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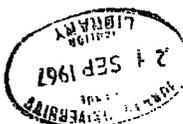
GERMYL AND HYDRIDO PALLADIUM COMPLEXES

by

E.H. Brooks, B.Sc.
(Grey)

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

July 1967



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PUBLICATIONS

The work described in this thesis has been the subject of the following publications:

Diphenylphosphino-organogermanes. J.C.S. 1965, 4283 -
with F. Glockling and K.A. Hooton.

With F. Glockling:-

A Palladium Hydride and Germyl-Palladium Complexes.

Chem. Commun. 1965, 510.

Triphenylgermylpalladium complexes. J.C.S. 1966, A, 1241.

Palladium Hydride Complexes. J.C.S. 1967, A. In press.

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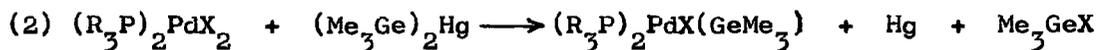
SUMMARY

This thesis describes the preparation, properties and reactions of germyl-palladium complexes and palladium hydride complexes. An appendix is concerned with some germanium-phosphorus compounds.

Germyl-Palladium Complexes

Germanium and other group IV metals form metal-metal bonds to platinum. The stability and reactivity of these compounds show many peculiarities, and the present work was undertaken partly in order to provide comparisons between platinum and palladium.

Two methods of preparation were investigated.



Only the first was successful and this gave the complexes where R = triethylphosphine and tri-n-propylphosphine. The Ge-Pd complexes are extremely sensitive to oxidation and decompose at about 100°. Reactions with HCl, 1,2-dibromoethane, KCN, H₂ and CO are described.

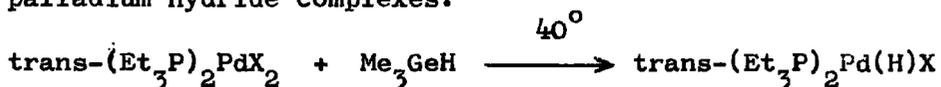
Palladium Hydride Complexes

In contrast to platinum which forms many stable hydride complexes, palladium has not hitherto yielded any isolable compounds containing a palladium hydrogen bond. Such compounds are of considerable interest since they are postulated in several palladium-catalysed reactions.



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An observation on the cleavage of Ge-Pd complexes by HCl led to the development of an almost quantitative reaction for preparing palladium hydride complexes:



By-products suggested that the reaction was taking place by a free radical mechanism. This evidence was supported by reactions carried out in the presence of a radical initiator and a radical inhibitor. The hydride $(\text{Pr}_3^{\text{n}}\text{P})_2\text{Pd(H)Cl}$ was formed but was too unstable to allow isolation, as also was a nickel hydride obtained from $(\text{Et}_3\text{P})_2\text{NiBr}_2$. Reactions of $(\text{Et}_3\text{P})_2\text{Pd(H)X}$ with KI, HCl/ Et_2O , $\text{NH}_3/\text{H}_2\text{O}$, CCl_4 , $\text{Me}_3\text{Sn.NMe}_2$, KCN/MeSH and KCN/MeOH are described. The latter two are of interest in that an intermediate hydridocyanide, $(\text{Et}_3\text{P})_2\text{Pd(H)CN}$ reacted with the solvents liberating hydrogen. Unsaturated compounds, $\text{CH}_2 = \text{CHCN}$, $\text{PhC}\equiv\text{CH}$, C_2F_4 and C_4H_6 reacted with $(\text{Et}_3\text{P})_2\text{Pd(H)Cl}$ giving a complexity of products.

Appendix

Chronologically this work, concerned with the formation and reactivity of germanium-phosphorus compounds, was carried out first and gave experience in handling air- and water-sensitive compounds. Lithium diphenylphosphide reacts with Ph_3GeCl giving $\text{Ph}_3\text{GePPh}_2$ and a few reactions of this compound are described. Ph_2PLi reacts

(x)

with all four chlorine atoms of GeCl_4 giving polymeric material instead of the expected $(\text{Ph}_2\text{P})_4\text{Ge}$. The polymer was shown to contain phosphorus as Ph_2P -groups only, and was probably formed by halogen-metal exchange reactions since $\text{Ph}_2\text{P}.\text{PPh}_2$ was also formed.

INTRODUCTION

The introduction to this thesis is concerned essentially with the chemistry of palladium (II) complexes. It will at times be necessary to make comparisons with nickel and platinum compounds, so the chemistry of these metals will be reviewed but particular emphasis is placed on the divalent state of palladium and platinum.

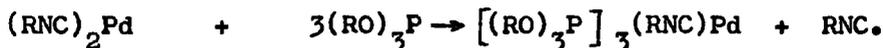
Although specific differences exist, the chemical properties of palladium and platinum are generally similar, but those of nickel are somewhat different. The dominant oxidation state of nickel is the +2 state, but the +4 oxidation state becomes increasingly important down the group.

1. Zerivalent Complexes

Each of these metals is known to form zerovalent complexes but all compounds involve strongly π -bonding ligands which remove electron density from the metal atom. Examples are $\text{Ni}(\text{CO})_4$, $\text{Ni}(\text{PF}_3)_4$, $(\text{Ph}_3\text{P})_4\text{Pd}$ and $(\text{Ph}_3\text{P})_3\text{Pt}$. Complexes of palladium (0) and platinum (0) with phosphine, phosphite and isonitrile ligands were prepared by reduction of divalent complexes in strongly alkaline media (1).



The products react with trialkylphosphites:



The chelate nickel complex, $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{Ni}$ was made by replacement of carbon monoxide from $\text{Ni}(\text{CO})_4$ (2). A series of complexes, ML_2 , MLL' and ML'_2 where $\text{M} = \text{Ni}, \text{Pd}$ or Pt , $\text{L} =$ chelating ditertiary phosphine and $\text{L}' =$ chelating ditertiary arsine have also been reported (3). Claims (4,5) to the preparation of the compounds $(\text{Ph}_3\text{P})_3\text{Pt}(\text{O})$, $(\text{Ph}_3\text{P})_4\text{Pt}(\text{O})$ and palladium analogues were later contested by Nyholm and co-workers (6) who suggested that these were in fact dihydrides, $(\text{Ph}_3\text{P})_3\text{PtH}_2$ and $(\text{Ph}_3\text{P})_4\text{PtH}_2$, but this has now been disproved (157).

2. The +4 Oxidation State

Relatively few compounds of nickel in this valence state are known. Stabilisation by coordination with highly electronegative elements such as oxygen and fluorine is necessary as in, for example, K_2NiF_6 . The +4 oxidation state becomes increasingly important as one proceeds down the triad. Palladium(IV) complexes are of two types, (8) halo-complexes $\text{M}_2(\text{PdX}_6)$ where M is an alkali-metal, and ammino-halo complexes, e.g. Pdpy_2Cl_4 . Both types are octahedral and readily lose halogen forming palladium (II) compounds. It has been pointed out recently that the 4-valent

state may play a more important part in the chemistry of simple compounds of palladium than was previously thought (9). Crystallisation from a solution obtained by dissolving palladium in nitric acid gave a product reported to be $\text{Pd(IV)(NO}_3)_2(\text{OH})_2$ which was previously described as hydrated $\text{Pd(NO}_3)_2$. Platinum forms a much larger number of stable 4-valent compounds. These are 6-coordinate and usually octahedral, but extraordinary structures are sometimes adopted for the metal to achieve 6-coordination. Trimethylplatinum iodide, first prepared in 1907 (10), has a tetrameric structure with the iodine and platinum atoms at the corners of a cube. Each platinum is coordinated to the three adjacent iodine atoms. Trimethylplatinum acetylacetonate has a dimeric structure. Each platinum atom adopts an octahedral environment by coordination with three methyl groups, the two oxygens of an acetylacetonate ligand and the C_3 carbon atom of the second acetylacetonate. An important series of platinum (IV) complexes is the range from halo complexes through ammino-halo complexes to the hexammines, e.g. Na_2PtCl_6 through intermediates $\text{Na [PtNH}_3\text{Cl}_5]$, $[\text{Pt(NH}_3)_2\text{Cl}_4]$, $[\text{Pt(NH}_3)_5\text{Cl}] \text{Cl}_3$ to $[\text{Pt(NH}_3)_6] \text{Cl}_4$. Combinations of various amines, ammonia, hydrazine, hydroxylamine and halogens or pseudohalogens including chlorine, bromine, iodine and thiocyanate are possible. Fluorine is found only in the complex ion PtF_6^{2-} which is much more stable than the palladium analogue.

3. Other Oxidation Levels

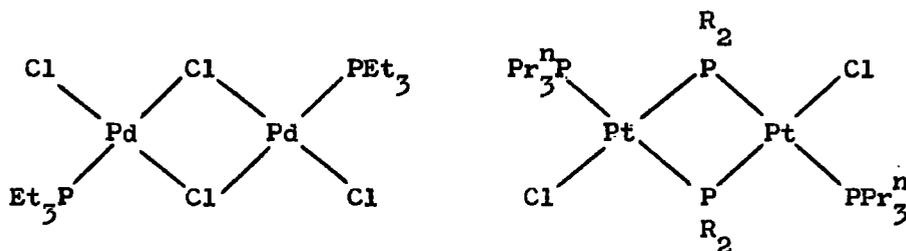
Oxidation states other than 0, +2 and +4 are not of great importance. Compounds of nickel (I) are very rare indeed but include $K_3Ni(CN)_4$ and $K_6[Ni_2(C\equiv CPh)_8]$. Palladium (I) and platinum (I) compounds are unknown. Tervalent halides of palladium and platinum have been claimed, but these may contain the metal in mixed oxidation levels +2 and +4. Nickel, on the other hand forms a few well defined Ni(III) complex. Oxidation of trans-bis(triethylphosphine)nickel bromide, $(Et_3P)_2NiBr_2$ with nitrosyl bromide yields a compound of composition $(Et_3P)_2NiBr_3$ (11). Only platinum forms compounds with the metal in oxidation state above +4. These are few in number and include PtF_5 and PtF_6 .

4. Divalent Complexes

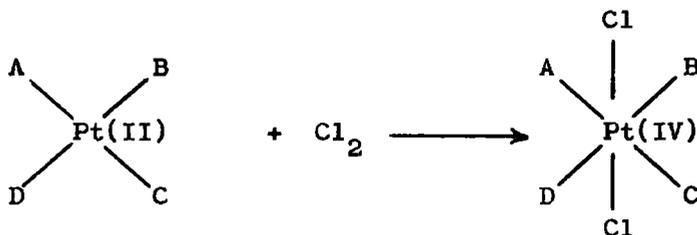
The complex chemistry palladium (II) and platinum (II) is rather similar, although palladium(II) complexes are kinetically more labile. Nickel shows distinct differences, however. Palladium (II) and platinum (II) complexes are usually 4-coordinate and square planar whereas nickel(II) complexes are commonly 4- or 6-coordinate and may have square planar, tetrahedral or octahedral structures (8). Square planar 4-coordinate complexes of nickel include $[Ni(CN)_4]^{2-}$ and the

chelate bis(N,N,N',N', -tetramethylethylenediamine)nickel (II). Such complexes are coordinatively unsaturated and coordination with strong donor ligands, e.g. H₂O, C₂H₅OH can increase the coordination number to six. A change in structure from square planar to octahedral results. Only relatively recently has the existence of tetrahedral nickel complexes been established, but these are now known to be quite numerous. Several classes have been characterised including [NiX₄]²⁻, [NiLX₃]⁻ and [NiL₂X₂] where L = a neutral ligand and X = halogen. In some cases the identity of the ligand is important. The complex (Et₃P)₂NiBr₂ is square planar, for example, while the triphenylphosphine analogue is tetrahedral (12). A number of compounds containing mixed alkyl-aryl phosphines have been prepared (13) e.g. bis(allyldiphenylphosphine)nickel bromide, (CH₂=CH-CH₂-PPh₂)₂NiBr₂ which exist in solution as an equilibrium mixture of the tetrahedral and square forms. The d⁸ electronic configuration of palladium (II) and platinum (II) gives rise to complexes which are characteristically square planar. In only a few cases is the coordination number increased beyond four. All types of mononuclear complexes of palladium and platinum, [ML₄]²⁺, [ML₃X]⁺, [ML₂X₂], [MLX₃]⁻ and [MX₄]⁻

have been prepared where L represents a neutral ligand and X an anionic ligand. In addition, bridged binuclear complexes having halogens, thiocyanate, RS and R_2P bridging groups exist (R represents an alkyl or aryl groups). Examples are: (14)



Nitrogen, halogens, cyanide ion and the heavy atom donors including phosphorus, arsenic, sulphur and selenium are the ligands for which palladium(II) and platinum(II) have the strongest affinity. The preference for heavy atoms is due largely to the formation of π -bonds between filled metal d orbitals (d_{xz} , d_{xy} and d_{yz}) and vacant ligand d orbitals. Platinum(II) complexes are generally more inert than palladium(II) complexes, kinetically and thermodynamically. This is reflected in the fact that certain reagents, e.g. chlorine, bromine, methyl iodide, oxidise platinum(II) to platinum(IV) complexes with retention of configuration:



5. Structure and bonding

The electrostatic crystal field theory predicts that if four ligands, either ionic or dipolar, lie two on each x and y axis with the metal atom at the centre, the d orbitals ($4d$ for Pd^{2+} and $5d$ for Pt^{2+}), $d_{x^2-y^2}$, d_{z^2} , d_{xy} , d_{xz} and d_{yz} will no longer be of equal energy (degenerate) since an electron in each of these orbitals would feel the influence of the four ligands to a differing degree. The theory predicts that the orbitals will be in the following order of increasing energy:

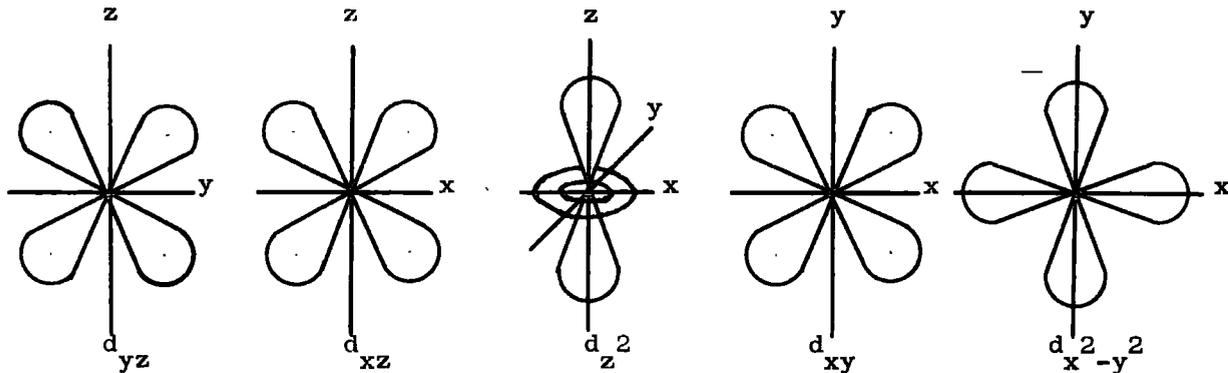


Fig.1.
Diagram of d atomic orbitals

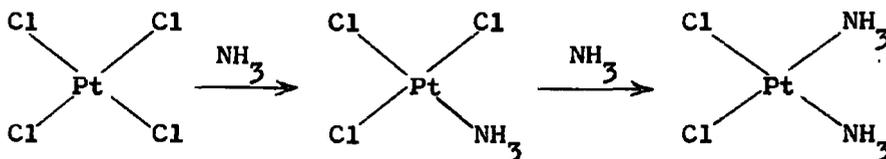
$d_{yz} \sim d_{xz} < d_{z^2} < d_{xy} < d_{x^2-y^2}$. Hund's rule states that orbitals shall be occupied singly as far as possible, but applies to

orbitals of equal energy. In the situation envisaged it is energetically more favourable for electrons to pair, leaving one vacant orbital, than for one electron to remain in the $d_{x^2-y^2}$ orbital. Thus, in d^8 square planar palladium(II) and platinum(II) complexes the d_{yz} , d_{xz} , d_z^2 and d_{xy} orbitals each contain two electrons while the $d_{x^2-y^2}$ orbital remains vacant. The result is that the four ligands can approach the central atom more closely in the x and y directions since electrostatic repulsions are reduced. The ligand field theory is a modification of the electrostatic crystal field theory which takes into account a moderate amount of covalent bond formation by overlap of metal and ligand orbitals. Expressed in these terms, the $4d_{x^2-y^2}$ palladium orbital can hybridise with the 5s, $5p_x$ and $5p_y$ orbitals forming dsp^2 square planar orbitals with which the ligands can overlap more effectively.

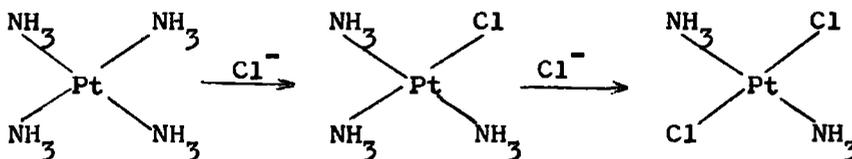
6. (a) The Trans Effect

The square planar structure of Pd(II) and Pt(II) complexes allows the possibility of geometrical isomerism in compounds of general formula ML_2X_2 . These can exist in cis or trans forms which have L groups at adjacent or opposite corners of the square respectively. The rates and isomeric products of ligand

replacement reactions are often dependent on the group trans to the leaving group. The theory of the trans effect has been developed to explain this and has proved quite useful as a guide to the preparation of isomers of complexes. The trans effect has been defined as the effect of a coordinated group on the rate of substitution reactions of ligands diagonally opposite (15). The synthesis of cis and trans isomers of $(\text{NH}_3)_2\text{PtCl}_2$ can be taken as an illustration of the operation of the trans effect. The cis isomer can be made by the action of buffered ammonia solution on $[\text{PtCl}_4]^{2-}$:



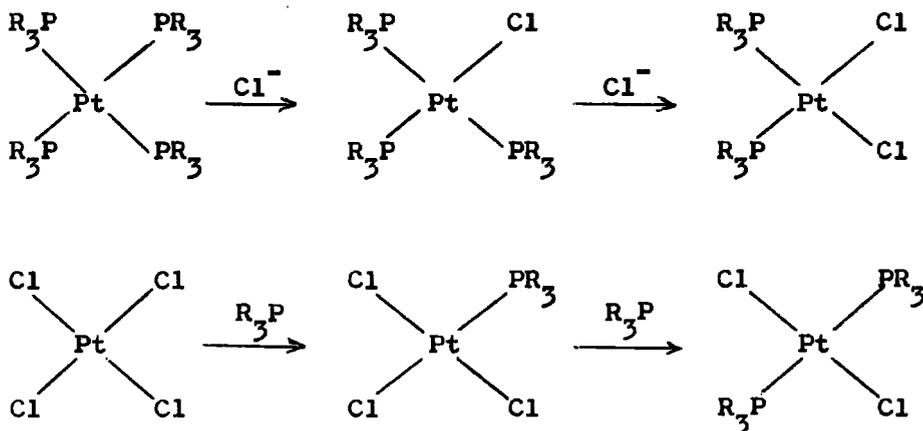
Treatment of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ with chloride ions gives the trans isomer, as indicated below. . . These reactions are explained by saying that chloride ion has a greater labilising effect on the group opposite than does ammonia, that is to say Cl^- has a greater trans effect than NH_3 . Study of similar substitution



reactions has enabled a correlation of the trans effects of

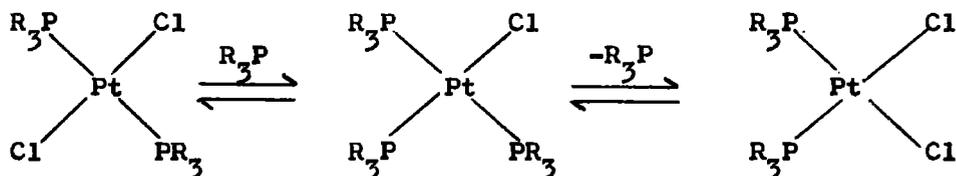
various ligands to be made. The usual sequence is $\text{H}_2\text{O} < \text{OH}^- < \text{NH}_3$, pyridine, $\text{RNH}_2 < \text{Cl}^- < \text{Br}^- < \text{I}^-$, $\text{SCN}^- < \text{NO}_2^- < \text{SC}(\text{NH}_2)_2$, R_3P , $\text{R}_2\text{S} < \text{CN}^-$, CO , C_2H_4 , $\text{NO} < \text{Me} < \text{Ph}$, H .

It would appear to be a general rule in substitutions of the above type that if the entering group has a greater trans effect than the groups already present, the product will be the trans isomer. Conversely, if the trans effect of the entering group is less than those groups present, the product will be the cis isomer. However, other factors may influence the situation, as will be seen from the following example. The relative trans effects of trialkyl-phosphines and chloride ion are in the order $\text{R}_3\text{P} > \text{Cl}^-$, so the cis and trans isomers of $(\text{R}_3\text{P})_2\text{PtCl}_2$ should be given by the following reactions:



Both sequences assume that R_3P has a greater trans labilising effect than Cl^- . In practice, each isomer can be obtained from

either system (16), the reason being that the trans form is thermodynamically more stable, but the cis form is less soluble in the solvent, benzene (17). A trace of free tertiary phosphine causes an equilibrium to be set up between the two forms, probably via a cationic intermediate:



The less soluble cis form crystallises on cooling and the equilibrium is displaced to the right. The addition of a slight excess of $[\text{PtCl}_4]^{2-}$ stops the equilibration by removal of the catalyst, trialkylphosphine, and then the thermodynamically more stable trans form crystallises.

(b) Kinetics and Mechanism

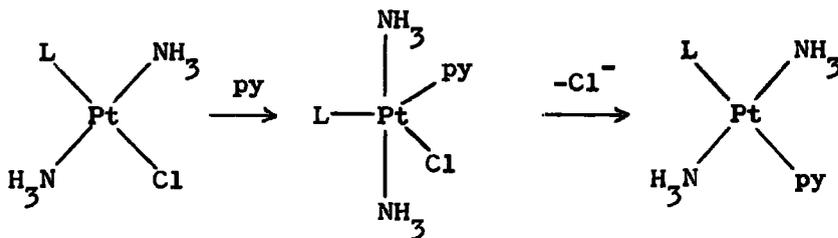
A considerable amount of work on the kinetics of substitution reactions has been done to give quantitative data on the trans effects of ligands and to establish a mechanism. The rate of substitution reactions of type



is given by the expression

$$\text{Rate} = k_1 [\text{Pt}(\text{A})_3\text{X}] + k_2 [\text{Pt}(\text{A})_3\text{X}] [\text{Y}]$$

where 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 (18). The solvent controlled reaction becomes more pronounced when the rate constant for direct substitution is lower, i.e. when the ligand Y is not a very good substituting reagent. It has been found that a ligand with high trans labilising ability is usually a very effective substituting reagent for platinum(II) complexes. This suggests that the activated complex of a substitution reaction is a trigonal bipyramid and the reaction can be represented as, for example:



(c) Structure Determination by X-ray Crystallography

The technique of X-ray diffraction is extremely useful for the determination of structures of metal complexes. Bond lengths and angles can be measured by this method. If the trans effect of a ligand L in complexes of type trans-

$[\text{PtA}_2\text{LX}]$ is due to a weakening of the Pt-X bond, the length of that bond should increase as the trans effect of L increases. However, such changes may be small and would require very accurate measurement of Pt-X distances. A correlation has not yet been attempted in detail, but the evidence available at present suggests that such trends do in fact take place in many cases. For example, the Pt-Br distances in the complex $\text{K} [\text{Pt}(\text{NH}_3)\text{Br}_3]$ have been measured (19). The Pt-Br bond length for bromine trans to NH_3 is 2.42A, which is approximately the sum of the covalent radii, but that for Br trans to Br is 2.70A. The structure of Zeise's anion, $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ shows a lengthening of that Pt-Cl bond which is trans to the ethylene ligand of high trans effect (20). The C-C bond is normal to the plane of the complex, and the mid point of this bond and each Cl atom form the square round platinum. The Pt-Cl bond trans to ethylene is 2.42A, compared with 2.32A for the sum of the atomic radii. A similar increase was observed in the corresponding bromo complex, $[\text{Pt}(\text{C}_2\text{H}_4)\text{Br}_3]^-$.

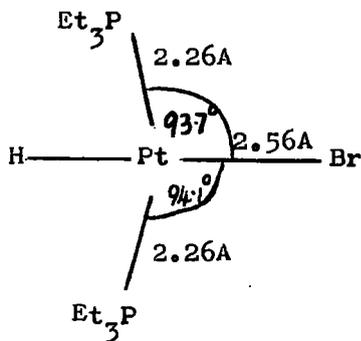
Although olefins have this tendency to lengthen trans platinum-halogen bonds, they do not increase platinum-nitrogen bond lengths in the same way.

The structure of trans- $[\text{Pt}(\text{C}_2\text{H}_4)\text{NH}(\text{CH}_3)_2\text{Cl}_2]$

has a Pt-N bond length 2.02Å which is normal (2.03Å), despite the very high trans effect of ethylene (21). The explanation has been put forward that the ligand which has high trans effect modifies the π -bonds of the system but has little effect on the σ -bonds. If the trans ligand has certain π -bonding character the strongly π -bonding ethylene will remove d electrons from the platinum atom. These will not then be available for bonding with the trans ligand and the result is that the trans bond to ethylene is longer than usual. This explains the lengthening of platinum-halogen bonds trans to ethylene, since Pt-Cl and Pt-Br bonds may have some π character. Nitrogen, however, has no vacant orbitals of suitable energy with which it can π -bond with the platinum d_{xz} , d_{yz} or d_{xy} orbitals and so is not influenced by the presence or absence of ethylene. This theory does not reconcile the observed high trans effect of hydrogen which does not have orbitals for π -bonding. Recently Parshall has shown by comparison of the nuclear shielding parameters of meta - and para-fluorophenylplatinum complexes that halogens do not accept d electrons from the metal, and that they may even be π -electron donors (22,23,24). This obviously conflicts

with the above theory explaining the anomaly of Pt-Cl and Pt-N bond lengths. It may be that the distances have not been measured with sufficient accuracy and will require further study.

The crystal structure of the platinum hydride, $(\text{Et}_3\text{P})_2\text{-PtHBr}$ has been determined and shows that the ligands are coplanar in a distorted square planar arrangement (25). The position of the hydridic hydrogen can only be inferred.



The Pt-Br distance, 2.56 Å is appreciably greater than the sum of the atomic radii (2.43 Å) while the Pt-P distances are shorter than expected (2.26 Å as opposed to 2.42 Å). The long Pt-Br distance may be the result of two effects, the high trans effect of hydrogen and the influence of the cis phosphorus atoms. The platinum d_{xy} orbital is available for π -bonding to bromine, as are the two phosphorus atoms. Partial removal of electrons from

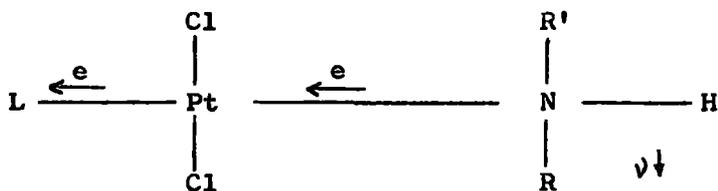
the metal d orbital into a phosphorus d orbital will reduce their availability to bromine. The Pt-Br π -bonding is therefore reduced, resulting in an increase in this bond length.

Conversely the Pt-P double bond character is increased and this is manifest in the short Pt-P distance. Support for this theory that the platinum 5d orbitals can interact with phosphorus 3d orbitals is obtained from the crystal structure of trans- $(Et_3P)_2PtBr_2$ (26). The observed Pt-P distances, 2.31Å are shorter than the sum of the covalent radii whereas the observed Pt-Br bond lengths had the normal value of 2.43Å.

(c) Infrared Spectra

Three methods have been used by Chatt and co-workers to investigate the trans effects of ligands and these will be considered in turn. The first, and ~~last~~ direct method (27) was a study of the N-H stretching frequencies of complexes of the type trans- $[PtLCl_2(NHRR')]$. This gave information on the Pt-N bond strength by the following argument. In the absence of hydrogen bonding, the N-H bond strength increases as $\nu(N-H)$ increases because the nitrogen atom is more negative. As a consequence, the Pt-N bond is weaker since the nitrogen atom withholds its electrons from platinum.

The results can be interpreted by reference to the diagram



Increasing electronegativity of L causes the ligand to withhold its electrons from platinum. This in turn increases the attraction of the platinum atom for the electrons in the Pt-N bond and the less negative nitrogen does not bind the proton so strongly. The result is a decrease in the N-H stretching frequency. Observations showed a decrease in $\nu(\text{N-H})$ as the ligand L is changed in the order $\text{R}_3\text{P} > \text{R}_3\text{Sb} > (\text{RO})_3\text{P} > \text{R}_3\text{As} > \text{R}_2\text{Te} > \text{C}_2\text{H}_4 > \text{R}_2\text{Se} > \text{R}_2\text{S} > \text{piperidine} > 4\text{-n-pentylpyridine}$. With the exception of ethylene and tertiary phosphines, the results indicate that the Pt-N bond strength increases as the tendency of the ligand to donate electrons to platinum decreases and this roughly parallels the decreasing trans effect of L. Ethylene and trialkylphosphines are anomalous. The latter cause higher N-H stretching frequencies than the less electronegative R_3As and R_3Sb groups.

Measurement of ν -(Pt-N) in the far infrared spectra of a few complexes trans- $[\text{PtL}(\text{NH}_3)\text{Cl}_2]$ gives results in agreement with the above order (28). The Pt-N stretching frequency increased in the series $\text{L} = \text{C}_2\text{H}_4 < \text{Et}_2\text{S} < \text{NH}_3$.

More direct evidence on the trans effects of ligands was obtained by measurement of the Pt-H stretching frequencies of a series of hydrides trans- $[(\text{R}_3\text{P})_2 \text{Pt}(\text{H})\text{X}]$ (29,30). Such complexes have sharp bands in the region $2000 - 2200 \text{ cm}^{-1}$.

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

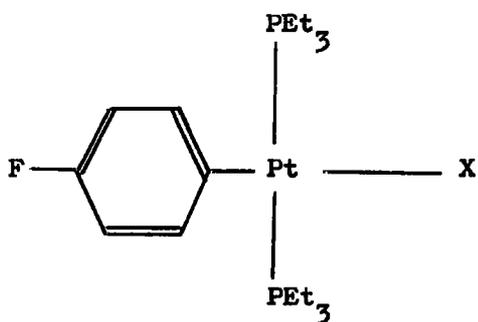
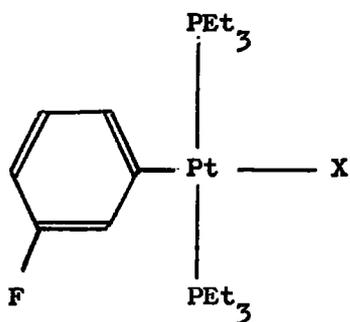
The values observed show that ν (Pt-H) decreases and therefore the Pt-H bond strength decreases as the trans effect of the ligand X increases. This supports a theory that the trans effect is due to a weakening of the Pt-H bond. The ligands in the cis positions also influence the Pt-H stretching frequency, but to a much lesser extent. The frequency increases with increasing electron withdrawal by the phosphine ligands, i.e. in the series $\text{PEt}_3 < \text{PEt}_2\text{Ph} < \text{PEtPh}_2 < \text{PPh}_3$.

Chatt's third type of spectroscopic study of the trans effects of ligands was the measurement of Pt-Cl and Pt-Br stretching frequencies of complexes e.g. trans-L₂PtClX (31). These absorptions are found in the far infrared region. There are two difficulties in relating ν -(Pt-Cl) or ν -(Pt-Br) to the platinum-halogen bond strength. To be rigorous, force constants and not stretching frequencies should be compared in order to obtain information about bond strengths. Since other bonds and angles may take some part in each vibration, a complete vibrational assignment of the molecule would be preferred. This is a formidable task with such a complicated molecule, but nevertheless, conclusions about trends in bond strengths of a closely related series of molecules should be correct, even if these trends are deduced from frequencies only. Another difficulty is that ν -(Pt-X) and ν -(Pt-Cl) may couple and show a frequency which is displaced from the true value, but the heavy platinum atom should minimise this. The results are in agreement with those from platinum hydride complexes and they also show that methyl, phenyl and hydride ligands have high trans effects. An exception was the complex (cycloocta-1,5-diene)platinum chloride. Although this ligand is known to have high trans effect, the Pt-Cl stretching frequency was one of the highest recorded. This

supports the view that the trans effect is the result of more than one cause.

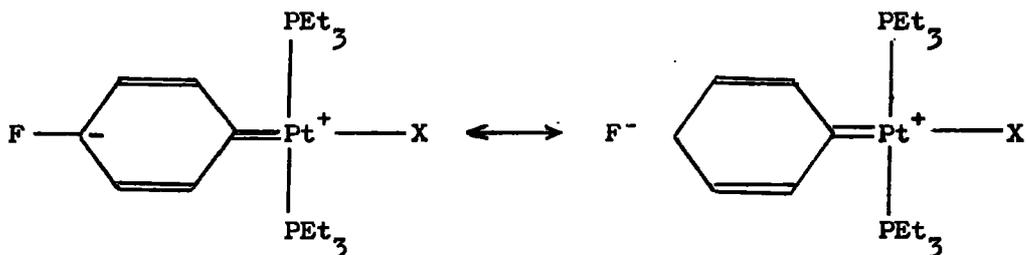
(d) N.M.R. Spectra

A study of ^{19}F nuclear shielding parameters has been carried out (22, 23, 24) with the object of correlating the trans effects of the ligands X in complexes (I) and (II):



The ^{19}F shielding parameters of these are very sensitive to the electronic effects of the other substituent of the ring, $[-\text{Pt}(\text{PEt}_3)_2\text{X}]$. Inductive electron donors increase the shielding of the ^{19}F nucleus (positive chemical shift relative to fluorobenzene) and vice versa. This inductive mechanism operates on both meta- and para-substituted complexes. In addition, groups which donate or withdraw electrons by π -bonding can further shield or deshield the ^{19}F nucleus of para-substituted

complexes by contributions such as



The ^{19}F n.m.r. spectra of complexes (I) and (II) show large positive shielding parameters indicating that the group $[-\text{Pt}(\text{PEt}_3)_2\text{X}]$ is an electron donor by both inductive and π -bonding mechanisms, but the actual value depends on the trans ligand, X.

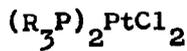
Meta-Fluorophenyl Complexes

Alkyl and aryl ligands have larger inductive electron donating effects than halide and pseudohalide ions. The observed sequence, $\text{CH}_3 > \text{Ph} > \text{PhC}\equiv\text{C} > \text{CN} > \text{Cl} > \text{Br} > \text{I}$ parallels the basicity of the ligand in non-polar solvents. This is reasonable since the shielding parameter should vary directly with the electron density induced in the σ -bonds of the complex by the trans ligand.

Para-Fluorophenyl Complexes

The ^{19}F shielding parameters of these complexes are much larger since both inductive and resonance effects are important. The methyl ligand does not have orbitals available for π -bonding to the metal so the shielding parameter of this complex was separated from each of the others to give a ' π -acceptor parameter' for each ligand. Results were, in most cases, in agreement with those obtained by other methods. Phenylethynyl, cyanide and SnCl_3^- have strong π -acceptor properties whilst aryl, substituted aryl and thiocyanate are modest π -acceptors. Halide ions actually show negative parameters and may therefore be π -electron donors.

Richards and co-workers have studied ^{195}Pt - ^{31}P coupling constants of tertiaryphosphine platinum halide complexes and the results have been interpreted in terms of the S character of the platinum-phosphorous bonds. (32) The coupling constant of the cis isomer of $(\text{Bu}_3\text{P})_2\text{PtCl}_2$ is about 1.5 times greater than that of the trans isomer (3508 as opposed to 2380 c.p.s.), implying that the S character of the Pt-P bond in cis complexes is greater than in trans isomers. The Pt-P bond strengths are greater in cis than in trans complexes, shown by the shorter bond distances and higher stretching frequencies.



	cis isomer	trans isomer
J (Pt-P)	3508 c.p.s.	2380 c.p.s.
l(Pt-P)	2.25A	2.31A
v(Pt-P)	442 cm ⁻¹ 427 cm ⁻¹	419 cm ⁻¹
l(Pt-Cl)	2.42A	2.32A
v(Pt-Cl)	303 cm ⁻¹ 281 cm ⁻¹	339 cm ⁻¹

If the π -component of a platinum-chlorine bond is small the data in the table can only be explained in terms of a directed inductive effect. The differences in the Pt-Cl bond lengths in the cis and trans complexes would then be due to a σ -effect only, and even if the phosphorus atom trans to chlorine in the compound cis $(R_3P)_2PtCl_2$ formed strong π -bonds to platinum, this would have little effect on the platinum-chlorine bond strength which would then be approximately the same as in the trans isomer. Thus, observations on bond lengths and stretching frequencies lead to the conclusion that phosphorus has a greater trans effect than chlorine, both operating through the σ -bonds. Unfortunately, this still leaves

open the question of why the π -bonding ligand, ethylene, causes lengthening of trans chlorine ligands but not trans amines (page 14).

(e) Theory of the Trans Effect

A satisfactory interpretation of the trans effect is by no means complete, but evidence available at present suggests that it is the result of more than one process.

The theories which have been proposed were reviewed by Basolo and Pearson (15) and were divided into two general classes, the polarisation theory and the π -bonding theory.

Polarisation Theory

This theory gives an explanation of how induced dipoles and polarisability of the ligands weaken to trans ligand. If the ligand L of a complex PtLX_3 has greater polarisability than X, the orientation of induced dipoles will be as shown

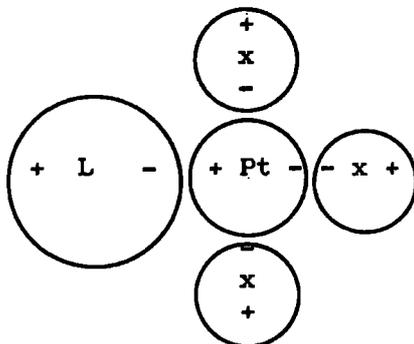


Fig.2. Dipoles induced in PtLX_3 by polarisation of ligand L

Thus the ligand X which is trans to L experiences a repulsive force which weakens and lengthens this Pt-X bond.

The polarisation theory accounts for the high trans effects of methyl and hydride ligands (29) where π -bonding is not possible. It also explains the correlation between the polarisability and trans effects of ligands and correctly predicts that the effect is most important where the ligand is itself polarisable. Thus the trans effect is more pronounced in platinum(II) than in the less polarisable palladium(II) or platinum(IV) complexes. The n.m.r. spectra of parafluorophenyl complexes (page 20) shows that halogens can act as weak π -electron donors, so the inductive effect may be important in the mechanism of the trans effect of these atoms. To support this, their trans effects increase in the series Cl < Br < I, the order of their polarisabilities.

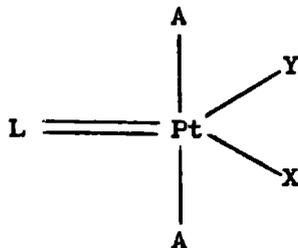
π -Bonding Theory

The high trans effects of such ligands as ethylene, and carbon monoxide is explained in terms of π -bonding in which electrons are donated from the metal d orbitals into ligand orbitals (33). These may be d orbitals as in phosphorus

or π^* antibonding orbitals as in ethylene, ethynyl or carbon monoxide. The type of bonding in olefin complexes is described later (page 49). If the activated complex of a substitution reaction



has trigonal bipyramidal structure, Chatt proposed (33) that removal of electrons from the metal by π -bonding to the ligand L will favour the approach of the substituting ligand Y to form the 5-coordinate intermediate:



Orgel prefers to regard it as stabilisation of the transition state by π -bonding since the electron density is reduced in the Pt-X and Pt-Y directions (34). This theory correctly predicts that both X and Y influence the rate of substitution.

It has been shown that the trans effects of ligands bonded to palladium are influenced more by the inductive electronic

properties of the ligands than by π -bonding (35). Since Pd(II) is not so readily oxidised to Pd(IV) as Pt(II) is oxidised to Pt(IV) it is likely that the palladium d orbitals lie at a lower energy and are not so available for π -bonding as are the platinum d orbitals.

To summarise, the trans effect can be transmitted by an inductive mechanism, a π -bonding mechanism or a combination of the two. The inductive mechanism is transmitted through the σ -bonds and usually involves weakening of the Pt-X bond. The π -bonding mechanism is transmitted through the platinum d orbitals and the ligand orbitals which may be d orbitals or vacant π orbitals. This mechanism may weaken the Pt-X bond if the ligand X can also form π -bonds to platinum or it may operate by stabilisation of the transition state for a 5-coordinate intermediate.

Chapter 2. Organic Derivatives of Divalent Nickel, Palladium and Platinum

2,1. Compared with non-transition metals, simple organic derivatives of transition metals are normally thermally unstable (36) and the reason must be connected with the fact that the energy of the d orbitals of transition metals in the penultimate shell is close to the energy of the valency s and p orbitals. Metal - halogen bonds are polar and any dissociation would be ionic.



The electrostatic attraction tends to keep those ions together and recombination would be likely. Metal - carbon bonds are more likely to dissociate by a radical mechanism and this would be enhanced if an electron could transfer to a metal - carbon σ^* antibonding orbital. It is suggested, therefore, that the main factor influencing the stability of metal to carbon bonds is the difference in energy, ΔE , between the highest energy occupied orbital and the lowest energy antibonding orbital.

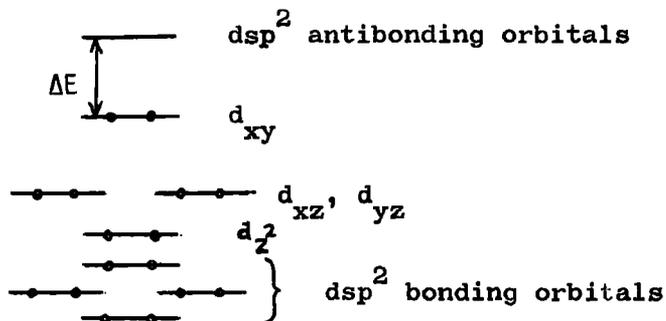


Fig. 3 Simplified energy level diagram showing molecular orbitals in square planar Pt(II) complexes.

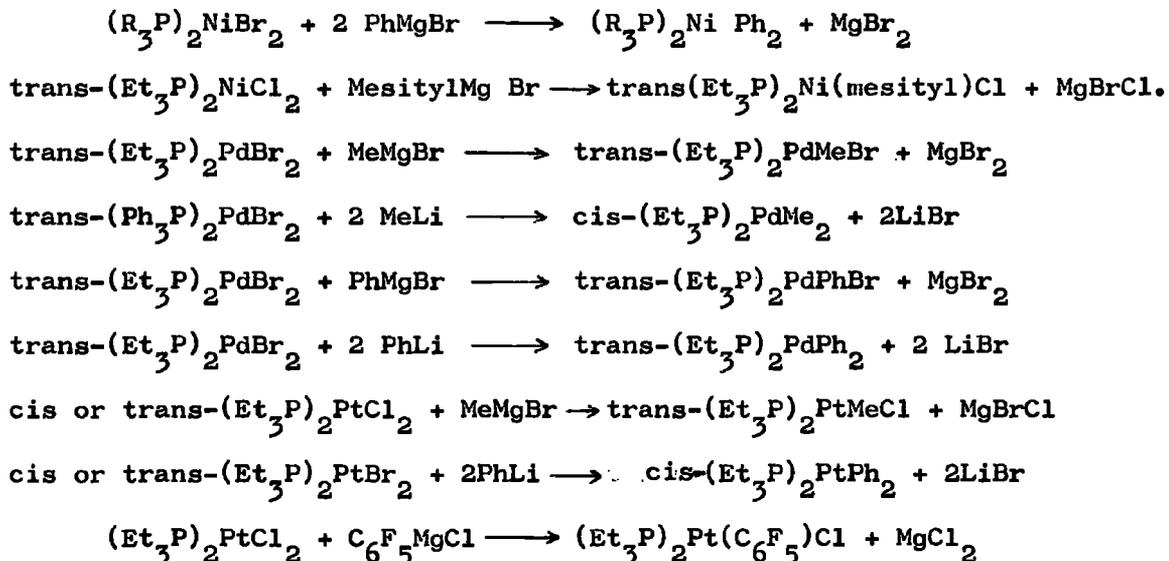
In the case of nickel(II), palladium(II) and platinum(II) complexes the relevant orbital energies are indicated in Fig. (2). If ΔE is small, electrons can be promoted from the highest energy occupied d orbital to σ^* antibonding orbitals of the metal - carbon bond. In many cases ΔE is too small for stable M-C bonds to be formed, but Chatt and Shaw (29, 37, 38) realised that coordination of the metal with π -bonding ligands increases ΔE by lowering the energy of the highest occupied orbital (d_{xy}).

Organic derivatives of nickel, palladium and platinum have been prepared which have π -bonding ligands such as tertiary phosphines and arsines, carbon monoxide, π -cyclopentadiene, complexed with the metal. Ligand field splittings caused by these ligands generally increase as one proceeds from light to heavier transition metals in the same group. This may explain the observation that stability of σ -bonded organic derivatives increases in the series nickel - palladium - platinum.

2,2. Preparations (a) Grignard and Organo-lithium reagents

The method of preparation most frequently encountered is the reaction between metal dihalide complexes and Grignard

or organo-lithium reagents. Grignard reagents are to be preferred for the preparation of monosubstituted complexes, but the more reactive organolithium reagents gave the best yields of disubstituted derivatives. One exception is benzylmagnesium chloride which gives disubstituted derivatives where purely aliphatic Grignards give monosubstituted complexes. Examples are given below (37, 38, 39, 40, 41, 42).

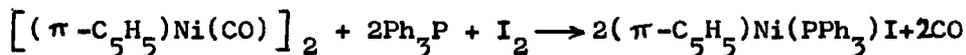


These methods of preparation were used for the preparation of mono- and dimethyls, phenyls and substituted phenyls of nickel, palladium and platinum, with the exception of nickel methyls which were probably formed but too unstable to be isolated.

Recently σ -bonded organometallic compounds of nickel stabilised by both cyclopentadiene and either tertiary phosphines, arsines or stibines have been described (43). Complex halides of the type $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)\text{Cl}$ were made either by reaction of nickelocene with bis (tertiary phosphine) nickel dihalides



or by reaction of π -cyclopentadienylnickel carbonyl dimer with triphenylphosphine and iodine.

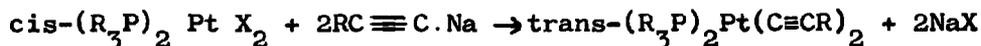


Reaction between complex halides of this type and Grignard reagents gave organonickel derivatives.

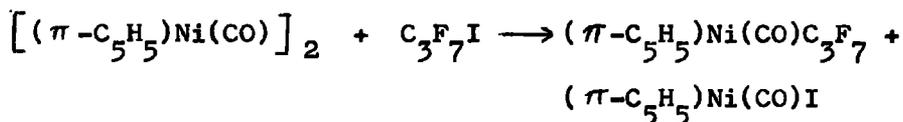


(b) Other methods of preparation

Although Grignard reagents $\text{RC}\equiv\text{C MgX}$ could be used for the preparation of diethynyl derivatives of nickel and platinum, yields were usually very low. A better method (38, 39) was the reaction between the tertiary phosphine nickel or platinum dihalide complex with the appropriate sodium acetylide in liquid ammonia.

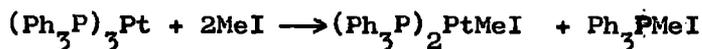


Stone and co-workers have prepared perfluoro-alkyl nickel complexes by treatment of dicyclopentadienyldinickel dicarbonyl with perfluoroalkyl iodides in benzene at room temperature (44, 45).



Triphenylphosphine reacted with $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}(\text{CO})\text{C}_2\text{F}_5$ displacing carbon monoxide to form $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}(\text{PPh}_3)\text{C}_2\text{F}_5$.

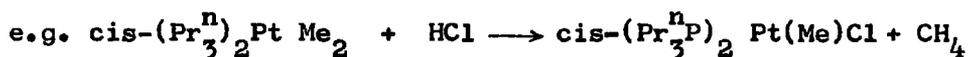
The monomethylplatinum derivative, $\text{trans}-(\text{Ph}_3\text{P})_2\text{PtMeI}$ can be prepared most conveniently by the addition of methyl iodide to tris(triphenylphosphine)platinum(0) (37, 38).



The ethyl complex, $\text{trans}-(\text{Et}_3\text{P})_2\text{Pt}(\text{Et})\text{Cl}$ has been made by reaction of bis(triethylphosphine)platinum hydrido-chloride with ethylene at $95^\circ/40\text{ atm.}$ (29).

As mentioned previously, the reaction between cis platinum dihalide complexes and 2 moles of Grignard or organo-lithium reagent usually gives the disubstituted derivative of cis configuration, whereas equimolar mixtures give the trans mono-substituted derivative.

Organoplatinum halides of cis configuration have been prepared by cleavage of one Pt-C bond with dry halogen acid (1 mol.), but the reaction is difficult to control.



Trans-dimethyl derivatives are difficult to obtain, but on a small scale this can be done by vacuum distillation of the cis form followed by chromatography of the distillate on alumina.

Benzyl complexes of these configurations, trans-(Et₃P)₂Pt(CH₂Ph)Cl and cis-(Et₃P)₂Pt(CH₂Ph)₂ are more easily formed but are more reactive.

A new type of organoplatinum carbonyl compound was described recently (46). Lithium tetrachloroplatinite warmed with 1-octene and formic acid in dimethyl-formamide gave the product (C₈H₁₇)Pt(CO)Cl. The infrared spectrum showed no sign of unsaturated C=C stretch in the 1500-1600 cm⁻¹ region, but an intense CO stretching band was observed at 2060cm⁻¹. This complex reacted with triphenylphosphine giving (C₈H₁₇CO)Pt-(PPh₃)₂Cl in which the carbonyl stretching frequency had disappeared and was replaced by an acyl C=O band at 1639 cm⁻¹.

2,3. Properties

(a) Infrared Spectra

The far infrared spectra of methyl-palladium complexes have been examined (40) and bands in the range 435 to 534 cm^{-1} were assigned to Pd-C stretching vibrations. One absorption was observed in the spectra of monomethyl derivatives, and two in dimethyls. The Pt-C stretching frequencies of platinum alkyls have been observed in the region 500 - 600 cm^{-1} . (47, 48). A comparison of analogous platinum and palladium compounds is interesting. The M-C stretching frequencies of $(\text{Et}_3\text{P})_2\text{PdMe}_2$ (457 and 491 cm^{-1}) are lower than those in $(\text{Et}_3\text{P})_2\text{PtMe}_2$ (506 and 523 cm^{-1}). If the methyl group is regarded as an atom of atomic weight 15 , the force constants of the M-C bonds may be calculated. These indicate that the palladium-carbon bond is considerably weaker than the platinum-carbon bond, which is in agreement with the chemical evidence. The low value of $\nu(\text{Pt-X})$ observed in monosubstituted derivatives indicates that the alkyl and aryl groups have high trans effects, as noted previously (31).

The metal-phosphorus stretching frequencies of some complexes $(\text{Et}_3\text{P})_2\text{M RX}$ and $(\text{Et}_3\text{P})_2\text{M R}_2$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$; $\text{R} = \text{Me}, \text{Ph}, \text{C}_6\text{F}_5$) have been observed (49, 50) in the far infrared region 410 - 440 cm^{-1} .

and they have been used to determine the stereochemistry. Trans complexes have only one Pt-P absorption, whereas cis isomers have two infrared active vibrations. By this means the stereochemistry of the first cis-bis(triethylphosphine)-palladium(II) complex, $(\text{Et}_3\text{P})_2\text{Pd}(\text{C}_6\text{F}_5)_2$ has been identified.

(b) Dipole Moments

Dipole Moments of organopalladium and organoplatinum complexes have been measured in order to elucidate the stereochemistry. A cis complex $(\text{R}'_3\text{P})_2\text{PdR}_2$ should have a high dipole moment whereas that of the trans isomer should be zero.

Methyl derivatives.

Freshly prepared palladium and platinum dimethyls have high dipole moments (37, 40) and therefore cis configuration, e.g. $(\text{Et}_3\text{P})_2\text{PdMe}_2$ (m.p. 46-47°) 4.68D, $(\text{Et}_3\text{P})_2\text{PtMe}_2$, 5.65D. On standing for six months under nitrogen the dipole moment and melting point of the palladium complex changed to 1.4D, (m.p. 66-67°) indicating that isomerisation to the trans form was taking place. The trans form of the platinum complex was difficult to obtain. Monomethyl derivatives of palladium and platinum prepared by the Grignard method have trans configuration with the low dipole moments, e.g. trans- $(\text{Et}_3\text{P})_2\text{PtMeCl}$, 3.4D. The cis isomer of this complex has moment 8.4D.

Aryl derivatives

All non-fluorinated aryl palladium complexes had the trans structures of the original dihalides (40) but cis and trans forms of $(Et_3P)_2PtPh_2$ and $(Et_3P)_2Pt(Ph)Cl$ have been obtained (38). Cis diarylpalladium complexes were very unstable and attempts to prepare them were unsuccessful. It has been shown (51) that the stereochemistry of non-chelate tertiaryphosphinepalladium dihalide complexes depends on the balance of an electrostatic factor favouring trans and a π -bonding factor favouring cis complexes. In addition, ring to ring conjugation through appropriate metal d orbitals could stabilise the trans isomers of aryl complexes (40).

Chelate Complexes

As would be expected, complexes with chelating ligands have necessarily cis configuration, e.g. $(MeSCH_2CH_2SMe)PdMe_2$ has dipole moment 6.4D. However, the magnitude of the dipole moments of the chelate platinum complexes $(Et_2PCH_2CH_2PEt_2)PtPh_2$ and the dimethyl analogue is a matter of some interest. They are both about 1.2 D greater than the corresponding non-chelate complexes, e.g. cis $(Et_3P)_2PtPh_2$ which has moment 7.2 D. Chatt and Shaw (38) suggest that complexes involving the strongly dipolar $Pt^- - P^+$ bonds are very sensitive to changes in the angle

between these bonds and that a smaller P-Pt-P bond angle in chelate complexes is responsible for the increase in dipole moment.

Direction of the Dipole Moment

Comparison of the moments of phenyl and tolyl complexes enables the direction of the dipole moments of organoplatinum complexes to be deduced. The organic groups are at the negative end of the dipole in complexes $\text{cis}-(\text{R}'_3\text{P})_2\text{PtR}_2$. The $\text{Ph}^- - \text{CH}_3^+$ moment opposes the molecular moment in the complex $\text{cis}-(\text{Et}_3\text{P})_2\text{Pt}(\text{p-tolyl})_2$ and the moment is less (6.75D) than that of the diphenyl analogue (7.2D). When the $\text{Ph}^- - \text{CH}_3^+$ moment reinforces the molecular moment as in $\text{cis}-(\text{Et}_3\text{P})_2\text{Pt}(\text{o-tolyl})_2$, the molecular moment is increased (7.5D). By similar reasoning it can be shown that the dipole moments of monosubstituted complexes $\text{trans}-(\text{R}'_3\text{P})_2\text{PtRX}$ are oriented such that the organic group is at the positive end of the dipole and that the Pt-P moment is polarized in the direction $\text{Pt}^- - \text{P}^+$.

The dipole moments of methylplatinumhalide complexes, $\text{trans}-(\text{R}'_3\text{P})_2\text{PtRX}$ show an increasing moment along the series $\text{Cl} < \text{Br} < \text{I}$, which is the reverse order to that found in carbon-halogen compounds. Parshall and co-workers (22, 23, 24) have found

that bromine and iodine are weak π -electron acceptors whereas chlorine acts as a π -electron donor in complexes of this type. Hence, if the electron drift from the metal to halogen increases in the series $\text{Cl} < \text{Br} < \text{I}$, this could reverse the order of decreasing electronegativity and explain the paradox. Another explanation is that the heavier halogen atoms could distort the phosphorus atoms away from the halogen. This would cause the strongly dipolar Pt-P bonds to make a contribution to the dipole moment in the direction $\overset{+}{\text{R}} - \text{Pt} - \overset{-}{\text{X}}$.

2,4. Stability relationships

Ligand field splittings caused by tertiary phosphines, for example, decrease as one proceeds from heavy to light transition metals in the same group. Organic derivatives of platinum are nearly all very stable thermally, so useful conclusions about stabilisation by different ligands are best drawn from a study of nickel and palladium complexes.

Effect of Organic Group

The stability of nickel complexes $(\text{R}'_3\text{P})_2\text{NiRX}$ and $(\text{R}'_3\text{P})_2\text{NiR}_2$ were found to increase in the order $\text{R} = \text{alkyl} < \text{phenyl} \sim \text{m- and p- substituted phenyl} < \text{ethynyl and phenylethynyl} < \text{o- substituted phenyl}$.

Palladium compounds differed in that the most stable compounds were methyls, phenylethynyl and aryls having an electron attracting substituent, the position of which was immaterial.

Ethynyls

The stability of ethynyl derivatives is due to overlap between the appropriate metal d orbitals and antibonding orbitals of the ethynyl groups, causing a drift of electrons from the metal in a similar manner to π -bonding ligands such as carbon monoxide.

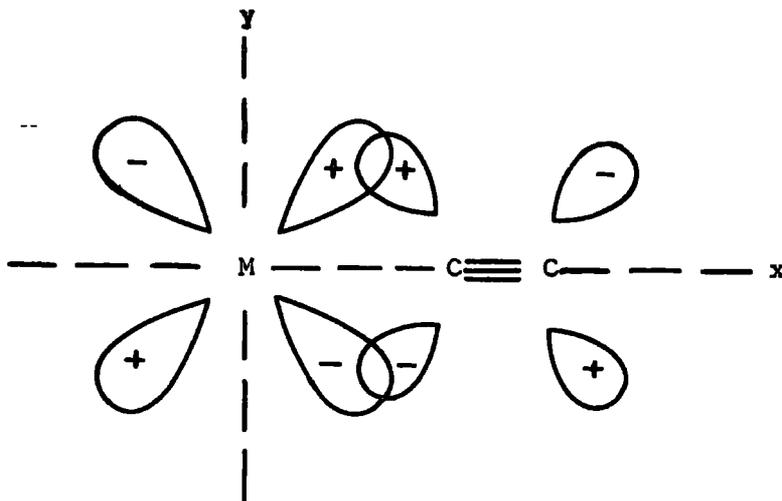


Fig.4. Overlap of metal d_{xy} orbitals with ethynyl π_g^* antibonding orbital

The ethynyl group has two unoccupied π_g^* antibonding orbitals which can overlap with the metal d orbitals. One is shown in Fig.4 and the other, which can overlap with the metal d_{xz} orbital, is in the xz plane and situated similarly with respect to the

C \equiv C axis. The energy of these metal orbitals is thereby reduced and stability is imparted to the complex by an increase of ΔE (Fig.3, section 2,1.)

Aryls

Although stable platinum phenyl complexes are relatively easy to prepare, simple phenyls of nickel and palladium could not be purified.

Stability is imparted to aryl palladium complexes if the aryl group is substituted by electron attracting groups. This is illustrated by the fact that the p-dimethylaminophenyl derivative $(Et_3P)_2Pd(p-C_6H_4NMe_2)_2$ was so unstable as to be difficult to purify. The dimethiodide, $[(Et_3P)_2Pd(p-C_6H_4NMe_3)_2]I_2$, in which electron attracting substituents replace electron releasing groups, was much more stable.

Steric effects were more important for the stabilisation of nickel complexes than were electronic effects. If the phenyl ring was substituted in the meta or para position, e.g. $trans-(Et_3P)_2Ni(m-tolyl)Br$, the product had much the same low thermal stability as the unsubstituted phenyl derivative. When the phenyl ring had large substituents in the ortho position, however, the complex was considerably more stable and the mesityl derivative, $trans-(Et_3P)_2Ni(mesityl)Cl$ which has two

ortho substituents in the ring, was extremely stable.

Phenyl groups have available π^* antibonding orbitals which can interact with the metal d orbitals and remove electron density from the metal. If the phenyl group, in the x direction say, rotates about the metal-carbon bond, the lowest energy unoccupied π^* antibonding orbital overlaps with the d_{yz} or the critical d_{xy} orbitals, depending on the plane of the phenyl ring relative to the plane of the complex. The effect of such a rotation of the plane of the ring about the metal-carbon bond will now be considered. When the plane of the ring is normal to the xy plane of the complex (Fig.5.)

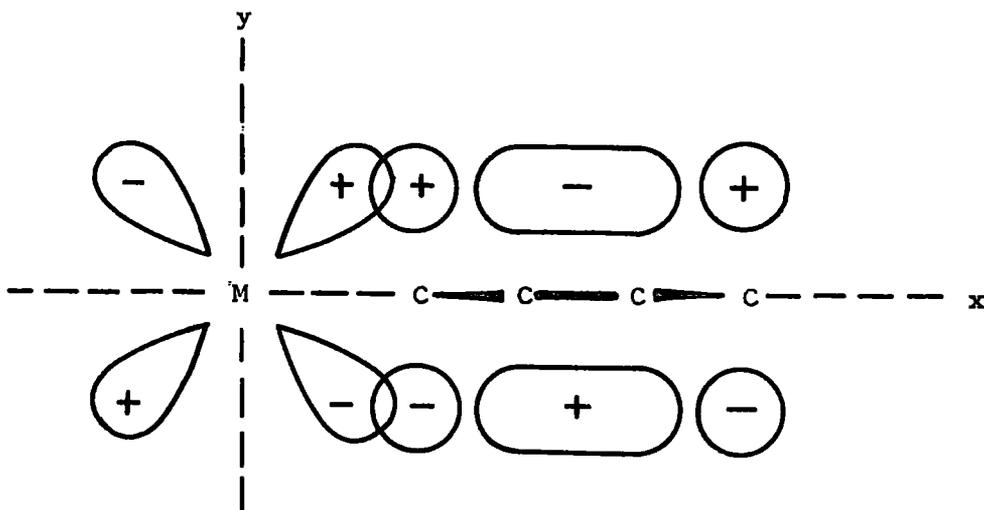


Fig.5. Diagram showing overlap between metal d_{xy} orbital and the π^* component of the metal bonded carbon atom.

the critical d_{xy} orbital energy is lowered and ΔE is raised (Fig.3.)

If the ring is in the plane of the complex the d_{xz} orbital can overlap with the aromatic π^* orbital, the energy of the d_{xy} orbital rises and ΔE is lowered so the complex will decompose most readily at this point. The average of free rotation of the phenyl ring is therefore a small increase in ΔE and a small stabilisation of phenyl complexes for this reason. In addition, the π -bonding introduced between the metal and metal-bonded carbon atom increases the M-C bond strength.

The extra stability of ortho substituted phenyl derivatives may be due to steric effects. Ortho substituents interfere with the coordinated tertiary phosphine ligands and in order to minimise these repulsions the phenyls become fixed in the xz plane. This configuration confers maximum stability by reducing the energy of the important d_{xy} orbital.

Fluorinated organic derivatives of nickel and palladium e.g. $(Et_3P)_2Ni(C_6F_5)Cl$, $(Et_3P)_2Pt(C_6F_5)_2$ prepared by Stone and co-workers were generally more stable than unsubstituted derivatives. (49, 52).

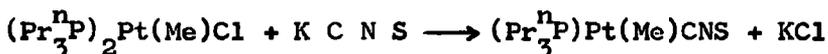
The complex $(bipy)PdMe_2$ showed extraordinary stability; no decomposition was apparent after six months at room temperature (40).

2,5. Chemical Reactions

Reactions of organic derivatives of nickel, palladium and platinum are usually of two types, cleavage of the organic groups and metathetical replacement of halogens in complexes of type $(R_3P)_2 M R X$.

(a) Metathesis

The halogen ligands of monosubstituted derivatives can be replaced on treatment with alkali-metal halides and pseudohalides in acetone solution, e.g.:



(b) Reactions with halogen acids

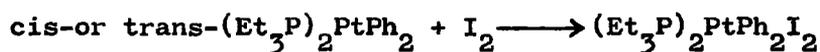
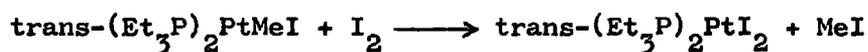
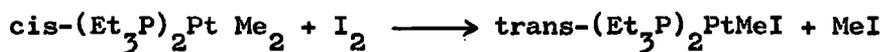
Dry ethereal hydrogen chloride cleaves the metal-carbon bonds. This has already been mentioned as a method of preparation of cis-monosubstituted platinum complexes (37) e.g.



The perfluoroarylcomplex $\text{cis-}(Et_3P)_2 Pt(C_6F_5)_2$ does not react with hydrogen chloride under the conditions which cause cleavage of non-fluorinated phenyl groups (49).

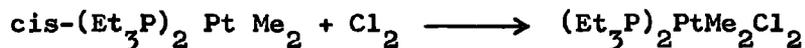
(c) Reactions with halogens

Organoplatinum compounds react with halogens and the products were dependent on the compounds involved. The possibilities were cleavage of the platinum-carbon bonds and oxidative addition giving an octahedral platinum(IV) complex. Iodine can react either way, depending on the organic groups involved. Methyls are cleaved but phenyls give octahedral complexes (38).



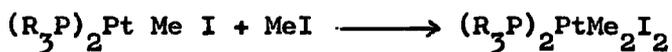
The analogous reaction between iodine and pentafluorophenyl platinum derivatives, e.g. $\text{cis}-(\text{Et}_3\text{P})_2\text{Pt}(\text{C}_6\text{F}_5)_2$ did not take place (48).

Chlorine reacts by oxidative addition to both dimethyl- and diphenyl-platinum complexes.



(d) Reactions with Organic Halides

Methyl iodide oxidatively adds to the monomethyl derivatives at 100° giving platinum(IV) compounds.



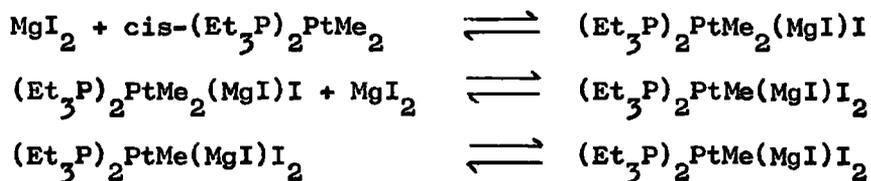
(R = Et, Prⁿ). The methyl iodide is loosely held and can be removed by pumping for 3 hours at 80°/10⁻² mm. That the methyl iodide is not held as solvent of crystallisation was shown by the fact that the adduct was not obtained at the boiling point of methyl iodide, except in very poor yield. The adduct loses ethane when heated to 100° for 20 hours.



The dimethyl complex, (Et₃P)₂PtMe₂ reacted with methyl iodide to give a mixture of products which could not be separated.

(e) Reactions with Magnesium Iodide

Magnesium iodide reacts with disubstituted derivatives of platinum in a manner which indicates that the Grignard method of preparation of organoplatinum compounds involves equilibria (37). A precipitate was formed immediately when magnesium iodide and the dimethyl, cis-(Et₃P)₂PtMe₂ were mixed. This suggested that an intermediate platinum (IV) complex was involved, since the starting materials and products, trans-(Et₃P)₂PtI₂, trans-(Et₃P)₂Pt MeI and MeMgI were all soluble in ether.



(f) Reaction with Carbon Monoxide

Organoplatinum compounds of type $(\text{Et}_3\text{P})_2\text{PtRX}$ ($\text{R}=\text{Me}, \text{Ph}$; $\text{X} = \text{halogen}$) react with carbon monoxide at $95^\circ/50$ to 100 atm . (53). The products are colourless or pale yellow acyl derivatives, $(\text{Et}_3\text{P})_2\text{Pt}(\text{COR})\text{X}$ having in the infrared spectrum a strong band between $1600\text{-}1700 \text{ cm}^{-1}$, $\nu(\text{C}=\text{O})$. Metathetical replacement of the halogen by other anions readily takes place.

Chapter 3. Olefin , Acetylene and π -Allyl Complexes

In addition to the σ -bonded organometallic complexes described previously, some transition metals, especially nickel, palladium and platinum form complexes with olefins, acetylenes and allylic ligands in which π -bonds are of great importance. These will be dealt with very briefly here, since they have been described in detail in two reviews (54,55).

3.1. Olefin Complexes

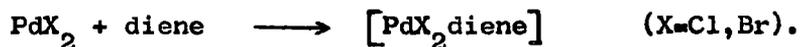
(a) Preparations

Olefins react with bis(benzonitrile)palladium dichloride (56) or with palladium dichloride in 50% acetic acid at room temperature (57) giving complexes $[\text{PdCl}_2 \text{un}]_2$ where un = olefin.



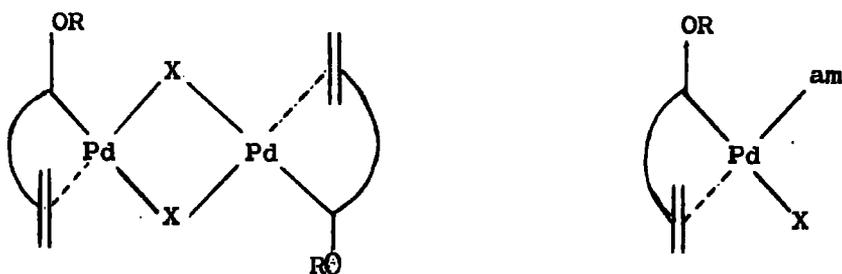
Complexes having cyclohexene, styrene, ethylene and isobutene ligands have been made and their stabilities decreased in this order.

Chelating diolefins e.g. hexa-1,5-diene (58), cycloocta-1,5-diene and dicyclopentadiene (59) gave far more stable complexes than the mono-olefins described above.



They can be converted by alcohols in presence of anhydrous

sodium carbonate into complexes $[\text{PdX}(\text{diene OR})]_2$ and the halogen bridge can be split by amines giving $[\text{Pd X}(\text{diene OR})\text{-amine}]$. The structures of these are represented below. (60).



Platinum - olefin complexes are generally more stable and less reactive than the palladium analogues. In addition to mono - olefin complexes of the type described, platinum also forms stable complexes of types $[\text{Pt X}_3\text{un}]^-$, trans- $[\text{PtX}_2\text{un}_2]$ and cis- and trans- $[\text{PtX}_2(\text{am})(\text{un})]$ where X = halogen, am = amine and un = olefin.

Nickel olefin complexes are few and unimportant.

(b) Structure.

The structure of platinum - olefin complexes is exemplified by that of Zeise's anion $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ (61).

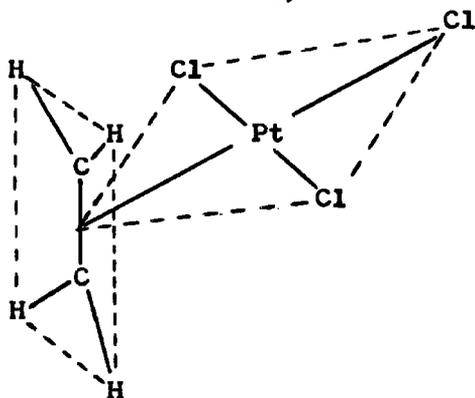


Fig. 6. Structure of Zeise's anion

The square plane of the complex is formed by the three chlorine atoms and the mid point of the C-C bond. Ethylene is situated with the C-C axis perpendicular to the plane of the complex. The hydrogen atoms lie in one plane which is displaced from the C-C axis, away from the platinum atom.

(c) Bonding

The bonding in transition metal - olefin complexes is believed to involve two parts in which the metal forms σ and π -type bonds with the olefin π_{2p} bonding and the π^*_{2p} antibonding orbitals respectively.

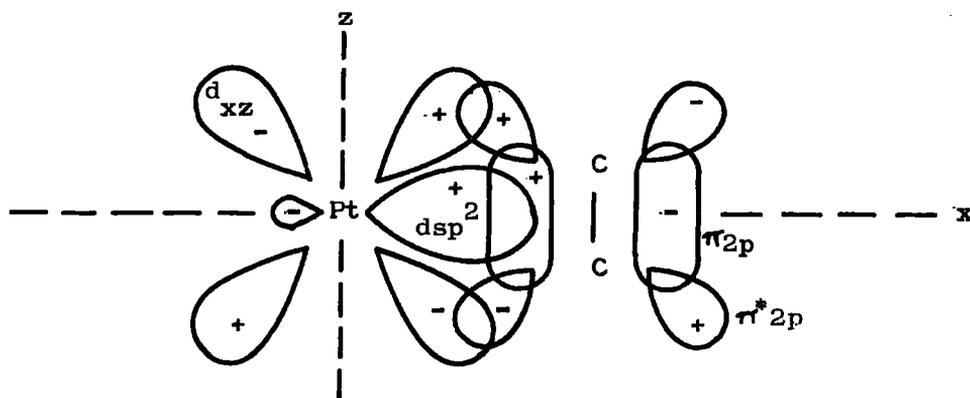


Fig.7. Bonding in platinum-olefin complexes

In the case of platinum the σ -bond is formed between the metal d_{sp^2} orbital and the olefin $\pi 2p_u$ orbital. This is described as a μ bond. A π -type 'back bond' is formed between the platinum $5d_{xz}$ orbital (which may have some 6p hybrid character) with the ethylene $\pi^* 2p_g$ orbital. The infrared spectra of platinum olefin complexes show that the olefinic double bond is retained intact, if of somewhat reduced order. This is indicated by a reduction in the C=C stretching frequency (61).

3.2. Acetylene Complexes

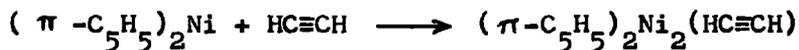
Nickel, palladium and platinum form acetylene complexes in which the acetylene structure is retained.

Preparations

Acetylene and substituted acetylenes (1 mol.) will displace 2 carbonyl groups from di- π -cyclopentadienyl-dinickel dicarbonyl giving the corresponding acetylene complex (62).

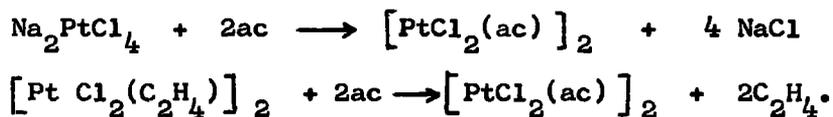


The unsubstituted complex has also been made from acetylene and nickelocene (63).



Acetylenes (ac) of the type $Bu^t-C\equiv CR$ (R=Me, Et, Pr^i , Bu^t) react

with PtCl_4^{2-} or displace ethylene from olefin complexes as follows: (64)

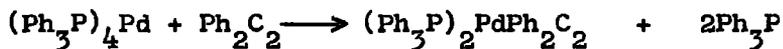


A different type of acetylene complex, $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{ac})]$ was obtained by reduction of an alcoholic suspension of cis- $(\text{Ph}_3\text{P})_2\text{PtCl}_2$ with hydrazine hydrate in presence of an acetylene (65).



Acetylenes will displace one another from complexes of this type in the following series: $\text{C}_2\text{H}_2 < \text{alk C}\equiv\text{CH} < \text{C}_2\text{alk}_2 \sim \text{Ph C}\equiv\text{CH} \sim \text{C}_2\text{Ph}_2$.

The analogous palladium complex with diphenyl-acetylene, $(\text{Ph}_3\text{P})_2\text{PdPh}_2\text{C}_2$ has recently been prepared from $(\text{Ph}_3\text{P})_4\text{Pd}$ and $\text{PhC}\equiv\text{CPh}$ (66).



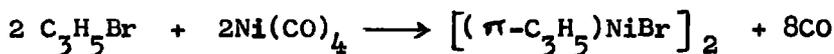
3,3. π -Allyl Complexes

π -Allyl complexes of all three metals, nickel, palladium and platinum are known (55). They are distinguished by the type of bonding from allyl complexes exemplified by allylmagnesium bromide, which have a purely σ -type metal - carbon bond. The bonding in π -allyl complexes is analogous to that in olefin

complexes in so far as the allyl group donates π electrons to the metal in a σ -bond and accepts electrons from the metal d orbitals into a π^* antibonding orbital.

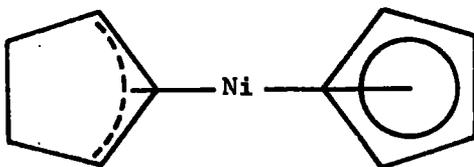
(a) Preparations

Nickel tetracarbonyl reacts with allyl bromide giving the violet complex, $[(\pi\text{-C}_3\text{H}_5)\text{NiBr}]_2$ (67).



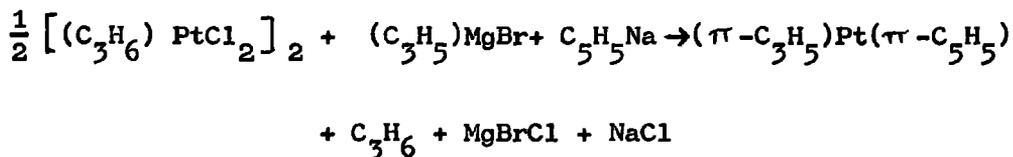
Cyclopentadiene reacts with nickel tetracarbonyl giving a red compound of empirical formula $\text{C}_{10}\text{H}_{12}\text{Ni}$ which was first thought to be dicyclopentadienyl-nickel(0), $\text{Ni}(\text{C}_5\text{H}_6)_2$ (68).

Proton magnetic resonance, which has been extremely useful in the investigation of π -allyl complexes, has shown that this complex is a π -allyl- π -cyclopentadienylnickel(II) (69).



This compound can also be made by treatment of nickel dibromide successively with cyclopentadienylsodium and cyclopentenylmagnesium chloride (70).

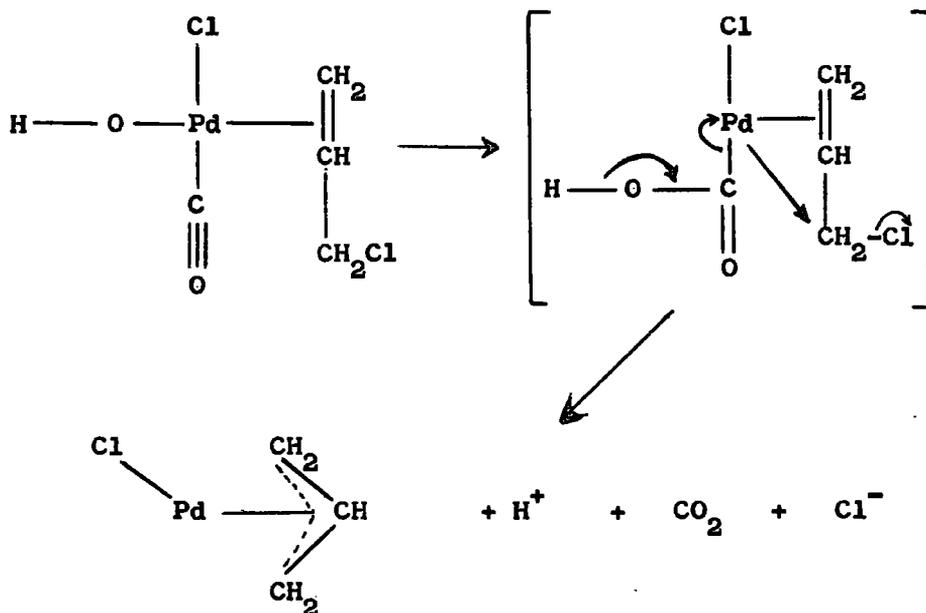
Palladium forms the largest number of π -allyl complexes of any metal and some of these will be described shortly. Platinum, in contrast, forms relatively few π -allyls. Treatment of propyleneplatinous chloride with allylmagnesium bromide (1 mol.) and cyclopentadienylsodium (1 mol.) gives π -allyl- π -cyclopentadienylplatinum(II) as yellow crystals (71).



π -Allyl palladium compounds are usually halogen-bridged dimers of the type $[\text{Pd Cl}(\text{all})]_2$ where 'all' represents the allylic ligand. By far the best and most versatile preparation is that described by Dent, Long and Wilkinson (72). The method involves the passage of carbon monoxide at atmospheric pressure through methanol solutions of allylic chlorides containing sodium chloropalladite. Water is involved in the mechanism since dry sodium chloropalladite gave only 20% yield of the allylpalladium chloride, whereas commercial material (usually the dihydrate) gave yields greater than 80%. Allyl chloride, methallyl chloride and 3-chloro-1-butene gave respectively allyl, methallyl and crotyl-palladium chloride complexes.

The mechanism of this reaction has been investigated (73) and it was found that one molecule of carbon monoxide per palladium

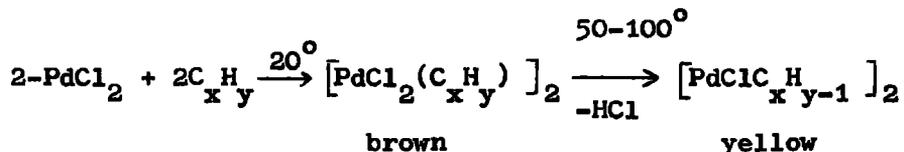
atom is oxidised to carbon dioxide. Allyl chloride, carbon monoxide and water coordinate to the palladium atom. Since water coordinated to this type of complex is known to be fairly acidic, it is proposed that some of the first species shown below is formed, which then reacts as indicated.



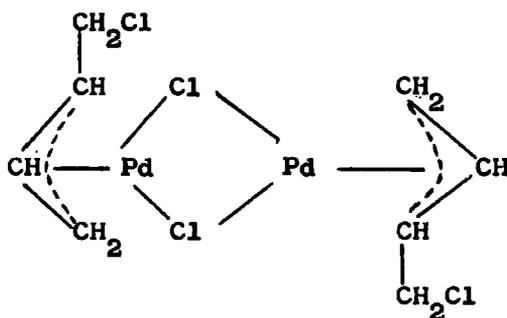
Hydroxyl migration gives the carboxylate complex which breaks down to form hydrogen chloride, carbon dioxide and π -allylpalladium chloride monomer which then dimerises.

The preparation of olefin complexes $[\text{PdCl}_2 \text{ olefin}]_2$ by reactions of olefins with palladium dichloride in 50% acetic

acid at room temperature has already been mentioned (section 3,1a). The complexes with isobutene, diisobutene, cyclohexene, 1-methylcyclohex-1-ene and α -methylstyrene lose HCl on heating to give the more stable π -allyl complexes (57).



Butadiene reacts with bis(benzonitrile)palladium dichloride giving an unstable yellow complex of empirical formula $\text{C}_4\text{H}_6\text{-PdCl}_2$ (74). The fact that the infrared spectrum did not show an isolated C=C absorption was difficult to explain and led to a controversy concerning the structure. The proton magnetic resonance spectrum of this complex has recently been interpreted in terms of a π -allyl structure (75).



(b) Reactions of π -allylpalladium complexes

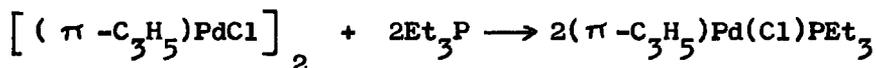
Metathesis

The bridging chlorine atoms of π -allylpalladium chloride

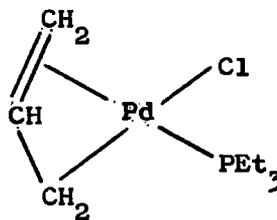
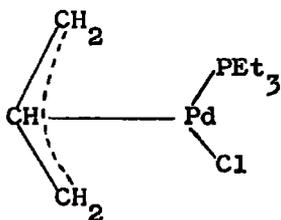
complexes can be readily replaced by heavier halogens or thiocyanate by treatment with alkali-metal salts in a suitable solvent such as acetone (76).

Bridge Splitting

An important reaction of π -allylpalladium chloride dimers is that with donor ligands, amines and trialkylphosphines. These result in splitting of the halogen bridges, and monomeric products result.

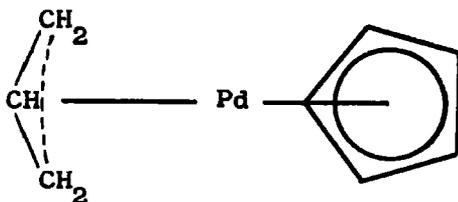


There has been speculation (77) as to whether the product is a π -allyl complex, a σ - π complex (a) or (b), or even a hybrid of the two forms:



The proton magnetic resonance spectrum and measurement of the palladium-carbon bond lengths by X-ray crystallography favour structure (b).

Treatment of π -allylpalladiumchloride with cyclopentadienyl-sodium gives π -allyl- π -cyclopentadienylpalladium(II) as dark red crystals. The n.m.r. spectrum indicates a sandwich structure in which palladium has the electronic configuration of xenon (71).



The platinum complex described on page 53 has a similar structure.

Proton Magnetic Resonance

The proton magnetic resonance spectra of π -allyl complexes show a characteristic pattern in the region 7-9 τ and this has been used widely as a diagnostic feature of the bonding in π -allyls. The usual numbering and the pattern produced by coupling is shown below:

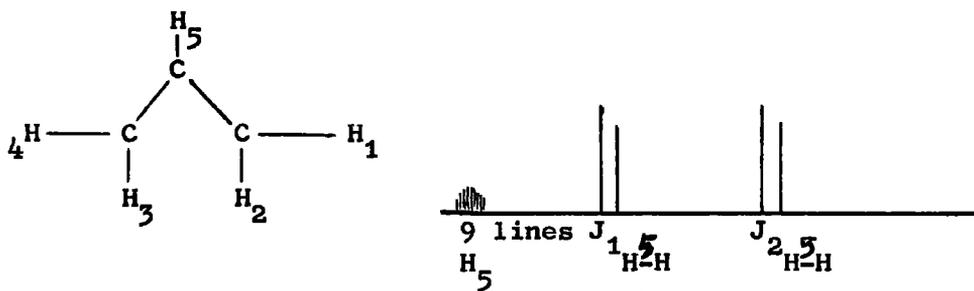


Fig.8. P.M.R. Spectra of π -allyl complexes

The protons 1 and 4 are magnetically equivalent, as are protons 2 and 3. If, however, the bridge is split by a donor ligand and the complex becomes a σ - π type, the spectrum changes. Chlorine is a relatively weak σ -donor, therefore the carbon atom trans to it is bonded more strongly to the metal.

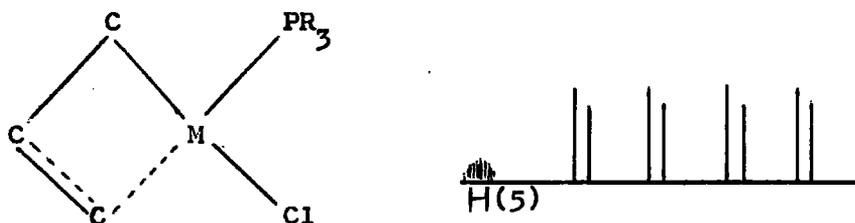


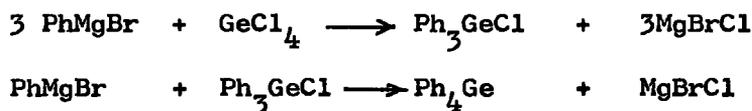
Fig.9. P.M.R. spectrum of ' σ - π ' metal tertiaryphosphine complexes

Each allyl proton becomes unique and the spectrum is shown in Fig.9.

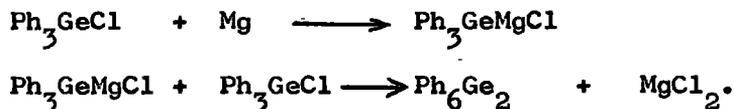
Chapter 4. Summary of the chemistry of germanium.

4,1. Organogermanes

Germanium tetrachloride reacts with Grignard reagents with the formation of Ge-C bonds (78). The reactions are difficult to stop at intermediate stages giving alkyl or aryl germanium halides. These can be prepared by other methods, but the Grignard method is good for the preparation of fully substituted derivatives. Various side reactions take place, illustrated in one case (79) by the reaction of GeCl_4 with phenylmagnesium bromide. Tetraphenyl germane is obtained if the Grignard reagent is filtered, or hexaphenyldigermane together with tetraphenylgermane if the reaction takes place in presence of excess magnesium. The formation of hexaphenyldigermane probably involves the formation of organogermeryl Grignard reagents:-



With free magnesium:-



4,2. Organogermanium halides

Tetraphenylgermane reacts with bromine giving first Ph_3GeBr and then Ph_2GeBr_2 , whereas tetraethylgermane reacts with excess bromine giving only Et_3GeBr . Redistributions of tetra-alkyl or -aryl germanes with germanium tetrachloride give any of three organogermanium halides, RGeCl_3 , R_2GeCl_2 or RGeCl_3 , depending on the stoichiometry.

Organogermanium halides are not so sensitive to hydrolysis as are organosilicon halides. Alkylgermanium halides are less stable in this respect than aryl compounds.

4,3. Germanium Hydrides

Germane itself, GeH_4 , is conveniently prepared in up to 75% yield by reducing GeO_2 with sodium borohydride in acid solution (80). The product is carried from the reaction vessel in a stream of nitrogen and trapped at -196° . Fractional condensation under high vacuum removes water and higher germanes. Germane can also be made by reduction of GeCl_4 with lithium aluminium hydride in ethereal solvents but the yield is much lower, 28% (81).

Organogermanium hydrides are most easily prepared from organogermanium halides, R_3GeX , R_2GeX_2 and RGeX_3 and lithium

aluminium hydride. They are also obtained by hydrolysis of the organogermyl Grignard reagents mentioned previously, and the organogermanium-alkali metal compounds mentioned below. The hydrides are stable in air for short periods and moderately thermally stable in the absence of oxygen.

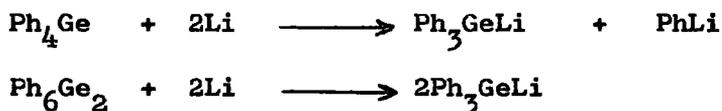
4,4. Germanium-alkali metal compounds

Germane reacts with sodium in liquid ammonia giving a yellow-green precipitate of germylene disodium (82). Germane is further taken up until the precipitate becomes grey when equimolar amounts of germane and sodium have reacted. The grey precipitate is solvated GeH_3Na .

Germane also reacts with lithium in liquid ammonia (83). When the solution is decolorised the excess ammonia can be removed leaving a grey solid having constitution $\text{GeH}_3\text{Li} \cdot 2\text{NH}_3$. On warming to room temperature the ammonia is evolved and a melt is formed over a solid phase. The solid decomposes on standing at 20° or on heating to 250° .

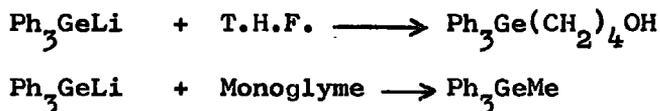
The reaction between potassium amide and germane in liquid ammonia has also been used to prepare germyl-~~lithium~~^{potassium} (84). The product reacted with bromobenzene giving benzene, GeH_2 and ~~sodium~~^{potassium} bromide.

Organogermanium-alkali metal compounds, e.g. Ph_3GeNa , Me_3GeLi can be prepared by cleavage of Ge-C or Ge-Ge bonds using solutions of the alkali metal in ammonia or an amine. The reactivity of the solvents limited the use of these reagents but recently their versatility was greatly extended by the introduction of ethereal solvents such as tetrahydrofuran (T.H.F.) and ethylene glycol dimethyl ether (Monoglyme) (85, 86).

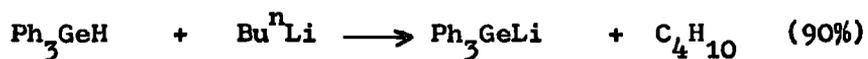


Phenyl-lithium formed in the first example usually reacts quickly with the solvent so the second method of the two is preferred.

The cleavage of hexaphenyldigermene by lithium gives a brown solution containing triphenylgermyl-lithium. It has never been isolated in the solid state, and slowly reacts with the solvent.



An even better method of preparation is the hydrogen-metal exchange reaction which takes place between n-butyl-lithium in hexane and triphenylgermane in diethyl ether. Butane is evolved and side reactions are minimised.



The above methods in ethereal solutions are not satisfactory for the preparation of trialkylgermyl-alkali metal compounds. These have recently been made by the reaction of bis(triethylgermyl)-mercury with lithium (87).

Organogermyl-lithium compounds undergo a variety of reactions. They are hydrolysed to the hydride, R_3GeH and lithium hydroxide. Bromination gives the digermene in 80% yield. Reaction with R_3^1SiX gives $\text{R}_3\text{Ge}\cdot\text{SiR}_3^1$ and with germanium tetrachloride, $(\text{R}_3\text{Ge})_4\text{Ge}$.

Chapter 5. Metal-Metal Bonds

In the past few years there has been increasing interest in molecular compounds containing metal-metal bonds. At one time these were thought to be very rare, but it is now known that they are quite common, especially in transition elements.

5.1. Metals in the solid state show one type of metal-metal bonding. The high electrical and thermal conductivities presented problems to the authors of the several theories which have been proposed to explain the nature of the bonding. Metals do not have enough valence electrons to form covalent bonds with all the neighbours. Sodium, for instance, has body centred cubic structure and therefore each atom has 8 near neighbours, but only one valence electron. The most reasonable explanation of the bonding in metals is that the electrons are situated in multicentre orbitals and delocalisation can occur through a very large system. These electrons can be made to move under the influence of an electric field.

Transition metals form metal-metal bonded compounds of great diversity, ranging from those in which there is only weak coupling of electron spins as in, for example, cupric acetate dimer, $\text{Cu}_2(\text{OCOCH}_3)_4 \cdot 2\text{H}_2\text{O}$, to those which have an authentic

metal-metal σ -bond, e.g.



5.2. Weakly Bonded Compounds

The two main techniques used to identify cases of metal-metal bonding, whether these be weak or strong, are structure determination by X-ray crystallography and the measurement of the magnetic susceptibility. Both require care to be exercised in their interpretation.

X-ray crystallography allows the measurement of bond lengths and angles. If the distance between the metal atoms is shorter than usual in complexes of the same type, and if there are no bridging groups in the molecule, the molecule must contain a metal-metal bond. This criterion is useful even when bridging groups are present, and the degree of metal-metal interaction can sometimes be related to the bond shortening but the bond length also depends on the oxidation states of the metals and the nature of the other ligands.

Magnetic susceptibilities of complexes are easily measured and they have been used to investigate cases of metal-metal bonding. The magnetic moments are reduced compared with those of free ions of the same type, due to pairing of electron spins.

One must again proceed with caution and be sure that spin-pairing is not due to some other cause.

Examples of complexes which contain weak metal-metal bonds include acetates of copper(II), chromium(II) molybdenum(II) and rhodium(II). These show shortening of the metal-metal bond lengths and electron spin pairing but the bond energy is very low.

Halides of certain transition metals show evidence of weak metal-metal bonding. Niobium tetraiodide has a structure of infinite chains of octahedra formed by the iodine atoms. (88). The metal atoms are distorted from the centres of the octahedra, adjacent pairs of atoms moving towards each other to form the weak metal-metal bonds,

Another important class of metal-metal bonded compounds are the cluster compounds consisting of halides of niobium, tantalum, molybdenum, technetium and rhenium in low oxidation states (89). There are many examples involving widely differing structure and only two cases will be described here. The anion $\text{Re}_2\text{Cl}_8^{2-}$ has a very short Re-Re bond length (2.24Å) implying a fairly strong metal-metal bond. The chlorine atoms are situated $\frac{1}{2}$ on each metal in the eclipsed configuration along the Re-Re bond (90). The metal atoms

in the ion in $\text{Re}_3\text{Cl}_{12}^{3-}$ form a triangle and three chlorine atoms are bonded directly to each metal while the remaining chlorines each bridge 2 metal atoms. The Re-Re bond lengths indicate strong metal-metal interaction but not so strong as in $\text{Re}_2\text{Cl}_8^{2-}$ (91).

5.3. Compounds Incorporating Metal-Metal σ -Bonds

This type of compound is much more numerous and can occur with a wide variety of metals. Compounds are known having main group metal to main group metal bonds, transition metal to transition metal bonds also main group metal to transition metal bonds. These compounds are formed when the metal contains one electron less than a closed shell or sub-shell (92). Thus, in the mercurous ion the formal mercury $6s^1$ atom becomes $6s^2$ and in hexaphenyldigermane the $4s^2 4p^5$ configuration becomes $4s^2 4p^6$.

Metal-metal bonding occurs in transition metal carbonyls so that the metal achieves the $d^{10} s^2 p^6$ configuration of the next noble gas. Chromium, iron and nickel achieve this configuration without metal-metal bonding in the compounds $\text{Cr}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$, but the intervening metals in the period achieve the krypton configuration by dimerisation in $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$.

The charge on the metal atoms also determines whether a metal-metal bond is formed, or two paramagnetic monomers. Increasing charge on the metal causes contraction of the metal d orbital containing the unpaired electron and if this is drawn away from the bonding region, stable monomers will be formed in preference to the dimer.

Other features which favour paramagnetic monomers are compounds having ligands which delocalise the unpaired electron, and steric repulsion which forces apart the two monomer units.

5,4. Main Group Metal-Main Group Metal Compounds

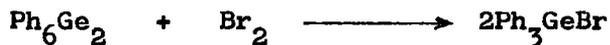
These most frequently involve the group IVb elements, silicon, germanium, tin and lead. Gilman and co-workers have prepared a range of analogues of hexaphenylethane $\text{Ph}_3\text{M}-\text{M}^1\text{Ph}_3$ (86, 93, 94, 95, 96) where M and M^1 are combinations of silicon, germanium and tin. These were prepared by reaction between an alkali-metal derivative and an organometal halide.



The distinction between the coordination number of the metal and its oxidation state must be pointed out. In hexaphenylditin for example, the tin atoms are 4-coordinate but in oxidation state + 3. The characteristic centre of reactivity of such compounds

is the metal-metal bond, but this is not invariably the case.

Halogens cleave the metal-metal bonds, as do alkali metals:



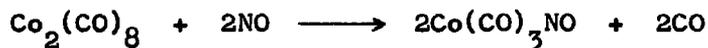
The reactivity of this bond increases as the atomic weight of the metals increases.

5,5. Transition Metal-Transition Metal Compounds

Transition metal carbonyls form one of the most important classes of compounds containing metal-metal bonds. These include the dimer obtained when metals try to achieve the inert gas configuration e.g. $\text{Mn}_2(\text{CO})_{10}$ (see section 5,3) and also polynuclear cluster compounds e.g. $\text{Co}_4(\text{CO})_{12}$. There may be bridging carbonyl groups between the metal atoms in addition to the metal-metal bonds. There are three bridging carbonyls in $\text{Fe}_2(\text{CO})_9$ for example. π -Cyclopentadienylmetal carbonyls also dimerise to achieve the closed shell configuration (cyclopentadiene as Cp^- donates 5 electrons) e.g. $[(\text{Cp})\text{Cr}(\text{CO})_3]_2$, $[(\text{Cp})\text{Fe}(\text{CO})_2]_2$ and $[(\text{Cp})\text{Ni}(\text{CO})]_2$.

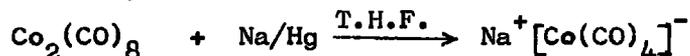
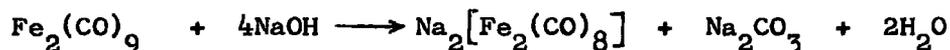
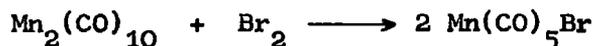
Reactions of metal-metal bonded carbonyls.

The metal-metal bond itself is the main reactive centre of these compounds. Nitric oxide acts as a 3-electron donor and can displace carbon monoxide from binuclear carbonyls (97,98):

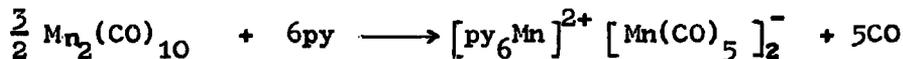


The monomeric product has closed shell configuration.

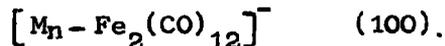
Other reactions which cleave the metal-metal bond are shown below:



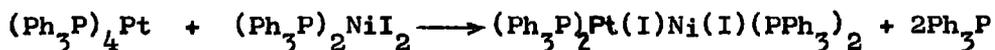
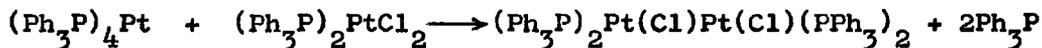
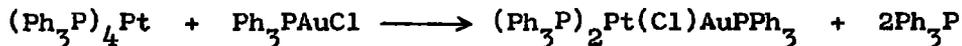
Disproportionation takes place on treatment with ammonia or pyridine:



Complexes having bonds between different transition metals are known e.g. $(\text{Cp})(\text{CO})_2\text{Fe}-\text{Mn}(\text{CO})_5$ (99) and



Nyholm and co-workers have recently reported compounds having Pt-Au, Pt-Pt and Pt-Ni bonds (101), prepared from tetrakis(triphenylphosphine)platinum (0) and metal halide complexes.

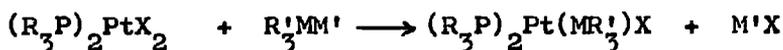


5,6. Main Group - Transition Metal Compounds

During the last 10 years or so, a wide variety of compounds of this type has been described. The main group metals are usually of group IV, and the chemistry of these compounds has in many cases been developed alongside that of σ -bonded organometallic compounds of the transition metal.

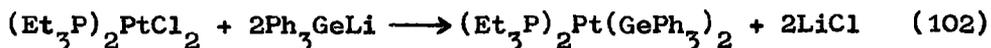
5,6.(i) Preparations

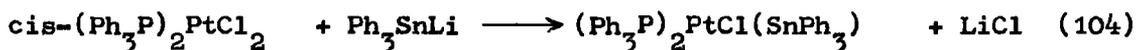
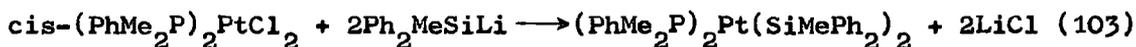
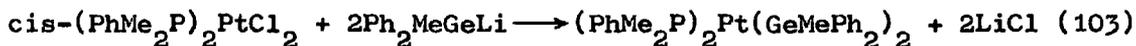
(a) One of the most versatile preparations of complexes having Pt-M bonds where M is a groupIV element is the reaction between a platinum halide complex and an alkali metal derivative of the groupIV element:



M = groupIV element; M' = alkali metal; R and R' are alkyl or aryl groups.

By this means, compounds having germanium-platinum, silicon-platinum, tin-platinum and germanium-platinum-silicon^{bonds} have been prepared. The usual method is to prepare the alkali metal derivative of the groupIV element in an ethereal solvent and then to add a solution of the platinum halide complex in ether. Examples are given below.





Copper, silver and gold-germanium complexes have also been made by this method (105).



M = Cu(I), Ag(I), Au(I); n = 1 for Au and 1 or 3 for Cu and Ag.

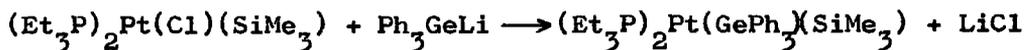
Triphenylgermyl-lithium in diglyme reacts with the complex $\text{Ph}_3\text{Ge} \cdot \text{Au PPh}_3$ giving a precipitate which, on addition of tetramethylammonium iodide, yielded $\text{Et}_4\text{N} [(\text{Ph}_3\text{Ge})_2\text{Au}]$. This remains the only known compound in which germanium is bonded to a transition element not stabilised by π -bonding ligands.

Limitations

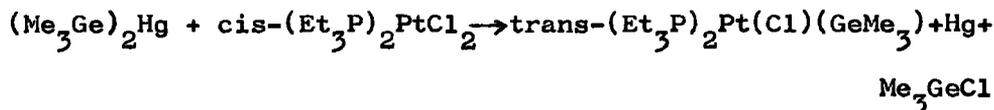
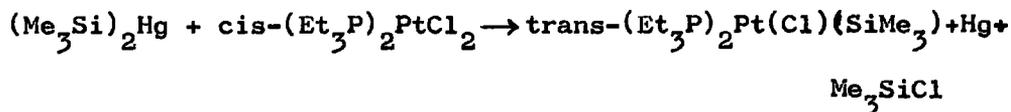
Equimolar amounts of the platinum dihalide complexes and either triphenylgermyl-lithium, diphenylmethylsilyl-lithium or diphenylmethylgermyl-lithium did not give monosubstituted derivatives. The product in each case was a mixture of the original platinum dihalide complex and the disubstituted derivative which was difficult to separate. Monosubstituted complexes can be made by cleavage of one Pt-M bond using hydrogen or hydrogen chloride.

Another restriction in this method until recently was that trialkylgermyl-lithium reagents could only be made in liquid ammonia or amine solvents which are themselves very reactive. Triethylgermyl-lithium and trimethylgermyl-lithium have now been made from lithium and bis(triethylgermyl)mercury or bis(trimethylgermyl)mercury (87). In the meantime, however, trimethylgermylplatinum complexes have been prepared by another method mentioned below.

The reaction between triphenylgermyl-lithium and a monosubstituted platinum-germanium or platinum-silicon compound can be used to obtain 'mixed metal' compounds (106)

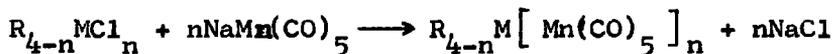
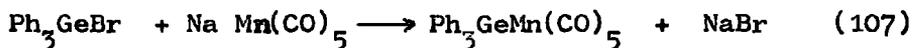


(b) A convenient method for the preparation of monosubstituted trimethylsilyl complexes is the reaction between a platinum dihalide complex and bis(trimethylsilyl)mercury (106). The trimethylgermyl analogue can be prepared in the same way.



Two moles of the mercury reagent did not substitute both chlorine atoms but gave an oil from which only a low yield of the monosubstituted complex was obtained.

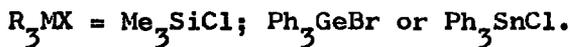
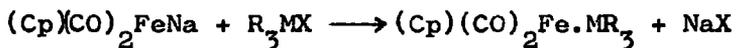
(c) Another versatile method which has similarities to (a) is the elimination of alkali metal halide from salts of transition metal carbonylate anions and a group IV metal halide.



M = Si, Sn, Pb; n = 1 or 2; R = alkyl or aryl. (108)

Oxidative stability increased in the order Si < Pb < Sn.

Silicon-, germanium- and tin-iron complexes have been prepared by similar reactions (107, 109).

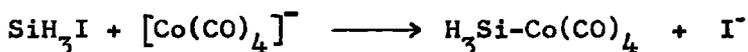


Tin-iron compounds of a different type are known. The reaction between dimethyldiphenyltin and iron pentacarbonyl gave a cluster compound, $[\text{Me}_2\text{SnFe}(\text{CO})_4]_2$ (110).

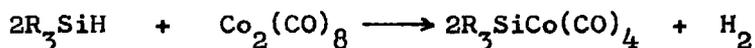
Tributyltin chloride reacts with iron pentacarbonyl giving $[\text{Bu}_2\text{Sn.Fe}(\text{CO})_4]_2$, $\text{Bu}_4\text{Sn}_3[\text{Fe}(\text{CO})_4]_4$ and $\text{Sn}[\text{Fe}(\text{CO})_4]_4$ in varying amounts depending on the temperature conditions (111).

These are also cluster compounds and the latter two have crystal structures involving SnFe_4 units.

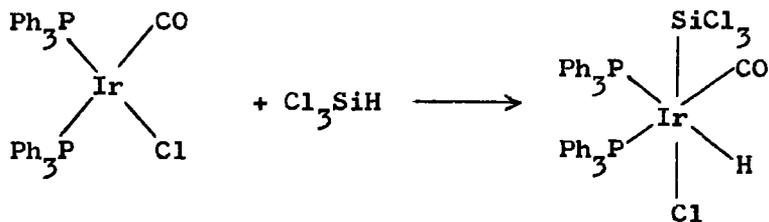
The reaction between a transition metal carbonylate ion and a metal halide has been used to obtain a new compound having hydrogen atoms attached to the group IVb element (112).



Other compounds having silicon-cobalt bonds were made from organosilicon hydrides and octacarbonyldicobalt (113).

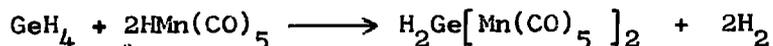


The reaction between the iridium(I) complex, $(\text{Ph}_3\text{P})_2\text{Ir}(\text{CO})\text{Cl}$ and silanes having electronegative substituents resulted in addition: (113b)



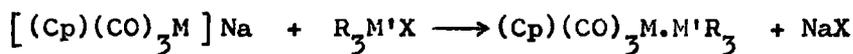
Organohalosilanes e.g. EtCl_2SiH and PhCl_2SiH behaved similarly.

The reaction of germane with manganesepentacarbonyl hydride in a sealed tube gave a compound having a bridging- GeH_2 -group (114).



Germanium(II) can expand its covalency by two, and this has been used in the synthesis of germanium-cobalt bonds. (115) Octacarbonyldicobalt reacts with GeI_2 in T.H.F. by insertion of the germanium atom between the cobalt-cobalt bond, giving red crystals of $\text{I}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$.

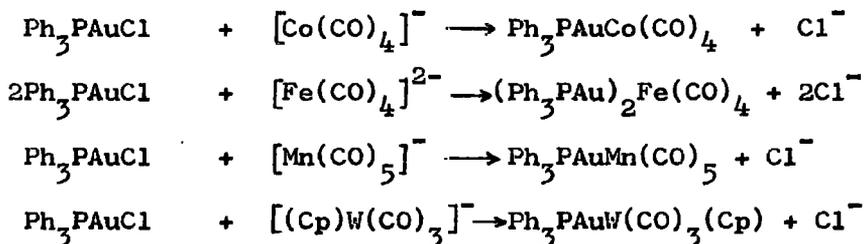
The carbonylate ion-metal halide reaction has been used to prepare metal-metal bonded compounds having bonds between groupVIa (Cr, Mo, W) and groupIVb metals (Ge, Sn, Pb) (116, 117).



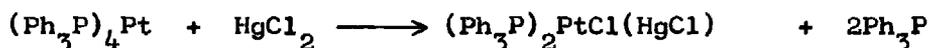
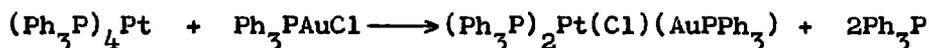
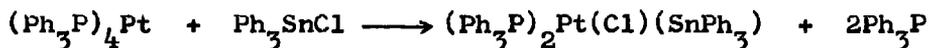
M = Cr, Mo, W; M' = Ge, Sn, Pb; R = Me, Ph.

Phenyl derivatives are more stable than methyls.

Nyholm and co-workers have used this type of reaction to synthesise gold-transition metal complexes (92). Gold can lose d electrons to form Au(III) complexes and is accordingly classed as a transition element. The reactions are similar to those above and are therefore included here.



(d) Tetrakis(triphenylphosphine)platinum(0) reacts with a variety of metal halides (101). Triphenylphosphine is displaced and metal-metal bonded compounds are formed:



These are analogous reactions to those which gave platinum-platinum and platinum-nickel bonded complexes described in section 5,5.

(e) Platinum hydridohalide complexes react with triphenyltin nitrate and triphenyllead nitrate as follows: (104).



Platinum-tin complexes

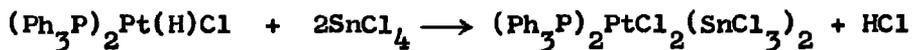
Such a wide variety of platinum-tin complexes containing SnCl_3^- ligands is known that these compounds can be regarded as a class of their own. The stability is greatly increased when the tin atom is bonded to three chlorine atoms as opposed to organic groups such as phenyl.

Trans-bis(triethylphosphine)platinum hydridochloride reacts with stannous chloride dihydrate in methanol (23).

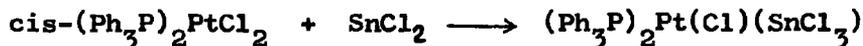


The infrared spectrum of $(Et_3P)_2Pt(H)SnCl_3$ showed $\nu(Pt-H)$ at $2105cm^{-1}$ and the low value indicates that $SnCl_3^-$ is a ligand of fairly high trans effect, intermediate between thiocyanate and cyanide (30). The proton magnetic resonance showed coupling of the CH_3 protons of the ethyl groups with the two phosphorus nuclei as well as with the CH_2 protons (23). This resulted in the appearance of a five-line pattern which partially collapsed into a 1:2:1 triplet by irradiation with the methylene signal, confirming the trans configuration of the complex.

An octahedral platinum(IV) complex has been isolated from a reaction between trans-bis(triphenylphosphine)platinum dichloride and stannic chloride (104).



The addition of triphenylphosphine in ethanol to a solution of potassium tetrachloroplatinite and stannous chloride in HCl gave $(Ph_3P)_2Pt(SnCl_3)_2$ (118). The complex with one Pt-Sn bond has also been described (119).



Anionic complexes containing platinum-tin bonds are also known. Wilkinson and co-workers have isolated salts of $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$ by direct replacement of ligands of Zeise's salt (119, 120)

$$\text{K}[(\text{C}_2\text{H}_4)\text{PtCl}_3] + 2\text{SnCl}_2 + \text{KCl} \rightarrow \text{K}_2[\text{PtCl}_2(\text{SnCl}_3)_2] + \text{C}_2\text{H}_4$$
A palladium-tin complex, $[\text{PdCl}(\text{SnCl}_3)_2]^{2-}$ has been reported (120b). This is thought to be a binuclear complex having Pd-Cl-Pd bridges.

Methyltriphenylphosphonium chloride reacts with a methanolic solution of chloroplatinic acid in stannous chloride (Sn:Pt-6:1) to give a quantitative yield of $[\text{Ph}_3\text{PMe}]_3[\text{Pt}(\text{SnCl}_3)_5]$ (121). A crystal structure determination has shown that this is one of the rare examples of 5-coordinate platinum. The structure is a trigonal bipyramid with a central platinum atom surrounded by five SnCl_3^- ligands, each attached by a Pt-Sn bond.

5,6(ii) Properties and Reactions

Metal-metal bonded compounds show a wide variety of thermal, oxidative and hydrolytic stabilities. The silicon-cobalt complex, for example, $\text{Me}_3\text{Si}[\text{Co}(\text{CO})_4]$ decomposes above -30° (122), but $\text{H}_2\text{Ge}[\text{Mn}(\text{CO})_5]$ is air stable and sublimable under high vacuum (114). Hydrolytic stability varies greatly even in closely

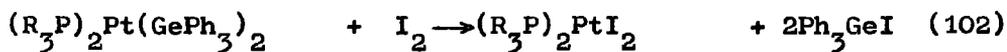
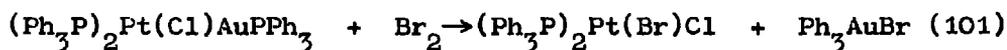
related compounds. $\text{Trans}-(\text{Et}_3\text{P})_2\text{Pt}(\text{Cl})(\text{SiMe}_3)$ is a very rapidly hydrolysed in moist air but the germanium analogue can be recovered unchanged from aqueous diglyme (106).

Measurement of the platinum-hydrogen stretching frequency of trans platinum hydride complexes shows that the ligands SnCl_3^- and GePh_3^- have high trans effects (30, 102, 118). Similarly, the platinum-chlorine stretching frequencies in the far infrared spectra of trans halide complexes shows that SiMePh_2^- and GeMePh_2^- also have high trans effects (31, 103).

The characteristic centre of reactivity of metal-metal bonded complexes is the metal-metal bond itself. This is cleaved by reaction with halogens, organic halides and halogen acids.

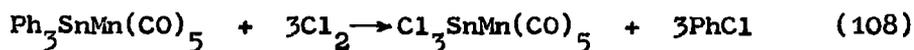
(a) Halogens

Halogens usually react in a straightforward manner, cleaving the metal-metal bonds:



One exception was the reaction of chlorine with $\text{Ph}_3\text{SnMn}(\text{CO})_5$.

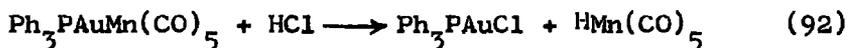
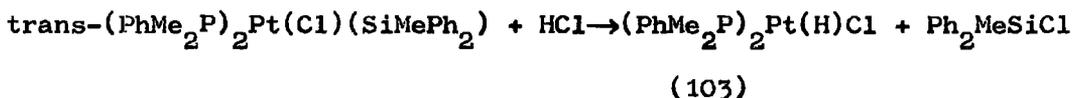
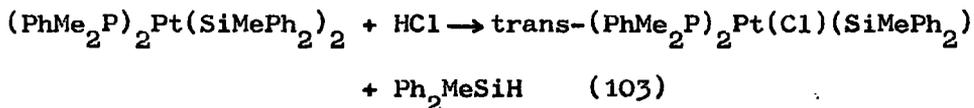
Phenyl groups were cleaved in preference to the metal-metal bonds:



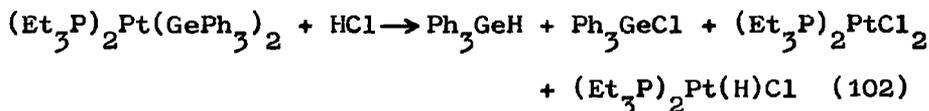
The Sn-Mn bond resisted further chlorination.

(b) Halogen Acids

Hydrogen halides cleave the metal-metal bonds.

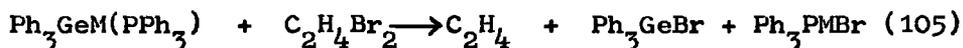


The platinum complex, $(\text{Et}_3\text{P})_2\text{Pt}(\text{GePh}_3)_2$ reacted with HCl giving a mixture of products suggesting that an octahedral intermediate was involved.

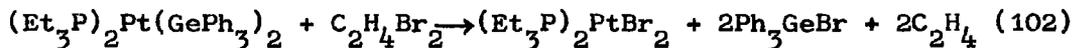


(c) Organic Halides

1,2-dibromoethane reacts with metal-metal bonded complexes giving ethylene.

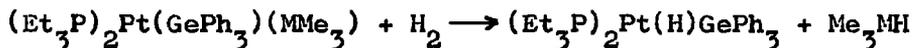


M = Cu(I), Ag(I), Au(I).



This can sometimes be used for quantitative estimation of metal-metal bonds if the ethylene is measured. The stoichiometric amount of ethylene was not obtained from the reaction with $(\text{Et}_3\text{P})_2\text{Pt}(\text{Cl})(\text{SiMe}_3)$, probably on account of partial hydrolysis of the platinum-silicon complex (106).

Hydrogenations of the mixed alkyl-aryl substituted compounds were very rapid at 0° and the alkyl substituted group was displaced exclusively: (106)



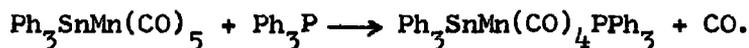
M = Si, Ge

A methanolic solution of $(\text{Et}_3\text{P})_2\text{PtCl}_2$ containing 2 mols. stannous chloride rapidly absorbed hydrogen at 25°/1atm. The addition of tetramethylammonium chloride gave yellow crystals of $\text{Me}_4\text{N}[(\text{Et}_3\text{P})_2\text{Pt}(\text{H})(\text{SnCl}_3)_2]$ which showed $\nu(\text{Pt-H})$ at 2108 cm^{-1} (121).

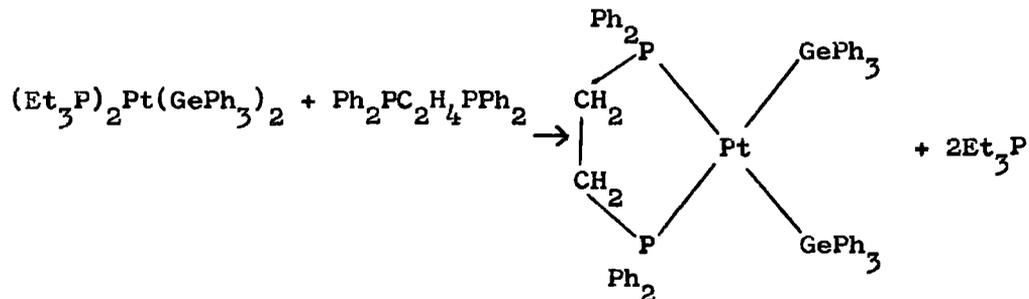
The 5-coordinate platinum complex $(\text{Me}_4\text{N})_3[\text{Pt}(\text{SnCl}_3)_5]$ reacts with hydrogen at 30°/3 atm. to form $(\text{Me}_4\text{N})_3[\text{Pt}(\text{H})\text{SnCl}_3]_4$ (121).

The complex, $(\text{Ph}_3\text{P})_2(\text{CO})\text{Cl}_2\text{Ir-HgCl}$ in benzene solution reacted with hydrogen giving mercury metal, mercurous chloride and the hydride $(\text{Ph}_3\text{P})_2(\text{CO})\text{Cl}_2\text{Ir-H}$. (126). This took place in the absence of catalyst over 20-30 hr. at room temperature.

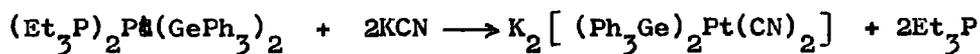
(f) A few ligand exchange reactions are known which do not result in cleavage of the metal-metal bond. Triphenyltinmanganese-pentacarbonyl reacts with triphenylphosphine and CO is displaced (108)



The chelating phosphine, 1,2-bis(diphenylphosphino)ethane displaces triethylphosphine from $(\text{Et}_3\text{P})_2\text{Pt}(\text{GePh}_3)_2$ (125).



Potassium cyanide reacted with $(\text{Et}_3\text{P})_2\text{Pt}(\text{GePh}_3)_2$ giving an ionic platinum-germanium complex:



Chapter 6. Molecular Hydrides of Transition Metals.

Several types of transition metal hydrides are known (127). The simplest are those which contain only hydrogen bonded to the transition metal e.g. ReH_9^{2-} and TcH_9^{2-} (128, 129, 130). These are unusual, however, and most transition metal hydrides have other ligands attached to the metal, including tertiary phosphines and arsines, cyclopentadiene, carbon monoxide and cyanide. In most cases π -bonding, which reduces the electron density on the metal atom, makes an important contribution to the stability of these hydrides. A convenient classification of transition metal hydrides is into groups having same types of ligands attached to the metal. These will be considered in turn.

6,1. Preparations

(a) Hydridometallates

Reduction of potassium perrhenate, KReO_4 , in an anhydrous mixture of ethylenediamine and alcohol using excess potassium metal gave K_2ReH_9 . The preparation of the technetium analogue is similar.

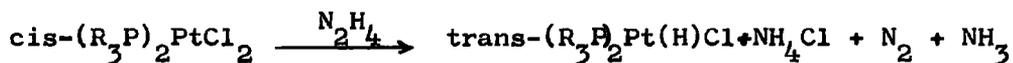
(b) Tertiary phosphine and arsine hydrides

The elements for which this class of compounds is important are Pt(II), Ir(III), Rh(III), Os(II), Ru(II), Fe(II) Re(III), Re(IV)

and Re(V). Most are monohydrides e.g. $\text{trans}-(\text{Et}_3\text{P})_2\text{Pt}(\text{H})\text{Cl}$, but polyhydrides are also known, e.g. $\text{trans}-(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)\text{OsH}_2$ (131), $(\text{Ph}_3\text{P})_2\text{ReH}_3$ (132). Platinum hydrides of this type have greater relevance to the work described in this thesis and more attention is devoted to them.

(i) Reduction with Hydrazine

Platinum hydridohalides are prepared most conveniently by reduction of the cis dihalide complex with hydrazine hydrate in aqueous or alcoholic solution: (29)

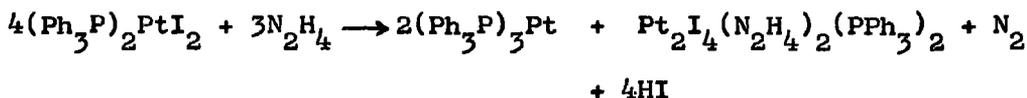


The trans dichloride is not reduced under the same conditions, and the difference in reactivity is probably due to the high trans effect of tertiary phosphine ligands.

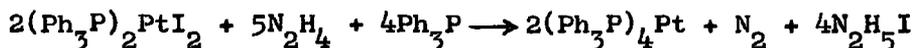
Chatt and Shaw reduced $\text{cis}-(\text{Ph}_3\text{P})_2\text{PtCl}_2$ with hydrazine hydrate in ethanol at 78° and obtained $\text{trans}-(\text{Ph}_3\text{P})_2\text{Pt}(\text{H})\text{Cl}$ (29). Re-examination of this reaction has shown that the cis isomer is the main product when the reaction is carried out in refluxing methanol-ether solution and at intermediate temperatures a mixture of the two isomers is obtained (133).

Reduction of the iodide complex $(\text{Ph}_3\text{P})_2\text{PtI}_2$ with anhydrous hydrazine in refluxing ethanol gave a platinum(0) complex and a

hydrazine complex which was inadequately described (134):

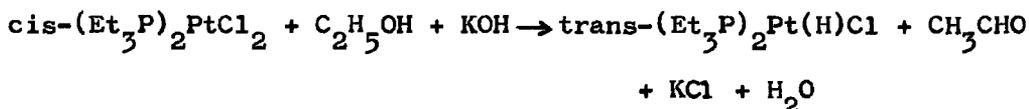


With excess triphenylphosphine:

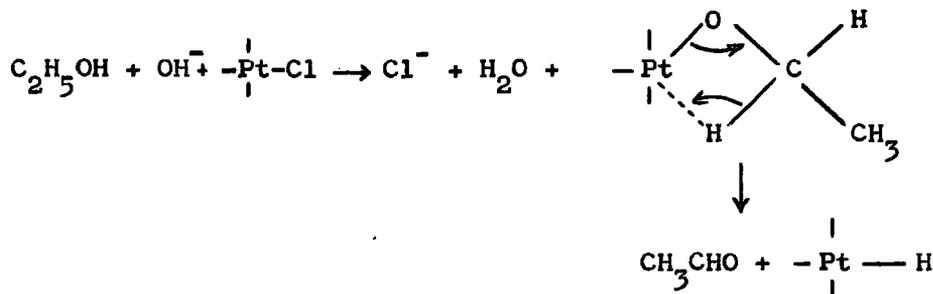


(ii) With Alcoholic KOH

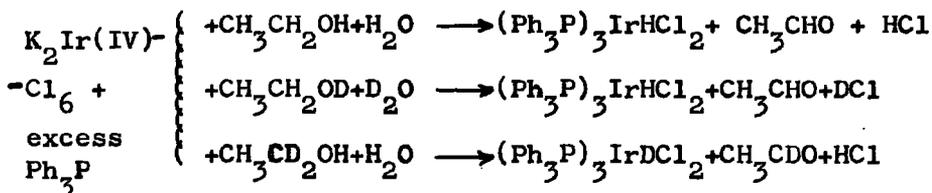
Alcoholic potassium hydroxide reduces cis platinum dihalide complexes on heating. Ethanol is oxidised to acetyldehyde (29).



This reaction is considered to take place by hydride ion transfer from the α carbon atom:



This mechanism is supported by tracer studies in the following reactions which give $(\text{Ph}_3\text{P})_3\text{Ir}(\text{III})\text{HCl}_2$ (135, 136).



The tris- and tetrakis(triphenylphosphine)platinum(0) complexes mentioned earlier were also prepared by the reduction of potassium tetrachloroplatinate by alcoholic KOH in presence of triphenylphosphine (134).

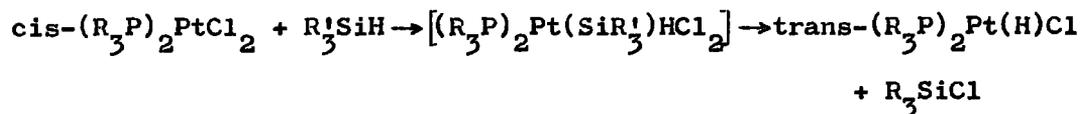
(iii) With Formic Acid

The reduction of cis platinum dihalides with hot formic acid also proceeds by a hydrogen transfer mechanism (29)



(iv) With Trialkylsilanes

Trialkylsilanes have been used to reduce cis-platinum dihalide complexes to trans-hydrido halides (113b). It is thought that the organosilane oxidatively adds to the platinum (II) complex giving an octahedral platinum(IV) intermediate which eliminates halotrialkylsilane:



This reaction gave only red polymeric material when triarylphosphine platinum complexes were used.

(v) With Metal Hydrides

Lithium aluminium hydride in ether or tetrahydrofuran (T.H.F.) is used to prepare the more reactive transition metal hydrides. However, as a method of preparation of platinum hydrides, it

suffers from the disadvantage that some platinum metal is also formed (29).

Chatt and Shaw reduced a palladium dihalide complex, $(Et_3P)_2PdCl_2$ and obtained a product with $\nu(Pd-H)$ at 2035 cm^{-1} which could not be purified (30). Decomposition was rapid in solution.

Sodium borohydride in T.H.F. was used in an attempt to prepare a nickel hydrido-chloride from $(Ph_3P)_2NiCl_2$ (137). The required product was not isolated but the presence of Ni-H species was suggested by a low intensity resonance to very high field in the proton magnetic resonance spectrum of the mixture.

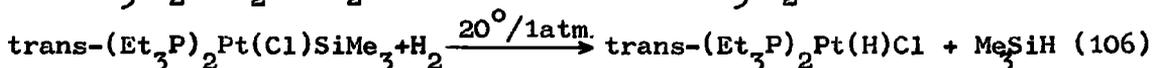
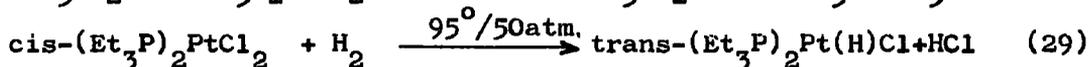
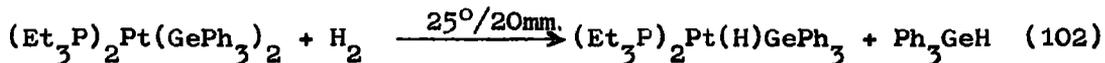
Iron, ruthenium and osmium hydrides have general formula $MHX(diphosphine)_2$ where $X = H, Cl, Br, I, SCN, CN$ and diphosphine is a chelating diphosphine, e.g. $Ph_2P \cdot CH_2CH_2 \cdot PPh_2$.

The trans hydrido-halides are prepared by reduction of the corresponding cis dihalide with lithium aluminium hydride in T.H.F. followed by treatment with ethanol to convert any dihydride into the monohydride (127, 131, 138).

(vi) With Hydrogen

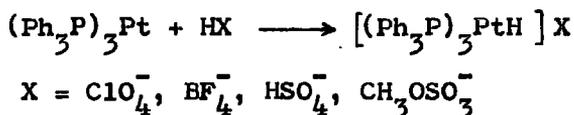
Gaseous hydrogen is absorbed by certain platinum complexes

with the formation of platinum hydrides. Reaction conditions are variable but can be very mild.

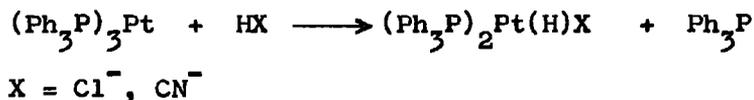


(vii) From Platinum(0) Complexes

Some unusual platinum hydrides have been prepared by reaction of platinum(0) phosphine complexes with acids (139). Tris(triphenylphosphine)platinum(0), $(\text{Ph}_3\text{P})_3\text{Pt}$ reacts with acids and the products are of two types according to the acid or reaction medium used. When a suspension of the platinum(0) compound reacted with aqueous or dilute alcoholic acid, an ionic platinum(II) hydride was formed:



The molar conductance in nitrobenzene showed that the complex was a uni-univalent electrolyte. If gaseous HX was bubbled through a benzene solution of the platinum(0) complex, a diamagnetic and non-conducting platinum hydride was produced:



Ionic platinum hydrides are formed if X is an anion of low coordinating power and covalent hydrides if X has high

coordinating power. Donor solvents such as ethanol give rise to the ionic hydride, even if the acid is HCl.

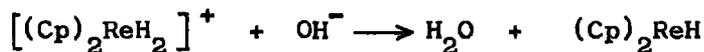
Similar reactions with zerovalent palladium and nickel complexes did not give the metal hydrides.

(c) Cyclopentadienyl Hydrides

Di- π -cyclopentadienyl hydride complexes of Re(I), Mo(II), Ta(III), W(II), Fe(0) and Ru(0) are known which are all iso-electronic in the valence shell.

Treatment of metal chlorides ReCl_5 , MoCl_5 , WCl_5 and TaCl_5 with sodium cyclopentadienide and sodium borohydride in T.H.F. gives respectively $(\text{Cp})_2\text{ReH}$, $(\text{Cp})_2\text{MoH}_2$, $(\text{Cp})_2\text{WH}_2$ and $(\text{Cp})_2\text{TaH}_3$ where Cp = π -cyclopentadiene (140, 141, 142).

Dilute mineral acids react with rhenium, molybdenum and tungsten cyclopentadienylhydrides giving cationic hydrides, $[(\text{Cp})_2\text{ReH}_2]^+$, $[(\text{Cp})_2\text{MoH}_3]^+$ and $[(\text{Cp})_2\text{WH}_3]^+$ which can be precipitated by large anions. The cations act as conjugate bases and the addition of alkali to an aqueous solution liberates the neutral hydrides which are insoluble in water.



(d) Carbonyl Hydrides

Carbonyl hydrides of chromium, molybdenum, tungsten, manganese, technetium, rhenium, iron, cobalt, rhodium and nickel are known.

The inert gas rule is obeyed by carbonyl hydrides. With the exception of manganese and rhenium, metals of odd atomic number form only mononuclear carbonyl hydrides but metals of even atomic number can also form polynuclear complexes of this type. Cationic carbonyl hydrides of some of these metals are also known.

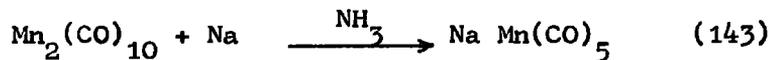
There is a wide variety of metal carbonyl hydrides and only a few examples can be given here, including $\text{H}_2\text{Cr}(\text{CO})_5$, $\text{HMn}(\text{CO})_5$, $\text{HRe}(\text{CO})_5$, $\text{H}_2\text{Fe}(\text{CO})_4$, $\text{H}_2\text{Fe}_2(\text{CO})_8$, $\text{HCo}(\text{CO})_4$, $\text{H}_2\text{Ni}_2(\text{CO})_6$ and $\text{H}_2\text{Ni}_3(\text{CO})_8$.

Preparations

The most general method of preparation of carbonyl hydrides is the hydrolysis of carbonylmetallate salts. Several reducing agents have been used to obtain the salts.

(i) Alkali Metal

The reduction of metal carbonyls in liquid ammonia or T.H.F. by alkali metal amalgam frequently gives the carbonylmetallate:



The pentacarbonylhydrides can best be obtained by treatment of these anions with concentrated phosphoric acid.

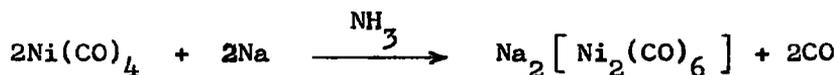
Hexacarbonyls of chromium, molybdenum and tungsten are reduced by alkali metals giving the mononuclear carbonylmetallate- (II) (145).



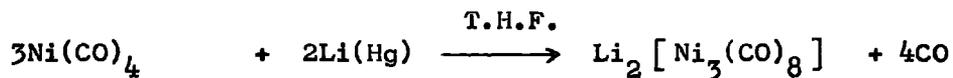
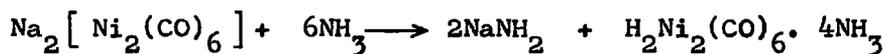
Precipitation with large cations from aqueous solutions of $Na_2 M(CO)_5$ (M = Cr, W) gives anionic hydrides:



Nickel tetracarbonyl is unique in that reductions with sodium in liquid ammonia or lithium amalgam in T.H.F. give polynuclear anions (146, 147).



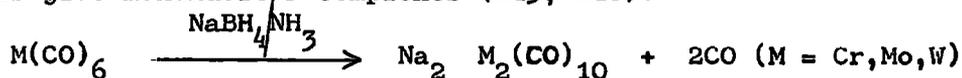
This is immediately solvolysed to the hydride:



(ii) Sodium Borohydride

Sodium borohydride in T.H.F. can often be used instead of alkali metals as the reducing agent for the preparation of carbonylmetallate ions. In a few cases, however, the weaker reducing properties give different products. For instance, the reduction of hexacarbonyls of chromium, molybdenum and

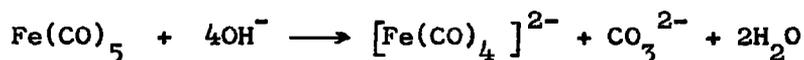
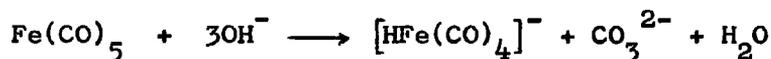
tungsten by NaBH_4 give polynuclear species where alkali metals give mononuclear complexes (145, 148).



(iii) Bases.

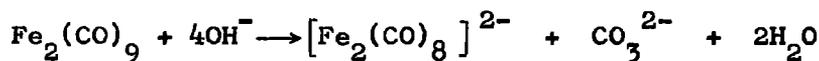
Treatment of $\text{Fe}(\text{CO})_5$ with aqueous alkali gives $[\text{HFe}(\text{CO})_4]^-$ or $[\text{Fe}(\text{CO})_4]^{2-}$, depending on the amount of alkali (149).

$\text{Fe}(\text{O})$ is reduced to $\text{Fe}(-\text{II})$ and one coordinated CO is oxidised to CO_3^{2-} .



Ammonia gives an analogous reaction (150). Acidification of the above tetracarbonylferrate ions gives $\text{H}_2\text{Fe}(\text{CO})_4$.

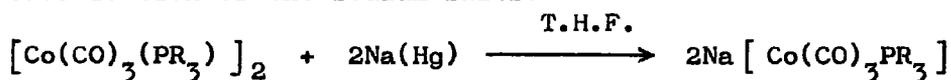
The action of bases on polynuclear iron carbonyls gives polynuclear carbonylferrates: (151)



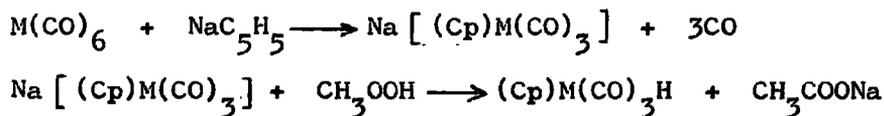
(e) Phosphine and Cyclopentadiene Carbonyl Hydrides.

In addition to the carbonyl hydrides mentioned above, complexes are known having carbon monoxide and either tertiary phosphines or cyclopentadiene bonded to the metal.

The former are quite numerous and are exemplified by $\text{HCo}(\text{CO})_3^-$ (PPh_3) and $\text{H.Mn}(\text{CO})_4(\text{PR}_3)$. They can be obtained by preparations similar to those of metal carbonyl hydrides, e.g. reduction of the phosphine substituted carbonyls by sodium amalgam, followed by acidification of the sodium salts:



Metal π -cyclopentadienylcarbonyl hydrides may be either neutral or cationic. The neutral chromium, molybdenum and tungsten compounds may be prepared by treatment of the metal hexacarbonyls with sodium cyclopentadienide in a polar solvent, followed by acidification.



M = Cr, Mo, W. Cp = π -cyclopentadiene

Cationic hydrides of this class are obtained by protonation of binuclear π -cyclopentadienylmetal carbonyls with strong acid (152) giving, e.g. $[(\text{Cp Mo}(\text{CO})_3)_2\text{H}]^+$ and $[(\text{Cp Fe}(\text{CO})_2)_2\text{H}]^+$. The proton magnetic resonance spectra showed the characteristic metal-bonded hydrogen resonance to high field.

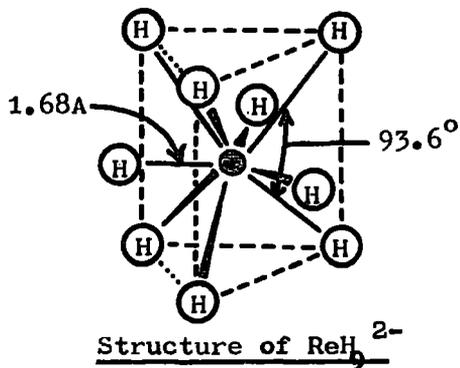
Properties of Transition Metal Hydrides.

The thermal and oxidative stability of transition metal hydrides varies greatly. Decomposition of HCo(CO)_4 takes place above -20° , for example, but platinum hydride complexes are thermally stable crystalline solids, remarkably resistant to oxidation and hydrolysis.

Structure Determination.

It appears that the metal-bonded hydrogen atom occupies a normal coordination position at the metal atom, linked by a σ -bond formed by the $\text{H}(1s)$ and the appropriate metal $(n-1)d(n)s(n)p$ hybrid orbital. The hydrogen atom can only be located in structural studies by neutron diffraction and this has been done in only a few cases. The hydrogen is not detectable unambiguously by X-ray diffraction, but its position can sometimes be inferred as in a study of $\text{trans-(Et}_3\text{P)}_2\text{Pt(H)Br}$ (25) reported earlier (page 15).

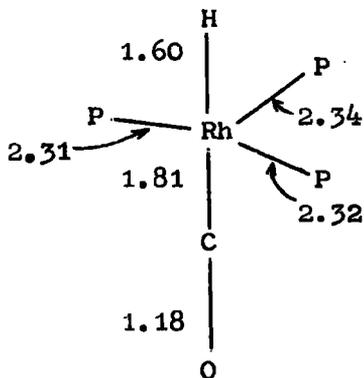
The structure of the enneahydridorhenate ion, ReH_9^{2-} has been determined by neutron diffraction by a single crystal (129).



Six hydrogens are at the corners of a trigonal prism having the rhenium atom at the centre, and the remaining three extend from the centre of each face as shown. Each ReH_9 prism is surrounded by a prism of 9 potassium ions rotated through 60° with respect to the first prism.

The molecular structure of $\text{Os}(\text{H})\text{Br}(\text{CO})(\text{PPh}_3)_3$ has been determined by X-ray crystallography, although the position of the hydrogen was not determined (153). The structure is an octahedron with three equatorial phosphines and axial bromine and CO ligands. The Os-P bond length trans to hydrogen (2.56\AA) was longer than the other two (2.34\AA). This, and the long Pt-Br distance in $\text{trans}-(\text{Et}_3\text{P})_2\text{Pt}(\text{H})\text{Br}$ (25) indicate that hydride has high trans effect.

The position of the hydrogen atom in $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ has been determined (154) and the Rh-H bond length was found to be approximately the sum of the covalent radii.



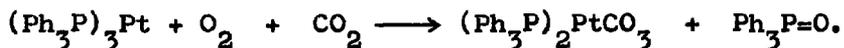
Structure of
 $\text{RhH}(\text{CO})(\text{PPh}_3)_3$

The structure is a trigonal bipyramid having axial H and CO ligands. In this case the Rh-CO distance was not increased by the high trans effect of the hydrogen.

Proton Magnetic Resonance

By far the most useful diagnostic property of transition metal-hydrogen bonds is the low intensity high field resonance of the metal-bonded hydrogen. This varies between about τ 12 to 45 (11.63 in $(Cp)_2TaH_3$ to 44.3 in $trans-(Et_2PCH_2CH_2^-PEt_2)FeHCl$). In some cases, e.g. $[(CpMo(CO)_3)_2H]^+$ (152), $(Ph_3P)_2Ni(H)Cl$ (137), this criterion has been used to show that metal-bonded hydride species exist in solution, even when they could not be isolated. The high-field proton resonance is so characteristic that any new claim to the preparation of a metal hydride without this supporting evidence must be suspected. Tri(triphenylphosphine)platinum(0), $(Ph_3P)_3Pt$ was prepared in 1958 by Malatesta (134) but was refuted by Nyholm et. al. who suggested that the compound is a dihydride, $(Ph_3P)_3PtH_2$ (155). The Pt-H p.m.r. signal was not observed, but a band in the infrared spectrum at $1670cm^{-1}$ was attributed to a very low Pt-H stretching frequency. Malatesta and Ugo replied that both compounds exist (156), but recently it was established that the 'dihydride' is in fact a

carbonatoplatinum complex having an abnormally high C=O stretching frequency (157). This was formed accidentally by the reaction:

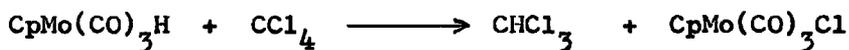


The platinum hydride complexes, $\text{trans}-(\text{Et}_3\text{P})_2\text{Pt}(\text{H})\text{X}$ show a metal-bonded hydrogen resonance of very characteristic pattern. The molecule contains two equivalent ^{31}P nuclei ($I = \frac{1}{2}$, abundance 100%) which split the Pt-H resonance into a 1:2:1 triplet. In addition, the ^{195}Pt nucleus ($I = \frac{1}{2}$, abundance 34%) further splits the triplet into two, while the remaining platinum isotopes with zero spin leave the central triplet unsplit. $J_{^{195}\text{Pt-H}}$ is extraordinarily large and the result is an easily recognisable pattern of a central triplet with a smaller triplet on either side (158).

The metal-hydrogen stretching frequency is another characteristic property of transition metal hydrides. These vary with the other ligands attached to the metal but are usually within the range $1750\text{-}2200\text{cm}^{-1}$. The M-H stretching frequency increases on going from light to heavy transition elements in the same group, if the other ligands are the same. This is the converse of the behaviour of main group elements and it indicates that transition metal-hydrogen bonds of the heavier metals are stronger.

Chemical properties of metal hydrides depend very much on the other ligands bonded to the metal. For example, HCo(CO)_4 behaves as an acid in aqueous solution, $(\text{Cp})_2\text{ReH}$ behaves as a base, $(\text{Et}_3\text{P})_2\text{Pt(H)Cl}$ does not react with water but K_2TcH_9 decomposes liberating hydrogen.

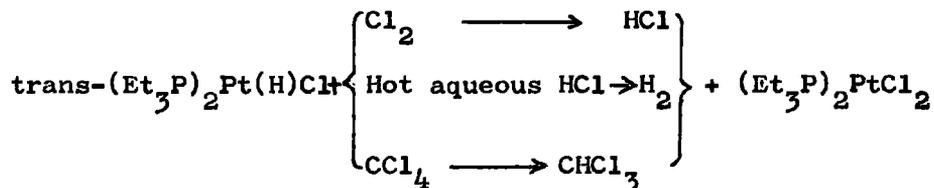
A more general reaction is that with halogenated hydrocarbon solvents. Hydrogen transfer takes place and carbon tetrachloride, for example, is reduced to chloroform.



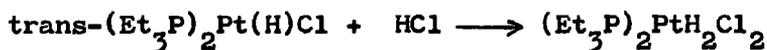
Reactions of platinum hydride complexes

(a) Hydrogen transfer.

Replacement of hydrogen by halogen takes place with decreasing ease when platinum hydrido-halide complexes are treated with halogen, hot aqueous acid and aliphatic halogeno-carbon (29).



The reaction with dry hydrogen chloride in ether gave an octahedral platinum(IV) complex which is unstable and slowly reverts to starting materials.



The infrared spectrum has bands at 2245 and 2265 cm^{-1} .

(b) Metathetical Reactions.

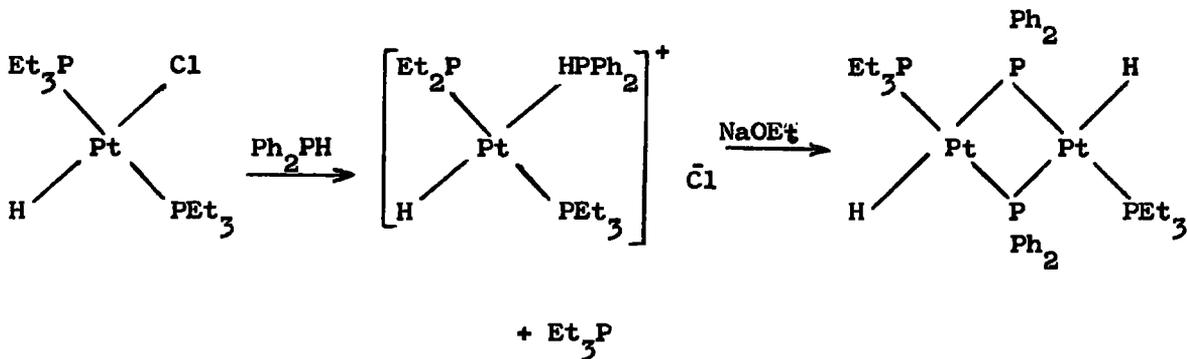
Hydrogen has high trans effect and a consequence is the lability of the chlorine atom of trans hydrido chlorides. The appropriate alkali metal salt in a suitable solvent replaces chloride by bromide, iodide, cyanide, cyanate, thiocyanate and nitrite. This extends the range of known platinum hydrides.

(c) Reactions with neutral ligands.

Ammonia reacts with platinum hydride complexes giving an ionic product (29).



The reaction with diphenylphosphine has been used as a route to a binuclear hydride of platinum (159).



The low Pt-H stretching frequency of this complex (2005cm^{-1}) suggests that the phosphido group has a higher trans effect than cyanide, since $\nu(\text{Pt-H})$ of $\text{trans}-(\text{Et}_3\text{P})_2\text{Pt}(\text{H})\text{CN}$ is at 2041cm^{-1} (30).

DISCUSSION

Chapter 7

Germyl-Palladium Complexes

The first compound described having germanium bonded to a transition metal was $(\text{Cp})(\text{CO})_2\text{FeGePh}_3$, prepared in 1956 by Wilkinson and co-workers (109). Since then complexes have been prepared which feature a wide variety of germanium-transition metal bonds including copper, silver and gold (105), platinum (102, 102b, 106), manganese (107, 114, 116), chromium, molybdenum and tungsten (116, 117).

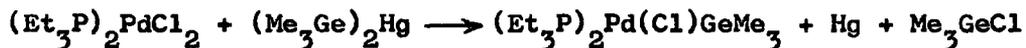
This study was undertaken with the aim of preparing compounds having nickel- and palladium-germanium bonds in order to compare their stability, properties and reactivity with germyl-platinum complexes and the other germanium-transition metal compounds.

There were in mind three possible routes to germanium-palladium complexes, all starting from palladium dihalide complexes e.g. $\text{trans}-(\text{Et}_3\text{P})_2\text{PdCl}_2$. The first method was to react the palladium dihalide with triphenylgermyl-lithium which should eliminate lithium halide and form the triphenylgermyl-palladium complex, e.g.:

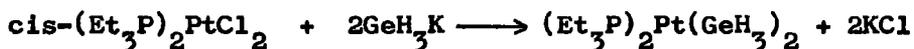


This method has been used to prepare the platinum analogue (102). The second type of reaction has also been used to make platinum complexes (106), but in this case stable compounds are formed with only one Pt-Ge bond in the molecule. This reaction involves

treatment of a solution of the dihalide complex with one mole of bis(trimethylgermyl)mercury and by analogy would proceed as follows:



The third method is analogous to the first in that a germanium-alkali metal compound is used. In this method, germyl-potassium, GeH_3K or germyl-lithium (82, 83, 84) is treated with the transition metal dihalide complex and elimination of alkali metal halide should again take place. In view of the novelty of this method, preliminary experiments were carried out with platinum dihalide complexes since experience had shown by that time that Pt- GeH_3 bonds were more likely to be stable than Pd- GeH_3 . One of the following reactions should take place:



1. Triphenylgermyl-lithium

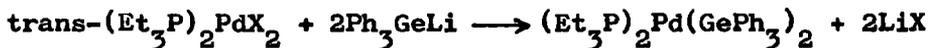
Triphenylgermyl-lithium was prepared for the first of these experiments by cleavage of hexaphenyldigermene with lithium shot in 1,2-dimethoxyethane (monoglyme). This reaction was often difficult to start and initiation periods ranged from 10 minutes to 4 hours at room temperature. Etheral solvents

are cleaved by triphenylsilyl-lithium and triphenylgermyl-lithium (160, 161, 162) and quantitative information on the yields of triphenylgermyl-lithium in various solvents after stated times was desired. Ph_3GeLi reacts with tetrahydrofuran (T.H.F.) probably giving $\text{Ph}_3\text{Ge}(\text{CH}_2)_4\text{OH}$ by analogy with the silicon compound (161) and with monoglyme giving Ph_3GeMe and $\text{Ph}_3\text{Ge}(\text{CH}_2)_2\text{OMe}$. The rate of reaction of triphenylgermyl-lithium with T.H.F. has been determined (160) and pseudo-first order kinetics with a rate constant $1.8 \times 10^{-3} \text{ hr.}^{-1}$ (corresponding to a half-life 385 hr.) are followed for the first part of the reaction. Thereafter the rate of reaction increased in a manner which suggested that catalysis by one of the products was taking place.

An examination of the reactions of triphenylgermyl-lithium with monoglyme and T.H.F. was planned and the products were to be examined by vapour phase chromatography on a Pye model 104 chromatograph. The most difficult separation of products which this involved would be the separation and estimation of methyltriphenylgermane and triphenylgermane, the latter being formed after hydrolysis of triphenylgermyl-lithium. This was attempted using a variety of column packings and oven temperatures.

The best separation which could be achieved was in 5' columns packed with 1% S.E. 30 on chromosorb Z at an oven temperature of 175° with a nitrogen flow rate 45 mls. per minute. Retention times of triphenylgermane and methyltriphenylgermane under these conditions were 4.6 and 5.2 minutes respectively. Although separate peaks were visible, the amount of overlap was such that it was impossible to determine the concentration of each compound by integration. For this reason the investigation was abandoned and yields of triphenylgermyl-lithium in monoglyme for the following reactions were assumed to be between 60% and 70%, depending on the time required for the preparation to go to completion.

Solutions of triphenylgermyl-lithium in monoglyme were difficult to filter through a glass sinter. Instead a rough filtration through a plug of glass wool removed unreacted lithium shot but invariably small particles of lithium passed through the glass wool. Triphenylgermyl-lithium in monoglyme reacted at -20° with solutions of palladium halide complexes, $(Et_3P)_2PdBr_2$ and $(Et_3P)_2PdCl_2$ giving yellow or orange solutions and a pale yellow precipitate.



The composition of the precipitate depended on the solvent used to dissolve the palladium dihalide complex. If the solvent was largely diethyl ether, the precipitate contained bis(triethylphosphine)bis(triphenylgermyl)palladium(II) which was isolated by filtration. This complex was soluble, however, if the solution consisted of more than $\frac{1}{3}$ benzene and isolation was by low temperature crystallisation from the hydrolysed solution.

The above method which gave $(Et_3P)_2Pd(GePh_3)_2$ as a precipitate had the disadvantage that the product was contaminated with hexaphenyldigermene. This could have been starting material which was not cleaved by lithium shot or it could have resulted from decomposition of $(Et_3P)_2Pd(GePh_3)_2$.

A modification of the preparation gave a product almost entirely free from hexaphenyldigermene. Triphenylgermyl-lithium is more conveniently prepared by metallation of triphenylgermane using n-butyl-lithium. This reaction is quicker, cleaner, minimises contamination of the product by hexaphenyldigermene and also eliminates the necessity for removal of excess lithium by filtration. The two methods were very similar after the preparation of triphenylgermyl-lithium. However, by this method the bis(tri-n-propylphosphine)complex, $(Pr_3^nP)_2Pd(GePh_3)_2$ was obtained from $(Pr_3^nP)_2PdCl_2$ and triphenylgermyl-

lithium. This compound was not isolable from a reaction using hexaphenyldigermane as the source of triphenylgermyl-lithium.

Other palladium halide complexes, $(\text{Ph}_3\text{P})_2\text{PdCl}_2$, $(\text{bipy})\text{PdCl}_2$ and $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{PdCl}_2$ have been treated with triphenylgermyl-lithium at -20° . Reaction took place in each instance, but pure germyl-palladium complexes were not obtained. The triphenylphosphine palladium dichloride complex was almost insoluble in ether-benzene (3:1) at -20° . The mixture became orange and then decomposed progressively to dark grey on adding triphenylgermyl-lithium. Only hexaphenyldigermane was isolated.

Bipyridylpalladium dichloride and triphenylgermyl-lithium decomposed even more rapidly. The colour changed from buff to black as half of the triphenylgermyl-lithium was added. Hexaphenyldigermane was recovered in about 60% yield.

The reaction with the chelate phosphine complex, $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{PdCl}_2$ showed more promise. The platinum complex $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Pt}(\text{GePh}_3)_2$ has been made (102b) both by displacement of triethylphosphine from $(\text{Et}_3\text{P})_2\text{Pt}(\text{GePh}_3)_2$ with 1,2-bis(diphenylphosphino)ethane and directly from the chelate platinum chloride complex and triphenylgermyl-lithium. A solution of triphenylgermyl-lithium was added to a suspension of $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{PdCl}_2$ in monoglyme at -30° giving a brown mixture.

Work-up procedure similar to those described previously gave hexaphenyldigermene, a small amount of starting material (palladium dihalide complex) and a similar quantity of a compound which was thought, on the basis of its infrared spectrum and elemental analysis, to be the impure complex, $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{-Pd}(\text{GePh}_3)_2$. Recrystallisation from ether at low temperature was attempted but the complex decomposed.

The nickel complexes, $(\text{Et}_3\text{P})_2\text{NiBr}_2$ (square planar) and $(\text{Ph}_3\text{P})_2\text{NiCl}_2$ (tetrahedral) both reacted with triphenylgermyl-lithium at low temperature but decomposition set in very rapidly. Brown solutions were obtained which yielded only hexaphenyldigermene and dark coloured tarry material.

The sequence of stability of compounds having germanium bonded to these group VIII metals parallels the stability of σ -bonded organic derivatives which increases in the series $\text{Ni} < \text{Pd} < \text{Pt}$.

2. Bis(trimethylgermyl)mercury, $(\text{Me}_3\text{Ge})_2\text{Hg}$.

The reaction between equimolar quantities of a platinum dihalide complex e.g. $\text{cis}-(\text{Et}_3\text{P})_2\text{PtCl}_2$ and bis(trimethylgermyl)-mercury gave the derivative with one Pt-Ge bond (106). Reactions with 2 mols of the mercury reagent did not give the bis(trimethylgermyl)platinum complex and the yield of monosubstituted derivative obtained from such a reaction was considerably reduced.

The reaction between bis(triethylphosphine)palladium dichloride, $\text{trans}-(\text{Et}_3\text{P})_2\text{PdCl}_2$ and bis(trimethylgermyl)mercury gave the expected yellow solution and deposit of mercury. Decomposition took place at -20° during the work-up procedure and a small quantity of the binuclear complex, $[(\text{Et}_3\text{P})\text{PdCl}_2]_2$ was the only pure substance isolated.

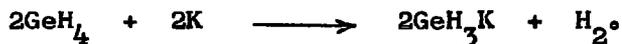
In a similar reaction with the dibromide, $(\text{Et}_3\text{P})_2\text{PdBr}_2$, the deposition of mercury was slow. Starting material, $(\text{Et}_3\text{P})_2\text{PdBr}_2$ was recovered (91%) together with a trace of $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Br}$ which might have been formed by hydrolysis of the desired product, $(\text{Et}_3\text{P})_2\text{Pd}(\text{Br})(\text{GeMe}_3)$. The infrared spectrum of the products showed no evidence of $\text{Ge}-\text{CH}_3$ rock or the $\text{Ge}-\text{C}$ stretching frequency.

The nickel complex, $(\text{Cp})\text{Ni}(\text{PPh}_3)\text{Cl}$ has recently been shown to form stable organic derivatives (43) when treated with Grignard reagents. It was hoped that nickel-germanium bonds would similarly be stabilised by the other ligands, cyclopentadiene and triphenylphosphine, on the metal. A solution of bis(trimethylgermyl)mercury was added dropwise to $(\text{Cp})\text{Ni}(\text{PPh}_3)\text{Br}$ in ether. The colour changed from maroon to dark brown as the first few drops of the mercury reagent were added. An intractable black tar remained after the solvent was removed.

3. Germyl-alkali metal compounds.

Metal-metal bonded complexes are known having hydrogen atoms attached to the group IV metal e.g. $\text{H}_3\text{SiCo}(\text{CO})_4$ (112) and $\text{H}_2\text{Ge}[\text{Mn}(\text{CO})_5]_2$. Reactions were carried out with the aim of preparing GeH_3 - complexes of platinum, palladium and possibly nickel. Platinum was chosen for the initial investigation since it was thought that M-GeH_3 bonds were likely to be more stable when M is a heavier metal, and the complexes would then be of the type $(\text{R}_3\text{P})_2\text{Pt}(\text{GeH}_3)_2$ or $(\text{R}_3\text{P})_2\text{Pt}(\text{GeH}_3)\text{X}$ where X is halogen.

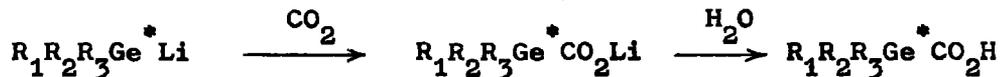
Germyl-potassium, GeH_3K was prepared by reaction of germane (40% excess) with potassium in liquid ammonia at -78° :



The solvent was removed to leave a grey powder which is, by analogy with the lithio derivative (83), $\text{GeH}_3\text{K} \cdot 2\text{NH}_3$. This was treated with $\text{cis}-(\text{Et}_3\text{P})_2\text{PtCl}_2$ in benzene. No reaction took place when the mixture was stirred for 4 hours at room temperature. At 60° the mixture began to decompose and an intractable black tar was formed.

Two possible reasons for this behaviour were considered. Germanium-alkali metal compounds having three organic compounds

groups on the germanium atom behave as 'gegen-ion' compounds, i.e. solvated ion pairs. This has been demonstrated by the fact that the asymmetric lithium derivative, $R_1R_2R_3GeLi$ where $R_1 = Me$, $R_2 = Ph$, $R_3 = \alpha$ -naphthyl undergoes substitution reactions without racemisation (163).



If germyl-potassium is also a gegen ion compound, the large potassium ion might hinder approach of the GeH_3 group to the platinum atom and prevent the formation of a σ -bond. This can be checked by replacing potassium by a smaller alkali metal ion, e.g. lithium. The second possibility is that the ammonia of solvation reacted with the complex as it was formed, causing decomposition. This problem is less easy to overcome since germyl-potassium is difficult to obtain free from ammonia and is very unstable in that state.

A reaction was carried out using equimolar quantities of germyl-lithium and cis-bis(triethylphosphine)platinum dichloride in benzene. Progressive decomposition again took place when the benzene was warmed above 60° .

Properties of triphenylgermyl-palladium complexes.

Bis(triethylphosphine)bis(triphenylgermyl)palladium(II), $(Et_3P)_2Pd(GePh_3)_2$ is moderately stable, thermally and oxidatively,

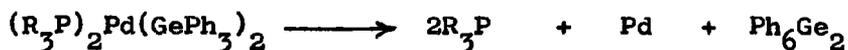
in the solid state. One sample has been kept in air at -20° for six months, but it showed signs of surface decomposition after two weeks at room temperature in a nitrogen atmosphere. A solution of the complex in benzene was completely oxidised within two minutes in air at room temperature giving intractable tarry material. Another sample of the complex was recovered unchanged from diethyl ether after dry oxygen had been bubbled through the solution for 3 hours at -40° . Heated under vacuum, the pale yellow complex, $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ began to decompose at 97° and was completely black at 107° . The tri-n-propylphosphine analogue was somewhat less stable and decomposed over the range 86 to 100° . The platinum analogues of these complexes were considerably more stable and began to decompose at 155° and 120° respectively (102).

Infrared Spectra.

The near and far infrared spectra of $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ showed the following absorptions: 3096sh, 3040m (aromatic C-H stretch), 2967m, 2933m, 2865 (aliphatic C-H stretch), 1949w, 1880w, 1818w, 1575m (aromatic C=C stretch), 1477m, 1449m, 1429s, 1379w, 1302w, 1253m, 1235sh, 1186w, 1155w, 1087m, 1075m, 1065w, 1030s, 997m, 909w, 852w, 762s, 729s, 700s, 629w, 480s, 457s (Ge-Car stretch), 403w (Pd-P stretch), 315s, 298 s, 280s.

Reactions of bis(triphenylgermyl)palladium complexes.

Pyrolysis of the complex $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ in a vacuum apparatus gave palladium metal, hydrogen, ethylene, benzene, triethylphosphine, hexaphenyldigermene and tetraphenylgermane. This indicates that not only were the Pd-Ge and Pd-P bonds cleaved, the stronger Ge-C, C-H and P-C bonds were also broken. This is very surprising, since the Ge-Pd bonds are clearly much weaker than the others and decomposition might be expected to proceed as follows:



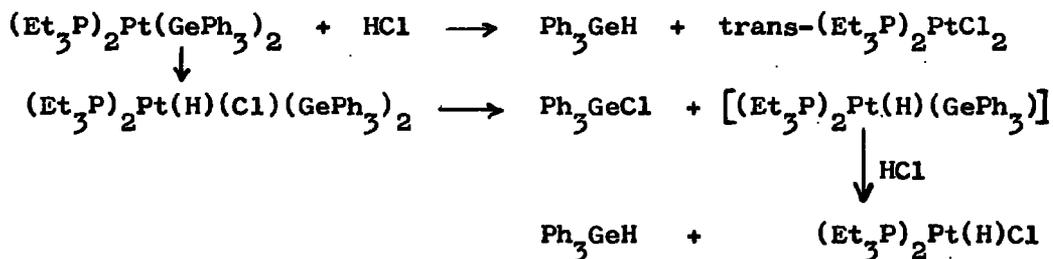
The products isolated strongly suggest that a variety of free radical processes take place, probably having been initiated by triphenylgermyl radicals. Pyrolysis of the platinum analogue yielded a similar mixture of products (102).

Chemical reactions of the platinum complexes $(\text{R}_3\text{P})_2\text{Pt}(\text{GePh}_3)_2$ often gave mixtures of products which suggested that the reactions were taking place via octahedral platinum(IV) intermediates, although in no case has such an intermediate been isolated. Reactions of the palladium complex $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ showed no such evidence that a palladium(IV) intermediate was involved, but this possibility was not disproved.

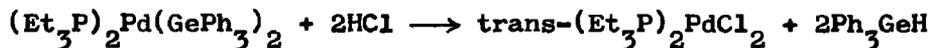
The lower stability of palladium(IV) compared with platinum(IV) complexes may be due to the stronger attraction of the palladium

nucleus for the 4d electrons as compared with the attraction of the platinum nucleus for the more diffuse 5d electrons. The result is that it will be energetically easier to remove outer d electrons from platinum(II) complexes than from palladium(II) complexes, and this is probably the reason for the difference in chemical behaviour of platinum-germanium and palladium-germanium complexes.

Hydrogen chloride, for example, reacted with $(Et_3P)_2Pt-(GePh_3)_2$ giving triphenylgermane, chlorotriphenylgermane, bis(triethylphosphine)platinum dichloride and bis(triethylphosphine)-platinum hydrido-chloride (102). These products could originate from addition of HCl to the complex followed by elimination of Ph_3GeH or Ph_3GeCl from the octahedral intermediate. This does not preclude the possibility that direct cleavage also occurred.



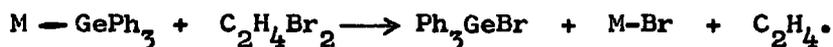
In contrast, dry hydrogen chloride in diethyl ether reacted with bis(triethylphosphine)bis(triphenylgermyl)palladium(II) giving only two products:



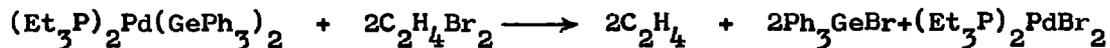
This could take place by direct cleavage or by oxidative addition giving the palladium(IV) intermediate followed by elimination of triphenylgermane exclusively.

Separation of the products by fractional crystallisation could not be effected and the mixture reacted further on sublimation giving palladium hydride species. This observation led to the separate investigation reported later.

Platinum-germanium and gold-germanium complexes reacted with 1,2-dibromoethane with the formation of ethylene, bromotriphenylgermane and the corresponding metal-halide complex (102, 105):



The palladium complex, $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ reacted with 1,2-dibromoethane in the expected manner. Ethylene was formed (90%), bromotriphenylgermane and the palladium dibromide complex.



Ligand exchange reactions of bis(triethylphosphine)bis(triphenylgermyl)palladium(II) have been carried out with varying

degrees of success. The phosphine ligands of the platinum analogue, $(Et_3P)_2Pt(GePh_3)_2$ were fairly strongly held (102b). Refluxing a solution of this complex with triphenylphosphine did not promote ligand exchange, but 1,2-bis(diphenylphosphino)ethane displaced triethyl phosphine giving the chelate complex.

Excess potassium thiocyanate did not react with $(Et_3P)_2Pd(GePh_3)_2$ in acetone solution and starting materials were recovered. It was thought that the triphenylgermyl group which has high trans effect might labilise the phosphine ligands and allow displacement by thiocyanate giving an ionic complex. However, the stereochemistry of $(Et_3P)_2Pd(GePh_3)_2$ is not known with certainty (it is probably trans on infrared spectral evidence) and the above hypothesis would only apply if there is at least a small equilibrium concentration of the cis isomer in solution. The complex, $(Et_3P)_2Pd(GePh_3)_2$ and 1,2-bis(diphenylphosphino)ethane in toluene solution were stirred together at room temperature. Decomposition took place over 30 minutes and products other than triethylphosphine and hexaphenyldigermene were not identified.

Potassium cyanide (2 mols.) reacted with a suspension of the complex in ethanol. A white precipitate of $K_2[(Ph_3Ge)_2Pd(CN)_2]$ was formed. The triethylphosphine liberated

was characterised by reaction with methyl iodide giving methyltriethylphosphonium iodide.

Addition of tetramethylammonium bromide (2 mols.) in methanol to a suspension of dipotassium bis(triphenylgermyl)-palladium dicyanide gave a solution from which a low yield of $(\text{Me}_4\text{N})_2 [(\text{Ph}_3\text{Ge})_2\text{Pd}(\text{CN})_2]$ crystallised on concentrating and cooling the solution. The thermal stability of the potassium salt $\text{K}_2 [(\text{Ph}_3\text{Ge})_2\text{Pd}(\text{CN})_2]$ is greater than that of the original complex, $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$, as indicated by the decomposition ranges, $112^\circ - 120^\circ$ and $97^\circ - 107^\circ$ respectively.

Booth and Chatt have studied the reactions of organoplatinum complexes $(\text{Et}_3\text{P})_2\text{PtR}_2$ (R = Me, Ph) with carbon monoxide, but products were isolable only in the case of the dimethyl complex (161). Biacetyl, $(\text{MeCO})_2$ and a novel platinum carbonyl complex $[\text{Pt}_3(\text{CO})_n(\text{PEt}_3)_4]$ (n = 3 or 4) which contained only bridging carbonyl groups ($\nu(\text{CO})$ 1766, 1773sh, cm^{-1}) were obtained.

Carbon monoxide at 70 atmospheres reacted with $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ in benzene solution over 5 days at 20° . The products were hexaphenyldigermane (80%) and a burgundy-red solution. On removal of the solvent a brown oil remained from which crystals could not be obtained. The infrared

spectrum of the oil showed characteristic triethylphosphine absorptions and 5 carbonyl bands. Aromatic C-H was absent.

Hydrogenolysis of platinum-germanium complexes has been studied in considerable detail (102, 106). The platinum complex $(\text{Et}_3\text{P})_2\text{Pt}(\text{GePh}_3)_2$ in ethyl acetate reacted with hydrogen at room temperature and 20 mm. pressure. Only one Pt-Ge bond was cleaved and the products were triphenylgermane and $(\text{Et}_3\text{P})_2\text{Pt}(\text{H})(\text{GePh}_3)$. The low value of the Pt-H stretching frequency (2051 cm^{-1}) indicated that the group trans to hydrogen had a high trans effect. Furthermore the tri-n-propylphosphine analogue showed $\nu(\text{Pt-H}) 1957 \text{ cm}^{-1}$ and the large difference suggests that one complex was of cis configuration and the other trans.

The chelate platinum-germanium complex, $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{-Pt}(\text{GePh}_3)_2$ and the palladium-germanium complex $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ can be effectively hydrogenated only at a higher pressure.

$(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Pt}(\text{GePh}_3)_2$ was recovered after stirring a suspension in xylene for 3 weeks in hydrogen at a pressure of just below 1 atmosphere (164). However, in benzene solution the complex reacted with hydrogen at 100 atmospheres over three days at 50° . Triphenylgermane and a platinum hydride showing $\nu(\text{Pt-H}) 1998 \text{ cm}^{-1}$ were obtained, together with a little

hexaphenyldigermane. The hydride, $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Pt} - (\text{H})\text{GePh}_3$ could not be obtained analytically pure, but the mass spectrum showed the molecular ion and the following calculated (165) and observed masses were recorded:

Calculated	Observed
895.1496	895.1446
896.1467	896.1460
897.1469	897.1443
898.1463	898.1457
899.1468	899.1464
900.1467	900.1497

This establishes without doubt the identity of the ion if allowance is made for the fact that the masses were measured by comparison with the heptacosafuorotributylamine 613.96473 peak.

The passage of hydrogen through a toluene solution of $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ at 0° at atmospheric pressure for 19 hours gave only brown tarry material. This did not contain triphenylgermane, indicating that hydrogenation did not precede decomposition. The complex was hydrogenated at 100 atmospheres over 7 days giving triphenylgermane and the unstable germyl-hydridopalladium complex, $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{GePh}_3$ which, as a semi-solid, showed $\nu(\text{Pd-H})$ 1890 cm^{-1} compared with 2035 cm^{-1} for a hexane solution of $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$. The low

value indicates that the Pd-H bond is very weak and the instability of this complex could be due to the easy promotion of an electron from this bond into an antibonding orbital (see page 28).

Recently it has been shown that hydrogenations of this type are reversible (164). Trimethylgermane reacts with bis(triethylphosphine)platinum hydrido-chloride giving hydrogen and $(Et_3P)_2Pt(Cl)GeMe_3$. This strongly suggests that the first step of the hydrogenation reaction is addition of hydrogen to give an octahedral platinum(IV) complex. This could explain why forcing conditions are necessary to hydrogenate the stereochemistry more rigid chelate phosphine platinum complex, and $(Et_3P)_2Pd(GePh_3)_2$.

Chapter 8

Palladium Hydride Complexes

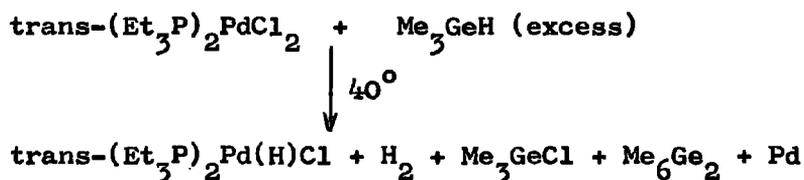
During the previous investigation, separation by sublimation of a mixture of triphenylgermane and bis(triethylphosphine)palladium dichloride showed evidence that a reaction was taking place giving chlorotriphenylgermane and a palladium hydride complex.

Difficulty experienced in removing excess triphenylgermane resulted in decomposition of the palladium hydride. This suggested that a study of the reaction of $(Et_3P)_2PdCl_2$ with trimethylgermane would be worthwhile since any germanium-containing products would be volatile and easily removed by pumping.

Methods of preparation of platinum hydride complexes usually involve a basic or an acidic environment (29, 30). Ethanolic potassium hydroxide, lithium aluminium hydride, hydrazine hydrate, hydrogen (which reacts forming HX) and formic acid have been used. One exception to this generalization is the preparation by Chalk and Harrod of bis(triethylphosphine)platinum hydrido-chloride using a trialkylsilane as the reducing agent (113b).

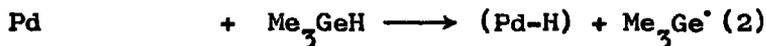
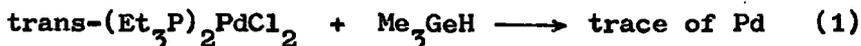
Trimethylgermane reacted with trans-bis(triethylphosphine)-palladium dichloride in periods ranging from 4 to 9 days at 35° giving a brown solution from which large colourless crystals of

trans-(Et₃P)₂Pd(H)Cl were obtained. The analogous bromide has been prepared but the reaction took longer (4 weeks at 35°). Other products, hydrogen, hexamethyldigermane and a trace of palladium metal suggested that the reaction took place by a free radical mechanism.



Mechanism of the reaction

The first process which takes place is probably decomposition of a small amount of the palladium dichloride complex in the presence of the reducing agent, trimethylgermane, to give the observed palladium mirror. The free radical reaction can then be initiated at the metal surface.



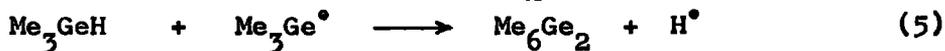
Two observations support this proposal. The first is that the reaction between bis(triethylphosphine)palladium dichloride and trimethylgermane to form the hydridochloride complex was accelerated by the addition of a small quantity of de-gassed

palladium black. A large proportion of the hydriochloride was then formed after 7 hours at 20° instead of 4 to 9 days at 35° in the absence of added palladium. The second observation which supports this initiation is that trimethylgermane was partly decomposed by palladium black at 20° giving hydrogen and hexamethyldigermene.

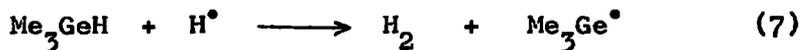
Having produced trimethylgermyl radicals, the following chain propagation stages could take place if a proportion of the $\text{Me}_3\text{Ge}^\bullet$ radicals escape into the solution.



The formation of hexamethyldigermene could be accounted for in two ways:

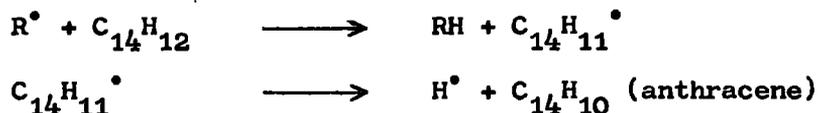


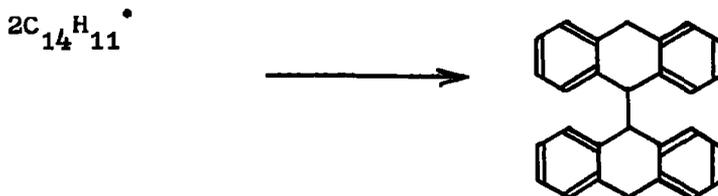
Step (5) is feasible only if it takes place at the palladium surface. If the highly reactive hydrogen radicals were formed in solution, a much larger variety of germanium-containing products would be expected. Hydrogen is probably formed as in step (7), again at the metal surface.



In further support of this theory that the reduction of $(\text{Et}_3\text{P})_2\text{PdCl}_2$ proceeds by a free radical mechanism the reactions have been carried out in the presence of a radical initiator and also a radical inhibitor. The initiator used was hexaphenylethane which exists in solution in equilibrium with triphenylmethyl radicals (166) and the inhibitor was 2,6-ditertiary butyl -4-methyl phenol (167). The initiated reaction was complete after 5 weeks at 20° but the inhibited reaction showed no sign of reacting after 4 months under the same conditions of temperature. It appears that hexaphenylethane is by no means as effective an initiator as palladium black which promoted complete reaction within 24 hours at 20° .

Finally, it has been shown that 9,10-dihydroanthracene can act as a free radical trap forming, transiently, hydroanthranyl radicals $\text{C}_{14}\text{H}_{11}^\bullet$ (168, 169). Opinions in the literature are divided concerning the nature of the final products. Anthracene or 9,9', 10, 10'-tetrahydrobianthranyl, produced by coupling of two $\text{C}_{14}\text{H}_{11}^\bullet$ radicals, have been reported.





When the reaction between bis(triethylphosphine)palladium dichloride and trimethylgermane was repeated in the presence of 9,10-dihydroanthracene a greater proportion of hydrogen was produced. Anthracene formed was isolated by column chromatography and hexamethyldigermene was not detected by mass spectrometry. 9, 9', 10, 10'-Tetrahydrobianthranyl was not detected. The increased quantity of hydrogen formed, and the appearance of anthracene are not in themselves evidence to support the radical mechanism since palladium metal is an effective dehydrogenation catalyst. However, the absence of hexamethyldigermene is significant in that trimethylgermyl radicals must preferentially attack the hydrocarbon rather than trimethylgermane.

Preparations

Trans-bis(triethylphosphine)palladium dichloride reacted with trimethylgermane at 35°. A faint palladium mirror was the first sign of reaction and then the yellow crystals were replaced by colourless prisms of bis(triethylphosphine)palladium

hydridochloride. Mixtures which contained palladium black reacted more quickly, but this convenience was offset by the difficulty of removing the metal.

The dibromide complex, $(Et_3P)_2PdBr_2$ reacted more slowly than the dichloride with trimethylgermane but a much cleaner product was obtained.

The complexes $(Pr_3^nP)_2PdCl_2$, $[(Et_3P)PdCl_2]_2$, $PhMeP(CH_2)_2 - PPhMe.PdBr_2$ and $(Ph_3P)_2PdCl_2$ did not give isolable hydridohalides. The bis(tri-n-propylphosphine) complex gave a brown viscous oil which showed $\nu(Pd-H) 2005\text{ cm}^{-1}$. Other complexes were reduced to the metal. The chlorine bridged binuclear complex began to decompose as the mixture was warmed to room temperature, but the triphenylphosphine complex, which was almost insoluble in trimethylgermane, gradually blackened over 1 week at 35° .

Attempts to prepare three different nickel hydrides were made. The green tetrahedral complex $(Ph_3P)_2NiCl_2$ was almost insoluble in trimethylgermane and did not form the hydride after 16 days at 35° . Colourless crystals which were isolated were identified as triphenylphosphine, and the other starting materials were recovered. The complex, $(Cp)Ni(PPh_3)Br$ was soluble in trimethylgermane at 35° and decomposition took place progressively over 6 hours giving a black residue

and brown viscous oil, neither of which contained nickel hydride species.

The purple square planar complex, $(\text{Et}_3\text{P})_2\text{NiBr}_2$ was freely soluble in trimethylgermane at 20° and reacted over 4 days at 20° giving a brown solution from which colourless crystals were obtained on cooling. The nickel containing product was liquid at room temperature and showed $\nu(\text{Ni-H})$ 1937 cm^{-1} . The product smelled strongly of triethylphosphine and could not be purified. The impure nickel hydride reduced carbon tetrachloride to chloroform which was identified by vapour phase chromatography. This is an established reaction of transition metal hydrides (127).

Trialkylsilanes have been used to reduce platinum dihalide complexes giving platinum hydridohalides (113b) and at first sight this seems analogous to the reduction of palladium dihalides by trimethylgermane. The analogy is quickly dispelled, however, since that reaction was considered to proceed via oxidative addition of trialkylsilane to form an octahedral platinum(IV) complex which eliminated halotrialkylsilane giving the palladium hydridohalide.

Reduction of $(\text{Et}_3\text{P})_2\text{PdCl}_2$ by trimethylsilane was attempted. Obvious advantages would be that trimethylsilane is much more readily available and less expensive than trimethylgermane.

However, up to the present time it has not been possible to prepare a useful quantity of bis(triethylphosphine)palladium hydriochloride by this method. The reaction has been examined over a range of temperature conditions and also in a quartz vessel with irradiation by ultraviolet light. Individual mixtures of bis(triethylphosphine)palladium dichloride and excess trimethylsilane did not appear to change during periods of 1-4 weeks at temperatures between 20 and 50°. Then in half an hour reaction took place giving palladium metal and alarming volumes of hydrogen. The residue after removal of volatile material showed $\nu(\text{Pd-H})$ 2033 cm^{-1} . The volatile products contained chlorotrimethylsilane but no hexamethyldisilane. One mixture of $(\text{Et}_3\text{P})_2\text{PdCl}_2$ and trimethylsilane gave traces of colourless crystals after 9 months at 20°.

The tin hydrogen bond is weaker than either the Si-H or Ge-H bond so trialkyltin hydrides ought to be much more effective than either organosilanes or organogermanes for the reduction of palladium dihalide complexes by a free radical mechanism. The reaction between triethyltin hydride and bis(triethylphosphine)-palladium dichloride was investigated. After 7 days at 18° a dark brown viscous oil was obtained which did not contain palladium hydride or tin hydride species. Hydrogen gas

accounted for all the Sn-H hydrogen. The liquid contained triethyltin chloride and hexaethylditin.

Properties of Palladium Hydrides

The complexes $(Et_3P)_2Pd(H)Cl$ and $(Et_3P)_2Pd(H)Br$ are colourless, crystalline solids. The chloride began to decompose at 55° in a nitrogen atmosphere and melted over the range $84-87^\circ$ (platinum analogue $82-83^\circ$). The bromide was somewhat more stable; it darkened at 64° and melted between 91 and 95° (platinum analogue $94-97^\circ$). Bis(triethylphosphine)palladium hydrido-chloride did not decompose in vacuum during 10 months at 20° . The crystalline complex was sufficiently stable in air to allow operations such as weighing to be done rapidly without any sign of decomposition. Solutions of the hydrides decomposed quickly on contact with air at room temperature although the bromide was somewhat less reactive than the chloride.

Infrared Spectra

The rate of reaction of $(Et_3P)_2Pd(H)Br$ was sufficiently low to allow measurement of $\nu(Pd-H)$ in chloroform solution. The values of $\nu(Pd-H)$ observed were $2029(KBr)$, $2025(CHCl_3)$ and 2002 cm^{-1} (hexane). These solvents were chosen since a particular transition metal hydride usually shows its highest (M-H) stretching

frequency in chloroform and its lowest (M-H) stretching frequency in hexane, which is non-polar (127). In the form of a KBr disc the (Pd-H) deformation at 712 cm^{-1} and characteristic triethylphosphine absorptions at $1453s$, $1414m$, $1376m$, $1263m$, $1248sh$, $1052s$, $1042sh$, $1001m$, $779sh$, $765s$, $691s$ and $630m$, cm^{-1} were observed.

Bis(triethylphosphine)palladium hydrido-chloride showed $\nu(\text{Pd-H})$ at 2035 (KBr), 2031 (CHCl_3), 2009 (hexane), $\delta(\text{Pd-H})$ 721 (KBr), $\nu(\text{Pd-Cl})$ 338 (Nujol mull) and the triethylphosphine absorptions mentioned above.

The iodide complex, $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{I}$ which was prepared by metathetical replacement of halogen but which was not analytically pure showed $\nu(\text{Pd-H})$ 2004 cm^{-1} (KBr).

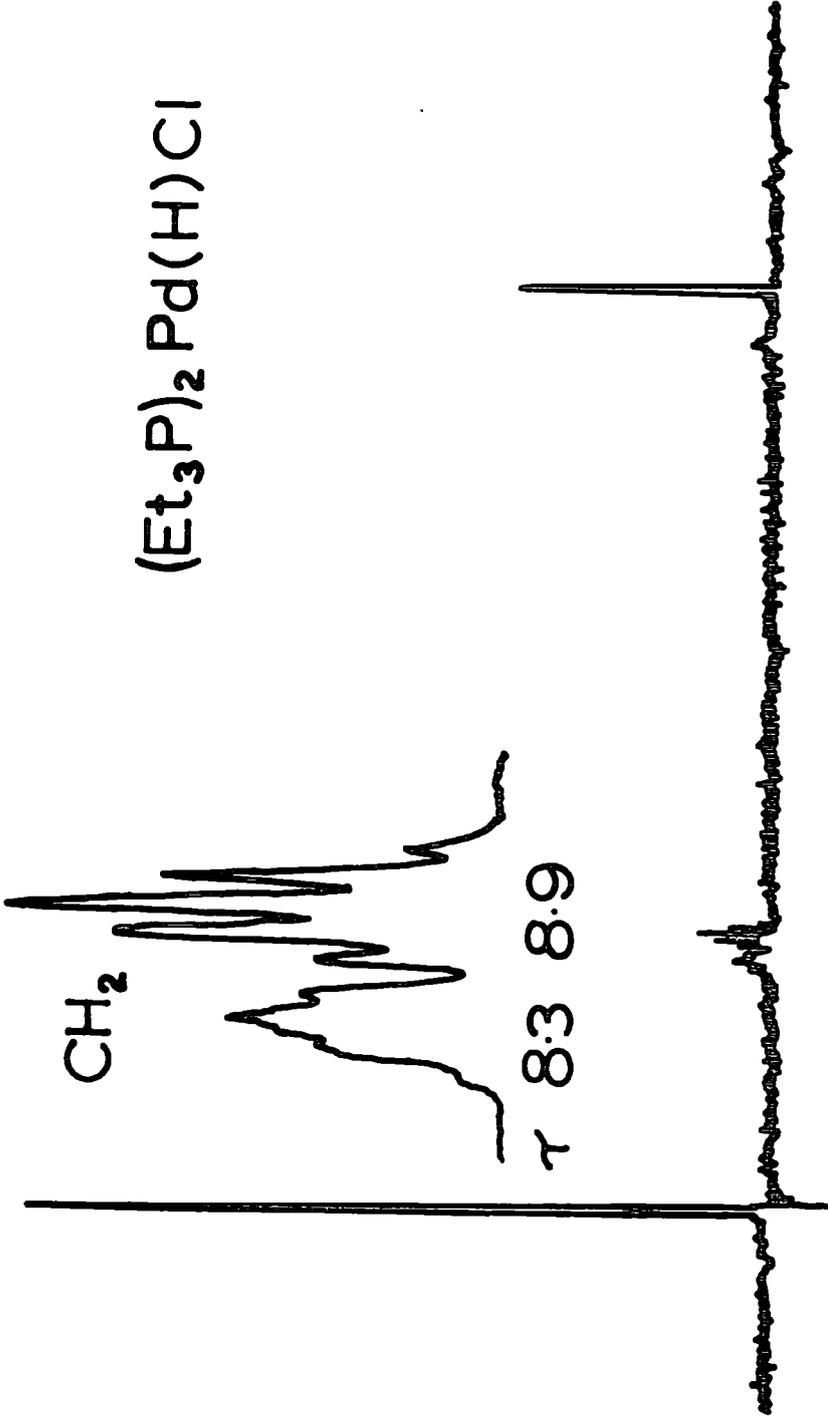
Proton Magnetic Resonance

The proton magnetic resonance spectrum of a 0.3M solution of $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ in benzene recorded at 60 Mc/s, is shown overleaf. The areas of the peaks are not in the direct ratios shown on the photograph; the signal level was changed from 20 μ volts to 1 m.volt for the Pd-H resonance and 400 μ volts for the expanded methyl proton resonances. The triethylphosphine proton resonances were located at $\tau 8.3$ and 8.9 relative to the internal standard, tetramethylsilane $\tau, 10$. The metal-bonded hydrogen shows the expected resonance at very high field, τ , 23.6 having

CH₃

CH₂

(Et₃P)₂Pd(H)Cl



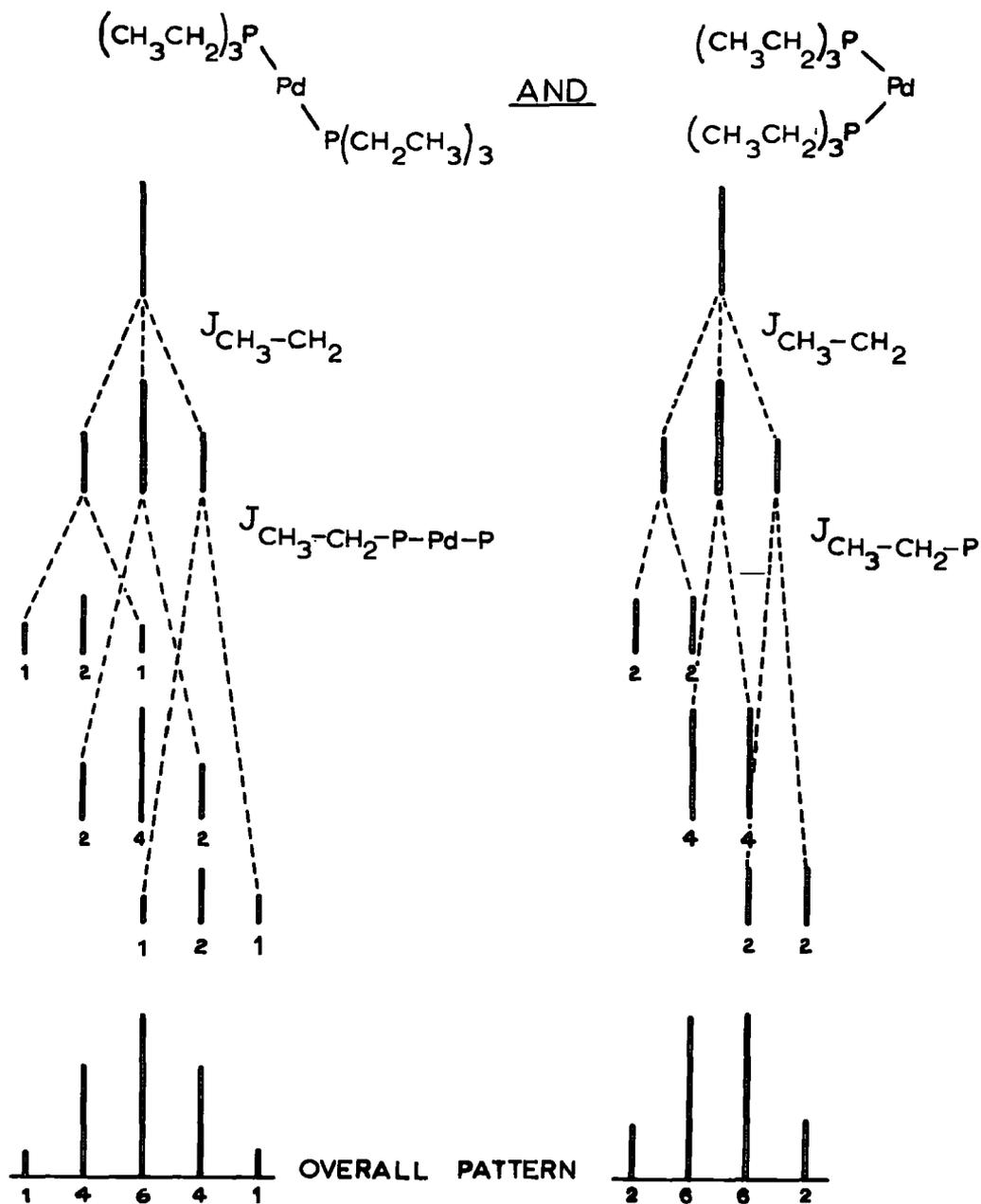
τ 2.7

C₆H₆

23.6

Pd-H

FIG. 10. METHYL PROTON RESONANCES OF



a half height line width 3 c.p.s. In contrast with the platinum analogue (see page 99), coupling with the metal was not observed, nor was coupling with phosphorus (^{105}Pd abundance 22%, spin $5/2$; ^{31}P abundance 100%, spin $1/2$). The hydridobromide complex, $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Br}$ showed the Pd-H resonance at τ 22.5

The triethylphosphine resonances provide a simple means of determining the stereochemistry of molecules (170, 171). A phenomenon known as virtual coupling has been observed in the p.m.r. spectra of tertiary phosphine complexes of platinum(II) and palladium(II). In complexes of trans configuration the methyl protons of triethylphosphine can couple with the methylene protons and both phosphorus nuclei (see Fig.10). It so happens that the coupling constants $J_{\text{CH}_3-\text{CH}_2}$ and $J_{\text{CH}_3-\text{CH}_2-^{31}\text{P}-^{105}\text{Pd}-^{31}\text{P}}$ are not resolved at 60 Mc/s. Coupling of the CH_3 with the CH_2 protons produces a 1:2:1 triplet and each of these lines is further split into a 1:2:1 triplet by long range coupling with the two phosphorus nuclei. Superimposition of these patterns produces a 1:4:6:4:1 quintet.

In cis complexes the methyl protons couple with the methylene protons and only the adjacent phosphorus nucleus.

Each of the 1:2:1 triplet lines produced by $\text{CH}_3 - \text{CH}_2$ coupling is split by the phosphorus nucleus into a symmetrical doublet. This gives as an overall pattern a 2:6:6:2 quartet.

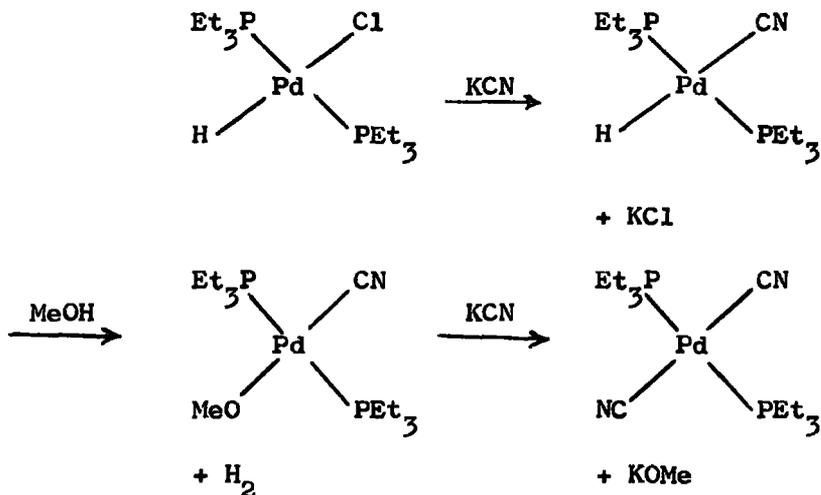
The photograph of the actual p.m.r. spectrum show the higher field ($\tau 8.9$) methyl proton resonances as a 1:4:6:4:1 quintet if allowance is made for the 'house roofing' effect. This indicates that $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ and $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Br}$ have trans configurations. The methylene proton resonances at $\tau 8.3$ are not well resolved and an analysis has not been possible.

Reactions of Palladium Hydrides

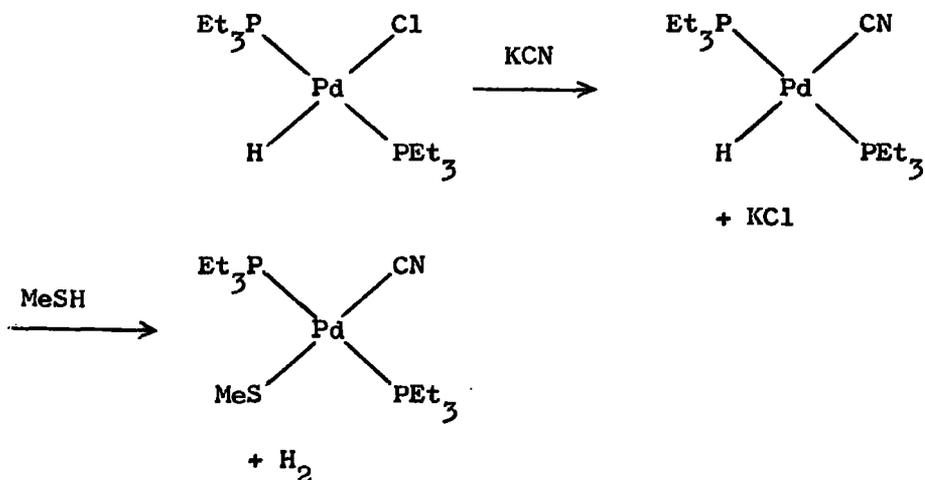
A few reactions of bis(triethylphosphine)palladium hydrido-chloride were carried out with the aim of metathetically replacing the chlorine ligand. An acetone solution of potassium iodide reacted giving the corresponding iodide which could not be obtained pure. The infrared spectrum with $\nu(\text{Pd-H})$ at the lower value of 2004 cm^{-1} (KBr) showed the greater trans effect of iodine.

Ammonium nitrate in acetone did not react with the hydrido-chloride complex and starting materials were recovered.

Potassium cyanide in acetone did not react with the hydridochloride, possibly because of the low solubility of the salt. However, in methanol an interesting series of reactions occurred with 2 mols. potassium cyanide. The palladium dicyanide complex, $\text{trans} - (\text{Et}_3\text{P})_2\text{Pd}(\text{CN})_2$ was formed together with 1 mol. of hydrogen per mol. of palladium hydridochloride used. Methanol must have taken part in the reaction to explain the formation of this quantity of hydrogen, but methanol alone did not react with $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ over 4 days at 20° . This suggested that the hydridochloride complex reacted with potassium cyanide giving initially the trans cyanohydride in which the hydrogen atom is labilised by the high trans effect of the cyanide ligand. The cyanohydride then reacted with methanol giving hydrogen and the methoxycyanide which reacted with the second mol. of potassium cyanide to form the dicyanide complex, $(\text{Et}_3\text{P})_2\text{Pd}(\text{CN})_2$.



The p.m.r. spectrum of the dicyanide complex showed a 1:4:6:4:1 quintet attributable to the CH_3 protons of the triethylphosphine ligands which, by the criteria described previously, indicates a trans configuration. To support this scheme, the reaction between $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ and 1 mol. of potassium cyanide was carried out in methanethiol solution. Sulphur is a much stronger ligand to palladium than is oxygen and the methylthiopalladium cyanide complex was isolated.



This behaviour contrasts with the lower reactivity of the analogous platinum hydrido-chloride. Potassium cyanide in aqueous methanol caused metathetical replacement of the chlorine ligand and the stable hydridocyanide, $(\text{Et}_3\text{P})_2\text{Pt}(\text{H})\text{CN}$ was isolated (29).

Dry hydrogen chloride in ethereal solution reacts with bis(triethylphosphine)platinum hydrido-chloride to form an octahedral platinum(IV) complex, $(Et_3P)_2PtH_2Cl_2$ (29, 139). This is sufficiently stable to allow isolation but slowly decomposes giving starting materials. Hot aqueous hydrochloric acid reacts giving hydrogen and $(Et_3P)_2PtCl_2$.

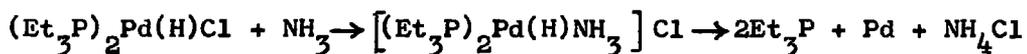
Dry hydrogen chloride in diethyl ether reacted rapidly at 20° with bis(triethylphosphine)palladium hydrido-chloride cleaving directly the Pd-H bond giving $(Et_3P)_2PdCl_2$ and hydrogen. This explains the failure to obtain palladium hydrido-halides from the reaction of hydrogen halides with tertiary phosphine palladium(0) complexes (139).

Carbon tetrachloride reacted with the palladium hydrido-chloride complex during 5 minutes at 20° . The products were bis(triethylphosphine)palladium dichloride and chloroform which was identified by vapour phase chromatography.

Ammonia reacted with $(Et_3P)_2Pt(H)Cl$ to form an ionic water-soluble salt, $[(Et_3P)_2Pt(H)NH_3]Cl$ (29). The palladium analogue reacted with concentrated ammonia solution giving immediately at room temperature a yellow solution, which quickly decomposed to a colourless solution over a black residue. No hydrogen was formed. Palladium and triethylphosphine oxide

(after distillation and sublimation in air) were obtained.

Ammonium chloride was expected but was not detected, possibly on account of the small scale of the reaction. The reaction probably proceeds as follows.



$(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Br}$ was treated with trimethyltin dimethylamine, $\text{Me}_3\text{-Sn.NMe}_2$ (1 mol.) in hexane. Although the mixture appeared to react and changed from colourless to light brown, only the original hydridobromide complex was isolated. The platinum hydrido-chloride complex, $\text{trans-}(\text{Et}_3\text{P})_2\text{Pt}(\text{H})\text{Cl}$ reacted with $\text{Me}_3\text{Sn.NMe}_2$ liberating dimethylamine and forming the platinum-tin complex, $(\text{Et}_3\text{P})_2\text{Pt}(\text{Cl})(\text{SnMe}_3)$. (172). More forcing conditions were used, and it may be possible to prepare the palladium-tin analogue if the mixture is refluxed in a higher boiling solvent.

Reactions with unsaturated compounds, acrylonitrile, phenylacetylene, tetrafluoroethylene and butadiene were carried out. In several cases the reactions appeared to be more complicated than those discussed previously.

Palladium complexes are good free radical polymerisation catalysts for unsaturated compounds. For this reason the complex $(\text{Ph}_3\text{P})_2\text{Pd}(\text{PhC}\equiv\text{CPh})$ could not be prepared by reduction of $(\text{Ph}_3\text{P})_2\text{Pd-Cl}_2$ with hydrazine in the presence of diphenylacetylene (66).

Acrylonitrile was polymerised by bis(triethylphosphine)-palladium hydrido-chloride giving a yellow plastic product. This incorporated triethylphosphine groups and left a residue of palladium on ignition.

Phenylacetylene reacted with $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Br}$ giving an oil from which a small quantity of orange crystals were obtained. This compound melted sharply without decomposition and the formula which best fitted the analytical data was $(\text{C}_8\text{H}_6)_7^- \text{Pd}(\text{PEt}_3)(\text{H})\text{Cl}$. The reaction could not be reproduced when an attempt was made to obtain material for further study.

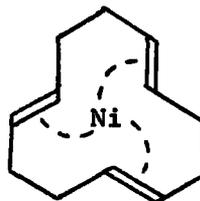
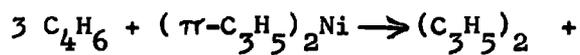
Tetrafluoroethylene reacted with $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ at room temperature. There was considerable decomposition with the formation of palladium metal and a mixture of white and yellow crystals was also formed. Chromatography on alumina separated the mixture into yellow and white components; the yellow crystals were identified as $(\text{Et}_3\text{P})_2\text{PdCl}_2$. The mass spectrum of the colourless crystals indicated that they were a mixture containing $(\text{Et}_3\text{P})_2\text{PdCl}_2$, $(\text{Et}_3\text{P})_2\text{Pd}(\text{C}_2\text{F}_4)\text{H}$ and $(\text{Et}_3\text{P})_2^- \text{Pd}(\text{C}_3\text{F}_5)\text{Cl}$. The latter product suggested that the tetrafluoroethylene contained hexafluoropropene. The mixture could not be separated by further chromatography. Reaction of the

platinum hydride, $(\text{Et}_3\text{P})_2\text{Pt}(\text{H})\text{Cl}$ with tetrafluoroethylene also gave a complexity of products (173) including $(\text{Et}_3\text{P})_2\text{Pt}(\text{Cl})-\text{CF}=\text{CF}_2$ by elimination of HF.

Butadiene reacted with $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ giving an orange oil and pale yellow crystals which both showed $\nu(\text{C}=\text{C})$, 1610cm^{-1} . The crystals melted sharply without decomposition, $24-25^\circ$. Butadiene reacts with cobalt carbonyl hydride, $\text{HCo}(\text{CO})_4$ to give two geometrical isomers of π -crotyltricarbonylcobalt (54). It was thought that the reaction of $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ with butadiene might follow an analogous course to give $(\pi\text{-crotyl})\text{Pd}(\text{PEt}_3)\text{Cl}$. An independent preparation of the latter compound from π -crotylpalladium chloride dimer and triethylphosphine established that these products were not identical. The mass spectrum indicated that the main component of the yellow crystals did not contain chlorine, although a trace of $(\text{Et}_3\text{P})_2\text{PdCl}_2$ was detected. Elemental analysis corresponded to an empirical formula $\text{C}_{30}\text{H}_{66}\text{P}_3\text{Pd}_2$ which can be formulated $(\text{Et}_3\text{P})_3\text{Pd}_2(\text{C}_4\text{H}_7)_3$. The n.m.r. spectrum was examined but was very complicated due partly to overlap of the triethylphosphine and the other proton resonances.

It has been shown that π -allyl complexes such as bis $(\pi\text{-allyl})\text{nickel}$ and $(\pi\text{-allyl})\text{Ni}(\text{PEt}_3)\text{Cl}$ bring about trimerisation

of butadiene to form cyclododecatriene (174). Biallyl was displaced from $(\pi\text{-C}_3\text{H}_5)_2\text{Ni}$ and intermediate nickel complexes were isolated.



Further reaction with butadiene gave cyclododecatriene.

EXPERIMENTAL

Germyl-Palladium Complexes

(1) $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ Method (1).

A solution of triphenylgermyl-lithium in monoglyme was prepared from hexaphenyldigermene (9.5 g.) and lithium shot (1.8g). The solution was filtered through glass wool and cooled to -20° . Bis(triethylphosphine)palladium dibromide (4.1 g.) in a mixture of diethyl ether (100 ccs) and benzene (30 ccs) was added dropwise with stirring. The colour changed from brown to orange and a pale yellow precipitate was formed. The mixture was hydrolysed with de-gassed water (50 ccs.) just above 0° to remove excess lithium, triphenylgermyl-lithium and precipitated lithium bromide. The yellow solid, bis(triethylphosphine)bis(triphenylgermyl)-palladium(II) was filtered from the solution. Yield 4.3 g, 55%. Purification was by extraction with toluene at 20° followed by filtration, rapid cooling to -20° , dilution with light petroleum (b.p. $40-60^\circ$) until the mixture became turbid and allowing the solid to crystallise overnight at low temperature. (Found C, 60.3; H, 6.1; P, 6.4. $\text{C}_{48}\text{H}_{60}\text{Ge}_2\text{P}_2\text{Pd}$ requires C, 60.6; H, 6.4; P, 6.5%). The crystals decomposed without melting, $96-107^\circ$. The solution from the filtration was dried over anhydrous magnesium sulphate but darkened on standing at -20° and deposited a white solid, hexaphenyldigermene.

Method (2).

Triphenylgermyl-lithium was prepared from triphenylgermane (7.3g.) and n-butyl-lithium (12.8ccs. 1.87M) in ether (50 ccs.) After stirring for 30 minutes, bis(triethylphosphine)palladium dichloride (5.0g) in a mixture of ether (100 ccs) and benzene (50 ccs) was added dropwise at room temperature. A pale yellow precipitate was formed and the solution became orange but darkened rapidly as the last 10 ccs. of palladium dihalide solution were added. The mixture was cooled rapidly to -78° , stirred for $1\frac{1}{2}$ hours and then filtered. The residue was washed with ether and dried. The infrared spectrum, flame and Beilstein tests showed that it contained lithium chloride and hexaphenyldigermene (4.0g.). The solution from the filtration was hydrolysed with water (50 ccs) and dried over anhydrous magnesium sulphate. By this time the solution had become dark brown. Yellow crystals formed overnight at -20° . The solution was decanted from the crystals which were washed with ether at -78° . The infrared spectrum and decomposition range were identical with those of a sample of $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ prepared previously. Yield 3.5g., 31%. The solution was treated with de-gassed decolorising charcoal which changed the colour from dark brown to pale yellow. Removal of the solvent left a semi-solid (1.0g) which consisted largely of hexaphenyldigermene.

(2) $(\text{Pr}_3^{\text{n}}\text{P})_2\text{Pd}(\text{GePh}_3)_2$.

Bis(tri-n-propylphosphine)palladium dichloride (1.6g) in ether (75ccs) was added to a solution of triphenylgermyl-lithium made from triphenylgermane (2.1g) and n-butyl-lithium (3.35ccs. 2.01M). The orange solution and precipitate were stirred for 1 hr. at -40° . Work up similar to that described previously gave pale yellow crystals (1.2g). (Found C, 65.2; H, 6.64; P, 5.1. $\text{C}_{54}\text{H}_{72}\text{Ge}_2\text{P}_2\text{Pd}$ requires C, 62.5; H, 6.96; P, 6.0%). The complex decomposed without melting $86-100^\circ$. The analytical data suggests that the product was contaminated with hexaphenyldigermene ($\text{C}_{36}\text{H}_{30}\text{Ge}_2$ requires C, 71.1; H, 4.94; P, 0%). Purification by recrystallisation from ether at low temperature was attempted but decomposition took place.

(3) $(\text{Ph}_3\text{P})_2\text{PdCl}_2 + \text{Ph}_3\text{GeLi}$.

A solution of triphenylgermyl-lithium from hexaphenyldigermene (6.4g) and lithium shot (1.5g) in monoglyme and filtered through glass wool) was added to a suspension of bis(triphenylphosphine)-palladium dichloride in ether (150 ccs) and benzene (50 ccs) at -20° . The solution, which was grey immediately after the addition of Ph_3GeLi , was treated as before and kept at temperatures between -15° and -50° except during hydrolysis and filtration.

Only hexaphenyldigermane and a black deposit containing palladium metal (X-ray fluorescence spectrum) were obtained.

(4) Bipyridylpalladium dichloride + Ph₃GeLi.

Bipyridylpalladium dichloride (3.4g) in monoglyme (100 ccs) at -20° was treated with a filtered solution of Ph₃GeLi prepared from hexaphenyldigermane (9.5g) and excess lithium shot. The mixture was black by the time half of the Ph₃GeLi had been added. Hexaphenyldigermane was the only pure material isolated.

(5) (Ph₂PCH₂CH₂PPh₂)PdCl₂ + Ph₃GeLi.

Ph₃GeLi (from hexaphenyldigermane (5.0g) and excess lithium shot) was added to a suspension of the chelate phosphine palladium dichloride complex (2.6g) in monoglyme (50 ccs) at -30°. The brown solution was filtered and the residue (0.4g) consisted largely of lithium chloride and hexaphenyldigermane. Benzene (50 ccs) and ether (100 ccs) were added to the solution which was hydrolysed and dried over magnesium sulphate. Solvent was partly removed by pumping and hexaphenyldigermane (0.7g) was filtered off. The solution was decolorised with charcoal and brown crystals (0.2g) formed on standing overnight at -20°. The crystals decomposed without melting 130-134°. (Found C, 65.4; H, 5.1; P, 6.1.

(Ph₂PCH₂CH₂PPh₂)Pd(GePh₃)₂ i.e. C₆₂H₅₄Ge₂P₂Pd requires C, 66.9; H, 4.9; P, 5.6%). Decomposition took place when recrystallisation

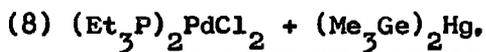
from ether was attempted. The mother liquors then yielded starting material, $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{PdCl}_2$ (0.1g) and a brown intractable tar.

(6) $(\text{Et}_3\text{P})_2\text{NiBr}_2 + \text{Ph}_3\text{GeLi}$.

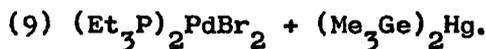
Bis(triethylphosphine)nickel dibromide (1.9g) in ether (25 ccs) was added to a solution of Ph_3GeLi made from hexaphenyldigermene (5.0g) and excess lithium. The mixture at -40° rapidly became dark brown and the emergent nitrogen smelled strongly of triethylphosphine. Solvent was removed after hydrolysis and a brown oil remained which showed $\nu(\text{Ge-H}) 2033 \text{ cm}^{-1}$. (Ph_3GeH formed by hydrolysis of excess Ph_3GeLi). Extraction of the oil successively with benzene and light petroleum (b.p. $40-60^\circ$) gave hexaphenyldigermene (0.1g) and impure starting material $(\text{Et}_3\text{P})_2\text{NiBr}_2$ (11mg).

(7) $(\text{Ph}_3\text{P})_2\text{NiCl}_2 + \text{Ph}_3\text{GeLi}$.

Triphenylgermyl-lithium, prepared from hexaphenyldigermene (5.0g) and excess lithium shot in monoglyme, was added to a suspension of bis(triethylphosphine)nickel dichloride (2.7g) in a mixture of ether (75 ccs) and benzene (75 ccs) at -20° . The brown solution was hydrolysed and filtered. Only hexaphenyldigermene (1.7g) and black tarry material were obtained.



A solution of bis(trimethylgermyl)mercury (0.9 g., 2.1 m.moles.) in benzene was added dropwise to a solution of bis(triethylphosphine)-palladium dichloride (0.85g., 2.1 mmoles) in 60 ccs. benzene-ether (1:5) at -10° . After stirring for 30 minutes at room temperature the yellow solution was filtered from the deposit of mercury formed. On standing overnight at -20° decomposition set in, 5mg. of the binuclear complex $[(\text{Et}_3\text{P})\text{PdCl}_2]_2$, identified by infrared spectrum and M.p. 235° , could be hand sorted from the grey deposit of palladium and only brown tar was recovered from the solution.



A mixture of bis(trimethylgermyl)mercury (1.15g., 2.6mmoles) and $(\text{Et}_3\text{P})_2\text{PdBr}_2$ (1.32g., 2.6 mmoles) in ether (200 ccs.) deposited mercury over 2 hours at temperatures between -30° and -78° . The mercury was removed by filtration. Starting material, $(\text{Et}_3\text{P})_2\text{PdBr}_2$ (1.2g, 91%) was recovered with a trace of $(\text{Et}_3\text{P})_2\text{Pd(H)Br}$ on removal of solvent. The infrared spectrum showed no evidence for Ge-CH₃ rock around 810 or Ge-C stretch at 550 cm^{-1} .



Potassium (0.175g., 4.5 m moles) was dissolved in liquid ammonia which had been dried over sodium in a vacuum apparatus. Germane (6.2 m moles) was condensed into the trap and the mixture was cautiously allowed to warm to -20° and the blue colour of the solution was discharged. The solvent was removed by pumping for 5 hours at -78° and 30 minutes at 20° to leave a grey powder, $GeH_3K \cdot 2NH_3$. A suspension of cis- $(Et_3P)_2PtCl_2$ (1.1g., 2.2 m moles) in warm benzene (150 ccs.) was added. On stirring the mixture for 4 hours with occasional warming to 40° the solution became pale yellow, but a grey solid settled out on standing. The solvent was removed from the filtered solution and starting material, $(Et_3P)_2PtCl_2$ was recovered (1.0g., 91%).

This reaction was repeated and the solution of $(Et_3P)_2PtCl_2$ and GeH_3K was heated. At 60° the mixture began to darken. The solution was rapidly cooled to -78° and the solvent was removed by pumping at low temperature. Further decomposition took place and an intractable black tar was obtained.



Germyl-lithium was prepared from lithium (14mg., 2 m moles) and germane (3 m moles) in liquid ammonia. The solvent was removed and the residue became yellow on pumping for 1 hr. at 20° . Cis- $(Et_3P)_2PtCl_2$ (1.0g., 2 m moles) in benzene was added and the

mixture was stirred and warmed. Decomposition began at 55° and only tarry material was obtained when the solvent was removed.

Reactions of $(Et_3P)_2Pd(GePh_3)_2$.

(12) Pyrolysis.

Bis(triethylphosphine)bis(triphenylgermyl)palladium(II) (0.242 g.) was heated in a vacuum apparatus. The colour began to change from yellow to pale grey at 97° and was dark charcoal grey at 107°. The volatile products were separated by fractional condensation and identified as hydrogen (0.9 cc. at N.T.P.; mass spectrum), ethylene (4.9 cc. at N.T.P. infrared spectrum), benzene (8 mg.) and triethylphosphine (33 mg.) (mass spectra). The solid residue was fractionally sublimed and gave tetraphenylgermane and hexaphenyldigermane at 140° and 180° respectively, and these were characterised by their far infrared spectra. The black residue was Soxhlet extracted with benzene and a mixture of tetraphenylgermane and hexaphenyldigermane (0.139 g.) was obtained. The black residue (32 mg.) consisted of finely divided palladium (X-ray fluorescence spectrum).

(13) Reaction with hydrogen chloride.

Dry hydrogen chloride was passed through a suspension of the complex (0.249 g.) in ether (20 ccs) at -20°. The solvent was removed and a mixture of triphenylgermane and trans- $(Et_3P)_2PdCl_2$ was obtained ($\nu(Ge-H)$, 2038, $\nu(Pd-Cl)$ 354;

characteristic triphenylgermane bands at 318 and 290 cm^{-1}).

$(\text{Et}_3\text{P})_2\text{PdCl}_2$ m.p. 135-136 $^\circ$ was obtained by crystallisation from light petroleum (b.p. 40-60 $^\circ$). The residue from the mother liquors was sublimed at 70 $^\circ$ /10 $^{-4}$ mms. The sublimate consisted of triphenylgermane with a small amount of palladium hydride showing $\nu(\text{Pd-H})$ 2012 as a shoulder on the Ge-H stretching frequency, 2035 cm^{-1} . The residue which contained chlorotriphenylgermane, $\nu(\text{Ge-Cl})$, 378 cm^{-1} , decomposed at 90 $^\circ$.

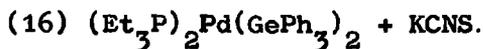
(14) Triphenylgermane and $\text{trans}-(\text{Et}_3\text{P})_2\text{PdCl}_2$

A finely ground mixture of Ph_3GeH and $(\text{Et}_3\text{P})_2\text{PdCl}_2$ was sublimed at 50 $^\circ$ /10 $^{-4}$ mm. The first sublimate consisted of pure triphenylgermane but the second fraction showed, in addition to $\nu(\text{Ge-H})$, a shoulder at 2011 cm^{-1} due (Pd-H) stretch in the complex $(\text{Et}_3\text{P})_2\text{Pd(H)Cl}$. The residue showed only (Ge-H) stretch in the 2000 cm^{-1} region so the palladium hydride complex sublimed as it was formed. Further sublimation and recrystallisation from hexane gave chlorotriphenylgermane, m.p. 112-114 $^\circ$.

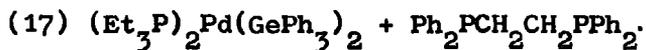
(15) $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ and 1,2-dibromoethane.

$(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ (0.107g) was stirred with 1,2-dibromoethane in a vacuum apparatus. Ethylene (4.54 ccs. at N.T.P., 90%) was removed by pumping through a trap at -78 $^\circ$ and was identified by its infrared spectrum. Excess 1,2-dibromoethane was removed

leaving a yellow residue which was extracted with methanol. The solution was filtered from white insoluble material which was identified by far infrared spectrum as hexaphenyldigermane (10 mg). A mixture of yellow $\text{trans}-(\text{Et}_3\text{P})_2\text{PdBr}_2$ (m.p. $135-136^\circ$) and colourless bromotriphenylgermane (m.p. $133.5-134.5$) crystals was obtained from the solution and these were separated by hand. They were further characterised by their infrared spectra.



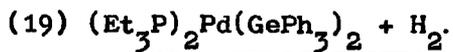
$(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ (9.5 mg) in acetone was treated with excess potassium thiocyanate in methanol. The mixture was stirred at room temperature for 30 minutes but the germanium-palladium complex was only partly soluble. The solvent was removed by pumping and the residue was washed with water leaving starting material $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$.



The palladium complex (0.5g) was treated with 1,2-bis(diphenylphosphino)ethane (0.2g) in toluene (15 mls.). The precipitate which formed was filtered off and recrystallised from toluene giving hexaphenyldigermane (0.2g). The deep red solution darkened as the solvent was removed by pumping at 20° and an intractable brown oil remained.



$(Et_3P)_2Pd(GePh_3)_2$ (0.295 g) in suspension in ethanol was treated with potassium cyanide (0.04g) dissolved in the minimum volume of water. A white precipitate formed as the mixture was stirred for 45 minutes. The precipitate was filtered off, washed with ethanol and dried. The solid decomposed without melting, 112-120°. (Found C, 54.6; H, 4.0; N, 3.0; $K_2 [(CN)_2Pd(GePh_3)_2]$ i.e. $C_{38}H_{30}Ge_2K_2N_2Pd$ requires C, 54.0; H, 3.6; N, 3.3%) The infrared spectrum showed $\nu(C\equiv N)$ 2084 cm^{-1} . and characteristic Ph_3Ge absorptions at 1477, 1425, 1074, 736 and 699 cm^{-1} . Yield 0.25g., 96%. The ethanolic filtrate containing triethylphosphine was distilled onto excess methyl iodide, giving methyltriethylphosphonium iodide after removal of excess methyl iodide and ethanol. Yield 0.104 g., 64%. Characterisation was by comparison of the infrared spectrum with an authentic sample. The experiment was repeated and the potassium complex in suspension in acetone was treated with 2 mols. tetramethylammonium bromide in methanol. A low yield (15%) of colourless needles of $(Me_4N)_2 [(CN)_2Pd(GePh_3)_2]$ was obtained. (Found C, 59.6; H, 5.8. $C_{46}H_{54}Ge_2N_4Pd$ requires C, 60.4; H, 5.9%). The infrared spectrum showed $\nu(C\equiv N)$ 2088 cm^{-1} and on recrystallisation from isopropanol, two additional cyanide bands were observed at 2109 and 2123 cm^{-1} .



(i) Atmospheric pressure

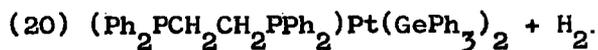
A slow stream of hydrogen was bubbled through a solution of $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ in toluene at 0° for 19 hrs. Extensive decomposition occurred giving a black residue which did not contain triphenylgermane, indicating that hydrogenation probably did not precede decomposition.

(ii) 100 atmospheres

$(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ (0.2 g.) in benzene (100 ccs.) was hydrogenated for 7 days at 20° at a pressure of 100 atmospheres. A dark green solution was obtained which, on removal of solvent, left a black residue showing $\nu(\text{Pd-H})$ 1890 and $\nu(\text{Ge-H})$ 2037 cm^{-1} .

Repeated extraction with pentane at -20° gave a brown solution from which an oil was obtained. Triphenylgermane sublimed from the oil at 50° . The residue which was insoluble in pentane had an infrared spectrum similar to $(\text{Et}_3\text{P})_2\text{Pt}(\text{H})\text{GePh}_3$. Recrystallisation at low temperature was attempted but the complex began to decompose.

(Found C, 57.0; H, 6.0; $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{GePh}_3$ i.e. $\text{C}_{30}\text{H}_{46}\text{GeP}_2\text{Pd}$ requires C, 55.6; H, 7.2%)



The chelate platinum-germanium complex $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{-Pt}(\text{GePh}_3)_2$ (0.4 g.), prepared by Dr. Cross, was hydrogenated in

benzene (15 ccs) at 100 atmospheres for 2 days at 20° and 2 days at 50°. A clear, colourless solution was obtained which gave a white powder on removal of the solvent. The powder was extracted with pentane (10 ccs) giving triphenylgermane (0.15 g.), characterised by its infrared spectrum; $\nu(\text{Ge-H})$ 2036 cm^{-1} . The residue was washed a further 3 times to remove triphenylgermane, and recrystallised from benzene. The product showed $\nu(\text{Pt-H})$ 1998 cm^{-1} (Nujol Mull) and the analytical data given below was obtained after repeated recrystallisation from benzene and then ethanol. (Found C, 57.4; H, 4.38; $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Pt}(\text{H})\text{GePh}_3$ i.e. $\text{C}_{44}\text{H}_{40}\text{GeP}_2\text{Pt}$ requires C, 58.7; H, 4.47%) Mp. 221-223° (dec). Satisfactory accurate mass measurements on the molecular ion of the platinum hydride were obtained.

(21) $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ and carbon monoxide.

The complex (1.0g) in benzene (20 ccs) was treated with carbon monoxide at 20° (70 atmospheres) for 6 days. A red solution and white solid were obtained. The solid was filtered off, washed with benzene and identified by infrared spectrum as hexaphenyldigermane (0.49g., 80%). Benzene was removed from the solution by pumping at 0° leaving a brown oil which showed characteristic triethylphosphine absorptions at 1453, 1412, 1377, 1260, 1038, 998, 764, 735 and carbonyl bands at 2040, 1960,

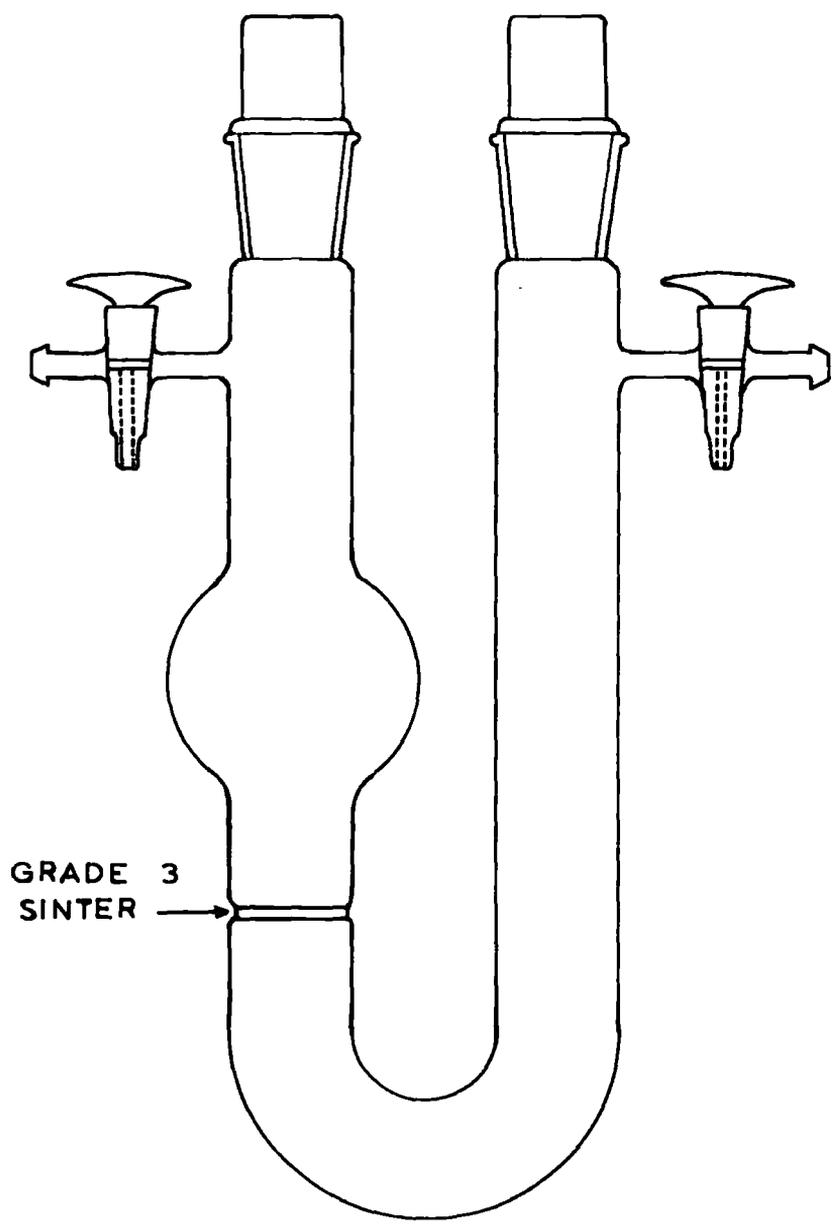
1923, 1852 and 1808 cm^{-1} . The residue was extracted with pentane and cooled repeatedly to -78° . Each time an oil was obtained which slowly decomposed.

Palladium Hydride Complexes

(1) Preparation of $(Et_3P)_2Pd(H)Cl$

Bis(triethylphosphine)palladium dichloride (2.76g) and trimethylgermane (1.8g) sealed in an evacuated tube fitted with a break-seal were warmed to 40° and the yellow crystals partly dissolved. After two days a faint palladium mirror was observed and the solution became progressively more brown. During a further two days at 40° the yellow palladium dichloride complex was totally replaced by colourless crystals. The tube was opened to a vacuum apparatus into which hydrogen (32.8 ccs. at N.T.P.) and volatile products were removed leaving a dark brown residue. The volatile material was examined by mass spectrometry and shown to contain chlorotrimethylgermane (Ge-Cl pattern with most abundant mass 154), hexamethyldigermane (Ge_2 pattern centred on 236 m.u.) and unreacted trimethylgermane. Vapour phase chromatography indicated that the liquid mixture contained Me_3GeCl and Me_6Ge_2 in the ratio 1:2.35 using a flame ionisation detector. The solid residue was transferred quickly in air onto the sintered disc of the apparatus shown in Fig.11 and washed with the minimum volume of diethyl ether at -78° to wash impurities through the sinter. The solution could easily be kept above the sinter or forced through it by

FIG. II. LOW TEMPERATURE
FILTRATION APPARATUS



manipulation of the nitrogen pressures on each side of the sinter. Yield of bis(triethylphosphine)palladium hydridochloride 1.7 g., 65%. (Found C, 38.0; H, 8.00; $C_{12}H_{31}ClP_2Pd$ requires C, 38.0; H, 8.24%). The crystals began to decompose at 55° and melted over the range $84-87^\circ$.

One reaction was stopped after the mixture had become brown but before the yellow crystals of $(Et_3P)_2Pd(H)Cl$ had been completely replaced by colourless palladium hydride complex. A mixture of crystals remained, therefore, after removal of the volatile products and laborious hand sorting was necessary to obtain pure hydride.

(2) $(Et_3P)_2PdCl_2$, Me_3GeH and palladium black

$(Et_3P)_2PdCl_2$ (1.0g), trimethylgermane (1.4g) and palladium black (0.1g) which had been heated and pumped for 4 hours ($80^\circ/10^{-4}$ mm). were sealed in an evacuated tube. After 7 hours at room temperature the yellow dichloride complex had not completely dissolved but colourless crystals formed when the solution was decanted and cooled to -20° . The reaction was complete after 24 hours at 18° . Volatile products were removed by pumping. The hydridochloride complex was dissolved in diethyl ether (15 ccs), filtered through a sintered disc (porosity 3) to remove palladium metal and crystallised on cooling to -40° . Yield 0.6g., 65%.

(3) Trimethylgermane and palladium black

Trimethylgermane (0.8g) and de-gassed palladium black (88 mg.) were sealed in an evacuated tube. After 4 days at 20°, permanent gas was removed and identified as hydrogen (mass spectrum). The mass spectrum of the liquid product showed that hexamethyldigermane was present. (The Ge₂ isotope pattern was observed having the most abundant isotope combination at 236 mass units, due to the molecular ion Me₆Ge₂. The Me₅Ge₂ ion was also observed having most abundant mass 221.)

(4) Preparation of (Et₃P)₂Pd(H)Br

Bis(triethylphosphine)palladium dibromide (1.5g), trimethylgermane (2.2g) and de-gassed palladium black were sealed together in an evacuated tube. After 1 day at 45° the yellow crystals had been completely replaced by large colourless crystals of bis(triethylphosphine)palladium hydridobromide. Volatile products were removed by pumping and the crystals were washed with ether on a sinter at -78° (Fig.11). The best crystals were selected for analysis and the last traces of palladium were removed mechanically. (Found C, 34.2; H, 6.94. C₁₂H₃₁Br₂P₂Pd requires C, 34.0; H, 7.3%). Yield of crude product 1.2g., 95%.

The reaction between bis(triethylphosphine)palladium dibromide and trimethylgermane in the absence of palladium black

took place much more slowly. It was complete after 4 weeks at 35° giving the hydridobromide crystals as large, highly refracting crystals. The inconvenience of the long reaction time was offset to some extent by the fact that by far the cleanest products were obtained from these reactions.

(5) $(Et_3P)_2PdCl_2 + Me_3GeH +$ radical initiator and inhibitor.

Bis(triethylphosphine)palladium dichloride (1.0g., 2.4 mmoles), hexaphenylethane (0.24g., 0.5 mmole) and trimethylgermane (2.2g.) were sealed together in vacuum. The initiator completely dissolved in the solvent at room temperature. After 3 weeks at 18° the first colourless crystals of $(Et_3P)_2Pd(H)Cl$ had formed and the reaction was complete after 5 weeks. Concurrently, a tube was sealed containing $(Et_3P)_2PdCl_2$ (1.0g., 2.4 m moles), trimethylgermane, (2.2g) and 4-methyl-2,6-di^{di}tertiary butyl phenol (0.11g., 0.5 mmole). The two tubes were kept under identical temperature conditions and this tube containing inhibitor showed no sign of reaction after 15 weeks at room temperature.

(6) $(Et_3P)_2PdCl_2, Me_3GeH$ and 9,10-dihydroanthracene

Bis(triethylphosphine)palladium dichloride (2.0g.), trimethylgermane (4.8g.) and 9,10-dihydroanthracene (0.3g) were sealed in an evacuated tube. The reaction had gone to

completion after 2 days at 20°. A large volume (192.3 ccs. at N.T.P.) of hydrogen was formed (identified by mass spectrum). The mass spectrum of the volatile products indicated that chlorotrimethylgermane and unreacted trimethylgermane were present. Hexamethyldigermane was not detected. The residue was transferred to a sintered disc at -78° and washed repeatedly with ethanol at -78° until infrared examination of the residue showed that anthracene and dihydroanthracene were no longer present. The colourless crystals remaining on the sinter were palladium hydrido-chloride complex. The residue from the filtrate was chromatographed on alumina using light petroleum (b.p. 40-60°) followed by benzene as eluents. Anthracene, identified by its ultraviolet spectrum (λ_{\max} 245 (sh) and 253m μ) and dihydroanthracene were recovered in combined yield 0.21g.

(7) (Et₃P)₂PdCl₂ and Me₃SiH

Bis(triethylphosphine)palladium dichloride (3.0g) was sealed in an evacuated tube with trimethylsilane (2.5g) in which it was almost insoluble. The tube was heated to 40° for 1 week with no obvious change but after a further 2 days at 60° the mixture became black as the palladium dichloride complex dissolved and reacted. Volatile products were removed by pumping. Hydrogen (101 ccs. at N.T.P.) was identified by mass spectrum. The vapour which condensed

at -196° contained chlorotrimethylsilane and unreacted trimethylsilane but no hexamethyldisilane. (The mass spectrum showed the Me_3SiCl isotope pattern at 108, 109 and 110 mass units and the Me_2SiCl pattern at 93, 94 and 95 mass units.) A black residue remained which showed $\nu(\text{Pd-H})$ 2033 cm^{-1} . An attempt to isolate $(\text{Et}_3\text{P})_2\text{Pd(H)Cl}$ by fractional sublimation at $40^{\circ}/10^{-5}\text{ mm}$. was not successful and led to further decomposition.

A mixture of $(\text{Et}_3\text{P})_2\text{PdCl}_2$ and Me_3SiH which had been kept at 20° for 4 weeks was heated to 45° for 2 hours without change but during the next 30 minutes extensive decomposition occurred giving a similar mixture of products. A tube containing $(\text{Et}_3\text{P})_2\text{PdCl}_2$ (0.5g) and excess trimethylsilane gave a slight palladium mirror inside the tube after 4 months at 18° and the first colourless crystals of $(\text{Et}_3\text{P})_2\text{Pd(H)Cl}$ were observed after 9 months at 18° .

(8) $(\text{Et}_3\text{P})_2\text{PdCl}_2$ and Et_3SnH

Bis(triethylphosphine)palladium dichloride (0.5g) and triethyltin hydride (4.3g., 21 m moles) were sealed together. During 2 weeks at 18° the yellow crystals almost completely dissolved to give a viscous solution which darkened progressively from yellow to brown. Hydrogen (230.5 ccs. at N.T.P., 10.3 m moles), which accounted for all the hydridic hydrogen, was removed.

The solution was separated from the dark semi-solid by pipette. The mass spectrum of the liquid showed the ion patterns of diethyltin chloride and hexaethylditin with most abundant peaks at 213 and 412 m.u. respectively. (the molecular ion Et_3SnCl was obscured). The infrared spectra of both liquid and solid products indicated that tin hydride and palladium hydride species were not present.

(9) $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ and Me_3GeH

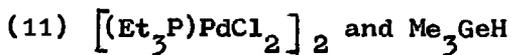
Bis(triphenylphosphine)palladium dichloride (2.0g) and excess trimethylgermane were sealed together. The solid was almost insoluble in trimethylgermane and darkened progressively at 35° until after 1 week it was black. Hydrogen (62.6 ccs. at N.T.P.) and volatile products (chlorotrimethylgermane and trimethylgermane, identified by mass spectra) were separated leaving the black solid, the infrared spectrum of which did not show a Pd-H stretching frequency.

The reaction was repeated in the presence of de-gassed palladium black. Decomposition again took place and the palladium hydride was not formed.

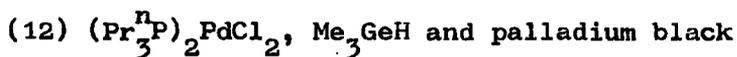
(10) $(\text{MePhPCH}_2\text{CH}_2\text{PPhMe})\text{PdBr}_2$, Me_3GeH and palladium black

1,2-bis(methylphenylphosphino)ethane palladium dibromide (1.0g), palladium black (0.1g) and trimethylgermane (1.2g) were sealed together. After 1 week at 20° and 1 week at 45° the

mixture had changed colour from yellow to deep red. Hydrogen (63.8 ccs. at N.T.P.) was removed. The colour of the residue changed back to yellow on removal of the volatile products and only palladium and the original dibromide complex were obtained.



A solution of the bridged binuclear complex $[(Et_3P)PdCl_2]_2$ (1.7g) in trimethylgermane (1 cc) darkened immediately at 20°. After 2 days hydrogen (256 ccs. at N.T.P.) and volatile products were removed. The black residue did not contain palladium hydride species.



Bis(tri-n-propylphosphine)palladium dichloride (1.0g), trimethylgermane (0.9g) and palladium black (0.1g) were sealed together. During 2 days at 20° a dark brown viscous solution was obtained. Hydrogen (41 ccs. at N.T.P.) and volatile products were separated leaving the impure hydride $(Pr_3^n P)_2 Pd(H)Cl$ as a brown oil. The infrared spectrum in hexane solution showed $\nu(Pd-H)$ 2005 cm^{-1} . Purification by low temperature crystallisation from ether solution was attempted, but was unsuccessful and decomposition occurred.

(13) $(Et_3P)_2NiBr_2$ and Me_3GeH

Bis(triethylphosphine)nickel bromide (1.0g) and trimethylgermane (1.0 cc.) changed colour from red to brown during 4 days at room temperature. Large, almost colourless crystals formed on cooling the solution to -20° . Volatile products were separated and identified by mass spectrometry as hydrogen (16.2 ccs at N.T.P.), chlorotrimethylgermane and unreacted trimethylgermane. Hexamethyldigermane was not detected. Extraction with light petroleum (b.p. $40-60^\circ$) and cooling to -78° gave light brown crystals which were recrystallised from petroleum at low temperature. The crystals melted at room temperature and decomposed to a dark brown liquid which smelled strongly of triethylphosphine. The infrared spectrum of the liquid showed $\nu(Ni-H)$ 1937 cm^{-1} (contact film). Carbon tetrachloride was added to the light brown crystals and after 24 hours at 18° the volatile products were removed by pumping. Vapour phase chromatography of the liquid using 10% apiezon L suspended on celite in 5 foot columns at 65° showed that it contained chloroform.

(14) $(Ph_3P)_2NiCl_2$ and Me_3GeH

The tetrahedral complex, bis(triphenylphosphine)nickel dichloride (0.5 g) and trimethylgermane (2.3g) were sealed together and heated to 35° for 2 weeks. After that time a small amount of

colourless crystals formed on cooling the solution. No hydrogen was formed. The colourless crystals were separated and identified as triphenylphosphine (infrared spectrum). Other than this, only unreacted trimethylgermane and bis(triphenylphosphine)nickel dichloride were isolated.

Reactions of $(Et_3P)_2Pd(H)Cl$ and $(Et_3P)_2Pd(H)Br$

(15) $(Et_3P)_2Pd(H)Cl + KI$

Bis(triethylphosphine)palladium hydridochloride (52 mg.) a 2-fold excess of potassium iodide (4.4 mg.) and acetone (2 ccs) were sealed in an evacuated tube. A flocculent yellow precipitate and a small amount of grey material were rapidly formed at room temperature. Hydrogen (0.31 cc. at N.T.P.) and acetone were removed. The infrared spectrum of the crude solid product showed $\nu(Pd-H)$ at 2004 cm^{-1} (KBr disc). Extraction of the solid with pentane at -30° followed by filtration and cooling to -78° gave colourless crystals of bis(triethylphosphine)palladium hydriodide which were washed with cold pentane and pumped at $-20^\circ/10^{-4}\text{ mm.}$ for 3 hours. (Found C, 32.8; H, 6.36; $C_{12}H_{31}IPd_2$ requires C, 30.6; H, 6.64%).

(16) $(Et_3P)_2Pd(H)Cl + NH_4NO_3$

The hydride complex (50.6 mg.) ammonium nitrate (21.1 mg.) and acetone (2 ccs.) were sealed together. After 1 week at room

temperature volatile products were removed leaving a semi-solid. Only the original complex, $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ was isolated on extraction with pentane.

(17) $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ and methanol

$(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ (0.22g.) was treated with methanol (1.5 ccs.) for 4 days at 18° . A negligible volume of hydrogen was formed (0.08 cc. at N.T.P.) and methanol was removed leaving the original hydridochloride complex (0.20 g., 91%).

(18) $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ and methanolic KCN

Bis(triethylphosphine)palladium hydridochloride (0.205g., 0.542 m mole), potassium cyanide (70 mg., 1.08 m mole) and methanol (1.0 cc.) were sealed together. At room temperature the solution rapidly became yellow and then changed to colourless as a white precipitate formed. Hydrogen (11.2 ccs. at N.T.P.) (0.50 m mole) and methanol were removed by pumping. The residue was extracted with benzene and yielded bis(triethylphosphine)-palladium dicyanide which was recrystallised from a mixture of propanol and pentane at -30° . (Found C, 42.6; H, 7.45; N, 7.12; $\text{C}_{14}\text{H}_{30}\text{N}_2\text{P}_2\text{Pd}$ requires C, 42.6; H, 7.66; N, 7.10%). $\nu(\text{C}\equiv\text{N})$, 2128 cm^{-1} (benzene solution). The proton magnetic resonance spectrum showed a 1:4:6:4:1 quintet attributable to coupling of the CH_3 protons with the methylene protons and virtual coupling with the two ^{31}P nuclei (see Fig.10), indicating that the complex had trans configuration.

(19) $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$, potassium cyanide and methanethiol

$(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ (0.187 g., 0.49 m mole), potassium cyanide (32 mg., 0.49 m mole) and methanethiol (1.5 cc.) were sealed in an evacuated tube. At room temperature the solution rapidly became yellow and a grey precipitate formed. Hydrogen (9.89 ccs. at N.T.P., 0.44 m mole) and excess methanethiol were removed. The residue was extracted with pentane and yellow crystals of bis(triethylphosphine)methylthiopalladium cyanide (0.13g., 63%) were obtained on cooling the solution to -50° . (Found C, 40.6; H, 7.7; N, 3.7. $(\text{Et}_3\text{P})_2\text{Pd}(\text{SMe})\text{CN}$, i.e. $\text{C}_{14}\text{H}_{33}\text{NP}_2\text{PdS}$ requires C, 40.5; H, 7.9; N, 3.4%).

(20) $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ and carbon tetrachloride

The complex (51 mg.) and carbon tetrachloride (0.2 cc.) reacted during 5 minutes at 20° giving a yellow solution. No hydrogen was formed. The volatile products were examined by v.p.c. and shown to contain chloroform (0.136 m mole, 63%). Extraction of the residue with ethanol gave bis(triethylphosphine)-palladium dichloride (49 mg., 88%) m.p. $139-139.5^\circ$.

(21) $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ and hydrogen chloride

$(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ (84 mg.) was sealed in vacuum with excess dry hydrogen chloride in ether. The solution rapidly became yellow

at room temperature. Hydrogen (4.47 ccs. at N.T.P., 91%) and solvent were removed. The solid product was recrystallised from ethanol giving $(\text{Et}_3\text{P})_2\text{PdCl}_2$, m.p. 139° (73 mg., 80%).

(22) $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ and aqueous ammonia

The hydride complex (51 mg.) and 0.880 ammonia (2.0 ccs.) gave a yellow solution at room temperature which then decomposed. After 12 hrs. there was a colourless solution above a black metallic residue. No hydrogen was formed. The solution was distilled to low volume in air and the residue was heated after it had been pumped to remove final traces of water. White crystals of triethylphosphine oxide (identified by infrared spectrum) sublimed. Ammonium chloride was expected but was not detected.

(23) $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Br}$ and $\text{Me}_3\text{Sn}\cdot\text{N Me}_2$

The hydridobromide complex (0.6 g.) was sealed in a tube with trimethyltindimethylamine (0.25g.) and pentane (5 ccs.). The mixture appeared to have reacted during 10 minutes at 20° giving a brown solution and pale cream crystals but only the original hydridobromide complex (0.55 g.) remained on removal of the solvent.

(24) $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ and acrylonitrile

The hydridochloride complex (50.8 mg.) was sealed with acrylonitrile (2.0 ccs.) and after 14 hours at 20° a pale yellow precipitate was observed. The only volatile product was unreacted

acrylonitrile (0.16g.) identified by v.p.c. A yellow plastic remained which was Soxhlet extracted with pentane and then benzene. A grey solid (2 mg.) was obtained which was infrared inactive and which contained palladium. The infrared spectrum of the yellow plastic showed $\nu(\text{C}\equiv\text{N})$ 2237 cm^{-1} . Ignition left a residue of palladium.

(25) $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ and phenylacetylene.

The hydridochloride complex (51.3 mg.) was sealed in a tube with phenylacetylene (0.6 cc.) Removal of volatile material (phenylacetylene only) from the brown solution left an orange oil. The infrared spectrum showed characteristic triethylphosphine bands and phenylacetylene absorptions including $\nu(\text{C}\equiv\text{C})$ 2105 cm^{-1} . Extraction with light petroleum (b.p. $40-60^\circ$) and cooling of the solution to -30° gave a small amount of orange crystalline material, m.p. $69-70^\circ$ without decomposition. Found, C, 77.8; H, 6.21% and a satisfactory formulation has not been made. The Beilstein test for halogen was positive and the crystals left a residue of palladium on ignition. The infrared spectrum showed that triethylphosphine was present. The reaction was not reproducible when attempts were made to repeat the reaction to obtain material for further study. A brown oil was obtained and efforts to induce crystallisation from various solvents, light petroleum, methylcyclohexane, ethanol

and methanol were not successful.

(26) $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ and tetrafluoroethylene

The hydrido-chloride complex (0.38g.), tetrafluoroethylene (0.5 g.) and pentane (3.0 ccs.) were sealed together in a 250 ml. bulb. After 2 days at 20° considerable decomposition had occurred giving palladium metal and a mixture of white and yellow crystals was observed inside the bulb. Hydrogen (3.6 ccs. at N.T.P.) was removed. Crystallisation from pentane at -78° gave a mixture of crystals (0.2g). The yellow crystals were separated by hand sorting and identified as $(\text{Et}_3\text{P})_2\text{PdCl}_2$. The remainder was chromatographed on alumina using benzene-pentane 1:1 as eluent. Yellow crystals and a colourless fraction (0.16g.) were obtained. The mass spectrum indicated that the colourless fraction was a mixture. The following ions were identified: $(\text{Et}_3\text{P})_2\text{PdCl}_2$ (PdCl_2 isotope pattern with most abundant mass 414), $(\text{Et}_3\text{P})_2\text{PdC}_2\text{F}_4\text{H}$ (Pd isotope pattern with most abundant mass 443), $(\text{Et}_3\text{P})_2\text{PdClC}_3\text{F}_4$ (PdCl pattern, 491) and $(\text{Et}_3\text{P})_2\text{PdClC}_3\text{F}_5$ (PdCl pattern 510). Chromatography of the colourless crystals did not give a further separation.

(27) $(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}$ and butadiene

The hydride complex (2.0g.) was sealed in a tube with butadiene (2.3g). The solution slowly became yellow at room temperature. No hydrogen was obtained from this reaction but

in other cases hydrogen has been obtained accounting for up to 11% of the hydridic hydrogen. Excess butadiene was removed leaving a yellow oil. Fractional crystallisation from pentane at low temperature gave first a yellow oil and then pale yellow crystals, m.p. 24-25°. The infrared spectrum showed triethylphosphine absorptions and $\nu_{C=C}$, 1640 cm^{-1} . The mass spectrum showed a minute trace of $(\text{Et}_3\text{P})_2\text{PdCl}_2$ as the only chlorine containing component. Ions having the palladium isotope pattern with most abundant masses at 332, 278 and 224 were thought to be $(\text{Et}_3\text{P})\text{Pd}(\text{C}_4\text{H}_6)_2$, $(\text{Et}_3\text{P})\text{PdC}_4\text{H}_6$ and $(\text{Et}_3\text{P})\text{Pd}$ respectively. Found C, 49.4; H, 8.97; P, 12.6%. If the crystals do not contain chlorine, this leads to an empirical formula $\text{C}_{30}\text{H}_{66}\text{P}_3\text{Pd}_2$ which can be formulated $(\text{Et}_3\text{P})_3\text{Pd}_2(\text{C}_4\text{H}_7)_3$. The p.m.r. spectrum was too complicated for interpretation due to overlapping of the triethylphosphine and other protons.

Experimental Methods

Nitrogen. All operations on air-sensitive compounds were carried out in an atmosphere of dry oxygen-free nitrogen. Commercial nitrogen was passed through copper turnings at 400° to remove oxygen and through a column containing molecular sieve and then a spiral trap at -196° to remove water.

Solvents. Hydrocarbon solvents, benzene, toluene, light petroleum, methylcyclohexane and also diethyl ether were dried by standing over sodium wire for 1 week. Methanol was refluxed with, and then distilled from magnesium methoxide immediately before use. Tetrahydrofuran and 1,2-dimethoxyethane were distilled from potassium and benzophenone and then from lithium aluminium hydride before use.

Analyses. Carbon, hydrogen, phosphorus and nitrogen analyses were carried out in the microanalytical laboratory of Durham University or by Drs. Weiler and Strauss, Banbury Road, Oxford.

Infrared Spectra in the region $2.5-25\mu$ were recorded on a Grubb-Parsons Spectromaster or G.S. 2A. Spectrophotometer. Solids were examined as pressed discs in KBr or KI or as Nujol Mulls. Liquids were examined as contact films between KBr plates. A Grubb-Parsons DM2. spectrophotometer was used to examine the region $20-50\mu$. Solids were examined as Nujol Mulls between CsI plates protected by thin polythene.

Proton Magnetic Resonance spectra were recorded, usually in benzene solution, on a Perkin-Elmer R10 spectrometer.

Preparation of Starting Materials

(1) Bis(triethylphosphine)palladium dichloride (175) Triethylphosphine (16.5 g., 0.14 mole) was added dropwise with stirring to a solution of sodium chloropalladite, $\text{Na}_2\text{PdCl}_4 \cdot 2\text{H}_2\text{O}$ (23.2g., 0.07 mole) in water (500 ccs.). The yellow precipitate was filtered off and recrystallised from ethanol containing a little triethylphosphine. Yield 23.8 g., 82%. M.p. 139°.

Other phosphine palladium halide complexes were prepared similarly.

(2) Hexaphenyldigermene (79) Phenylmagnesium bromide was prepared from bromobenzene (886 g., 4.1 moles) and magnesium (155g., 6.5 moles) in 2.5 litres of diethyl ether. Germanium tetrachloride (100 g., 0.47 mole) in toluene (1 litre) was added slowly to the Grignard reagent in the presence of free magnesium. The solid was filtered off in air and washed with dilute acetic acid to destroy magnesium. The hexaphenyldigermene was purified by Soxhlet extraction with chloroform. Yield 93.8 g., 66%.

(3) Bromotriphenylgermane. Bromine (10.0g., 0.063 mole) was added dropwise with stirring to a solution of hexaphenyldigermene (38 g., 0.063 mole) in 1,2-dibromoethane (250 ccs.) at reflux temperature. The solvent was removed by distillation and the product was reduced without purification.

(4) Triphenylgermane (176) The crude bromotriphenylgermane, dissolved in ether and benzene (1:1; 400 ccs), was added to lithium aluminium hydride (5g.) in ether (500 ccs.). The mixture was refluxed for 2 hours and then hydrolysed with 2N sulphuric acid.

Triphenylgermane was separated by ether extraction and purified by vacuum distillation ($140-147^{\circ}/10^{-3}$ mm.) and recrystallisation from light petroleum (b.p. $40-60^{\circ}$).

(5) Triphenylgermyl-lithium (a) (86) Hexaphenyldigermene (10.0g) was added to freshly prepared lithium shot (5g.) in thoroughly dry apparatus. The crystals were moistened with 1,2-dimethoxyethane (monoglyme) and the appearance of a yellow colour was awaited. The mixture was then stirred slowly and monoglyme was added (up to 20 ccs.) as the colour of the solution deepened. The reaction was deemed complete when no crystals settled to the bottom of the solution on standing. Reaction times varied from 3 to 15 hours. Yields of Ph_3GeLi were assumed to vary between 70% and 60% respectively, to allow for any loss by reaction with the solvent. The solution was filtered through glass wool before use.

(b) (177). Triphenylgermane (7.3g., 0.024 mole) was dissolved in ether (50 ccs.) and the solution was cooled to 0° . n-Butyllithium (0.024 mole) in hexane was added dropwise and the mixture was stirred at room temperature for 30 minutes to ensure complete reaction. A yield of 95% was assumed.

(6) Tetramethylgermane. Methylmagnesium bromide was prepared from magnesium (120 g., 4.9 moles) and methyl bromide (380g., 4.0 moles) in di-n-butyl ether. The mixture was cooled in ice-water during the addition of the halide and then refluxed for 3 hours. Germanium tetrachloride (150 g., 0.70 mole) in 200 ccs. di-n-butyl ether was added dropwise and the mixture was maintained at 60° for a further 3 hours. The fraction containing Me₄Ge was distilled from the mixture without hydrolysis, and the product was separated from di-n-butyl ether by fractionation. Boiling range 41.5-44°; Yield 66g., 71%.

(7) Bromotrimethylgermane. Tetramethylgermane (76g., 0.58 mole) was sealed in a tube with excess bromine (115g., 0.72 mole). After 1 week at 20° the mixture was fractionated giving first bromine then Me₃GeBr, b.p. 114°. Final traces of bromine were removed by shaking the product with mercury. Yield 102g., 89%.

(8) Trimethylgermane. Dioxane was dried by refluxing with sodium and distilled on to lithium aluminium hydride (3.0g.) Bromotrimethylgermane (45g.) was added dropwise and the apparatus was arranged so that dioxane refluxed and trimethylgermane distilled as it was formed into a flask at -78°. Yield 22.4g., 83%. The product was separated from dioxane by passage through two traps at -78° and condensation at -196° in a vacuum apparatus.

(9) Bis(trimethylgermyl)mercury.(178) Sodium amalgam, prepared from mercury (230g.) and sodium (1.15g., 0.05g.atom), was shaken for three weeks in a sealed flask with cyclohexane (20 ccs.) and bromotrimethylgermane (9.7g., 0.049 mole). The organic layer was extracted with cyclohexane and filtered from mercury. Solvent was removed by pumping and the yellow product was purified by sublimation at $83^{\circ}/10^{-2}$ mm. Yield 3.6g., 34%.

APPENDIX

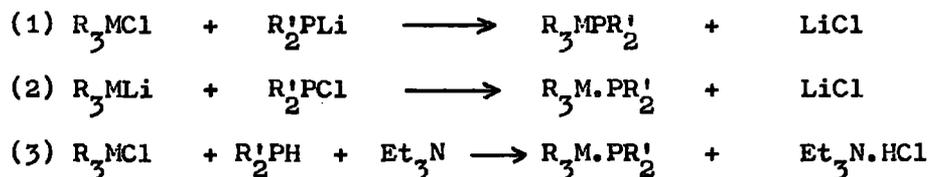
Diphenylphosphino-organogermanes

The object of this work was to study the preparation and properties of compounds in which germanium is bonded to phosphorus and to prepare tetrakis(diphenylphosphino)germane, $(\text{Ph}_2\text{P})_4\text{Ge}$.

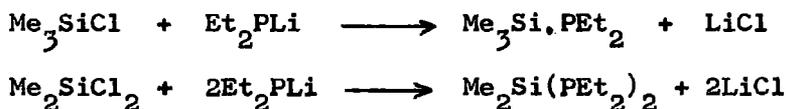
Introduction

All of the group (IVb) elements form covalent bonds to phosphorus in compounds of the type $\text{R}_3\text{M.PR}'_2$ and $\text{R}_2\text{M.}(\text{PR}'_2)_2$ (M = Si (179, 180), Ge, Sn (180, 181, 182) and Pb (179)).

Three methods of preparation have been used:



The first method has been used to prepare a variety of silicon phosphorus compounds in ethereal solution (179, 180).

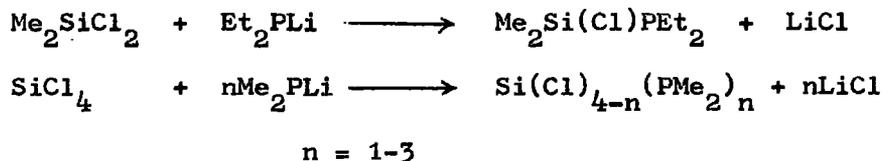


Sodium diphenylphosphide has been used successfully, instead of lithium diethylphosphide.



The reaction of silicon tetrachloride with lithium-diethylphosphide (1:4) showed the complication that tetraethyl-diphosphine was formed in addition to tetrakis(diethylphosphino)-silane.

Partially substituted halophosphinosilanes have been isolated by reaction of halosilanes with less than the amount of lithium dimethylphosphide required for complete replacement of the halogens (179).



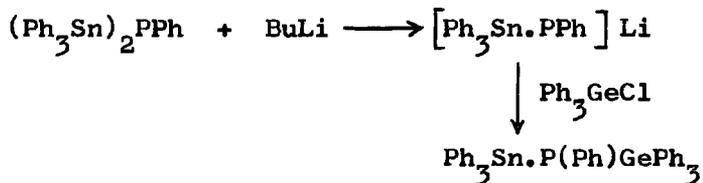
This type of reaction has been used to prepare triethylgermyldiphenylphosphine from bromotriethylgermane and lithium diphenylphosphide in tetrahydrofuran (T.H.F.) (184).



Kuchen and Buchwald (180) prepared the first tin-phosphorus compound by reaction of sodium diphenylphosphide with triethyl tin bromide in ether.



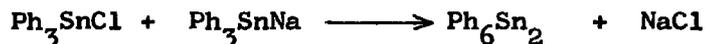
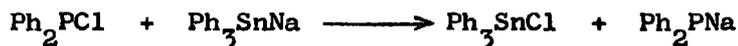
Compounds having both germanium- and tin-phosphorus bonds have recently been made (185) e.g.



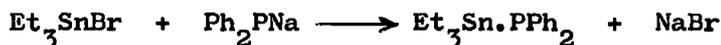
Reactions of type 2, using a chlorophosphine and an organotin-alkali metal compound, have been carried out but there is some doubt about the nature of the products. Schumann, Kopf and Schmidt (182, 186) claimed that the reaction



gave a good yield of the tin-phosphorus compound, but they also claim to have isolated a cyclic trimer $(\text{Ph}_2\text{Sn.PPh})_3$ formed by the cleavage of phenyl-tin and phenyl-phosphorus bonds. This must be suspected since alkali metals in T.H.F. cleave only one phenyl group from triphenylphosphine. Campbell, Fowles and Nixon obtained only hexaphenylditin from a similar reaction by halogen-metal exchange.



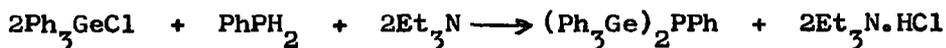
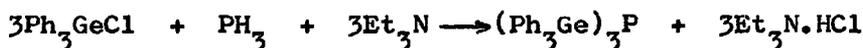
These workers were able to isolate $\text{Ph}_3\text{Sn.PPh}_2$ from diphenylphosphinomagnesium bromide and triphenyltin chloride in ether-benzene. The melting points reported do not agree ($103-105^\circ$ (181), $127-130^\circ$, (182, 186)). A reaction in liquid ammonia was more satisfactory for the preparation of liquid trialkyltin compounds.



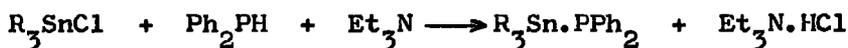
Any unreacted triethyltin bromide was removed as the solid ammoniate before distillation.

Treatment of phenylphosphine sodium, PhPHNa, with triethyltin bromide did not give the expected hydride but phenylbis(triethyltin)phosphine $(Et_3Sn)_2PPh$. Attempts to make compounds having P-Sn-P links were successful only in the case of $Ph_2Sn(PPh_2)_2$. Diethylbis(diphenylphosphine)tin, $Et_2Sn(PPh_2)_2$ was probably formed but distillation caused disproportionation.

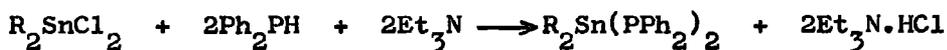
The third type of reaction using triethylamine as a base to eliminate HCl from diphenylphosphine and the organometal halide has been used to prepare germanium, tin and lead compounds. (187, 182, 183).



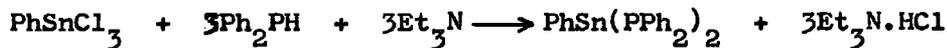
Compounds having 1 to 4 tin-phosphorus bonds have been made.



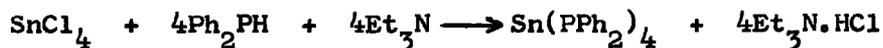
M.p. (R = Ph) 127-130°; (R = n-Bu) 90-96°.



M.p. (R = Ph) 78-80°; (R = n-Bu) 98-102°.

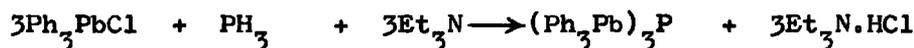
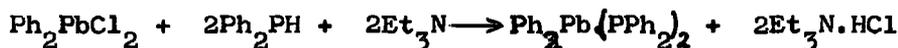
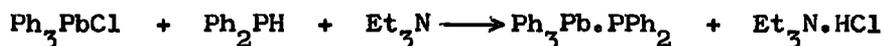


M.p. 115-117°.



Organolead-phosphorus compounds were prepared in benzene solution by reaction of stoichiometric amounts of the lead chloride,

diphenylphosphine and triethylamine (183, 185).



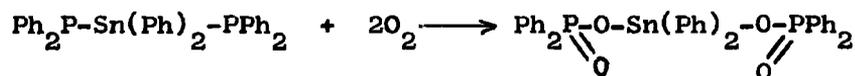
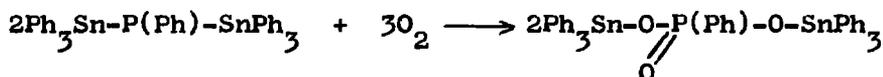
Organolead-phosphorus compounds were less stable than the analogous tin compounds.

Properties and Reactions

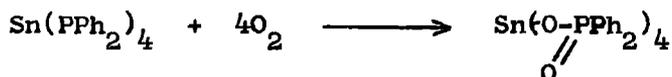
Silicon-,germanium-, tin-and lead-phosphorus compounds are colourless or very pale yellow. Purely aliphatic compounds are usually liquids at room temperature, purely aromatic compounds are solids and mixed aliphatic-aromatics are intermediate, usually low-melting solids.

These compounds are very sensitive to oxidation and hydrolysis.

Oxidation by dry oxygen gave characteristic phosphorus(V) esters, e.g.



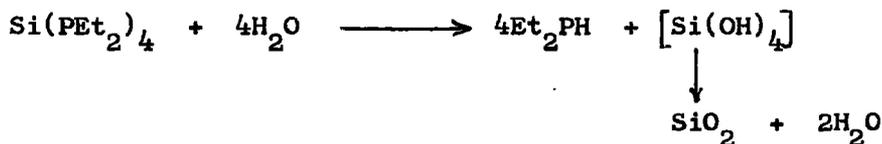
Tetrakis(diphenylphosphine)tin is oxidised to tetrakis(diphenylphosphonate), a white solid m.p. 168-175°.



Triphenyllead-diphenylphosphine was quantitatively oxidised to triphenyllead-diphenylphosphonate on standing in dry air or on treatment with alcoholic hydrogen peroxide.

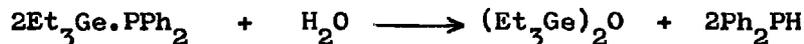


Hydrolysis in the absence of air liberated dialkyl- or diarylphosphine from these compounds.

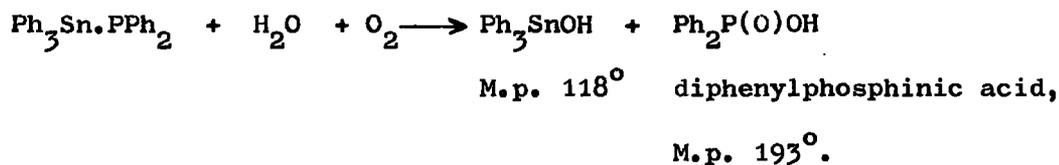


This hydrolysis was quantitative on warming the mixture.

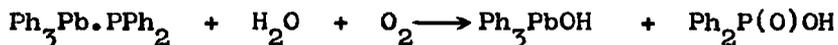
Triethylgermyl-diphenylphosphine was hydrolysed in less than 5 minutes at room temperature in a 10% solution of water in 1,2-dimethoxyethane.



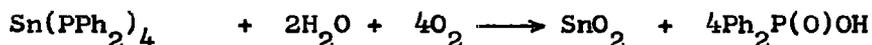
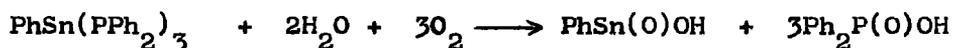
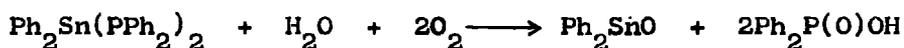
Oxidative Hydrolysis. Simultaneous oxidation and hydrolysis by heating compounds with aqueous caustic soda in the presence of air caused cleavage of tin-phosphorus bonds



The lead compound, $\text{Ph}_3\text{PbPPh}_2$ gave analogous products.



Higher substituted organotin-diphenylphosphines always gave diphenylphosphinic acid as one product of oxidative hydrolysis but the tin-containing product varied according to the number of tin-phosphorus bonds in the original compound.

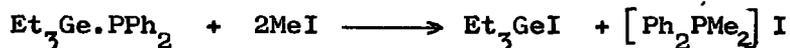


The same products could also be obtained by successive oxidation and hydrolysis.

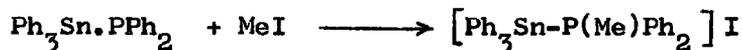
Bromine in carbon tetrachloride rapidly cleaved the germanium-phosphorus bond.



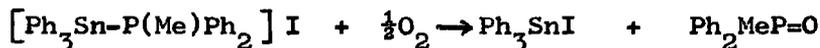
Methyl iodide also cleaved the Ge-P bond of $\text{Et}_3\text{Ge.PPh}_2$:-



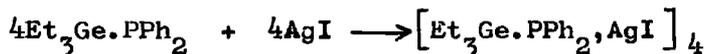
In contrast, a 1:1 adduct with triphenyltin-diphenylphosphine was obtained.



The product was readily oxidised to methyl-diphenylphosphine oxide and triphenyltin iodide



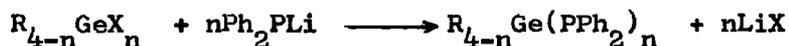
Silver iodide gave a tetrameric 1:1 adduct with triethylgermyldiphenylphosphine.



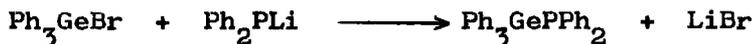
These addition reactions show that the phosphorus atom retains its donor character in the metal-phosphorus compounds.

Discussion

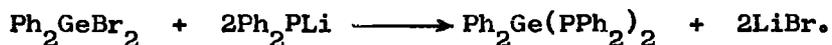
Organohalogermanes have been found to undergo substitution reactions with lithium diphenylphosphide to give organophosphinogermanes with the elimination of lithium halide.



However, the reaction was not general and applied only to the cases where $n = 1$ and 2 .



Triphenylgermyldiphenylphosphine, a white crystalline solid M.p. $153-156^\circ$ was obtained in reasonable yield.

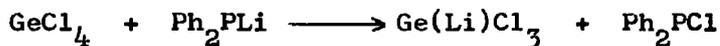


Diphenylbis(diphenylphosphino)germane was obtained in smaller yield and tetraphenyldiphosphine (10%) was also isolated (188). Complications occurred in the cases where $n = 3$ and 4 .

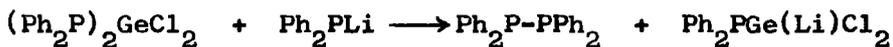
Neither of the expected products, phenyltris(diphenylphosphino)germane or tetrakis(diphenylphosphino)germane were isolated.

This is remarkable since tetrakis(diethylphosphino)silane and tetrakis(diphenylphosphine)tin are known (179, 182) although in the preparation of the former compound a considerable quantity of tetraethyldiphosphine was also formed.

The reaction between germanium tetrachloride and lithium diphenylphosphide showed distinct peculiarities. The reaction mixture remained colourless until 1.9 equivalents of Ph_2PLi had been added and it was not possible to isolate intermediate halophosphinogermanes by stopping the reaction at this stage. As the addition of lithium diphenylphosphide continued the solution changed colour, passing through yellow and orange to deep red-brown. Estimation of the lithium diphenylphosphide before and after reaction showed that all four chlorines of GeCl_4 reacted. Hydrolytically stable but air-sensitive polymeric material of varying composition was produced. No tetrakis(diphenylphosphino)germane was obtained. Analytical data on one sample of the polymer indicated the approximate composition $\text{Ph}_6\text{P}_4\text{Ge}_5$ while material from another preparation approximated to Ph_2PGe . Reactions between germanium tetrachloride or phenyltribromogermane and lithium diphenylphosphide both gave tetraphenyldiphosphine which may be formed by halogen-metal exchange.

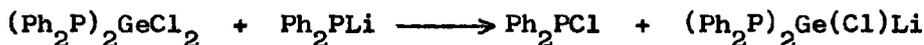


Other reactions e.g.

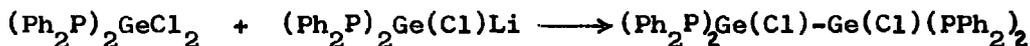


may also give tetraphenyldiphosphine. Attempts to show the presence of Ge-Li groups proved inconclusive. (188)

The empirical formula (based on C,H and P analyses) of the red polymer from one preparation corresponded approximately to $\text{Ph}_6\text{P}_4\text{Ge}_5$. The high germanium to phosphorus ratio is indicative of a high degree of metal-metal bonding and the phenyl to phosphorus ratio (1.5 rather than 2), if correct, requires the cleavage of phenyl groups from phosphorus at some stage of the reaction. Germanium-germanium bond formation is readily accounted for by processes of the type

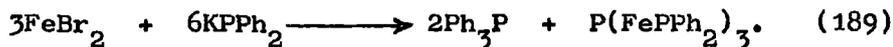


followed by coupling



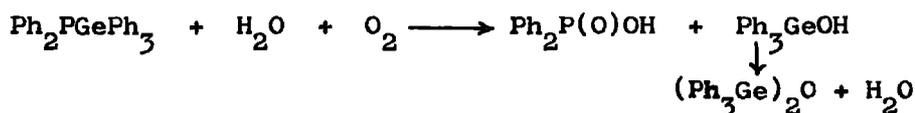
and so on.

In only two cases, however, has cleavage of a phenyl group from $\text{Ph}_2\text{P-}$ under mild conditions has been reported. Schumann et. al. observed that the reaction between triphenyltin lithium and chlorodiphenylphosphine gave a cyclic trimer $(\text{Ph}_2\text{SnPPh})_3$ (186) and Issleib and Frohlich described the reaction:

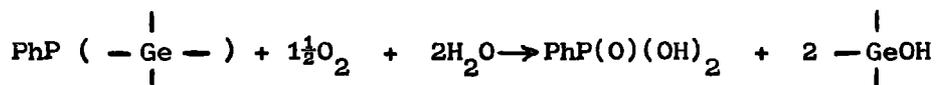


These are most unusual since alkali metals in ethereal solvents cleave only one group from triphenylphosphine. On the available evidence there is little point in speculating on processes which could involve cleavage of Ph-P bonds during the formation of the polymer and give the above mean composition. It must be pointed out that there is no evidence to suggest that the polymer is homogeneous.

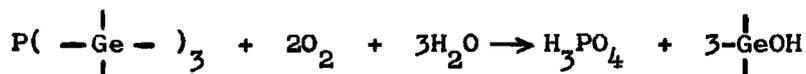
Oxidative hydrolysis of the polymer was carried out to investigate the nature of the organic groups bonded to phosphorus. Oxidative hydrolysis^{was} by caustic soda solution in the presence of air or hydrogen peroxide. Diphenylphosphorus-germanium bonds are cleaved giving diphenylphosphinic acid: (187)



Phenylphosphorus-germanium groups hydrolyse to give phenylphosphonic acid.



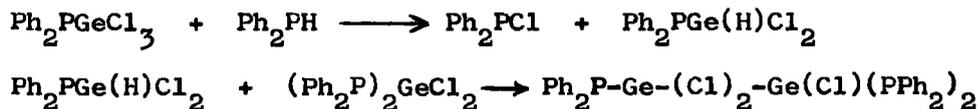
Phosphorus-germanium groups hydrolyse giving phosphoric acid.



A sample of the polymer was stirred with aqueous alkaline hydrogen peroxide. Acidification of the mixture produced a copious white precipitate. Investigation of the filtrate and residue showed that diphenylphosphinic acid only was formed. This means

that only Ph_2P - groups are present in the polymer and casts doubts on the analysis $\text{Ph}_6\text{P}_4\text{Ge}_5$ in favour of $(\text{Ph}_2\text{PGe})_n$. The method of purification was thought to be a possible reason for the unsatisfactory analysis. This was by precipitation from a concentrated benzene solution by petroleum; attempts to induce crystallisation at low temperature were not successful.

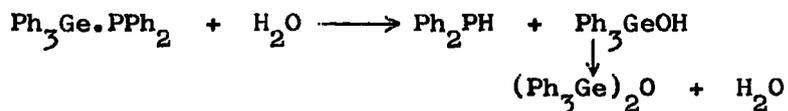
Germanium tetrachloride will not react with diphenylphosphine alone but the reaction in the presence of a base was investigated as another possible route to tetrakis(diphenylphosphino)germane. A strong base was required to remove HCl and cause the reaction to proceed. Pyridine was not sufficiently basic but triethylamine was effective in promoting the reaction between germanium tetrachloride and diphenylphosphine. Again, however, tetrakis(diphenylphosphino)germane was not obtained. Addition of the base to the reaction mixture caused the solution to become a dark red-brown colour. A precipitate appeared which was identified as triethylammonium chloride. Tetraphenyldiphosphine and a red-brown polymer were obtained. The latter was air-sensitive but hydrolytically stable. A suggested method for the formation of the polymer includes hydrogen-halogen exchange reactions to give Ge-H intermediates:



Oxidative hydrolysis of this polymer led to the isolation of only diphenylphosphinic acid. This shows that the polymer contained only the original Ph_2P - groups.

Hydrolysis of triphenylgermyldiphenylphosphine, $\text{Ph}_3\text{GePPh}_2$.

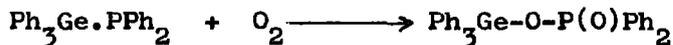
A dilute solution of $\text{Ph}_3\text{GePPh}_2$ in monoglyme was mixed with a solution of water in monoglyme in the correct proportion to effect complete hydrolysis. The reaction was followed spectrophotometrically by measuring the appearance of $\nu(\text{P-H})$ at 4.374μ .



The absorption became maximum after 6 hours from the time of mixing. This contrasts with the hydrolysis of triethylgermyldiphenylphosphine which was complete within 5 minutes from the time of mixing (188).

Oxidation of triphenylgermyldiphenylphosphine.

$\text{Ph}_3\text{Ge.PPh}_2$ was oxidised by bubbling dry oxygen through the solution. The ester, triphenylgermyldiphenylphosphonate was formed.



The infrared spectrum of the product showed $\nu(\text{Ge-O-P})$, 947 cm^{-1} which is close to that in $\text{Et}_3\text{Ge-O-P(O)Ph}_2$ (954 cm^{-1}) (188) and

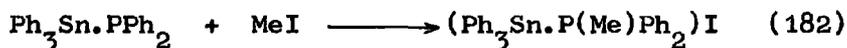
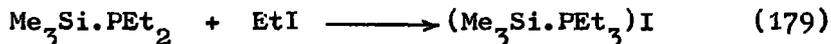
$\nu(\text{P=O}), 1198 \text{ cm}^{-1}$.

Triphenylgermyldiphenylphosphine and methyl iodide.

$\text{Ph}_3\text{GePPh}_2$ reacted with excess methyl iodide. Cleavage of the Ge-P bond took place giving iodotriphenylgermane and dimethyldiphenylphosphonium iodide.



This contrasts with the behaviour of silicon and tin compounds in which the phosphorus atom retained its donor character.



Hydrogenation of triphenylgermyldiphenylphosphine.

Hydrogen was bubbled through a solution of $\text{Ph}_3\text{Ge.PPh}_2$ containing Adams' catalyst for 4 hours at room temperature/1 atmosphere. No reaction took place and starting material was recovered.

Triphenylgermyldiphenylphosphine and silver iodide.

A solution of $\text{Ph}_3\text{GePPh}_2$ in methylcyclohexane was stirred for 3 days with a suspension of freshly prepared dry silver iodide. No reaction took place and $\text{Ph}_3\text{Ge.PPh}_2$ was recovered from the solution.

This contrasts with triethylgermyldiphenylphosphine which formed a 1:1 adduct with silver iodide (188).



Experimental

1. Preparation of triphenylgermyldiphenylphosphine

Bromotriphenylgermane (13.2g., 34.4 mmoles) was dissolved in T.H.F. and lithium diphenylphosphide (34.4. m moles) was added to the colourless solution. The cherry red colour of lithium diphenylphosphide was immediately discharged in an exothermic reaction. The bulk of the solvent was removed by distillation and the crude triphenylgermyldiphenylphosphine, a colourless solid, was dried at $130^{\circ}/10^{-4}$ mm. The product was purified by recrystallisation from methylcyclohexane at -20° . Yield 8.6 g., 51%. M.p. $153-156^{\circ}$.

2. Hydrolysis of triphenylgermyldiphenylphosphine

Triphenylgermyldiphenylphosphine (0.4g., 0.82 m mole) was dissolved in 1,2-dimethoxyethane (monoglyme) (11.5g.) to give a 3.5 weight % solution. 4.0 mls. of a 10% solution of water in monoglyme was mixed with the triphenylgermyldiphenylphosphine solution and immediately an infrared cell with KBr windows (1.0 mm spacer) was filled with the mixture. The cell was quickly placed in the beam of an infrared spectrometer which had previously been set at wavelength 4.374μ - $\nu(\text{P-H})$. The same thickness of monoglyme was used to compensate the reference beam. The absorption at this frequency increased with time and reached a maximum after 6 hours from the time of mixing.

3. Oxidation of triphenylgermyldiphenylphosphine

Triphenylgermyldiphenylphosphine (0.5g., 1.02 m moles) was dissolved in benzene (30 ccs.) Oxygen, dried by passage through a spiral trap at -78° was bubbled through the solution and a pale yellow colour developed. The solvent was removed by pumping leaving a yellow viscous oil from which crystals would not be obtained. Found, C, 69.7; H, 5.28: $C_{30}H_{25}GeO_2P$ requires C, 69.2; H, 4.84%. The infrared spectrum of the product showed the Ge-O-P absorption at 947 and $\nu(P=O)$ at 1198 cm^{-1} .

4. Triphenylgermyldiphenylphosphine and hydrogen

Ph_3GePPh_2 (0.3 g., 0.61 m mole) was dissolved in benzene (10 ccs.) A few milligrammes of Adams' catalyst were added and a slow stream of hydrogen was passed through the solution for 4 hours. The solution became dark brown in colour, presumably due to colloidal platinum from the catalyst. Solvent was removed by pumping leaving a residue which had an infrared spectrum identical to that of the starting material.

5. Triphenylgermyldiphenylphosphine and methyl iodide

Ph_3GePPh_2 (0.4g., 0.82 m mole) was dissolved in benzene (15 ccs.) and excess methyl iodide was added (0.5 cc.) After 24 hours a white precipitate had formed. This was filtered,

washed with benzene and recrystallised from methanol. Yield 0.20 g. M.p. 255-256^o Found C, 48.5; H, 4.63.

(Ph₂PMe₂)I, i.e. C₁₄H₁₆IP requires C, 49.1; H, 4.67%

(Ph₃GeP(Me)Ph₂)I, i.e. C₃₁H₂₈GeIP requires C, 59.0; H, 4.44%.

The infrared spectrum of this solid was identical with that of dimethyldiphenylphosphonium iodide. The benzene solution was pumped dry and left a white solid. This was purified by sublimation and had near and far infrared spectra identical with iodotriphenylgermane. Particularly characteristic is $\nu(\text{Ge-I})$, 282 cm⁻¹. M.p. 153-154^o Yield 0.3g., 85%.

6. Triphenylgermyldiphenylphosphine and silver iodide

Silver iodide (0.43g., 1.84 m moles), which had been dried by pumping overnight and then heating for 1 hour in vacuum, was stirred with a small volume of methylcyclohexane. Ph₃GePPh₂ (0.9g., 1.8 m moles) was dissolved in methylcyclohexane (40 ccs.) and the solution was added to the suspension of silver iodide. After stirring for 2 days it appeared that no reaction had taken place. Benzene (20 ccs.) was added and the mixture was stirred for a further day. Filtration and removal of solvent from the solution left triphenylgermyldiphenylphosphine (i.r. characterisation).

7. Germanium tetrachloride and lithium diphenylphosphide.

(Molar ratio 1:85). A solution of lithium diphenylphosphide in T.H.F. was prepared as indicated on page 197. The solution was

standardised by hydrolysing a 2.0 ml. aliquot and potentiometrically titrating the lithium hydroxide against 0.1 N H_2SO_4 . In this way it was shown that the total volume of solution (202 mls.) contained 0.173 mole of lithium diphenylphosphide (99% based on diphenylphosphine used). The lithium diphenylphosphide solution was added dropwise to germanium tetrachloride (4.2g., 0.02 mole) in T.H.F. (40 mls.) and the solution was stirred magnetically. The emergent nitrogen was passed through a trap at -196° to condense solvent vapour and allow measurement of its volume. At first the red colour of lithium diphenylphosphide was immediately discharged in an exothermic reaction. After 43 mls. of the lithium diphenylphosphide had been added the solution became yellow (i.e. after the addition of 1.89 moles Ph_2PLi per mole of GeCl_4). The addition of Ph_2PLi was continued and the colour passed through the red colour of lithium diphenylphosphide to a deep red-brown. The solution was stirred for three hours and unreacted lithium diphenylphosphide was estimated as before. The new volume of the reaction mixture was estimated and thus it was shown that 4.23 moles of Ph_2PLi reacted per mole of GeCl_4 . Solvent was removed by distillation and pumping. The brown residue was extracted with toluene (50 ccs.) and the solution was filtered from the white solid. The latter did not change on

exposure to air, did not contain $(\text{Ph}_2\text{P})_4\text{Ge}$, and was identified as lithium chloride. The organic layer was hydrolysed with de-gassed water (100 ccs.) which did not destroy the colour. Toluene and diphenylphosphine (4.3g.) were removed by distillation first at atmospheric pressure and then at $130^\circ/10^{-4}\text{ mm}$. Tetraphenyldiphosphine (about 0.2g.) then sublimed onto a cold finger at -78° (near and far infrared characterisation). The residue was dissolved in boiling benzene (80 ccs.) giving a dark brown solution. Light petroleum (b.p. $40-60^\circ$) was added and a red-brown polymer precipitated. (Found C, 41.9; H, 3.4; P, 13.8% which approximates to $\text{Ph}_6\text{P}_4\text{Ge}_5$).

8. Oxidative hydrolysis of polymer This was carried out to determine whether cleavage of phenyl groups from phosphorus took place during the formation of the polymer. The polymer, prepared as described above from GeCl_4 (3.36g., 16 m moles) and Ph_2PLi (65 m moles) was oxidatively hydrolysed with aqueous alkaline hydrogen peroxide (100 mls. 3% H_2O_2 containing 10 g. sodium hydroxide). After stirring overnight a white solid was filtered from the solution. This was later identified as diphenylphosphinic acid. Yield 1.7g. The solution was acidified to congo red and a copious white precipitate appeared, which was filtered and recrystallised from methanol. Yield 6.2g.

The infrared spectra of both solids were identical with that of diphenylphosphinic acid, $\text{Ph}_2\text{P}(\text{O})\text{OH}$. M.p. 195.5-196.5. M.p. of a sample prepared independently, 194.5-195.5. Mixed m.p. 195.5-196.5. A sample of the acid filtrate was warmed with excess ammonium molybdate solution. The non-appearance of a yellow precipitate indicated that phosphoric acid was not formed. The remainder of the solution was evaporated to dryness leaving a white solid which had no infrared structure and which was totally insoluble in methanol. Phenylphosphonic acid was therefore not formed.

9. Germanium tetrachloride, diphenylphosphine and base

Germanium tetrachloride (3.7g., 17.4. m moles) was added dropwise to a solution of pyridine (6.0g.) in benzene (50 ccs.) A white complex was formed exothermically. Diphenylphosphine (13.0g., 70 m moles) was added dropwise. The solution was refluxed but no reaction was apparent. Triethylamine (15 ccs.) was added and the solution became orange and then brown in colour. After refluxing for 2 days a white water and air stable solid was filtered off (triethylammoniumchloride) and solvent was removed from the solution by pumping. Heating at $110^\circ/10^{-4}$ mm. caused the excess diphenylphosphine to distil and condense higher up the walls of the Schlenk tube. On further heating a white sublimate

appeared on the wall of the tube which had near and far infrared spectra identical with tetraphenyldiphosphine. The dark brown residue did not yield tetrakis(diphenylphosphino)germane.

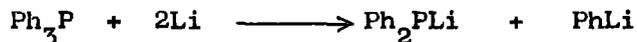
A repeat experiment was performed with a different order of addition of the reactants to see if halogen-hydrogen exchange reactions of the type $\text{Ph}_2\text{PH} + \text{GeCl}_4 \longrightarrow \text{Ph}_2\text{PCl} + \text{HGeCl}_3$ were taking place leading to the formation of polymer at the expense of $(\text{Ph}_2\text{P})_4\text{Ge}$. Triethylamine (2.02g., 20 m moles) was added dropwise with stirring to germanium tetrachloride (1.0g., 4.7 m moles) and then diphenylphosphine (3.7g., 20 m moles) was added slowly. The colour gradually darkened through yellow to red brown, and a white precipitate was filtered off and identified as Et_3NHCl (liberated triethylamine on treatment with NaOH). Solvent was removed by pumping leaving a red brown solid which was oxidatively hydrolysed by adding 50 mls. 10% sodium hydroxide and bubbling air through the solution for 24 hours. The mixture was acidified to congo red and the white precipitate was filtered off and recrystallised from methanol. This was identified (infrared and m.p. 193-194.5) as diphenylphosphinic acid. The aqueous solution was evaporated to dryness leaving a white solid which had no infrared structure and which was insoluble in methanol. No evidence was obtained to suggest that phosphoric acid or

phenylphosphonic acid were present.

An attempt to repeat the preparation of the polymer for analysis showed that the reaction was not reproducible. A brown oil was consistently obtained from hydrocarbon solvents. Fresh samples of triethylamine and diphenylphosphine were used but other conditions appeared to be identical.

Preparation of starting materials

Diphenylphosphine (190)



Triphenylphosphine (70g.,) in T.H.F. (150 ccs.) was added dropwise to a stirred suspension of lithium shot (10g.) in T.H.F. The solution became an intense cherry red colour. After stirring overnight the solution was filtered through glass wool to remove excess lithium shot. The solution was hydrolysed with dilute HCl until the pH was reduced to 7-7.5. The layers were separated and the aqueous layer was washed with ether (50 ccs) which was added to the organic layer. The organic layer was then washed with de-gassed water, dried over solid caustic soda and flash distilled to remove solvent. Vacuum distillation at $74^{\circ}/10^{-4}$ mm. gave diphenylphosphine. Yield 36g., 73%.

Lithium diphenylphosphide. Lithium chips (0.25g., 0.038 g.atom) were placed in a 250 ml. 3-necked flask containing T.H.F. (70 ccs.)

Diphenylphosphine (7.0g. 38 m moles) in T.H.F. (15 ccs.) was added dropwise with stirring. The solution was stirred for 3 hours and filtered through glass wool before use.

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