influence of the hydride. The position of the Pt-H hydrogen atom was not revealed.

Recently the crystal structure of $Pt_2Cl_4(AsMe_3)_2$ has been reported[33] as dimeric with two platinum atoms unsymmetrically bridged by two chlorine atoms. The structure shows three types of chlorine atom: bridging trans to arsenic, bridging trans to chlorine and terminal trans to chlorine. The mutually trans Pt-Cl bond lengths of 2.268 and 2.312A are in reasonable agreement with other X-ray observations[28,34]. However the Pt-Cl bond length trans to arsenic of 2.39A approaches the value of 2.42A found in trans-$(PPh_2Et)_2PtHCl$[31], suggesting that the trimethylarsine ligand exerts a strong trans-influence.

(b) Infra-red Spectra

Chatt et al[35], in investigating the *trans*-influence of various ligands, studied the N-H stretching frequencies in complexes of the type *trans*-$[(NHRR')LPtCl_2.]$



$$L \xLeftarrow{e} \underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Pt}} \xLeftarrow{e} \underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{N}} - H \qquad \nu(N\text{-}H)\downarrow$$

Fig. 3

As the electron withdrawing power of L increases there is a movement of electrons as shown in fig. 3 causing the proton to be less strongly bonded to the nitrogen and hence resulting in a decrease in ν(N-H). The results showed a decrease in ν(N-H) as the ligand L was changed in the order

$$PR_3 > SbR_3 > P(OR)_3 > AsR_3 > TeR_2 > C_2H_4 > SeR_2 > SR_2$$

i.e. the Pt-N bond strength increased as the tendency of the ligand to donate electrons to platinum decreased. With the exception of ethylene the order roughly parallels the *trans*-effect order. A linear relationship between ν(N-H) and the electronegativities of the ligand atoms was also observed. The tertiary phosphines were anomalous however, and this was attributed to relatively strong π-bonding between platinum and phosphorus.

A more direct measure of the *trans*-influence of ligands was obtained by investigating the change in Pt-H stretching frequency with changing *trans* ligand[35,36] (see Table 2) in a series of complexes *trans*-$(PR_3)_2PtHX$. The decrease in ν(Pt-H), which gives a measure of the Pt-H bond strength, again parallels an order of increasing *trans*-effect. Values of ν(Pt-H)

Table 2

X	NO_3	Cl	Br	I	NO_2	SCN	CN
ν(Pt-H)cm^{-1}	2242	2183	2178	2156	2150	2112	2041

for hydride trans to a tertiary phosphine[37,38] suggest that the trans-influence of tertiary phosphines is similar to that of CN^-.

The far infra-red spectra of a series of compounds of the type cis- and trans- L_2PtX_2 (X = Cl or Br, L = neutral ligand), and trans- $(PEt_3)_2PtXR$[39] (X = Cl or Br, R = H, Me or Ph), have been recorded and the values obtained for ν(Pt-X) compared. The lowest values of ν(Pt-X) were found for the complexes trans-$(PEt_3)_2PtXR$ and the highest values of ν(Pt-X) for trans-L_2PtX_2 agreeing with results from platinum hydride complexes. They also show that hydride, methyl and phenyl ligands have a high trans-influence. Measurements of ν(Pt-Cl) in complexes containing a platinum-group-IVb bond[40,41] have shown that silicon and germanium organometallic groups have a very high trans-influence, but it has been found[42] that cis- and trans- $(PPh_3)_2PtCl(SnCl$ have the same infra-red spectra with ν(Pt-Cl) appearing at 315 $cm.^{-1}$ as a shoulder on the tin-chlorine stretching frequencies, suggesting that Ph_3P and $SnCl_3$ have similar trans-influences.

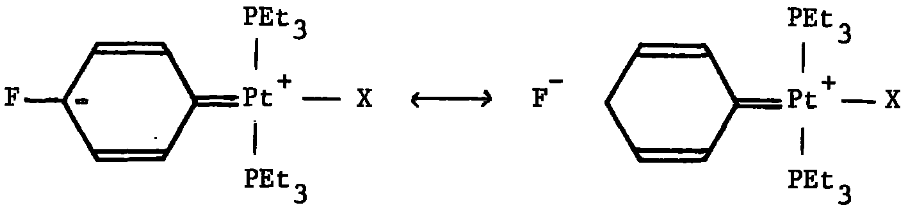
(c) N.m.r. spectra

The ^1H n.m.r. spectra for the series of compounds trans- $(PEt_3)_2PtLH$ (L = NO_3, Cl, Br, I, NO_2, SCN, $SnCl_3$, CN) have been recorded[19,36]. The resonance due to the hydridic proton is found at high-field (discussed on p. 43) and shows a large change in chemical shift with change in L.

e.g. L = NO_3 τ = 33.8
L = CN τ = 17.8

The gradual decrease in τ correlates with increasing trans-influence of L.

Parshall[43], using a series of fluorophenyl platinum complexes studied the ^{19}F n.m.r. in an attempt to estimate the σ and π-bond contributions to the trans-influence. The ^{19}F shielding parameters give a measure of the ability of the fluorophenyl group to compete with the ligand X for the electron density on the platinum. Electrons from X donated by an inductive effect increase the shielding of the ^{19}F nucleus in both the meta- and para-substituted compounds, but groups which donate or withdraw electrons by π-bonding can further shield or deshield the ^{19}F nucleus thus:



Therefore, by varying X and noting the change in the shielding parameters, σ and π contributions are obtained. The results provided data supporting the view that the trans-effect ligands are of two types: strong σ-donor ligands of low electronegativity such as H and CH_3, and strong π-bonding ligands such as CN and PR_3.

Trans-Effect Theory

No one theory has been put forward which can satisfactorily explain the trans-effect. The two main theories advanced are the polarisation or inductive theory and the mesomeric or π-bonding theory.

1. Polarisation theory

In a square planar platinum complex $LPtX_3$ the charge on the metal will induce a dipole in the ligand L, this will in turn, induce a dipole on the metal such that this second dipole will be unfavourable to a negative charge on X and will lead to repulsion between X and the metal atom thus weakening the metal-X bond.

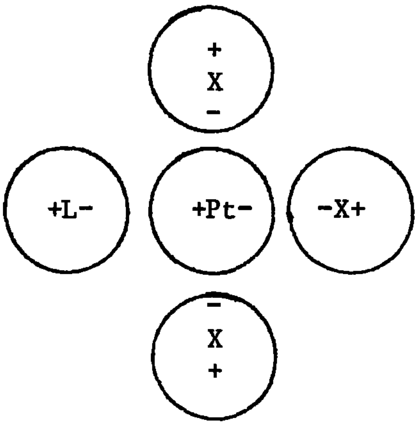


Fig. 4 Induced dipoles in $LPtX_3$

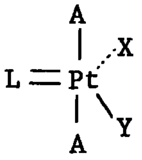
The dipole on X will only be induced provided that L is more polarisable than X. This theory accounts for the high trans-effect of hydride and methyl ligands where π-bonding cannot be invoked.

2. π-bonding theory

This theory proposes that ligands such as C_2H_4, PR_3 and CO are high in the trans-effect series because of their tendency to stabilise the transition state for a reaction by removal of electron density from the platinum through π-bonding. In a substitution reaction of the type

$$LPtA_2X + Y \longrightarrow LPtA_2Y + X$$

the transition state is believed to be trigonal bipyramidal in structure (p.8), Chatt[22] proposed that removal of charge from the platinum atom by π-bonding to the ligand L will encourage the addition of Y to form a five-coordinate intermediate.



An alternative approach was put forward by Orgel[44] in which he suggested that the stability of the intermediate was increased by the reduction of electron density in the Pt-X and Pt-Y directions by π-bonding. The theory is supported by experimental results such as retention of configuration and that Y and L will affect the rate of reaction. This theory explains why ethylene in trans-$Pt(C_2H_4)NH(CH_3)_2Cl_2$, although having a strong trans labilising effect, shows no Pt-N bond lengthening[45], i.e. large trans-effect but little trans-influence, the high trans-effect being due to stabilisation of transition states and not due to some ground-state effect. In the structure determination of Zeise's salt[46] some Pt-Cl bond lengthening was observed for the bond trans to ethylene, the difference between this and the lack of bond lengthening with platinum-nitrogen was explained by the fact that the platinum-chlorine bond may have some π-character and removal of electron density from the platinum by the ethylene will reduce the π-bonding in the Pt-Cl bond thereby causing bond lengthening. Nitrogen, however, has no vacant orbitals of suitable energy with which it can π-bond to the platinum and is thus not affected by the ethylene.

Recent ^{195}Pt n.m.r.[47] studies on a number of platinum phosphine halide complexes suggest that the high trans-influence of phosphorus is probably due to a σ-bonding mechanism. From theory, it can be concluded that a change in the platinum-phosphorus coupling constant reflects a change in the s-character of the Pt-P bond. The n.m.r. results show that the Pt-P bond is stronger in cis complexes than in trans for both Pt(II) and Pt(IV) complexes the difference being similar in both states, as dπ-dπ bonding is considered less important in Pt(IV) complexes a difference in bond strengths between the Pt(II) and Pt(IV) oxidation states would be expected if π-bonding formed a major contribution to the Pt-P bond, that no difference is observed suggests that the bonding between platinum and phosphorus is mainly σ-bonding.

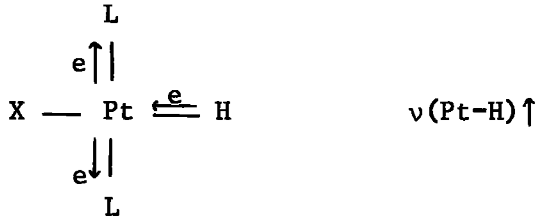
Gray and Langford[48], based a trans-effect theory on the size of M-L and M-X σ-overlap integrals in complexes of the type $LPtA_2X$. If the M-L σ-overlap > M-X σ-overlap then the M-L bond is strengthened whilst the M-X bond is weakened. These calculations gave a similar *trans*-influence order to that obtained from X-ray measurements (p. 9).

Summary

The *trans*-effect can be considered to be transmitted by an inductive effect, a mesomeric effect or a combination of both. The inductive effect is transmitted via 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 often referred to as the *trans*- influence. The π-bonding mechanism is transmitted through d-orbitals of the platinum and ligand orbitals which can be either d-orbitals or vacant π-orbitals. It operates by stabilisation of the transition state for a 5-coordinate intermediate though weakening of the *trans* bond can occur if the *trans* ligand is able to π-bond to the platinum.

Cis-Effect

The effect on Pt(II) systems of *cis* ligands is considered to be small. The influence of *cis* phosphines on the Pt-H stretching frequency was investigated[35] and ν(Pt-H) was found to rise as the electron withdrawing ability of the *cis* ligands increased (Table 3).



X = Cl

Table 3

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

The smallness of infra-red shifts[39] has prevented a satisfactory characterisation of the cis-influence of ligands, however the ^{35}Cl nuclear quadrupole resonance frequency of a coordinated chlorine is sufficiently sensitive to changes in the cis ligands and can give a measure of their cis-influence[49]. From the observed frequencies for a series of compounds trans- L_2MCl_2 M = Pd(II) or Pt(II) the M-Cl bond is weakened as the cis ligand L is changed from left to right:

For M = Pd^{II} L = PhCN, EtCN, n-Bu_3P, n-Bu_3As, pyridine, piperidine

For M = Pt^{II} L = n-Bu_3P, pyridine, $(CH_3)_2NH$, NH_3

i.e. the cis-influence increases left to right. This ground-state weakening of the M-Cl bond appears to assist nucleophilic substitution in trans-L_2PtCl_2 as the rate of substitution of chlorine by weak nucleophiles increases in a similar order[50] L = Et_3P < Et_3As < pyridine < piperidine. The cis-influence is virtually the reverse order of the trans-influence, a possible explanation is that in the trans-influence series

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

the π-acceptor abilities of the ligands increases left to right giving an increased trans-influence in the same order whereas the total charge donated by ligands (σ-donation - π-withdrawal) increases right to left therefore, for the ligands in a cis position the M-Cl band will become increasingly polarised and therefore weakened.

CHAPTER 2

ORGANIC DERIVATIVES OF PLATINUM

2.1 σ-Organocomplexes

Although methyl derivatives of Pt(IV) have been known for over fifty years[51], σ-bonded organo-derivatives of platinum(II) were first reported in 1957[52]. The thermal stability of the σ-bonded organo compounds decreases in the order Pt>Pd>>Ni and for variation of organic groups decreases Me>Et>Pr[53].

Metal carbon bonds are thought likely to dissociate by a radical dissociation[54], this could occur by transfer of an electron to an antibonding orbital in the M-C bond or promotion of one electron from the M-C bonding orbital. It would therefore appear that the energy difference, ΔE, between the highest energy bonding orbital and the unfilled orbital of lowest energy is the governing factor on the kinetic stability of the bond. As ΔE increases the M-C bond stability increases. Coordination of the metal with π-bonding ligands leads to greater stability as π-bonding between ligands and non-σ-bonding metal orbitals forms molecular orbitals of lower energy than the non-σ-bonding d-orbitals thereby increasing ΔE. All the known complexes L_2MRX and L_2MR_2 contain π-bonding ligands where L = tertiary phosphines or arsines, sulphur ligands, aromatic nitrogen ligands or olefins.

(i) Preparation

The alkyl and aryl derivatives are usually prepared by treating the halide with Grignard or organolithium reagents, e.g. (54, 55, 56, 57).

$$(R_3P)_2NiBr_2 + 2PhMgBr \longrightarrow (R_3P)_2NiPh_2 + MgBr_2$$

$$\underline{trans}\text{-}(Et_3P)_2PdBr_2 + MeMgBr \longrightarrow \underline{trans}\text{-}(Et_3P)_2PdMeBr + MgBr_2$$

$$\underline{trans}\text{-}(Ph_3P)_2PdBr_2 + 2MeLi \longrightarrow \underline{cis}\text{-}(Ph_3P)_2PdMe_2 + 2LiBr$$

$$(Et_3P)_2PtCl_2 + C_6F_5MgCl \longrightarrow (Et_3P)_2Pt(C_6F_5)Cl + MgCl_2$$

The monomethylplatinum derivative trans-$(Ph_3P)_2PtMeI$ can be prepared by the addition of methyl iodide to tris(triphenylphosphine)platinum(o)[54,55].

$$(Ph_3P)_3Pt + 2MeI \longrightarrow (Ph_3P)_2PtMeI + Ph_3PMeI$$

The ethyl complex, trans-$(Et_3P)_2Pt(Et)Cl$ has been made by reaction of bis(triethylphosphine)platinumhydridochloride with ethylene at 95°/45 atm.[36] In general, reactions between cis-platinum dihalides with two equivalents give the cis disubstituted derivatives and reaction of equimolar mixtures gives the trans monosubstituted derivatives. However, if cis-$(Et_3P)_2PtMe_2$ is distilled in vacuo the condensate contains the trans isomer[54]. Cis monosubstituted halomethyl derivatives can be obtained by cleavage of one methyl group from a disubstituted derivative using one equivalent of dry hydrogenhalide[54,55].

$$\text{e.g.}\qquad \text{cis-}(Et_3P)_2PtMe_2 \xrightarrow{HCl} \text{cis-}(Et_3P)_2PtMeCl$$

Some of the platinum(II) organic complexes will react further with halogens or alkylhalides to give octahedral platinum(IV) organic derivatives[54].

$$\text{e.g.}\qquad \text{trans-}(Et_3P)_2PtMeI + MeI \longrightarrow (Et_3P)_2PtMe_2I_2$$

$$\text{cis or trans-}(R_3P)_2PtPh_2 + I_2 \longrightarrow (R_3P)_2PtPh_2I_2$$

(ii) Properties

The dipole moments of many of the palladium and platinum derivatives have been measured in order to determine their stereochemistry. Cis complexes should have a high dipole moment and the trans derivatives zero dipole moments. An interesting phenomenon demonstrated by dipole moment measurements was the apparent isomerisation of cis-$(Et_3P)_2PdMe_2$ (dipole moment 4.68D.) to trans-$(Et_3P)_2PdMe_2$. After six months the dipole moment had dropped to 1.4D., indicating a cis→trans isomerisation was taking place[56].

The reactions of organic derivatives of nickel, palladium and platinum are generally of two types: those similar to inorganic platinum(II) complexes such as isomerisation and oxidation to platinum(IV) compounds and cleavage of the organic group.

(a) Reactions with hydrogen halides

As mentioned earlier (p. 19) cleavage of the organic group occurs with dry hydrogen halide, but the perfluoroaryl complex cis-$(Et_3P)_2Pt(C_6F_5)_2$ does not react with hydrogen chloride under the conditions which would cleave a non-fluorinated phenyl group[58].

(b) Reaction with hydrogen and reducing agents

The M-C bond is often cleaved by hydrogen under very mild conditions[36,59]

e.g. $\text{cis-}(Et_3P)_2PtClPh + H_2 \xrightarrow[1\ atm.]{20^o} \text{trans-}(Et_3P)_2PtHCl + C_6H_6$

$(\pi\text{-}C_3H_5)NiCH_3 + H_2 \xrightarrow{-40^o} CH_4 + C_3H_6 + Ni$

(c) Reaction with halogens and alkylhalides

Halogens either cleave the M-C bond or give an oxidative-addition reaction yielding an octahedral platinum(IV) derivative[54,55].

e.g. $\text{cis-}(Et_3P)_2PtMe_2 + Br_2 \longrightarrow \text{cis-}(Et_3P)_2PtBr_2 + 2MeBr$

$\text{trans-}(Et_3P)_2PtMeI + I_2 \longrightarrow \text{trans-}(Et_3P)_2PtI_2 + MeI$

$\text{cis or trans-}(Et_3P)_2PtPh_2 + I_2 \longrightarrow (Et_3P)_2PtPh_2I_2$

With iodine, methyl groups are cleaved whereas with phenyl groups octahedral complexes are obtained, chlorine however reacts by oxidative-addition in both the dimethyl and diphenyl cases to give octahedral platinum(IV) derivatives. Methyl iodide similarly gives an octahedral adduct[54]:

$\text{trans-}(Et_3P)_2PtMeI + MeI \longrightarrow (Et_3P)_2PtMe_2I_2$

(d) Reactions with metal halides

The platinum dimethyl complex $\underline{cis}\text{-}(Et_3P)_2PtMe_2$ reacts with magnesium iodide giving transfer of a methyl group to yield methyl Grignard reagent, $\underline{trans}\text{-}(Et_3P)_2PtI_2$ and $\underline{trans}\text{-}(Et_3P)_2PtMeI$[54]. This reaction gave evidence of the formation of an intermediate complex as an immediate precipitate was formed when the components were mixed though both reactants and final products were soluble in the solvent (diethylether). Stannous chloride also reacts with organoplatinum halides to produce platinum-tin compounds[19].

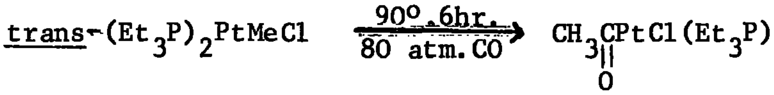
$$\underline{trans}\text{-}(Et_3P)_2Pt(C_6H_4F)Cl + SnCl_2 \longrightarrow \underline{trans}\text{-}(Et_3P)_2Pt(C_6H_4F)SnCl_3$$

(e) Other reactions

The insertion reaction by which $\underline{trans}\text{-}(Et_3P)_2PtEtCl$ is made can be reversed by heating the organo derivative to 180°.[36]

$$\underline{trans}\text{-}(Et_3P)_2PtEtCl \quad \xrightleftharpoons[95^{o}/45\ atm.]{180^{o}} \quad \underline{trans}\text{-}(Et_3P)_2PtHCl + C_2H_4$$

With carbon monoxide insertion reactions occur giving acyl derivatives[60]



$$\underline{trans}\text{-}(Et_3P)_2PtMeCl \quad \xrightarrow[80\ atm. CO]{90^{o}, 6hr.} \quad CH_3\underset{\underset{O}{\|}}{C}PtCl(Et_3P)_2$$

The palladium analogue carbonylates under much milder conditions requiring only 1 atmosphere pressure of carbon monoxide[60].

2.2 Olefin, Acetylene and π-allyl Complexes

Since the first olefin complex, $K^+\left[PtCl_3(C_2H_4)^-\right]$ was prepared in 1830[61] a large number of olefin, acetylene and π-allyl complexes have been reported, and have been described in detail in reviews[62,63,64].

(a) Olefin complexes

(i) Bonding

The bonding in transition metal-olefin complexes is believed to involve two types in which the metal forms σ- and π-bonds with the olefin

π-2p bonding and π^*-sp antibonding orbitals respectively[65].

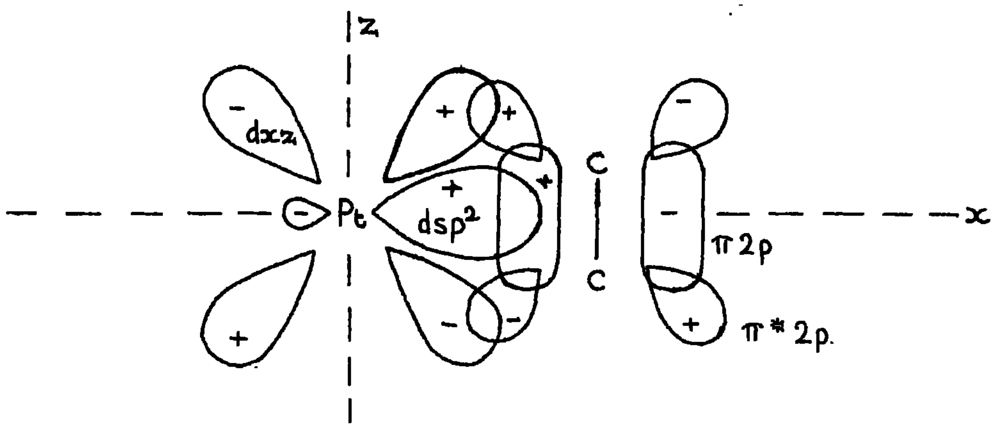


Fig. 5 Bonding in platinum-olefin complexes

(ii) Preparations

The treatment of a palladium(II) or platinum(II) complex with an olefin either refluxing or under pressure has been widely used for the preparation of olefin complexes of palladium and platinum[64].

The displacement of ligands such as benzonitrile from palladium and platinum(II) complexes is another commonly used route to olefin complexes[65];

$$2(PhCN)_2PdCl_2 + 2\ \text{olefin} \longrightarrow [\text{olefin}PdCl_2]_2 + 2PhCN$$

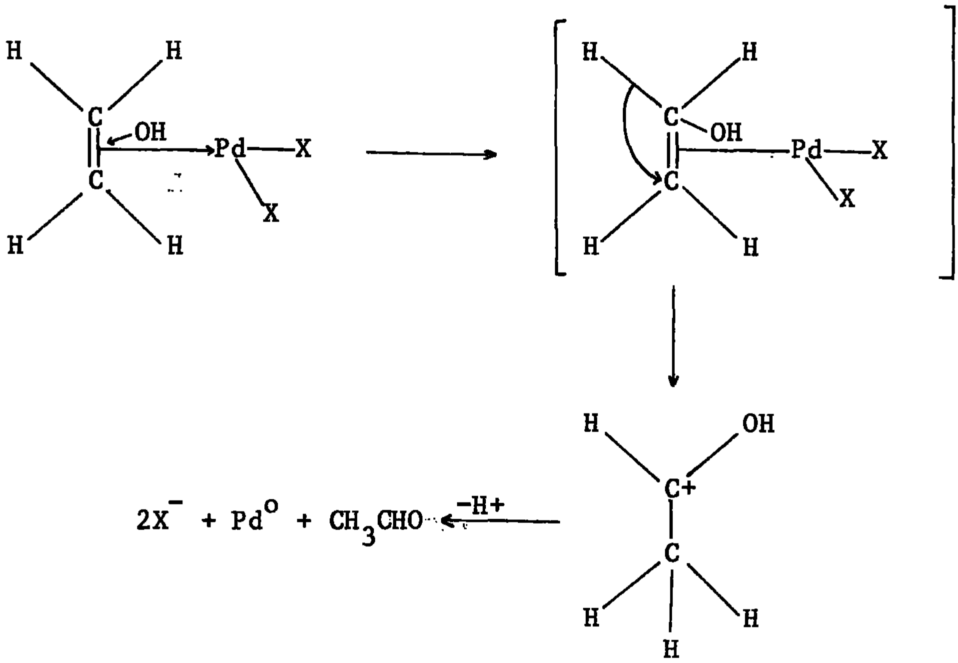
The use of zerovalent palladium and platinum compounds also provides a route to olefin complexes and a number of chloro-olefin derivatives have been prepared utilising this method[67].

$$(PPh_3)_4Pt + C_2Cl_4 \longrightarrow (PPh_3)_2Pt(C_2Cl_4)$$

This reaction worked successfully for trichloroethylene, 1,2-dichloroethylene and 1,1-dichloroethylene. Reduction of cis-$(PPh_3)_2PtCl_2$ with hydrazine followed by the addition of an olefin has led to the formation of olefin complexes with trans-stilbene and trans-4,4'-dinitrostilbene[68].

(iii) Chemical properties

The olefin complexes are susceptible to nucleophilic attack and the basis of the industrial conversion of ethylene to acetaldehyde is the nucleophilic attack by OH$^-$ on a palladium-olefin complex, a proposed mechanism[69] is illustrated below.



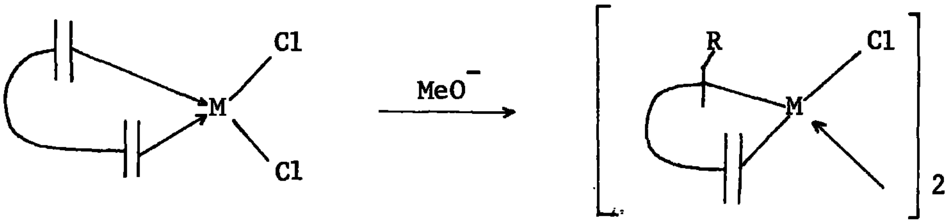
Usually aqueous solutions of $PdCl_2$ are treated with ethylene and the ethylene-palladium complex formed is hydrolysed giving acetaldehyde and palladium metal.

This process is not catalytic, but can be made continuous by oxidising the palladium metal with copper(II) chloride

$$Pd + 2Cu^{2+} + 6Cl^- \longrightarrow PdCl_2 + 2\left[CuCl_2\right]^-$$

$$2\left[CuCl_2\right]^- + 2H^+ + \tfrac{1}{2}O_2 \longrightarrow 2Cu^{2+} + 4Cl^- + H_2O$$

Another example of nucleophilic attack is the reaction of methoxide ion[71] on diolefin palladium and platinum complexes:



The complexes also react with carbon monoxide, alcohols and silanes but as these reactions have been extensively reviewed[64,70] they will not be described further.

(b) π-Allyl complexes

The three metals, nickel, palladium and platinum all form π-allyl complexes; nickel and palladium forming the largest number of π-allyl derivatives, by comparison platinum derivatives are relatively few.

(i) Bonding

The bonding in π-allyl complexes is similar to that in olefin complexes as the allyl group donates π-electrons to the metal in a σ-bond and accepts electrons from the metal d-orbitals into π*-antibonding orbitals.

(ii) Preparations

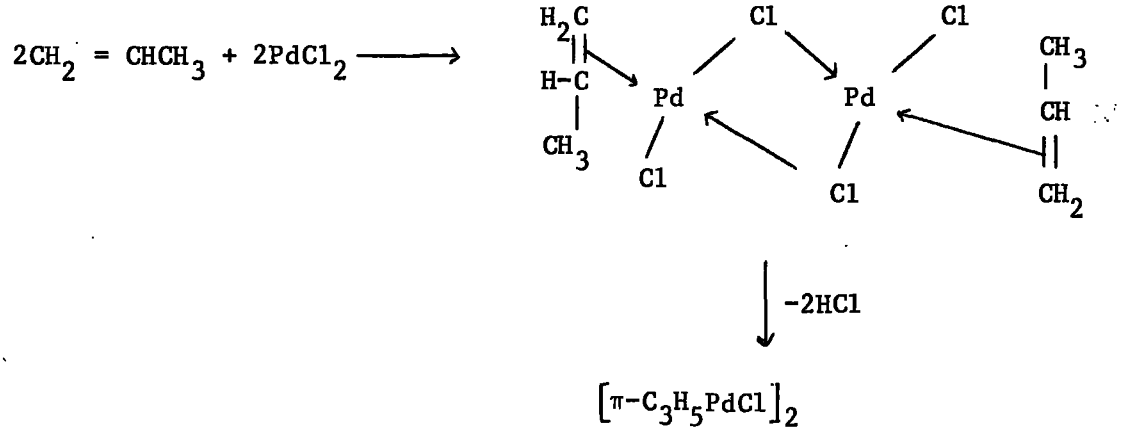
There are several methods available for the preparation of π-allyl complexes, one of the best is the treatment of a metal salt with a π-allyl Grignard reagent:

$$2C_3H_5MgBr + NiCl_2 \xrightarrow[-10^{o}]{\text{Diethyl Ether}} (C_3H_5)_2Ni \qquad 72$$

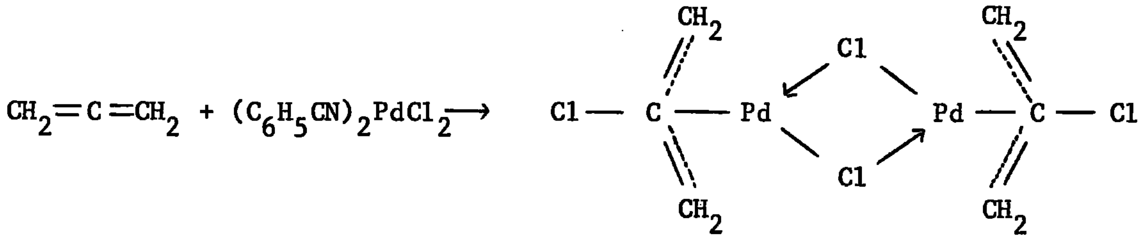
The reaction of allyl halides and alcohols with anionic metal salts also yields π-allyl-metal complexes:

$$Na_2PdCl_4 + CH_2{=}CH{-}CH_2{-}Cl \longrightarrow [\pi\text{-}C_3H_5PdCl]_2 \qquad 73$$

Other preparative methods include the reaction of olefins with a metal salt[74].



The displacement of benzonitrile from bis-benzonitrile palladium dichloride with allene has also been utilised to prepare π-allyl complexes[75]



Recently[76] a π-allyl acetylacetonate platinum complex, $[Pt_2(acac)_2(C_3H_5)_2]$, has been prepared from bis-π-allyl platinum and thallium acetylacetonate.

(iii) Reactions of π-allyl complexes

In general, the bis-π-allyl derivatives are more active than the chlorobridged complexes of the type $[\pi\text{-}C_3H_5MCl]_2$. Bis-π-allyl-nickel is highly reactive and undergoes reactions in which the π-allyl groups are displaced by ligands such as CO and tertiary phosphines[72].

e.g. $(\pi\text{-allyl})_2Ni + CO \longrightarrow \text{diallyl} + Ni(CO)_4$

$(\pi\text{-allyl})_2Ni + R_3P \longrightarrow \text{diallyl} + Ni(R_3P)_4$

Recently the bis-π-allyl palladium and platinum derivatives have been shown[77] to react with sulphur dioxide which is inserted into one of the π-allyl ligands:

$$(C_3H_5)_2Pt + SO_2 \longrightarrow C_3H_5Pt(SO_2CH_2CH=CH_2).$$

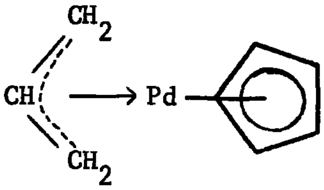
An important reaction of the π-allyl metal chloride dimers is with donor ligands such as amines and trialkylphosphines[78] when the halogen bridge is split to give monomeric products

$$[\pi\text{-}C_3H_5PdCl]_2 + 2Et_3P \longrightarrow 2(\pi\text{-}C_3H_5)PdClEt_3P$$

The dimers are also hydrolysed readily at room temperature[74].

$$[\pi\text{-}(C_3H_5)PdCl]_2 \xrightarrow{H_2O} CH_2=CHCHO + CH_2=CHCH_3 + 2Pd + 2HCl$$

Treatment of π-allylpalladium chloride with cyclopentadienyl-sodium gives π-allyl-π-cyclopentadienyl-palladium(II), its n.m.r. spectrum indicating a sandwich structure[79].



(iv) 'H nuclear magnetic resonance

The 'H n.m.r. spectra show three characteristic resonances as shown in Fig. 6[53].

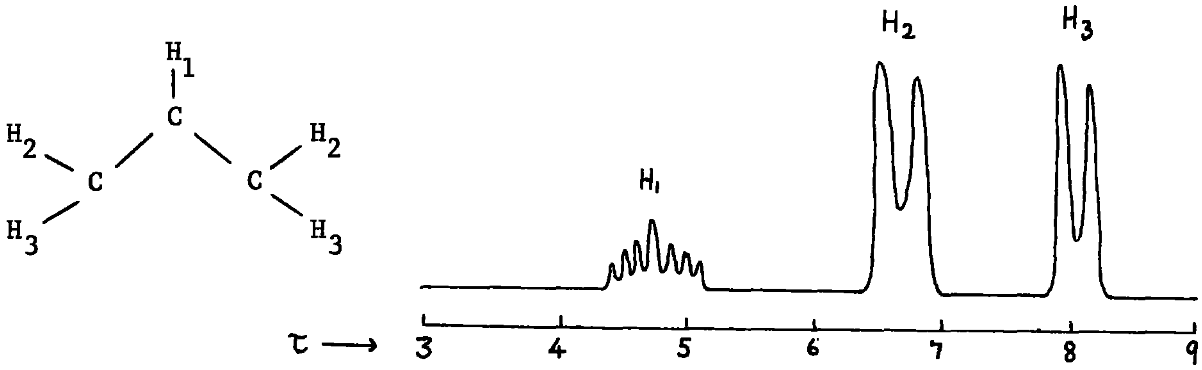
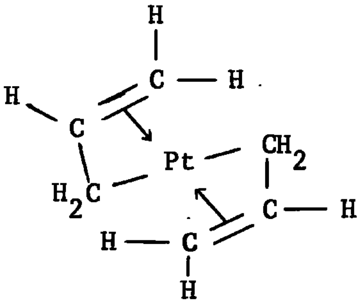
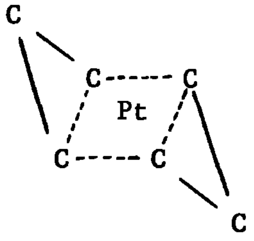


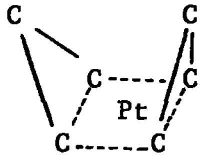
Fig. 6 Typical 'H n.m.r. of a π-allyl complex

Recent investigations at 220 MHz[77] suggest that the 'H n.m.r. spectra of bis-π-allylplatinum and palladium arise from an asymmetrical (σ-π) structure:





(I)



(II)

and not from an equilibrium mixture of the two isomeric forms (I) and (II) as previously believed[80].

(c) Acetylene Complexes of Nickel, Palladium and Platinum

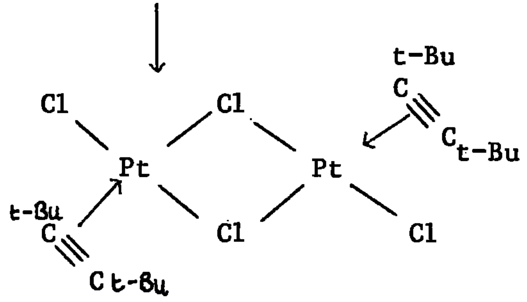
(i) Bonding

The bonding is believed to be similar to that in olefin-platinum derivatives where π-electrons are donated from the acetylene to the metal and back bonding occurs when electrons are donated from the metal d-orbitals into π* antibonding orbitals of the acetylene. The platinum-acetylene complexes are less stable than the ethylene derivatives.

(ii) Preparations

The acetylene complexes are prepared by methods analogous to the preparations of olefin complexes

e.g. $NaPtCl_4 + t\text{-}BuC\equiv Ct\text{-}Bu$ 81



Chatt and co-workers found that complexes of the above type were only stable when the acetylene had at least one tertiary carbon substituent.

$$(Ph_3P)_4Pd + PhC\equiv CPh \longrightarrow (PPh_3)_2Pd(PhC\equiv CPh) \qquad 82$$

CHAPTER 3

HYDRIDE COMPLEXES OF NICKEL, PALLADIUM AND PLATINUM

Since the discovery in 1957 of a platinum hydride[83] much work has been done on the preparation and properties of platinum hydrides but the first palladium hydride was not reported until 1965[84] with the first stable nickel hydride complex being prepared some four years later[85]. The time differences are, perhaps, some indication of the relative stabilities of the compounds, platinum hydrides being very much more stable than those of palladium and nickel.

Preparations

(1) From phosphine platinum halides

There are several methods available for the preparation of platinum hydrides the most general being the reduction of the halides, $(R_3P)_2PtX_2$, with a variety of reducing agents as will now be described. The *cis* phosphine halide complexes are generally preferred as starting material, being more reactive than the corresponding *trans* compounds due to the greater *trans*-effect of phosphine ligands compared with halides.

(a) Reduction of Hydrazine

The reduction of *cis*-$(Et_3P)_2PtCl_2$ and similar phosphine complexes with aqueous hydrazine gives good yields of the hydride *trans*-$(Et_3P)_2PtHCl$ with the evolution of nitrogen[36]. The first step in the reaction is the formation of a hydrazine complex:

$$\begin{tikzcd}
\underline{cis}\text{-}(Et_3P)_2PtCl_2 \arrow[r, "N_2H_4"] & {[(Et_3P)_2Pt(N_2H_4)Cl]Cl} \arrow[d, "N_2H_4"] \\
 & \underline{trans}\text{-}(Et_3P)_2PtHCl + NH_4Cl + N_2 + NH_3
\end{tikzcd}$$

The reduction works for *cis*-trialkyl and triaryl phosphine or arsine complexes, but the *trans*-dichloride complexes are not reduced by hydrazine.

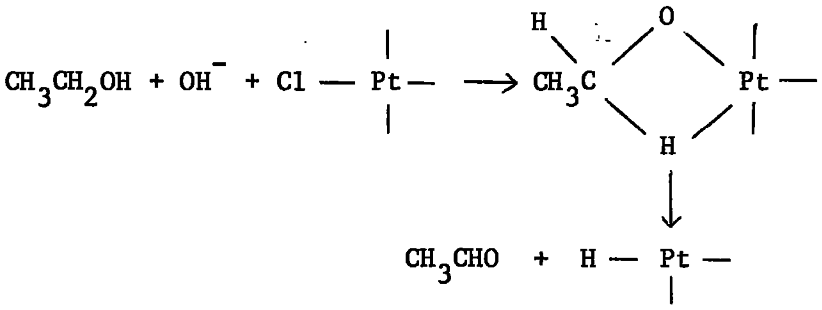
In contrast to the above reductions, $(Ph_3P)_2PtI_2$ with anhydrous hydrazine in ethanolic solution produced the zerovalent complex $(Ph_3P)_3Pt$[2].

(b) Reduction with Alcoholic KOH

On heating cis-phosphine platinum dihalides with alcoholic KOH the trans-phosphine hydridochloride is produced in good yield[36].

$$\text{cis-}(Et_3P)_2PtCl_2 + EtOH + KOH \longrightarrow \text{trans-}(Et_3P)_2PtHCl + CH_3CHO + KCL + H_2$$

Deuteration studies have shown that the proton is transferred from the α-carbon of the alcohol[86]. Chatt and Shaw[36] have suggested a possible mechanism involving an alkoxyplatinum complex.



As with the hydrazine reduction, triphenylphosphine derivatives tend to form zerovalent platinum complexes[2].

(c) Reduction with Formic Acid

This reaction is very similar to the ethanol reaction, trans-$(Et_3P)_2PtHCl$ being formed on heating cis-$(Et_3P)_2PtCl_2$ with formic acid[36].

(d) Reduction with Metal Hydrides

Chalk and Harrod[87] found that reactions of platinum(II) phosphine dihalide complexes with silanes fell into three categories:

(i) No reaction, as found with all except the trialkyl- and triarylsilanes.

(ii) Exchange between chloride of the platinum complex and hydride of the silane.

(iii) Reaction between bis(triphenylphosphine)platinum(II) dichloride and trialkyl- or triarylsilanes.

Only the second category of reactions yielded platinum hydrides according to the equation:

$$(R_3P)_2PtCl_2 + R'_3SiH \longrightarrow (R_3P)_2PtHCl + R'_3SiCl$$

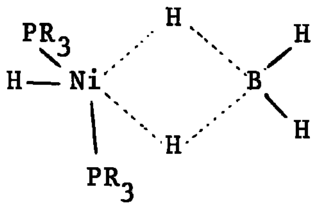
R = alkyl, R' = alkyl or aryl

These reactions were carried out by heating the platinum complex with the silane under nitrogen. With bis(triphenylphosphine)platinum(II) dichloride only a red polymeric material was obtained giving no indication of Pt-H.

The reduction of trans-$(Et_3P)_2PdCl_2$ with trimethylgermane at 40° yielded a palladium hydride[88], trans-$(Et_3P)_2PdHCl$, a free radical mechanism is believed to be involved. The reduction of trans-$(Et_3P)_2PdBr_2$ was slow in the absence of palladium black. No parallel to those reductions could be obtained using trimethylsilane though trans-$(Et_3P)_2PdCl_2$ after being sealed for four weeks with trimethylsilane showed evidence (infra-red) of the presence of a palladium hydride.

The purple nickel complex $(Et_3P)_2NiBr_2$ also reacted with trimethylgermane giving a brown solution from which colourless crystals were obtained at -20°. The nickel containing product was liquid at room temperature and its infra-red spectrum showed ν(Ni-H) at 1937 $cm.^{-1}$, but no pure product could be obtained[88]. Further evidence for the formation of a nickel hydride from this reaction was obtained later[89] when the 'H n.m.r. spectrum of $(Et_3P)_2NiBr_2$ sealed with Me_3GeH in benzene, showed a resonance at 31.7τ attributable to a nickel hydride. Lithium aluminium hydride has been used to prepare platinum hydrides[36] but is not a particularly satisfactory method due to the formation of some metallic platinum, it does, however, have the advantage that it will reduce both cis and trans phosphine platinum dihalides. Chatt and Shaw[90] applied this method to $(Et_3P)_2PdCl_2$ and although no pure product was isolated an infra-red frequency ascribable to ν(Pd-H) was observed.

Sodium borohydride in T.H.F.-ethanol (4:1) has been used to prepare a stable nickel hydride[85]. The reduction of bis(tricyclohexylphosphine)-nickeldichloride with sodium borohydride under argon produced a stable nickel hydride, trans-(bistricyclohexylphosphine)nickel hydridochloride. It was later shown[91] that this nickel hydride, when treated with sodium borohydride in a mixed acetone-ethanol solvent gave a crystalline complex formulated as (I)



R = cyclohexyl

I

This complex acts as a hydridic reducing agent and will reduce $(R_3P)_2MX_2$ (M = Ni or Pd) forming new hydride complexes. For R = Et, Pr^n or Bu^n and M = Ni, nickel hydride resonances in the 'H n.m.r. of the reaction solutions indicated the presence of both cis-and trans-$(R_3P)_2NiHX$ species.

(e) Reduction with Hydrogen

Gaseous hydrogen has been used in a number of cases to produce platinum hydrides though reaction conditions vary widely as can be seen from the examples:

$$\text{cis-}(Et_3P)_2PtCl_2 + H_2 \xrightarrow[50\ \text{atm.}]{95^o} \text{trans-}(Et_3P)_2PtHCl \qquad 36$$

$$\text{trans-}(Et_3P)_2PtCl(SiMe_3) + H_2 \xrightarrow[1\ \text{atm.}]{20^o} \text{trans-}(Et_3P)_2PtHCl + Me_3SiH \qquad 41$$

$$(\text{Diphos})Pt(GePh_3)_2 + H_2 \xrightarrow[100\ \text{atm.}]{50^o} (\text{Diphos})Pt(GePh_3)H + Ph_3GeH \qquad 37$$

The reaction of hydrogen with palladium complexes has however failed to give any pure palladium hydrides as products[93]. On reacting $(Et_3P)_2Pd(GePh_3)_2$

with hydrogen at one atmosphere extensive decomposition occurred but no hydridic species produced, hydrogenation at 100 atm. pressure did produce a residue showing infra-red bands attributable to ν(Pd-H) but no pure palladium-hydride product could be isolated.

(f) Reaction with Grignard and Lithio Reagents

It was observed during the reaction of cyclohexyl- and styrylmagnesium bromides with $\underline{\mathrm{cis}}$-$(Et_3P)_2PtCl_2$ that moderate yields of the hydride $\underline{\mathrm{trans}}$-$(Et_3P)_2PtHBr$ were obtained[55]. A re-examination[94] of this reaction concluded that a two stage process was involved with the formation of a platinum Grignard reagent by halogen-metal exchange.

$$\begin{tikzcd}
 & \underline{\mathrm{trans}}\text{-}\mathrm{(Et_3P)_2PtHBr} \\
\underline{\mathrm{cis}}\text{-}\mathrm{(Et_3P)_2PtBr_2} + \mathrm{C_6H_{11}MgBr} \arrow[r] & \mathrm{(Et_3P)_2Pt(MgBr)Br} \arrow[u, "\mathrm{H_2O}"] \arrow[d, "\mathrm{D_2O}"'] \\
 & \underline{\mathrm{trans}}\text{-}\mathrm{(Et_3P)_2PtDBr}
\end{tikzcd}$$

Similar halogen-metal exchange reactions have been observed between bistriethylphosphineplatinum(II)iodide complexes and triphenylgermyllithium[95].

$$\begin{tikzcd}
\mathrm{(Et_3P)_2PtI_2} + \mathrm{Ph_3GeLi} \arrow[r] & \mathrm{Ph_3GeI} + \mathrm{(Et_3P)_2PtLiI} \arrow[d, "\mathrm{H_2O}"] \\
 & \underline{\mathrm{trans}}\text{-}\mathrm{(Et_3P)_2PtHI}
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{(Et_3P)_2PtI(GePh_3)} + \mathrm{Ph_3GeLi} \arrow[r] & \mathrm{(Et_3P)_2Pt(GePh_3)_2} + \mathrm{(Et_3P)_2PtLi(GePh_3)} \arrow[d, "\mathrm{H_2O}"'] \\
 & \mathrm{(Et_3P)_2PtH(GePh_3)}
\end{tikzcd}$$

(2) From Zerovalent Platinum Complexes

The reaction of zerovalent platinum phosphine complexes with acids has produced a number of ionic platinum hydrides[14]. Tris(triphenylphosphine)-platinum(o) gave different reaction products depending on the acid or reaction medium used. Reaction of aqueous or dilute alcoholic acid with a suspension of the platinum complex produced an ionic platinum(II) hydride according to the equation:

$$(Ph_3P)_3Pt + HX = [(Ph_3P)_3PtH]^+X^-$$

$$X^- = ClO_4^-,\ BF_4^-,\ HSO_4^-\ ,\ CH_3OSO_3^-$$

Conductance data agreed with their formulation as 1:1 electrolytes. When gaseous HX ($X^- = Cl^-$, CN^-) was bubbled through a benzene solution of the zerovalent platinum complex no ionic hydride was produced, only a diamagnetic, non-conducting hydride:

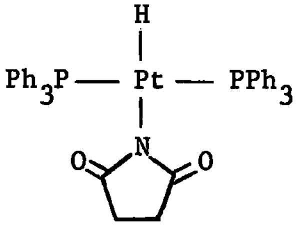
$$(Ph_3P)_3Pt + HX = (Ph_3P)_2PtHX + Ph_3P$$

Aqueous HCl and HNO_3 gave hydrides but the conductance data were low for a 1:1 electrolyte, It rose however, to the correct value on the addition of excess triphenylphosphine, this was explained by an equilibrium reaction:

$$(Ph_3P)_2PtHX + Ph_3P \rightleftharpoons [(Ph_3P)_3PtH]^+\ X^-$$

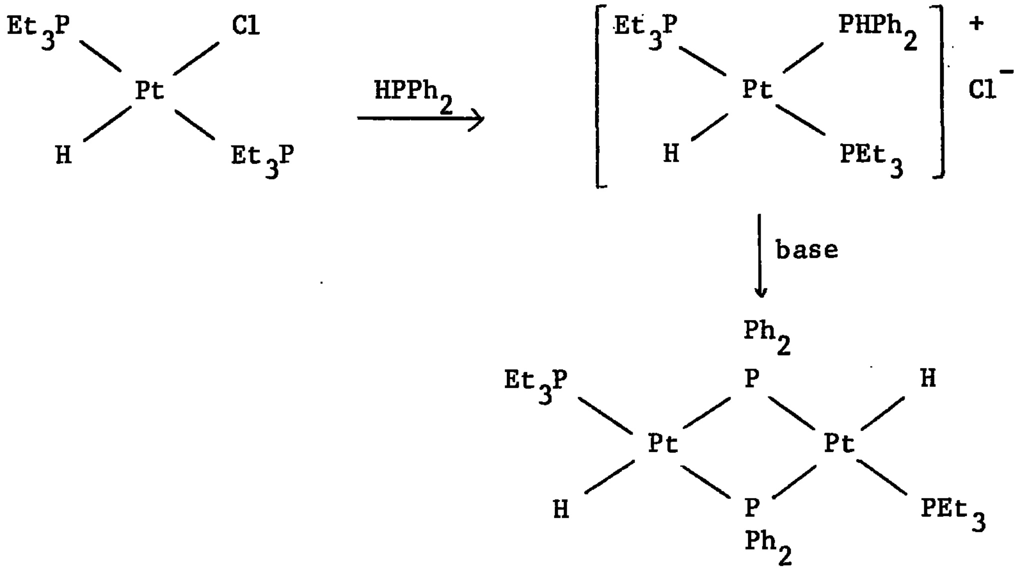
Thus it seems that when X is an anion of low coordinating power ionic hydrides are formed and if X has a high coordinating power covalent hydrides are produced. For ions, such as Cl^-, NO_3^-, of intermediate coordinating power either ionic or covalent hydrides were formed according to reaction conditions. Palladium and nickel zerovalent compounds gave no hydridic species in analogous reactions, similarly the reaction of bis(1,2-bisdiphenylphosphinoethane)platinum(o) with acids produced no Pt-H bonds but formed platinum(II) salts of the type $[(Ph_2PCH_2CH_2PPh_2)_2Pt]^{2+}2X^-$

Platinum hydrides have also been formed by the oxidative-addition of hydrogen cyanide and 1-ethynylcyclohexanol to zerovalent phosphine platinum derivatives[96]. It has now be shown that some imides can be oxidatively added to tetrakis(triphenylphosphine)platinum(o) to give, in good yield, imide-hydride complexes of platinum.[96a] Derivatives characterised have been prepared from succinimide, phthalimide and saccharin. From the 'H n.m.r. a trans configuration is postulated:



(3) By Ligand Exchange

These ligand exchange reactions convert one hydrido platinum complex into another, for example, trans-$(Et_3P)_2PtHCl$ can be converted into the analogous bromide, iodide, cyanide, cyanate, thiocyanate and nitro complexes by solutions of the appropriate alkali-metal salt[36]. A binuclear dihydride has been prepared[18] by a ligand exchange reaction on trans-$(Et_3P)_2PtHCl$:



Similarly a platinum-tin complex, trans-$(Et_3P)_2PtH(SnCl_3)$ has been prepared by adding stannous chloride to the analogous hydridochloride[19].

The addition of a chelating phosphine (1,2-bisdiphenylphosphinoethane) to $\underline{trans}$-$(Et_3P)_2PtHCl$ has recently been shown[97] to result in a cationic hydride.

$$\underline{trans}\text{-}(Et_3P)_2PtHCl + \text{diphos} \xrightarrow{C_6H_6} [(\text{diphos})Pt(Et_3P)H]^+Cl^- \qquad \text{(II)}$$

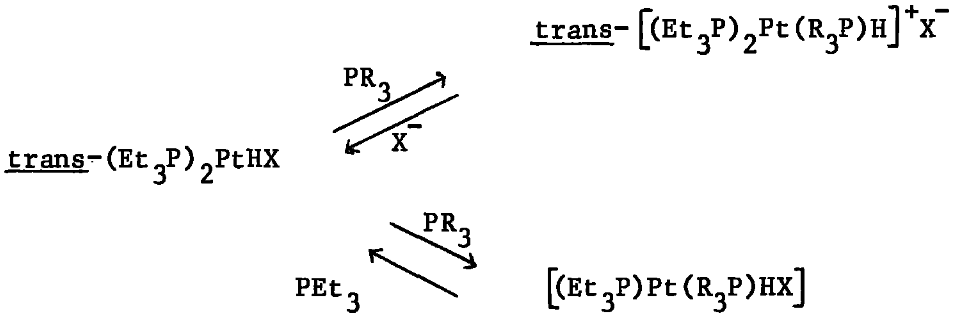
diphos = 1,2-bisdiphenylphosphinoethane

Complex II had previously been prepared[38] by the hydrogenation of $[(\text{diphos})Pt(MMe_3)PEt_3]^+Cl^-$, M = Si or Ge. Addition of stannous chloride to II converts the anion to $SnCl_3^-$ leaving the cation unaffected . The use of monodentate phosphine ligands instead of a chelating ligand also results in cationic hydrides analogous to II.

$$\underline{trans}\text{-}(Et_3P)_2PtHX + PR_3 \xrightarrow[C_2H_4Cl_2]{C_6H_6\ \text{or}} [(Et_3P)_2Pt(R_3P)H]^+X^-$$

$(X = Cl \text{ or } CN,\ R_3 = Et_3,\ Bu_3,\ EtPh_2 \text{ or } Ph_3)$

When R = Bu or Ph the replacement of X in dichloroethane is accompanied by a slower, partial displacement of triethylphosphine. An equilibrated mixture ($Pt:PPh_3 = 1$) displayed a slight decrease in conductivity with time, a simultaneous change in $\nu(Pt-H)$ also being observed, thus the reaction can be summed up as two equilibria as follows:



Cationic platinum(II) hydrides have also resulted from ligand exchange reactions of trans-$(Et_3P)_2PtHCl$ in the presence of sodium perchlorate[98] or tetraphenylborate[99].

$$\text{trans-}(Et_3P)_2PtHCl \xrightarrow[NaClO_4]{L} \text{trans-}[(Et_3P)_2PtHL]^+ClO_4^-$$

(L = CO, Ph_3P, Et_3P, $(MeO)_3P$, $(PhO)_3P$, Me_3CNC).

The values obtained for ν(Pt-H) and the chemical shift of the hydrides gave an indication of the trans-influences of the ligands.

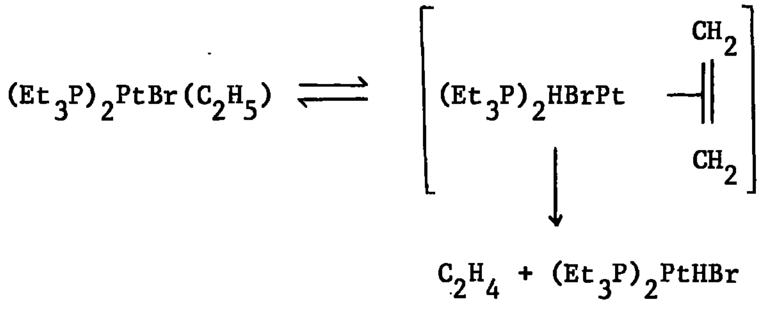
(4) Miscellaneous Preparations

(a) Pyrolysis of organoplatinum complexes

Chatt and Shaw[36] demonstrated that trans-$(Et_3P)_2PtHCl$ could be obtained by heating the ethyl derivative trans-$(Et_3P)_2PtClEt$, ethylene being eliminated. The reaction is in fact an equilibrium:

$$\text{trans-}(Et_3P)_2PtClEt \xrightleftharpoons[95^\circ/40\ \text{atm.}]{180^\circ} \text{trans-}(Et_3P)_2PtHCl + C_2H_4$$

Deuterium studies[92] on this reaction show that the platinum hydride originates from both the α and β carbon atoms of the ethyl group. The action of heat on trans-$(Et_3P)_2Pt(CD_2CH_3)Br$ evolves a mixture of platinum hydride and deuteride in proportions not significantly different from the statistical ratio (1.5:1). This hydrogen-deuterium scrambling is consistent with the carbon atoms of the ethyl group being symmetrically placed with respect to the platinum atom in the transition state



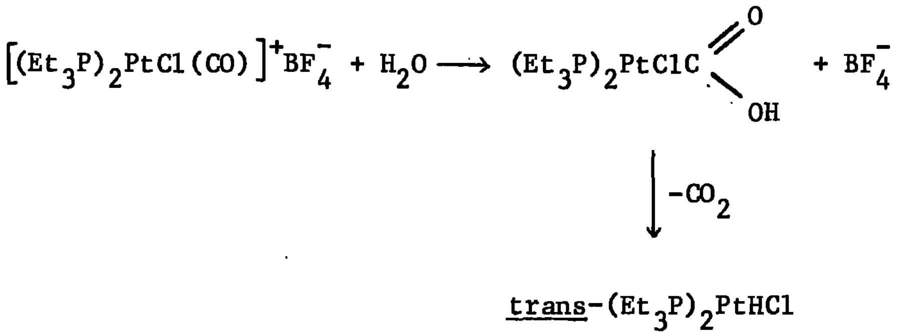
$$(Et_3P)_2PtBr(C_2H_5) \rightleftharpoons \left[(Et_3P)_2HBrPt - \overset{CH_2}{\underset{CH_2}{\|}}\right] \longrightarrow C_2H_4 + (Et_3P)_2PtHBr$$

(b) Cleavage of group-IVb derivatives

The cleavage of platinum-group-IVb bonds by HCl and H_2 has led to the formation of platinum-hydride complexes. These reactions will be treated later as reactions of platinum-group-IVb derivatives.

(c) From carbonyl derivatives

Platinum hydridohalides, trans-$(R_3P)_2PtHX$, X = halide, R = Et or Ph, have been prepared[100] from cationic carbonyl complexes, trans-$[(R_3P)_2PtXCO]^+BF_4^-$. The carbonyl complexes which can be synthesised by a variety of routes,[98,99] can be hydrolysed to give good yields of the hydridohalide. The reaction is thought to proceed via a carboxylic acid:



$$[(Et_3P)_2PtCl(CO)]^+BF_4^- + H_2O \longrightarrow (Et_3P)_2PtClC\begin{matrix}{}^{\diagup\!\!\diagup O}\\ {}_{\diagdown OH}\end{matrix} + BF_4^-$$

$$\big\downarrow -CO_2$$

$$\text{trans-}(Et_3P)_2PtHCl$$

A novel palladium hydridocarbonyl has resulted from the reaction of palladous chloride and carbon monoxide in alcoholic solution[101].

$$PdCl_2 + CO \longrightarrow [PdH(CO)Cl_2]^-$$

The addition of triphenylarsine to the solution afforded the neutral carbonyl complex $[PdCO(AsPh_3)Cl_2]$ with no hydridic species.

Properties of the Hydrides

(1) Stability

The stability of the hydrides of nickel, palladium and platinum varies enormously, the trans-hydridoplatinum(II) complexes are air and water stable whereas palladium and nickel hydrides are much less stable, decomposing in solution, and $(Et_3P)_2PdHCl$ decomposes above 55° in a nitrogen atmosphere. The nickel hydride, bis(tricyclohexylphosphine)nickelhydridochloride decomposes within minutes when a solution is exposed to air[85]; the solid form is, however, stable in air over several hours. The high stability of this hydride relative to other tertiary phosphine nickel derivatives is believed due to the bulky tricyclohexylphosphine groups hindering rearrangement of the square-planar form to a tetrahedral arrangement and also limiting attack of other molecules.

The lower alkylphosphine derivatives of platinum are surprisingly volatile and thermally stable[36], trans-$(Et_3P)_2PtHCl$, for example, can be sublimed at $75^{o}/10^{-2}$mm.

(2) Chemical Reactions

The reactions of platinum hydrides can be generally regarded as being of two types:

(a) those similar to normal platinum(II) complexes such as ligand exchange, oxidation to platinum(IV) derivatives and isomerisation;

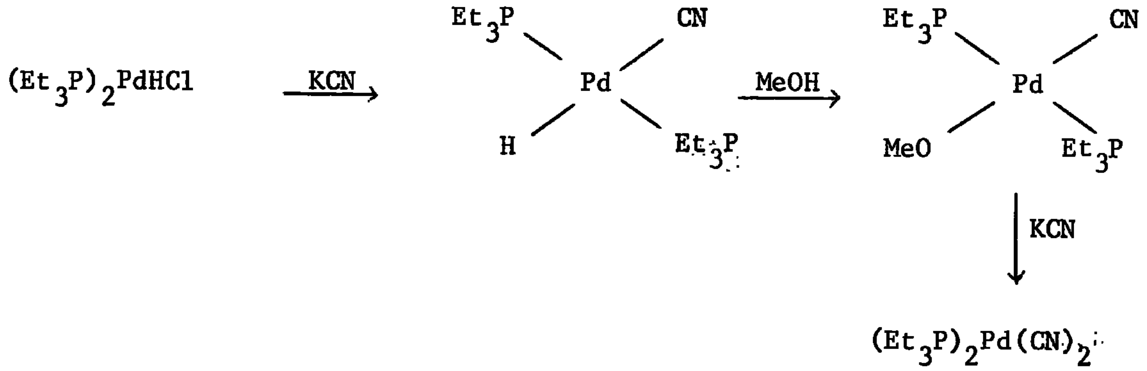
(b) those involving the hydride directly such as reductions and additions to unsaturated compounds.

Many of the ligand exchange reactions where a new hydride complex is produced have already been discussed (p. 34). The hydride can be replaced in some reactions to give cationic complexes[98,100], addition of water to the cationic derivatives yields the original hydrido complex:

$$\begin{tikzcd}
\underline{\text{trans}}\text{-}(Et_3P)_2PtHCl + CO + HBF_4 \arrow[r, "120^{o}", "C_6H_6"'] & \underline{\text{trans}}\text{-}\left[(Et_3P)_2PtCl(CO)\right]^{+}BF_4^{-} \arrow[d, "H_2O"] \\
 & \underline{\text{trans}}\text{-}(Et_3P)_2PtHCl + CO_2
\end{tikzcd}$$

$\left[(Et_3P)_3PtH\right]^{+}X^{-}$ ($X^{-} = Cl^{-}$ or CN^{-}) does not however react with carbon monoxide[97]. It is a general feature of σ-bonded platinum-hydride and -carbon complexes that the most stable derivatives occur when the platinum atom is bonded to strong π-accepting groups (p. 18) which can remove negative charge from the metal, thus one would expect positively charged σ-bonded platinum complexes to be more stable than neutral complexes.

The palladium hydride $(Et_3P)_2PdHCl$ reacted with potassium iodide to give the corresponding iodide, with potassium cyanide, in methanol however, the straightforward exchange was not observed, the final product being the dicyanide derivative[93]. The reaction was believed to proceed via the hydridocyanide derivative.



The oxidative-addition of hydrogen chloride to trans-$(Et_3P)_2PtHCl$ has resulted in an octahedral dihydride complex[36] which can be reverted to the hydridochloride by heat or water. A similar reaction occurs for the triphenylphosphine analogue[14].

Deuterium oxide with a catalytic amount of hydrogen chloride reacts with trans-$(Et_3P)_2PtHCl$ replacing the hydride thus[36].

$$\underline{\text{trans}}\text{-}(Et_3P)_2PtHCl + D_2O \longrightarrow \underline{\text{trans}}\text{-}(Et_3P)_2PtDCl$$

The role of the hydrogen chloride is believed to be to produce platinum(IV) intermediates[102] such as $(Et_3P)_2PtHDCl_2$, elimination of HCl then produces the deuteride.

The platinum hydrides are mild reducing agents, MeI, EtI, n-BuBr, CCl_4 and $CHCl_3$ all react with trans-$(Et_3P)_2PtHCl$ to give the corresponding dihalide[36]. Carbon tetrachloride undergoes an analogous reaction with $(Et_3P)_2PdHCl$ to give the palladium dihalide and chloroform[93]. Cleavage of the Pt-H bond also occurs with halogens[36], again giving the platinum dihalide complex.

Hydride derivatives of platinum are known to react with group-IVb compounds to give platinum-metal bonds, for example, trans-$(Ph_3P)_2PtHCl$ reacts with stannic chloride to give the platinum(IV) complex $(Ph_3P)_2PtCl_2(SnCl_3)_2$[42]. Trichlorosilane and triarylsilanes react with trans-$(PhMe_2P)_2PtHCl$ to give trans-$(PhMe_2P)_2PtClSiR_3$, this provides a useful route for the synthesis of platinum-silicon complexes[103].

An important and interesting class of reactions of the hydrides is their reaction with unsaturated organic compounds. The reaction of trans-$(Et_3P)_2PtHCl$ with ethylene has already been discussed. Hex-1-ene reacts with trans-$(Et_3P)_2PtHCl$ only under forcing conditions (22 hours at 180°) when 22% is converted to the hex-2-ene[104], however in the presence of hydrochloric or perchloric acid in ethanol trans-$(Et_3P)_2PtHCl$ will reduce olefins to the corresponding alkane[105]. The reduction has been carried out for hex-1-ene, cyclohexene, oct-1-ene and 2-methyl-2-butene. No hex-2-ene was produced during the course of the reaction. The proposed reaction mechanism can be seen in Fig. 7.

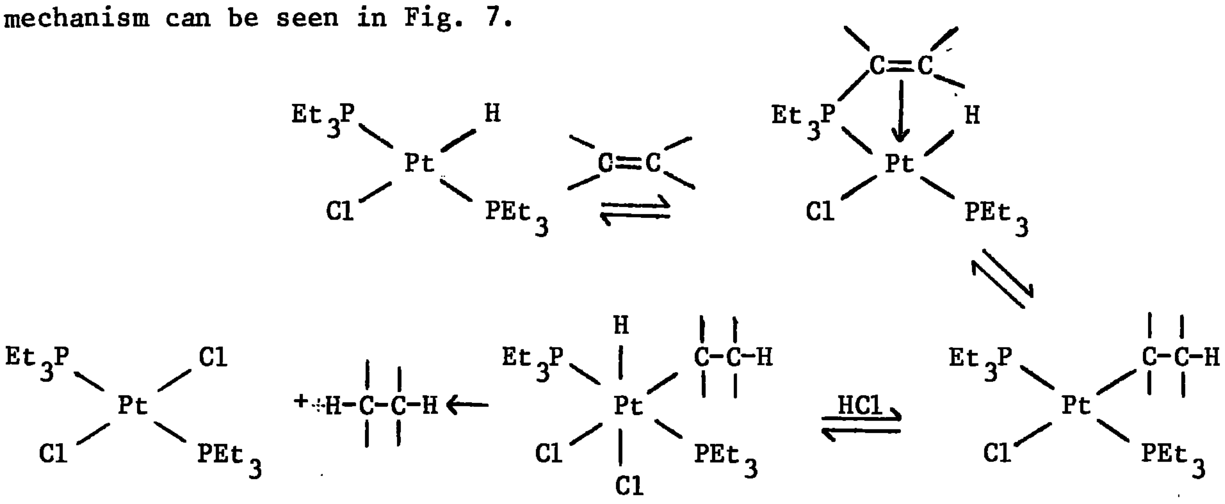


Fig. 7

The reaction was investigated kinetically under pseudo-first-order conditions by using an excess of all other reactants with respect to the metal complex concentration. The data thus obtained indicated that the pseudo-first-order rate constants were dependent on the concentration of mineral acid, chloride ion and olefin. The dihydride $(Et_3P)_2PtH_2Cl_2$ was found[36] to be ineffective towards olefin hydrogenation. Perfluoro-olefins react differently, eliminating HF to produce fluorovinyl derivatives[106].

$$\underline{\text{trans}}\text{-}(Et_3P)_2PtHCl + C_2F_3H \longrightarrow \underline{\text{trans}}\text{-}(Et_3P)_2Pt(CF = CFH)Cl + HF$$

In an analogous reaction an olefin intermediate complex was detected.

$$\begin{array}{ll} \underline{\text{trans}}\text{-}(Et_3P)_2PtHCl + C_2F_4 \longrightarrow & (Et_3P)_2PtHCl(C_2F_4) \\ & \qquad\downarrow \\ & \underline{\text{trans}}\text{-}(Et_3P)_2Pt(CF = CF_2)Cl + HF \end{array}$$

Reactions of tetracyanoethylene with the complexes *trans*-$(R_3P)_2PtHX$ R = Et, X = Cl, Br, I, NO_2, CN, NCO; R = Ph, X = Cl, Br, I, CN, have been studied[107]. $(R_3P)_2Pt(C_2CN_4)$ was obtained in good yield for X = Cl and Br but only in trace amounts or not at all for other X groups. Kinetic data obtained indicated a 1:1 adduct forming as an intermediate. Fig. 8 depicts a possible reaction mechanism:

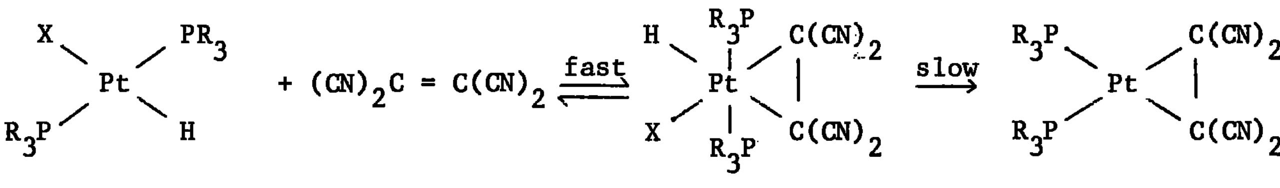
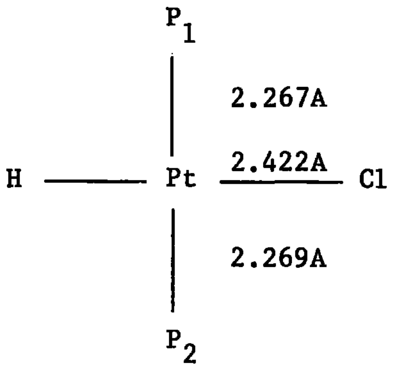


Fig. 8

Tetrachloroethylene behaves differently leading to $(Et_3P)_2PtCl_2$[106]. A useful synthetic route to arylplatinum derivatives has been devised from the ability of *trans*-hydridoplatinum complexes to add to aryldiazonium compounds, treatment of the resulting salts with base produces azoplatinum complexes which on the addition of neutral alumina liberate nitrogen to yield the arylplatinum derivative[108].

(3) Structure Determination

For the series of compounds trans-$(R_3P)_2PtHX$ infra-red and nuclear magnetic resonance data support a square-planar arrangement of the ligands about the platinum. The structures of trans-$(Et_3P)_2PtHBr$ and trans-$(Ph_2EtP)_2PtHCl$ have been determined by X-ray studies[32,31]. Both structure determinations show that the phosphorus atoms are trans to each other and together with the chlorine (or bromine) atom lie at three of the four corners of a distorted square. The hydride is assumed to be at the fourth corner as its position has not been determined.



Bond Angles

P_1 - Pt - Cl	92.6°
P_2 - Pt - Cl	94.5°
P_1 - Pt - P_2	188.8°

The Pt-Cl distance is longer than that predicted by the sum of the covalent radii (2.30A), consistent with the high trans-influence of the hydride. Similarly in trans-$(Et_3P)_2PtHBr$ the Pt-Br bond distance is greater than that predicted by radii sum calculations. During the structure determination the hydridobromide, which was mounted in air, was found to be sensitive to X-rays and thus not allowing as greater refinement as was achieved for the hydridochloride.

Infra-red Spectra

The metal-hydrogen stretching frequency is very characteristic of transition metal hydrides. The values for ν(M-H) vary, depending on the ligands attached to the metal, but are usually in the 1,900 to 2,200 cm.$^{-1}$ region for nickel, palladium and platinum. Typical values are given in Table 4.

Table 4

Compound	ν(M-H) cm^{-1}	Reference
trans-$(Et_3P)_2PtHCl$	2183	36
trans-$(Ph_3P)_2PtHCl$	2235	40
(Diphos)PtH$(GePh_3)$	1998	37
$[(Diphos)PtHPEt_3]^+Cl^-$	2043	38
trans-$(Et_3P)_2PdHCl$	2035	88
trans-$(Et_3P)_2PdHI$	2004	88
$[(C_6H_{11})_3P]_2NiHCl$	1916	85

As can be seen from the table, for variation of the metal down the group there is an increase in ν(M-H) implying an increase in metal-hydrogen bond strength on going from nickel to platinum.

The value of ν(M-H) is particularly dependent on the other ligands bonded to the metal atom, with ν(M-H) decreasing as the trans-influence of the group trans to the hydride increases.

Nuclear Magnetic Resonance

The high-field resonance of the metal bonded hydride can, in many cases, allow the stereochemistry of the complex to be unambiguously assigned. The hydridic protons show a large chemical shift to high field, generally in the 15-35τ region. The large chemical shifts have been explained by paramagnetic shielding of the proton by the d-electrons of the transition metal[110]. According to this theory the paramagnetic shielding constant and hence τ is most significantly changed by changes in the distance the proton is from the metal atom. The variation in τ with trans ligands can thus be explained by changes in Pt-H bond length associated with changes in the ligands.

In the complexes, trans-$(R_3P)_2PtHX$, the hydride resonance appears as three triplets[36]. The molecule contains two equivalent ^{31}P nuclei (spin = ½, 100% abundant) which couple with the hydride and split the resonance into a 1:2:1 triplet, the coupling constant $J(^{31}P\text{-}H)$ being in the region of 15Hz. This triplet is further split by the ^{195}Pt nucleus (spin = ½, 33.8% abundant) giving two triplet systems, one upfield and one downfield of the central triplet, (the isotopes not of spin ½ leave this central triplet unsplit), thus the overall hydride resonance occurs as three triplet systems in the ratio of 1:4:1.

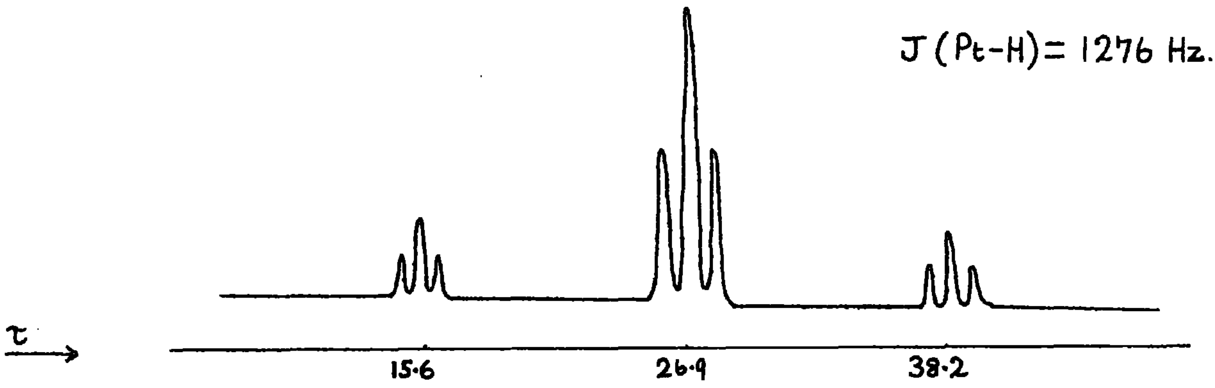


Fig. 9 Hydride resonance of trans-$(Et_3P)_2PtHCl$

The corresponding arsine complexes however, show only a triplet due to coupling with the ^{195}Pt nucleus[109]. The coupling constant $J(^{195}Pt\text{-}H)$ is very large being about 1200 Hz, for both phosphine and arsine complexes.

Trans-$(Et_3P)_2PdHCl$ showed the hydride as a singlet resonance, in contrast to the platinum analogues coupling with the ^{31}P nucleus was not observed[88], presumably because of reversible dissociation of triethyl phosphine in solutions of the complex. The hydride resonance in the 'H n.m.r. spectrum of $[(C_6H_{11})_3P]_2NiHCl$ appeared as a triplet at τ34.6, again coupling with the ^{31}P nuclei is observed and a trans configuration assigned[85].

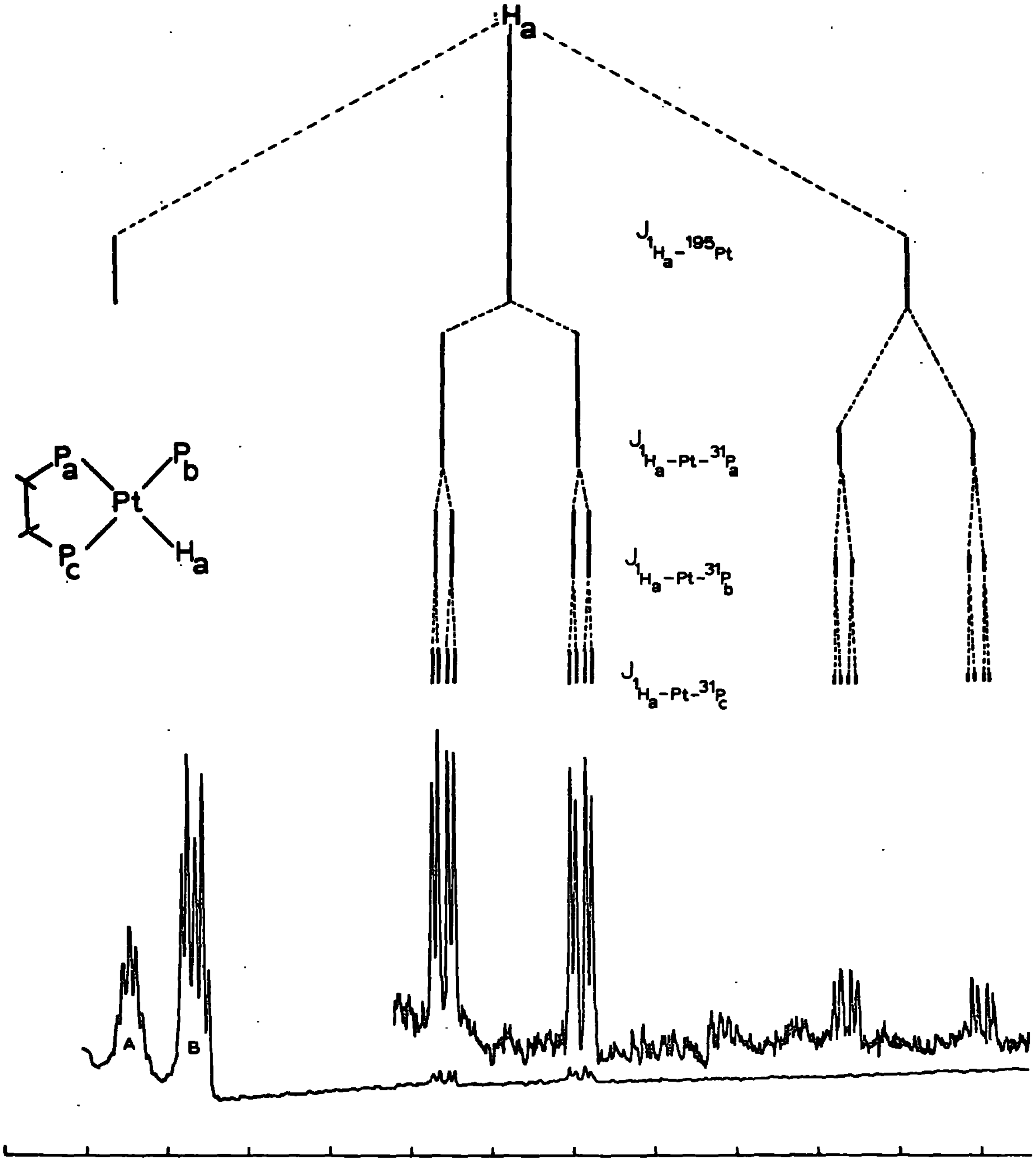


Fig 10 Highfield 100M Hz spectrum of $[(Ph_2PCH_2CH_2PPh_2)Pt(PEt_3)H]$ Cl

The 'H n.m.r. spectrum of the cis hydride $[(Ph_2PCH_2CH_2PPh_2)Pt(PEt_3)H]Cl$ differed significantly from the spectra of the trans hydride complexes[38]. The hydride couples to the trans ^{31}P nucleus with a coupling constant $J(^{31}P\text{-}H) = 168.1$ Hz to give a doublet, which is further split by the two non-equivalent cis ^{31}P nuclei into an eight lined signal (Fig. 10). The upfield satellite system due to coupling with the ^{195}Pt nucleus was observed but the low field system was obscured by other signals. As with the platinum-hydrogen stretching frequency the chemical shift of the hydride is susceptible to changes in ligand bonded to the metal (see p. 12). The chemical shifts of the hydrides and the platinum-hydrogen stretching frequencies were measured in various solvents for a series of complexes trans-$(Et_3P)_2PtHL$ (L is an o-, m- or p- substituted benzoato ligand or acetato ligand)[111]. A linear correlation was found between ν(Pt-H) and τPt-H thus supporting the view of Buckingham and Stephens[110] that changes in the platinum-hydride distance is the main contributing factor to changes in the paramagnetic shielding constant and hence in the chemical shift of the hydride. The platinum-hydrogen coupling constant has been shown[111,112] to depend mainly on the amount of platinum 6*s* orbital involved in the platinum-hydrogen bond, if the *s*-character is increased then the coupling constant is increased. A consequence of the increase in *s*-character of the bond is a shortening of the bond which in turn will increase the chemical shift of the proton (discussed earlier), thus a correlation between J(Pt-H) and τ(Pt-H) is predicted and has been found[111]. It has thus been concluded that variation in *s*-character of the bond is the most likely source of variation in the platinum-hydrogen coupling constant.

The ^{31}P n.m.r. spectra of the series trans-$(Et_3P)_2PtHX$ (X = Cl, Br, I, CN, NCO, NCS, SCN, NO_3, NO_2) have been reported[113,159], a good correlation was found between the chemical shift of the ^{31}P resonance and the Pt-H stretching frequency, also the chemical shift is shifted to lower field as the electronegativity of X is increased.

CHAPTER 4

GROUP-IVb DERIVATIVES OF NICKEL, PALLADIUM AND PLATINUM

Over the last decade there has been a great interest shown in compounds containing metal-metal bonds, and complexes containing silicon, germanium, tin or lead bonded to most of the d-block transition elements have been isolated. This upsurge of interest in metal-metal bonded compounds is probably due to two reasons: the increased sophistication of spectroscopic techniques for the detection of metal-metal interactions and their possible industrial applications as catalysts. The chemistry of metal-metal bonded complexes has been the subject of a number of reviews in recent years[114,115,116,117].

(1) Synthesis of Transition-metal-group-IVb Bonds

(a) From alkali metal derivatives of group-IVb

The use of alkali metal derivatives of the group-IVb elements provides perhaps the most versatile route available for the preparation of platinum and palladium-group-IVb complexes.

$(Et_3P)_2PtCl_2 + 2Ph_3GeLi \longrightarrow (Et_3P)_2Pt(GePh_3)_2 + 2LiCl$ 95

$(Et_3P)_2PdCl_2 + 2Ph_3GeLi \longrightarrow (Et_3P)_2Pd(GePh_3)_2 + 2LiCl$ 93

$(Diphos)PtCl_2 + 2(MePh_2SiLi) \longrightarrow (Diphos)Pt(MePh_2Si)_2 + 2LiCl$ 103

$(Et_3P)_2PtCl_2 + Ph_3SnLi \longrightarrow (Et_3P)_2PtCl(SnPh_3) + LiCl$ 42

$(Et_3P)_2PdCl_2 + 2PbPh_3Li \longrightarrow (Et_3P)_2Pd(PbPh_3)_2 + 2LiCl$ 118

By this method, Pt-Si, Pt-Ge, Pt-Sn, Pt-Pb, Pd-Ge and Pd-Pb bonds have been prepared, the use of Ph_3GeLi with $(Et_3P)_2NiBr_2$[93] did not result in a nickel germanium bond, only starting material and hexaphenyldigermane were isolated. Equimolar quantities of phosphine platinum dihalide and Ph_3GeLi resulted in a mixture of unreacted platinum dihalide and the disubstituted complex, no monosubstituted derivative was isolated. Triphenylphosphine platinum(II) bromide and Ph_3GeLi gave only a yellow polymeric material[95]. A further limitation on the reaction is the availability of the alkali-metal derivative, trimethylgermyl-lithium, for example, has to be prepared from bis(trimethylgermyl)mercury, or in very reactive solvents such as liquid ammonia or amines.

'Mixed metal' complexes have also been prepared by reacting triphenylgermyl-lithium with monosubstituted platinum-silicon or platinum-germanium complexes[41]:

$$\underline{\text{trans}}\text{-}(Et_3P)_2PtCl(SiMe_3) + Ph_3GeLi \longrightarrow (Et_3P)_2Pt(GePh_3)(SiMe_3) + LiCl$$

This method of preparation is also applicable to the titanium and copper groups[119,120].

(b) <u>From transition-metal anions</u>

This method is complementary to (a), but has not been applied to the nickel group. It has been used extensively for chromium, molybdenum, tungsten, manganese, iron and cobalt where the transition metal anions are easily prepared:

$$NaMn(CO)_5 + Me_3GeBr \longrightarrow Me_3GeMn(CO)_5 + NaBr \qquad 121$$

$$\pi\text{-}C_5H_5Mo(CO)_3Na + R_3GeCl \longrightarrow \pi\text{-}C_5H_5(CO)_3MoGeR_3 + NaCl \qquad 122$$

(R = Me, Et or n-Pr)

(c) <u>From metal-metal bonded complexes</u>

A convenient method for the preparation of monosubstituted trimethylsilyl- and trimethylgermyl-platinum derivatives is the use of bis(trimethylsilyl)mercury or [(trimethylgermyl)mercury][41].

$$(Me_3Si)_2Hg + \underline{\text{cis}}\text{-}(Et_3P)_2PtCl_2 \longrightarrow \underline{\text{trans}}\text{-}(Et_3P)_2PtCl(SiMe_3) + Hg + Me_3SiCl.$$

$$(Me_3Ge)_2Hg + \underline{\text{cis}}\text{-}(Et_3P)_2PtCl_2 \longrightarrow \underline{\text{trans}}\text{-}(Et_3P)_2PtCl(GeMe_3) + Hg + Me_3GeCl$$

The use of two equivalents of the mercury reagent failed to give the disubstituted complexes, forming a red oil from which only the monosubstituted derivative could be isolated in low yield.

The reported[123] preparation of trans-$(Et_3P)_2PtCl(PbPh_3)$ from bis(triphenyllead)mercury and cis-$(Et_3P)_2PtCl_2$ was later refuted[124] as bis(triphenyllead)mercury had not in fact been prepared.

(d) From zerovalent complexes

The use of zerovalent platinum complexes has led to the formation of Pt-Si, Pt-Sn and Pt-Pb bonds. Tetrakis(triphenylphosphine)platinum(o) on reaction with Cl_3SiH, Ph_2SiH_2 or Si_2Cl_6 gives the disubstituted complexes[15,171]:

$$(Ph_3P)_4Pt + Cl_3SiH \xrightarrow{\text{reflux}} (Ph_3P)_2Pt(SiCl_3)_2 + H_2$$

Fluorinated silanes of the type $(C_6H_4X)_3SiH$ (X = F or CF_3) produced hydrido silyl complexes:

$$(Ph_3P)_4Pt + (C_6H_4F)_3SiH \longrightarrow \underline{\text{trans}}\text{-}(Ph_3P)_2Pt(H)Si(C_6H_4F)_3$$

With triphenylsilane no reaction occurred. Platinum-tin bonded complexes have been prepared from $(Ph_3P)_4Pt$ using hexamethyldistannane[125] and triphenyltin chloride[6]:

$$(Ph_3P)_4Pt + Me_6Sn_2 \longrightarrow \underline{\text{trans}}\text{-}(Ph_3P)_2Pt(SnMe_3)_2$$

The same product is obtained reacting hexamethyldistannane with the ethylene complex, $(Ph_3P)_2Pt(C_2H_4)$.

The use of triphenyltin chloride gives the monosubstituted derivative

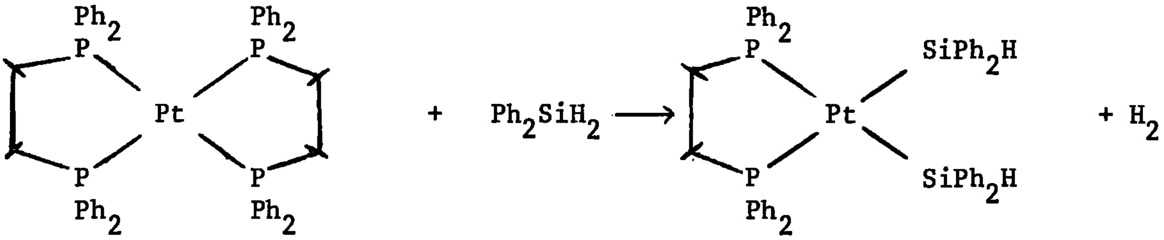
$$(Ph_3P)_4Pt + Ph_3SnCl \longrightarrow \underline{\text{trans}}\text{-}(Ph_3P)_2PtCl(SnPh_3) + 2Ph_3P.$$

By analogous reactions, Pt-Au and Pt-Hg bonded compounds have been produced[6].

$$(Ph_3P)_4Pt + Ph_3PAuCl \longrightarrow (Ph_3P)_2PtCl(AuPPh_3) + 2Ph_3P.$$

In a similar reaction triphenyllead chloride and tetrakis(triphenylphosphine)platinum(o) gave the monosubstituted lead derivative trans-$(Ph_3P)_2PtCl(PbPh_3)$[126].

Cis disubstituted silyl derivatives have been obtained[15] using $(diphos)_2Pt(o)$ (diphos = 1,2-bisdiphenylphosphinoethane) and Cl_3SiH or Ph_2SiH_2



(e) From platinum-hydrides

Several silicon hydrides have been found to react with trans-$(PhMe_2P)_2PtHX$ (X = Cl or Br), eliminating hydrogen and forming the monosubstituted silyl derivative[40,103]:

$$R_3SiH + \text{trans-}(PhMe_2P)_2PtHCl \longrightarrow \text{trans-}(PhMe_2P)_2PtCl(SiR_3) + H_2$$

(R = C_6H_5, C_6F_5, m-FC_6H_4, p-ClC_6H_4, m-, p-$CF_3C_6H_4$, Cl_3SiH).

The analogous Ph_3Ge- and Et_3Sn- derivatives were prepared similarly using Ph_3GeH and Et_3SnH. Trimethyl-, triethyl- and tribenzyl-silanes did not react at all. Trimethylgermane has however, been shown to react with trans-$(Et_3P)_2PtHCl$ to give trans-$(Et_3P)_2PtCl(GeMe_3)$ in low yield[38]. Compounds of the type trans-$(Et_3P)_2PtX(MH_2Y)$ (M = Si or Ge; X,Y = Cl, Br or I) have been prepared from the analogous platinum hydridohalide and the substituted silane or germane[127].

$$\text{trans-}(Et_3P)_2PtHCl + H_3SiCl \longrightarrow \text{trans-}(Et_3P)_2PtCl(SiH_2Cl) + H_2$$

The interaction of platinum hydrido complexes and amido derivatives of tin has resulted in platinum-tin compounds[128].

$$\underline{trans}\text{-}(Ph_3P)_2PtHCl + Me_3Sn\text{-}NMe_2 \longrightarrow \underline{trans}\text{-}(Ph_3P)_2PtCl(SnMe_3) + Me_2NH.$$

(f) Miscellaneous Preparations

A series of compounds containing platinum-germanium bonds has been prepared by reacting solutions of trichlorogermane in concentrated hydrochloric acid with potassium tetrachloroplatinite followed by the addition of tetramethylammonium chloride or triphenylphosphine, or alternatively with bis(triphenylphosphine)platinum(II) chloride[129].

e.g. $$Cl_3GeH + K_2PtCl_4 \xrightarrow[Me_4N^+Cl^-]{conc.\ HCl} [Me_4N]\left[(GeCl_3)_5PtH\right]$$

No analogous reactions occurred when using trichlorosilane. A trichlorosilyl derivative of nickel has been prepared by heating $[\pi\text{-}C_5H_5NiCO]_2$ with trichlorosilane[130].

$$[\pi\text{-}C_5H_5NiCO]_2 + Cl_3SiH \xrightarrow{100\text{-}180^o} Cl_3SiNi(CO)C_5H_5$$

A series of nickel-germanium complexes, $NiCp(R_3P)GeCl_3$ have been made[131] by the reaction of caesium trichlorogermanite with $NiCp(R_3P)X$:

$$NiCp(R_3P)X + CsGeCl_3 \longrightarrow NiCp(R_3P)GeCl_3$$

(Cp = cyclopentadienyl, X = Cl, Br or I, R_3 = Et_3, Et_2Ph, Ph_3, nPr_3, nBu_3).

Finally, the interaction of organsilicon hydrides with <u>cis</u>-$(PhMe_2M)_2PtCl_2$ (M = P or As) in benzene-triethylamine has resulted in platinum-silicon derivatives[103] according to the equation

$$R_3SiH + \underline{cis}\text{-}(PhMe_2M)_2PtX_2 + Et_3N \longrightarrow \underline{trans}\text{-}(PhMe_2M)_2PtCl(SiR_3) + Et_3NHCl$$

The silicon hydrides, $PhMe_2SiH$, $(PhCH_2)_3SiH$, Me_3SiH and Et_3SiH did not undergo the reaction. Excess of the silicon hydride did not replace the second chlorine atom to give the disubstituted derivatives.

Chlorotin Derivatives

As such a wide variety of platinum-tin complexes containing the $SnCl_3^-$ ligand are known, these compounds will be treated as a class of their own. The simpler reactions involve insertion of $SnCl_2$ into a Pt-Cl bond; trans-bis(triethylphosphine)platinum(II) hydridochloride reacts with stannous chloride in methanol[19]:

$$\underline{trans}\text{-}(Et_3P)_2PtHCl + SnCl_2 \longrightarrow (Et_3P)_2PtH(SnCl_3)$$

The platinum-hydrogen stretching frequency at 2105 $cm.^{-1}$ indicated that $SnCl_3^-$ is a ligand of fairly high trans-influence.

The reaction of stannic chloride with trans-bis(triphenylphosphine) platinum(II)hydridochloride results in an octahedral platinum(IV) complex[42]:

$$\underline{trans}\text{-}(Ph_3P)_2PtHCl + SnCl_4 \longrightarrow (Ph_3P)_2PtCl_2(SnCl_3)_2$$

Anionic complexes containing platinum-tin bonds are numerous and are prepared from mixtures of tin and platinum chlorides e.g. the addition of methyltriphenylphosphonium chloride to a solution of chloroplatinic acid and stannous chloride (ratio 1:6) in methanol precipitates out $[(C_6H_5)_3PCH_3]_3\,[Pt(SnCl_3)_5]$ as a red crystalline solid. Similarly the addition of triphenylphosphine in ethanol to a solution of K_2PtCl_4 and stannous chloride (ratio 1:10) in 3M, hydrochloric acid gave orange crystals of $[Ph_3P]_2\,[Pt(SnCl_3)_2]$[132].

Determination of the crystal structure of the $[Pt(SnCl_3)_5]^{3-}$ anion[133] has shown it to be a trigonal bipyramid with a central platinum atom surrounded by five $SnCl_3^-$ ligands attached through platinum-tin bonds. Parshall and co-workers[19] have studied the σ- and π-bonding properties of the $SnCl_3^-$ ligand using ^{19}F n.m.r. shielding parameters of fluorophenyl platinum complexes (see p. 13). As a result of this investigation it was concluded that the $SnCl_3^-$ ligand is a weak σ-donor, but can π-bond strongly.

Mössbauer studies on a number of chlorotin platinum derivatives[160] such as $(Et_4N)_3Pt(SnCl_3)_5$ have shown that the tin is in the +4 oxidation state and not +2 as had previously been thought.

Trichlorotin derivatives of platinum have been used as catalysts in the reduction of acetylenes and short chain olefins to alkanes under mild conditions[132,134]. A solution of stannous chloride and chloroplatinic acid in methanol effected quantitative hydrogenation of mixtures of ethylene with hydrogen and acetylene with hydrogen at room temperature and one atmosphere pressure. The hydrogenation of polyenes to dienes and monoenes[135,136] and the isomerisation of polyenes,[137] is also catalysed by trichlorotin derivatives of platinum.

The most important steps in these catalytic reactions are the formation of a platinum-hydride and coordination of the olefin to the platinum. A hydride species, $[HPt(SnCl_3)_4]^{3-}$, has been detected under conditions of catalysis[133,137].

In contrast to the behaviour of platinum complexes and stannous chloride, the analogous palladium(II)-tin(II) chloride system is unstable, metallic palladium eventually precipitating out of ethanolic solutions[138]. An ill-defined palladium-tin complex has been isolated[139] and on the basis of analytical data only has been formulated as $[PdCl(SnCl_3)_2]_2^{4-}$.

(2) Reactions of the Complexes

The characteristic reactions are (1) cleavage of the metal-metal bond with halogens, organic halides, halogen acids and hydrogen; (2) exchange reactions

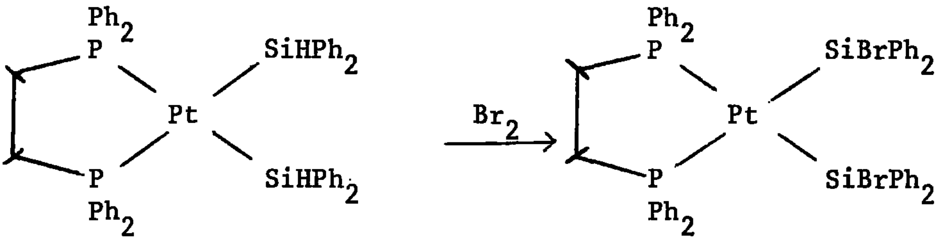
(a) Halogens and hydrogen halides

With halogens the reaction is usually straightforward with the metal-metal bond being cleaved giving the corresponding transition metal and group-IVb halides.

$(Et_3P)_2Pt(GePh_3)_2 + 2I_2 \longrightarrow (Et_3P)_2PtI_2 + 2Ph_3GeI$ 95

$(Et_3P)_2Pt(PbPh_3)_2 + 4Br_2 \longrightarrow (Et_3P)_2PtBr_2 + 2Ph_2PbBr_2 + 2PhBr$ 140

In both reactions, no evidence of single cleavage was obtained. The reaction of _cis_-$(PhMe_2P)_2Pt(SiMePh_2)_2$ did however react with chlorine (molar ratio 1:0.5) to give _trans_-$(PhMe_2P)_2PtCl(SiMePh_2)$. With equimolar ratios cleavage of both silyl groups resulted[103]. An exception to the cleavage of a metal-metal bond occurred when hydrogen was bonded to the silicon[15]



The hydrogen being replaced in preference to cleavage of the metal-metal bond. Hydrogen halides cleave the metal-metal bond, the products varying on the type of complex. With disubstituted platinum silicon complexes of non-chelating phosphines, the Pt-Si bond is cleaved in opposite directions on reaction firstly with 1 molar quantity of HCl and then with a second molar quantity[40]:

cis-$(PhMe_2P)_2Pt(SiMePh_2)_2 \xrightarrow{HCl}$ _trans_-$(PhMe_2P)_2PtCl(SiMePh_2) + Ph_2MeSiH$

trans-$(PhMe_2P)_2PtCl(SiMePh_2) \xrightarrow{HCl}$ _trans_-$(PhMe_2P)_2PtHCl + Ph_2MeSiCl$

(I)

The platinum-lead complex, _trans_-$(Et_3P)_2Pt(PbPh_3)_2$, with 1 molar quantity reacts as the silicon complex but the addition of a second molar quantity gives the platinum dihalide and not the hydridochloride[140].

$$\begin{tikzcd}
\underline{\text{trans}}\text{-}(Et_3P)_2Pt(PbPh_3)_2 \arrow[r, "HCl"] & \underline{\text{trans}}\text{-}(Et_3P)_2PtCl(PbPh_3) + Ph_3PbH \arrow[d, "HCl"] \\
 & \underline{\text{trans}}\text{-}(Et_3P)_2PtCl_2 + PbCl_2 + C_6H_6
\end{tikzcd}$$

The monosubstituted silyl and germyl platinum derivatives, t-$(Et_3P)_2PtCl(MMe_3)$ (M = Si or Ge) cleave as for the above complex, (I), giving the hydridochloride and the chlorotrimethylsilane (germane)[38].

The palladium complexes $(Et_3P)_2Pd(MPh_3)_2$ (M = Ge, Pb) with HCl gave no compound resulting from a single cleavage but in both cases the palladium dihalide was produced:

$$(Et_3P)_2Pd(GePh_3)_2 \xrightarrow{HCl} (Et_3P)_2PdCl_2 + Ph_3GeH \qquad 93$$

$$(Et_3P)_2Pd(PbPh_3)_2 \xrightarrow{HCl} (Et_3P)_2PdCl_2 + Ph_3PbCl + Ph_2PbCl_2 + PbCl_2 \quad 118$$

These reactions probably indicate the greater reluctance of Pd(II) compared with Pt(II) to undergo oxidative-addition reactions leading to 6-coordinate intermediates.

The disubstituted tin complex trans-$(Ph_3P)_2Pt(SnMe_3)_2$ undergoes a unique reaction with HCl, giving the platinum hydridochloride and hexamethyldistannane[125].

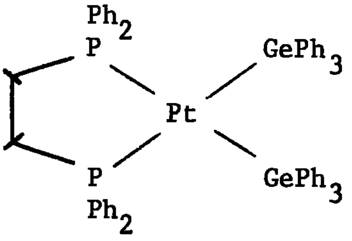
$$\underline{\text{trans}}\text{-}(Ph_3P)_2Pt(SnMe_3)_2 \xrightarrow{HCl} \underline{\text{trans}}\text{-}(Ph_3P)_2PtHCl + Me_6Sn_2$$

The hydrogen chloride cleavage of trans-$(Et_3P)_2Pt(GeMe_3)(GePh_3)$ is extremely selective[38], the trimethylgermyl group being cleaved, predominantly as Me_3GeH. It has been suggested[140] that the course of the cleavage reactions depends greatly on the group-IVb metal, particularly on its electronegativity.

With a chelating phosphine complex both platinum-silicon bonds are cleaved in the same direction to give the platinum dichloride complex[103].

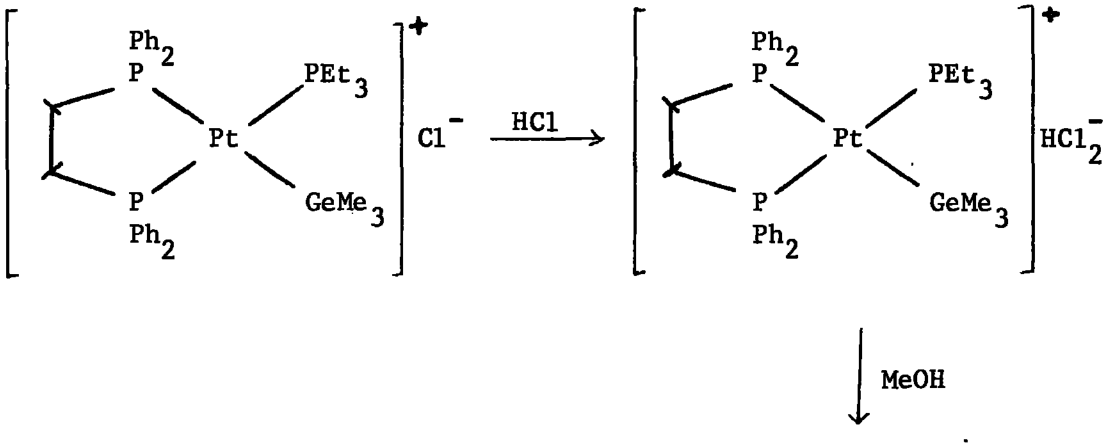
This contrasts with the non-chelating phosphine derivatives, the difference being attributed to the high trans-effect of the silyl group. In the chelate complex both silyl groups are necessarily trans to the phosphine ligand, whereas in the non chelate complexes one silyl group is trans to a phosphine ligand but in trans-$(PhMe_2P)_2PtCl(SiMePh_2)$ i.e. the second stage of the cleavage, the silyl group is trans to a chloride ion.

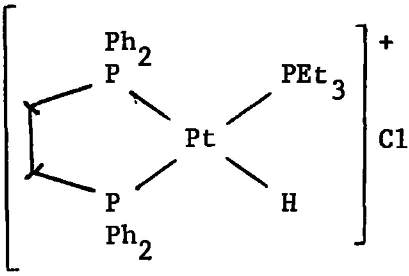
The disubstituted complex,



only reacted with an excess of hydrogen chloride giving $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ and triphenylgermane. Samples of the complex with one and two equivalents of HCl did not undergo reaction[37].

The cleavage reactions probably proceed via an octahedral intermediate, complexes of the type trans-$(Et_3P)_2PtH_2Cl_2$, formed by the addition of HCl to trans-$(Et_3P)_2PtHCl$, being known[36]. The reaction of an ionic platinum-germanium complex with hydrogen chloride gave initially an intermediate complex containing the HCl_2^- anion. This intermediate, on solution in methanol, formed an ionic platinum hydride and Me_3GeCl[38].





$Cl^- + Me_3GeCl$

After reacting for several days in benzene a number of products were isolated:

$[(Ph_2PC_2H_4PPh_2)Pt(PEt_3)Cl]^+Cl^-$; $[(Ph_2PC_2H_4PPh_2)_2Pt]^{2+}2Cl^-$; trans-$(Et_3P)_2PtHCl$, $[(Ph_2PC_2H_4PPh_2)Pt(PEt_3)H]^+Cl^-$; Me_3GeH and Me_3GeCl.

Recently[141] an octahedral platinum complex formed by the addition of HI has been isolated. The adduct decomposed slowly at room temperature with the evolution of hydrogen:

$$\text{trans-}(Et_3P)_2Pt(SiH_2I)I \xrightarrow{HI} (Et_3P)_2PtI_2(H)(SiH_2I) \xrightarrow{-H_2} \text{trans-}(Et_3P)_2Pt(SiHI_2)I$$

No analogous hydrogen chloride adduct was detected.

(b) Organic halides

1,2-Dibromoethane reacts with metal-metal bonded complexes liberating ethylene, often quantitatively:

$$(Et_3P)_2Pt(GePh_3)_2 + C_2H_4Br_2 \longrightarrow (Et_3P)_2PtBr_2 + 2Ph_3GeBr + C_2H_4 \qquad 95$$

Trans-$(Et_3P)_2PtCl(SiMe_3)$ with ethylene dichloride[41] did not however give the stoichiometric quantity of ethylene, the amount of chlorotrimethylsilane formed was in excess of that expected from the amount of $(Et_3P)_2PtCl_2$ isolated.

Methyl iodide also reacts with metal-metal bonds[95,103] cleaving the metal-metal bond:

$$\underline{cis}\text{-}(PhMe_2P)_2Pt(SiMePh_2)_2 \xrightarrow{CH_3I} (PhMe_2P)_2PtI_2 + Ph_2SiMe_2 + \text{trace } Ph_2MeSiH$$

(c) Hydrogenation

The hydrogenation of metal-metal bonds has received much attention and the reaction conditions vary widely from room temperature and low pressure to high temperature and pressure conditions.

$$(Et_3P)_2Pt(GePh_3)_2 \xrightarrow[\text{20 mm partial pressure}]{H_2,\ \text{Room Temp.}} \underline{trans}\text{-}(Et_3P)_2PtH(GePh_3) + Ph_3GeH \qquad 95$$

The palladium analogue required more forcing conditions (100 atm. for 1 week), the reaction then proceeding as for the platinum complex[93]. The palladium-lead complex; $(Et_3P)_2Pd(PbPh_3)_2$ however, hydrogenated at 0°C, to give palladium metal, triethylphosphine and hexaphenyldiplumbane[118], this contrasted also with the platinum analogue which gave the platinum hydride.

$$(Et_3P)_2Pt(PbPh_3)_2 + H_2 \xrightarrow[1.5\ \text{atm.}]{20^o} \underline{trans}\text{-}(Et_3P)_2Pt(PbPh_3)H \qquad 140$$

These hydrogenations again show the different tendencies of palladium(II) and platinum(II) complexes towards oxidative-addition reactions.

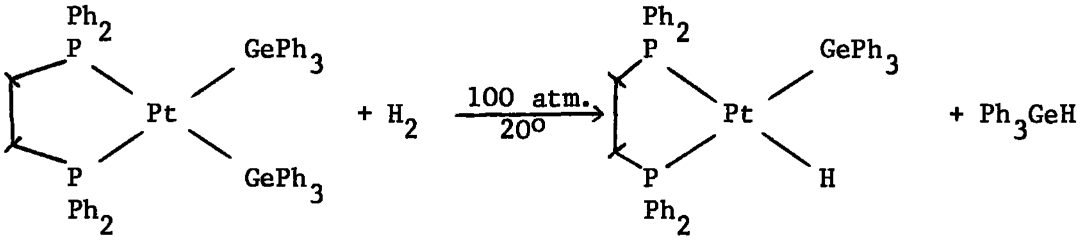
The trans complexes, trans-$(Et_3P)_2PtCl(MMe_3)$, (M = Si or Ge) reacted smoothly with hydrogen at room temperature and atmospheric pressure giving the hydridochloride[41]:

$$\underline{trans}\text{-}(Et_3P)_2PtCl(MMe_3) + H_2 \xrightarrow[1\ \text{atm.}]{\text{Room Temp.}} \underline{trans}\text{-}(Et_3P)_2PtHCl + Me_3MH$$

The reversibility of this reaction has also been demonstrated[38]. Similar reactions, the hydrogenation of cis-$(PhMe_2P)_2Pt(SiMePh_2)_2$ and trans-$(PhMe_2P)_2PtCl(SiMePh_2)$ have also been shown to be reversible[103],

$$\underline{cis}\text{-}(PhMe_2P)_2Pt(SiMePh_2)_2 + H_2 \rightleftharpoons \underline{trans}\text{-}(PhMe_2P)_2PtH(SiMePh_2) + Ph_2MeSiH.$$

(The products, trans-$(PhMe_2P)_2PtH(SiMePh_2)$ and Ph_2MeSiH were indicated by infra-red spectra, but a separation was not achieved). The reversibility of these reactions suggests that a common intermediate is involved, most readily formulated as a 6-coordinate intermediate. The chelate phosphine complexes $(Ph_2PCH_2CH_2PPh_2)Pt(GePh_3)_2$ and $(Ph_2PCH_2CH_2PCH_2)Pt(SiMePh_2)_2$ did not react with hydrogen at low pressure and temperature[41,103], however at 100 atmospheres pressure the germyl complex reacted but only one germyl group was cleaved.



(d) Ligand replacement reactions

In complexes $(R_3P)_2PtCl(MR'_3)$ RR' = alkyl, M = (Si or Ge), replacement of chloride ion can be carried out by Br^-, I^-, OH^-, OR^-, CN^- or NCS^- by using the appropriate salt[41,95]. With the compounds *trans*-$(Et_3P)_2M'(PbPh_3)_2$ (M' = Pd or Pt) the reaction with CN^- leads to breakage of the M'-Pb bond giving the tetracyano cation and hexaphenyldiplumbane[118,140];

$$\textit{trans}\text{-}(Et_3P)_2Pt(PbPh_3)_2 + CN^- \longrightarrow [Pt(CN)_4]^{2-} + Ph_6Pb_2 + Et_3P$$

The replacement of the phosphine ligands in some cases has been achieved, in complexes having only one metal-metal bond, chelating phosphines produce either anionic or zerovalent complexes[37,38]:

$$\textit{trans}\text{-}(Et_3P)_2PtCl(SiMe_3) + \text{Diphos} \longrightarrow [(\text{Diphos})Pt(Et_3P)(SiMe_3)]^+Cl^- + Et_3P$$

$$\textit{trans}\text{-}(Et_3P)_2Pt(GePh_3)H + 2Ph_2PCH_2CH_2PPh_2 \longrightarrow (\text{Diphos})_2Pt + Et_3P + Ph_3GeH$$

The addition of a chelating phosphine to disubstituted complexes results in a direct replacement of the two non-chelating phosphine ligands[103+140].

$$\underline{\text{trans}}\text{-}(Et_3P)_2Pt(PbPh_3)_2 + Ph_2PCH_2CH_2PPh_2 \longrightarrow (Ph_2PCH_2CH_2PPh_2)Pt(PbPh_3)_2 + 2Et_3P$$

The silyl group in $(Et_3P)PtCl(SiH_2Cl)$ can be displaced by chlorogermane to give $(Et_3P)_2PtCl(GeH_2Cl)$ which slowly decomposes[127].

(e) Miscellaneous reactions

(i) Pyrolysis

The pyrolysis of a number of compounds has been studied and free radicals are involved. The palladium complex decomposes in vacuo to give a variety of products[93] which parallel those from the pyrolysis of the platinum analogue[95].

$$(Et_3P)_2Pd(GePh_3)_2 \xrightarrow{97\text{-}107^o} Pd + Ph_6Ge_2 + Ph_4Ge + Et_3P + C_6H_6 + C_2H_4 + H_2$$

A much higher temperature (230°) was required to effect pyrolysis of the platinum complex.

Pyrolysis of the lead derivative, $(Et_3P)_2Pt(PbPh_3)_2$ again gave a variety of products[140].

$$\underline{\text{trans}}\text{-}(Et_3P)_2Pt(PbPh_3)_2 \longrightarrow Pt + Et_3P + Ph_6Pb_2 + Ph_4Pb + \text{unidentified residue containing Pt and P.}$$

(ii) Hydrolysis

The Me_3Ge and Me_3Si derivatives are moisture sensitive[38,41], the silyl derivatives being more susceptible to hydrolysis than the germyl complexes.

$$\underline{\text{trans}}\text{-}(Et_3P)_2PtCl(SiMe_3) + H_2O \longrightarrow \underline{\text{trans}}\text{-}(Et_3P)_2PtHCl + \tfrac{1}{2}(Me_3Si)_2O$$

The reaction is thought to proceed by proton attack on the platinum. Phenyl analogues do not undergo reaction with water[95].

(3) The Complexes

(a) The transition metal

It has been observed that in metal-metal bonded complexes the complexes of the third row transition metals are generally more stable than those of the first and second rows. For example, the platinum compound $(Et_3P)_2Pt(GePh_3)_2$ is air and water stable[95], decomposing at 230° whereas the palladium analogue decomposes at 107° in the solid state and -20° in solution[93]. The nickel analogue has so far eluded preparation. The germanium- and tin-transition metal complexes appear to be more stable than silicon and lead derivatives. Similarly for the series of complexes π-$C_5H_5(CO)_3M$-$M'R_3$ (M = Cr, Mo or W; M' = Ge, Sn or Pb; R = Me or Ph), decomposition under nitrogen occurs after several weeks for the chromium complexes but the molybdenum and tungsten derivatives remain stable indefinitely[142].

(b) Ligands bonded to the transition metal

Metal-metal bonded complexes not having π-bonding ligands such as tertiary phosphines and carbon monoxide bonded to the transition metal are few, a notable exceptions being $Li[(Ph_3Ge)_2Au].4Et_2O$ 120

A change in the ligand bound to the transition metal can greatly affect reactions. For example, the reaction of $(R_3P)_2PtCl_2$ and Ph_3GeLi gives satisfactory yields of $(R_3P)_2Pt(GePh_3)_2$ for R = Et and n-Pr, but for R = Ph only ill-defined polymeric material could be isolated[95]. In the gold complexes, $Ph_3PAuGePh_3$ and $Me_3PAuGePh_3$, the phenyl complex is stable to air and water whereas the methyl analogue decomposes rapidly in air[120], the difference probably being due, in part, to stabilisation by π-bonding between the metal and the triphenylphosphine ligand removing negative charge from the gold into the aromatic rings.

(c) The group-IVb metal

Although little systematic work has been done on the stability of complexes with different group-IVb elements some trends do occur. The silicon complexes, trans-$(Et_3P)_2PtCl(SiMe_3)$ and $[(Ph_2PCH_2CH_2PPh_2)Pt(Et_3P)(SiMe_3)]^+Cl^-$

are hydrolysed more readily than the germanium analogues[38,41]. In the series of complexes, $Ph_3MMn(CO)_5$, M = (Si,Sn or Pb) thermal stability increases in the order Sn>Pb>Si[143]. Although compounds containing germanium, tin and lead bonded to palladium have all been isolated, no palladium-silicon complexes have been prepared, this again giving some indication of the lower stability of complexes having a silicon-metal bond.

Platinum complexes involving Ph_3Pb, Ph_3Sn, Ph_3Ge and Ph_3Si have all been prepared[42,95,140], on the basis of decomposition temperatures, germanium and tin derivatives appear to be more stable than those of silicon and lead, it therefore seems probably that optimum overlap conditions occur with germanium and tin.

(d) Effect of the substituent on the group-IVb metal

The general order of stability of metal-metal bonded complexes for variation of the group-IVb metal substituent is found to be $X_3M>R_3M>R'_3M>H_3M$ (X = halogen, R = aryl, R' = alkyl, M = group-IVb metal). This stability of complexes with halogen as substituent is best illustrated by a series of rhodium complexes (Table 5)[144].

Table 5

Stability of the complexes $(Ph_3P)_2RhH(SiMe_nCl_{3-n})Cl$

	Decomposition temp.	Solution stability
$(Ph_3P)_2RhH(SiMe_3)Cl$	95°	instant dissociation
$(Ph_3P)_2RhH(SiMe_2Cl)Cl$	125°	
$(Ph_3P)_2RhH(SiMeCl_2)Cl$	145°	slow dissociation
$(Ph_3P)_2RhH(SiCl_3)Cl$	170°	stable

The difference between alkyl and aryl groups as substituents can be seen from the complexes *trans*-$(PhMe_2P)_2PtCl(SiPh_3)$ and *trans*-$(Et_3P)_2PtCl(SiMe_3)$, the triphenylsilyl complex being water stable[103] whereas the trimethylsilyl complex is rapidly hydrolysed to hexamethyldisiloxane and trans-$(Et_3P)_2PtHCl$[41]. Similarly the complex π-$C_5H_5(CO)_2FeSiMe_3$[145] is unstable towards oxygen but the triphenylsilyl analogue is unreactive[142].

The Nature of the Metal-metal Bond

The metal-metal bond in these compounds is thought to consist of a σ-bond and a d-π-bond contribution. Metal-metal bond distances, infra-red and nuclear magnetic resonance data support d→d π-bonding. Nearly all reported metal-metal distances show shortening from lengths calculated from covalent radii, though steric effects and electronic effects other than dπ-dπ bonding can cause bond shortening. In the series R_3Sn-$Mn(CO)_5$ the Mn-Sn bond length was found to be independent of R and less than the sum of the covalent metal radii[146,147], replacement of a carbonyl group trans to R_3Sn by a tertiary phosphine group of lower π-bonding ability produced a further shortening of the Mn-Sn bond[148], consistent with an increase in multiple bond character of the Mn-Sn bond as a result of less competition by the phosphine group for the d-electrons of the manganese.

The Fe-Sn bond lengths in the series $[\pi\text{-}C_5H_5Fe(CO)_2]_2SnX_2$ (X = ONO, Cl, C_5H_5 or Me) have been measured[149,150]. It was found that as the electron withdrawing ability of the substituent X increased, a shortening of the Fe-Sn bond occurred, again consistent with π-bonding between the iron and tin. An order of π-bonding thus appeared to be $Cl_2Sn>(ONO)_2Sn>(C_5H_5)_2Sn>Me_2Sn$.

^{19}F n.m.r. has been used to estimate the relative importance of σ- and π- effects in $SnCl_3^-$ when bonded to platinum (p.13) from the data it was concluded that the $SnCl_3^-$ anion is a weak σ-donor but a strong π-acceptor.

Tin-proton coupling constants ($J^{119}Sn$-Me) from the n.m.r. of Me_4Sn, Me_3Sn-M and Me_2Sn-M_2 (M = transition metal) have been found to decrease as a methyl group is replaced, this implies that the S-character of the tin orbitals bonding to the methyl groups is decreased[151], or equivalently that the tin atom uses a high degree of S-character in its bonds to transition metals[142,152,153]. This is supported by Mössbauer studies on tin-transition metal derivatives (using ^{119}Sn), these spectra also suggest some dπ-character[154]

Nuclear quadrupole resonance spectra of X_3M-$Co(CO)_4$ complexes (M = Si, Ge, Sn or Pb; X = Cl, Br, I or Ph) show that the Co-M bonds have appreciable π-character as well as a strong σ-component[155].

In square planar platinum(II) complexes the R_3M (M = Si, Ge, Sn or Pb) have a high <u>trans</u>-influence as can be seen from the lowering of Pt-H and Pt-Cl stretching frequencies (Table 6 and 7). This high <u>trans</u>-influence is indicative of a strong Pt-M σ-bond (the $SnCl_3$-group being an exception as mentioned earlier).

Determination of Stereochemistry

(a) Infra-red

In square planar platinum(II) complexes the strong platinum-hydrogen and platinum-chlorine stretching frequencies are dependent on the <u>trans</u>-ligand. From Tables 2 and 6 it can be seen that the range of values of ν(Pt-H) are from 1940 $cm.^{-1}$ (<u>trans</u> to Ph_3Pb) to 2242 $cm.^{-1}$ (<u>trans</u> to NO_3^-); for ν(Pt-Cl) (Table 7), from 238 $cm.^{-1}$ (<u>trans</u> to Me_3Ge) to 340 $cm.^{-1}$ (<u>trans</u> to Cl), thus, the values for ν(Pt-H) and ν(Pt-Cl) in the complexes are indicative of their stereochemistry.

(b) X-ray determination

The X-ray structure determination of a number of nickel group - group-IVb complexes has been carried out[95, 131,133].

The ethoxy complex, $(Et_3P)_2Pt(OEt)(GePh_3)$, has been subjected to a partial X-ray study[95], which suggests a square planar, <u>trans</u> configuration.

The configuration of the $[Pt(SnCl_3)_5]^{3-}$ anion has been described on p. 53.

The structure of the nickel complex, π-$C_5H_5Ni(Ph_3P)GeCl_3$, has also been determined[131], the nickel, germanium and phosphorus atoms are located in a plane approximately perpendicular to that of the cyclopentadienyl ring which is significantly distorted. The nickel-germanium bond length is considerably shorter than the sum of the covalent radii, this is probably due to appreciable dπ-dπ bonding between the nickel and germanium.

(c) Nuclear magnetic resonance spectroscopy

(i) 'H n.m.r.

The 'H n.m.r. spectra of compounds containing Me_3Ge, Me_3Si and Ph_2MeSi allow the stereochemistry of the complexes to be assigned unambiguously, this is perhaps best illustrated by the examples *trans*-$(Et_3P)_2PtCl(GeMe_3)$ and *cis*-$(Et_3P)_2PtPh(GeMe_3)$[41], (Fig. 11).

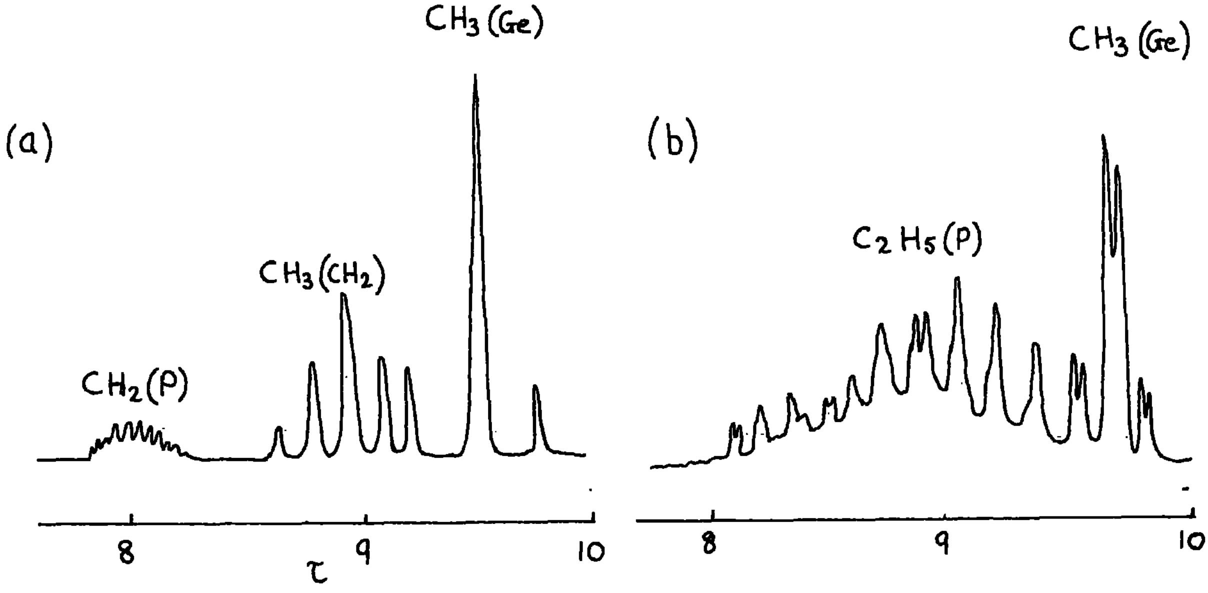


Fig. 11 'H n.m.r. spectra of (a) *trans*-$(Et_3P)_2PtCl(GeMe_3)$ and (b) *cis*-$(Et_3P)_2PtPh(GeMe_3)$

In the *trans* complex the methyl protons of the germyl group appear as a 1:4:1 triplet due to coupling with the ^{195}Pt nucleus (spin ½, 34% abundant) (see n.m.r. of hydrides, p.44), $J(^{195}Pt\text{-}Ge\text{-}C\text{-}'H) = 20$ Hz. In the *cis* complex however the three lines due to the coupling with the ^{195}Pt nucleus

Table 6

Characteristic Platinum-hydrogen Stretching Frequencies in Platinum-IVb Complexes

Complex	ν(Pt-H) cm.$^{-1}$	Reference
trans-$(Et_3P)_2PtHCl$	2183	36
$(Ph_2PCH_2CH_2PPh_2)PtH(GePh_3)$	1998	37
$(n\text{-}PrP)_2PtH(GePh_3)$	1957	95
$(Et_3P)_2PtH(SiPh_3)$	2056	42
trans-$(PhMe_2P)_2PtH(SiMePh_2)$	2040	103
trans-$(Ph_3P)_2PtH(SnMe_3)$	2042	125
trans-$(Et_3P)_2PtH(PbPh_3)$	1940	140

Table 7

Characteristic Platinum-chlorine Stretching Frequencies in Platinum-IVb Complexes

Complex	ν(Pt-Cl) cm.$^{-1}$	Reference
trans-$(Et_3P)_2PtCl_2$	340	39
trans-$(Ph_3P)_2PtCl_2$	345	42
trans-$(Et_3P)_2PtHCl$	269	39
trans-$(Et_3P)_2PtCl(SiMe_3)$	238	41
trans-$(Et_3P)_2PtCl(GeMe_3)$	235	41
trans-$(Et_3P)_2PtCl(SnMe_3)$	278	128
trans-$(Ph_3P)_2PtCl(PbPh_3)$	286	42

are each further split into doublets due to coupling with the trans ^{31}P nucleus (spin ½, 100% abundant), $J(^{31}P\text{-Pt-Ge-C-}^{1}H)$ = 1.4 Hz, this six line signal being indicative of a cis configuration.

The ^{1}H n.m.r. of the protons of the phosphine groups can also allow the stereochemistry of complexes to be assigned, this has been applied to phosphine-platinum hydrides and halides[156,157,159] as well as group-IVb complexes[41,103], for example, in trans-$(PhMe_2P)_2PtBr(GePh_3)$ the methyl groups of the phosphine appear as a 1:4:1 triplet due to coupling with the ^{195}Pt nucleus, each line of the triplet is further split by the two trans ^{31}P nuclei into a 1:2:1 triplet, giving as an overall signal three 1:2:1 triplets. In cis complexes e.g. cis-$(Ph_2Me_2P)_2PtCl_2$, the methyl resonances appear as a 1:4:1 triplet as before, but each of these is split into a doublet by coupling with a ^{31}P nucleus, (coupling with the cis ^{31}P nucleus is not observed[157]), thus the overall resonance appears as three doublets.

Recently[158] the ^{31}P n.m.r. of a number of platinum-group-IVb complexes has been reported. For a series of complexes, $(PhMe_2P)_2PtXY$ (X = Cl or Br; Y = alkyl or aryl silicon or germanium grouping) the ^{31}P resonance appears as a singlet line split into a 1:4:1 triplet due to coupling with the ^{195}Pt nucleus, the complexes are therefore assigned a trans configuration. (A cis configuration would have resulted in two ^{31}P resonances as the two phosphorus atoms would then be in different environments). The platinum-phosphorus coupling constant has been shown to depend on the covalency of the Pt-P bond and the magnitude of the S-character of the platinum orbital involved in the Pt-P bond[47], therefore when the Pt-P bond is trans to a group of high trans-influence such as Me, Ph, or Silyl the coupling constant J(Pt-P) is reduced because the covalency of the bond is reduced, this has been utilised[158] to establish the configurations of disubstituted silyl- and germyl-platinum complexes $(R_3P)_2Pt(MR'_3)_2$ (RR' = alkyl or aryl;

M = Si or Ge), by comparing the coupling constants J(Pt-P) with those of isomeric bisphenylplatinum phosphine complexes $(R_3P)_2PtPh_2$.

CHAPTER 5

DISCUSSION

Platinum Hydride Complexes

During the investigation into the reactions of platinum-group-IVb complexes, the hydrogenation of the silyl derivative, $(Ph_2PCH_2CH_2PPh_2)PtCl(SiMe_3)$, at atmospheric pressure yielded $(Ph_2PCH_2CH_2PPh_2)PtHCl$. Previously only one cis hydridohalide of platinum, cis-$(Ph_3P)_2PtHCl$, had been reported[161]. This had been prepared by the reduction of cis-bis(triphenylphosphine)platinum(II) chloride with hydrazine hydrate. This reported cis hydride showed two bands in its infra-red spectrum ascribable to ν(Pt-H) at 2260 and 2225 cm^{-1}. The hydride, $(Ph_2PCH_2CH_2PPh_2)PtHCl$, however showed only one band in this region at 2002 cm^{-1}. As this complex and the reported cis hydride complex both have phosphine ligands trans to the hydride (i.e. a P-Pt-H arrangement) the difference in the platinum-hydrogen stretching frequencies seemed unduly large and led to a reinvestigation of the reported cis hydridochloride.

Chatt and Shaw[36] established that trans-hydridochlorides were produced from a variety of cis-or trans-platinum dichloride complexes, e.g.

$$\text{cis- or trans-}(Et_3P)_2PtCl_2 \xrightarrow{N_2H_4} \text{trans-}(Et_3P)_2PtHCl$$

By contrast, cis-bis(triphenylphosphine)platinum(II) chloride was reported[161] to yield both cis- and trans- hydridochlorides on reduction with hydrazine hydrate, the trans form separating from a benzene-methanol mixture as colourless prisms of the methanol adduct and the cis-form, prepared at a lower temperature, separating with one molecule of benzene of recrystallisation as colourless scaly crystals from a benzene-diethylether mixture.

The preparations were repeated and the 'H n.m.r. spectra of the cis and trans samples were recorded. In chloroform solution the platinum hydride resonance of both complexes appeared as a 1 : 2 : 1 triplet (τ26.0) due to coupling of the Pt-H proton to two equivalent ^{31}P nuclei [spin½, 100% abundant, $J(^{31}P\text{-Pt-H}) = 13.2Hz$], flanked by two satellite systems (1 : 2 : 1 triplets) due to coupling to the ^{195}Pt nucleus [spin½, 34% abundant, J(^{195}Pt-H) = 1184 Hz]. The high chemical shift indicated that the Pt-H proton was trans to a group of low trans-influence[36], i.e. Cl rather than Ph_3P. The splitting of the Pt-H proton is consistent with a trans configuration not a cis (discussed earlier), thus, on the 'H n.m.r. evidence, in solution both forms have the trans configuration. This was confirmed by their solution infra-red spectra in chloroform when both complexes gave only one band ascribable to ν(Pt-H) at 2235 cm^{-1}.

On the above evidence however, the possibility exists that the 'cis form' isomerises rapidly in solution to yield the trans isomer, therefore the platinum-hydrogen and platinum-chlorine infra-red stretching frequencies of the cis and trans forms were measured with the complexes in the solid state. The trans form, either as a hexachlorobutadiene mull or as a potassium bromide disc, had a single Pt-H stretching frequency at 2230 $cm.^{-1}$, whereas the 'cis isomer ' had four bands in this region at 2210, 2232, 2265 and 2279 $cm.^{-1}$, the strongest and sharpest being the 2232 $cm.^{-1}$ band. Fractional recrystallisation of the 'cis-isomer' at room temperature from a benzene-diethylether mixture yielded two fractions, the first showing two bands at 2211 and 2232 $cm.^{-1}$ whereas the second fraction had only one band in this region at 2232 cm^{-1}. Crystallisation of the trans form under similar conditions produced crystals having three bands in this region attributable to ν(Pt-H) at 2211, 2250 and 2265 $cm.^{-1}$, the same sample on crystallisation from a benzene-methanol mixture had previously shown only one band at 2230 cm^{-1}. As can be seen from Table 8, all the values of ν(Pt-H) are consistent with structures in which hydrogen is trans to chlorine rather than phosphorus. In two authenticated hydrido-platinum complexes having the grouping trans-R_3P-Pt-H the platinum-hydrogen stretching frequencies are much lower (2043, 1998 $cm.^{-1}$) due to the higher trans-influence of the tertiary phosphine compared to that of the chloride.

Fig. 12

HIGH-FIELD SPECTRUM OF
TRANS-$(Ph_3P)_2PtHCl$.
220 MHz.

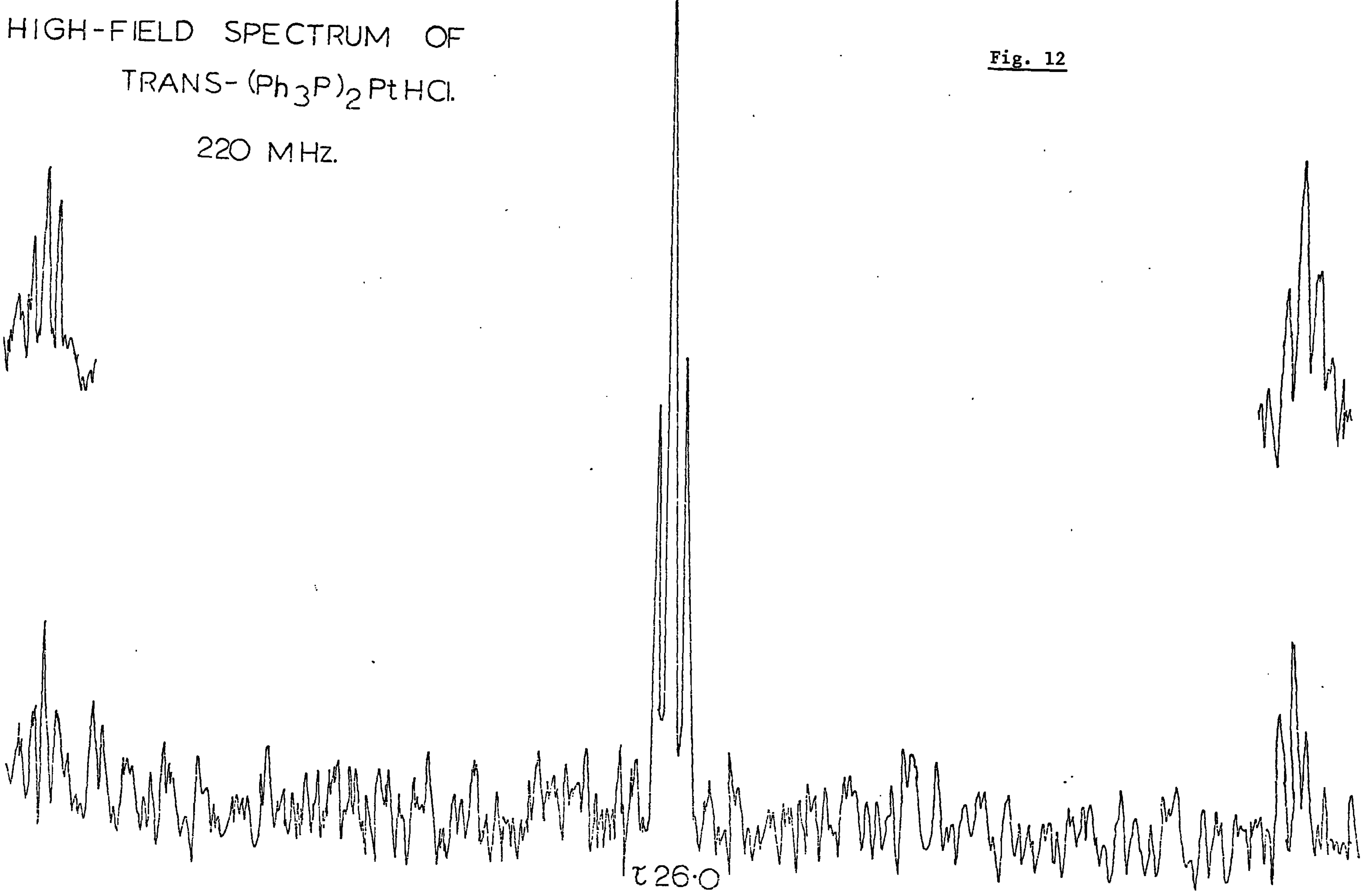


Table 8

Platinum-hydrogen and -chlorine Stretching Frequencies

Complex	ν(Pt-H) cm.$^{-1}$	ν(Pt-Cl) cm.$^{-1}$*	Ref.
trans-$(Et_3P)_2PtHCl$	2183 (C_6H_{14})	269.3	35,36,39
trans-$(PhMe_2P)_2PtHCl$	2205 (Nujol)	282	40
trans-$(Ph_3P)_2PtHCl$	2235 ($CHCl_3$)	274	This work
(diphos)PtH($GePh_3$)	1998 (Nujol)		37
$[(diphos)PtH(PEt_3)]^+Cl^-$	2043 (Me_2CO)		38
(diphos)PtHCl	2002 (KBr)	286	This work
(diphos)$PtCl_2$	?	292,315	165

*As nujol mulls

The platinum-chlorine stretching frequencies of these supposedly *cis* and *trans* isomers were examined as nujol mulls and were very similar, the values obtained were consistent with chlorine being *trans* to hydrogen ν(Pt-Cl), *trans* form: 274s, '*cis* form': 277s, cm^{-1}. Thus from the solid state infra-red data it can be concluded that both the *trans* and reported *cis* isomers are in fact *trans* hydridochlorides having the grouping Cl-Pt-H. The multiplicity of bands in the region attributable to ν(Pt-H) being due to different crystallographic forms of the *trans* isomer, this is supported by conversion of crystals of the *trans* form having a single ν(Pt-H) band to crystals having a multiplicity of bands and vice-versa by varying the solvents during the crystallisation process.

Similar solid state effects have been observed for other metal-hydride complexes. For example, as a mull *trans*-$(PhEt_2P)_2PtHCl$ shows a variable number of bands in the 2200 cm.$^{-1}$ region ascribable to ν(Pt-H), though its 'H n.m.r. spectrum is that of the trans-complex[162]. Wilkinson et al[163] found a multiplicity of bands due to ν(Ir-H) in the solid phase spectra of $(Ph_3P)_3IrHCl_2$ and $(Ph_3P)_3IrHCl(SnCl_3)$. For solids, the selection rules applicable when discussing infra-red spectra are, in general, different from those used for isolated molecules. A unit cell containing more than one molecular unit can therefore, by intermolecular coupling, give rise to more than one metal-hydride stretching frequency even though the individual molecular units have only one metal-hydrogen bond. It can therefore be concluded that the reported cis and trans isomers are in fact different crystallographic forms of the trans isomer and in solution a unique trans form exists.

A recent publication[164] confirmed these findings and observed three crystalline modifications which were easily interconverted according to the method of purification. Adducts of methanol, benzene and acetone were also isolated. Molecular weight determinations showed that a single species was always present in solution.

The hydridochloride, $(Ph_2PCH_2CH_2PPh_2)PtHCl$, prepared from the hydrogenation of $(Ph_2PCH_2CH_2PPh_2)PtCl(SiMe_3)$ (this reaction will be discussed more fully in the next chapter) exhibits platinum-hydrogen and platinum-chlorine stretching frequencies consistent with the groupings P-Pt-H and P-Pt-Cl (see Table 8). Unfortunately, due to the low solubility of the complex its 'H n.m.r. spectrum was not obtained, its mass spectrum did however, at a source temperatureof 270-280°, produce ions due to the loss of hydrogen from the parent ion, i.e. $[(\text{diphos PtCl})]^+$. High resolution mass measurements on the main PtCl isotope combinations agreed to within 10 p.p.m.

A number of attempts were made to prepare this cis-hydridochloride by methods other than the hydrogenation reaction. The reduction of

$(Ph_2PCH_2CH_2PPh_2)PtCl_2$ with hydrazine hydrate proved unsuccessful. During the course of the reaction a pale yellow solution was obtained and some platinum metal deposited. Removal of all volatile material left a pale yellow residue which contained in its infra-red spectrum no band attributable to $\nu(Pt-H)$. An attempt to prepare a cis-hydridochloride by reducing $(Me_2PCH_2CH_2PMe_2)PtCl_2$ with lithium aluminium hydride under mild or vigorous conditions has also proved unsuccessful[162], coloured solutions being obtained from which only unchanged starting material could be isolated.

Cariati and co-workers[14] reacted the zerovalent platinum complexes $(Ph_3P)_4Pt$ and $(Ph_3P)_3Pt$ with various acids e.g. HCl, $HClO_4$ (aqueous and alcoholic) and obtained both ionic and covalent hydrides. With the bischelate complex $(Ph_2PCH_2CH_2PPh_2)_2Pt$, however, no hydride species were produced only the salts $\left[(Ph_2PCH_2CH_2PPh_2)_2Pt\right]^{2+} 2X^-$ ($X^- = Cl^-$, ClO_4^- or HSO_4^-).

The use of anhydrous hydrogen chloride with the bischelate platinum(o) complex again did not yield the cis-hydridochloride. On bubbling HCl into a benzene solution of $(Ph_2PCH_2CH_2PPh_2)_2Pt$ a white precipitate of $\left[(Ph_2PCH_2CH_2PPh_2)_2Pt\right]^{2+}2Cl^-$ immediately formed and no hydridic material was obtained. This difference in reactivity between the chelate platinum complex and the monodentate ligand complex, $(Ph_3P)_4Pt$, is probably due to the triphenylphosphine complex dissociating in solution to give the reactive $(Ph_3P)_3Pt$ and $(Ph_3P)_2Pt$ species which then react with the hydrogen chloride.

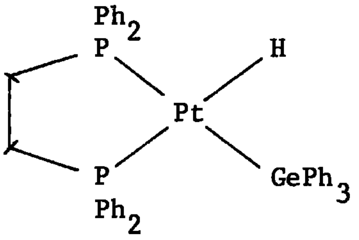
$$\begin{tikzcd}
(Ph_3P)_4Pt \arrow[r, shift left, "-Ph_3P"] & (Ph_3P)_3Pt \arrow[l, shift left] \arrow[r, shift left, "HX"] \arrow[d, shift right, "-Ph_3P"'] & PtH(Ph_3P)_3\ X \arrow[l, shift left] \arrow[d, shift right, "-Ph_3P"'] \\
 & (Ph_3P)_2Pt \arrow[u, shift right] \arrow[r, shift left, "HX"] & (Ph_3P)_2PtHX \arrow[l, shift left] \arrow[u, shift right]
\end{tikzcd}$$

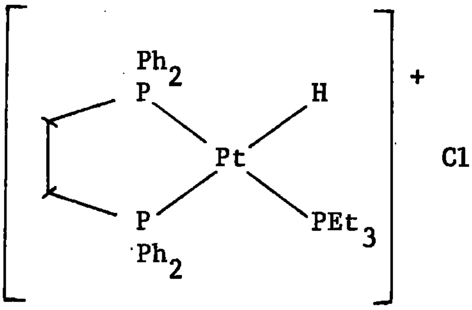
A similar dissociation would be unlikely to occur for the bischelate complex.

Thus attempts to prepare the cis-hydridochloride other than by hydrogenation of the silyl complex have so far failed.

The cis-hydridochloride is a golden-yellow air stable solid, too insoluble in benzene to obtain a proton nuclear magnetic resonance spectrum, though recrystallisation from benzene can be achieved.

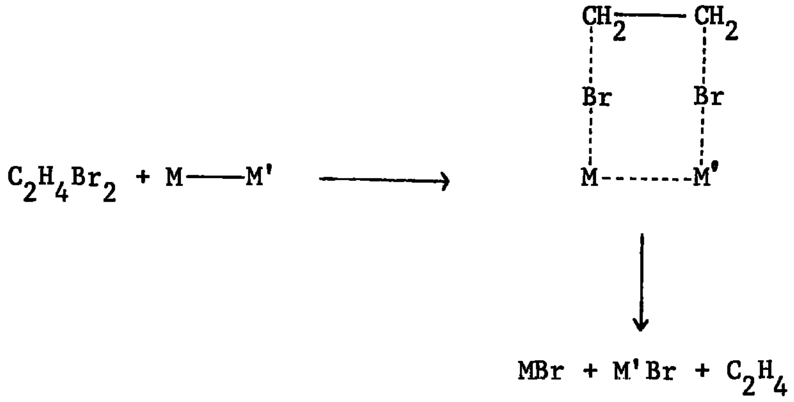
Hydrogenolysis of Pt-Si and Pt-Ge bonds has been used to prepare the complexes I and II in which hydrogen is trans to one phosphorus atom of a chelating phosphine[37,38].


(I)


(II)

The structure of (II) is fully confirmed by its 'H n.m.r. spectrum (p.45) whereas complex (I) , because of its low solubility failed to show the expected 'H n.m.r. spectrum due to the platinum proton, though the n.m.r. integration of phenyl to methylene protons was correct. Confirmation of its structure was obtained by deuteriolysis of $(Ph_2PCH_2CH_2PPh_2)Pt(GePh_3)_2$ at 5 atmospheres pressure and 60^o. This reaction yielded the deuterium analogue of (I), showing ν(Pt-D) at 1428 and δ(Pt-D) at 538 $cm.^{-1}$, together with deuteriotriphenylgermane, ν(Ge-D) at 1471 cm^{-1}.

The reaction of complex (I) with 1,2-dibromoethane proved very interesting as the two products (1,2-bisdiphenylphosphinoethaneplatinum(II) bromide and triphenylgermane) were not those expected by the normal mechanism. The reaction with 1,2-dibromoethane has become diagnostic of a metal-metal bond[93,95,120] usually cleaving it to give the appropriate metal bromides according to the scheme:



However, this four centre intermediate does not explain the products obtained in the reaction of complex(I) with 1,2-dibromoethane. They are perhaps best explained by postulating a concerted attack by the dibromoethane as in Fig. 13.

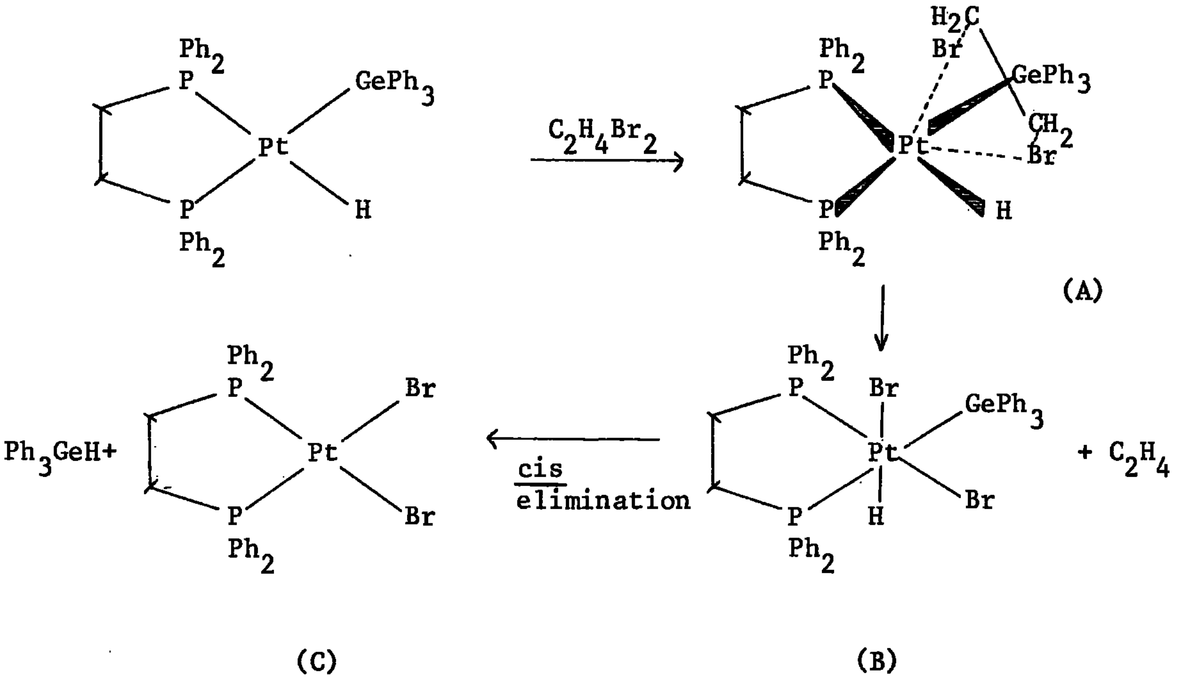


Fig. 13.

The dibromoethane attacks in the plane perpendicular to the plane of the complex as in intermediate (A), this is followed by the elimination of ethylene quantitatively to give the octahedral complex (B), which then undergoes a *cis* elimination of triphenylgermane to give the platinum dibromide complex (C).

The reaction probably proceeds by this mechanism rather than a 4-centre intermediate as previously postulated because of the bulky phenyl groups on the phosphorus and germanium sterically hindering attack by the dibromoethane along the Pt-Ge bond. The dibromoethane cleavages of other platinum complexes, e.g. $(Et_3P)_2Pt(GePh_3)_2$[95] could also be explained by this mechanism.

The reversibility of the reaction,

$$\underline{trans}\text{-}(Et_3P)_2PtCl(GeMe_3) + H_2 \longrightarrow \underline{trans}\text{-}(Et_3P)_2PtHCl + Me_3GeH \qquad (1)$$

has been demonstrated[38], though the hydrogenation of the germyl complex is the most favoured reaction, being quantitative during 24 hours at 20°[41]. From the reversibility of the reaction it is probable that a common intermediate exists in both the forward and reverse reactions, possibly an octahedral complex of the type $(Et_3P)_2PtH_2Cl(GeMe_3)$. Similar reversible processes have been reported for iridium complexes[87,166]. Little thermodynamic work has been reported on the reactions of platinum(II) complexes, and so reaction (2) was selected for more detailed study, aimed at obtaining further information on the mechanism of the reaction:

$$\underline{trans}\text{-}(Et_3P)_2PtCl(SiMe_3) + H_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underline{trans}\text{-}(Et_3P)_2PtHCl + Me_3SiH \qquad (2)$$

The hydridochloride, $\underline{trans}$-$(Et_3P)_2PtHCl$, and an equimolar quantity of trimethylsilane were reacted in benzene in a sealed flask, the hydrogen produced in the reaction was measured to give the position of equilibrium. The flasks were sealed for a period of six weeks to allow the reaction to reach equilibrium.

At 25°, equilibrium constant, $K = 4.4 \times 10^{-3}$.

At 35°, equilibrium constant, $K = 2.7 \times 10^{-3}$.

These values give a heat of reaction for process (2) of -8.8 kcal.mole^{-1}. (For calculation see appendix). This implies an exothermic reaction i.e.

a decrease in equilibrium constant as the temperature is raised. Thus, an increase in temperature favours the hydrogenation of the silyl complex, i.e. in reaction (2), the rate constant $k_1 >> k_2$. The hydrogenation of the germyl complex (equation (1)) was reported to be quantitative after 24 hours at 20°, this is supported to some extent by the small equilibrium constants, in fact at equilibrium at 25° only 6.2% of the platinum hydridochloride had been converted into the silyl complex, implying that the hydrogenation of the silyl complex proceeds to about 94% completion. The fact that the reaction of the hydridochloride with the trimethylsilane proceeds to such a small extent perhaps brings in the greatest errors in the experiment as such small quantities of hydrogen are being measured (c.a. 3 N.c.c.).

The equilibrium constants and heats of reaction for reactions of the type ,

$$Ir(CO)X(L_2) + H_2 \rightleftharpoons Ir(CO)X(L_2).H_2$$

X = Cl, Br or I L = tertiary phosphine

have been measured recently[185], as with the hydrogenation of the platinum-silicon complexes, these reactions have a small equilibrium constant and are exothermic reactions with a heat of reaction of the order of -10 kcals.

CHAPTER 6

Platinum - Group-IVb Complexes

Since the preparation in 1956 by Wilkinson and co-workers of the first silicon- and germanium-transition metal derivatives[145], $Me_3Si-Fe(CO)_2Cp$ and $Ph_3Ge-Fe(CO)_2Cp$, complexes of the group-IVb elements bonded to most of the transition metals have been isolated. For a particular transition metal the stability of the complexes is usually in the order $Sn \sim Ge > Si$. Many of the cleavage reactions of the platinum - Group-IVb compounds are believed to proceed via an oxidative-addition reaction giving an octahedral platinum(IV) intermediate. (Discussed in detail later in this chapter).

This work was undertaken to prepare platinum complexes of silicon, germanium and tin to obtain a comparison of their stabilities and reactions. In order to clarify to some extent the stereochemistry of octahedral intermediates formed in cleavage reactions chelating phosphine platinum complexes were employed in most of the reactions discussed. (Chelate = 1,2-bisdiphenylphosphinoethane).

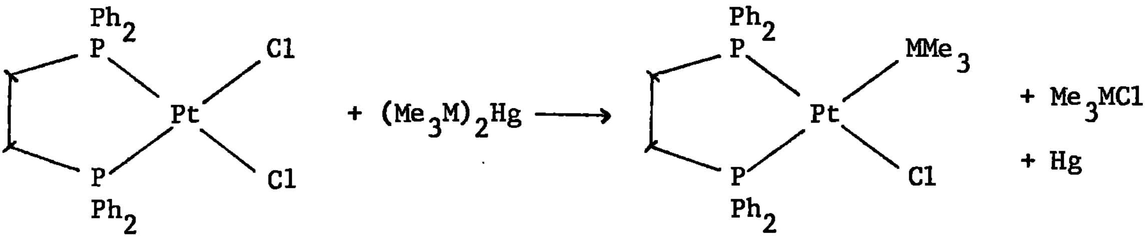
The silyl and germyl complexes were prepared from the chelate platinum dichloride with bis(trimethylsilyl- or germyl)mercury. Before the preparations of these compounds are treated some comments on the synthesis of the bis(trimethylsilyl- and germyl)mercury are perhaps pertinent. Two methods previously described[167,168] for the preparation of bis(trimethylgermyl)mercury and bis(trimethylsilyl)mercury involved the reaction of bromotrimethylgermane or chlorotrimethylsilane in cyclohexane with sodium amalgam and in the case of the germylmercury reacting trimethylgermane with diethylmercury. The first method was adapted, instead of shaking the reactants in a sealed flask they were stirred under nitrogen, as shaking was not involved it was thought that larger quantities could be prepared. This method however, gave only a 9% yield, the low yield was probably due to two reasons:

1. Leakage of air into the reaction flask during the reaction time (c.a. three weeks.)
2. The rather difficult work up, requiring a number of extractions of the reaction mixture with cyclohexane.

Undoubtedly the best method for the preparation of the complexes was shaking (under argon) bromotrimethylgermane or chlorotrimethylsilane with a 0.5% sodium amalgam in a round bottomed flask fitted with a 'rotaflo' tap. The 'rotaflo' tap greatly facilitated both the setting up and work up of the reaction as the flask could be sealed without requiring stoppers or glassblowing and easily opened against a current of dry nitrogen. The yield by this method was about 30%. The major disadvantage was that only about 5-6 grams of the mercury complex could be made because the flask required vigorous shaking thus limiting the amount of sodium amalgam used. An attempt was made to prepare bis(trimethylsilyl)mercury by sealing trimethylsilane and dimethylmercury in an evacuated flask. After three days at room temperature no visible change occurred and the flask was heated at 40° for one week again with no visible change. This lack of reaction is possibly due to the greater energy (58.4 Kcals.)[169] required to dissociate dimethylmercury ($Me_2Hg \longrightarrow Hg + 2R$) compared with that required to dissociate diethylmercury (48.4 Kcals)[169], and the Si-H bond strength being greater than the Ge-H bond strength. Ditertiarybutylmercury has recently been shown[170] to give good yields of $(R_3M)_2Hg$ compounds (R = alkyl, M = Si, Ge or Sn) when reacted with R_3MH, again the low energy required for dissociation of the $(t\text{-}Bu)_2Hg$ probably being the prime reason for the reaction proceeding.

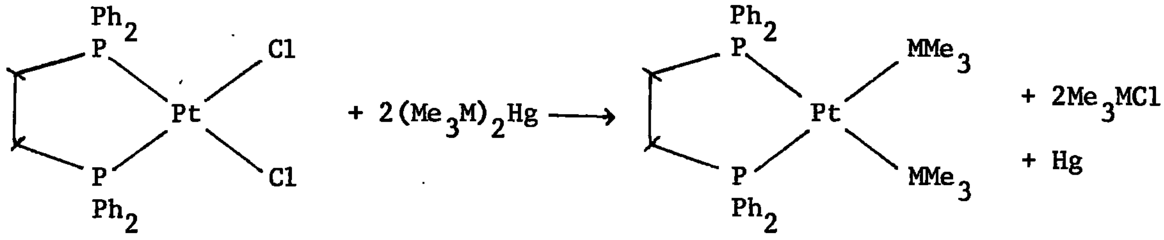
Preparations of Platinum-Group-IVb Complexes

Bis(trimethylsilyl)- and bis(trimethylgermyl)-mercury have been used to prepare platinum-silicon and platinum-germanium complexes. The reaction of $(Et_3P)_2PtCl_2$ with an equimolar quantity of the mercury complex replaced one chloride to give the *trans* derivative $(Et_3P)_2PtCl(MMe_3)$ M = Si or Ge. The use of two moles of the mercury reagent failed to replace the second chloride ion[41]. We have found that the chelate phosphine platinum complex, $(Ph_2PCH_2CH_2PPh_2)PtCl_2$, as a suspension in hot benzene, reacted with an equimolar amount of bis(trimethylsilyl)- or bis(trimethylgermyl)-mercury giving the monosubstituted derivative $(Ph_2PCH_2CH_2PPh_2)PtCl(MMe_3)$ M = Si or Ge. The use of two moles of mercury compound did in fact give the disubstituted complex in good yield (c.a. 60-70%). This contrasts markedly with the $(Et_3P)_2PtCl_2$ reaction when two moles of $(Me_3M)_2Hg$ gave deep red or green solutions from which only the monosubstituted derivatives could be isolated in low yield. This difference in reactivity is most probably due to the high *trans*-influence of the Me_3M moiety, with $(Et_3P)_2PtCl_2$ the first replacement gives *trans*-$(Et_3P)_2PtCl(MMe_3)$ the second replacement would involve the Me_3M-Pt-MMe_3 grouping and as the Me_3M groups have a high *trans*-influence this is probably unstable at room temperature and thus cannot be isolated. With the chelate phosphine complex however, both Me_3M moieties must be *trans* to a phosphine group which has a relatively lower *trans*-influence, leading to a greater stability of the complexes.



(III)

(IV)



(V)

The chelate platinum complex (III), due to its very low solubility in benzene, was reacted as a suspension with no apparent side reactions. This again contrasts with the behaviour of bis(triethylphosphine)platinum (II) chloride when complete solution in benzene was found to be essential to obtain high yields of the silyl or germyl derivatives[41].

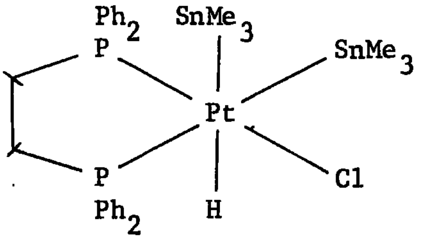
The silyl and germyl derivatives (IV) and (V) are white crystalline solids and in the solid state are stable in air.

Attempts to prepare the complexes (IV) and (V) and the analogous tin derivatives by other methods were also made:

1. <u>From $(Ph_2PCH_2CH_2PPh_2)PtCl_2$</u>

The chelate phosphine complex (III) was reacted with excess trimethylsilane, trimethylgermane and trimethylstannane in benzene. The reactants were sealed in break-seal tubes. After heating for one week at 40° the trimethylsilane and trimethylgermane wereunreacted. The reaction with trimethylstannane did however yield $(Ph_2PCH_2CH_2PPh_2)PtCl(SnMe_3)$ in low yield (8%). The reaction of trimethylstannane with (III) possibly reflects the greater reducing ability of trimethylstannane compared with trimethylsilane and trimethylgermane.

The trimethylstannane reaction was repeated without solvent, a yellowish reaction mixture was obtained which, over ten days, gradually changed to red-brown and some platinum metal was deposited. Removal of the volatile material which contained Me_6Sn_2 and Me_3SnCl left a dark solid showing $\nu(Pt-H)$ at 1960 $cm.^{-1}$ and a broad absorption between 280-290 $cm.^{-1}$ attributable to $\nu(Pt-Cl)$. On recrystallisation from benzene $(Ph_2PCH_2CH_2PPh_2)PtCl(SnMe_3)$ was obtained. The experiment was repeated but the recrystallisation of the dark solid was carried out in a sealed tube and the volatiles examined to give trimethylstannane, tetramethylstannane and hydrogen. From the products obtained and the Pt-H stretching frequency, the dark solid is best formulated as the octahedral complex.



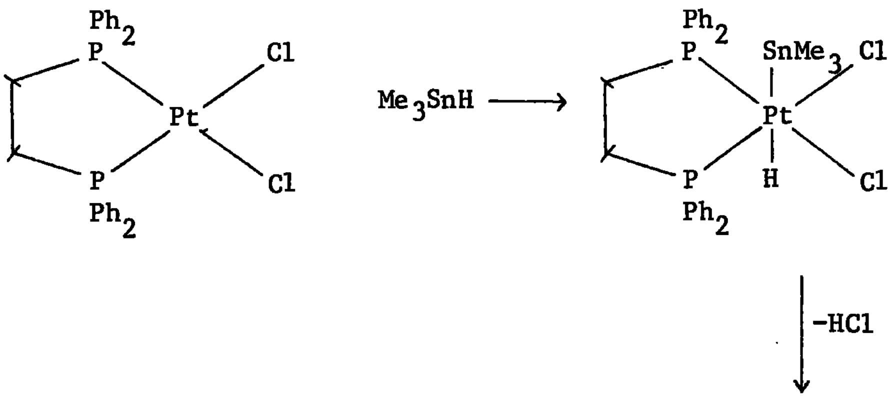
(VI)

This, on dissolving in benzene, eliminates trimethylstannane to give the trimethyltin derivative $(Ph_2PCH_2CH_2PPh_2)PtCl(SnMe_3)$. The isolation of some tetramethylstannane is however, puzzling and is probably formed by decomposition of the trimethylstannane thus:

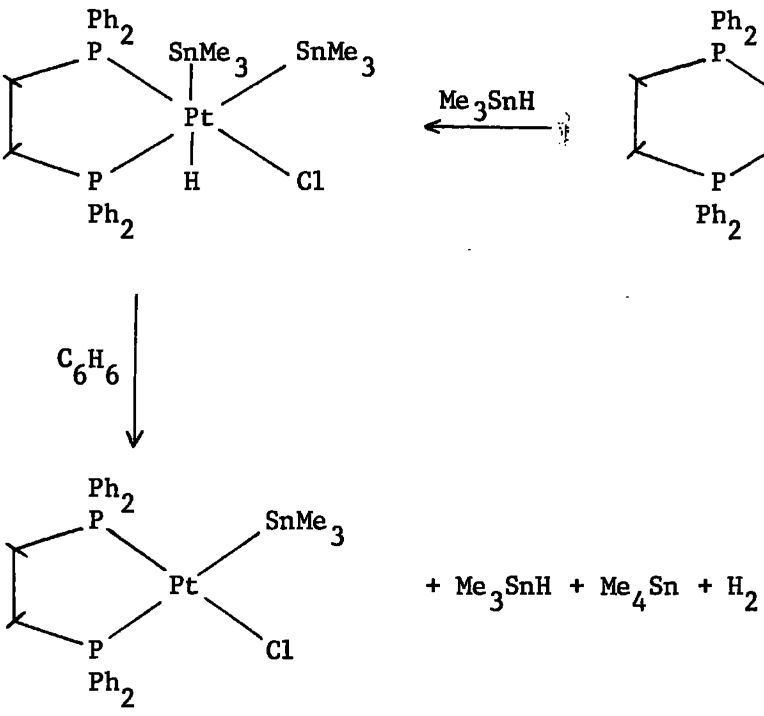
$$4Me_3SnH \longrightarrow 3Me_4Sn + Sn + 2H_2$$

Such decompositions are known to occur for the alkyl tin hydrides in the presence of metals, grease or acids[53]. The isolation of hydrogen is also indicative of some decomposition. The low platinum-hydrogen stretching frequency is consistent with the hydrogen being <u>trans</u> to a group of very high <u>trans</u>-influence, i.e. Me_3Sn rather than Cl or phosphine, thus an overall reaction mechanism can be postulated as a series of oxidative-additions and eliminations:

Scheme A

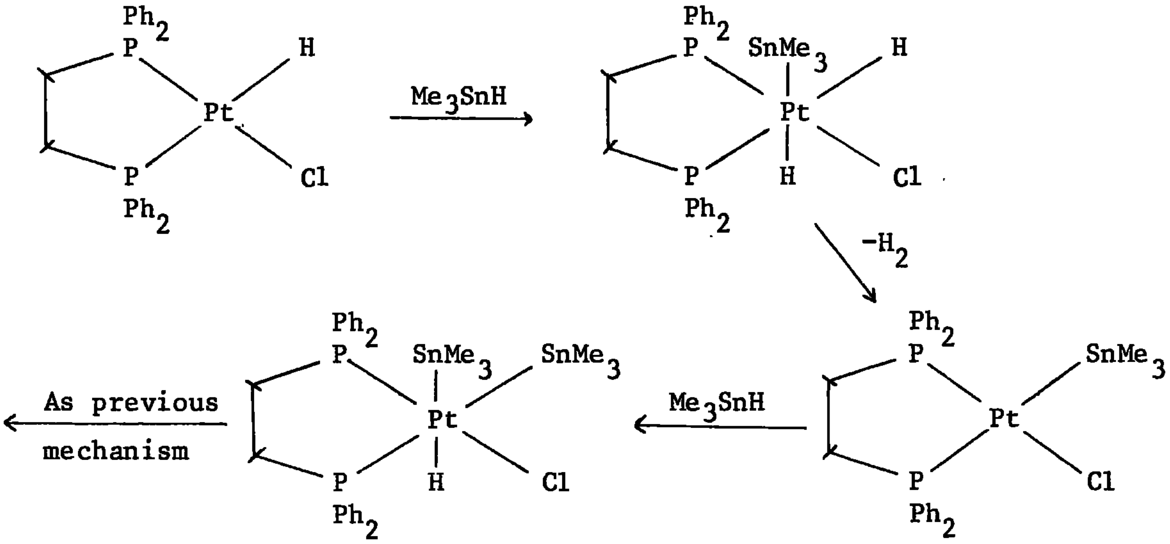


(VII)



(VIII)

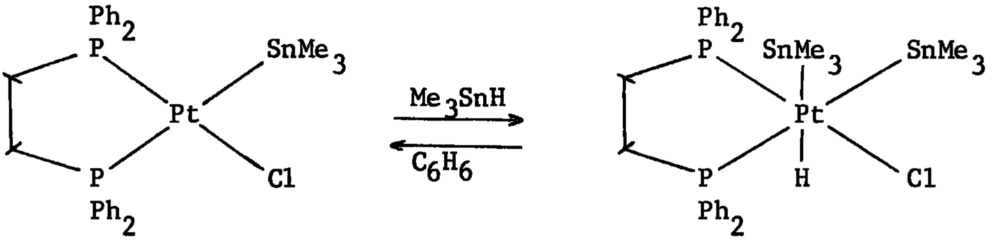
The chlorotrimethylstannane found is probably formed by cleavage of trimethylstannane with hydrogen chloride as no hydrogen chloride was detected. An alternative mechanism could involve the elimination of chlorotrimethylstannane from (VII) giving the platinum hydridochloride which then undergoes further reaction thus:



(VI)

It is perhaps surprising that the octahedral complex (VI) does not eliminate HCl or Me_3SnCl, but it is quite stable as a solid, being unaffected by air after three months. Only in solution in the absence of trimethylstannane does decomposition occur to give $(Ph_2PCH_2CH_2PPh_2)PtCl(SnMe_3)$. This final process has been shown to be reversible, the addition of trimethylstannane to complex (VIII) yields the octahedral derivative (VI).

Scheme B

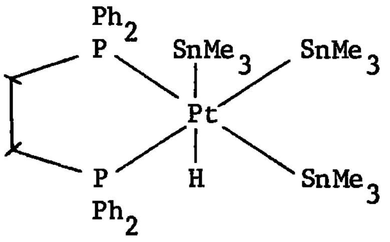


As mentioned earlier, transition metal-tin complexes are more stable than those of the other group-IVb elements, this seems to be supported by the isolation of this tin complex. Hexamethyldistannane, hydrogen and platinum metal were produced in both Schemes (A) and (B); they most likely result from a free radical decomposition of trimethylstannane. (These products were also obtained in other experiments where an excess of trimethylstannane was reacted). Trimethylstannane is known to react by both ionic and free radical mechanisms[53], although the production of hydrogen, hexamethyldistannane and platinum is best explained by free radical decomposition, the isolation of an octahedral adduct would indicate a polar mechanism, so it seems likely that both free radical and polar mechanisms are operative.

2. From Zerovalent Complexes

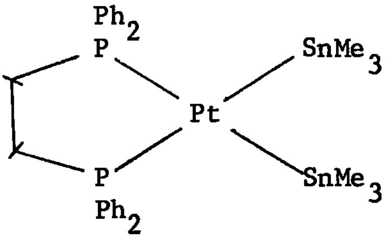
The preparation of platinum-group-IVb complexes from zerovalent platinum derivatives has been reported (p. 50), it was therefore decided to attempt to prepare complexes with a platinum-metal bond by the reaction of the bischelate platinum(o) complex, $(Ph_2PCH_2CH_2PPh_2)_2Pt$, with the alkyl metal hydrides Me_3MH (M = Si, Ge or Sn).

The platinum complex was sealed with a large excess of the neat group-IVb metal hydride. The trimethylsilane and trimethylgermane showed no sign of reaction even after 5 weeks at 70^o. The trimethylstannane however, reacted immediately at room temperature to give a white solid. This again illustrates the greater reactivity of the trimethylstannane over the analogous silicon and germanium hydrides. The white solid showed $\nu(Pt-H)$ at 1960 $cm.^{-1}$ and by infra-red comparison with a previously prepared sample was shown to be



(IX)

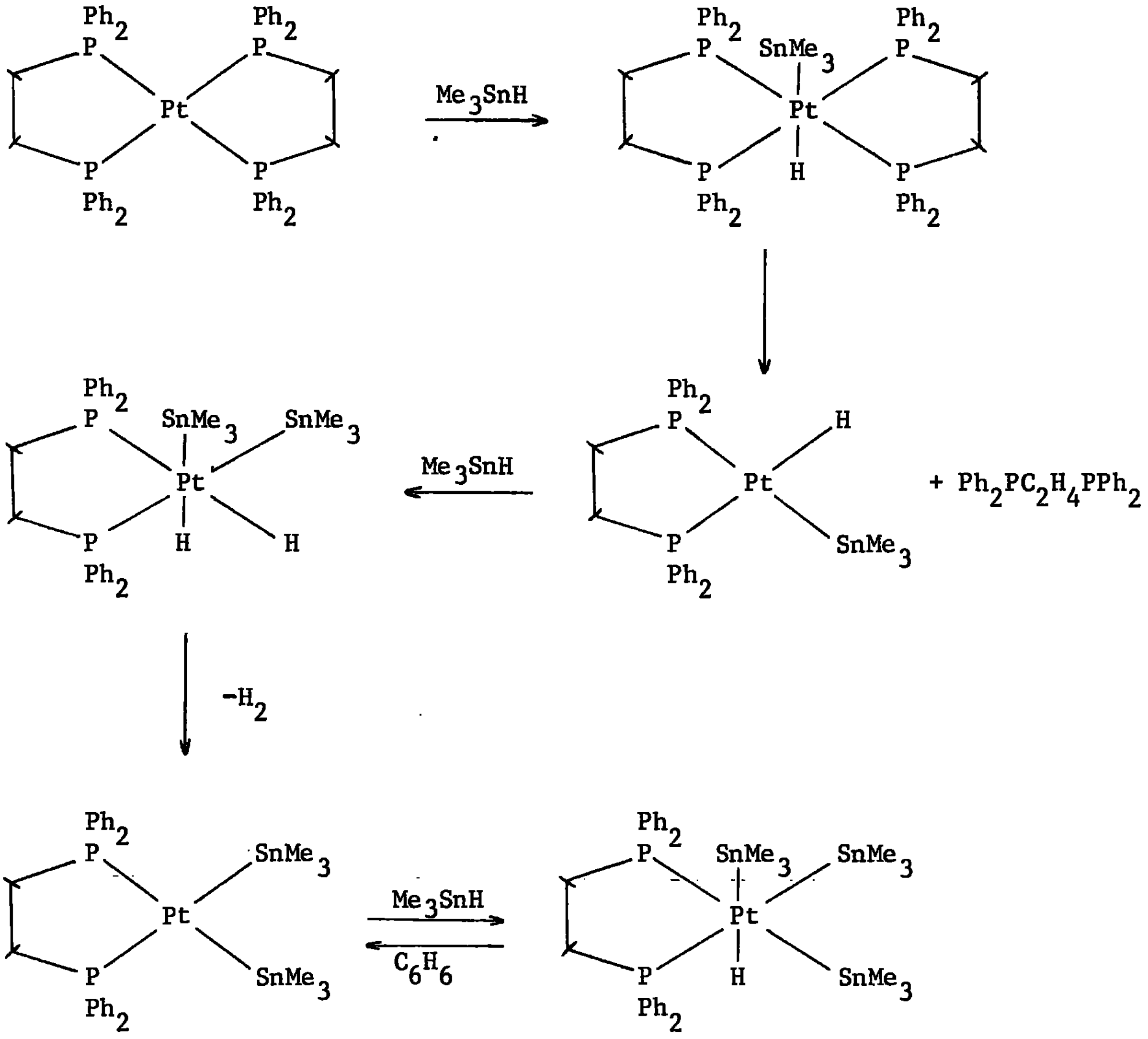
Recrystallisation of complex (IX) from benzene gave the disubstituted derivative (X).



(X)

(These complexes had previously been obtained from the reaction of $(Ph_2PCH_2CH_2PPh_2)PtCl(SiMe_3)$ with excess of trimethylstannane, their full characterisation will therefore be dealt with later when the reactions of the silyl complexes are discussed).

Due to the similar solubility of complex (X) and free chelate in benzene, the presence of free chelate was not detected. An oxidative-addition mechanism can again be postulated for this reaction:



(X) (IX)

As with the complexes (VI) and (VIII) the interconversion of (IX) and (X) was demonstrated by adding trimethylstannane to the disubstituted derivative (X).

The reaction of tetrakis(triphenylphosphine)platinum(o) with trimethylstannane has been reported to give low yields of the disubstituted tin complex[125], the above reaction however, produced the disubstituted complex in 80% yield. As with other reactions involving an excess of trimethylstannane hydrogen was produced. The reaction did however proceed cleanly without separation of platinum metal, and this provides the best route for the preparation of the disubstituted complex.

Attempts to prepare platinum-silicon and -tin complexes were made by reacting the bis chelate platinum(o) complex with chlorotrimethylsilane and chlorotrimethylstannane. Excess of the group-IVb compound was added to a benzene solution of the platinum complex. In both cases an immediate reaction took place at room temperature to produce a yellow sticky solid which after stirring or shaking for thirty minutes gave a white microcrystalline solid. Removal of volatile material and washing the solid with hot benzene yielded the bis chelate salt $[(Ph_2PCH_2CH_2PPh_2)_2Pt]^{2+}2Cl^-$. This was confirmed by the addition of sodium tetraphenylborate to a methanol solution of the complex when a flocculent white precipitate of the tetraphenylborate salt was obtained. The volatile material contained $(Me_3M)_2$ (M = Si or Sn).

Platinum-lead and -tin complexes have been prepared by reacting triphenyllead- and triphenyltin chlorides with tetrakis(triphenylphosphine)-platinum(o)[42,126], the non-formation of platinum-metal bonds with the chelating phosphine complex is probably due to the lack of dissociation of the complex in solution whereas with the triphenylphosphine complexes dissociation does occur.

Summary

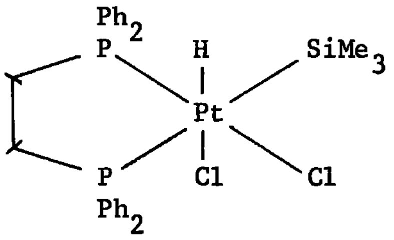
Of the preparative methods attempted only the reactions of $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ with trimethylsilyl- and (trimethylgermyl)mercury were found to be successful for the production of trimethylsilyl (or germyl) platinum complexes. The reaction of trimethylstannane with

$(Ph_2PCH_2CH_2PPh_2)PtCl_2$ and $(Ph_2PCH_2CH_2PPh_2)_2Pt$ did give the mono- and disubstituted tin derivatives respectively. The failure to obtain silyl and germyl complexes by analogous methods is probably due to the weaker and more polar nature of the tin-hydrogen bond compared to the silicon- or germanium-hydrogen bonds. The reaction of the zerovalent platinum complex with trimethylstannane provides a convenient route to the disubstituted tin complex. The monosubstituted derivative, although it can be prepared as discussed above, is perhaps prepared more conveniently by hydrogen chloride cleavage of the disubstituted derivative as will be discussed in the next Section.

Reactions of the Complexes

The reactions involving cleavage of platinum-metal bonds are, in general, believed to proceed via an octahedral platinum(IV) intermediate[172]. In the reactions studied the products can be shown to be consistent with such a mechanism, and in a number of cases octahedral adducts were isolated.

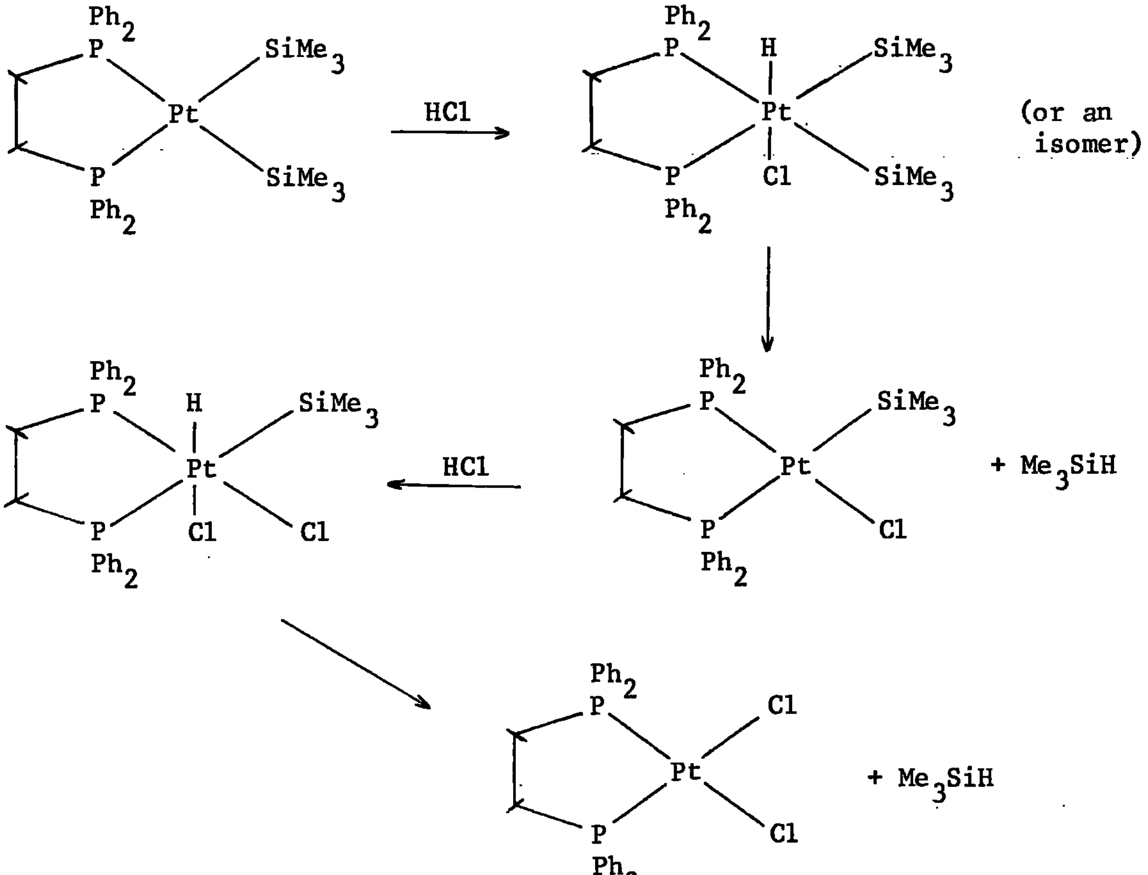
Hydrogen chloride reacted with the monosubstituted silyl derivative $(Ph_2PCH_2CH_2PPh_2)PtCl(SiMe_3)$ in equimolar quantities, cleaving the platinum-silicon bond to give the phosphine platinum dichloride complex and trimethylsilane. These products could originate from addition of HCl to the complex followed by the elimination of trimethylsilane from the resulting octahedral complex. No evidence of a Pt-H bond was obtained and chlorotrimethylsilane was not detected, thus the cleavage appears to be quite specific. If <u>cis</u> elimination from the octahedral intermediate is assumed then it can be best formulated as (XI)



(XI)

or an isomer.

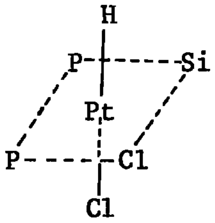
The Me_3Si group will always be cis to a Cl, but elimination as trimethylsilane rather than chlorotrimethylsilane occurs. This contrasts with the behaviour of non-chelate trans complexes when the Me_3M moiety (M = Si or Ge) is cleaved as the chloroderivative yielding the platinum hydridochloride. Similarly, the reaction of the disubstituted silyl complex $(Ph_2PCH_2CH_2PPh_2)Pt(SiMe_3)_2$ with two equivalents of hydrogen chloride cleaves both Me_3Si moieties in the same direction producing the phosphine platinum dichloride and eliminating the Me_3Si exclusively as trimethylsilane. Again no evidence of a Pt-H bond was obtained. This reaction is also in sharp contrast to the cleavage of cis disubstituted non-chelate complexes when the two silyl groups are cleaved in opposite directions to give the hydridochloride, R_3SiH and R_3SiCl[103]. Thus it appears that chelate complexes give the platinum dichloride and non-chelate complexes yield the hydridochloride. The overall reaction of the chelate derivatives with HCl can be explained by oxidative-addition of HCl followed by elimination of trimethylsilane:



The cleavage of the monosubstituted derivative being the second stage of the disubstituted complex cleavage. The actual stereochemistry of the octahedral derivatives cannot be assigned unambiguously from a knowledge of the products but assuming cis elimination the Me_3Si and H must always be cis.

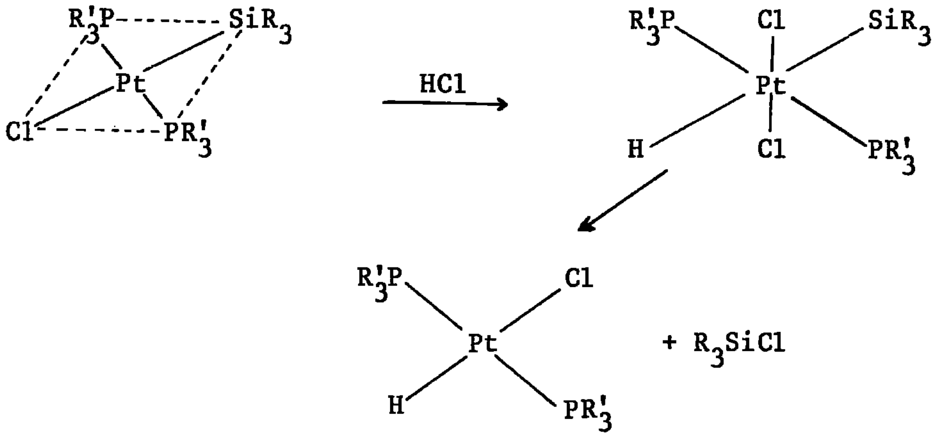
This high degree of specificity in the cleavage reactions can be due purely to kinetic factors, but the relative stabilities of the products may also be important in determining the course of the reaction. The non-chelate complexes yield the hydridochloride and eliminate chlorotrimethylsilane whereas the chelate complexes give the dichloride and eliminate trimethylsilane. This elimination may be preferred due to the formation of the stable phosphine platinum dichloride rather than the elimination of chlorotrimethylsilane, which would leave the less kinetically stable cis hydridochloride in which the Pt-H bond is trans to a phosphine group of high trans-influence thus making it quite labile. In the non-chelate complexes the hydridochloride formed is the trans compound in which the hydride is trans to Cl which has a relatively low trans-influence, and is therefore kinetically more stable.

The differences in behaviour can also be interpreted in terms of the stereochemistry of the 6-coordinated intermediate, the cleavage of the first Pt-Si bond in both chelate and non-chelate complexes results in elimination of R_3SiH. If then the phosphine groups are mutually cis, as in the chelate complexes they must necessarily be, then the silicon group is most likely to be cis to the hydrogen of the second molecule of HCl as in (XI)



(XI)

and elimination of R_3SiH occurs again. In non-chelate complexes however, after the cleavage of one Pt-Si bond the phosphine groups may not be *cis* and on addition of a further mole of HCl the silyl group may be *trans* to hydrogen as in (XII) and *cis* elimination of R_3SiCl occurs to yield the platinum hydridochloride.



(XII)

The omplex $(Et_3P)_2Pt(GePh_3)_2$,which exists in solution as both *cis* and *trans* forms, on reaction with HCl gave both $(Et_3P)_2PtHCl$ and $(Et_3P)_2PtCl_2$.[95] This supports the above mechanism that if the phosphine groups are *trans* then elimination of the chloro-metal compound occurs to yield the hydridochloride whereas with *cis* phosphine groups the group-IVb-metal hydride is eliminated to leave the platinum dichloride complex.

The cleavage of the disubstituted tin derivative $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$ with one equivalent of hydrogen chloride yielded the monosubstituted tin compound $(Ph_2PCH_2CH_2PPh_2)PtCl(SnMe_3)$ and trimethylstannane, again the group-IVb moiety being cleaved exclusively as the hydride and not as the chloroderivative. The cleavage proceeded smoothly at room temperature in benzene and provides perhaps the best route for the preparation of the monosubstituted tin derivative. These products are also consistent with an oxidative-addition mechanism to give an octahedral intermediate followed by elimination of trimethylstannane.

The hydrogenations of the mono- and disubstituted silyl derivatives have been studied, and both react with hydrogen at atmospheric pressure. Earlier reports of hydrogenations of chelate complexes indicated that high pressure conditions were required[37,103]. The ease of hydrogenation of these trimethylsilyl derivatives reflects the general trend in platinum-group-IVb complexes of greater reactivity of methylsubstituted group-IVb complexes compared to aryl substituted.

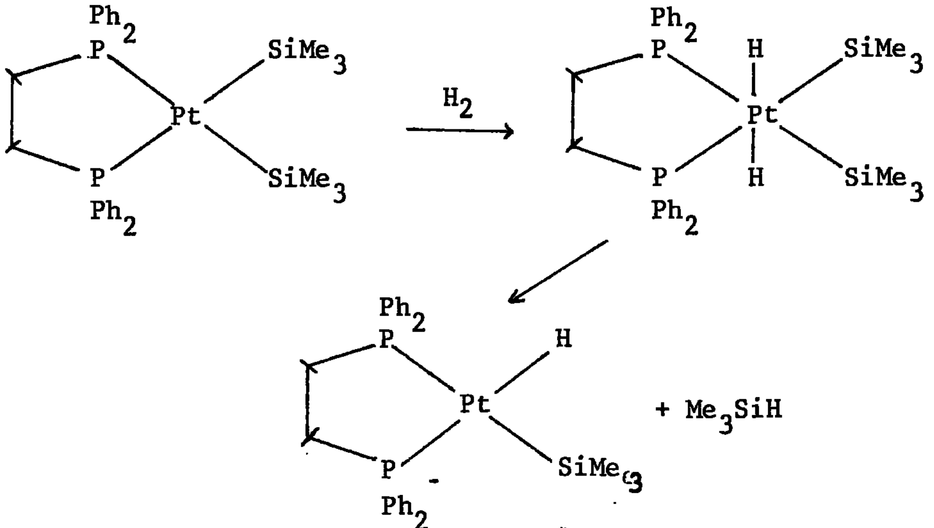
The complex $(Ph_2PCH_2CH_2PPh_2)PtCl(SiMe_3)$ hydrogenated at one atmosphere pressure and 70° to yield the cis hydridochloride $(Ph_2PCH_2CH_2PPh_2)PtHCl$. Trimethylsilane and hexamethyldisilane were identified in the volatile material. Removal of the volatile material left the hydridochloride as a yellow-brown solid, (ν(Pt-H) at 2002 $cm.^{-1}$), which proved difficult to purify. A recrystallisation from benzene was finally achieved by slow evaporation of the solvent. The 'H n.m.r. spectrum of the hydridic proton was not obtained due to insufficient solubility of the complex, the phenyl and methylene proton resonances however, were obtained and the observed ratio of protons was 4.8 : 1; (the cis hydridochloride requires 5 : 1). Its mass spectrum at a source temperature of 270-280° produced ions due to loss of hydrogen from the parent i.e. $(\text{chelate PtCl})^+$. High-resolution mass measurements on the main PtCl isotope combinations agreed to within 10 p.p.m. (Table 9).

Hydrogenation of the disubstituted silyl complex proceeded at 1 atmosphere pressure, but the product was found to be dependent on the reaction temperature. Between 25° and 40° cleavage of one silyl group occurred, but at 60-80° both silyl groups were cleaved.

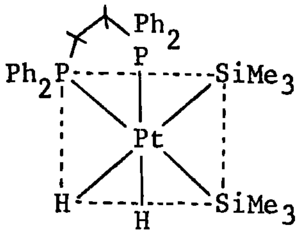
Table 9

Nominal mass	Ion	Mass observed	Mass calc.	Δm. p.p.m.
627	chelate^{194}Pt^{35}Cl	627.06428	627.07045	9
628	chelate^{195}Pt^{35}Cl	628.06996	628.07245	3
629	chelate^{194}Pt^{37}Cl	629.06888	629.06750	2
630	chelate^{195}Pt^{37}Cl	630.06841	630.06950	1
631	chelate^{196}Pt^{37}Cl	631.06856	631.06970	1

The cleavage of one silyl group as trimethylsilane, (some hexamethyldisiloxane was also found due to the admission of some air during work up of the volatiles), yielded the hydrido derivative $(Ph_2PCH_2CH_2PPh_2)PtH(SiMe_3)$ as a yellow brown solid showing ν(Pt-H) at 2000 $cm.^{-1}$, (KBr disc). This is consistent with the hydride being trans to a phosphine group, c.f. ν(Pt-H) at 2002 $cm.^{-1}$ in the cis-hydridochloride. The solid was obtained by removal of the solvent onto a vacuum line and a satisfactory recrystallisation was not achieved. As with the cis hydridochloride the complex was not sufficiently soluble to allow the detection of the highfield hydridic proton in its 'H n.m.r. spectrum. The reaction mechanism can again be postulated as addition of hydrogen forming an octahedral intermediate, followed by elimination of trimethylsilane:



The addition of hydrogen could be a cis addition if, in solution, a Pt-P bond is momentarily broken, this would give the octahedral complex (XIII).



(XIII)

Cis elimination of trimethylstannane from this complex would then give the required product, $(Ph_2PCH_2CH_2PPh_2)PtH(SiMe_3)$.

The reaction of the disubstituted silyl derivative with hydrogen (1 atm., 70^o) resulted in cleavage of both silyl groups as trimethylsilane. Removal of volatiles left a yellow-brown solid, its infra-red spectrum showed neither ν(Pt-H) nor methyl rock of the Me_3Si moiety. Only resonances due to protons of the chelate were obtained in its 'H n.m.r. spectrum, therefore, from this evidence and the analytical data the product can be postulated as a zerovalent cluster compound $\left[(Ph_2PCH_2CH_2PPh_2)_3Pt_4\right]$. An osmometer molecular weight determination gave a molecular weight of 2,190, this agrees to within 10% of the 1974 required for the cluster compound. A possible structure of this complex could involve an approximately tetrahedral arrangement of the four platinum atoms with the three phosphine chelates bonding between different platinum atoms. (Fig. 14)

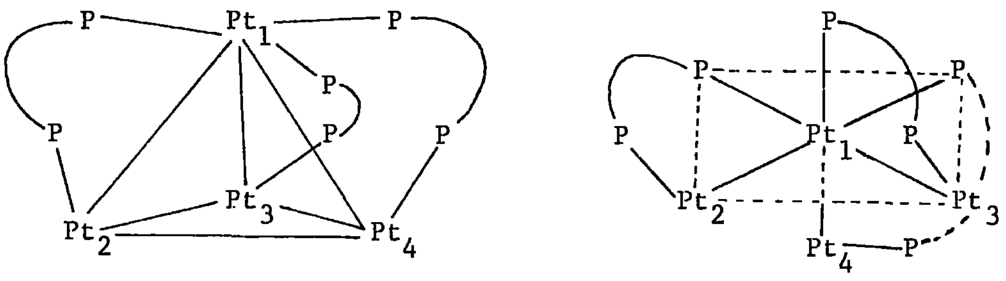


Fig. 14

Pt_1 will be in an approximately octahedral environment.

Hydrogenation of the disubstituted tin complex $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$ at 25° was not achieved, reflecting the general trend that platinum-tin compounds are more stable than analogous platinum-silicon complexes. The tin compound, *trans*-$(Ph_3P)_2Pt(SnMe_3)_2$, has been hydrogenated to give the hydride *trans*-$(Ph_3P)_2PtH(SnMe_3)$[125]. This difference in reactivity is probably due to the high *trans*-influence of the Me_3Sn group facilitating cleavage in the *trans* complex, $(Ph_3P)_2Pt(SnMe_3)_2$.

The complexes $(Ph_2PCH_2CH_2PPh_2)PtHCl$, $(Ph_2PCH_2CH_2PPh_2)PtH(SnMe_3)$ and $[(Ph_2PCH_2CH_2PPh_2)_3Pt_4]$ are all yellow-brown solids and in the solid state are air-stable. Apart from the hydridochloride the complexes do not melt sharply but decompose over a temperature range. The cluster compound showed no visible change on heating to 150° in vacuo, but slowly darkened and charred as heating was continued.

An interesting series of reactions was carried out on the mono- and disubstituted derivatives (IV) and (V) involving exchange with Me_3MH compounds (M = Si, Ge or Sn). For the monosubstituted complexes, the exchange reactions proceed as in Fig. 15.

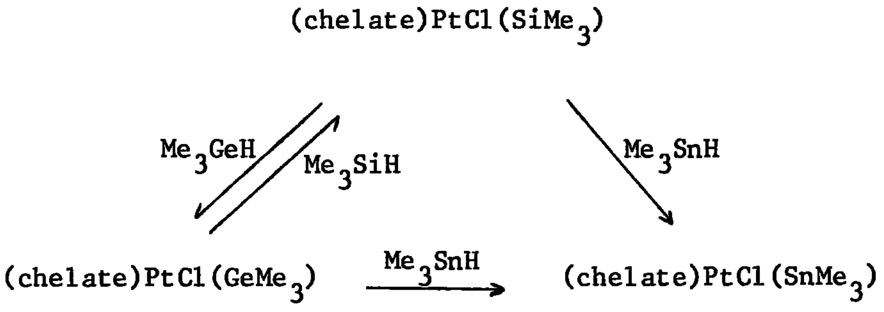


Fig. 15

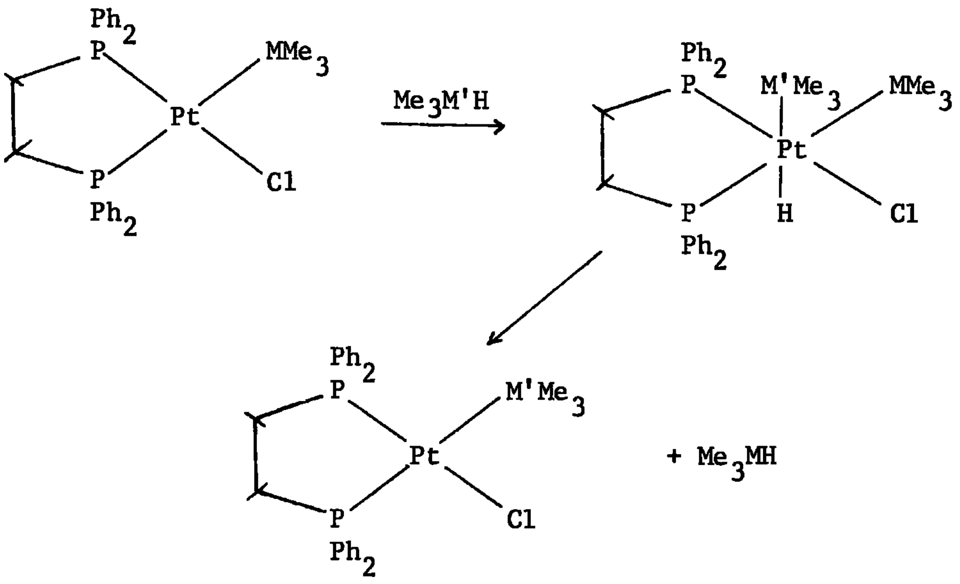
Similarly, for the disubstituted complexes the exchange reactions proceed as in Fig. 16.

$$\begin{tikzcd}
 & \text{(chelate)Pt}(\text{SiMe}_3)_2 \arrow[dl, shift right, "2\text{Me}_3\text{GeH}"'] \arrow[dr, "2\text{Me}_3\text{SnH}"] & \\
\text{(chelate)Pt}(\text{GeMe}_3)_2 \arrow[ur, shift right, "\text{Me}_3\text{SiH}"'] \arrow[rr, "2\text{Me}_3\text{SnH}"] & & \text{(chelate)Pt}(\text{SnMe}_3)_2
\end{tikzcd}$$

Fig. 16

The reactions were carried out in benzene in break-seal tubes and the exchanges favoured (chelate)Pt-MMe_3 products in the order M = Sn>Ge>Si, i.e. the exchanges Pt-Si→Pt-Ge→Pt-Sn proceeded smoothly (typically 12 hours at 40°), giving the product in an almost quantitative yield eliminating Me_3MH. However, the reverse order exchanges could not be achieved except for a small Pt-Ge→Pt-Si conversion. For both the mono- and disubstituted derivatives in the Pt-Ge to Pt-Si conversion no solid product could be isolated containing a Pt-Si bond due to its formation in very small yield, but the eliminated trimethylgermane was detected. A large excess of trimethylsilane was required to effect elimination of a small quantity of trimethylgermane in the reverse reactions, whereas the exchanges in the order Pt-Si→Pt-Ge→Pt-Sn could be achieved using the stoichiometric amounts of Me_3MH.

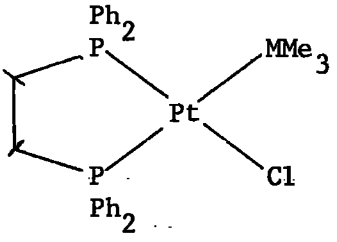
The reversibility of the Pt-Si⇌Pt-Ge conversions suggests that they are equilibrium reactions with the position of equilibrium favouring the product with platinum bonded to the heavier metal. This is further evidence supporting the general trend that complexes involving Pt-Sn and Pt-Ge bonds are more stable than the analogous Pt-Si complexes. Again an oxidative-addition mechanism can be postulated, from the reversibility of the reaction Pt-Si⇌Pt-Ge it seems reasonable that there is a common intermediate which can be formulated as the 6-coordinated platinum(IV) intermediate (XIV). c.f. the hydrogenation of trans-$(Et_3P)_2PtCl(GeMe_3)$ [38].



(XIV)

(M,M' = Si, Ge or Sn)

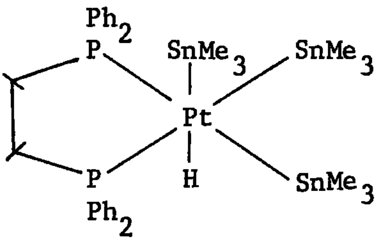
None of the stoichiometric reactions in Figs. 15 and 16 produced direct evidence of octahedral adducts but the reaction of complexes



(IV)

(M = Si or Ge)

with excess trimethylstannane did yield an octahedral platinum(IV) complex (IX):

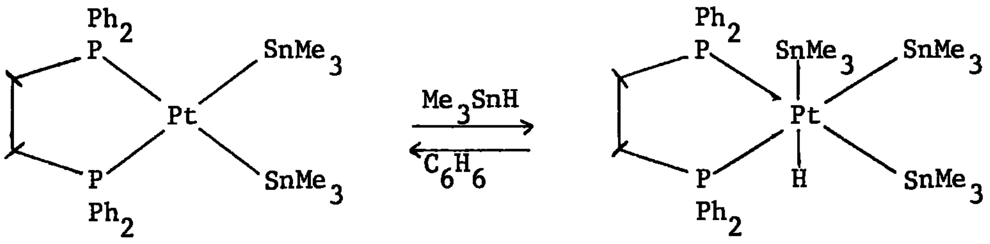


(IX)

(The same complex was also isolated in the reaction of $(Ph_2PCH_2CH_2PPh_2)_2Pt$ (o) with Me_3SnH (p. 87), chronologically it was first obtained from the exchange reactions above therefore its characterisation will be treated here).

On removal of the volatile material which contained H_2, Me_3MH, Me_3SnCl and Me_6Sn_2, from the reaction of complexes of the type (IV) with excess trimethylstannane a white crystalline solid was obtained (IX). This solid (contaminated with some platinum metal formed in the reaction) showed ν(Pt-H) at 1960 cm^{-1}.

The same complex was obtained when either the platinum-silicon or the platinum-germanium compound was used as the starting material. Recrystallisation of the complex (IX) from benzene yielded the disubstituted tin complex $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$. Recrystallisation of the complex in a sealed system and an examination of the volatile products again produced the disubstituted tin complex together with trimethylstannane and small quantities of tetramethylstannane and hydrogen. The addition of trimethylstannane to the disubstituted tin complex produced a white solid showing ν(Pt-H) at 1960 $cm.^{-1}$, its infra-red spectrum being identical to that of the solid obtained from the exchange reaction. Thus it appears that the octahedral solid, in solution, is only stable in the presence of excess trimethylstannane, its decomposition however being reversible:



The low Pt-H stretching frequency of 1960 $cm.^{-1}$ is consistent with the hydride being trans to a group of high trans-influence i.e. the Me_3Sn group, therefore the stereochemistry of the octahedral complex can be assigned uniquely as that shown in (IX).

Although the octahedral complex decomposes rapidly in benzene solution, like the octahedral complex $(Ph_2PCH_2CH_2PPh_2)PtHCl(SnMe_3)_2$ (VI), it is air-stable in the solid state, a sample being unchanged after three months in air.

Further information on the reaction was obtained by reacting the monosubstituted silyl complex with excess trimethylstannane and obtaining the 'H n.m.r. spectrum of the resulting mixture. This spectrum showed a broad resonance centred on 15.25τ attributable to the Pt-H proton. The broadness is probably due to the proton being coupled to ^{195}Pt(spin½, 34% abundant), both ^{31}P nuclei (spin½, 100% abundant) and both magnetic isotopes of the three tin atoms: ^{117}Sn (spin½, 7.61%abundant; ^{119}Sn (spin½, 8.5% abundant). The hydridic proton of the displaced Me_3SiH showed eight of the expected ten lines due to coupling with the nine protons of the methyl groups, $J(H\text{-}Si\text{-}CH_3) = 3.5$ Hz. whereas the resonance due to the hydridic proton of Me_3SnH was not resolved (the spectrum of Me_3SnH in benzene did have the Sn-H resonance resolved), but merely broadened* This implies a rapid exchange of free trimethylstannane with the octahedral complex (IX). This rapid exchange would also lead to broadening of the Pt-H resonance as was observed. The 9-10τ region of the spectrum proved complex, due to methyl resonances of Me_3SnH, Me_3SiH and Me_3Sn bonded to platinum together with its coupling to ^{195}Pt, ^{31}P, ^{117}Sn and ^{119}Sn.

As described earlier, a similar octahedral platinum (IV) complex $(Ph_2PCH_2CH_2PPh_2)PtHCl(SnMe_3)_2$ was isolated from the reaction of $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ and trimethylstannane.

A satisfactory analysis of the complex (IX)had previously been marred by the fact that some platinum metal was formed in the reaction and due to decomposition of the solid a recrystallisation was not possible. However some colourless crystals which appeared to be free of platinum metal were formed in the n.m.r. tube and a satisfactory elemental analysis for $(Ph_2PCH_2CH_2PPh_2)PtH(SnMe_3)_3$ was obtained.

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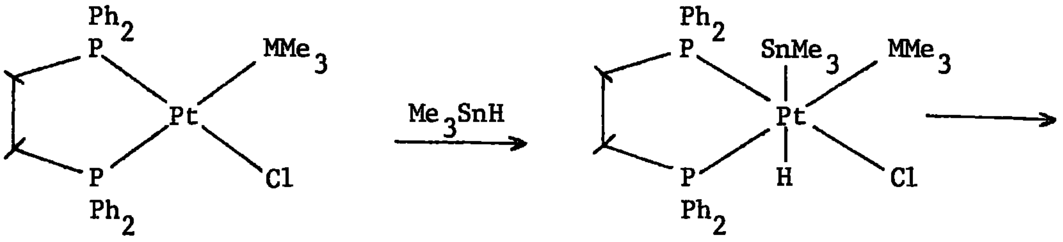
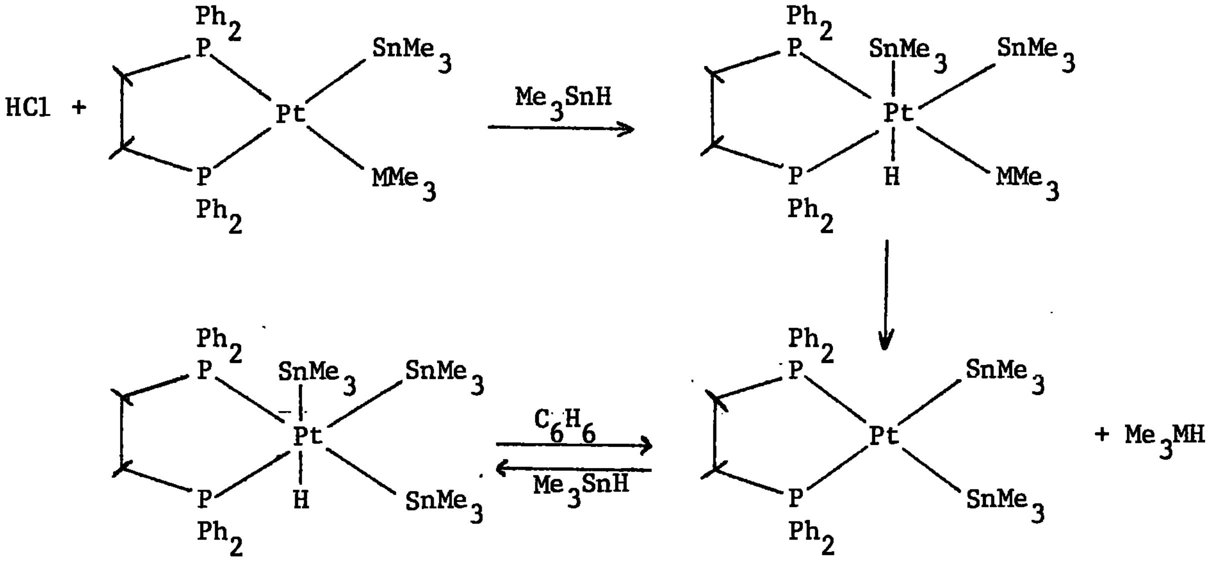
*See p. 142

As with other reactions involving excess trimethylstannane quantities of hydrogen, hexamethyldistannane and some platinum metal were produced, most likely from free radical decomposition of some trimethylstannane. However, the reaction mechanism can be best explained by a series of oxidative-additions followed by cis eliminations:



(M = Si or Ge)



The complexes, $[(Ph_2PCH_2CH_2PPh_2)PtH(Et_3P)]^+Cl^-$, $[(Ph_2PCH_2CH_2PPh_2)PtSiMe_3(Et_3P)]^+BPh_4^-$, trans-$(Et_3P)_2PtPh(GeMe_3)$ and trans-$(Et_3P)_2PtCl(SiMe_3)$ were all tested for catalytic activity in hydrogenations but were found to be negative. The reactions of $[(Ph_2PCH_2CH_2PPh_2)PtGeMe_3(Et_3P)]^+BPh_4^-$, trans-$(Et_3P)_2PtCl(GeMe_3)$ and $[(Ph_2PCH_2CH_2PPh_2)PtGeMe_3(Et_3P)]^+Cl^-$ with hex-1-ene were also carried out, but even after heating at 60° for several days no reaction occurred, possibly due to steric reasons.

Infra-red Spectra

The infra-red spectra of the platinum-group-IVb complexes prepared were very similar, the bands due to ν(Pt-Cl), ν(Pt-H) and methyl rock, $\rho(CH_3)$ of the Me_3M grouping being the most characteristic features of the spectra. These values are summarised in Table 10.

Table 10

Complex	$\rho(CH_3)$	ν(Pt-Cl)	ν(Pt-H)
(chelate)PtCl($SiMe_3$)	825	299	
(chelate)Pt$(SiMe_3)_2$	822		
(chelate)PtCl($GeMe_3$)	818	300	
(chelate)Pt$(GeMe_3)_2$	815		
(chelate)PtCl($SnMe_3$)	742	280	
(chelate)Pt$(SnMe_3)_2$	742		
(chelate)PtH($SiMe_3$)	819		2000
(chelate)PtHCl$(SnMe_3)_2$		280-290 (broad)	1960
(chelate)PtH$(SnMe_3)_3$	742		1960

Values are in cm^{-1}; samples run as CsI discs.

Proton Magnetic Resonance

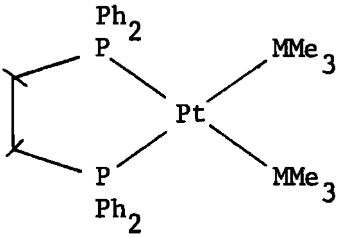
The use of 'H n.m.r. spectroscopy in determining the stereochemistry of platinum-group-IVb complexes has already been described (p. 66). The 'H n.m.r. parameters of the complexes are given in Table 11. The silyl and germyl derivatives gave the expected spectrum for the methyl protons of the Me_3Si and Me_3Ge groupings in a cis configuration.

Table 11

Complex	τ(MMe_3)	J(^{195}Pt-M-C-'H)	J(^{31}P-Pt-M-C-'H)	J(^{117}Sn-C-'H)	J(^{119}Sn-C-'H)
(chelate)Pt($SiMe_3$)$_2$	9.36	26.0	2.5		
(chelate)PtCl($SiMe_3$)	9.41	16.9	2.9		
(chelate)PtH($SiMe_3$)	9.2	31.5	2.9		
(chelate)Pt($GeMe_3$)$_2$	9.23	18.1	2.3		
(chelate)PtCl($GeMe_3$)	9.37	12.2	2.6		
(chelate)Pt($SnMe_3$)$_2$	9.62	8.9		29.9	39.2
(chelate)PtCl($SnMe_3$)	9.5	8.3		28.4	36.9

Samples run in C_6D_6.

i.e.

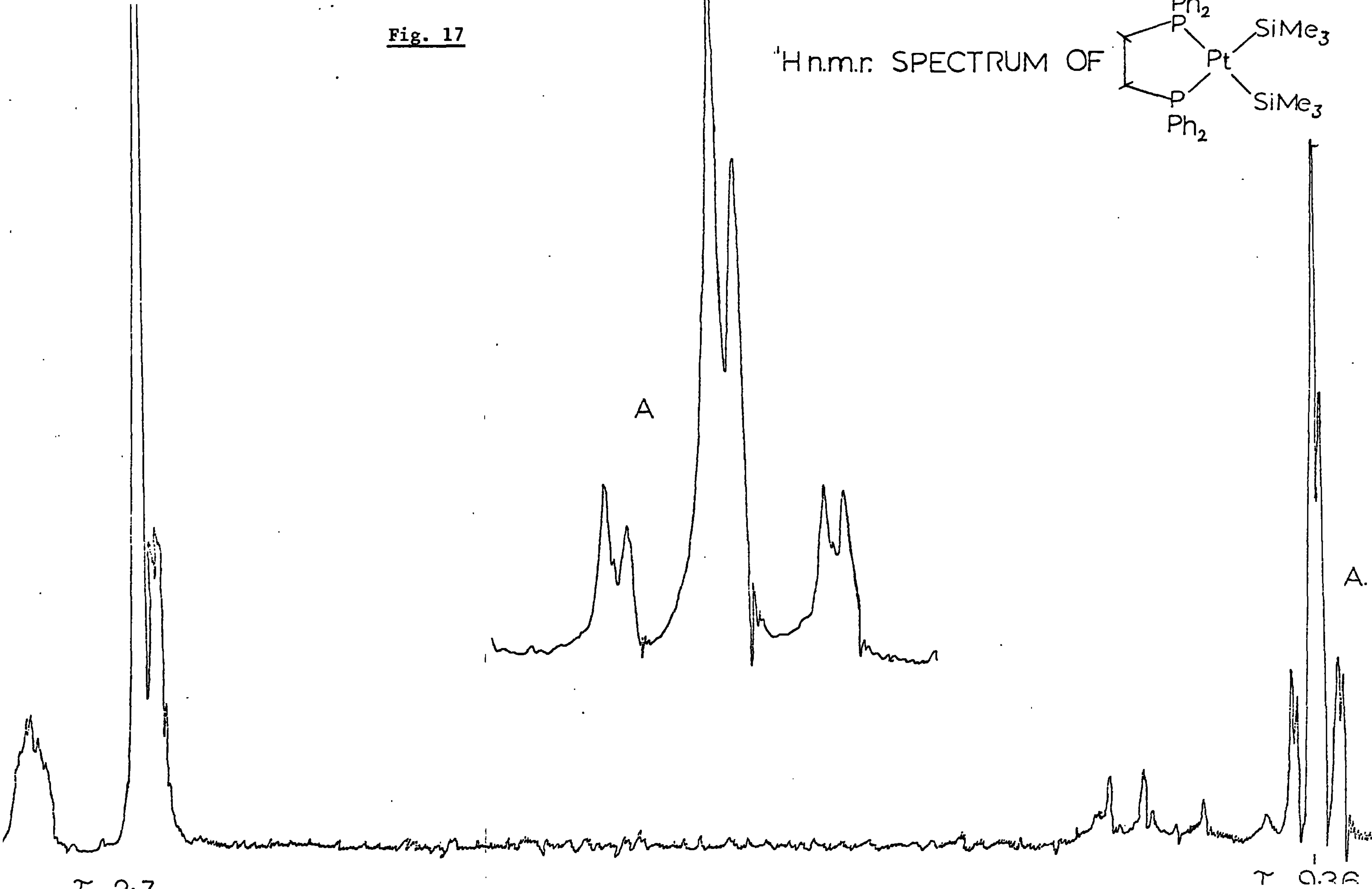


M = Si or Ge

The methyl resonance appeared as a six line signal (three doublets) in the ratio 1:1:4:4:1:1 due to coupling with the ^{195}Pt nucleus and the trans ^{31}P nucleus as explained on p. 66 (Fig. 17). The coupling constants, J(^{195}Pt-M-C-'H) and J(^{31}P-Pt-M-C-'H) are consistent with values reported for other platinum-group-IVb complexes[38,41]. The solubilities of the complexes proved a difficulty in obtaining the spectra, and the methylene protons of the phosphine were not well resolved because of this poor solubility.

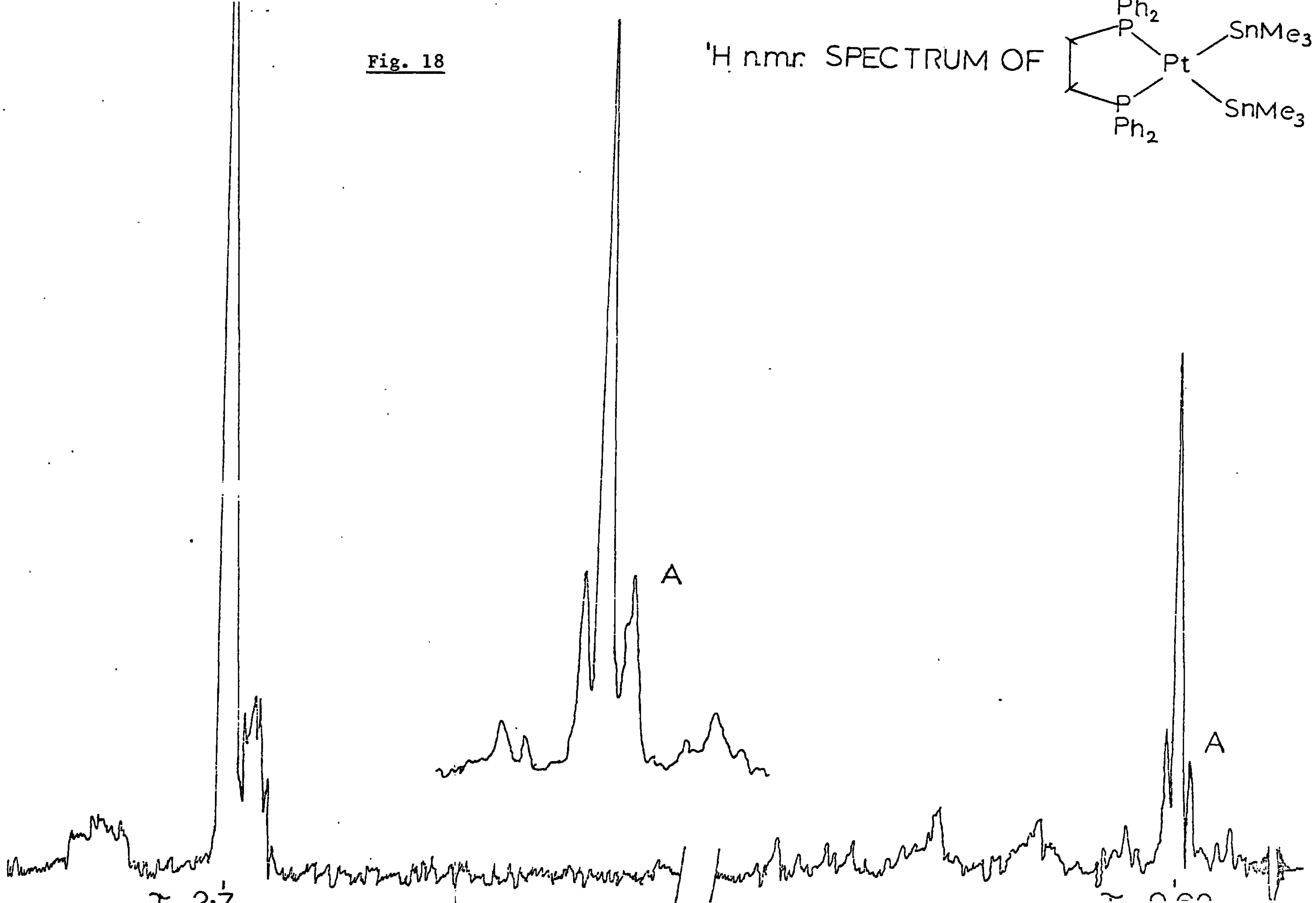
The 'H n.m.r. spectra of the mono- and disubstituted tin derivatives differed from the analogous silyl and germyl complexes in that coupling with the ^{31}P nucleus was not observed, hence the methyl resonance appeared as a 1:4:1 triplet due to coupling with the ^{195}Pt nucleus, flanked by two doublets due to coupling with the ^{117}Sn and ^{119}Sn nuclei (Fig. 18). This absence of observable long range coupling to the trans phosphorus nucleus is probably due to the high trans-influence of the Me_3Sn group producing reversible breaking of the Pt-P bond. The $^{119}Sn-CH_3$ coupling constants shows a decrease from the value in tetramethylstannane (54.0 Hz)[151]. As mentioned in the introduction, this phenomenon was also observed in trimethylstannyl derivatives of molybdenum and tungsten[142] and indicates that the tin orbitals used in bonding to the platinum have appreciable s-character leaving the methyl-bonded tin orbitals with reduced s-character resulting in a smaller coupling constant.

Fig. 17



¹H n.m.r. SPECTRUM OF

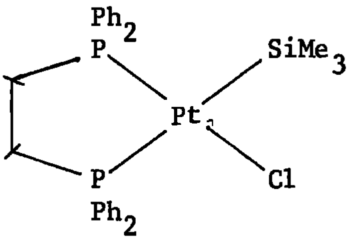
Fig. 18



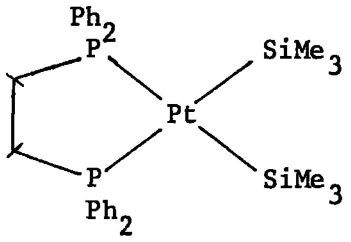
¹H n.m.r. SPECTRUM OF

Mass Spectra

The complexes (III) and (IV)



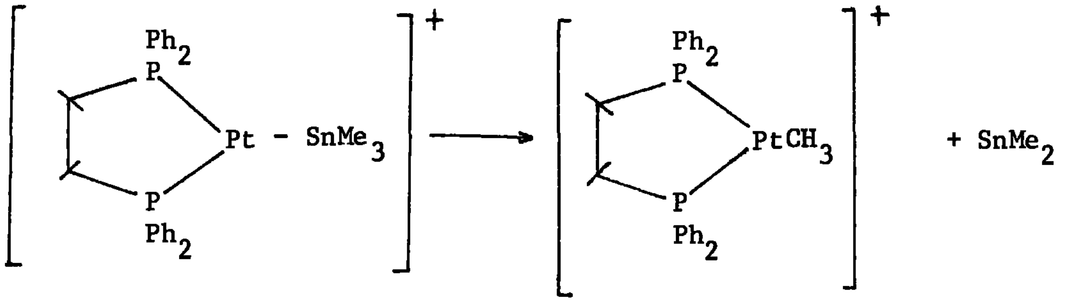
(III)



(IV)

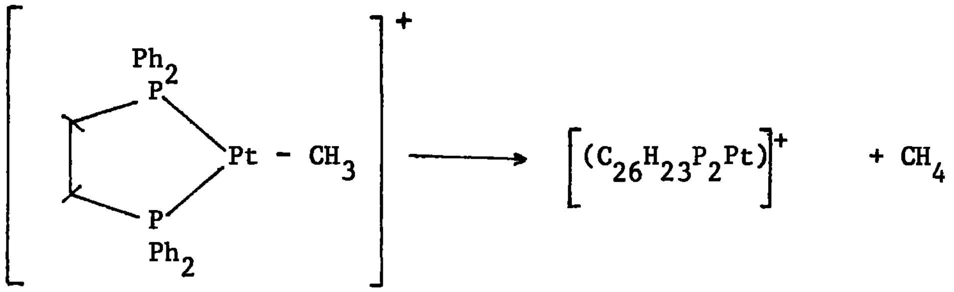
differed in their mass spectra in that the disubstituted derivative gave a molecular ion at m = 739 whereas the monosubstituted complex gave the parent—methyl at m = 686, no molecular ion being observed. The other ions observed can be seen from the fragmentation diagrams in Figs. 19 and 20. The analogous germanium complexes showed similar fragmentation patterns, the most abundant ions in the four complexes being due to (chelate)Pt^{+}, (chelate)Pt(SiMe$_3$)$^{+}$, (chelate)Pt(GeMe$_3$)$^{+}$, (chelate)Pt(SiMe$_3$)-(SiMe$_2$)$^{+}$ and (chelate)Pt(GeMe$_3$)(GeMe$_2$)$^{+}$.

The mass spectra of the two tin complexes $(Ph_2PCH_2CH_2PPh_2)_2Pt(SnMe_3)_2$ and $(Ph_2PCH_2CH_2PPh_2)PtCl(SnMe_3)$ however, differed from the silicon and germanium analogues in that their spectra showed ions at masses = 608 and 592 whereas the silicon and germanium complexes showed only an ion at mass = 593 i.e. $[(chelatePt)]^{+}$. The ion at mass = 608 can be attributed to $[(chelate)Pt{-}CH_3]^{+}$ and must be formed by transfer of a methyl group across a Pt–Sn bond. Processes of this type are well established[186], and in this case may be due to the following decomposition:



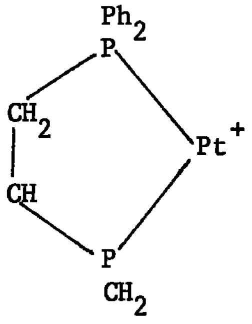
(XV)

The ion at mass = 592 is formed by the elimination of methane from (XV), and this process is supported by a metastable peak at 576.4.

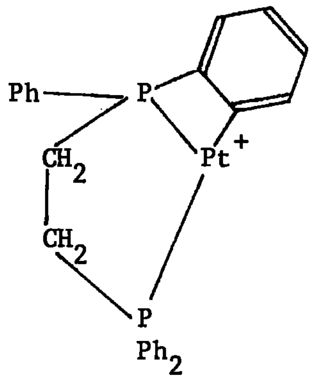


(XV) (XVI)

The ion (XVI) could presumably have the structure (XVII) or (XVIII).



(XVII)



(XVIII)

The disubstituted complex showed a weak molecular ion at mass = 920. The monosubstituted complex however, did not give a molecular ion but an ion due to methyl loss at mass = 777 was detected. In both complexes, the ion at mass = 758 $[(\text{chelate})\text{Pt}(\text{SnMe}_3)]^+$ was the most abundant. The mass spectrum of the monosubstituted derivative did contain ions of higher mass than the molecular weight of the complex, e.g. $\left[(\mathrm{chelate})\mathrm{Pt}(\mathrm{SnMe_3})\text{-}(\mathrm{SnMe_2})\right]^+$, these are presumably due to rearrangements in the mass spectrometer. The fragmentation diagram of the disubstituted complex is given in Fig. 21.

Kinetic Study of the Hydrogenation of $(Ph_2PCH_2CH_2PPh_2)Pt(SiMe_3)_2$

The hydrogenation of the complex was carried out in toluene solution at 25° with an initial hydrogen pressure of 613mm. Hg. The data showed that the reaction appeared to be first order with respect to hydrogen and first order with respect to the platinum complex. The rate constants were calculated to be: (1) 4.14×10^{-2} $\mathrm{l.m^{-}s^{-1}}$

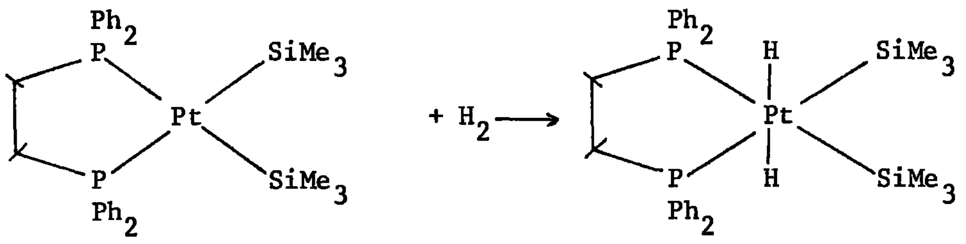
(2) 6.0×10^{-2} $\mathrm{l.m^{-}s^{-1}}$

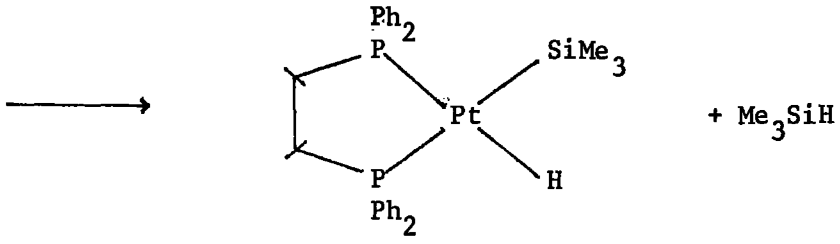
(1) was calculated from the reduction in hydrogen pressure, (2) was calculated from the rate of reaction of the platinum-silyl compound. (For calculation and results see appendix). The discrepancy in the two measurements is considered to be within experimental error for such rate determinations. The rate constants and order are in agreement with values obtained in kinetic experiments involving addition of hydrogen to square planar iridium complexes[166].

e.g. <u>trans</u>-$IrX(CO)(Ph_3P)_2 + H_2 \longrightarrow IrXH_2(CO)(Ph_3P)_2$

X = Cl, Br or I

and are consistent with an oxidative-addition of hydrogen to the platinum followed by elimination of trimethylsilane.





Work up of the reaction mixture gave $(Ph_2PCH_2CH_2PPh_2)PtH(SiMe_3)$ and under the conditions of the experiment, the reaction went essentially to completion, but cleavage of only one silyl group occurred.

A description of the experimental technique and apparatus used is given on p.131.

An attempt to study the kinetics of the hydrolysis of trans-$(Et_3P)_2PtCl(GeMe_3)$ using ultra-violet spectroscopy was made, but preliminary measurements on the spectra of the starting material and the hydrolysed sample containing trans-$(Et_3P)_2PtHCl$ and $(Me_3Ge)_2O$ showed insufficient differences in the spectra for the method to be used hence no kinetic measurements were made.

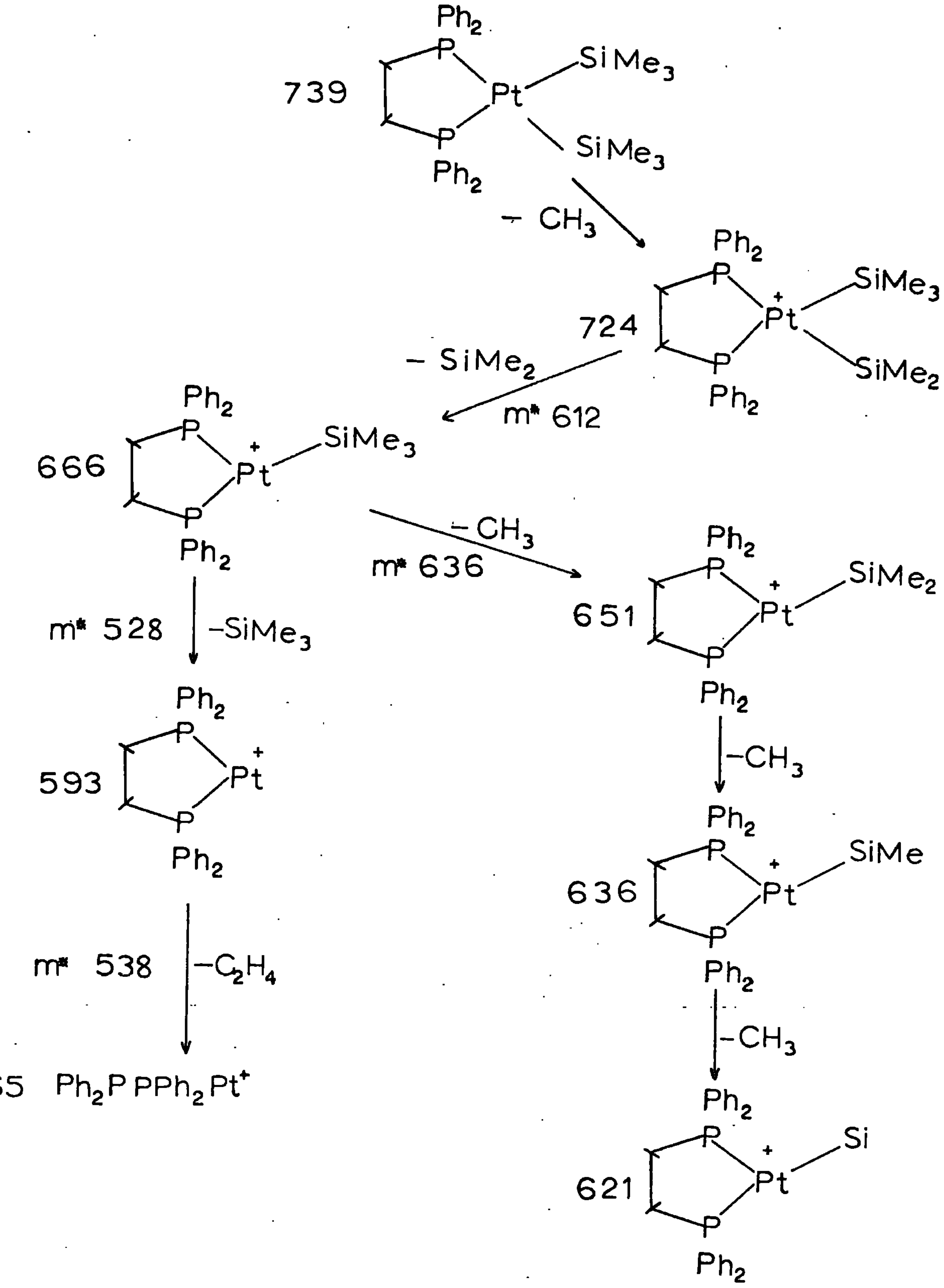


Fig. 19 Fragmentation Diagram of $(Ph_2PCH_2CH_2PPh_2)Pt(SiMe_3)_2$

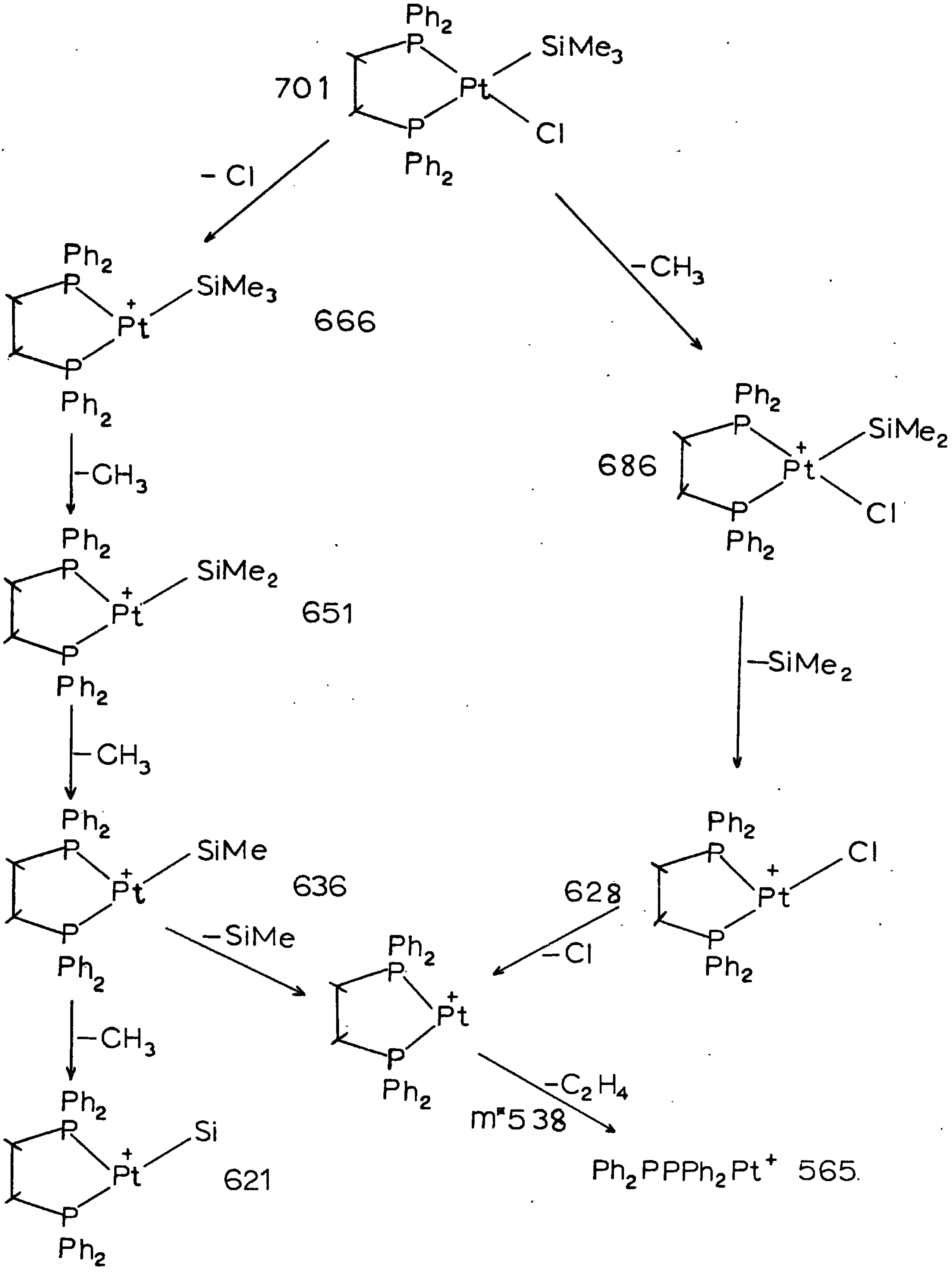


Fig. 20 Fragmentation Diagram of $(Ph_2PCH_2CH_2PPh_2)PtCl(SiMe_3)$

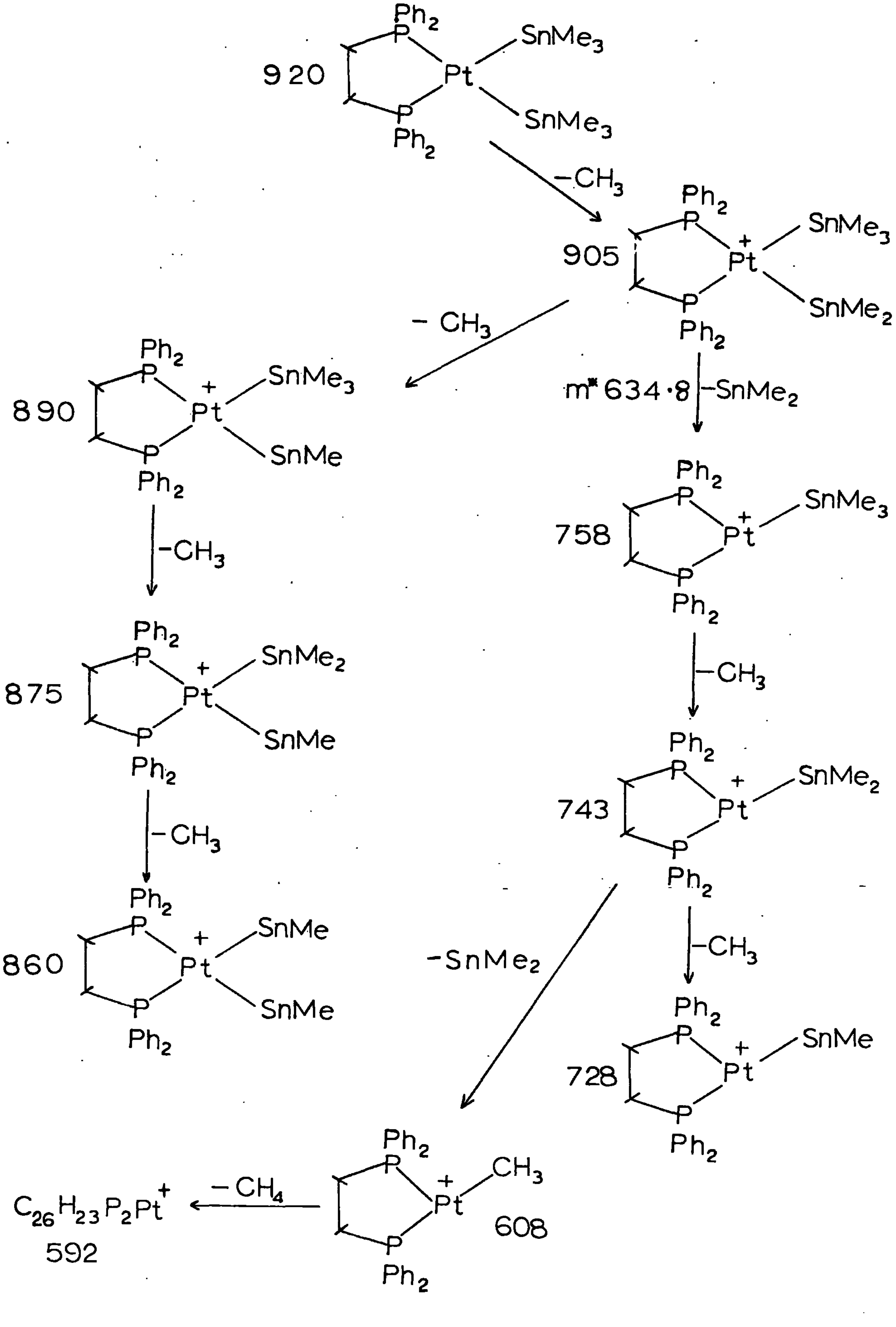


Fig. 21. Fragmentation Diagram of $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$

CHAPTER 7

EXPERIMENTAL

SECTION A

Platinum-Group-IVb Complexes

1. The Preparation of 1,2-bisdiphenylphosphinoethanetrimethylsilylplatinum(II) chloride

Bistrimethylsilylmercury (1.04g., 3.0 mmole) in benzene (20 ml.) was added dropwise to a suspension of $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ (2g., 3.0 mmole) in benzene (650 ml.) at 60°. Mercury was deposited and the reaction mixture turned yellow-brown. The reaction mixture was stirred for 2 hours at 60°, cooled and filtered to remove mercury. The solvent, which was removed under vacuum, contained chlorotrimethylsilane (v.p.c.). The light brown solid was transferred to a schlenk and recrystallised from benzene to give white crystals of 1,2-bisdiphenylphosphinoethanetrimethylsilylplatinum(II) chloride, $(Ph_2PCH_2CH_2PPh_2)Pt(Cl)SiMe_3$, m.p. 205-208°. [0.7g., 64%; ν(Pt-Cl) at 299 cm^{-1}. Found: C, 49.4; H, 4.86%. $C_{29}H_{33}ClP_2PtSi$ requires C, 49.6; H, 4.7%.].

Further crystallisation of the remaining solid yielded 1,2-bisdiphenylphosphinoethanebistrimethylsilylplatinum(II), $(Ph_2PCH_2CH_2PPh_2)Pt(SiMe_3)_2$, m.p. 220-223° (d) (0.12g.).

2. The preparation of 1,2-bisdiphenylphosphinoethanebistrimethylsilylplatinum(II) $(Ph_2PCH_2CH_2PPh_2)Pt(SiMe_3)_2$

Bistrimethylsilylmercury (1.7g., 4.9 mmole) in benzene (20 ml.) was added dropwise to $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ (1.60g., 2.41 mmole) in benzene (500 ml.) at 60°. Mercury was deposited and the reaction mixture turned yellow-brown. The mixture was stirred for 2 hours at 60°, cooled and filtered to remove mercury. The solvent, which was removed under vacuum, contained chlorotrimethylsilane (v.p.c.). The pale-brown solid was recrystallised from benzene to give 1,2-bisdiphenylphosphinoethanebistrimethylsilylplatinum(II) m.p. 220-223° [1.3g., 73%; Found: C, 52.2; H, 5.8%. $C_{32}H_{42}P_2PtSi_2$ requires C, 51.98; H, 5.7%.]

3. The preparation of 1,2-bisdiphenylphosphinoethanetrimethylgermylplatinum(II) chloride $(Ph_2PCH_2CH_2PPh_2)Pt(Cl)GeMe_3$

Bistrimethylgermylmercury (1.5g., 3.4 mmole) in benzene (20 ml.) was added dropwise to $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ (2.0g., 3.7 mmole) in benzene (500 ml.) at 60°. Mercury was deposited and the reaction mixture became a yellow-brown colour. After stirring for 2 hours at 60° the mixture was cooled and filtered. After removal under vacuum of the solvent, which was shown to contain chlorotrimethylgermane (v.p.c.), the light brown solid remaining was recrystallised from benzene to yield white crystals of 1,2-bisdiphenylphosphinoethanetrimethylgermylplatinum(II) chloride $(Ph_2PCH_2CH_2PPh_2)Pt(Cl)GeMe_3$ m.p. 216-220° [1.8g., 72%; ν(Pt-Cl) at 300 $cm.^{-1}$ (nujol); Found: C, 46.71; H, 4.23%. $C_{29}H_{33}ClGeP_2Pt$ requires C, 46.6; H, 4.42%].

4. The preparation of 1,2-bisdiphenylphosphinoethanebistrimethylgermylplatinum(II) $(Ph_2PCH_2CH_2PPh_2)Pt(GeMe_3)_2$

Bistrimethylgermylmercury (4.4g., 10.0 mmole) in benzene (20 ml.) was added dropwise to $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ (3g., 5.0 mmole) in benzene (500 ml.) at 60°. During the reaction mercury was deposited and the reaction mixture turned yellow-brown. After stirring for 2 hours at 60° the mixture was cooled, filtered and the solvent, which contained chlorotrimethylgermane (v.p.c.), was removed under vacuum. The remaining light-brown solid was recrystallised from benzene to give white crystals of 1,2-bisdiphenylphosphinoethanebistrimethylgermylplatinum(II), $(Ph_2PCH_2CH_2PPh_2)Pt(GeMe_3)_2$ m.p. 210-215 (d). [2.8g., 75%; Found: C, 46.50; H, 5.30%; $C_{32}H_{42}Ge_2P_2Pt$ requires C, 46.21; H, 5.05%].

5. Reaction of $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ with trimethylsilane

Trimethylsilane (excess) and benzene (5 ml.) were condensed onto $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ (0.6g., 9.0 mmole) in a tube fitted with a break-seal. After heating at 60° for six days the tube was opened to a vacuum line and volatile products removed. An infrared spectrum of the remaining solid showed only starting material.

6. Reaction of $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ with trimethylgermane

Trimethylgermane (excess) and benzene (5 ml.) were condensed onto $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ (0.5g., 0.78 mmole) in a break-seal tube and heated at 60° for six days. The tube was opened to a vacuum-line and volatiles removed, leaving only starting material.

7. Reaction of $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ with trimethylstannane

Trimethylstannane (excess) and benzene (5 ml.) were condensed onto $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ (0.5 g., 7.8 mmole) in a break-seal tube. After one week at 40° a small amount of platinum metal was deposited. The tube was opened to a vacuum line. Hydrogen gas (70.0 N.c.c.) and volatiles were removed. The benzene solvent contained chlorotrimethylstannane, hexamethyldistannane and trimethylstannane (v.p.c. identification). The white solid was washed with hot benzene, leaving insoluble starting material. Removal of the benzene gave a white solid, which was recrystallised from benzene to give 1,2-bisdiphenylphosphinoethanetrimethylstannylplatinum(II) chloride, m.p. 205-208 (d). [0.052g., 8.8%].

8. Reaction of $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ with neat trimethylstannane

The complex (1g., 1.5 mmole) was sealed with trimethylstannane (3 ml.) and heated at 40°. After one week a yellow solution was formed which, after heating for a further week, turned to a reddish-brown solution. The tube was opened to a vacuum line, hydrogen gas (80.8 N.c.c.) and chlorotrimethylstannane were identified (mass spectrum and v.p.c.) in the volatiles. The remaining reddish-brown solid showed ν(Pt-H) at 1960 $cm.^{-1}$ and a broad band attributable to ν(Pt-Cl) at 280-290 cm^{-1}. Recrystallisation of the solid from benzene gave colourless crystals of 1,2-bisdiphenylphosphinoethanetrimethylstannylplatinum(II) chloride $(Ph_2PCH_2CH_2PPh_2)Pt(Cl)SnMe_3$, m.p. 205-208 (d). [0.51 g., 43%; Found: C, 43.02; H, 4.56; Cl, 4.1%; $C_{29}H_{33}ClP_2PtSn$ requires C 43.8; H, 4.2; Cl, 4.4%].

9. Reaction of $(Ph_2PCH_2CH_2PPh_2)_2Pt$ with Me_3SiH

Trimethylsilane (excess) was condensed into a break-seal tube containing the complex (0.25 g., 0.25 mmole) in benzene (3 ml.). After heating at 70° for 1 week the tube was opened to a vacuum line and the volatiles removed leaving a yellow solid which by its infra-red spectrum was shown to be starting material.

The experiment was repeated using neat trimethylsilane. The complex (0.2 g., 0.2 mmole.) was sealed with trimethylsilane (excess). After heating at 70° for 1 month no visible change had occurred; removal of volatile material yielded only the original starting material.

10. Reaction of $(Ph_2PCH_2CH_2PPh_2)_2Pt$ with Me_3GeH

The complex (0.2 g., 0.2 mmole) was heated at 80° for 1 month with excess trimethylgermane. No visible change took place and removal of the trimethylgermane left only solid starting material.

11. Reaction of $(Ph_2PCH_2CH_2PPh_2)_2Pt$ with Me_3SnH

Trimethylstannane (excess) was condensed onto the complex (0.25 g., 0.25 mmole) in a tube fitted with a break-seal. On warming to room temperature a reaction took place, the yellow starting material turning white, some effervescence occurring. The tube was then heated at 60° for three hours before opening to a vacuum line. Work up of the volatiles yielded hydrogen (26.7 N.c.c.), trimethylstannane and hexamethyldistannane (v.p.c. identification). The white solid residue showed ν(Pt-H) at 1962 $cm.^{-1}$ and its infra-red spectrum was identical to that of the solid obtained in experiment 24. Recrystallisation of the solid from benzene yielded colourless crystals of 1,2-bisdiphenylphosphinoethanebistrimethylstannylplatinum(II), $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$, m.p. 207-210 (d). [0.18 g., 78%, Found: C, 41.88; H, 4.54; $C_{32}H_{42}P_2PtSn_2$ requires C, 41.6; H, 4.55%].

12. Reaction of $(Ph_2PCH_2CH_2PPh_2)_2Pt$ with Me_3SiCl

Chlorotrimethylsilane (1 ml.) was condensed onto the complex (0.3 g., 0.3 mmole) in benzene (3 ml.). After warming to room temperature a greenish-yellow sticky solid formed which, on shaking, became an off-white in colour. After being heated at 60° for two days the tube was opened and all volatile material, which contained Me_6Si_2, removed. Recrystallisation of the solid residue from methanol yielded white crystals of bis(1,2-bisdiphenylphosphinoethane)platinum(II) dichloride, $[(Ph_2PCH_2CH_2PPh_2)_2Pt]^{2+}2Cl^-$, m.p. > 300 (d). [0.27 g., 90%].

13. Reaction of $(Ph_2PCH_2CH_2PPh_2)_2Pt$ with Me_3SnCl

Chlorotrimethylstannane (0.2 g.,) in benzene (2 ml.) was added slowly to a solution of the complex (0.2 g., 0.2 mmole) in benzene (8 ml.).

The resulting mixture was stirred for 5 minutes when a yellow oil formed which after 30 minutes at 70° gradually changed to a white precipitate, the mixture also became a paler yellow. The mixture was filtered and the solid recrystallised from methanol to give white crystals of bis(1,2-bisdiphenylphosphinoethane)platinum(II)dichloride, $\left[(Ph_2PCH_2CH_2PPh_2)_2Pt\right]^{2+}2Cl^-$, m.p. > 300° (d). [0.17 g., 85%].

14 Reaction of $\left[(Ph_2PCH_2CH_2PPh_2)_2Pt\right]^{2+}2Cl^-$ with Me_3SiH

The complex (0.4 g., 0.4 mmole) in benzene (4 ml.) was sealed with an excess of trimethylsilane in a tube fitted with a break-seal. The tube was heated at 70° for one week and then opened to a vacuum line to yield hydrogen (7.4 N.c.c.), trimethylsilane, hexamethyldisilane (n.m.r. detection), and unreacted solid starting material.

Reactions of $(Ph_2PCH_2CH_2PPh_2)Pt(SiMe_3)_2$

15. With Anhydrous Hydrogen Chloride

Anhydrous hydrogen chloride (8.16 N.c.c., 0.36 mmoles) and benzene (5 ml.) were condensed onto the complex (0.135g., 0.18 mmole) in a break-seal tube. After two days at room temperature the tube was opened to a vacuum line and hydrogen gas (0.56 N.c.c.) removed. The volatiles were collected and separated by fractional condensation to yield trimethylsilane (5.2 N.c.c. 84%) and the benzene solvent. The remaining white solid was washed several times with hot benzene leaving $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ (0.084 g., 93%).

16. With Hydrogen at 40°

The complex (0.3 g., 0.405 mmole) in benzene (4 ml.) was reacted with hydrogen at atmospheric pressure. After four days at 40° a brown solution was formed. The tube was opened and the volatiles removed to yield trimethylsilane (4.1 N.c.c., 45% available silicon). The residual yellow solid showed ν(Pt-H) at 2000 cm^{-1}. Attempts to recrystallise the solid from benzene and cyclohexane proved unsuccessful but after washing several times with cold hexane $(Ph_2PCH_2CH_2PPh_2)PtH(SiMe_3)$ was obtained as a yellow-brown solid; decomposes > 165°, [0.21 g., 78%, Found: C, 51.74; H, 5.11%; $C_{29}H_{34}P_2PtSi$ requires C, 52.1; H, 5.09%].

17. With Hydrogen at 80°

The complex (0.2 g., 0.27 mmole) in benzene (4 ml.) was reacted with 1 atmosphere of hydrogen in a sealed tube at 80°. After one hour the solution became pale brown and gradually darkened over one week. The tube was opened to a vacuum line, excess hydrogen was removed by pumping and the remaining volatiles were fractionated to yield trimethylsilane (11.4 N.c.c., 94%) and the benzene solvent. The yellow-brown solid remaining was recrystallised from a benzene-cyclohexane mixture to yield a yellow-brown solid showing no bands attributable to ν(Pt-H) or $\rho(CH_3)$ in its infra-red spectrum and its 'H n.m.r. spectrum gave only resonances due to phenyl and methylene protons. The complex was formulated as $[(Ph_2PCH_2CH_2PPh_2)_3Pt_4]$, [0.09 g., 69%:

Found: (a) C, 47.8; H, 3.9; P, 10.4%

(b) C, 48.1; H, 3.6; P, 10.1%.

Osmometer Molecular Weight: 2190

$C_{78}H_{72}P_6Pt_4$ requires C, 47.4; H, 3.6; P, 9.4%; Molecular Weight: 1974.

$C_{104}H_{96}P_8Pt_4$ i.e. $(chelatePt)_4$ requires C, 52.6; H, 4.0; P, 10.5%; Molecular Weight: 2372].

18. With Trimethylgermane

The complex (0.5 g., 0.67 mmole) was reacted in benzene (5 ml.) in a break-seal tube with trimethylgermane (30.3 N.c.c., 1.3 mmole). After three days at 50° some white solid crystallised out of the pale yellow solution. The tube was opened to a vacuum line, the volatiles removed and separated by fractional condensation to yield hydrogen gas (1.15 N.c.c.)

and trimethylsilane contaminated with a trace of trimethylgermane (30.3 N.c.c.). The solid was recrystallised from benzene to give colourless crystals of 1,2-bisdiphenylphosphinoethanebistrimethylgermylplatinum(II), m.p. 210-215 (d). [0.47 g., 84%].

19. With Trimethylstannane

Trimethylstannane (30.3 N.c.c., 1.3 mmole) and benzene (5 ml.) were condensed onto the complex (0.5 g., 0.67 mmole) in a vacuum tube. After one week at 50° the volatiles were removed and separated to give hydrogen (3.35 N.c.c.) and trimethylsilane (29.9 N.c.c., 98%). The white solid remaining was recrystallised from benzene to yield colourless crystals of $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$, m.p. 205-210 (d). [0.54 g., 87%].

Reactions of $(Ph_2PCH_2CH_2PPh_2)PtCl(SiMe_3)$

20. With Anhydrous Hydrogen Chloride

Anhydrous hydrogen chloride (6.6 N.c.c., 0.29 mmole) and benzene (4 ml.) were condensed onto the complex (0.21 g., 0.29 mmole) in a tube fitted with a break-seal. After two days the tube was opened to a vacuum line and the volatiles removed. The volatiles were separated by fractionation to yield hydrogen (1.3 N.c.c.), trimethylsilane (5.7 N.c.c., 86%) and the solvent benzene. The residual solid was refluxed with benzene and filtered to give insoluble $(Ph_2PCH_2CH_2PPh_2)PtCl_2$, m.p. > 325°, (0.16 g., 84%) and some solid starting material (0.012 g., 5%) recovered from the benzene.

21. With Hydrogen

The complex (0.73 g., 1.04 mmole) was hydrogenated in benzene (6 ml.) at atmospheric pressure for four days at 60°. A brown solution was obtained. The volatiles were removed and separated by fractionation to yield trimethylsilane (5.8 N.c.c., 25%) and hexamethyldisilane ('H n.m.r. identification). The solid showed ν(Pt-H) 2004 $cm.^{-1}$ (KBr), and after repeated recrystallisations from benzene gave $(Ph_2PCH_2CH_2PPh_2)Pt(H)Cl$. [(0.41 g., 61%; Found: C, 48.6; H, 4.12%. $(Ph_2PCH_2CH_2PPh_2)Pt(H)Cl$, $C_{26}H_{25}ClP_2Pt$ requires C, 49.6; H, 3.97%). Satisfactory accurate mass measurements were obtained on $(C_{26}H_{24}ClP_2Pt)^+$].

22. With Trimethylgermane

Trimethylgermane (8.9 Nc.c., 0.4 mmole) and benzene (3 ml.) were condensed onto the complex (0.28 g., 0.4 mmole) in a sealed vacuum tube and heated at 60° for three days when colourless crystals separated out. The tube was opened to a vacuum line and hydrogen gas (1.8 N.c.c.), trimethylsilane (7.8 N.c.c., 88%) and benzene were removed. The remaining white solid was recrystallised from benzene to give colourless crystals of 1,2-bisdiphenylphosphinoethanetrimethylgermylplatinum(II) chloride, $(Ph_2PCH_2CH_2PPh_2)PtCl(GeMe_3)$, m.p. 216-220°. [0.28 g., 95%].

23. With Trimethylstannane

Trimethylstannane (9.5 N.c.c., 0.42 mmole) and benzene (3 ml.) were condensed onto the complex (0.3 g., 0.42 mmole) in a sealed vacuum tube. After two weeks at 60° the volatiles were removed and separated to give trimethylsilane (5.8 N.c.c., 61%) and benzene. The white residual solid was recrystallised from benzene to give colourless crystals of 1,2-bisdiphenylphosphinoethanetrimethylstannylplatinum(II) chloride, $(Ph_2PCH_2CH_2PPh_2)PtCl(SnMe_3)$, m.p. 205-208° (d), [0.21 g., 60%, ν(Pt-Cl) at 284 cm^{-1}. (CsI disc)].

24. With Trimethylstannane (excess)

Trimethylstannane (excess) and benzene (5 ml.) were condensed onto the complex (0.5 g.,) in a vacuum tube and heated for three days at 60°. A green solution resulted with some platinum metal deposited. The tube was opened to a vacuum line and the volatiles were removed and fractionated to yield hydrogen gas (16.1 N.c.c.), trimethylsilane (14.4 N.c.c., 91% available silicon) and chlorotrimethylstannane (v.p.c. identification). The off-white solid showed ν(Pt-H) at 1960 $cm.^{-1}$ and was recrystallised from benzene to give colourless crystals of $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$, m.p. 207-210°, [0.59 g., 91%; Found: C, 41.71; H, 4.75%; osmometric molecular weight: 891, $C_{32}H_{42}P_2PtSn_2$ requires C, 41.6; H, 4.55%; molecular weight: 923]. After the recrystallisation, the Schlenk smelled strongly of trimethylstannane. The experiment was repeated to investigate the volatile products obtained on recrystallising the solid showing ν(Pt-H) at 1960 cm^{-1}. A sample (0.5 g.,) of this solid was transferred to a break-seal tube and benzene was condensed onto it. After heating for three days at 40° the tube was opened to a vacuum line and the volatiles removed. Hydrogen gas (6.9 N.c.c.), trimethylstannane and tetramethylstannane were identified in the volatiles. The white solid residue, which did not now show a band attributable to ν(Pt-H), was recrystallised from benzene to give $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$.

25. With trimethylstannane (excess) for 'H n.m.r.

The complex in deuterobenzene was sealed in an n.m.r. tube with excess trimethylstannane and the spectrum recorded (discussed on p.101). After two weeks, large colourless crystals separated out of the green solution. The tube was opened and the volatiles removed. An analysis of the crystals which showed ν(Pt-H) at 1960 $cm.^{-1}$ gave C, 37.62; H, 4.83%; $C_{35}H_{52}P_2PtSn_3$ requires C, 38.5; H, 4.77% .

Reactions of $(Ph_2PCH_2CH_2PPh_2)PtCl(GeMe_3)$

26. With Trimethylstannane (excess)

Trimethylstannane (excess) and benzene (5 ml.) were condensed onto the complex (0.17 g., 0.23 mmole) in a break-seal tube. A yellow-green solution was formed after heating for twenty four hours at 40°. Hydrogen gas (4.36 N.c.c.), trimethylgermane (contaminated with some trimethylstannane) and benzene were removed. A complete separation of the trimethylgermane and trimethylstannane was not achieved, 6.2 N.c.c. of the mixture were obtained, (a 100% yield of trimethylgermane = 5.2 N.c.c.). The off-white residue showed ν(Pt-H) at 1961 $cm.^{-1}$ in its infra-red spectrum which was identical to the spectrum of the solid obtained in experiments 11, 24 and 25. Recrystallisation of this solid from benzene gave colourless crystals of $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$, [0.17 g., 81%].

27. With Trimethylstannane (equimolar)

Complex (0.16 g., 0.2 mmole) in benzene (4 ml.) was reacted with trimethylstannane (4.8 N.c.c., 0.2 mmole) at 40° in a break-seal tube. After 6 days the tube was opened to a vacuum line and the volatile material removed. The volatiles were separated by fractional condensation to give hydrogen (0.3 N.c.c.), trimethylgermane and benzene. Recrystallisation of the solid from benzene yielded colourless crystals of $(Ph_2PCH_2CH_2PPh_2)PtCl(SnMe_3)$, [0.13 g., 76%].

28. With Trimethylsilane (excess)

Excess trimethylsilane and benzene (5 ml.) were condensed onto the complex (0.23 g., 0.31 mmole) in a break-seal tube. After six days at 70° no visible change had taken place and the tube was opened to a vacuum line. Hydrogen gas (0.3 N.c.c.) was evolved. The other volatile material was removed and separated by fractional condensation to give trimethylsilane with a small amount of trimethylgermane (identified by infra-red comparison). Successive crystallisations of the solid remaining produced only starting material $(Ph_2PCH_2CH_2PPh_2)PtCl(GeMe_3)$. No compound having a Pt-Si bond could be isolated.

Reactions of $(Ph_2PCH_2CH_2PPh_2)Pt(GeMe_3)_2$

29. With Trimethylstannane

The complex (0.15 g., 0.18 mmole) in benzene (4 ml.) was reacted with trimethylstannane (8.1 N.c.c., 0.36 mmole) in a sealed tube. After 24 hours at 40° some colourless crystals formed on the side of the tube which was then opened to a vacuum line. A small quantity (0.15 N.c.c.) of hydrogen was evolved. Removal of the volatiles and separation by fractionation yielded trimethylgermane (7.2 N.c.c., 89%) and the solvent benzene. Recrystallisation of the remaining white solid from benzene gave colourless crystals of $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$, [0.15 g., 88%.]

30. With Trimethylsilane (excess)

Trimethylsilane (excess) was condensed onto the complex (0.16 g., 0.19 mmole) in benzene (4 ml.). After two weeks at 60° the tube was opened to a vacuum line, hydrogen gas (0.15 N.c.c.) was evolved. The remaining volatile material was separated by fractionation to give trimethylsilane with a trace of trimethylgermane, and benzene. Only starting material, $(Ph_2PCH_2CH_2PPh_2)Pt(GeMe_3)_2$, could be isolated from the solid residue.

Reactions of $(Ph_2PCH_2CH_2PPh_2)PtCl(SnMe_3)$

31. With Trimethylgermane (excess)

A benzene solution of the complex (0.2 g., 0.25 mmole in 5 ml.) was reacted with excess trimethylgermane in a vacuum tube. No visible change occurred after one week at 70° when the tube was opened to a vacuum line. A small quantity of hydrogen gas was evolved. Removal and separation of the volatiles produced only trimethylgermane and benzene leaving unreacted starting material, $(Ph_2PCH_2CH_2PPh_2)PtCl(SnMe_3)$.

32. With Trimethylsilane (excess)

The complex (0.2 g., 0.25 mmole) in benzene (5 ml.) was reacted with excess trimethylsilane in a tube fitted with a break-seal. After five days at 70° the tube was opened to a vacuum line. Hydrogen gas (0.6 N.c.c.) was evolved. Separation of the remaining volatiles produced only trimethylsilane and benzene, leaving unreacted solid starting material.

33. With Trimethylstannane (excess)

The complex (0.2 g., 0.25 mmole) was heated at 50° with neat trimethylstannane (approx. 1 liquid ml.). After 24 hours the tube was opened to a vacuum line and the volatile material removed leaving a pale yellow solid with some platinum metal. The infra-red spectrum of this solid was identical to the spectrum of the solid in experiment 8, and showed ν(Pt-H) at 1960 $cm.^{-1}$ and a broad absorption between 280-290 $cm.^{-1}$ attributable to ν(Pt-Cl). This solid, formulated as $(Ph_2PCH_2CH_2PPh_2)PtHCl(SnMe_3)_2$ was then sealed with benzene (3 ml.) and heated at 60° for three days. Work up of the volatile material yielded hydrogen (1.3 N.c.c.), trimethylstannane and tetramethylstannane (v.p.c. identification). The remaining solid which did not now show a band attributable to ν(Pt-H) was recrystallised from benzene to give colourless crystals of starting material, $(Ph_2PCH_2CH_2PPh_2)PtCl(SnMe_3)$.

Reactions of $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$

34. With Trimethylgermane (excess)

Excess trimethylgermane was condensed onto a benzene solution of the complex (0.15 g., 0.16 mmole in 4 ml.) in a tube fitted with a break-seal. After nine days at 50^o the tube was opened and the volatiles removed leaving unreacted starting material. Work up of the volatiles gave only trimethylgermane and benzene.

35. With trimethylsilane (excess)

The complex (0.13 g., 0.14 mmole) in benzene (4 ml.) was heated at 50^o for 10 days with excess trimethylsilane. The tube was opened to a vacuum line and volatile material removed leaving unreacted starting material, $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$. Examination of the volatile material yielded only trimethylsilane and benzene.

36. With Anhydrous Hydrogen Chloride (one equivalent)

Anhydrous hydrogen chloride (4.6 N.c.c., 0.21 mmole) and benzene (4 ml.) were condensed onto the complex (0.19 g., 0.21 mmole) in a tube fitted with a break-seal. After one week at room temperature, the tube was opened and volatile products were removed and separated by fractional condensation to yield hydrogen (1.9 N.c.c.), trimethylstannane and benzene. (A complete separation of the trimethylstannane and benzene was not achieved). The white solid residue was recrystallised from benzene to give colourless crystals of $(Ph_2PCH_2CH_2PPh_2)PtCl(SnMe_3)$, [0.13 g., 81%; ν(Pt-Cl) at 285 cm^{-1} . (CsI disc)].

37. With Trimethylstannane (excess)

Excess trimethylstannane (approx. 1 liquid ml.) was condensed onto the complex (0.15 g., 0.16 mmole) in a vacuum tube. The tube was heated at 40° for two weeks during which time some platinum metal was deposited. The tube was then opened and hydrogen (14.5 N.c.c.) evolved. The off-white solid showed a band attributable to ν(Pt-H) at 1964 $cm.^{-1}$ in its infra-red spectrum which was identical to the spectra of the solids obtained in experiments 11, 24 and 26. The solid was therefore formulated as $(Ph_2PCH_2CH_2PPh_2)PtH(SnMe_3)_3$. A satisfactory analysis could not be obtained due to the platinum metal. Recrystallisation of the solid from benzene yielded colourless crystals of starting material, $(Ph_2PCH_2CH_2PPh_2)$-$Pt(SnMe_3)_2$, thus in the experiment trimethylstannane adds on to the complex giving the octahedral complex $(Ph_2PCH_2CH_2PPh_2)PtH(SnMe_3)_3$ which on recrystallisation eliminates trimethylstannane to give the original starting material.

38. With Hydrogen at 25°

The complex (0.17 g., 0.18 mmole) in toluene (40 ml.) was vigorously stirred at 25° for 20 hours under 1 atmosphere of hydrogen. Removal of the hydrogen and toluene left only unreacted starting material.

In all the preceeding reactions where an excess of trimethylsilane, trimethylgermane or trimethylstannane is referred to approximately 0.5 to 1.0 liquid ml. were used.

39. Reaction of $(Ph_2PCH_2CH_2PPh_2)Pt(GePh_3)_2$ with Deuterium

(a) Atmospheric Pressure

$(Ph_2PCH_2CH_2PPh_2)Pt(GePh_3)_2$ (0.25 g., 0.21 mmole) was sealed with benzene (20 ml.) and deuterium at atmospheric pressure. The tube was opened after three weeks at room temperature, removal of the deuterium and benzene left only starting material.

(b) Five Atmospheres

$(Ph_2PCH_2CH_2PPh_2)Pt(GePh_3)_2$ (0.25g., 0.21 mmole) was reacted in benzene (20 ml.) with deuterium at five atmospheres. After heating for four days at 60° the deuterium and benzene were removed by pumping. Extraction of the remaining solid with light petroleum ether gave insoluble $(Ph_2PCH_2CH_2PPh_2)PtD(GePh_3)$ which was recrystallised from benzene to give light buff crystals, m.p. 157-162°, [0.17 g., 91%, ν(Pt-D) 1428 cm^{-1}; δ(Pt-D) 538 cm^{-1}; Found: C, 58.74; H, 4.73%; $C_{44}H_{39}DGeP_2Pt$ requires C, 58.67; H, 4.56%]. The light petroleum ether was pumped from the filtrate to leave deuterotriphenylgermane (characterised by its mass and infra-red spectra, ν(Ge-D) 1471 cm^{-1}.).

40. Reaction of $(Ph_2PCH_2CH_2PPh_2)PtH(GePh_3)$ with 1,2-dibromoethane

The chelate platinum-hydride complex $(Ph_2PCH_2CH_2PPh_2)PtH(GePh_3)$ (0.16 g., 0.18 mmole) was reacted in a sealed tube with 1,2-dibromoethane (4 ml.). A colourless solution was formed after heating for two days at 70°. The tube was opened and the volatiles removed. Separation of the volatiles by fractional condensation gave ethylene and 1,2-dibromoethane. The solid was extracted with 60-80° petroleum ether to give insoluble $(Ph_2PCH_2CH_2PPh_2)PtBr_2$, [0.11 g., 84%]. Removal of the petroleum ether from the filtrate left triphenylgermane [0.06 g., 70%, ν(Ge-H) at 2036 cm^{-1}].

41. Reaction of $[(Ph_2PCH_2CH_2PPh_2)Pt(Et_3P)(SiMe_3)]^+BPh_4^-$ with Hex-1-ene

The complex (0.18 g., 0.16 mmole) was sealed with hex-1-ene (5 ml.) in a vacuum tube and heated at 60°. After 20 days the tube was opened to a vacuum line and the volatile material removed leaving only unreacted starting material.

42. Reaction of $[(Ph_2PCH_2CH_2PPh_2)Pt(Et_3P)(GeMe_3)]^+Cl^-$ with Hex-1-ene

Hex-1-ene (5 ml.) was condensed onto the complex (0.17 g., 0.2 mmole) in a break-seal tube. The tube was heated at 60° for eight days then opened to a vacuum line and the volatile material removed leaving unreacted starting material.

43. Kinetic Study of the Reaction of $(Ph_2PCH_2CH_2PPh_2)Pt(SiMe_3)_2$ and Hydrogen

The complex (0.1843 g.) in toluene (43.89 ml.) was reacted with hydrogen at 25° at an initial pressure of 613.57 mm. Hg. The rate of reaction was followed by measuring the reduction in hydrogen pressure using a 'Langham-Thompson Type U.P.4' transducer. The signal from the transducer was fed to an amplifier, the output from which was fed into a chart recorder having a linear calibration, hence a direct measure of pressure reduction and time was obtained.

The hydrogenation was carried out in a glass reaction vessel connected to the transducer. The thermostating was achieved by circulating water at 25° through the glass jacket of the reaction vessel. (Schematic diagrams of the apparatus and reaction vessel are given in Figs. 22 and 23).

I would like to thank Dr. M.G. Burnett and Mr. R.J. Morrison for the use of the hydrogenation apparatus and their helpful discussion of the results.

44. Attempted Preparation of bis(trimethylsilyl)mercury

Trimethylsilane (5 ml.) and dimethylmercury (5 ml.) were condensed into a flask fitted with a break-seal, to give a colourless solution. After three days at room temperature no visible change occurred so the flask was heated at 40° for one week, again no formation of bis(trimethylsilyl)mercury occurred.

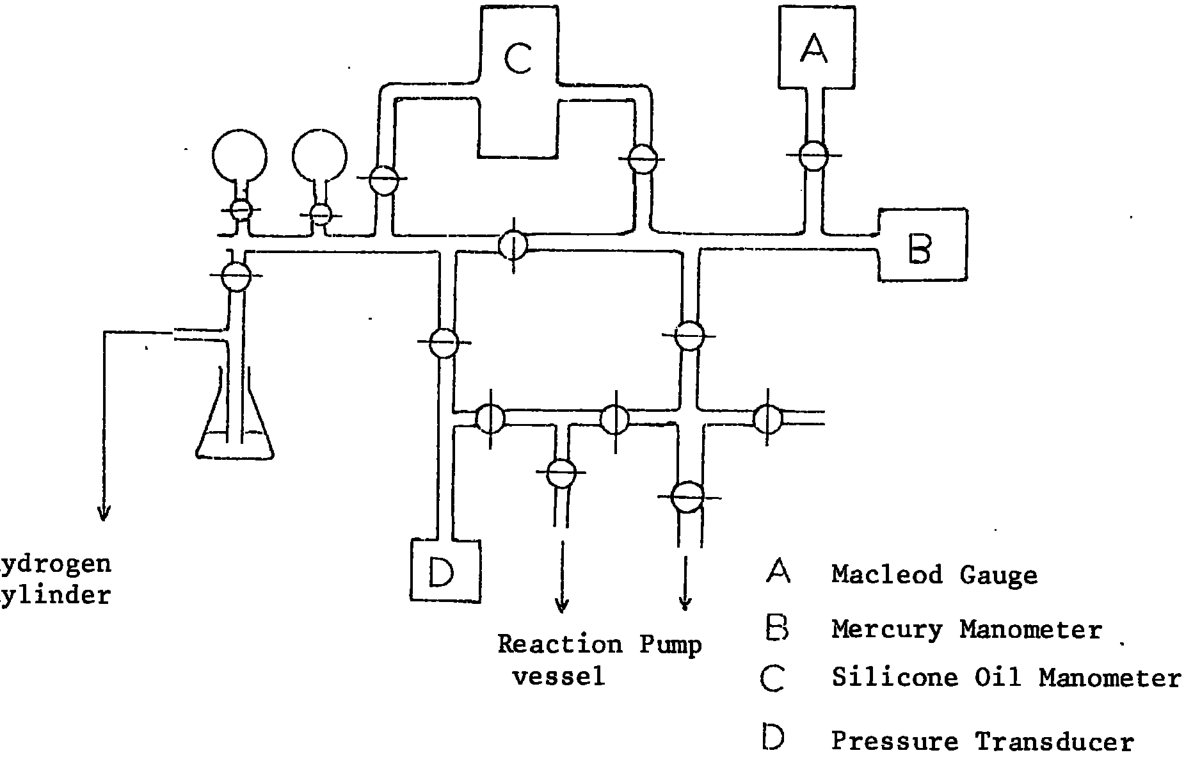


Fig. 22 Hydrogenation Apparatus

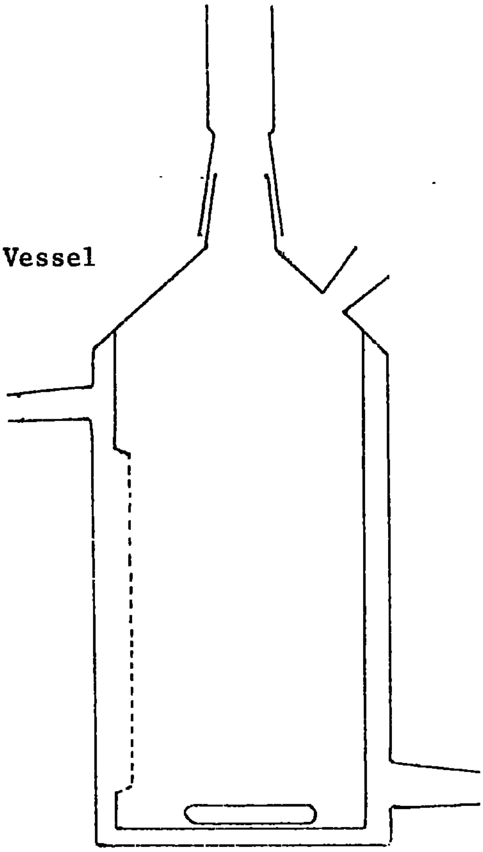


Fig. 23 Reaction Vessel

SECTION B

Platinum Hydride Complexes

1. The samples of trans-$(Ph_3P)_2PtHCl$ used to show that the reported cis and trans isomers were both trans species were made as reported by Bailar and Itatani[161].

Trans-$(Ph_3P)_2PtHCl$

Bis(triphenylphosphine)platinum(II) chloride (3 g., 3.8 mmole) was dissolved in ethanol (75 ml.) containing hydrazine hydrate (1.9 g., 3.8 mmole). The solution was refluxed on a steam bath for 5 minutes, acetic acid (1.8 g.), water (30 ml.) and ethanol (15 ml.) were added. The mixture was then cooled and colourless crystals separated out. The crystals were filtered, washed with methanol and recrystallised from a benzene-methanol mixture (1:2) to give colourless crystals of trans-$(Ph_3P)_2PtHCl.\ CH_3OH$, [ν(Pt-H) at 2230 $cm.^{-1}$].

Reported cis-$(Ph_3P)_2PtHCl$

Cis-bis(triphenylphosphine)platinum(II) chloride (2 g., 2.6 mmole) was dissolved in a mixture of methanol (80 ml.) and diethyl ether (80 ml.) containing hydrazine hydrate (1.3 g., 2.6 mmole). The mixture was refluxed on a steam bath for 15 minutes then acetic acid (0.9 g.) and water (60 ml.) were added. On cooling, colourless crystals separated out. These were collected, washed with methanol and recrystallised from benzene and diethyl ether at room temperature to give colourless crystals of "cis"-$(Ph_3P)_2PtHCl.C_6H_6$ ν(Pt-H) at 2210, 2232, 2265 and 2279 cm^{-1}. The strongest and sharpest being at 2232 $cm.^{-1}$, (hexachlorobutadiene or KBr).

A slow fractional recrystallisation of the "cis" form from a benzene-diethyl ether mixture gave two fractions, the first showing ν(Pt-H) at 2232 and 2211 $cm.^{-1}$, the second showing only one band at 2232 cm^{-1}.

Crystallisation of the trans form from a benzene-diethyl ether mixture yielded crystals showing three bands at 2211, 2250 and 2265 cm^{-1}.

2. Reaction of $(Ph_2PCH_2CH_2PPh_2)_2Pt(o)$ with HCl

The complex (0.2 g., 0.2 mmole) was dissolved in benzene (8 ml.) giving a yellow solution. Anhydrous hydrogen chloride was bubbled through the solution and a white precipitate formed immediately, the solid showed no ν(Pt-H) and recrystallisation of this precipitate from methanol gave white crystals of $\left[(Ph_2PCH_2CH_2PPh_2)_2Pt\right]^{2+}2Cl^-$, m.p. 300-310° (d). [0.18 g., 90%].

3. Reaction of $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ with Hydrazine Hydrate

The complex (1.0 g., 1.4 mmole) was heated in refluxing benzene (60 ml.) containing hydrazine hydrate (0.6 g., 1.2 mmole) for 2 hours. Some platinum metal was deposited and removal of solvent from the pale yellow solution left a yellow solid, showing no bands attributable to ν(Pt-H), from which only starting material could be isolated.

4. Reaction of trans-$(Et_3P)_2PtHCl$ with Trimethylsilane

Trimethylsilane (59.8 N.c.c., 2.67 mmole) and degassed benzene (15 ml.) were condensed onto the complex (1.25 g., 2.67 mmole) in a flask fitted with break-seal and stirrer. The flask was sealed and the contents vigorously stirred in a thermostat at 25°. After six weeks, when it was assumed that the reaction had reached equilibrium, the flask was opened to a vacuum line and the quantity of hydrogen measured using a Töpler pump. The experiment was repeated at 25° and two further flasks were set up at 35°. The equilibrium constants at 25° and 35° were then calculated (see appendix).

At 25° quantity of hydrogen liberated = 3.72 N.c.c.

At 35° quantity of hydrogen liberated = 2.83 N.c.c.

Experimental Methods

Nitrogen

All operations involving air-sensitive compounds were carried out in an atmosphere of dry, oxygen-free nitrogen. Purification was effected by passing commercial nitrogen through copper turnings at 400° to remove oxygen and through a molecular sieve column and a spiral trap at -196° to remove water.

Solvents

Hydrocarbon solvents, benzene, toluene, petroleum-ether, ether and cyclohexane were redistilled from phosphorus pentoxide and dried by standing over sodium wire for 1 week. Tetrahydrofuran was distilled from lithium aluminium hydride before use.

Analyses

Analyses were carried out in the microanalytical laboratories of Durham and Queen's Universities or by Drs. Weiler and Strauss, Banbury Road, Oxford.

Infra-red Spectra

Infra-red spectra in the region 2.5-25μ were recorded on a Grubb-Parson's Spectromaster, G.S.2A or Perkin-Elmer 457 Spectrophotometers. Solids were examined as pressed discs in KBr or as Nujol Mulls unless otherwise stated. Liquids were examined as contact films between KBr plates. A Grubb-Parson's DM2 Spectrophotometer and a Perkin-Elmer 457 Spectrophotometer were used to examine the region 20→50μ, solids being examined either as Nujol mulls between polythene protected CsI plates or as CsI discs.

Proton Magnetic Resonance

Proton magnetic resonance spectra were recorded, usually in benzene or deuterobenzene on either a Perkin-Elmer R10 Spectrometer or a Varian H.A.100 Spectrometer.

Mass Spectra

Mass spectra were recorded on an A.E.I. M.S.9 instrument.

Preparation of Starting Materials

1. 1,2-Bisdiphenylphosphinoethane[173]

Lithium foil (10.6 g., 2 equivalents) was dissolved, by stirring for one hour, in a solution of triphenylphosphine (200 g.) in T.H.F. (1000 ml.), during which the temperature rises to 48°. The golden-brown mixture was then cooled in ice-water and ethylene dichloride (60 ml.) in T.H.F. (100 ml.) was added over one hour. The mixture was then boiled for 20 minutes and cooled. Methanol (1500 ml.) was added, followed by the slow addition, with stirring, of sufficient water to precipitate the crystalline phosphine which was then filtered and recrystallised from 40-60° petroleum ether. Yield 70%.

2. 1,2-Bisdiphenylphosphinoethaneplatinum(II) chloride[174]

Sodium tetrachloroplatinite (8 g.) in ethanol (100 ml.) was treated with 1,2-bisdiphenylphosphinoethane (6 g.) in methylene chloride (30 ml.). A pink precipitate formed immediately and was collected, washed with water, then heated with equal volumes of concentrated hydrochloric acid and ethanol (100 ml. total) under reflux for four hours. The residue was separated, washed with ethanol and recrystallised from dimethylformamide by the addition of equal volumes of light petroleum and diethyl ether to give 1,2-bisdiphenylphosphinoethaneplatinum(II) chloride. [10g., 80%].

3. Bis(1,2-bisdiphenylphosphinoethane)platinum(II) dichloride[174]

$(Ph_2PCH_2CH_2PPh_2)PtCl_2$ (2.8 g.) in dimethylformamide (60 ml.) was treated with 1,2-bisdiphenylphosphinoethane (1.7g.) in chloroform (10 ml.). A few millilitres of water were added to ensure solution, followed by methanol (75 ml.) and diethyl ether (700 ml.). A precipitate was formed which was recrystallised from hot dimethylformamide by the addition of methanol to give $\left[(Ph_2PCH_2CH_2PPh_2)_2Pt\right]^{2+}2Cl^-$.

4. Bis(1,2-bisdiphenylphosphinoethane)platinum(o)[3]

Sodium borohydride (conc. aqueous solution) was added in small quantities to a hot ethanol/water (8%) solution of $\left[(Ph_2PCH_2CH_2PPh_2)_2Pt\right]Cl_2$. A vigorous reaction ensued and the bis chelate platinum (o) complex precipitated out. It was filtered and recrystallised from a benzene/methanol mixture to give the complex as bright yellow crystals, m.p. 252-255°.

5. Bistrialkylphosphineplatinum(II) chlorides

Bistrialkylphosphineplatinum(II) chlorides were prepared by adding a slight excess of two equivalents of the phosphine to a suspension of $PtCl_2$ in refluxing ethanol. $(Et_3P)_2PtCl_2$ was recrystallised from ethanol and $(Ph_3P)_2PtCl_2$ by dissolving in chloroform and precipitating out with pentane or hexane. $(Ph_3P)_2PtCl_2$ can also be prepared by the addition of triphenylphosphine to an aqueous solution of potassium tetrachloroplatinite[175].

6. Trans-(bistriethylphosphine)platinum(II) hydridochloride

Trans-(bistriethylphosphine)platinum(II) hydridochloride was prepared by the method of Chatt and Shaw[36] by reducing $(Et_3P)_2PtCl_2$ with hydrazine hydrate.

7. Germanium- and Tin-tetramethyls

These were prepared by the standard method of reacting excess Grignard reagent with the metal tetrachloride and distilling the tetramethyl derivative from the reaction mixture[176,177].

8. Bromotrimethylgermane

Bromotrimethylgermane was synthesised by the method of Mironov and co-workers[178].

Bromine (64 g.) was added to tetramethylgermane (50 g.) in n-propyl bromide (50 ml.). The mixture was refluxed for 24 hours, the temperature rising to 80^{o} and the solution gradually decolourising. The mixture was then fractionated through a column packed with glass helices, the fraction boiling between 90 and 120^{o} was redistilled to give bromotrimethylgermane b.p. 113.5^{o}. Yield 95%

9. The Group-IVb Hydrides

Me_3SnH, Me_3GeH and Me_3SiH were synthesised by reduction of the trialkyl metal halide with lithium aluminium hydride in dioxane or di-n-butyl ether[179,180], the product being distilled from the reaction mixture and purified by fractionation on a vacuum line.

10. Triphenylgermyl-lithium

Triphenylgermyl-lithium was made by reacting triphenylgermane[176] with one equivalent of n-butyl-lithium in ether[181]. It can also be prepared by cleaving hexaphenyldigermane with lithium in 1,2-dimethoxyethane[182].

11. The Platinum-germanium Complexes

$(Ph_2PCH_2CH_2PPh_2)Pt(GePh_3)_2$ and $(Ph_2PCH_2CH_2PPh_2)PtH(GePh_3)$ were prepared from $(Ph_2PCH_2CH_2PPh_2)PtCl_2$ and triphenylgermyl-lithium, the hydride was then obtained by high pressure hydrogenation of the disubstituted germyl complex[37].

12. Bis(trimethylsilyl)mercury and Bis(trimethylgermyl)mercury

Sodium amalgam, prepared from mercury (200 g.) and sodium (2 g.), was shaken in a flask fitted with a 'rotaflo' tap with cyclohexane (30 ml.) and chlorotrimethylsilane or bromotrimethylgermane (10 ml.) until an intense green colouration formed (this varied between one to four weeks). The mixture was extracted with cyclohexane, which was then removed by pumping and the yellow residue purified by sublimation. Yield 10-35%[167].

APPENDIX

1. Kinetic Study of Hydrogenation of $(Ph_2PCH_2CH_2PPh_2)Pt(SiMe_3)_2$

The results of the kinetic study are tabulated in Tables 1 and 2. The pressure reduction at the completion of reaction (P_∞) is obtained by extrapolation from graph 1. The rate constants with respect to hydrogen and platinum complex were calculated by standard methods[183]. Assuming a first order rate with respect to hydrogen, the integrated rate equation becomes

$$\ln \frac{P_\infty - Pt}{P_\infty} = k_1 t$$

$$\log \frac{P_\infty - Pt}{P_\infty} = \frac{k_1 t}{2.303}$$

Pt = pressure reduction at any time

t = time in seconds

k_1 = rate

Graph 2 is a plot of $\log \frac{P_\infty - Pt}{P_\infty} / t$

$$\text{gradient} = \frac{k_1}{2.303}$$

From graph (2), gradient = 4.9×10^{-5}

$$\therefore\ k_1 = 1.13 \times 10^{-4}\ S^{-1}$$

The rate constant is obtained by dividing this rate by the concentration of hydrogen in solution.

In toluene at 298 K, hydrogen concentration = 2.73×10^{-3} ml^{-1}.

$$\text{rate constant } k_2 = \frac{k_1}{[H_2]} = \frac{1.13 \times 10^{-4}}{2.73 \times 10^{-3}}$$

$$= \underline{4.14 \times 10^{-2}}\ lm^{-1}s^{-1}$$

Similarly, with respect to platinum complex, the concentration of the platinum-silyl complex in moles litre^{-1} is obtained from the expression

$$\text{concentration} = \frac{n}{v} = \frac{P}{RT} \qquad R = 0.08206 \text{ l atm m}^{-1}$$

$$T = 298 \text{ K}$$

As before, the gradient of a plot of log $\dfrac{[Pt]_o}{[Pt]_o - [Pt]_t}$ /t

(graph 3) gives $k_1/2.303$.

From graph 3, gradient $= \dfrac{0.475}{6,600}$

$$\therefore k_1 = \frac{0.475}{6,600} \times 2.303 = 1.65 \times 10^{-4} \text{ S}^{-1}$$

rate constant, $k_2 = \dfrac{1.65 \times 10^{-4}}{2.73 \times 10^{-3}}$

$\therefore$ rate constant, $k_2 = \underline{6.0 \times 10^{-2}}$ l m^{-1}s^{-1} with respect to platinum complex.

Therefore, as the plots of graphs 2 and 3 are linear the reaction appears to be first order with respect to hydrogen and first order with respect to the platinum complex.

N.B. The calculation does not include an allowance for the volume difference of hydrogen in liquid and gas phases, i.e. gas phase is three times the volume of the liquid phase, as the reduction in pressure of the gas phase is measured, for the system to remain in equilibrium the pressure reduction in the liquid phase must be three times the measured gas phase reduction, but for the first order rate equation this does not affect the calculation as in the $\dfrac{P_\infty - Pt}{P_\infty}$ expression this factor of three would cancel out thus $\dfrac{3P_\infty - 3Pt}{3P_\infty}$.

2. Reaction of trans-$(Et_3P)_2PtHCl$ with Me_3SiH

$$\text{trans-}(Et_3P)_2PtHCl + Me_3SiH \rightleftharpoons \text{trans-}(Et_3P)_2PtCl(SiMe_3) + H_2$$

$$\text{Equilibrium constant}\quad K = \frac{[(Et_3P)_2PtCl(SiMe_3)]\,[H_2]}{[(Et_3P)_2PtHCl]\,[Me_3SiH]}$$

At 25°, hydrogen liberated = 3.72 N.c.c. = 0.166 mmole.

Initial concentrations of hydridochloride and Me_3SiH = 2.67 mmole.

$$K = \frac{[0.166]\,[0.166]}{[2.67-0.166]\,[2.67-0.166]}$$

$$K_{25} = \underline{4.4 \times 10^{-3}}$$

Similarly at 35°, hydrogen liberated = 2.83 N.c.c. = 0.131 mmole.

$$K = \frac{[0.131]\,[0.131]}{[2.67-0.131]\,[2.67-0.131]}$$

$$K_{35} = \underline{2.7 \times 10^{-3}}$$

$$\frac{d\ \ln K}{d(1/T)} = \frac{-\Delta H}{R}$$

Integrating, $$\ln\frac{K_{25}}{K_{35}} = \frac{-\Delta H}{R}\left(\frac{1}{298} - \frac{1}{308}\right)$$

$$\ln\frac{4.4}{2.7} = \frac{-\Delta H}{8.3143} \qquad (0.00011)$$

$$\therefore\ \Delta H = \underline{-8.8\ \text{kcals}}.$$

Table 1

Rate Constant Results with Respect to Hydrogen

T.min.	Pressure Reduction mm.Hg.	$\frac{1}{T}$	$\frac{P\infty-Pt}{P\infty}$	$\log \frac{P\infty-Pt}{P\infty}$
10	11.14	0.1000	0.9119	0.0401
20	19.91	0.0500	0.8426	0.0744
30	27.64	0.0333	0.7815	0.1070
40	35.15	0.025	0.7221	0.1414
50	40.79	0.02	0.6791	0.1680
60	46.28	0.0167	0.6341	0.1978
70	52.20	0.0143	0.5923	0.2275
80	57.77	0.0125	0.5433	0.2650
90	62.64	0.0111	0.5048	0.2969
100	66.12	0.0100	0.4773	0.3212
120	73.36	0.00833	0.4200	0.3768
140	80.04	0.00714	0.3672	0.4351
160	86.48	0.00625	0.3165	0.4996
180	90.83	0.00556	0.2819	0.5499
200	93.26	0.00500	0.2627	0.5806
210	94.72	0.00476	0.2512	0.6000
220	95.70	0.00455	0.2434	0.6137
230	95.97	0.00435	0.2413	0.6175

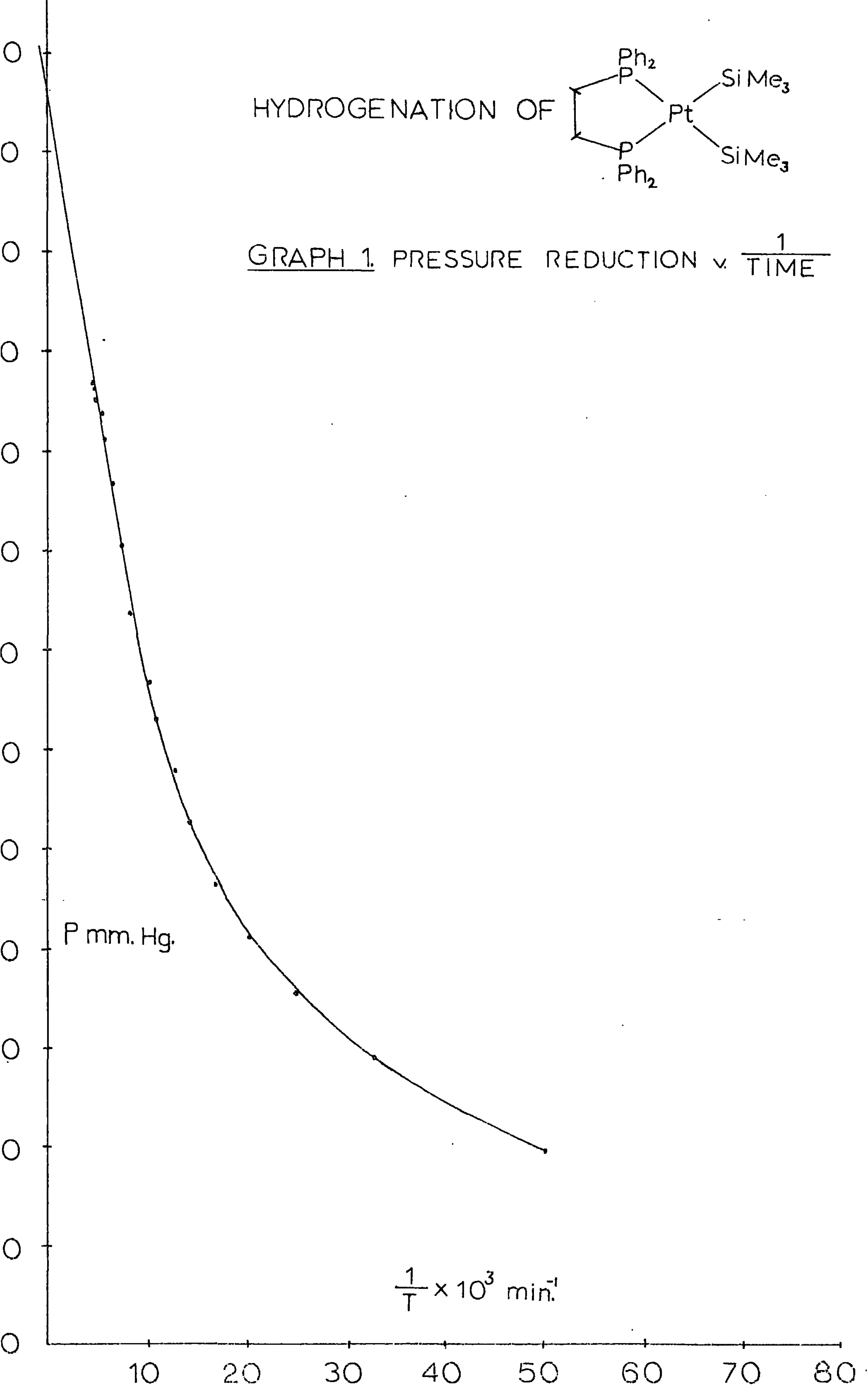
$P\infty = 126.5$ mm.Hg.

Table 2

Rate Constant Results with Respect to Platinum Complex

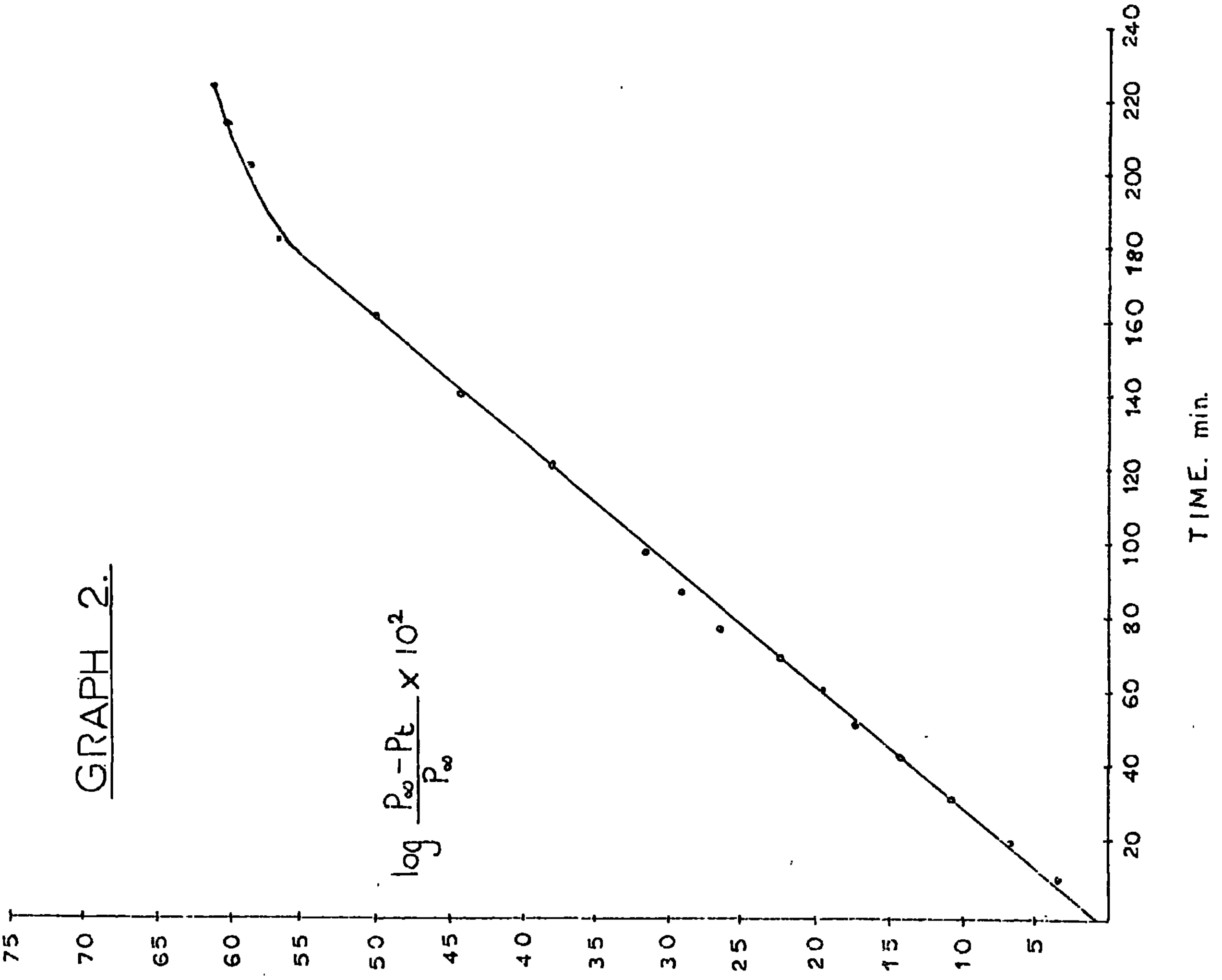
.min	Pressure Reduction mm.Hg.	$\frac{P}{RT}$ ml^{-1}	$[Pt]_o-[Pt]_t$	$\frac{[Pt]_o}{[Pt]_o-[Pt]_t}$	$\log\left[\frac{[Pt]_o}{[Pt]_o-[Pt]_t}\right]$
10	11.14	0.000599	0.005083	1.1178	0.0483
20	19.91	0.001071	0.004611	1.2323	0.0906
30	27.64	0.001487	0.004195	1.3545	0.1319
40	35.15	0.001891	0.003791	1.4988	0.1759
50	40.79	0.002194	0.003488	1.6290	0.2119
60	46.28	0.002490	0.003192	1.7801	0.2504
70	52.20	0.002808	0.002874	1.9770	0.2961
80	57.77	0.003108	0.002574	2.2075	0.3439
90	62.64	0.003370	0.002312	2.4576	0.3906
00	66.12	0.003557	0.002125	2.6739	0.4272
20	73.36	0.003947	0.001735	3.2749	0.5152
40	80.04	0.004306	0.001376	4.1294	0.6158
60	86.48	0.004653	0.001029	5.5219	0.7421
80	90.83	0.004887	0.000795	7.1472	0.8541
00	93.26	0.005018	0.000664	8.5572	0.9324
10	94.72	0.005096	0.000586	9.6962	0.9868
20	95.70	0.005149	0.000533	10.6604	1.0278
30	95.97	0.005164	0.000518	10.9691	1.0403

= 0.08206 l.atm.m^{-1}; T = 298K; Pt$_o$ = 0.005682 ml^{-1}.

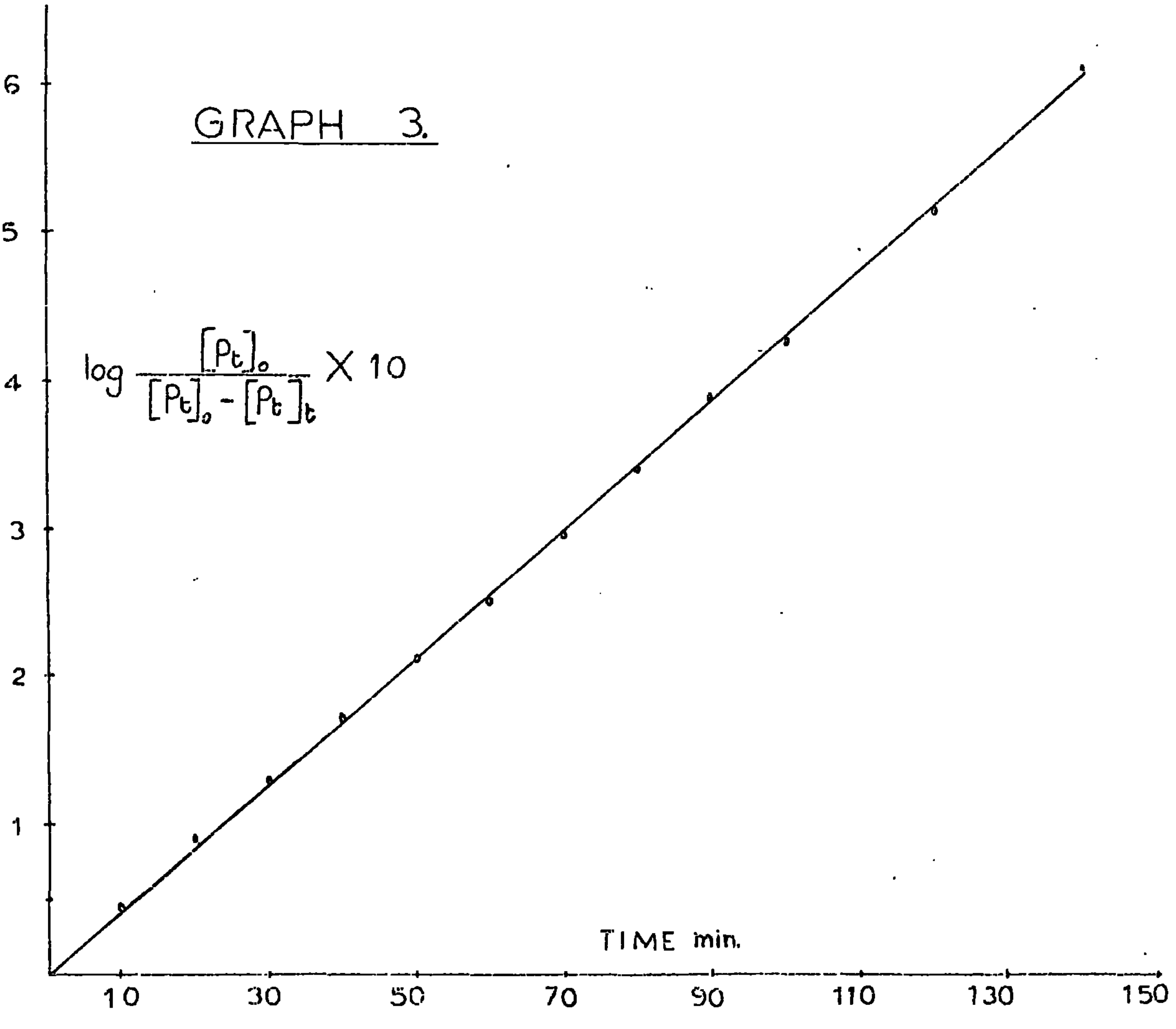


HYDROGENATION OF (Ph$_2$P)$_2$Pt(SiMe$_3$)$_2$

GRAPH 1. PRESSURE REDUCTION v. $\frac{1}{\text{TIME}}$



GRAPH 2.



GRAPH 3.

The 'H n.m.r. spectrum of the complex $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$ with excess trimethylstannane in deuterotoluene was run at +25, +10, -10 and -30°. The resonance due to the hydride of trimethylstannane at 25° appeared as a broad signal which on cooling resolved into eight of the expected ten lines due to coupling with the protons of the methyl groups (Fig. 24). This confirms that the initial broadening is due to the trimethylstannane being in rapid exchange with the octahedral complex (IX), on cooling the exchange slows down (or ceases) and the coupling is then observed..

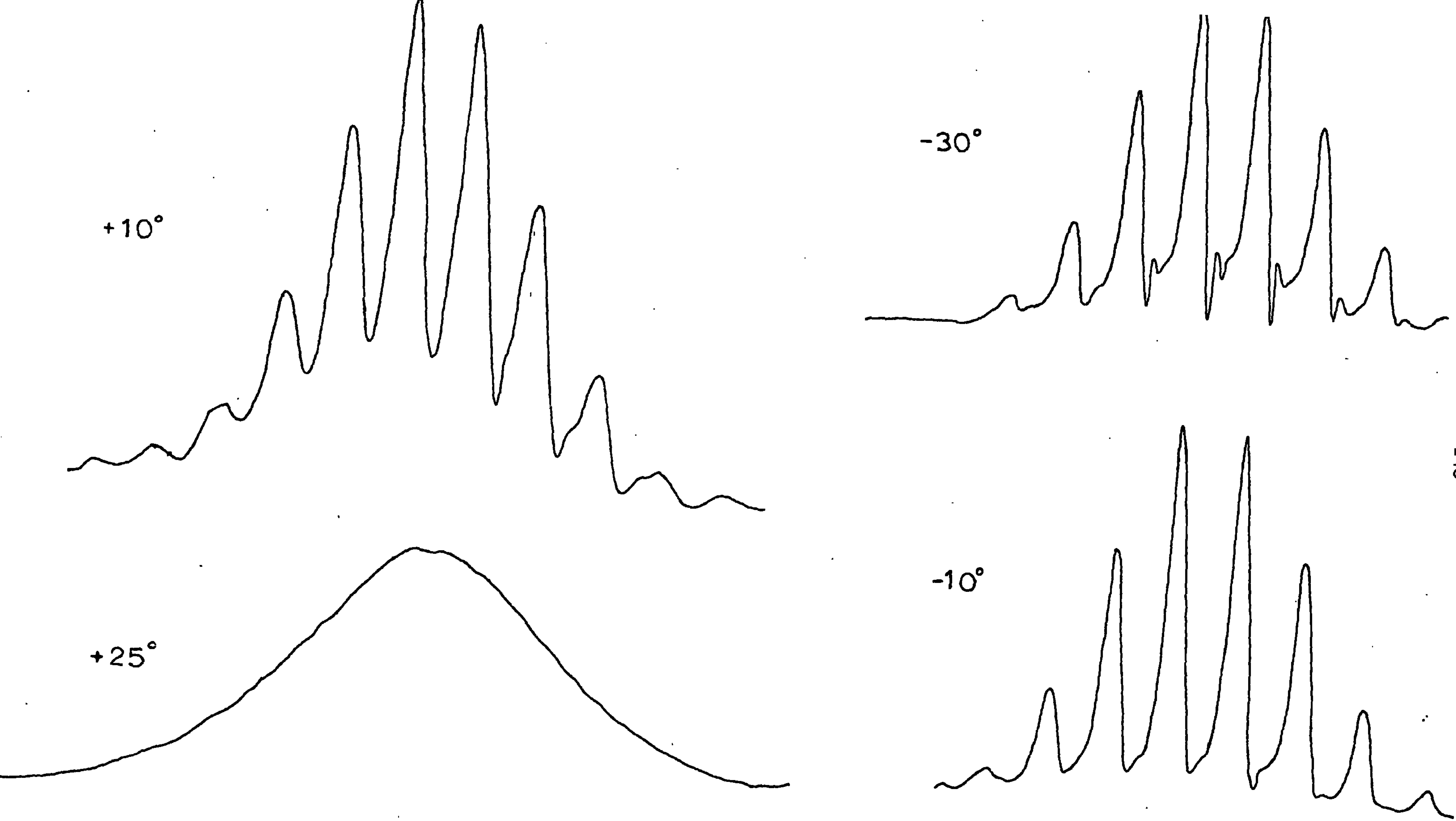


Fig. 24 Variable temperature 'H n.m.r. of $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$ + Me_3SnH, showing hydride resonance of Me_3SnH.

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