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BENZYL AND PLATINUM DERIVATIVES OF ORGANOGERMANES

by R.J. Cross

Abstract of Thesis

The work described in this thesis is conveniently divided into three parts.

PART A. Benzyl Derivatives of Germanium.

Tetrabenzylgermane is cleaved by lithium in 1,2-dimethoxyethane to give moderate yields of tribenzylgermyl-lithium, but some dibenzyl-germyl-dilithium is also produced. The germyl-lithium reagent does not attack the solvent at 0°, but at reflux temperature in the presence of an excess of lithium a progressive series of reactions takes place giving $(PhCH_2)_3GeMe$, $(PhCH_2)_2GeMe_2$ and $PhCH_2GeMe_3$. Many reactions of tribenzylgermyl-lithium are similar to those of other organolithium reagents.

The reaction between tribenzylgermane and lithium is not selective. Both Ge-H and Ge-CH_2Ph bonds are cleaved, and this lack of selectivity is also shown by hexabenzyldigermane. Similar complications are evident in the reaction between butyl-lithium and tribenzylgermane. Both hydrogen-metal exchange to give $(PhCH_2)_3GeLi$, and nucleophilic attack of Bu^- with displacement of either H^- or $PhCH_2^-$ occurs.

PART B. Triphenylgermylplatinum Complexes.

Triphenylgermyl-lithium reacts with the complexes cis or trans $(R_3P)_2PtCl_2$ [R = Et, n-Pr] to give $(R_3P)_2Pt(GePh_3)_2$. The iodide $(R_3P)_2PtI_2$ reacts with triphenylgermyl-lithium partly by halogen-metal exchange, however, giving the lithio platinum derivatives $(R_3P)_2Pt(Li)I$

and $(R_3P)_2Pt(Li)GePh_3$.

The complexes $(R_3P)_2Pt(GePh_3)_2$ are stable to air and water but decompose at 150° with cleavage of Ge-Pt, Ge-C and P-C bonds. Iodine, HCl, MeI, MgI$_2$, $C_2H_4Br_2$, PhLi and LiAlH$_4$ all cleave both Ge-Pt bonds, and in some cases at least the reaction probably proceeds via platinum(IV) intermediates. Hydrogenolysis of one Ge-Pt bond takes place under extremely mild conditions, and this may also proceed via oxidation to a Pt(IV) complex.

Stable alkoxy-platinum complexes, $(R_3P)_2Pt(OR')GePh_3$, were produced by the action of alcohols on the intermediate $(R_3P)_2Pt(I)GePh_3$.

PART C. Infrared Spectra.

Characteristic infrared frequencies are given for 90 organogermanes, including alkyls, aryls, hydrides, deuterides, halides and oxides, with the main object of assisting characterisation of similar compounds. Germanium-carbon stretching frequencies for trans and gauche forms of n-butylgermanes have been observed.

BENZYL AND PLATINUM DERIVATIVES

OF ORGANOGERMANES

by

R.J. Cross, B.Sc.

A Thesis submitted for the degree of Doctor of Philosophy in

the University of Durham.

July 1965.

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MEMORANDUM

The work described in this thesis was carried out in the University of Durham between September 1962 and June 1965. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

PUBLICATIONS

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

"Benzyl Derivatives of Germanium", J. Chem. Soc., 4125 (1964).

"Uncatalysed Hydrogenolysis of Metal-Metal Bonds", Proc. Chem. Soc., 143 (1964).

"Infrared Spectra of Organogermanes", J. Organometal. Chem., 3, 146 (1965).

"Platinum(II) Grignard and lithio derivatives", J. Organometal. Chem., 3, 253 (1965).

"Triphenylgermylplatinum Complexes",

J. Chem. Soc. In the press.

CONTENTS

SUMMARY

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Triphenylgermyl-lithium reacts with the complexes <u>cis</u> or <u>trans</u> $(R_3P)_2PtCl_2$ [R = Et, n-Pr] to give $(R_3P)_2Pt(GePh_3)_2$. The iodide $(R_3P)_2PtI_2$ reacts with triphenylgermyl-lithium partly by halogen-metal exchange, however, giving the lithioplatinum derivatives $(R_3P)_2Pt(Li)I$ and $(R_3P)_2Pt(Li)GePh_3$.

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Characteristic infrared frequencies are given for 90 organogermanes, including alkyls, aryls, hydrides, deuterides, halides and oxides, with the main object of assisting characterisation of similar compounds. Germanium–carbon stretching frequencies for trans and gauche forms of n-butylgermanes have been observed.

INTRODUCTION

This introduction is concerned with a general review of organo-germanium chemistry. Certain aspects of the organometallic chemistry of platinum and of compounds containing metal-metal bonds are also summarised. A more detailed account is provided of aspects which are particularly relevant to the work described in this thesis.

A. General Characteristics of the Group IVb Elements.

The atoms of Group IVb resemble carbon and silicon in having the ns^2np^2 electron configuration, and it is often advantageous to include these elements in comparisons as many trends can be followed through the whole group; carbon, silicon, germanium, tin and lead. The trend from electronegative to electropositive character with increasing atomic number is very striking. Carbon is strictly non-metallic and silicon essentially so. Although germanium has many metallic properties, it is best considered as a semi-metal. Tin and lead, however, are definitely metallic, although their oxides are amphoteric.

All the elements of Group IVb form tetrahedral covalent bonds by sp^3 hybridisation and give a large number of organic derivatives. The fully substituted compounds of the type R_4M (R = alkyl or aryl, M = Si, Ge, Sn or Pb) differ from the fully alkylated or arylated compounds of the adjacent groups in their relative stability. For example, trimethyl-indium and trimethylstibine inflame in air, whereas tetramethyltin is stable to air and water. The high reactivity of the Group III organic compounds may be attributed mainly to their vacant orbital and electron-deficient character. For Group V (the trivalent compounds) the reactivity

is due to their unsaturated character and to the presence of a lone pair of electrons. The alkyls and aryls of Group IV behave as saturated compounds and show no tendency to expand their covalency above four.

The thermal and chemical stability of compounds of the type R_4M decreases as the group is descended. This may be illustrated by the action of chlorine on the tetra-alkyls. Et_4C and Et_4Si undergo atomic chlorination with retention of the ethyl to C or Si bonds. Et_4Ge reacts smoothly to give $Et_3GeCl + EtCl$, and Et_4Sn reacts so readily that care is necessary to stop the reaction at Et_3SnCl. Et_4Pb is completely degraded by chlorine. Covalent bonds between Group IVb metals and hydrogen or another Group IVb metal also become more reactive as the group is descended. These tendencies are not continuous, however. The thermal stability of R_4M compounds probably reaches a maximum at silicon, and SiH_4 is more reactive than CH_4 or GeH_4.

The atoms of the Group IVb elements can also enter into compounds in a divalent state, and these become more stable as the tetravalent compounds become more reactive, i.e. in the heavier elements. In these compounds the s electrons are presumably retained as an "inert pair". Divalent inorganic lead compounds are generally more stable than the tetravalent ones, and many show ionic properties. The divalent compounds of tin are less stable, and those of germanium are powerful reducing agents. Little is known at present about silicon (II) compounds and divalent carbon compounds ("Carbene ions") have been postulated only as reactive intermediates. The increasing energy gap between the s and p

electrons in the heavier atoms, making sp^3 hybridisation less favourable, is at least partly responsible for the increasing stability of the divalent state.

With very electronegative groups attached, the Group IVb elements can expand their coordination number to 5 or 6, giving compounds of the type Na_2SiF_6 and $(NH_4)_2SnCl_6$. This is achieved by using the unoccupied d orbitals for bonding. Carbon, of course, having no low energy d orbitals available, cannot expand its covalency above 4.

Carbon is also exceptional in Group IV in forming $p\pi-p\pi$ multiple bonds, giving rise to such compounds as alkynes, alkenes, ketones and imines. There are no examples known of the other Group IV elements forming compounds of these types. However, there is evidence that the other Group IVb elements can form multiple bonds (at least partially) by $d\pi-p\pi$ interactions. For example, in disilyl ether, $H_3Si-O-SiH_3$, the Si-O-Si bonds are colinear where the normal tetrahedral angle about oxygen would be expected, as in dimethyl ether. $d\pi-p\pi$ bonds between silicon and oxygen are thought to be responsible for this. Less evidence is available about this phenomenon in the heavier elements.

B. The Organic Chemistry of Germanium.

The organic chemistry of germanium was reviewed in 1951 by Johnson (1), who described some 230 compounds. Since that time the number of organogermanes described in the literature has increased rapidly at a rate parallel to the increase in interest in organometallic chemistry in general. Reviews by Rijkens (2) in 1960 and by Quane and Bottei (3) in

1963 have summarised most of the recent advances, and a survey by Dub (4)
lists the preparation and properties of over 400 compounds. For aspects
of the organic chemistry of germanium not described below these reviews
are recommended.

1 THE FULLY SUBSTITUTED GERMANES.

a) The monogermanes, R$_4$Ge.

The standard method for the preparation of tetra-alkyl and tetra-
aryl germanes is the reaction between a germanium (IV) halide and a
Grignard reagent in ether or ether/toluene solution (5,6,7).

$$GeX_4 + 4RMgX \longrightarrow R_4Ge + 4MgX_2$$

The reaction proceeds via the intermediates RGeX$_3$, R$_2$GeX$_2$ and R$_3$GeX, and,
in cases where the reaction is slow, the conditions can be adjusted to
give a principal yield of one of these compounds. Mixed alkyl- or aryl-
germanes can be obtained by the stepwise alkylation or arylation of
these intermediates. The use of alkyl- or aryl-lithium reagents instead
of the Grignard reagents often leads to improved yields of the tetra-
organogermanes (8).

Coupling reactions of the Wurtz type have been used to prepare both
alkyl- and arylgermanes (7). Germanium(IV)chloride and bromobenzene react
vigorously with sodium to give tetraphenylgermane.

$$GeCl_4 + 4PhBr + 8Na \xrightarrow{ether} Ph_4Ge + 4NaCl + 4NaBr$$
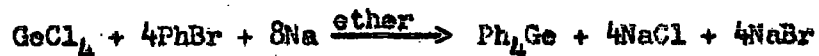
Direct substitution reactions between alkyl halides and elementary
germanium in the presence of a copper catalyst also produces some R$_4$Ge,

but the yields are low, the principal products being partially substituted organogermanium halides (9).

Another method of producing symmetrical fully substituted organogermanes is the use of dialkylzinc and germanium tetrachloride. This reaction is interesting historically as it was by this route that Winkler (11) produced the first organogermanium compound in 1887.

$$GeCl_4 + 2ZnEt_2 \longrightarrow Et_4Ge + 2ZnCl_2$$

A more recent variation involves the use of trialkylaluminium instead of dialkylzinc (12).

Compounds containing Ge-H bonds can be made to react with olefinic or acetylenic carbon-carbon bonds to prepare fully substituted organogermanes. Gilman and Gerow (13, 14) demonstrated that the germanium became attached to the terminal carbon of an olefin:

$$Ph_3GeH + CH_2=CH(CH_2)_{15}CH_3 \longrightarrow CH_3(CH_2)_{17}GePh_3$$

The reaction is catalysed by benzoyl peroxide or ultra-violet radiation. More useful applications of this method are in the synthesis of tetra-organogermanes with side-chains containing a reactive center or an unsaturated group. For example:

$$n-Bu_3GeH + HC{\equiv}CCR_2OH \longrightarrow n-Bu_3GeCH=CR_2OH \quad (15)$$

and $R_3GeH + CH_2=CHY \longrightarrow R_3GeCH_2CH_2Y \quad (16)$ where R = alkyl and Y = -CN, -COOH, -COOR, -CH_2OH or -CHO.

Germanium dihydrides behave similarly, an interesting example being:

$$Bu_2GeH_2 + (CH_2=CH)_2GeEt_2 \longrightarrow Bu_2Ge \underset{CH_2-CH_2}{\overset{CH_2-CH_2}{\diamond}} GeEt_2 + \text{polymeric material (17)}$$
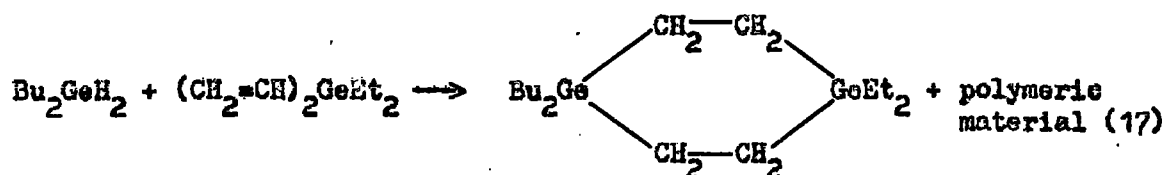
Germyl-lithium and potassium compounds can give tetra substituted monogermanes by reaction with organic halides. They also react with olefins in a manner similar to the hydrides (13).

$$Ph_3GeLi + Ph_2C=CH_2 \xrightarrow{H_2O} Ph_2CHCH_2GePh_3$$
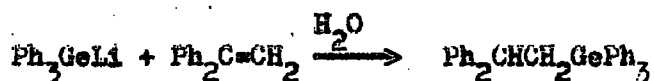
This reaction is not general, however, and does not proceed with trans-stilbene, 1-octene or cyclohexene. Two further reactions of triphenylgermyl-lithium which produce fully substituted germanes are with formaldehyde and benzophenone (18), giving Ph_3GeCH_2OH and $Ph_3GeC(OH)Ph_2$ respectively in about 30% yield after hydrolysis.

Another method, useful in the synthesis of β-substituted organogermanes, is the reaction between trialkylgermanium hydrides and various diazo compounds (16, 19). Ethyl diazoacetate, $N_2CHCOOEt$, diazoacetone, $N_2CHCOCH_3$, and diazoacetophenone, $N_2CHCOPh$ all react in refluxing benzene or toluene to give yields in the order of 40%:

$$R_3GeH + N_2CHCOCH_3 \xrightarrow{Cu \text{ catalyst}} R_3GeCH_2COCH_3 + N_2$$
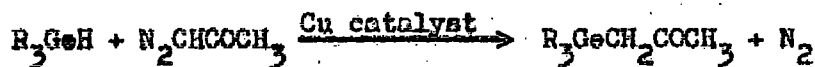
The compounds prepared by these methods can often be converted to other fully-substituted germanes by reactions involving the organic groups only. These reactions are not described here. Many attempts to prepare tetra-iso-propylgermane have met with failure, presumably due to steric hindrance (20). This has now been isolated in small amounts from the

reaction between iso PrMgBr and $GeCl_4$ (10) and tetra-iso-butylgermane has also been prepared by the alkylaluminium method (21).

Properties of the fully substituted monogermanes.

Tetra-alkyl- and tetra-arylgermanes are very stable thermally and chemically. The lower alkyls are volatile liquids: Me_4Ge, b.p. 43.4°; Et_4Ge, b.p. 162.5°. The aryls are crystalline solids which melt without decomposition: Ph_4Ge, m.p. 236°; $(PhCH_2)_4Ge$, m.p. 110°. Mixed alkyl-aryl compounds have intermediate properties. Compounds of the type R_4Ge are stable to air and water (unless the R group is reactive) and are generally soluble in organic solvents.

Halogens react with the fully substituted germanes, cleaving off an organic group to give the halide R_3GeX. Hydrogen halides are less effective halogenating agents, only HF giving reasonable yields of R_3GeF (R = Me or Et) (22), although it has been reported that HBr reacts with tetramethylgermane in the presence of $AlBr_3$ to give Me_3GeBr (23).

Bromine reacts with tetraethylgermane in ethyl bromide to give Et_3GeBr (24,25). Further cleavage to give Et_2GeBr_2 does not occur. Aryl groups are cleaved from germanium more readily, however. Tetra-phenylgermane can be converted to triphenylbromgermane, Ph_3GeBr, by bromine in refluxing carbon tetrachloride (5), or more effectively in 1,2-dibromoethane at room temperature (26). In the latter solvent at reflux temperature, removal of a second phenyl group occurs giving diphenyldibromgermane, Ph_2GeBr_2 (27). The cleavage by bromine of a series of mixed tetra-alkylgermanes has been examined by Lesbre and

Mazerolles (21,28) who stated that lighter radicals were split off in preference to heavier ones, but that phenyl groups were more easily cleaved than alkyl groups. This was demonstrated by Flood (29) who prepared diethyldibromgermane by the reaction scheme:

$$Ph_2GeBr_2 + 2EtMgBr \longrightarrow Ph_2GeEt_2 \xrightarrow{Br_2} Et_2GeBr_2$$
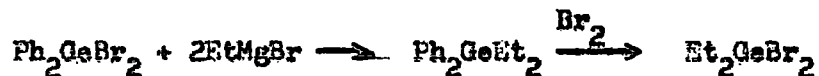
Organic groups can be cleaved from germanium by alkali-metals in solvents such as liquid ammonia or tetrahydrofuran. These experiments also suggest that aryl groups can be cleaved easier than alkyl groups. Calculations from the heats of combustion of R_4Ge compounds indicate that the dissociation energy for the Ge-C bond is 32.2 k-cals. per mole for Ph_4Ge (30) and 56.6 k-cals. per mole in Et_4Ge (31).

b) **The fully substituted higher germanes.**

Fully substituted derivatives of the higher germanes, $R_3Ge(GeR_2)_nGeR_3$, (n = 0, 1, 2 ...) are generally more difficult to prepare than mono-germanes, as the Ge-Ge bonds tend to be more reactive than Ge-C bonds. The compounds become less stable as the chain-length increases.

Hexaphenyldigermane, Ph_6Ge_2, was first prepared by Morgan and Drew in 1925 by the reaction between triphenylbromgermane and sodium in refluxing xylene (32).

$$2Ph_3GeBr + 2Na \longrightarrow Ph_3GeGePh_3 + 2NaBr$$

The reaction presumably proceeds via the intermediate Ph_3GeNa. Hexa-benzyldigermane, $(PhCH_2)_6Ge_2$, has been made by a similar reaction (33)

but bromtriethylgermane reacts with sodium only at higher temperatures in the absence of a solvent (24).

The reaction between triphenylgermane and phenyl-lithium has been shown to give hexaphenyldigermane under some conditions (34). Gilman and Gerow (35) showed that most conditions for this reaction favoured the formation of triphenylgermyl-lithium, which then reacts further to give the digermane.

$$Ph_3GeH + PhLi \longrightarrow Ph_3GeLi + C_6H_6$$

$$Ph_3GeH + Ph_3GeLi \longrightarrow Ph_6Ge_2 + LiH$$

The reaction between germanium tetrachloride and Grignard reagents to give monogermanes has already been described, but in certain cases appreciable yields of digermanes were also isolated (36, 37). The yields varied considerably, however (38) and in some cases no digermane was formed. In 1962 this reaction was examined by Glockling and Hooton (39) who showed that the coupling reaction proceeded via a germyl-Grignard intermediate. If the substitution of the intermediate R_3GeX to give R_4Ge is slow due to steric reasons or to a relatively unreactive Grignard reagent, then this compound can react with excess magnesium to give the germyl magnesium halide, R_3GeMgX, which can react further to give the digermane.

$$GeX_4 + RMgX \longrightarrow R_3GeX$$

$$R_3GeX + RMgX \longrightarrow R_4Ge$$

$$R_3GeX + Mg \longrightarrow R_3GeMgX$$

$$R_3GeMgX + R_3GeX \longrightarrow R_6Ge_2$$
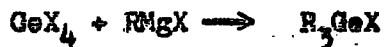
High yields of the digermane can be obtained using aryl Grignard reagents with an excess of magnesium. In the complete absence of free magnesium small amounts of the digermane can still occasionally be isolated. This is formed from germyl magnesium halide which is produced by halogen-metal exchange, a common phenomenon in Group IVb.

$$R_3GeX + RMgX \longrightarrow R_3GeMgX + RX$$

The reaction between germanium-alkalimetal compounds and a germanium halide can also produce digermanes, and this is a very useful reaction in preparing unsymmetrical compounds: for example:

$$Ph_3GeNa + Et_3GeBr \longrightarrow Ph_3GeGeEt_3 + NaBr \quad (40)$$
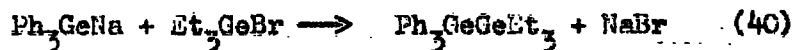
Comparatively few organo-substituted higher germanes are known. Octaphenyl trigermane was prepared by Kraus and Brown (41, 42) by the action of triphenylgermyl-sodium on diphenyldichlorogermane in benzene.

$$2Ph_3GeNa + Ph_2GeCl_2 \longrightarrow Ph_3Ge(GePh_2)GePh_3 + 2NaCl$$
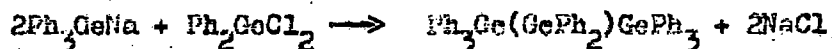
Two compounds of a tertiary butane type structure, tristriphenylgermyl-germane and tristriphenylgermylmethylgermane, have been prepared from the reaction between germanium(II) iodide and triphenylgermyl-lithium (43).

$$3Ph_3GeLi + GeI_2 \longrightarrow [Ph_3Ge]_3GeLi$$

$$[Ph_3Ge]_3GeLi \xrightarrow{H_2O} [Ph_3Ge]_3GeH$$

$$[Ph_3Ge]_3GeLi \xleftarrow{BuLi}$$

$$[Ph_3Ge]_3GeLi \xrightarrow{MeI} [Ph_3Ge]_3GeMe$$
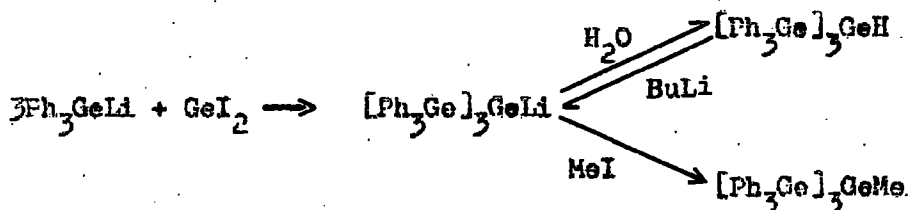
Attempts to prepare tetrakistriphenylgermylgermane were unsuccessful (44),
and no simple substituted compounds containing more than four linked
germanium atoms have yet been prepared, although there is no reason to
suspect that they cannot be made. Kraus and Brown obtained a compound
which appeared to be a cyclic tetragermane, $(Ph_2Ge)_4$, in low yield from
the reaction between diphenyldichlorogermane and sodium in refluxing
xylene (42). Recently this compound has been prepared by a different
reaction and its cyclic structure confirmed (121). Reaction with iodine
followed by phenyl-lithium gives the normal tetragermane, $Ph_3Ge(GePh_2)GePh_3$

$$
\begin{array}{c}
Ph_2 \qquad Ph_2 \\
Ge\text{---}Ge \\
| \qquad\quad | \\
Ge\text{---}Ge \\
Ph_2 \qquad Ph_2
\end{array}
\quad\xrightarrow{I_2,\ PhLi}\quad
Ph_3Ge\text{-}GePh_2\cdot GePh_2\cdot GePh_3
$$
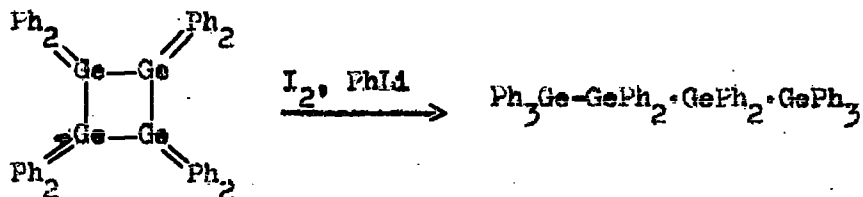
The reaction between phenyl-lithium or phenyl magnesium bromide and
germanium(II)iodide produces organogermanium compounds which almost
certainly have greater chain lengths than those mentioned above (43).
The products, however, are non-homogeneous polymers which contain
germanium atoms in all stages of substitution (Ge, GePh, $GePh_2$ and
$GePh_3$. Tetraphenylgermane is also produced).

Properties of the fully substituted higher germanes.

In their physical properties the digermanes parallel the mono-
germanes: Ph_6Ge_2 melts at 351°, whereas Et_6Ge_2 melts at 90°. The com-
pounds are stable to air and water. As has been mentioned above, the
strength of the Ge-Ge bond is less than that of the Ge-C bonds, so

cleavage reactions usually involve rupture of the metal-metal bond. Cleavage of the M-M bond by alkali metals is discussed later.

Bromine reacts readily with R_6Ge_2 to give R_3GeBr (5,24), and with Ph_8Ge_3 to give a mixture of Ph_3GeBr and Ph_2GeBr_2 (41,42). The Ge-Ge bonds of the phenylgermanium polymers are also cleaved by bromine under mild conditions, and this reaction, followed by alkylation of the resulting halides by EtMgBr, has been used to elucidate their structure (43).

2. THE ORGANOHALOGERMANES.

The complete series of these compounds, R_3GeX, R_2GeX_2 and $RGeX_3$ where R = alkyl or aryl and X = F, Cl, Br or I is known; their relatively high reactivity makes them important in synthetical work.

The preparation of the more highly substituted compounds R_3GeX and R_2GeX_2 by the halogenation of fully substituted monogermanes and digermanes has been described (page 7) and this is the preferred method for these compounds. A variation of this method is the reaction of halogens on organogermanium hydrides. These are converted completely and smoothly to the halides. Diphenylgermane is halogenated to diphenyl-dibromgermane by bromine in ether at $0°$ (27).

$$Ph_2GeH_2 + 2Br_2 \longrightarrow Ph_2GeBr_2 + 2HBr$$

The partial substitution of germanium(IV)chloride by a Grignard reagent to give organohalogermanes has also been mentioned (page 4). If the R group is bulky enough to make substitution beyond R_3GeX difficult, then high yields of this product can be obtained. For example an excess of

1-naphthyl magnesium bromide on $GeCl_4$ gives mainly tri-1-naphthylbrom-germane (45). Tri-iso-propylbromgermane can be made in a similar way (20, 28).

The direct reaction between alkyl or aryl halides and germanium metal proceeds at temperatures above 320°. A copper catalyst is needed, the main products being the di- and tri-halo-organogermanes (46).

$$MeCl + Ge \longrightarrow Me_2GeCl_2 + MeGeCl_3$$

$$EtCl + Ge \longrightarrow Et_2GeCl_2 + EtGeCl_3$$

$$PhCl + Ge \longrightarrow Ph_2GeCl_2$$
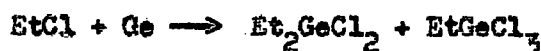
The method is of limited application as the high reaction temperatures tend to cause decomposition via the evolution of hydrogen halides. Another preparative method for organohalogermanes which involves similar reaction conditions is the redistribution between R_4Ge and $GeCl_4$, $RGeCl_3$ or R_2GeCl_2 (47, 48, 49)

$$e.g. \quad Ph_4Ge + 3GeCl_4 \longrightarrow 4PhGeCl_3$$

These reactions proceed at temperatures above 200° in the presence of aluminium trichloride or an organo-aluminium halide. The method is applicable to both alkyl and aryl halides, although methyl compounds seem resistant to rearrangement (48). The rearrangement between tetra-n-butyl-tin and germanium tetrachloride or between tetra-n-butylgermane and tin tetrachloride proceeds without added catalyst (50).

$$Bu_4Sn + GeCl_4 \longrightarrow Bu_3SnCl + BuGeCl_3$$

$$Bu_4Ge + SnCl_4 \longrightarrow Bu_3GeCl + BuSnCl_3$$
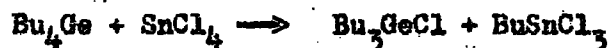
Germanium (II) halides form a convenient starting point in the preparation of many lower substituted organohalogermanes. The reaction between alkyl or aryl iodides and germanium di-iodide proceeds to completion when heated in a sealed tube.

$$MeI + GeI_2 \longrightarrow MeGeI_3 \quad (51)$$

Equimolar amounts of GeI_2 and diarylmercury react (in refluxing toluene) to give mainly R_2GeI_2 with small amounts of $RGeI_3$ and R_3GeI (52)

$$R_2Hg + GeI_2 \longrightarrow R_2GeI_2 + Hg$$
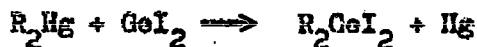
The reaction between $GeCl_2$ and caesium chloride has been reported to give the complex salt $CsGeCl_3$, which can react with organic halides to give organohalogermanes (53).

$$GeCl_2 + CsCl \longrightarrow CsGeCl_3 \xrightarrow{EtI} EtGeCl_3$$

Many of the reactions mentioned above produce a mixture of mono-, di-, and tri-halides and separation can often be difficult. This is facilitated, however, by two common methods. The halides can be hydrolysed to the oxides which are more easily separated, and can be re-converted to the halides by the appropriate halogen acid (44). Alternatively, the halides can be reduced using lithium aluminium hydride to the hydrides, which can often be separated by fractional vacuum distillation, then converted back by the action of halogen.

A reaction which produces an organotrihalogermane exclusively is the addition of trichlorgermane, $HGeCl_3$, to an olefin (28, 54, 55). Benzoyl peroxide or chloroplatinic acid have been used as catalysts, though some-

times they are not needed.

$$Cl_3GeH + CH_2=CH(CH_2)_3CH_3 \longrightarrow Cl_3Ge(CH_2)_5CH_3$$

Another reaction which produces a specific halide is the reaction between diazomethane and $GeCl_4$ or $MeGeCl_3$. Seyferth and Rochow (56) found that this reaction proceeded in ether at $-60°$.

$$GeCl_4 + CH_2N_2 \longrightarrow ClCH_2GeCl_3 + N_2$$

$$MeGeCl_3 + CH_2N_2 \longrightarrow ClCH_2(Me)GeCl_2 + N_2$$

Dimethyldichlorgermane does not react with diazomethane.

Few organohalo derivatives of digermane are known, but two phenyl compounds have been made by the action of lithium amalgam on phenyl-tribromgermane or diphenyldibromgermane (57).

$$2PhGeBr_3 + 2Li \longrightarrow PhBr_2Ge-GeBr_2Ph + 2LiBr$$

$$2Ph_2GeBr_2 + 2Li \longrightarrow Ph_2BrGe-GeBrPh_2 + 2LiBr$$
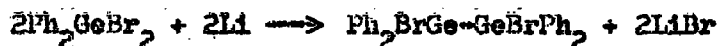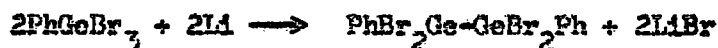
Also the reaction between germanium (II) iodide and di-n-butylmercury in acetone gives a solid product which analyses for $Bu_2IGe-GeIBu_2$ (58).

Properties of the organohalogermanes.

The organohalogermanes are high-boiling liquids or solids (Et_3GeCl, b.p. $176°/760$ mm: Ph_3GeCl, m.p. $116°$) and the majority can be distilled under reduced pressure without decomposition. The halides are stable to dry air but are slowly hydrolysed by moisture. Their stability towards both thermal decomposition and hydrolysis is in the order $F > Cl > Br > I$. The halogen atoms appear to have a stabilizing influence on the organic

groups of the molecules. Thus in the reaction between compounds of the type R_4Ge (R = alkyl or aryl) and halogens, the reaction ceases after one or two R groups have been cleaved.

Organogermanium halides are rapidly hydrolysed by aqueous or ethanolic solutions of sodium hydroxide. The germanium hydroxides produced usually condense with themselves to form oxides, eliminating water.

$$R_3GeX \longrightarrow [R_3GeOH] \rightleftharpoons (R_3Ge)_2O$$

$$R_2GeX_2 \longrightarrow [R_2Ge(OH)_2] \rightleftharpoons (R_2GeO)_n$$

$$RGeX_3 \longrightarrow [RGe(OH)_3] \rightleftharpoons RGeOOH \rightleftharpoons ((RGeO)_2O)_n$$
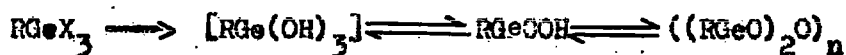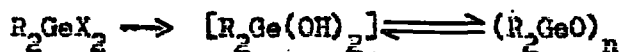
Rochow and Allred compared the hydrolysis of organogermanium halides with that of analogous compounds of the other Group IVb elements (59). In their reaction with water, most carbon halides resist hydrolysis, and silicon halides are rapidly and completely hydrolysed. Germanium halides reach an equilibrium, however. Ionic intermediates have been postulated in these reactions (60) although ionisation of organohalogermanes in non-aqueous solvents does not seem to occur (61, 62). Also, Johnson and Schmall, (63) showed that the hydrolysis of the monohalides R_3GeX proceeded via the pentacovalent intermediate $R_3Ge(OH_2)X$, and not via a germonium ion R_3Ge^+.

$$R_3GeX + H_2O \underset{\text{fast}}{\rightleftharpoons} R_3Ge\begin{subarray}{l} X \\ OH_2 \end{subarray} \underset{\text{slow}}{\rightleftharpoons} R_3GeOH_2^+ + X^-$$
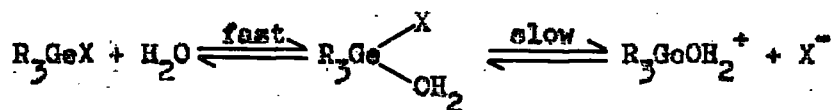
Attempts to show the presence of Ph_3Ge^+ in liquid hydrogen chloride saturated with Ph_3GeCl were not successful (64). The carbonium ion

Ph_3C^+ is known to exist in similar conditions.

The germanium halides react with anhydrous ammonia in a manner similar to water. Monohalides can produce the germanium analogues of primary, secondary and tertiary amines, where dihalides produce imine type compounds. Like the oxides, these tend to associate and do not give germanium-nitrogen double bonds. This is probably the case also with the nitrides produced from trihalides and ammonia.

The reaction between compounds of the type R_3GeX and alkali metals to produce digermanes has been discussed. This is thought to proceed via an intermediate alkali-metal compound R_3GeM, and under the correct conditions this can be the major product. The reaction of diphenyldichlorgermane and sodium to give $(Ph_2Ge)_4$ has also been mentioned. The reaction of germanium trihalides with alkali metals is more obscure. In 1936 Schwarz and Schmeisser (47) treated phenyltrichlorgermane with sodium in refluxing xylene. They isolated a compound which they analysed as $(PhGe)_6$. However, a reinvestigation of this reaction by Metlesics and Zeiss (57) using potassium gave a compound which contained 1-5% of chlorine and 5-10% of oxygen; it is unlikely that (PhGe) was, in fact, obtained.

3. THE GERMANIUM HYDRIDES.

a) The simple germanes.

Although monogermane, GeH_4, was first prepared in 1902 (65), it was not until 1924 that reasonable amounts were prepared in a pure state. Dennis, Corey and Moore (66) found that treatment of a germanium-zinc or germanium-magnesium alloy with dilute acids gave moderate yields of mono-

germane, together with some digermane, Ge_2H_6, and trigermane, Ge_3H_8. Better methods have been developed more recently involving the reduction of GeO_2 (67) and $GeCl_4$ (68) by sodium borohydride, yields being in the order of 80%. Lithium tri-tert-butoxyaluminium hydride also gives good results (69) but stronger reducing agents are less effective. Lithium aluminium hydride, for example, gives monogermane in only 10-40% yield (69, 70), germanium(II)chloride being produced as a major product.

$$GeCl_4 + 2LiAlH_4 \longrightarrow GeCl_2 + H_2 + 2LiCl + 2AlH_3$$

$$GeCl_4 + AlH_3 \longrightarrow GeCl_2 + H_2 + AlHCl_2$$
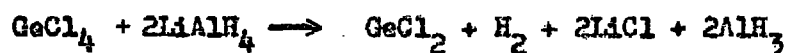
The germanium hydride series has been extended by Amberger (71) who prepared tetragermane and pentagermane (Ge_4H_{10} and Ge_5H_{12}) along with the simpler germanes by the action of 10% aqueous hydrochloric acid on a germanium-magnesium alloy. Iso-tetragermane, iso-pentagermane and neo-pentagermane were among the products obtained by Drake and Jolly (72) who subjected GeH_4 to a silent electrical discharge. Normal germanes up to nonagermane were also detected. Separation was achieved by vapour-phase chromatography and for identification, vapour pressures, infrared spectra, mass spectroscopy and proton magnetic resonance were employed. Some fully deuterated germanes have also been prepared from a magnesium-germanium alloy by treating it with DCl in D_2O (73)

The higher germanes have lower thermal stabilities than monogermane. On pyrolysing, they break down producing monogermane and "germanoethylene", $(GeH_2)_x$. Complete breakdown to germanium and hydrogen occurs above 350°.

GeH_4: b.p. -90° at 760 mm. Decomposes at 350°

Ge_5H_{12}: b.p. 20° at 10^{-5} mm. Decomposes at 100°

The hydride $(GeH_2)_x$ has been prepared by a number of methods (74,75, 76,77), for example:

$$CaGe + 2HCl \longrightarrow CaCl_2 + GeH_2 \longrightarrow (GeH_2)_x$$

and
$$NaGeH_3 + PhBr \longrightarrow NaBr + PhH + (GeH_2)_x$$
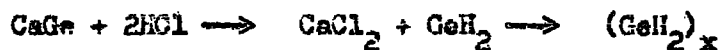
It has a low solubility and volatility and explodes in air. Bromination gives germanium(IV)bromide and hydrolysis proceeds according to the scheme

$$(GeH_2)_x \xrightarrow{H_2O} (HGeOH)_x \underset{aq.KOH}{\overset{aq.HCl}{\rightleftharpoons}} (HGeCl)_x$$
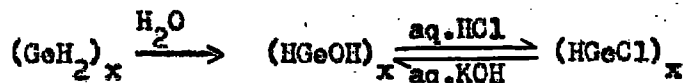
Prolonged heating with aqueous potassium hydroxide gives K_2GeO_2, H_2 and GeH_4.

b) The partially substituted germanes.

Compounds of the type $RGeH_3$, R_2GeH_2 and R_3GeH are well known. They are usually prepared by reducing the corresponding organo halides, oxides or sulphides. The most convenient and now almost standard method of preparing these hydrides is the action of lithium aluminium hydride on a germanium halide in ether (16, 27, 78, 79, 80, 81).

$$R_nGeX_{4-n} \xrightarrow{LiAlH_4} R_nGeH_{4-n}$$

Similar reactions using sodium borohydride in tetrahydrofuran (19) or lithium hydride in dioxan (55, 82) have also been used, the yields being slightly lower than for $LiAlH_4$ (70-90%). Germanium halides have been

roduced by zinc and hydrochloric acid (83). This method is of little use as the yields are small, but it is of interest since silicon and tin hydrides cannot be reduced in this way.

The hydrolysis or ammonolysis of germyl-sodium or lithium reagents produces the equivalent hydrides (5, 24), and recently it has been shown that germyl Grignard reagents behave similarly (39). Methylgermane, MeGeH$_3$, has been prepared by the action of methyliodide on germyl-sodium in liquid ammonia (84).

$$NaGeH_3 + RI \longrightarrow RGeH_3 + NaI$$
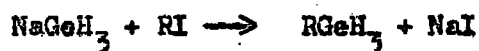
Partially halogenated derivatives of monogermane have been obtained by the action of hydrogen halides on monogermane (85) and by reactions such as

$$Ge + HCl \xrightarrow{600^o} GeHCl_3 \quad (86)$$
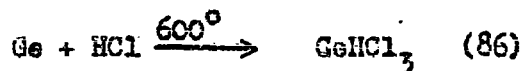
Also, compounds containing an organic group, hydrogen and a halogen bonded to a central germanium atom were recently prepared by Anderson (87) who reacted di- and tri-hydrides of germanium with a deficiency of mercuric halide or iodine.

Properties of the partially substituted germanes.

The organogermanium hydrides are relatively stable to air, although signs of oxidation have been noticed with Ph$_3$GeH on long standing. The alkylgermanium hydrides differ markedly from the corresponding silicon and tin compounds in their resistance to hydrolysis by basic solutions (88). Triphenylgermane, however, does react with ethanolic potassium hydroxide with the evolution of hydrogen (89).

The hydrogen atoms bonded to germanium are very easily displaced by halogens (79, 27) or by alkali metals: for example

$$Et-(iso-amyl)GeH_2 \xrightarrow{\text{Li in ethylamine}} Et-(iso-amyl)GeHLi + \tfrac{1}{2}H_2 \quad (90)$$
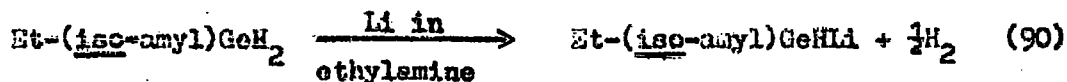
The addition of germanium hydrides to olefinic or acetylenic systems has been mentioned (page 5).

Germanium hydrides are quite strong reducing agents.   Triethylgermane reduces salts of platinum, palladium, gold and mercury to the metals, and copper(II), titanium(IV) and vanadium(V) compounds to lower valency states (78).   Alkylgermanium hydrides reduce certain organic halides without catalysis and in a selective manner (91):

$$PhCOCl \longrightarrow PhCHO$$

$$CCl_3COOH \longrightarrow CH_3COOH$$

$$ClCH_2OCH_3 \longrightarrow CH_3OCH_3$$

$$CCl_4 \longrightarrow CHCl_3$$
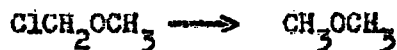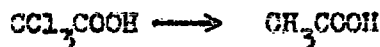
From the reaction of triphenylgermane with organolithium reagents arises one of the most pronounced differences between germanium compounds and those of silicon and tin (35).   Triphenylgermane metallates, whereas the stannane and silane alkylate.

$$Ph_3SiH + RLi \longrightarrow Ph_3SiR + LiH$$

$$Ph_3GeH + RLi \longrightarrow Ph_3GeLi + RH$$

In this respect triphenylgermane resembles triphenylmethane.   The reaction between Et_3GeH and n-butyl-lithium yields less than 10% of Et_3GeLi,

however (92).

4. ORGANOGERMANES INVOLVING OTHER NON-METALS.

a) Oxides and sulphides.

Organogermanium halides are readily hydrolysed, but the immediate products – germanium hydroxides (germanols) – are usually unstable and tend to dehydrate in a bimolecular reaction.

$$2R_3GeOH \rightleftharpoons R_3GeOGeR_3 + H_2O$$
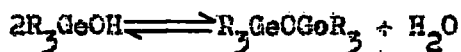
However, some germanols have been isolated in a pure state (93, 94, 5, 20, 45). Some of these (e.g. iPr_3GeOH and $(\alpha\ naphth)_3GeOH$) are too sterically hindered to allow the bimolecular elimination and can be prepared without difficulty. Triphenylgermanol has been prepared by the oxidation of triphenylgermyl-sodium, followed by careful hydrolysis (5).

$$Ph_3GeNa \xrightarrow{O_2} Ph_3GeONa \xrightarrow{H_2O} Ph_3GeOH$$
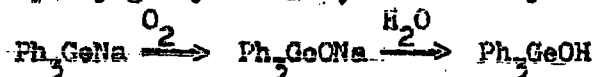
Germanium analogues of ketones are unknown, and compounds of the type R_2GeO associate to polymers or cyclic oligomers. Thus $(Me_2GeO)_{3,4\ or\ n}$ (95), $(Et_2GeO)_{2,3\ or\ 4}$ (1), $(nPr_2GeO)_{3\ or\ 4}$ (79,96), $(iPr_2GeO)_3$ (20,97) and $(Ph_2GeO)_{3,4\ or\ n}$ (1,98) are known. The structures are probably of the type:
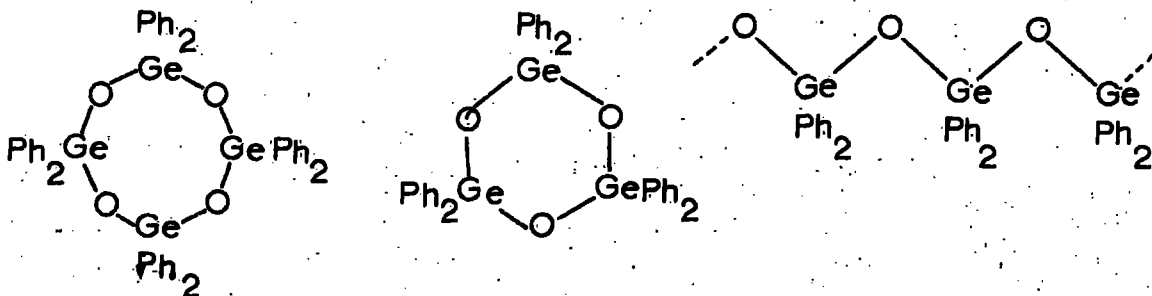
$(PrGeO)_2O$ also occurs in tetrameric form (99).

Other germanium oxygen compounds which have been studied include the alkoxides and esters. These can be made by the action of sodium alkoxides on germanium halides (100, 101) and by the reaction between acid anhydrides and germanium oxides (102, 103) respectively.

$$nRONa + R'_{4-n}GeX_n \longrightarrow R'_{4-n}Ge(OR)_n + nNaX$$

$$(R_3Ge)_2O + (R'CO)_2O \longrightarrow 2R_3GeOOCR'$$
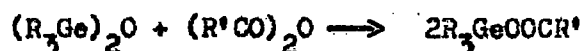
Less is known about the sulphur analogues of the oxygen compounds, but the general trends seem similar to the oxides.

b) Nitrogen and phosphorus compounds.

The ammonolysis of organohalogermanes has been extensively studied. Trimethylbromgermane reacts with ammonia in benzene to give the amine Me_3GeNH_2 and ammonium bromide, whereas when ammonia is condensed onto triethylbromgermane, $(Et_3Ge)_2NH$ is given. This is a colourless liquid which is rapidly hydrolysed by water to give hexaethyldigermoxane (24). Et_2GeBr_2 reacts with NH_3 to give the imine, Et_2GeNH, which is probably tetrameric (29) resembling the oxide Et_2GeO. Ethyltribromgermane, $EtGeBr_3$, is similarly ammonolysed to give $(EtGeN)_n$ which is hydrolysed by water to the germanoic anhydride, $(EtGeO)_2O$ (104).

The conditions of the reaction between triphenylbromgermane and ammonia can be varied to give good yields of either Ph_3GeNH_2, $(Ph_3Ge)_2NH$ or $(Ph_3Ge)_3N$ (5, 105). The amines react with hydrogen chloride to give triphenylchlorgermane.

Recently, compounds have been prepared involving germanium bonded to phosphorus (106).

$$Et_3GeBr + Ph_2PLi \longrightarrow Et_3GePPh_2 + LiBr$$

Most of the reactions of this and related compounds which have been studied involve rupture of the Ge-P bond.
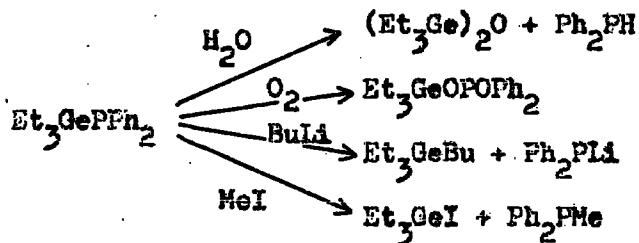
5. ORGANOGERMANIUM – ALKALIMETAL COMPOUNDS AND GRIGNARD REAGENTS.

a) Alkalimetal compounds.

Alkali metal derivatives of germanium are very reactive species and are therefore useful in synthetic reactions. Few of the methods of preparation so far tried are quantitative, however, and experimental conditions often need to be stringently controlled. Nevertheless continued interest has been shown in this field since Kraus and Foster demonstrated the existence of triphenylgermyl-sodium in 1927.

Triphenylgermyl-sodium, Ph$_3$GeNa, was prepared by adding tetraphenylgermane to a solution of sodium in liquid ammonia (5).

$$Ph_4Ge + 2Na \xrightarrow{NH_3} Ph_3GeNa + NaNH_2 + C_6H_6$$
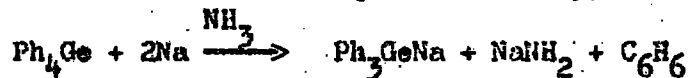
The sodamide and benzene were probably produced by the reaction between phenylsodium and ammonia. Hexaphenyldigermane was also cleaved by sodium in ammonia to produce triphenylgermyl-sodium. These reactions are slow, probably due to the small solubility of the starting materials

in liquid ammonia. The alkalimetal compounds were generally not isolated (although $Ph_3GeNa.3NH_3$ has been crystallised); their existence being demonstrated by the isolation of the products of their reactions.

e.g. $Ph_3GeNa + Me_3SnBr \longrightarrow Ph_3GeSnMe_3 + NaBr$ (5)

Cleavage of Ge-H bonds, as well as Ge-C and Ge-Ge, also produced germyl-sodium compounds.

$$Ph_3GeH + Na \xrightarrow{NH_3} Ph_3GeNa + \tfrac{1}{2}H_2$$

In all of these reactions involving an excess of alkali metal, a red colour was observed after the formation of the yellow Ph_3GeNa. This was assumed to be the disodio derivative, diphenylgermyl-disodium. This was further investigated by the reaction of sodium in liquid ammonia on octaphenylcyclotetragermane, Ph_8Ge_4 (42). The colour changes observed indicated that the reaction proceeded by the following path:

$(Ph_2Ge)_4 \longrightarrow 2Ph_2(Na)Ge-Ge(Na)Ph_2$ (yellow) $\longrightarrow 4Ph_2GeNa_2$ (red)
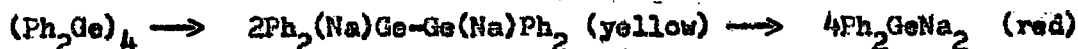
In no case was the existence of these compounds confirmed by isolating their reaction products, however.

In 1932, Kraus and his co-workers turned their attention to ethylgermanium derivatives (24). The reaction between hexaethyl-digermane and lithium in ammonia was not a very satisfactory route to trimethylgermyl-alkalimetal compounds, as the reaction was slow, and the compound reacted readily with solvent.

$$Et_6Ge_2 \xrightarrow{Li\ in\ NH_3} Et_3GeLi \xrightarrow{NH_3} Et_3GeH + LiNH_2$$
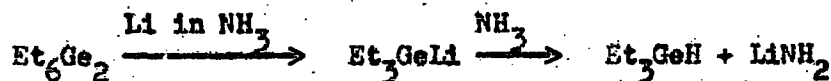
Ethylamine proved a better solvent than liquid ammonia, and potassium
reacted smoothly to give yellow solutions of tri-ethylgermyl-potassium
which did not cleave the solvent.

Hexaethyldigermoxane (24) and triethylsilyltriphenylgermane (107)
were also cleaved by lithium in ethylamine, but those gave mixtures of
lithio derivatives.

$$Et_3GeOGeEt_3 \xrightarrow{\text{Li in EtNH}_2} Et_3GeLi + Et_3GeOLi$$

$$Et_3SiGePh_3 \xrightarrow{\text{Li in EtNH}_2} Et_3SiLi + Ph_3GeLi$$
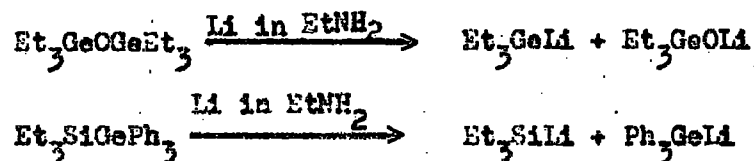
A sodio derivative of monogermane was prepared by bubbling the gas into
a solution of sodium in liquid ammonia (75), and more recently the
corresponding lithio compound has been made by the same method (108).

$$GeH_4 + Na \xrightarrow{NH_3} H_3GeNa$$
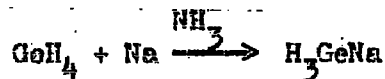
Germylpotassium has been prepared by the reaction of monogermane on
potassamide.

$$GeH_4 + KNH_2 \xrightarrow{NH_3} H_3GeK + NH_3 \quad (90)$$

Glarum and Kraus investigated the reaction between sodium in
ammonia and lithium in ethylamine on many other germanium hydrides (90)

$$e.g. \quad EtGeH_3 \xrightarrow{\text{Na in NH}_3} EtH_2GeNa + \tfrac{1}{2}H_2$$
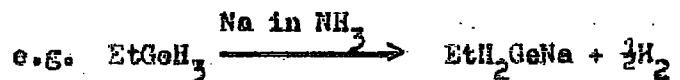
Often the amount of hydrogen given was less than the stoichiometry
required but some reactions were quantitative:

$$(\underline{iso}\text{-Amyl})EtGeH_2 \xrightarrow{\text{Li in EtNH}_2} (\underline{iso}\text{-Amyl})EtHGeLi$$

An important advance was made in 1955 when Gilman and Gerow prepared triphenylgermyl-lithium in an ether solvent (109). Hexaphenyl-digermane, tetraphenylgermane and triphenylchlorgermane all react with lithium in 1,2-dimethoxyethane to give triphenylgermyl-lithium in yields of about 65%.

$$Ph_6Ge_2 + 2Li \longrightarrow 2Ph_3GeLi$$
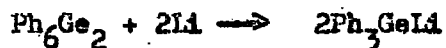
A large excess of lithium (preferably finely divided) and the minimum of dry, peroxide-free solvent are necessary to initiate the reaction. After an induction period (usually from 5 minutes to 3 hours) the reaction proceeds smoothly at room temperature over about 2 hours. When tetra-phenylgermane is used, the phenyl-lithium also produced reacts with the solvent much more rapidly than the triphenylgermyl-lithium. Triphenyl-bromgermane (110) and triphenylgermane (111) also react with lithium in 1,2-dimethoxyethane to give triphenylgermyl-lithium. The halides probably react via the intermediate formation of hexaphenyldigermane.

The cleavage by alkalimetals of hexaphenyldigermane has been examined under a number of conditions (38). At reflux temperatures, no reaction was produced by sodium in xylene, caesium in ether, or by a 1:5 sodium-potassium alloy in diethylether, di-n-butylether, benzene or xylene. Yields of 60% of triphenylgermyl potassium were produced by cleavage by the sodium-potassium alloy in ether when an initiator (tetrahydrofuran, tetraphenylgermane, or phenylbromide) was added, however.

In another similar series of experiments Gilman and his co-workers examined the cleavage of organic groups other than phenyl from germanium

by alkalimetals (112). Evidence was obtained that phenyl groups were cleaved more easily than others. When mixed alkylarylgermanes were reacted with lithium in monoglyme, a phenyl group was eliminated.

$$(n\text{-}C_{18}H_{37})Ph_3Ge \xrightarrow{\text{Li in monoglyme}} (n\text{-}C_{18}H_{37})Ph_2GeLi$$

$$(PhCH_2CH_2)Ph_3Ge \xrightarrow{\hspace{3cm}} (PhCH_2CH_2)Ph_2GeLi$$

Gilman also examined the reaction of lithium or sodium-potassium alloy on other fully substituted organogermanes. In no cases was positive evidence for germyl-alkalimetal compounds found, but in many reactions (for example tetraethylgermane with 1:5 Na-K alloy) no starting material was recovered. In the reaction between tetrabenzylgermane and lithium in 1,2-dimethoxy-ethane, a brown colour developed, which was discharged on addition of ethylbromide. No product was isolated, however. The first part of this thesis describes a re-examination of this reaction.

Another method which can produce good yields of triphenylgermyl-lithium is the reaction between triphenylgermane and an organolithium reagent in ether (35). n-Butyl-lithium has been reported to give almost quantitative yields, but phenyl-lithium and methyl-lithium give some tetraorganogermane as well.

$$Ph_3GeH + BuLi \longrightarrow Ph_3GeLi$$

$$Ph_3GeH + PhLi \longrightarrow Ph_3GeLi\ (86\%) + Ph_4Ge$$

$$Ph_3GeH + MeLi \longrightarrow Ph_3GeLi\ (80\%) + Ph_3GeMe$$
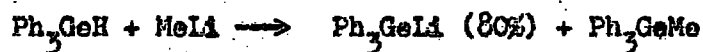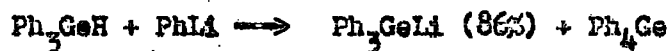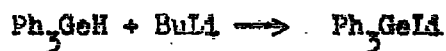
Earlier, the reaction between Ph_3GeH and PhLi had been reported to give either Ph_4Ge on Ph_6Ge_2 under more drastic conditions (34). The metallation reaction does not appear to be general to all organogermanium hydrides, however. Triethylgermane gives only 10% of Et_3GeLi with n-butyl-lithium (92), although $(Ph_3Ge)_3GeH$ and $(\alpha-Naph)MePhGeH$ both react smoothly to give the lithio reagent in good yield (43, 113). The reaction between alkyl-lithium reagents and germanium hydrides is also further examined in the present work.

Properties of the alkali metal compounds.

Solutions of triphenylgermyl-sodium in liquid ammonia are yellow or orange depending on the concentration, and $Ph_3GeNa.3NH_3$ can be crystallised from these solutions. Triphenylgermyl-lithium is generally brown in 1,2-dimethoxyethane, but yellow in diethylether. The germyl-alkali metal compounds are very similar to organolithium reagents in their reactions.

Triphenylgermyl-sodium reacts rapidly with oxygen to give the germanolate (5).

$$Ph_3GeNa + (O) \longrightarrow Ph_3GeONa$$
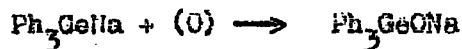
Reaction with moisture or acids (e.g. NH_4Cl in NH_3) converts the alkalimetal compounds to hydrides.

$$Ph_3GeLi + H_2O \longrightarrow Ph_3GeH + LiOH$$

Carbonation of a solution of triphenylgermyl-potassium produces, after acidifying, triphenylgermyl carboxylic acid, $Ph_3GeCOOH$ (114,115). This

compound decarbonylates on heating, giving finally hexaphenyldigermoxane.

$$Ph_3GeCOOH \xrightarrow{200^o} [Ph_3GeOH] \xrightarrow{Ph_3GeCOOH} Ph_3GeOC:OGePh_3 \xrightarrow{250^o} Ph_3GeOGePh_3$$

Several esters of this acid are known. Methyl triphenylgermylcarboxylate, for example, can be made by reaction with diazomethane.

$$Ph_3GeCOOH + CH_2N_2 \longrightarrow Ph_3GeCOOMe + N_2$$
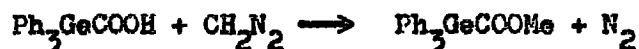
This ester also decarbonylates at high temperatures (116)

$$Ph_3GeCOOMe \xrightarrow{250^o} Ph_3GeOMe + CO$$
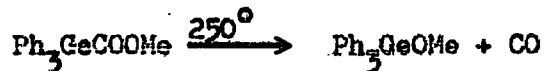
The reactions of triphenylgermyl-lithium with certain olefins and carbonyls have already been mentioned (page 6). The reaction between triphenylgermyl-lithium and azoxybenzene has also been studied (117). The first step is reduction to azobenzene, which then reacts further

$$Ph_3GeLi + PhN\overset{O^-}{=}\overset{\uparrow^+}{N}Ph \longrightarrow PhN=NPh + Ph_3GeOLi$$

$$PhN=NPh + Ph_3GeLi \longrightarrow PhN\overset{Li}{\underset{GePh_3}{-}}NPh \xrightarrow{H_2O} PhN\overset{H}{\underset{GePh_3}{-}}NPh$$
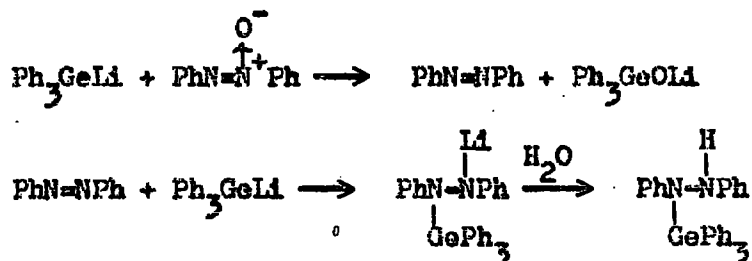
With methyl triphenylgermyl carboxylate or diethylcarbonate, however, instead of adding across the carbonyl double bond, Ph₃GeLi produces hexaphenyldigermane with decarbonylation (109).

$$Ph_3GeLi + Ph_3GeCOOMe \longrightarrow Ph_6Ge_2 + CO + LiOMe$$

$$2Ph_3GeLi + (EtO)_2CO \longrightarrow Ph_6Ge_2 + CO + 2LiOEt$$
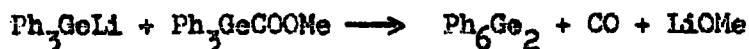
Triphenylgermyl-lithium undergoes hydrogen-metal exchange with "acidic" hydrocarbons (14). For example fluorene is metallated in the 9 position.
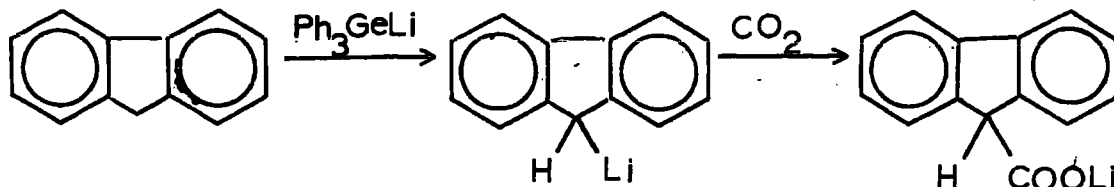
Some of the reactions of germyl-sodium, H_3GeNa, are anomalous due to the germanium hydrogen bonds (75). The action of heat causes decomposition to NaGe alloy and hydrogen, and oxygen reacts with the Ge-H bonds as well as the Ge-Na link.

The reaction between germyl-alkalimetal compounds and organic halides usually gives rise to the expected coupling products. For example:

$$Ph_3GeNa + PhBr \longrightarrow Ph_4Ge \qquad\qquad (5)$$

$$(C_{18}H_{37})Ph_2GeLi + PhCH_2CH_2Br \longrightarrow (C_{18}H_{37})Ph_2GeCH_2CH_2Ph \quad (112)$$

$$Et(i\text{-}Amyl)HGeLi + EtBr \longrightarrow Et_2(i\text{-}Amyl)GeH \qquad\qquad (90)$$
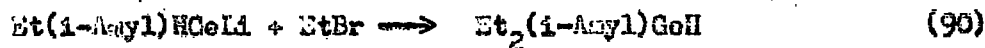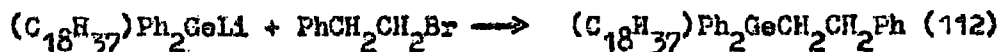
Reactions with Group IV metal halides also usually proceed in a similar manner.

$$Ph_3GeNa + Me_3SnBr \longrightarrow Ph_3GeSnMe_3 \qquad\qquad (5)$$

$$2Ph_3GeNa + Ph_2GeCl_2 \longrightarrow Ph_3Ge(Ph_2Ge)GePh_3 \qquad\qquad (42)$$

A common complication, however, is halogen-metal exchange. Subsequent coupling reactions can give a mixture of products, often difficult to separate. The reaction between triphenylgermyl-potassium and triphenyl-chlorsilane (115, 118) is an example of this.

$$Ph_3GeK + Ph_3SiCl \longrightarrow Ph_3GeSiPh_3$$

$$Ph_3GeK + Ph_3SiCl \longrightarrow Ph_3GeCl + Ph_3SiK$$

$$Ph_3GeK + Ph_3GeCl \longrightarrow Ph_6Ge_2$$

$$Ph_3SiK + Ph_3SiCl \longrightarrow Ph_6Si_2$$
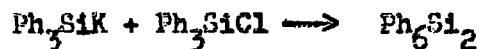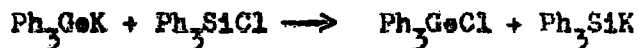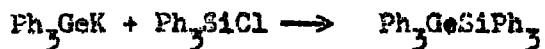
A more recent example of the synthetical value of germylalkalimetal compounds is the coupling of triphenylgermyl-lithium with certain transition-metal halides to give germanium-transition metal compounds (119).

$$Me_3PAuCl + Ph_3GeLi \longrightarrow Me_3PAuGePh_3 + LiCl$$
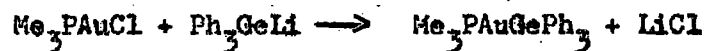
b). <u>Grignard reagents.</u>

Compared with the alkali metal compounds, much less is known about germyl Grignard reagents. No method has yet been devised which can produce a good yield of R_3GeMgX for subsequent reaction, but very strong evidence is available that these compounds exist as intermediates in many systems.

Attempts to prepare trimethylgermyl-magnesium chloride by reacting Me_3GeCl with metallic magnesium failed (37). The reaction between an organolithium reagent and triphenylgermane to give triphenylgermyl-lithium has been described (page 28) and Gilman and his co-workers attempted to carry out the equivalent reaction:

$$RMgX + Ph_3GeH \longrightarrow Ph_3GeMgX + RH$$
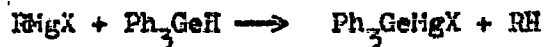
Allyl- and n-butyl-magnesium halides failed to react in refluxing diethyl ether (55). The use of tetrahydrofuran as a solvent was more successful, however. Carbonation after a reaction using allyl-magnesium

chloride gave some triphenylgermyl carboxylic acid. Some 4-hydroxy-butyltriphenylgermane was also isolated from a side reaction involving cleavage of the solvent. When phenyl or allyl Grignard reagent was used as the metallating agent, only the cleavage product was obtained after refluxing for 2 days (120).

$$Ph_3GeMgCl + \underset{\underset{O}{\overset{CH_2\text{---}CH_2}{|\qquad\qquad|}}{CH_2\quad CH_2}} \longrightarrow Ph_3Ge(CH_2)_4OMgCl \xrightarrow{H_2O} Ph_3Ge(CH_2)_4OH$$
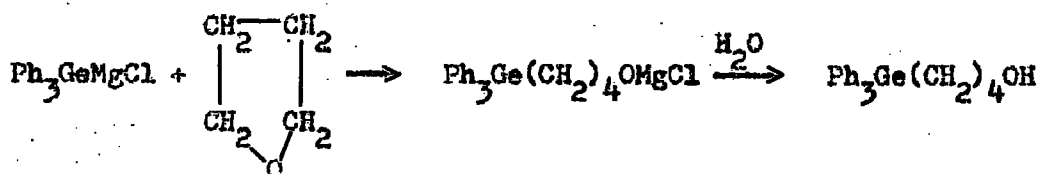
No reaction was reported for n-butyl-magnesium halides.

In the reaction between vinyl-magnesium bromide and $GeCl_4$, Seyferth isolated $(Vinyl)_4Ge$ and $(Vinyl)_6Ge_2$, and he postulated $(Vinyl)_3GeMgBr$ as an intermediate (37). The reaction between i-PrMgBr and $GeCl_4$ has produced i-Pr$_3$GeH after hydrolysis and this reaction has been assumed to proceed via i-Pr$_3$GeMgBr (28). Recently Glockling and Hooton (39) showed that germyl Grignard reagents were produced as intermediates in the reaction of aryl Grignard reagents and $GeCl_4$ to produce R_6Ge_2 (see page 9). These are produced primarily by the reaction between an intermediate organogermanium halide and the reactive magnesium left after the formation of the Grignard reagent, but also by halogen-metal exchange (to a lesser extent).

$$R_3GeX + Mg \longrightarrow R_3GeMgX$$

$$R_3GeX + R'MgX' \longrightarrow R_3GeMgX' + R'X$$
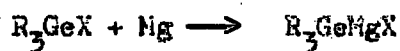
The presence of the germyl Grignard reagents in reactions which were not allowed to proceed to completion was shown by hydrolysis or carbonation.

$$(\text{o-tolyl})_3\text{GeMgBr} \xrightarrow{\text{H}_2\text{O}} (\text{o-tolyl})_3\text{GeH}$$

$$(\text{p-tolyl})_3\text{GeMgBr} + \text{CO}_2 \xrightarrow{\text{H}_2\text{O}} (\text{p-tolyl})_3\text{GeCOOH}$$
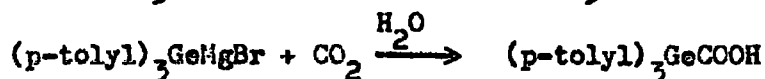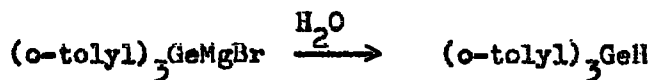
C. Organic Compounds of Divalent Platinum.

Although organic compounds of platinum(IV) have been known since 1909 (122), compounds containing divalent platinum sigma-bonded to carbon were first isolated only a few years ago (123). Since then a large number of thermally stable hydrido, alkyl and aryl complexes of platinum(II) have been prepared, and these afford some interesting comparisons and contrasts with the germyl-platinum complexes described in the second part of this thesis. All of these compounds involve π-bonding ligands, and a knowledge of the coordination chemistry of divalent platinum is necessary to explain some of their properties.

1. COORDINATION COMPLEXES OF PLATINUM(II).

(a) Structure.

Stable coordination complexes of the types PtX_4^{2-}, $PtLX_3^{-}$, PtL_2X_2, PtL_3X^{+} and PtL_4^{2+} (where X^{-} is an anionic ligand and L is a neutral ligand) are known. They are all square planar and diamagnetic. A few octahedral complexes of platinum(II) have also been characterised, but always four of the ligands in a square configuration are closer to and more strongly held by the platinum than the other two. These structures are explained by the arrangement of the platinum 5d electrons.

The free ion Pt^{2+} has eight electrons available to occupy its five degenerate 5d orbitals, and these should be distributed to give the least spin-pairing according to Hund's rule. In chemical compounds, however,

free Pt^{2+} is unknown; the ion is always solvated or complexed. In the ensuing electric field the degeneracy of the outer d orbitals is lifted and the electrons are located in the low energy orbitals with spin-pairing. Thus the d_{xy}, d_{yz}, d_{zx} and d_{z^2} orbitals each contain two electrons and the $d_{x^2-y^2}$ orbital is vacant.

$$d_{xy} \qquad d_{zx} \qquad d_{yz} \qquad d_{z^2} \qquad d_{x^2-y^2}$$
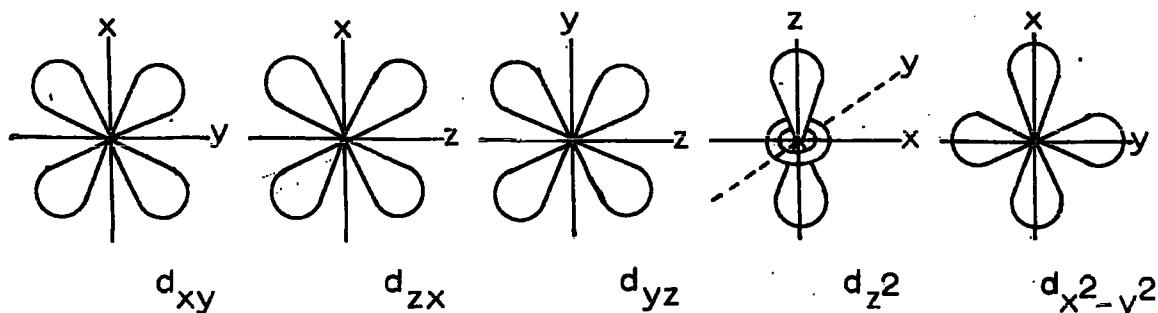
Distribution of electron density in the five d orbitals.

The vacant $5d_{x^2-y^2}$ orbital leads to a decrease in nuclear shielding in the directions of the x and y coordinates, allowing four ligands to approach the nucleus more closely in these directions. Alternatively, for covalent bonding, the $d_{x^2-y^2}$ orbital is available to form square-planar dsp^2 hybrid orbitals with the 6s and 6p orbitals.

(b) The trans-effect.

The square configuration of 4-coordinate platinum(II) allows complexes of the type PtL_2X_2 to exist as either cis or trans geometrical isomers. Both isomers are known for most complexes; indeed it was mainly the discovery of these geometrical isomers which lead to the idea that their structure is planar.

An examination of ligand replacement reactions in these compounds shows that the ligand situated <u>trans</u> to the leaving group has a great influence on its stability (124) whereas the neighbouring <u>cis</u> groups have a relatively small effect. The classical illustration of this is the reactions leading to the isolation of <u>trans</u> $(NH_3)_2PtCl_2$ by Reiset in 1844 (125) and <u>cis</u> $(NH_3)_2PtCl_2$ by Peyrone in 1845 (126). Reiset heated the salt $[Pt(NH_3)_4]Cl_2$, liberating two NH_3 molecules and replacing them by Cl^- ions.
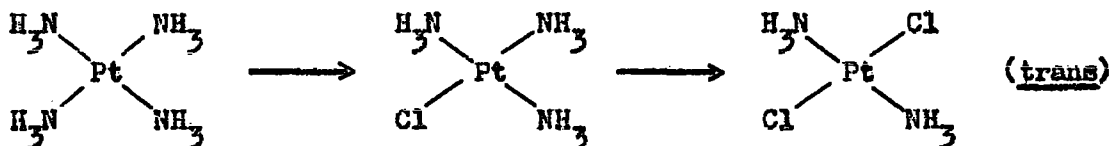
In the second step the ammonia <u>trans</u> to the chloride ion is replaced more readily than the ammonia opposite ammonia. A similar case is Peyrone's reaction from which the <u>cis</u> compound is obtained by treating $PtCl_4^{2-}$ with a buffered ammonia solution.
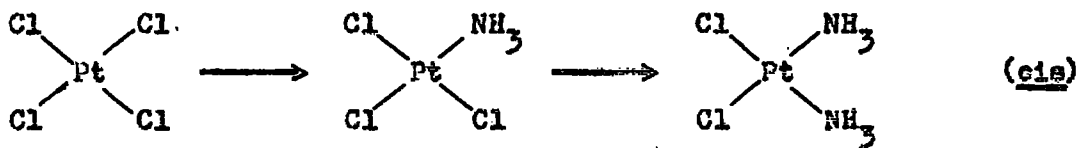
Here the chloride ion opposite another Cl^- is labilised, rather than the one <u>trans</u> to NH_3. A chloride ion has a greater labilising influence than ammonia on the group <u>trans</u> to it: the "<u>trans</u> effect" order is $Cl^- > NH_3$.

Similar studies have allowed a series of the relative <u>trans</u> effects of ligands to be assembled. The usual order is CN^-, CO, C_2H_4, NO > $SC(NH_2)_2$, PR_3, SR_2 > NO_2^- > I^-, SCN^- > Br^- > Cl^- > NH_3, py, RNH_2 > OH^- > H_2O (127). The importance of the <u>trans</u> effect in the synthesis of platinum complexes was recognised by Chernyaev (128). With the ability

to predict which group will be replaced, different isomers can be produced often merely by reversing the order in which ligands are added to $PtCl_4^{2-}$. Chernyaev demonstrated the principles involved in his synthesis of the three possible isomers of $[PtNH_3py(NH_2OH)NO_2]Cl$ in 1926.

There are limitations to the application of the _trans_ effect in this manner. The leaving group and entering group in ligand exchange reactions have an influence and small variations in the normal _trans_ effect order can occur. Also, certain systems are able to isomerise, leading to un-expected products. For example, as the relative _trans_ effects are $PR_3 >$ Cl^-, _cis_ and _trans_ $(R_3P)_2PtCl_2$ should be obtained by the reactions

(cis)

and
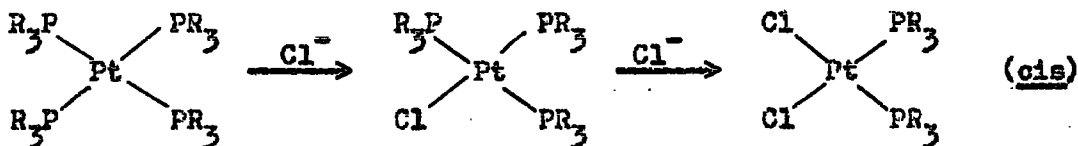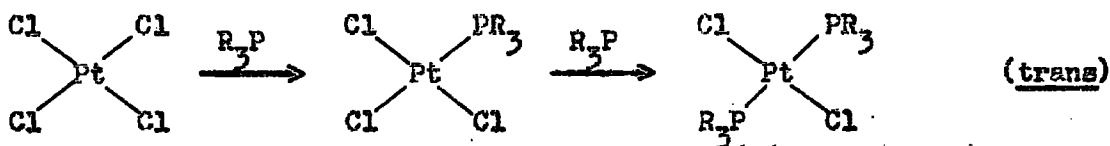
(trans)

It was found, however, that either isomer can be obtained from either system. The reason is that when an excess of phosphine is present, isomerisation can occur.
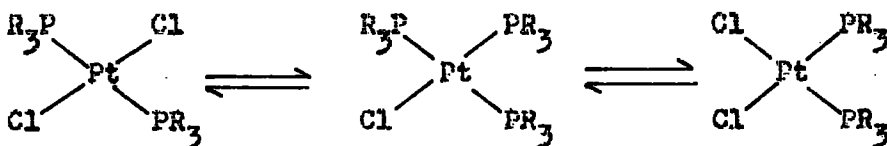
In solution the _trans_ form is thermodynamically more stable than the _cis_

form, and is present to a greater extent at equilibrium (129). If excess $PtCl_4^{2-}$ is added to remove the phosphine and freeze the equilibrium, the trans form can then be crystallised. With excess PR_3 present the equilibrium is maintained and the less soluble cis isomer crystallises. This method of synthesis can also be applied to arsine complexes (130).

As defined, the trans effect is a measure of the trans labilising ability of a given ligand relative to other ligands. An increase in reactivity could come about by a lowering of the Pt-X bond strength (where X is the leaving group) or from factors leading to a decrease in activation energy for the reaction. The trans effect series has been supplemented by various kinetic studies and physical measurements in attempts to explain the phenomenon.

The rates of several reactions of the type $[Pt(trien)X] + Y \longrightarrow$ $[Pt(trien)Y] + X$ (where (trien) $= H_2NCH_2CH_2NHCH_2CH_2NH_2$) have been measured (131, 132) and the results show differences of 10^5 for different X groups, although the trans ligand is the same in each case. The rates tend to decrease with increasing bond strength of Pt-X. Further kinetic studies (131, 132, 133) indicate that the reactions are first order with respect to the entering group, Y, and that the relative effect of different Y groups on the rate of reaction gives a series similar to the trans effect order.

These and other observations have led to the conclusion that the ligand replacement reactions proceed via an S_N2 mechanism, probably involving a trigonal bipyramidal intermediate (127). For example:
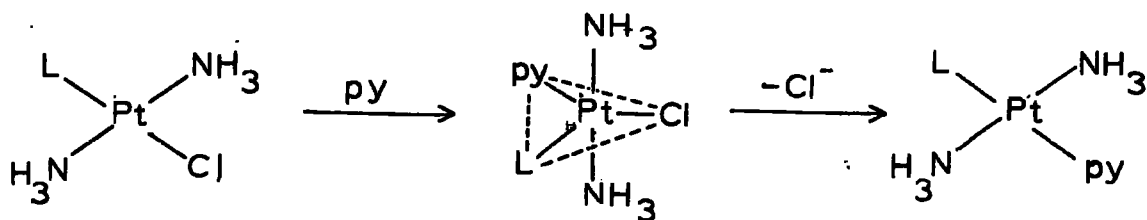
(c) Physical consequences of the trans effect.

The effects of ligands on the strengths of trans Pt-X bonds have been compared by various physical techniques, the most important being X-ray studies and infrared spectra.

Changes in the bond length of Pt-X brought about by changing the trans group have not been extensively studied, but the structures of some 4-coordinate platinum(II) compounds have been elucidated by X-ray methods. Differences in bond length resulting from the trans effect are small and precise measurements are needed. For example in the compound $K[Pt(NH_3)Cl_3]$ no significant difference was found in the bond lengths of the Pt-Cl bonds trans to Cl^- or NH_3 (134). However, for the corresponding compound $K[Pt(NH_3)Br_3]$ the Pt-Br distance trans to NH_3 is 2.42Å (near the sum of the atomic radii) but the bond trans to Br^- is 2.7Å. Similar lengthening of bonds opposite ligands of high trans effect has been detected in the anion of Zeise's salt $[Pt(C_2H_4)Cl_3]^-$ (135) and its bromine analogue $[Pt(C_2H_4)Br_3]^-$ (136). The structure of trans $(Et_3P)_2Pt(H)Br$ has also been determined, and the Pt-Br bond length is longer than normal (137). H^- is known to have a large trans effect.

These results indicate that groups of high trans effect weaken

(and thereby lengthen) the Pt-X bond. The Pt-N bond length in trans [Pt(C$_2$H$_4$)(NHMe$_2$)Cl$_2$] is anomalous in this respect however. Although opposite a group of very high trans effect (ethylene) the Pt-N distance is essentially normal (138). The difference between the effect of the trans ethylene in this compound and in the halogen compounds mentioned above can be accounted for if the trans effect of π bonding ligands is due to modifications in the π bonding system. Nitrogen has no π bonding character here, where chlorine and bromine may have.

Infrared measurements, mainly by Chatt and his co-workers, have led to information on the relative strength of Pt-X bonds by various routes. Examination of the N-H stretching frequencies in the series of compounds trans [PtL(NHR$_2$)Cl$_2$] leads to the relative strengths of Pt-N by the following argument (139): ν(N-H) increases as its bond strength increases because the N atom is more negative. Therefore the Pt-N bond is weaker, because the N is with-holding its electrons from platinum. The results indicate that the Pt-N bond strength decreases as the electronegativity of the trans ligand, L, decreases, and that this series roughly parallels the trans effect series. Ethylene is again exceptional: although it has a large trans effect it does not reduce the Pt-N bond strength. The position of tertiary phosphines in this series is also rather anomalous compared to the trans effect series.

More direct infrared evidence has been obtained from a series of platinum hydrides, trans (R$_3$P)$_2$Pt(H)X, (140). ν(Pt-H), which falls at about 2100 cm.$^{-1}$, decreases with ligands of increasing trans effect,

supporting the view that the labilising effect is due mainly to the weakening of the Pt-X bond. Recently, improved spectrometers have opened regions of the far infrared to study, and examinations of ν(Pt-Cl) and ν(Pt-Br) have been made (141,142). The results obtained are similar to those obtained from ν(Pt-H): they also demonstrate that CH_3^-, Ph^- and H^- have very high _trans_ effects. Once again, evidence was obtained which indicated that two mechanisms were operative to produce the _trans_ effect.

(d) Interpretation of the _trans_ effect.

The available chemical and physical evidence on square-planar platinum(II) compounds indicates that the _trans_-effect is transmitted by more than one mechanism. The many theories which have been proposed have been summarised by Basolo and Pearson (127). Essentially they can be classified into two theories.

The polarisation theory has developed from an idea by Grinberg (143) and is necessary to explain the high _trans_ effect of ligands such as H^- and CH_3^- where π bonding is unlikely to contribute. The theory begins from the consideration that the primary charge on platinum(II) will induce a dipole in the ligand L, which in turn induces a dipole in the metal atom which is unfavourable to X.
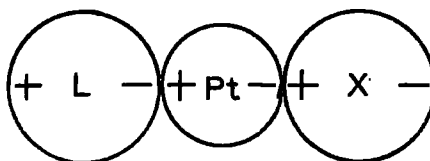
The orientation of the dipole repels charge in X and weakens the Pt-X bond. Recent extensions of this concept involve covalent bonding. The theory accounts for the parallel in the _trans_ effect and the polarisability of a ligand. It also correctly predicts that the effect should be greater in platinum(II) than in either palladium(II) or platinum(IV), as these nuclei are less polarisable. The effect is stereospecific to the _trans_ group.

The second mechanism is required to explain the high _trans_ effect of π bonding ligands such as ethylene. Physical measurements indicate that the _trans_ Pt-X bond is not weakened, and it seems reasonable to seek the explanation in the π bonding system.
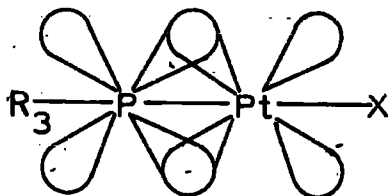
Overlap in dπ bonding

Chatt (144) has pointed out, however, that π bonding will lead to charge removal from the Pt nucleus and this will probably stabilise the other three groups, rather than labilise the _trans_ group. The current explanation, therefore, is that π bonding ligands have high _trans_ effects not by weakening the Pt-X bond but by stabilising the transition state for the reaction (144,145). Thus in a 5 coordinate transition intermediate of trigonal bipyramidal structure (see page 39), π bonding to L will reduce the electron density towards both the leaving group X and the

entering group Y, correctly predicting that the properties of Y and L will affect the rate of reaction in a similar way.

(e) Other aspects of the chemistry of platinum(II)

Although the most important consideration in the reactions of platinum(II) complexes is the _trans_ effect, ligands in the _cis_ position do exert a small influence. $v(\text{Pt-H})$ in _trans_ $(R_3P)_2Pt(H)X$ varies slightly with different phosphines, increasing electron withdrawal giving a higher stretching frequency. Also changes in the rate of reaction of systems varying only in _cis_ ligands have been noted.

The oxidation of square platinum(II) compounds to octahedral platinum(IV) compounds by oxidising agents such as halogens or H_2O_2 has been known for many years: the two additional groups add above and below the square (146).
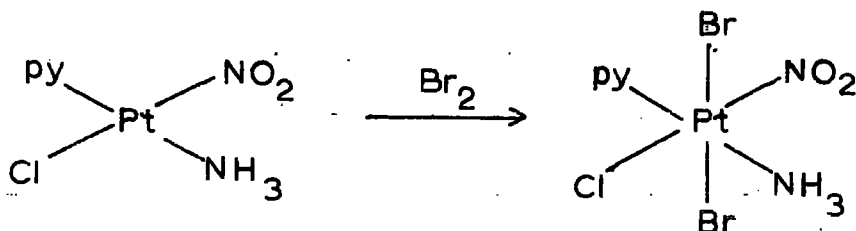
The steric course of this reaction has been utilised greatly in synthesising platinum(IV) complexes, although it does not seem to apply to certain organic compounds discussed later.

Another class of platinum(II) compounds worthy of note is the binuclear complexes.

- 44 -

$$
\begin{array}{c}
\text{L} \qquad \text{X} \qquad \text{Y} \\
\diagdown \quad \diagup \diagdown \quad \diagup \\
\text{Pt} \qquad \text{Pt} \\
\diagup \quad \diagdown \diagup \quad \diagdown \\
\text{Y} \qquad \text{X} \qquad \text{L}
\end{array}
$$
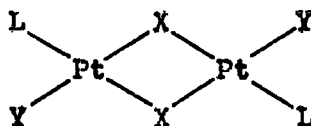
The bridging groups can be halogens, thio-compounds, phosphines or arsines. Less is known about these compounds than the mononuclear type, but they display some interesting stability relationships, and some aromatic character has been ascribed to certain of the four-membered rings (147).

2. ALKYL DERIVATIVES OF PLATINUM(II).

The addition of an electron to an antibonding molecular orbital frequently leads to the rupture of the bond. Metal-halogen bonds in complexes of the types mentioned are usually very polar and any bond dissociation is likely to be ionic:

$$L_2PtX_2 \rightleftharpoons L_2PtX^+ + X^-$$
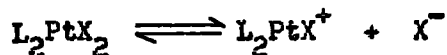
The halogen will probably detach itself as an ion (or remain as an ion pair) and the process can reverse when the anti-bonding orbital is vacated. Metal to carbon bonds tend to split homolytically, however, and the resulting free radical, $R^\bullet$, will react irreversibly with a neighbouring molecule, and the complex decomposes. The critical factor governing the stability of transition-metal to carbon bonds is the energy difference, ΔE, between the highest-energy occupied orbital and the lowest-energy antibonding orbital. This is illustrated by the simplified energy-level diagram for planar Pt(II) complexes below.

$$\Delta E \qquad \begin{array}{ll} \text{———————} & d_{sp}2 \text{ antibonding orbitals} \\[4pt] \text{—— oo ——} & d_{xy} \\[4pt] \text{— oo — — oo —} & d_{xz} \text{ and } d_{yz} \\[4pt] \text{—— oo ——} & d_{z}2 \\[4pt] \text{oo oo oo oo} & d_{sp}2 \text{ bonding orbitals.} \end{array}$$
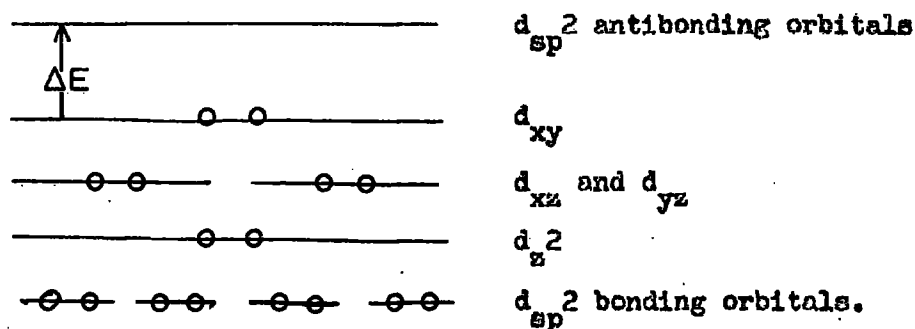
For simple transition-metal organic compounds it is considered ΔE is too small for stable bonds to result (148).

It was realised, however, that ΔE may be increased by lowering the energy of the occupied d orbitals (the d_{xy} orbital in particular for platinum(II)) by allowing them to overlap with π bonding ligands. Chatt and Shaw (140, 123, 149) isolated a series of alkyl, aryl and hydrido derivatives of platinum(II) with tertiary phosphine ligands. These ligands are particularly successful since they are relatively strong donors and have pronounced π bonding acceptor properties.

(a) Preparations.

In general, mono- and di-alkyl derivatives of platinum(II) can be prepared from a Grignard or organolithium reagent and the halide cis or trans $(R_3P)_2PtX_2$ in ether or ether-benzene solution. Complexes of the type $(R_3P)_2PtR'_2$ and $(R_3P)_2PtR'X$ have been isolated where R = Me, Et, n-Pr or Ph and R' = Me, Et, n-Pr, n-Bu and CH_2Ph (123, 149). Donors other than tertiary phosphines have been used, such as R_3As and R_2S.

The Grignard reaction appears to involve a series of equilibria, giving a mixture of products (with $(R_3P)_2PtR'X$ as the major part) even

with a large excess of R'MgX. Organolithium reagents are more suitable for preparing the fully substituted compounds.

$$\underline{cis} \; (Et_3P)_2PtCl_2 + 2MeLi \xrightarrow{90\%} \underline{cis} \; (Et_3P)_2PtMe_2 + 2LiCl$$
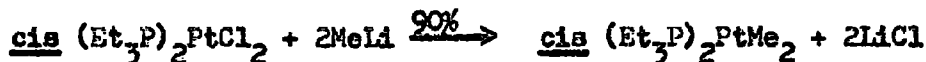
The products of these reactions have the configuration $\underline{cis} \; (R_3P)_2PtR'_2$ and $\underline{trans} \; (R_3P)_2PtR'X$ whatever the configuration of the starting material. Attempts to isolate $\underline{trans} \; (R_3P)_2PtR'_2$ have met with failure, and $\underline{cis}$ $(R_3P)_2PtR'X$ is best prepared by reacting $\underline{cis} \; (R_3P)_2PtR'_2$ with one mol. of dry HX. As expected, the $\underline{cis}$ dihalide is more reactive in these preparations, but the $\underline{trans}$ starting material gives higher yields in preparations of mono-alkyl derivatives.

The monomethyl derivative $\underline{trans} \; (Ph_3P)_2PtMeI$ can also be prepared by the reaction between methyl iodide and the platinum (0) complex, $(Ph_3P)_3Pt.$

$$(Ph_3P)_3Pt + 2MeI \longrightarrow \underline{trans} \; (Ph_3P)_2PtMeI + [Ph_3PMe]I$$

This reaction is not generally applicable to other alkyl groups. For example ethyl iodide gives a very poor yield of $(Ph_3P)_2PtEtI$, and benzyl iodide produces a mixture of products.

Triphenylmethyl sodium, cyclopentadienyl sodium, cyclohexyl magnesium bromide and β-styryl magnesium bromide failed to give stable organo platinum derivatives with $\underline{cis} \; (Et_3P)_2PtCl_2$. The hydridoplatinum complex, $\underline{trans} \; (Et_3P)_2PtHBr$, was isolated in both cases from the reactions with the Grignard reagents.

(b) <u>Properties of the alkyl-platinum(II) complexes.</u>

Alkyl-platinum(II) compounds stabilised by tertiary phosphines are remarkably inert, colourless and usually crystalline. They are soluble in organic solvents, stable to air and water and are not hydrolysed by dilute acids. <u>cis</u> $(Me_3P)_2PtMe_2$ sublimes slowly at 110° in air at 1 atmosphere and <u>cis</u> $(Et_3P)_2PtMe_2$ can be distilled at $85^o/10^{-4}$ mm. The higher alkyl and benzyl derivatives are less stable, however.

The reactions of the alkyl platinum compounds are usually of two types: reactions similar to normal platinum(II) complexes, such as isomerisation and oxidation to Pt(IV) compounds, and reactions involving cleavage of the alkyl groups.

<u>Cis</u> $(Et_3P)_2PtMeCl$ in benzene solution is rapidly converted to the <u>trans</u> isomer by a trace of free phosphine. The Cl^- ligand of the <u>trans</u> isomer is very labile and can be replaced by other halides, thiocyanate or nitrate groups on treatment with the corresponding alkali-metal or silver salt.

<u>trans</u> $(Et_3P)_2PtMeCl$ + LiBr $\longrightarrow$ <u>trans</u> $(Et_3P)_2PtMeBr$
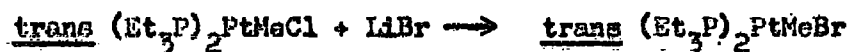
In contrast to the alkali-metal halides, magnesium iodide in ether reacts to cleave the alkyl groups giving Grignard reagents and the <u>trans</u> platinum iodides.

<u>cis</u> $(Et_3P)_2PtMe_2 \xrightarrow{MgI_2}$ <u>trans</u> $(Et_3P)_2PtI_2$ + <u>trans</u> $(Et_3P)_2PtMeI$ + MeMgI
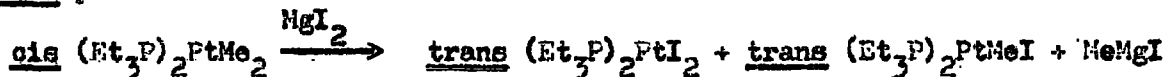
There is evidence that the first step in this reaction is oxidation to a platinum(IV) compound, since a precipitate is initially produced but all the products are soluble in ether. Hydrogen chloride and iodine also cleave the metal-carbon bond, the former producing <u>cis</u> isomers and the

latter <u>trans.</u>

$$\text{cis } (Et_3P)_2PtMe_2 \xrightarrow{HCl} \text{cis } (Et_3P)_2PtMeCl + CH_4$$

$$\text{cis } (Et_3P)_2PtMe_2 \xrightarrow{2HCl} \text{cis } (Et_3P)_2PtCl_2 + 2CH_4$$

$$\text{cis } (Et_3P)_2PtMe_2 \xrightarrow{I_2} \text{trans } (Et_3P)_2PtMeI + MeI$$

$$\text{trans } (Et_3P)_2PtMeI \xrightarrow{I_2} \text{trans } (Et_3P)_2PtI_2 + MeI$$
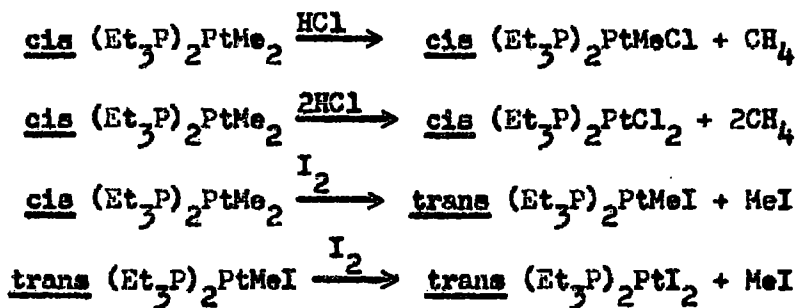
Unlike iodine, chlorine reacts with the dimethyl platinum complex to form a stable platinum(IV) complex, $(Et_3P)_2PtMe_2Cl_2$. The reaction between <u>trans</u> $(Et_3P)_2PtMeI$ and methyl iodide at 100° gives a similar complex, $(Et_3P)_2PtMe_2I_2$. Dipole moment studies have established the structure of these compounds as either

or
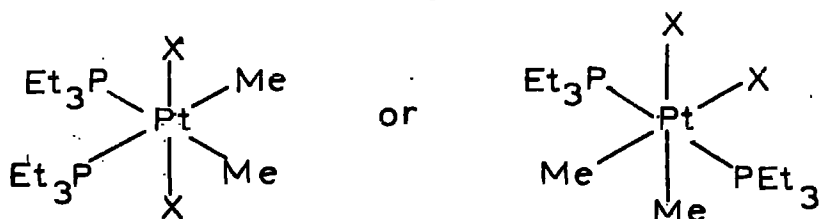
The methyl iodide in $(Et_3P)_2PtMe_2I_2$ is loosely held and can be removed at $80^\circ/10^{-2}$ mm. or slowly in boiling solvents. When heated at 100° for 20 hours in a sealed tube, cleavage of the methyl groups occurs.

$$(Et_3P)_2PtMe_2I_2 \longrightarrow (Et_3P)_2PtI_2 + C_2H_6.$$

Methyl iodide does not react with <u>trans</u> $(Et_3P)_2PtI_2$ under similar conditions, and with <u>cis</u> $(Et_3P)_2 PtMe_2$, a mixture of products is given. The benzyl-platinum derivative <u>cis</u> $(Et_3P)_2Pt(CH_2Ph)_2$ reacts with benzyl iodide to give bibenzyl.

$$\text{cis } (Et_3P)_2Pt(CH_2Ph)_2 + 2PhCH_2I \longrightarrow \text{trans } (Et_3P)_2PtI_2 + 2PhCH_2CH_2Ph$$

3 ARYL-PLATINUM COMPOUNDS.

In 1959 Chatt and Shaw reported the isolation of several aryl compounds of platinum(II) (149). By comparison with the alkyl platinum complexes, the increased stability and the higher dipole moments of the aryl complexes indicates that a certain amount of π-bonding occurs from the platinum d orbitals to the "aromatic" orbitals.

The preparation of these compounds from Grignard or aryl-lithium reagents is generally easier than for the alkyl complexes. Both cis and trans isomers of $(Et_3P)_2PtPh_2$ and $(Et_3P)_2PtPhX$ can be isolated. Cis $(Et_3P)_2PtCl_2$ reacts with PhLi at 20° or PhMgX at 80° to give cis $(Et_3P)_2PtPh_2$ in good yield. The corresponding trans halide is more sluggish in reaction and gives a mixture of cis and trans products. The mono-aryl compounds cis and trans $(Et_3P)_2PtPhCl$ are best obtained by cleaving one aryl group from the diaryl compounds with HCl in dry ether.

A supply of trans $(Et_3P)_2PtPh_2$ for conversion to trans $(Et_3P)_2PtPhCl$ is usually difficult to obtain, and trans $(Et_3P)_2PtPhCl$ is therefore better prepared from the cis isomer, which is rapidly converted to the trans form when a trace of free Et_3P is added to the solution. This isomerisation strongly supports the view that the reactions proceed by ionic inter- mediates such as $[(Et_3P)_3PtPh]Cl$ rather than by a five-coordinate inter- mediate, as complexes of the type $(Et_3P)_2PtPh_2$ which do not contain an ionic ligand do not rapidly isomerise under these conditions.

The reactions of the aryl compounds of platinum(II) are similar to those of the alkyls, but with a few exceptions. In contrast to cis $(Et_3P)_2PtMe_2$, which loses a methyl group by reaction with one molecule of iodine, both cis and trans $(Et_3P)_2PtPh_2$ add iodine to give the same stable Pt(IV) derivative $(Et_3P)_2PtPh_2I_2$. Chlorine behaves similarly. The structures of these platinum(IV) complexes (below) have been deduced from their dipole moments.
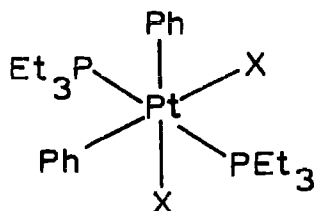
The oxidation of $(Et_3P)_2PtPh_2$ to a Pt(IV) complex follows a different course to the oxidation of inorganic Pt(II) complexes, where the entering groups attach above and below the plane (146). Methyl iodide reacts with both cis and trans $(Et_3P)_2PtPh_2$ to give a mixture of products.

4. HYDRIDO-PLATINUM COMPOUNDS.

The discovery of a stable hydrido-complex of platinum, trans $(Et_3P)_2PtHCl$, was announced in 1957 (150), and this was followed by the study of a series of compounds of this type (140). The hydrides are remarkably stable, hydridic rather than acidic in character, and are resistant to oxydation and hydrolysis. Studies on these compounds and on hydrido-complexes of other Group VIII metals have shown that as a ligand, H^- has both a high ligand field strength and a high trans effect.

Although attempts to prepare compounds of the type cis $(R_3P)_2PtHX$ have met with failure, the dihydrides $(R_3P)_2PtH_2$ (151) and $(R_3P)HPt(PR_2)_2Pt(PR_3)H$ (147) have been isolated. Their properties have not yet been studied in detail, however.

(a) Preparations of trans $(R_3P)_2PtHX$

The hydrido-complexes, trans $(R_3P)_2PtHX$, are conveniently made by the action of reducing agents on cis $(R_3P)_2PtX_2$. The trans complexes, trans $(R_3P)_2PtX_2$, react more slowly and are not generally suitable.

Hydrazine hydrate gives very good results as a reducing agent for these reactions. Used in water, methanol or ethanol (depending on the solubility of the particular platinum complex) yields of about 90% are obtained. The reaction proceeds at $90°$ and probably follows the course:

$$\text{cis } (Et_3P)_2PtCl_2 \xrightarrow{N_2H_4} [(Et_3P)_2Pt(N_2H_4)Cl]Cl \xrightarrow{N_2H_4} \text{trans } (Et_3P)_2PtHCl$$
$$+ NH_4Cl + N_2 + NH_3.$$
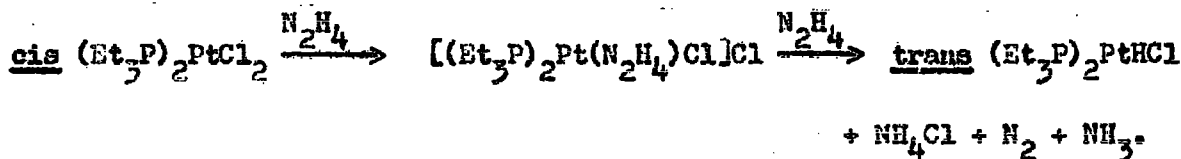
Lithium aluminium hydride is too powerful a reducing agent, and although it reacts with both cis and trans $(Et_3P)_2PtCl_2$ to give the hydrido-complex, some metallic platinum is also produced.

On heating an ethanolic solution of potassium hydroxide with cis $(R_3P)_2PtX_2$, acetaldehyde and trans $(R_3P)_2PtHX$ are produced. Tracer studies have shown that the mechanism of the reaction is:

$$CH_3CH_2OH + OH^- + X-Pt- \longrightarrow CH_3-\overset{H}{\underset{H}{\overset{|}{C}}}\!\!-O\!\!\rightharpoonup Pt- + X^- + H_2O$$

$$\downarrow$$

$$CH_3CHO + H-Pt-$$
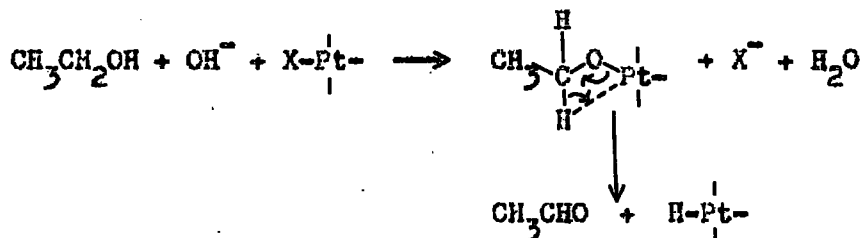
KOH in iso-propanol also gives yields of about 90%, acetone being produced instead of acetaldehyde. Formic acid has also been used as the reducing agent.

$$\text{cis } (Et_3P)_2PtCl_2 + HCOOH \longrightarrow \text{trans } (Et_3P)_2PtHCl + HCl + CO_2$$

The reaction between cis $(Et_3P)_2PtCl_2$ and either styryl magnesium bromide or cyclohexyl magnesium bromide produces some hydrido-complex.

$$\text{cis } (Et_3P)_2PtCl_2 + C_6H_{11}MgBr \longrightarrow \text{trans } (Et_3P)_2PtHBr + C_6H_{10} + MgCl_2$$
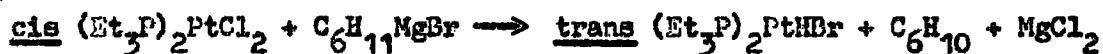
The presence of the cyclohexene produced by this mechanism was not shown (149) and an alternative route to the hydride is proposed in the present work.

The pyrolysis of trans $(Et_3P)_2PtEtCl$ at 180° gives the hydrido-complex by a reversible reaction.

$$\text{trans } (Et_3P)_2PtEtCl \underset{95^{\circ}/40 \text{ atm.}}{\overset{180^{\circ}}{\rightleftharpoons}} \text{trans } (Et_3P)_2PtHCl + C_2H_4$$
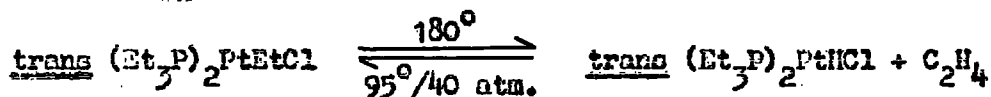
The aryl platinum complex, cis $(Et_3P)_2PtPhCl$, can be converted to the hydrido complex by gaseous hydrogen at room temperature and pressure.

$$\text{cis } (Et_3P)_2PtPhCl + H_2 \longrightarrow \text{trans } (Et_3P)_2PtHCl + C_6H_6$$
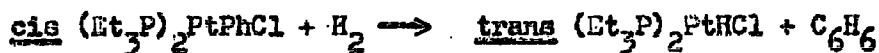
The halide cis $(Et_3P)_2PtCl_2$ can also be reduced by hydrogen but under less mild conditions ($95^{\circ}/50$ atm.).

The chlorine in the hydridochloride complexes is very labile and is readily replaced by other anionic ligands on treatment with the appropriate salt. Thus trans $(Et_3P)_2PtHCl$ is converted almost quantitatively into the corresponding bromide, iodide, cyanate, thiocyanate, nitro or cyanide complex by the action of alkali-metal salts in acetone or aqueous methanol,

or into the nitrate by treatment with 1 mol. of silver nitrate.

(b) Properties of the hydrido-complexes.

The hydrides are colourless crystalline solids, soluble in organic solvents. They are remarkably stable: at 0·01 mm., trans $(Et_3P)_2PtHCl$ sublimes slowly at 75° and distils at 130°.

A sharp band near 2100 cm.$^{-1}$ in the infrared spectra of these compounds is assigned to $\nu(Pt-H)$ and the corresponding bending mode, $\delta(Pt-H)$, is found near 820 cm.$^{-1}$. The deuterium analogues of several compounds have been prepared and the expected isotopic shifts are observed. The effects of different ligands in trans position to the hydrogen atoms on $\nu(Pt-H)$ have been mentioned (139, 152).

The nuclear magnetic resonance spectra of many hydrides have also been examined. The proton resonance of the hydridic hydrogen shows a large chemical shift (about $20-30$ τ). It is split into a triplet of relative intensities 1:2:1 by the two equivalent ^{31}P nuclei of spin $\frac{1}{2}$ (100% abundance) and this triplet is further split by the ^{195}Pt nucleus of spin $\frac{1}{2}$ (33% abundance) to give a characteristic structure of three triplets.

The H^- ligand has a high trans effect, labilising the Cl^- ion in trans $(Et_3P)_2PtHCl$. Metathetical replacement reactions with anionic ligands have been mentioned, and the Cl^- can also be replaced reversibly by neutral ligands such as ammonia to give ionic water-soluble salts.

$$(Et_3P)_2PtHCl + NH_3 \rightleftharpoons [(Et_3P)_2PtH(NH_3)]Cl$$
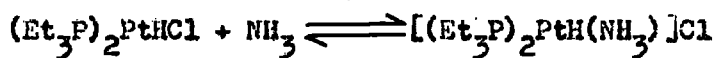
The hydridic hydrogen can be replaced by deuterium or by halogens. Although little H-D exchange occurs when $(Et_3P)_2PtHCl$ is shaken with hot D_2O, rapid exchange takes place in the presence of HCl (10^{-3} molar). Complexes containing ligands of greater _trans_ effect than Cl^- (e.g. CN, OCN, SCN) undergo exchange in neutral solution, however. Halogens, hot aqueous halogen acids, and aliphatic halogenocarbons replace the hydride ligand by halide. For example:

$$\underline{trans} \ (Et_3P)_2PtHCl + CCl_4 \longrightarrow \underline{cis} \ (Et_3P)_2PtCl_2$$

$$\underline{trans} \ (Et_3P)_2PtHI + MeI \longrightarrow \underline{trans} \ (Et_3P)_2PtI_2$$
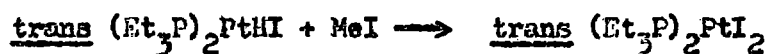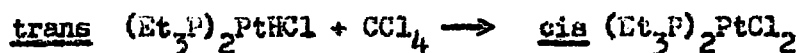
Dry HCl in ether reacts with _trans_ $(Et_3P)_2PtHCl$ to give an adduct which is probably a platinum(IV) hydride halide.

$$\underline{trans} \ (Et_3P)_2PtHCl + HCl \rightleftharpoons (Et_3P)_2PtH_2Cl_2$$

This unstable, crystalline complex can only be stored under HCl and loses HCl when treated with H_2O or on heating. Its infrared spectrum in nujol shows a strong band at 2254 cm.$^{-1}$ with a shoulder at 2265 cm.$^{-1}$ attributable to $\nu(Pt-H)$.

(e) Other platinum hydrides.

To settle a controversy concerning the existence of the Pt (0) complexes, $Pt(PPh_3)_3$ and $Pt(PPh_3)_4$, Malatesta and Ugo prepared the hydrido-platinum complex $(Ph_3P)_2PtH_2$ (151). This compound was prepared by the action of gaseous hydrogen at 200 atm. on a benzene solution of $Pt(PPh_3)_3$ or $Pt(PPh_3)_4$. This method of preparation took 5 hours, but it was also reported that the Pt (0) complexes were converted to the

dihydride simply on standing in benzene for 1 week. The authors proposed that water present in the solution as an impurity might account for the reaction:

$$Pt(PPh_3)_3 + H_2O \longrightarrow (Ph_3P)_2PtH_2 + Ph_3PO$$

The platinum dihydride is a crystalline solid, stable to air and water and sparingly soluble in organic solvents. Its infrared spectra showed $\nu(Pt-H)$ at 1670 cm.$^{-1}$ and $\delta(Pt-H)$ at 816 cm.$^{-1}$. These assignments have been confirmed by deuteration studies (153). In contrast to the monohydrides of Chatt, this compound did not react with CCl_4. With iodine, one equivalent of hydrogen was evolved.

$$(Ph_3P)_2PtH_2 + I_2 \longrightarrow (Ph_3P)_2PtI_2 + H_2$$

A phosphido-bridged binuclear dihydride of platinum has also been isolated (147). Reaction of trans $(Et_3P)_2PtHCl$ with $PHPh_2$ in benzene gave a yellow solution which, on treatment with a base, gave the binuclear complex.

$$+ \; 2PEt_3 + 2HCl$$
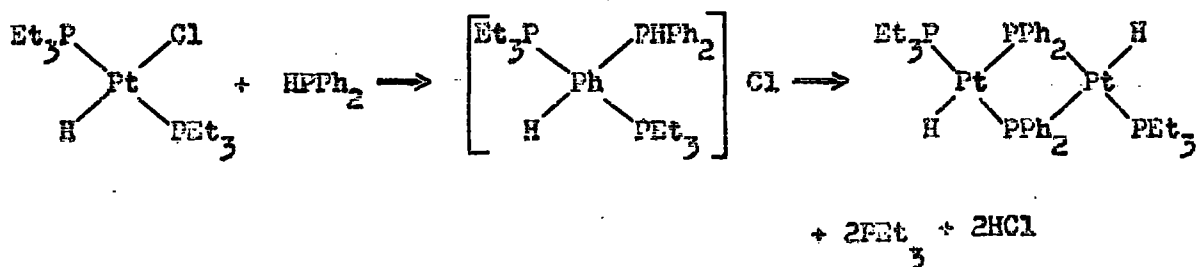
The low Pt-H stretching frequency of this hydride (2005 cm.$^{-1}$) suggests that the bridging PPh_2 groups have a high trans effect.

D. Metal-Metal Bonds.

1. GENERAL CONSIDERATIONS.

In recent years an extensive study of compounds containing metal-metal bonds has been initiated, mainly as a result of the interesting catalytic properties which some of these compounds exhibit. Nevertheless compounds containing metal-metal bonds are more common than has often been supposed (154) and many systems containing such links have been known for several years.

The solid metals themselves show one extreme type of metal-metal bonding, involving multicenter delocalised molecular orbitals. "Concentrated metal" compounds, with properties intermediate between metals and covalent halides, form a second class of compounds containing metal atoms close enough to produce some electronic interaction. An example is $MoCl_2$, which contains $[Mo_6Cl_8]^{4+}$ units showing many features of molybdenum metal. Another type of metal-metal bond occurs in certain transition-metal complexes and involves $d\pi$ bonding. These compounds are comparatively rare: the cupric acetate dimer is one example (155).

This summary is concerned only with compounds containing sigma covalent bonds between two metals. In these compounds it is necessary to differentiate between the oxidation state and valency of the metals. For example in Hg_2Cl_2, where the mercury atoms are linked by a metal-metal bond, the mercury is divalent but the oxidation state is +1. Similarly the germanium atoms in the cyclic compound $(Ph_2Ge)_4$ are tetravalent but the oxidation state is +2.

Due to the great diversity of compounds containing metal-metal bonds and to the fact that the systematic study of these compounds is comparatively young, little is known about the formation and stability of these bonds compared with, for example, metal-carbon bonds. Certain of the factors involved are discussed in a recent paper by Nyholm and his co-workers describing compounds of gold bonded to transition-metals (156). In order to form these links the metals must have available unpaired electrons which are in the bonding region. The latter consideration is of particular importance in transition metal compounds where an unpaired electron can often be accommodated in the d orbitals, sufficiently removed from the bonding region to give a stable paramagnetic monomer rather than a complex involving a metal-metal bond.

The effect of the formal charge of the metals is also important. In general, as the oxidation state rises, the tendency to form paramagnetic monomers increases. This is probably due to the contraction of the orbitals involved away from the bonding region. Thus for the d^9 series Cu (+2), Ni (+1), Co (0) and Fe (-1), copper shows little tendency to form metal-metal bonds, whereas iron forms stable compounds of the type $[Fe_2(CO)_8]^{2-}$.

In descending a vertical triad in the transition series the bonding orbitals become bigger, and it is likely that overlap will increase, leading to greater stability. The germanium-gold compound $Ph_3PAu\cdot GePh_3$ is stable to air and water, whereas the silver and copper analogues are susceptible to oxidation and hydrolysis at room temperature (119). Also,

in the carbonyl series, $Fe_2(CO)_9$ has bridging carbonyls as well as an Fe-Fe bond, but the ruthenium compound $Ru_3(CO)_{12}$ is stable with Ru-Ru bonds alone and no bridging groups.

The attached ligands have a large effect on the stability of metal-metal bonded complexes. The formal charge of the metal atom can be modified by the ligand via its inductive effect or by an ability to form dπ bonds. The situation is more complicated than for metal-carbon bonds and the net result is difficult to predict. The attached ligand will tend to stabilise the M-M bond if it increases the energy gap between the highest energy occupied orbitals and the lowest energy antibonding orbitals (see page 45) and also if it removes charge from M, leading to a decrease in the repulsion between the non-bonding electrons on the two metals. Rupture of the M-M bond producing paramagnetic monomers will be enhanced if the ligands stabilise the monomer or destabilise the dimer. Factors which force the reaction RM-MR $\longrightarrow$ 2RM$^{\bullet}$ to the right are (1) ligands which lead to the delocalisation of the unpaired electron: (2) groups which contract the orbital containing the unpaired electron and remove it from the bonding region: (3) steric repulsion of the ligands on the two metal atoms. The effect of various ligands L on the Mn-Mn bond in $[L(CO)_4Mn]_2$ has been examined (156): also it has been noted that the compound $Ph_3PAu \cdot GePh_3$ is more stable than $Me_3PAu \cdot GePh_3$ (119).

2. PREPARATIONS AND PROPERTIES.

Compounds containing metal-metal bonds are common among the group

IVb elements and many examples have been examined. Gilman and his co-workers prepared a series of analogues of hexaphenylethane with one or both of the central atoms replaced by Si, Ge or Sn (38, 114, 115, 118, 157, 158). They were prepared by the reaction of an alkali metal derivative with a halide (or occasionally an ester).

$$Ph_3MM' + Ph_3MX \longrightarrow Ph_3M-MPh_3 + M'X$$
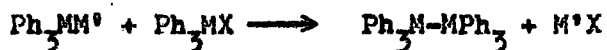
(M = Si, Ge, Sn. M' = alkali metal. X = halogen).

The general properties of these compounds are similar to those previously described for substituted digermanes. The M-M bond can be cleaved either by halogens or alkali metals, and they do not tend to dissociate into $R_3M^{\cdot}$ radicals, as does Ph_6C_2. Cleavage by lithium aluminium hydride has been reported for the Sn-Sn bond (159). The compounds tend to become more reactive as the atomic weight of the metals increases: thus in the cleavage of Me_3M-MMe_3 by F_3CI, ease of reaction decreases in the order Pb-Pb, Sn-Sn, Ge-Ge, Si-Si (160).

Except for mercury, metal-metal bonds between main-group elements other than group IV are comparatively rare, although isolated examples have been reported. In group III, metal-metal bonding has been reported in Ga_2S_3 (161). Gold vapour contains Au_2 molecules.

Many examples of metal-metal bonding amongst the transition metals are known, especially in complexes where the metals are in a low oxidation level. Carbonyl complexes in particular frequently contain M-M bonds. These complexes obey what has become known as the "noble-gas rule", in that they try to achieve the same number of electrons as the next noble-

gas shell. Each carbon monoxide group formally donates two electrons to the metal (or one for a bridging group) (162). When the next noble-gas configuration is not reached by the metal and ligands alone, dimerisation via covalent metal-metal bonds can attain this. This is strikingly demonstrated by the carbonyls of the first transition series which dimerise alternately with spin pairing: $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Fe(CO)_5$, $Co_2(CO)_8$ and $Ni(CO)_4$.

Similar series can be obtained with other ligands. π-Cyclopentadienyl, for example, formally donates 5 electrons giving rise to the series $\pi C_5H_5V(CO)_4$, $[\pi C_5H_5Cr(CO)_3]_2$, $\pi C_5H_5Mn(CO)_3$, $[\pi C_5H_5Fe(CO)_2]_2$, $\pi C_5H_5Co(CO)_2$ and $[\pi C_5H_5NiCO]_2$. Also, metal-metal bonded carbonyls can be produced if the molecule has an apparent deficiency of carbon monoxide. For example in addition to $Fe(CO)_5$, iron can give $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $[Fe_2(CO)_8]^{2-}$, $[Fe_3(CO)_{11}]^{2-}$ and $[Fe_4(CO)_{13}]^{2-}$, all containing Fe-Fe bonds (162). Compounds with two different metals are also known: for example $(CO)_4Co-Mn(CO)_5$ (156) and $\pi C_5H_5(CO)_2Fe-Mn(CO)_5$ (163).

The M-M bonds in these complexes are reactive. Ligand exchange reactions introducing groups which allow the next noble-gas configuration to be achieved without a M-M bond leads to its rupture (164).

$$Fe_3(CO)_{12} + 6NO \longrightarrow 3Fe(CO)_2(NO)_2 + 6CO$$

$$Co_2(CO)_8 + 2NO \longrightarrow 2Co(CO)_3NO + 2CO.$$

Alkali metals, halogens and strong bases also cleave the metal-metal bond.

$$Mn_2(CO)_{10} + 2Na \longrightarrow 2NaMn(CO)_5$$

$$Mn_2(CO)_{10} + I_2 \longrightarrow 2IMn(CO)_5$$

$$Fe_2(CO)_9 \xrightarrow{KOH} K_2Fe(CO)_4 \xrightarrow{acid \quad -10^o} H_2Fe(CO)_4.$$
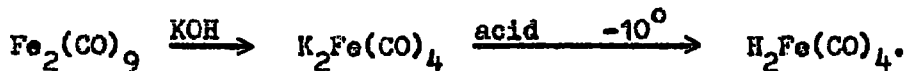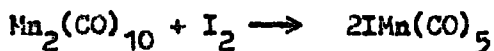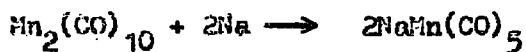
Many of the compounds mentioned above were isolated long before it was realised that they contained metal-metal bonds. Recently, however, many compounds have been prepared with the prime object of synthesising M-H bonds and many of them contain main group metals bonded to transition metals. The compound $\pi C_5H_5Fe(CO)_2SiMe_3$ which contains a silicon to iron sigma bond was reported in 1956 (165). It was prepared by the reaction:

$$\pi C_5H_5Fe(CO)_2Na + Me_3SiCl \longrightarrow \pi C_5H_5Fe(CO)_2SiMe_3 + NaCl$$

It is stable thermally up to 200°, but is air sensitive.

Gorsich has isolated a number of compounds containing tin or lead bonded to manganese (166).

$$R_{4-n}MCl_n + nNaMn(CO)_5 \longrightarrow R_{4-n}M[Mn(CO)_5]_n$$
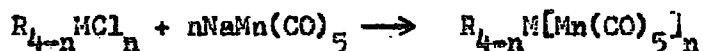
(M = Sn or Pb. n = 1 or 2. R = alkyl or aryl).

π-Cyclopentadienyldicarbonyl-σ-triphenylstannyliron, $\pi C_5H_5Fe(CO)_2SnPh_3$, was also prepared by a reaction similar to that for the Si-Fe derivative. These complexes undergo ligand exchange reactions in a similar manner to other metal carbonyls. CO groups in $Ph_3SnMn(CO)_5$ were readily replaced by tertiary phosphines or arsines.

$$Ph_3SnMn(CO)_5 + PPh_3 \longrightarrow Ph_3SnMn(CO)_4PPh_3 + CO.$$

Somewhat surprisingly, halogenation failed to cleave the M-M bond, tin-phenyl groups being cleaved instead:

$$Ph_3SnMn(CO)_5 + 3Cl_2 \longrightarrow Cl_3SnMn(CO)_5 + 3PhCl.$$

The presence of the Sn-Mn bonds has been demonstrated by X-ray measurements for two compounds. $Ph_3Sn-Mn(CO)_4PPh_3$ has a Sn-Mn bond length of 2.55 Å (167) and $Ph_2Sn[Mn(CO)_5]_2$ has Mn-Sn bonds of 2.7 Å with the angle Mn-Sn-Mn = 117° (168).

Several tin-platinum compounds have been prepared by adding tin(II) chloride to various platinum chlorides. Complexes such as $[NMe_4]_3[Pt(SnCl_3)_5]$, $(Ph_3As)_2Pt(SnCl_3)_2$ and $(Ph_3P)_2PtCl(SnCl_3)$ have been identified (169, 170) and their properties indicate the presence of anionic $SnCl_3^-$ ligands. A later infrared examination of some of these compounds has shown the presence of a platinum-tin bond with $\nu(Pt-Sn)$ near 200 cm.$^{-1}$ (171).

Many compounds containing a transition metal bonded to mercury are known. With metal carbonyls, complexes such as $MeHg-Fe(CO)_4$ and $Hg[Mn(CO)_5]_2$ have been isolated, and although comparatively little is known about the nature of these M-M links, many interesting synthetical methods have emerged.

The mercury-tantalum compounds $RHg-Ta(CO)_6$ (where R = Me, Et or Ph) have been prepared by a reaction similar to that used for the group IV compounds (172).

$$RHgX + Na[Ta(CO)_6] \longrightarrow RHg-Ta(CO)_6 + NaX.$$

These complexes are stable to air and water for short periods, but are decomposed by halogenated solvents. Their thermal stability is greatest for R = Et. In some preparations, the alkali metal derivative can be replaced by a hydride.

$$
\begin{array}{c}
\text{H} \\
\text{Ph}_3\text{P}\diagdown \;|\; \diagup \text{CO} \\
\text{Ir} \\
\text{Ph}_3\text{P} \diagup \;|\; \diagdown \text{Cl} \\
\text{Cl}
\end{array}
\;+\; \text{HgCl}_2 \longrightarrow
\begin{array}{c}
\text{Cl} \\
\text{Hg} \\
\text{Ph}_3\text{P}\diagdown \;|\; \diagup \text{CO} \\
\text{Ir} \\
\text{Ph}_3\text{P} \diagup \;|\; \diagdown \text{Cl} \\
\text{Cl}
\end{array}
\;+\; \text{HCl} \quad (173).
$$
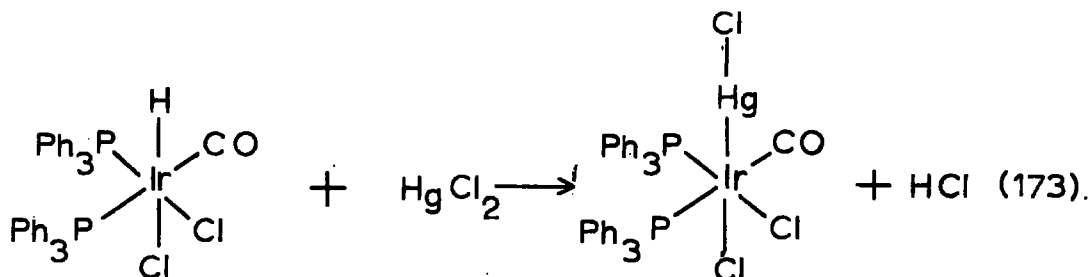
The HCl produced is either evolved as gas or removed by adding a base. The same iridium-mercury complex shown above was also made simply by oxidising an Ir(I) complex with mercuric chloride.

$$
\begin{array}{c}
\text{Ph}_3\text{P}\diagdown \;\;\; \diagup \text{CO} \\
\text{Ir} \\
\text{Cl} \diagup \;\;\; \diagdown \text{PPh}_3
\end{array}
\;+\; \text{HgCl}_2 \longrightarrow
\begin{array}{c}
\text{Cl} \\
\text{Hg} \\
\text{Ph}_3\text{P}\diagdown \;|\; \diagup \text{CO} \\
\text{Ir} \\
\text{Ph}_3\text{P} \diagup \;|\; \diagdown \text{Cl} \\
\text{Cl}
\end{array}
$$
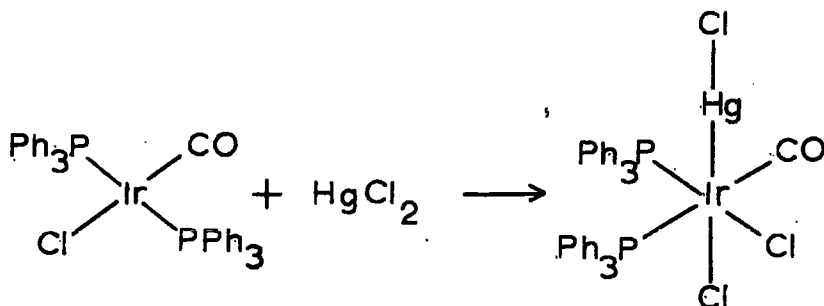
Similar reactions with mercury(II) bromide, iodide and acetate have also been studied (173). Mercurous chloride gives the same product, together with mercury.

An even simpler preparation of a new metal-metal bond was the reaction of mercury metal with a cyclopentadienyl-iron-cobalt carbonyl complex (174). This reaction proceeded at room temperature to give a complex with two M-M bonds.

$$\pi C_5H_5Fe \underset{\underset{O}{\overset{CO}{|}}}{\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{\underset{C}{\overset{C}{\diagdown}}}}} Co(CO)_3 \xrightarrow{\text{Hg}} \pi C_5H_5Fe \underset{CO}{\overset{CO}{|}} Hg-Co(CO)_4$$
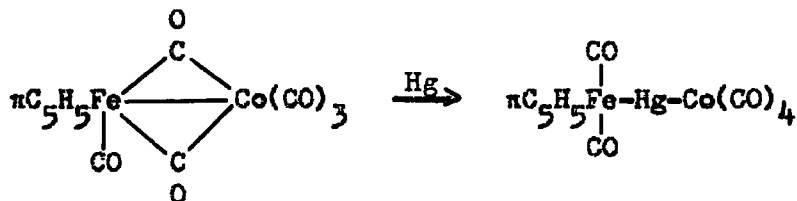
$Ph_3PAu-Co(CO)_4$, $(Ph_3PAu)_2Fe(CO)_4$, $Ph_3PAu-Mn(CO)_5$ and $Ph_3PAu-W(CO)_3\pi C_5H_5$ have recently been prepared by reactions of the type:

$$2Ph_3PAuCl + Na_2Fe(CO)_4 \longrightarrow (Ph_3PAu)_2Fe(CO)_4 + 2NaCl \quad (156).$$
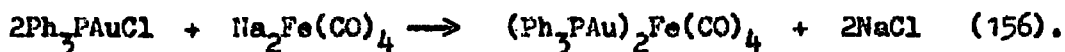
These compounds are pale brown crystalline solids, stable to air and water, diamagnetic, monomeric in benzene and non-electrolytes in nitro-benzene. The gold-transition metal bonds are cleaved by hydrogen chloride or iodine.

$$Ph_3PAu-Mn(CO)_5 + HCl \longrightarrow Ph_3PAuCl + HMn(CO)_5$$

$$(Ph_3PAu)_2Fe(CO)_4 + 2I_2 \longrightarrow 2Ph_3PAuI + I_2Fe(CO)_4.$$

Complexes with copper and silver bonded to manganese have now also been prepared (175).

$$(\text{triarsine})CuBr + NaMn(CO)_5 \longrightarrow (\text{triarsine})Cu-Mn(CO)_5 + NaBr.$$

$$\text{triarsine} = MeC \underset{\diagdown}{\overset{\diagup}{-}} \underset{CH_2AsMe_2}{\overset{CH_2AsMe_2}{}} CH_2AsMe_2$$
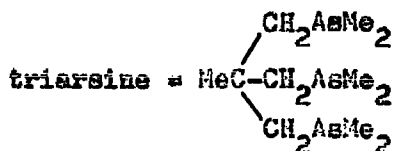
3. GERMANIUM COMPOUNDS.

Compounds containing germanium bonded to metals other than those of group IVb are rare. An early example, however, was the boron compound $(Ph_3Ge)_3B$ which was prepared from triphenylgermyl-lithium and boron trichloride (176). More recently, Seyferth and his co-workers carried out a similar reaction between Ph_3GeLi and Ph_3B (177). The product, lithium

triphenylgermyltriphenylborate, $Li^+[Ph_3GeBPh_3]^-$, was too unstable to be isolated, but the tetramethylammonium and triphenylmethylphosphonium salts gave stable crystalline products.

$$Ph_3GeLi + Ph_3B \longrightarrow Li^+[Ph_3GeBPh_3]^- \xrightarrow{Me_4NI} Me_4N^+[Ph_3GeBPh_3]^-$$

These compounds, which contain germanium-boron bonds, do not have definite melting points and decompose above 200°. The Me_4N^+ salt reacts with bromine to give Ph_3GeBr and $Me_4N^+Br^-$.

Russian workers have prepared compounds of germanium bonded to mercury and cadmium (178, 179) by heating triethylgermane with diethylmercury or diethylcadmium in a sealed tube.

$$Et_3GeH + Et_2Hg \xrightarrow{120^o} (Et_3Ge)_2Hg + C_2H_6$$

$$Et_3GeH + Et_2Cd \xrightarrow{80^o} (Et_3Ge)_2Cd + C_2H_6$$
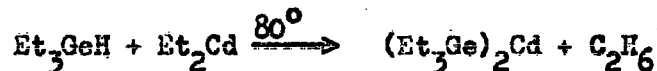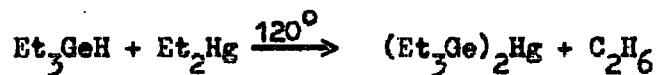
Silicon-mercury compounds were prepared in a similar way, and a Si-Hg-Ge compound has also been isolated (180).

$$Et_3Si-HgEt + Et_3GeH \xrightarrow{100^o} Et_3Si-Hg-GeEt_3 + C_2H_6$$
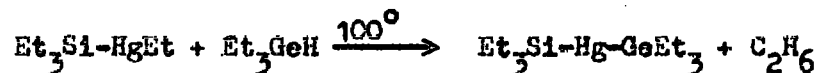
These compounds are yellow liquids, sensitive to ultra-violet radiation and oxygen.

$$(Et_3Ge)_2Hg \xrightarrow{h\nu} Hg + Et_3GeGeEt_3$$

$$(Et_3Ge)_2Cd \xrightarrow{O_2} Cd + Et_3GeOGeEt_3$$
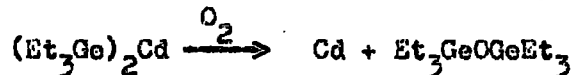
Their reactions with benzoyl peroxide are similar, although metallic mercury is given from the mercury compound, and cadmium benzoate from the cadmium compound.

$$(Et_3Ge)_2Hg + Bz_2O_2 \longrightarrow Et_3GeOBz + Hg$$

$$(Et_3Ge)_2Cd + Bz_2O_2 \longrightarrow Et_3GeOBz + Cd(OBz)_2$$
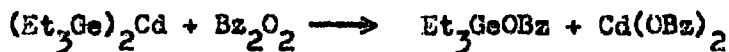
A notable difference between the cadmium and mercury compounds, however, is their reaction with organic halides. The reaction between bistriethyl-germylmercury and bromobenzene is catalysed by u.v. radiation and gives triethylbromgermane and diphenylmercury, whereas the germyl-cadmium compound reacts with benzyl bromide or ethyl bromide to give the tetra-organogermane and cadmium bromide.

$$(Et_3Ge)_2Hg + PhBr \xrightarrow{h\nu} Et_3GeBr + Ph_2Hg$$

$$(Et_3Ge)_2Cd + EtBr \longrightarrow Et_4Ge + CdBr_2$$
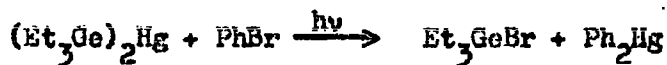
The first reported compounds containing a germanium-transition metal bond, $Ph_3Ge-Mn(CO)_5$ and $Ph_3Ge-Fe(CO)_2\pi C_5H_5$, were isolated by Seyferth and his co-workers at the same time as Gorsich prepared the tin and lead analogues (181).

$$Ph_3GeBr + NaMn(CO)_5 \longrightarrow Ph_3Ge-Mn(CO)_5$$

$$Ph_3GeBr + NaFe(CO)_2\pi C_5H_5 \longrightarrow Ph_3Ge-Fe(CO)_2\pi C_5H_5$$
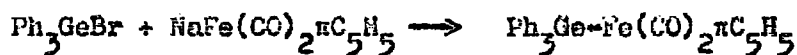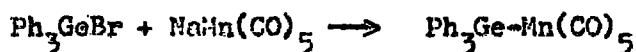
No properties of these compounds were given, except that they were air and moisture stable only in the solid state.

Another complex containing a germanium-manganese bond has been prepared by allowing monogermane to react with manganese pentacarbonyl hydride. The reaction proceeds in a sealed tube at room temperature over a period of 8 days (182).

$$GeH_4 + HMn(CO)_5 \longrightarrow H_2Ge[Mn(CO)_5]_2 + H_2$$

No $H_3GeMn(CO)_5$ or $HGe[Mn(CO)_5]_3$ was produced in the reaction and it was

suggested that the reaction proceeds via reduction to the germanium(II) intermediate, GeH_2. The bispentacarbonylmanganesegermane is an air-stable solid, melting at $87-88^\circ$. It can be sublimed in vacuum at $80^\circ/10^{-3}$ mm. Iodine decomposes the complex liberating hydrogen and carbon monoxide.

Triphenylgermyl complexes of copper, silver and gold have been examined in some detail (119). They were prepared by the reaction:

$$Ph_3GeLi + (R_3P)_nMX \longrightarrow Ph_3Ge-M(PR_3)_n + LiX$$

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

The stability of the compounds depends greatly on the ligand, and alters from metal to metal. For example, $Ph_3Ge-AuPPh_3$ is more stable than $Ph_3Ge-AuPMe_3$, and whereas $Ph_3Ge-AuPPh_3$ is stable to air and water, the silver analogue is less stable and the equivalent copper complex fumes in air. The copper and silver complexes were stabilised by the addition of excess triphenylphosphine and $(Ph_3P)_3AgGePh_3$ was isolated.

The group Ib complexes all reacted with 1,2-dibromethane to liberate ethylene and the germanium and transition metal bromides.

$$Ph_3Ge-AuPMe_3 + BrCH_2CH_2Br \longrightarrow C_2H_4 + Ph_3GeBr + Me_3PAuBr$$
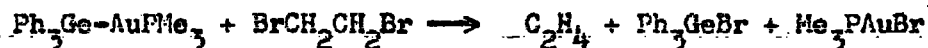
Ethyl bromide and ortho-dichlorobenzene failed to react and it has been suggested (183) that the 1,2-dibromethane reacts via a four-centered transition state.

The reaction of the gold complex with phenyl-lithium was surprisingly complicated. As expected, etherial PhLi first cleaved the gold-germanium bond.

$$Ph_3Ge-AuPPh_3 + PhLi \longrightarrow Ph_3GeLi + Ph_3PAuPh$$
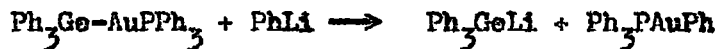
The triphenylgermyl-lithium reacted immediately with more of the gold complex, however, to produce the solvated salt $Li[(Ph_3Ge)_2Au].4Et_2O$.

$$Ph_3Ge-AuPPh_3 + Ph_3GeLi \xrightarrow{\text{Et}_2\text{O}} Li[Ph_3Ge-Au-GePh_3].4Et_2O + Ph_3P$$
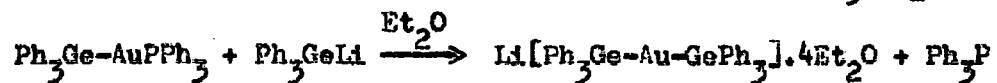
The lithium salt was too unstable to be isolated, but addition of $Et_4N^+I^-$ produced a stable, unsolvated complex $Et_4N[(Ph_3Ge)_2Au]$ which was crystallised from acetone.

EXPERIMENTAL

PART A. Benzyl Derivatives of Germanium.

1. Preparation of tribenzylgermane by reduction of tribenzylbromgermane.

Bromine (28·8 g.) in 1,2-dibromoethane (200 c.c.) was added to a solution of tetrabenzylgermane (70 g.) in the same solvent (500 c.c.); the reaction was complete after 6 hr. at room temperature. The solvent and benzyl bromide were removed by vacuum distillation and the residue, dissolved in a 1:1 ether-benzene mixture (700 c.c.), was added slowly to lithium aluminium hydride (30 g.) in ether (400 c.c.). After refluxing for 2 hr. the excess lithium aluminium hydride was destroyed by the cautious addition of 2N-sulphuric acid. The organic part was dried $(MgSO_4)$ and the solvent removed by distillation. Vacuum distillation of the residue gave tribenzylgermane, $(PhCH_2)_3GeH$ (47·4 g., 85%. B.p. 160-180°/10^{-3} m.m. M.p. 80-82° ex methanol. $\nu(Ge-H)$ at 2034 cm^{-1}). (Found: C, 73·0; H, 6·2; Ge, 21·5%. $C_{21}H_{22}Ge$ (i.e. $(PhCH_2)_3GeH$) requires: C, 72·7; H, 6·4; Ge, 20·9%).

2. Hexabenzyldigermane.

a) Wurtz reaction.

Tribenzylbromgermane (29 g.) in xylene (250 c.c.) was refluxed with sodium (2 g.) for 20 hr. during which time the mixture turned black. The solvent was removed by distillation after hydrolysis with water. Attempted crystallisation from chloroform, methyl-cyclo-hexane and methanol gave no hexabenzyldigermane. The material recovered (13·1 g.) contained no halogen. Its infrared spectrum contained a weak band attributable to ν_{asym} (Ge-O-Ge) at 11·5μ, but no $\nu(Ge-H)$.

In a similar experiment using 20 g. of tribenzylbromgermane and 5 g. of sodium, the refluxing was continued for 3 days. A small amount of hexabenzyldigermane (1·5 g., 9%) was obtained (m.p. 182–184° ex xylene) as well as the intractable residue. It was concluded that the Wurtz method of Bauer and Burschkies (33) was unsuitable for large scale reactions.

b) <u>Grignard coupling reaction.</u>

This method, based on the coupling of an intermediate germyl Grignard reagent, was more successful (39).

$$PhCH_2MgCl + GeI_4 \longrightarrow (PhCH_2)_3GeMgCl + (PhCH_2)_3GeI \longrightarrow (PhCH_2)_6Ge_2$$

Germanium (IV) iodide (169 g.) in toluene (500 c.c.) was added to etherial (2·5 lit.) benzyl magnesium chloride prepared from benzyl chloride (370 g.) and magnesium (80 g.) and the mixture, containing the excess magnesium, was refluxed for 44 hr. Hydrolysis yielded a semi-solid organic product which was extracted with boiling ether giving hexabenzyldigermane (11·5 g., 11·4%) as the insoluble part, m.p. 185° ex chloroform.

3. <u>Preparation of the benzylbutylgermanes.</u>

Dropwise addition of a filtered solution of butyl magnesium bromide (0·26 mole), prepared from butyl bromide (35·6 g.) and magnesium (7 g.) in ether (250 c.c.), to germanium (IV) chloride (20 g.) in ether (50 c.c.) was followed immediately by the addition of etherial benzyl magnesium chloride (0·4 mole). The resulting mixture was refluxed for 2 hr. and then hydrolysed by 2N-hydrochloric acid. Vacuum distillation of the

organic extract gave:

benzyltributylgermane (7.4 g., 27%) b.p. 100-110°/10⁻³ mm. (Found: C, 67.8; H, 10.0. $C_{19}H_{34}Ge$ (i.e. $PhCH_2GeBu_3$) requires C, 68.1; H, 10.2%);

dibenzyldibutylgermane (16 g., 46%) b.p. 130-133°/10⁻³ mm. (Found: C, 70.6; H, 9.3. $C_{22}H_{32}Ge$ (i.e. $(PhCH_2)_2GeBu_2$) requires C, 71.6; H, 8.8%);

and tribenzylbutylgermane (5.9 g., 16%) b.p. 150-163°/10⁻³ mm. (Found: C, 74.7; H, 7.5. $C_{25}H_{30}Ge$ (i.e. $(PhCH_2)_3GeBu$) requires C, 74.5; H, 7.5%).

4. Cleavage of tetrabenzylgermane.

a) Isolation of tribenzylgermane.

Tetrabenzylgermane (10 g.), lithium shot (2.5 g.) and ethylene glycol dimethyl ether (1 c.c.) were stirred to a paste which turned yellow after a few minutes and then deepened to brown with spontaneous warming. Additional solvent (7 c.c.) was added and after 1 hr. the excess lithium was separated by filtration through glass wool. Hydrolysis of the filtrate by 10% aqueous monoglyme was exothermic and discharged the brown colour. Distillation of ether extracts gave tribenzylgermane (6 g., 76%), b.p. 164°/10⁻³ mm., as colourless needles, m.p. 80-82° ex methanol. The residue from the distillation gave tetrabenzylgermane as needles from propanol (m.p. and mixed m.p. 110°).

b) Isolation of tribenzylgermane and dibenzylgermane.

Tetrabenzylgermane (50 g.) and lithium shot (4 g.) were stirred at room temperature with 1,2-dimethoxyethane (5 c.c.) until yellow specks

appeared (5 min.). The mixture was then kept at 0° for 16 hr. after the addition of further solvent (40 c.c.). Hydrolysis by the slow addition of 10% aqueous monoglyme (100 c.c.) followed by benzene-water extraction gave an organic layer (40.5 g.) which was distilled in vacuo giving a trace of bibenzyl, dibenzylgermane (2.3 g., 7.8%) b.p. $80\text{-}85^{\circ}/10^{-3}$ mm. (Found: Ge, 26.1. $C_{14}H_{16}Ge$ (i.e. $(PhCH_2)_2GeH_2$) requires Ge, 28.5%), and tribenzyl-germane (8.3 g., 21%) b.p. $176\text{-}187^{\circ}/10^{-3}$ mm. The residue consisted of tetrabenzylgermane.

Dibenzylgermane showed in addition to the Ge-H stretch at 2034 cm^{-1}, a strong band at 866 cm^{-1}. This band is also present in the spectrum of diphenylgermane and is probably a GeH_2 deformation frequency (184). The ^1H nuclear magnetic resonance spectrum of dibenzylgermane at 60 Mc./sec. showed a large unresolved peak at low fields, a quintet at midfields and a triplet at high fields. The relative intensities of 10:2:4 are in agreement with the structure $(PhCH_2)_2GeH_2$.

c) Tribenzyldeuterogermane and dibenzyldideuterogermane.

An experiment similar to part b) with tetrabenzylgermane (10 g.) and lithium shot (0.8 g.), followed finally by the addition of deuterium oxide (5 c.c.), gave on vacuum distillation a few drops of liquid which appeared to be dibenzyldideuterogermane ($\nu(Ge\text{-}D)$ at 1464 cm^{-1}; GeD_2 deformation at 612 cm^{-1}). The main product was tribenzyldeuterogermane (5.4 g., 77%) b.p. $170\text{-}176^{\circ}/10^{-3}$ mm., m.p. 81° ex methanol and $\nu(Ge\text{-}D)$ at 1464 cm^{-1} (Found: C, 72.4; H, 6.6; Ge, 21.35. $C_{21}H_{21}DGe$ (i.e. $(PhCH_2)_3GeD$) requires C, 72.5; H, 6.7; Ge, 20.9%).

5. Tribenzylethylgermane.

Tribenzylgermyl-lithium was prepared from tetrabenzylgermane (15 g.) and lithium shot (5 g.) in ethylene glycol dimethyl ether (20 c.c.). The reaction started after stirring for 2 minutes. After 48 hr. at 0° the deep brown solution was filtered through glass wool and added to an excess of ethyl bromide in ether. The colour was discharged in an exothermic reaction. Normal work up of the organic extract gave a few drops of a liquid (B.p. $60-140^{\circ}/10^{-3}$ mm.) which appeared to be a mixture of dibenzyl-diethylgermane and tribenzylethylgermane (n.m.r. and i.r. spectra) and tribenzylethylgermane, 8.2 g., 64%. B.p. $170-183^{\circ}/10^{-3}$ mm. (Found: C, 73.0; H, 6.9; Ge, 19.1. $C_{23}H_{26}Ge$ (i.e. $(PhCH_2)_3GeEt$) requires C, 73.6; H, 7.0; Ge, 19.4%). After repeated crystallisation from methanol it had m.p. $34-35^{\circ}$ (in contrast to the literature value (33) of $56-57^{\circ}$).

6. Tribenzylgermyltrimethylsilane.

Tribenzylgermyl-lithium was prepared from tetrabenzylgermane (6.8 g.) as described above. The reaction commenced after 15 minutes and was allowed to proceed for 2.5 hr. at 5°. After filtration through glass wool, the tribenzylgermyl-lithium in monoglyme was added to trimethyl-chlorsilane (3.2 g., 2 mol.). The colour was discharged with evolution of heat. Hydrolysis and ether extraction followed by distillation of the organic extract gave a mixture containing toluene and hexamethyldisiloxane (v.p.c. characterisation). Vacuum-distillation gave tribenzylgermyltri-methylsilane, b.p. $183^{\circ}/10^{-3}$ mm., m.p. $63.5-64.5^{\circ}$ (needles, ex methanol).

(Found: C, 68·6; H, 7·1%; M (freezing benzene), 415. $C_{24}H_{30}GeSi$

(i.e. $(PhCH_2)_3Ge \cdot SiMe_3$) requires C, 68·8; H, 7·2%; M, 419). The residue

from the distillation consisted of tetrabenzylgermane.

7. Reaction of tribenzylgermyl-lithium with triethylbromgermane.

a) Sym-tribenzyltriethyldigermane.

Triethylbromgermane (5·5 g.) in ether (50 c.c.) was added to a

solution of tribenzylgermyl-lithium prepared from tetrabenzylgermane

(10 g.) as previously described (initiated after 10 minutes: stirred for

2 hr. at 20°). Normal work-up gave unreacted tetrabenzylgermane (4·3 g.)

and sym-tribenzyltriethyldigermane, 6·1 g., b.p. 220-230°/10^{-3} mm. (Found:

C, 67·6; H, 7·3%; M (freezing benzene) 541. $C_{27}H_{36}Ge_2$ (i.e. $(PhCH_2)_3Ge \cdot$

$GeEt_3$) requires C, 64·1; H, 7·2%; M, 506). The n.m.r. spectrum at 60

Mc./sec. showed three peaks of relative intensity 5:2:4·8, corresponding to

phenyl, methylene (of $PhCH_2$), and ethyl groups respectively. Attempts to

purify the compound from traces of tetrabenzylgermane failed.

b) Halogen-metal exchange.

In a similar experiment, tribenzylgermyl-lithium in monoglyme was

added to pure Et_3GeBr. No tribenzyltriethyldigermane was detected in the

products. Instead, the organic part yielded hexaethyldigermane (b.p. 261°/

765 mm.) and hexabenzyldigermane (m.p. 182-183° ex methyl-cyclohexane).

8. Reaction of tribenzylgermyl-lithium with carbon dioxide.

a) Failure to isolate tribenzylgermylcarboxylic acid.

Tribenzylgermyl-lithium prepared from tetrabenzylgermane (7·2 g.)

in monoglyme (15 c.c.) (initiation period 15 minutes: reaction proceeded

2.5 hr. at 5°) was cooled to -78° and treated with solid CO_2 and ether (50 c.c.). The colour discharged on warming up to room temperature. Ether-water extraction of the mixture gave an organic layer containing 2 g. of unreacted tetrabenzylgermane. Addition of hydrochloric acid to the aqueous part gave a white precipitate which was ether extracted. Removal of the solvent and sublimation at $120°/10^{-3}$ mm. to remove any phenylacetic acid left a semi-solid residue which was insoluble in NaOH solution.

In a similar experiment the acidified part was worked up at room temperature or below and purification of the products was attempted by chromatography on alumina. The products were again non-acidic, however, and it was assumed that the tribenzylgermylcarboxylic acid formed had decomposed thermally by decarbonylation.

b) Tribenzylphenylacetoxygermane and Tribenzylgermyltribenzylgermane carboxylate.

Tribenzylgermyl-lithium, prepared from tetrabenzylgermane (10 g.) and excess lithium as previously described (initiation 30 minutes: reaction 2 hr. at 20°), was treated with solid carbon dioxide and then water. Ether extraction of the alkaline solution gave unreacted tetrabenzyl-germane (4.1 g.). Acidification of the aqueous solution and extraction with ether gave a mixture of non-acidic products (5 g.). Extraction with hexane gave first tribenzylphenylacetoxygermane, $(PhCH_2)_3GeOCOCH_2Ph$ (1.5 g.) as colourless crystals, m.p. 146-148° (Found: C, 72.1; H, 5.5; Ge, 15.0. $C_{29}H_{28}GeO_2$ (i.e. $(PhCH_2)_3GeOCOCH_2Ph$) requires C, 72.4; H, 5.9;

Ge, 15·1%). Concentration of the hexane solution yielded <u>tribenzylgermyl-tribenzylgermanecarboxylate</u>, $(PhCH_2)_3GeOCOGe(CH_2Ph)_3$, m.p. 77-80° ex methanol. (Found: C, 70·1; H, 5·7; Ge, 19·6. $C_{43}H_{42}Ge_2O_2$ (i.e. $(PhCH_2)_3GeOCOGe(CH_2Ph)_3$) requires C, 70·2; H, 5·8; Ge, 19·7%). Both compounds evolved gas (carbon monoxide) vigorously at about 180°.

9. <u>Reaction of tribenzylgermyl-lithium and trichlorsilane.</u>

Tribenzylgermyl-lithium, prepared from tetrabenzylgermane (26 g., 59·5 mmole) as previously described (initiation took 6 hr.: reaction proceeded 18 hr. at 0°), was added to trichlorsilane (2·7 g., 20 mmole) in ether (60 c.c.) at -70°, allowed to warm to room temperature and finally refluxed for 30 minutes. Hydrolysis and ether extraction gave polymeric material (18·1 g.) which was obtained as a white powder from iso-propanol, m.p. 35-45° (Found: C, 69·6; H, 6·7%; M (freezing benzene) 2030-1320). This material showed a weak Si-H stretch at 2101 cm.$^{-1}$

10. <u>Cleavage of 1,2-dimethoxyethane by tetrabenzylgermane and lithium.</u>
a) <u>Reaction time 4 hr.</u>

Tetrabenzylgermane (10 g.) and lithium shot (2·5 g.) in monoglyme (5 c.c.) were stirred until the yellow colour developed, when further solvent (25 c.c.) was added and the mixture heated under reflux for 4 hr. The mixture was filtered through glass-wool to remove excess lithium. After hydrolysis, the organic extract gave <u>tribenzylmethyl-germane</u>, (2·2 g., 27%) as colourless needles from methanol, m.p. 82-85° (Found: C, 73·6; H, 6·3; Ge, 20·4%; M (freezing benzene), 356.

$C_{22}H_{24}Ge$ (i.e. $(PhCH_2)_3GeMe$) requires C, 73·2; H, 6·7; Ge, 20·1%; M, 361).

b) **Reaction time 19 hr.**

In a similar experiment to above in which the refluxing was continued for 19 hr., the organic extract contained toluene and ethylbenzene (ratio 9:1) in amounts consistent with the cleavage of two benzyl groups from tetrabenzylgermane (v.p.c. characterisation). Vacuum distillation gave a liquid (0·5 g.), b.p. 26-82°/10⁻³ mm., consisting of benzyltri-methylgermane and dibenzyldimethylgermane (v.p.c. characterisation) and dibenzyldimethylgermane (2·3 g.), b.p. 82-100°/10⁻³ mm., m.p. 53-55°, ex methanol (Found: C, 67·3; H, 7·2%; M, 273. $C_{16}H_{20}Ge$ (i.e. $(PhCH_2)_2$ $GeMe_2$) requires C, 67·4; H, 7·1%; M, 285).

c) **Reaction time 6 days.**

Tetrabenzylgermane (20 g.) and lithium shot (8 g.) in 1,2-dimethoxy-ethane were heated under reflux for 6 days in a nitrogen atmosphere, the emergent gases being passed through a trap at -78°. Fractional condensation of the contents of the trap (in a vacuum apparatus) gave methyl vinyl ether (1185 c.c. at N.T.P.; 3·07 g.) (Found: M, 56·2. C_3H_6O (i.e. MeOCH=CH₂) requires M, 58) but no tetramethylgermane. The final organic extract gave benzyltrimethylgermane (3·6 g.) b.p. 204-206°/760 mm. (Found: C, 57·7; H, 7·8. $C_{10}H_{16}Ge$ (i.e. $PhCH_2GeMe_3$) requires C, 57·5; H, 7·7%) and an unidentified high boiling fraction (3·7 g.).

11. **Cleavage of hexabenzyldigermane by lithium.**

Hexabenzyldigermane (4·75 g., 4·68 mmole) and lithium shot (1·2 g.)

were mixed to a paste with 1,2-dimethoxyethane (4 c.c.). Golden-brown specks appeared after 10 min. and spread throughout the mixture in $2\frac{1}{2}$ hr., when more solvent (8 c.c.) was added. The mixture was stirred at $0°$ for 22 hr., when the deep brown solution was filtered from excess lithium (glass wool) and hydrolysed with 10% aqueous monoglyme. Ether-water extraction, and vacuum distillation of the organic part gave tribenzyl-germane (1.2 g., 25%). The residue from the distillation gave unreacted hexabenzyldigermane (2.4 g.) m.p. 182-185° ex toluene. Examination of the solvent mixture by vapour-phase chromatography showed a trace of toluene, indicating that some cleavage of benzyl groups had occurred.

12. Cleavage of tribenzylgermane by lithium.

Tribenzylgermane (2.2 g., 6.35 mmole), lithium shot (0.5 g.) and ethylene glycol dimethyl ether (2 c.c.) were mixed to a paste. After 45 minutes, black specks formed on the lithium surface and the solution turned pale brown. More monoglyme was then added (14 c.c.) and the mixture was stirred at $0°$. The solution was dark green after 7 hr. and black after 24 hr. when excess lithium was separated and methyl iodide (7 g.) in ether (20 c.c.) was added. Most of the colour was discharged in an exothermic reaction. Normal work-up gave a liquid, b.p. 120-140°/10^{-3} mm. (0.1 g.) consisting of dibenzyldimethylgermane (v.p.c. characterised) and a more volatile component. Since the mixture showed a strong Ge-H absorption at 2034 cm.$^{-1}$, the unidentified component was probably di-benzylmethylgermane, $(PhCH_2)_2MeGeH$. Toluene was detected in the solvent mixture and tribenzylmethylgermane (0.8 g.), m.p. 82-84° ex methanol, was also isolated by vacuum-distillation.

13. Reaction of tribenzylgermane and n-butyl-lithium.

a) 1 mol. at -10°

Tribenzylgermane (10 g., 28.8 mmole) in ether (200 c.c.) was added over $3\frac{1}{2}$ hr. to butyl-lithium (28.8 mmole) in ether (40 c.c.) at -10°. The yellow solution containing suspended solid was stirred at -12° for 20 hr. when methyl iodide (6 g.) was added. The colour was discharged. Hydrolysis with water gave hydrogen. Hexabenzyldigermane (1.25 g., 12.5%) was separated by filtration. Vacuum distillation of the organic extract gave a liquid mixture (6.5 g.) b.p. 150-200°/10^{-3} mm. Tetrabenzylgermane (2 g., 16%), m.p. and mixed m.p. 106-110°, was isolated from the residue of the distillation. Fractional vacuum distillation of the volatile part gave tribenzylbutylgermane (3 g., 26%), b.p. 150-163°/10^{-3} mm., tribenzyl- methylgermane (1.25 g., 12%), b.p. 140-160°/10^{-3} mm., m.p. 78-81° (ex methanol) and a liquid mixture (0.6 g.), b.p. 50-140°/10^{-3} mm. Infrared and n.m.r. spectra on the mixture indicated that this was probably benzyl- dibutylgermane, $PhCH_2Ge(Bu)_2H$ and dibenzylbutylgermane, $(PhCH_2)_2GeBuH$. The 'H n.m.r. spectrum at 60 Mc./sec. of a higher-boiling cut from this mixture showed three peaks of relative intensity 10:4:12; and its infra- red spectrum showed $\nu(Ge-H)$ at 2020 cm.$^{-1}$

b) 2 mols. at room temperature

A similar experiment carried out at room temperature using tribenzyl- germane (12 g.) and butyl-lithium (2 mols.) gave hexabenzyldigermane (0.9 g., 7.5%), tetrabenzylgermane (3 g., 20%) and tribenzylbutylgermane (7 g., 50%). A lower boiling fraction (1.3 g.), b.p. 90-140°/10^{-3} mm.,

was shown by vapour-phase chromatography (using the authentic compounds for comparison) to contain dibenzyldibutylgermane, benzyltributylgermane and tetrabutylgermane. No tribenzylmethylgermane was isolated from this experiment, and no volatile products containing Ge-H bonds were detected.

A separate experiment with tribenzylgermane (0·6 g.) and butyl-lithium (2 mols. in 30 c.c. of ether) was carried out under the same conditions. Hydrolysis with de-aerated water gave hydrogen (19·6 c.c. at N.T.P.).

14. Reaction of tribenzylgermane with benzyl-lithium.

Tribenzylgermane (3·8 g., 11 mmole) in ether (100 c.c.) was treated at room temperature with a tetrahydrofuran-ether solution of benzyl-lithium (185) (11 m.mole) and, after 18 hr. excess methyl iodide was added. Normal work-up gave by distillation a trace of dibenzyldimethylgermane, b.p. 80-100°/10^{-3} mm. (v.p.c. characterised), tribenzylmethylgermane, b.p. 165°/10^{-3} mm. (0·5 g., 12%) and tetrabenzylgermane, b.p. 200-210°/10^{-3} mm. (2·9 g., 60%).

15. Tetraorganogermanes and hexabenzyldigermane with n-butyl-lithium.

a) Dibenzyldibutylgermane and benzyltributylgermane.

To a mixture of 0·55 g. of benzyltributylgermane (35%) and dibenzyl-dibutylgermane (65%) in ether (25 c.c.) was added 3 mmoles of butyl-lithium (2 mols.) in ether. The mixture was stirred 18 hr. at room temperature, then hydrolysed by water. After work-up in the usual way the product consisted of dibenzyldibutylgermane (65·5%) and benzyltributyl-germane (34·5%) (estimated by v.p.c.). No tetrabutylgermane was given.

b) Tetrabenzylgermane.

Tetrabenzylgermane (10 g., 22.9 mmole) and butyl-lithium (25 mmole) in ether (50 c.c.) were stirred at 20° for 10 hr. Hydrolysis and normal work-up gave an almost quantitative recovery of starting material. A trace of toluene was detected in the solvent mixture by v.p.c., but no tribenzyl-butylgermane or tribenzylgermane was detected. A similar experiment using 3 equivalents of butyl-lithium produced the same result.

c) Hexabenzyldigermane.

Hexabenzyldigermane (6.8 g., 98.5 mmole) in ether (100 c.c.) was stirred with an excess of butyl-lithium for 20 hr. at room temperature. Normal work-up after hydrolysis gave only starting material (6.5 g.).

16. Attempted reduction of tetrabenzylgermane and tribenzylgermane.

a) Tetrabenzylgermane.

Tetrabenzylgermane (3 g.) and lithium shot (2 g.) were stirred with monoglyme. Before cleavage could take place, the lithium was destroyed by adding an excess of 10% aqueous monoglyme. Normal work-up gave only tetrabenzylgermane and no tribenzylgermane.

In another experiment, tetrabenzylgermane (2.8 g.) in ethyl acetate (40 c.c.) was shaken with molecular hydrogen at atmospheric pressure and in the presence of Adam's catalyst. No hydrogen was absorbed by the tetrabenzylgermane.

b) Tribenzylgermane.

Lithium shot (1 g.) in a solution of tribenzylgermane (2 g.) in monoglyme was hydrolysed by 10% aqueous monoglyme. Normal work-up gave only $(PhCH_2)_3GeH$. No dibenzylgermane was produced, as evidenced by the absence of the GeH_2 deformation band at 11.55μ.

17. Pyrolysis of tribenzylgermane.

Tribenzylgermane (1 g.) was sealed in an evacuated tube and heated for 24 hr. The compound was stable at 240°, and only slight decomposition took place at 370°. At 390°, complete decomposition took place, giving a trace of a non-condensable gas (probably H_2), toluene (0·55 g.), bibenzyl (0·1 g.), a trace of trans-stilbene, and a dark brown polymer (0·3 g.) which was shown by X-ray powder photograph to contain no germanium metal (Found: C, 40·4; H, 3·0%).

18. Triphenylbutylgermane.

Triphenylgermyl-lithium, from hexaphenyldigermane (2·5 g.) and lithium shot (0·25 g.) in 1,2-dimethoxyethane (5 c.c.), was treated with n-butyl bromide (1·3 g.). Hydrolysis and ether extraction gave butyl-triphenylgermane (2·0 g.) b.p. 160°/10^{-2} mm., m.p. 80-81° ex methanol (Found: C, 73·2; H, 6·8. $C_{22}H_{24}Ge$ (i.e. Ph_3GeBu) requires C, 73·2; H, 6·7%). The reaction between triphenylgermane and butyl-lithium in ether also produced small amounts of this compound (mixed m.p. and infra-red spectra) contrary to earlier reports (35).

19. Reaction of diphenylgermane and n-butyl-lithium.

Diphenylgermane (5 g., 22 mmole) in ether (100 c.c.) was treated with n-butyl-lithium (44 mmole) at -10°. After 4 hr. ethyl bromide (4·8 g.) was added to the cloudy yellow solution with discharge of the colour. Hydrogen was evolved on hydrolysis and the organic extract (4 g.) gave a liquid distillate (2·4 g.), b.p. 20-140°/10^{-3} mm., con-sisting of (i) diphenyldiethylgermane (0·1 g., 2%) (v.p.c. characterisa-

tion); (ii) <u>n-butylethyldiphenylgermane</u> (1·4 g., 20·5%), b.p. 100-110°/
10⁻³ mm. (Found: C, 69·0; H, 7·7%; M, 327. C₁₈H₂₄Ge (i.e. Ph₂Ge(Bu)Et)
requires C, 69·1; H, 7·7%; M, 313); (iii) <u>Dibutyldiphenylgermane</u>
(0·9 g., 12%); b.p. 130-140°/10⁻³ mm. (Found: C, 70·5; H, 8·3%; M,
350. C₂₀H₂₈Ge (i.e. Ph₂GeBu₂) requires C, 70·4; H, 8·3%; M, 341). The
residue from the distillation gave <u>1,2-diethyl,1,1,2,2,-tetraphenyldi-
germane</u> from propanol (1·5 g., 28%), m.p. 125-126·5° (Found: C, 64·7;
H, 5·8. C₂₈H₃₀Ge₂ (i.e. Ph₂EtGe·GeEtPh₂) requires C, 65·7; H, 5·9%).
Its infrared spectrum and mixed m.p. were identical with a compound of
similar formula (but unknown structure) isolated from degradative ex-
periments on phenylgermanium polymers (43).

PART B. Triphenylgermylplatinum Complexes.

1. Bistriethylphosphinebistriphenylgermylplatinum(II) $(Et_3P)_2Pt(GePh_3)_2$.

a). From trans $(Et_3P)_2PtCl_2$

Triphenylgermyl-lithium, from n-butyl-lithium (20.4 mmole) and triphenylgermane (6.2 g., 20.4 mmole) in ether (120 c.c.) was added dropwise to a solution of trans-bistriethylphosphineplatinum(II) chloride (5.0 g., 10 mmole) in ether (100 c.c.). A yellow precipitate was produced, and triethylphosphine was detected by smell in the emergent nitrogen stream. After 1 hr. under reflux the ether was removed by distillation and the residue extracted with benzene. Filtration from lithium chloride, and removal of benzene from the orange solution gave bistriethylphosphinebistriphenylgermylplatinum(II), (9.5 g., 91%), as pale yellow needles from methylcyclohexane. (Found: C, 55.9; H, 5.8; Pt, 19.5%; M (freezing benzene), 1004. $C_{48}H_{60}Ge_2P_2Pt$ (i.e. $(Et_3P)_2Pt(GePh_3)_2$) requires C, 55.9; H, 5.8; Pt, 18.8%; M, 1039).

This germylplatinum complex is stable to air and water oven in solution. It does not react with alcohols or ethanolic potassium hydroxide. It decomposes above 160°, and is only sparingly soluble in common organic solvents. Its u.v. spectrum in cyclohexane shows two main bands at 2075 Å, $\log \mathcal{E} = 5.0$ and 3005 Å, $\log \mathcal{E} = 4.36$.

b). From cis $(Et_3P)_2PtCl_2$

A similar experiment was carried out using cis-bistriethylphosphineplatinum(II) chloride. The reaction proceeded as above except that it appeared to be slightly more exothermic. $(Et_3P)_2Pt(GePh_3)_2$ was isolated

in 65% yield. An X-ray powder photograph showed that this material
was essentially the same as that isolated from a), but with a few weak
extra lines. These may be due to a small amount of <u>cis</u> material in an
essentially <u>trans</u> product.

2. Bistri-n-propylphosphinebistriphenylgermylplatinum(II), $(n-Pr_3P)_2Pt(GePh_3)_2$.
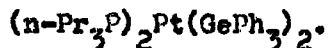
Triphenylgermyl-lithium, prepared from butyl-lithium (36 mmole) and
Ph_3GeH (11 g., 36 mmole) in ether (100 c.c.), was added slowly to a
suspension of <u>trans-bistri-n-propylphosphineplatinum(II)</u> chloride (9 g.,
15·4 mmole) in ether (100 c.c.). The reaction proceeded as above
(tri-n-propylphosphine detected by smell) giving <u>bistri-n-propylphosphine-</u>
<u>bistriphenylgermylplatinum(II)</u> (17 g., 98%). Purification from benzene
gave the solvated complex as pale yellow crystals (Found: C, 60·7;
H, 6·5; C_6H_6, 7·2. $C_{60}H_{78}Ge_2P_2Pt$ (i.e. $(n-Pr_3P)_2Pt(GePh_3)_2 \cdot C_6H_6$)
requires C, 60·0; H, 6·5; C_6H_6, 7·0%). The unsolvated complex was
obtained by heating at 40° <u>in vacuo</u>. (Found: C, 57·5; H, 6·5; P, 5·45.
$C_{54}H_{72}Ge_2P_2Pt$ (i.e. $(n-Pr_3P)_2Pt(GePh_3)_2$) requires C, 57·7; H, 6·5;
P, 5·5%). This material is also stable to air and water in solution.
Its dipole moment in benzene solution was 2·4D (assuming atom
polarisation to be 15% of the electron polarisation).

3. Reaction of Ph_3GeLi with <u>cis</u> $(Ph_3P)_2PtBr_2$.

Triphenylgermyl-lithium, from butyl-lithium (19 mmole) and tri-
phenylgermane (5·8 g., 18·9 mmole) in ether (100 c.c.), was added slowly

to a suspension of cis-bistriphenylphosphineplatinum(II) bromide in
ether (120 c.c.). A heavy yellow precipitate developed, and the mixture
was refluxed for 3 hr. The solvent was distilled off, and the residue
extracted with benzene, leaving lithium bromide (1·1 g.) undissolved.
Removal of the benzene from the red solution gave a yellow powder (9·3 g.).
Attempts to purify this from methylcyclohexane, petroleum, acetone and
ethyl acetate gave a red oil. Addition of petroleum ether to benzene
solutions precipitated an inhomogeneous orange powder (Found: Pt,
11·5%; N, 584) which decomposed without melting at 90°.

4. Reaction between Ph_3GeH and $(Et_3P)_2PtBr_2$.

a). Trans$(Et_3P)_2PtBr_2$ and Ph_3GeH in solution.

Triphenylgermane (0·1 g.) and trans-bistriethylphosphineplatinum(II)
bromide (0·1 g.) were stirred overnight in ether solution at room
temperature. After removal of the solvent, infrared examination showed
the presence of the starting materials only.

b). Trans$(Et_3P)_2PtBr_2$ and Ph_3GeH heated together.

Triphenylgermane (170 mg.) and trans $(Et_3P)_2PtBr_2$ (80 mg.) were mixed
together and sublimed at $140°/10^{-4}$ mm. Infrared examination of the
sublimate showed that triphenylbromgermane was present as well as tri-
phenylgermane. Three bands attributable to $v(Pt-H)$ were also observed
at 2212, 2183 and 2004 cm.$^{-1}$ The band at 2183 cm.$^{-1}$ is close to that
expected for trans $(Et_3P)_2Pt(H)Br$ (140). Only a trace of non-volatile
material remained after the sublimation.

c). <u>Cis(Et$_3$P)$_2$PtBr$_2$ with Ph$_3$GeH in the presence of triethylamine.</u>

Triphenylgermane (1.8 g.), <u>cis-bis</u>triethylphosphineplatinum(II) bromide (1.75 g.) and triethylamine (0.6 g., 2 mol.) were refluxed in benzene (100 c.c.). No triethylamine hydrochloride was produced, and, after removing the solvent, the starting materials were recovered un- changed.

5. <u>Trans</u> (Et$_3$P)$_2$PtI$_2$ and Ph$_3$GeLi.

a). <u>Using 2 equivalents of Ph$_3$GeLi.</u>

A filtered solution (glass wool) of triphenylgermyl-lithium, pre- pared from hexaphenyldigermane (5 g.) and lithium shot (1.5 g.) in 1,2- dimethoxyethane (20 c.c.), was added dropwise to <u>trans-bis</u>triethyl- phosphineplatinum(II) iodide in a 1:1 ether-benzene solution (120 c.c.). A precipitate formed during the exothermic reaction, and triethylphosphine was detected by smell in the emergent nitrogen stream. Hydrolysis with de-aerated water after 1$\frac{1}{2}$ hr. under reflux gave hexaphenyldigermane (1.4 g., 28%) as the insoluble part. The mixed solvents were distilled from the organic extract, and extraction with petroleum ether (50 c.c., b.p. 40-60°) removed a small amount of tarry material. The residue was extracted with hot <u>iso</u>-propanol (150 c.c.) leaving (Et$_3$P)$_2$Pt(GePh$_3$)$_2$ (3.9 g., 54%) undissolved. The <u>iso</u>-propanol solution yielded <u>bistriethyl- phosphinetriphenylgermylhydridoplatinum(II)</u>,(Et$_3$P)$_2$Pt(H)GePh$_3$, (0.3 g.) as colourless plates, m.p. 150° (dec.). (Found: C, 49.3; H, 6.2. C$_{30}$H$_{46}$GeP$_2$Pt (i.e. (Et$_3$P)$_2$Pt(H)GePh$_3$) requires C, 48.9; H, 6.3%). The Pt-H stretching frequency of this compound shows a marked shift when

measured as a pressed disc in KBr ($v_{max.}$, 2042 cm.$^{-1}$) compared with the value in benzene solution ($v_{max.}$, 2051 cm.$^{-1}$).

b). <u>Using less than 2 equivalents of Ph$_3$GeLi.</u>

In a similar experiment, triphenylgermyl-lithium prepared from hexaphenyldigermane (6 g.) in monoglyme (15 c.c.) was added to <u>trans</u> (Et$_3$P)$_2$PtI$_2$ (5.5 g.) in a 2:1 ether-benzene solution (100 c.c.). Hydrolysis, after 3 hr. of reflux, gave hexaphenyldigermane (1.5 g., 25%). Infrared examination of the organic residue, after solvent had been removed, showed <u>trans</u> (Et$_3$P)$_2$Pt(H)I (v(Pt-H), 2163 cm.$^{-1}$) and (Et$_3$P)$_2$-Pt(H)GePh$_3$ (v(Pt-H), 2042 cm.$^{-1}$). Extraction with hot ethanol (150 c.c.) left (Et$_3$P)$_2$Pt(GePh$_3$)$_2$ (2.8 g., 33%) undissolved. The ethanol solution yielded <u>bistriethylphosphinetriphenylgermylethoxyplatinum(II)</u>, (Et$_3$P)$_2$Pt-(OEt)GePh$_3$, (0.4 g.) as colourless plates, m.p. 160-170° (dec.). (Found: C, 49.3; H, 6.35; P, 7.8, 7.2%; M, (X-rays) 772 (density 1.48). C$_{32}$H$_{60}$GeOP$_2$Pt (i.e. (Et$_3$P)$_2$Pt(OEt)GePh$_3$) requires C, 49.25; H, 6.5; P, 7.9%; M, 780). The ^{1}H n.m.r. spectrum of this complex at 60 Mc./sec. showed a quartet at 6.26 due to the methylene of the ethoxide. The ratio of this methylene resonance to that of the other aliphatic protons was 1:15.5. (Et$_3$P)$_2$Pt(OEt)GePh$_3$ requires 1:16.5. The ethanolic mother liquors gave a brown tar from which <u>trans</u> (Et$_3$P)$_2$Pt(H)I (0.5 g.) (v(Pt-H), 2163 cm.$^{-1}$ ^{1}H n.m.r. in C$_6$D$_6$ (Pt)H, τ, 22.8) was isolated by sublimation (100°/10^{-4} mm.). Chromatography of the non-volatile residue on alkaline alumina (eluant 1:1 benzene-petroleum (b.p. 40-60°)) gave a trace of (Et$_3$P)$_2$PtI$_2$ (Found: C, 21.0; H, 4.8. C$_{12}$H$_{30}$I$_2$P$_2$Pt requires C, 21.0;

H, 4.4%), tetraphenylgermane and <u>bistriethylphosphineiodophenylplatinum(II)</u>, $(Et_3P)_2Pt(I)Ph$, (0.22 g.) m.p. 101-102° ex methanol (Found: C, 34.0; H, 5.5. $C_{18}H_{35}IP_2Pt$ (i.e. $(Et_3P)_2Pt(I)Ph$) requires C, 34.0; H, 5.55%).

A similar experiment using half the amount of triphenylgermyl-lithium gave some hexaphenyldigermane and $(Et_3P)_2Pt(GePh_3)_2$ (1.0 g.). Crystallisation from ethanol gave the ethoxyplatinum complex, $(Et_3P)_2^-$ $Pt(OEt)GePh_3$, (0.5 g.) and unreacted $(Et_3P)_2PtI_2$ (2 g., 36%). The tarry residue (1.5 g.) again contained <u>trans</u> $(Et_3P)_2Pt(H)I$.

6. <u>Iodotrimethylplatinum(IV) and triphenylgermyl-lithium.</u>

A filtered solution of triphenylgermyl-lithium, from hexaphenyl-digermane (1.3 g.) and lithium (1.0 g.) in 1,2-dimethoxyethane (20 c.c.), was added slowly to Me_3PtI (1.25 g.) in a 2:1 mixture of benzene-ether (100 c.c.). The mixture was stirred at room temperature for 18 hr., during which time the colour deepened as a black precipitate was given. The soluble part yielded only triphenylmethylgermane, Ph_3GeMe ($\rho CH_3(Ge)$, 788 cm.$^{-1}$; $\nu(Ge-CH_3)$, 586 cm.$^{-1}$). The black residue (1.1 g.) showed no infrared bands and ignited in air.

<u>Reactions of the Germylplatinum complexes, $(R_3P)_2Pt(GePh_3)_2$.</u>
7. <u>Thermal decomposition.</u>
a). <u>Pyrolysis of $(n-Pr_3P)_2Pt(GePh_3)_2$.</u>

The complex (0.332 g.) decomposed <u>in vacuo</u> at 120° and at 175° collapsed to a black tar. Fractional sublimation (250°/10^{-4} mm. for 1 hr.) gave tetraphenylgermane (35 mg., m.p. 227-235°) and hexaphenyldigermane

(25 mg., m.p. 351-353°) together with benzene, propylene, and tri-n-propylphosphine. The black, X-ray amorphous residue (170 mg.) was freely soluble in benzene giving a brown solution. (Found: C, 42.9; H, 5.9%). Prolonged heating at 230°/10^{-4} mm. resulted in further loss of Ph_4Ge and Ph_6Ge_2 (50 mg.), when the black amorphous residue was insoluble in benzene. Its infrared spectrum still showed bands associated with phenyl and propyl groups (Found: C, 20.0; H, 2.2%).

b). Pyrolysis of $(Et_3P)_2Pt(GePh_3)_2$.

The complex (0.203 g.) darkened _in vacuo_ at 155° and at 180° a white sublimate (Ph_4Ge) formed. At 193° the compound collapsed to a black liquid which became increasingly viscous as the temperature was held at 230° for 30 minutes. Ph_4Ge (41 mg.), Ph_6Ge_2 (15 mg.) and a black, benzene soluble residue (87 mg.) were isolated as previously described, together with benzene, ethylene and triethylphosphine.

8. $(n-Pr_3P)_2Pt(GePh_3)_2$ with triphenylphosphine.

The complex $(n-Pr_3P)_2Pt(GePh_3)_2$ (0.3 g.) and triphenylphosphine (0.3 g.) were stirred in benzene for 3 days at room temperature. After removal of the benzene under vacuum, extraction of the residue with hot methanol (50 c.c.) removed the triphenylphosphine and left only $(n-Pr_3P)_2Pt(GePh_3)_2$. Infrared examination of the products gave no evidence for a triphenylphosphine complex.

9. $(n-Pr_3P)_2Pt(GePh_3)_2$ and diazomethane.

To a solution of $(n-Pr_3P)_2Pt(GePh_3)_2$ (333 mg., 0.3 mmole) in benzene

(10 c.c.) was added a solution of diazomethane (1 mmole) in ether (2·7 c.c.). After stirring for 24 hr. the solvents and CH_2N_2 were removed under vacuum. The **bistri-n-propylphosphinebistriphenylgermylplatinum(II)** was recovered intact.

10. $(R_3P)_2Pt(GePh_3)_2$ with phenylacetylene, Ph_3GeBr and Ph_3GeH.

a). Phenylacetylene.

The complex $(Et_3P)_2Pt(GePh_3)_2$ (0·24 g.) was dissolved in PhC≡CH (10 c.c.) and heated to 95° for 1 hr. The phenylacetylene was distilled off and the residue extracted with petroleum ether (b.p. $40-60^\circ$, 20 c.c.), leaving unchanged $(Et_3P)_2Pt(GePh_3)_2$ undissolved.

b). Triphenylbromgermane.

$(Et_3P)_2Pt(GePh_3)_2$ (0·25 g.) and Ph_3GeBr (0·186 g., 2 mol.) were dissolved in benzene (25 c.c.) and the mixture was refluxed for 1 hr. Removal of the solvent and extraction with hot ethanol left $(Et_3P)_2Pt-(GePh_3)_2$ undissolved. The ethanol solution contained triphenylbromgermane.

c). Triphenylgermane.

An experiment similar to b) was attempted using $(n-Pr_3P)_2Pt(GePh_3)_2$ (0·25 g.) and Ph_3GeH (68 mg.). No reaction took place after refluxing in benzene for 24 hr.

11. $(Et_3P)_2Pt(GePh_3)_2$ and iodine.

Dropwise addition of iodine (89 mg., 0·35 mmole) in benzene (13·8 c.c.) to the complex $(Et_3P)_2Pt(GePh_3)_2$ (0·36 g., 0·34 mmole) in benzene (20 c.c.) resulted in immediate discharge of the iodine colour. The residue, after

removal of benzene, was extracted with petroleum ether (b.p. 60-80°) giving starting material as the insoluble part (0.15 g., 42%). Sublimation (110°/10^{-4} mm.) of the petroleum soluble material followed by crystallisation from ethanol gave triphenyliodogermane, m.p. 149-154°, and trans-bistriethylphosphineplatinum(II) iodide, m.p. 133-135° (Found: C, 21.2; H, 4.5. $C_{12}H_{30}I_2P_2Pt$ requires C, 21.0; H, 4.4%). A trace of hexaphenyldigermoxane was also isolated, presumably produced by hydrolysis of triphenyliodogermane during work-up.

12. $(Et_3P)_2Pt(GePh_3)_2$ and carbon tetrachloride.

A few crystals of the germylplatinum complex were boiled in carbon tetrachloride for 5 min. Removal of the solvent left triphenylchlorgermane and trans-bistriethylphosphineplatinum(II) chloride (Ph$_3$GeCl: ν(Ge-Cl), 379 cm.$^{-1}$; ν(Ge-Ph) 328 cm.$^{-1}$; characteristic band at 257 cm.$^{-1}$ Trans (Et$_3$P)$_2$PtCl$_2$: ν(Pt-P), 415 cm.$^{-1}$; ν(Pt-Cl), 340 cm.$^{-1}$).

13. Reaction with 1,2-dibromethane.

a) $(Et_3P)_2Pt(GePh_3)_2$

Bistriethylphosphinebistriphenylgermylplatinum(II), (0.4 g.) and 1,2-dibromethane (20 c.c.) were heated under reflux in a slow stream of nitrogen for 20 hr., the emergent gases being passed through traps at -78° and -198°. Ethylene (9.84N.c.c.; 57%) was isolated from the liquid nitrogen trap. Sublimation of the residue (100°/10^{-3} mm.), after removal of the excess 1,2-dibromethane, gave trans-bistriethylphosphineplatinum (II) bromide, (Et$_3$P)$_2$PtBr$_2$, m.p. 128-133° ex ethanol, and triphenylbromgermane, Ph$_3$GeBr, m.p. 135-137° ex ethanol in a combined yield of 0.25 g.

The residue from the sublimation (0·17 g.) gave cis-bistriethylphosphine-platinum(II) bromide, m.p. 200-202° ex ethanol, and hexaphenyldigermoxane, $(Ph_3Ge)_2O$, m.p. 176-179°. The latter was presumably formed by hydrolysis of bromtriphenylgermane in the working up process.

b) $(n-Pr_3P)_2Pt(GePh_3)_2$

The tri-n-propylphosphine complex, $(n-Pr_3P)_2Pt(GePh_3)_2$ (49 mg.) and 1,2-dibromethane (10 c.c.) were stirred at room temperature in a vacuum apparatus. The reaction was complete after 12 days, giving ethylene (1·95N.c.c.; 99·6%). The rate of production of ethylene slowed considerably after half the gas had evolved.

14. $(R_3P)_2Pt(GePh_3)_2$ and hydrogen chloride.

The triethylphosphine complex, $(Et_3P)_2Pt(GePh_3)_2$, (0·22 g.) in benzene (20 c.c.) was treated with an excess of dry hydrogen chloride. The yellow solution rapidly paled. Sublimation of the reaction products (90°/10⁻⁴ mm.) left a trace of hexaphenyldigermoxane as residue. The oily sublimate contained triphenylgermane, triphenylchlorgermane, trans-bistriethylphosphinehydridoplatinum(II) chloride and trans-bistriethyl-phosphineplatinum(II) chloride. (Ph_3GeH: $\nu(Ge-H)$, 2036 cm.⁻¹; ¹H n.m.r., $\tau(Ge)H$, 4·2. $(Et_3P)_2Pt(H)Cl$: $\nu(Pt-H)$, 2185 cm.⁻¹; ¹H n.m.r., $\tau(Pt)H$, 26·7. Ph_3GeCl: $\nu(Ge-Cl)$, 379 cm.⁻¹ trans $(Et_3P)_2PtCl_2$: $\nu(Pt-Cl)$, 341 cm.⁻¹; $\nu(Pt-P)$, 412 cm.⁻¹).

An analagous experiment using the tri-n-propylphosphine complex gave similar products, and in this case cis-bistri-n-propylphosphine-platinum(II) chloride, m.p. 145-150°, was isolated by fractional

crystallisation from methanol. As it was established that hydrogen-halogen exchange can take place under certain conditions (Experiment 4), separate experiments on both complexes confirmed the presence of all the products before the sublimation stage.

15. **Reaction with methyl iodide.**

a). $(n-Pr_3P)_2Pt(GePh_3)_2$.

The complex (0.45 g., 0.4 mmole) and methyl iodide (6 c.c.) were heated in an evacuated sealed tube for 6 hr. at 118°. Methane (3.56N c.c., 0.16 mmole) and ethane (6.02N c.c., 0.27 mmole) were isolated when the tube was opened to a vacuum system. Removal of the excess methyl iodide left a complex mixture of products (0.53 g.) which yielded, by fractional crystallisation first from acetone then from ethanol, iodotriphenyl-germane, m.p. 144-147°, trans-bistri-n-propylphosphineplatinum(II) iodide, m.p. 112-114°, and, in small yield, red crystals of the binuclear complex, trans $(n-Pr_3P)_2Pt_2I_4$, m.p. 198-201° (Found: C, 18.0; H, 3.5. $C_{18}H_{42}I_4P_2Pt_2$ requires C, 17.7; H, 3.5%).

In a similar experiment the crude reaction mixture was boiled with ethanolic potassium hydroxide. Sublimation of the ether soluble part gave triphenylmethylgermane as the only volatile component, m.p. 68-69° ex methanol. (Found: C, 70.9; H, 5.6. $C_{19}H_{18}Ge$ (i.e. Ph_3GeMe) requires C, 71.5; H, 5.7%).

b) $(Et_3P)_2Pt(GePh_3)_2$.

The complex $(Et_3P)_2Pt(GePh_3)_2$ (0.3 g.) was heated in a sealed, evacuated tube with methyl iodide (5 c.c.) for 6 hr. at 115°. As before,

the main products were the iodides Ph_3GeI (60 mg.) (m.p. 143-148° ex acetone) and <u>trans</u> $(Et_3P)_2PtI_2$ (100 mg.) (m.p. 133-135° ex acetone). The residue (0·1 g.) which contained mainly Ph_3GeMe, gave trace quantities of unidentified white and red crystalline compounds by fractional crystallisation from benzene and acetone. Both compounds appeared to contain Et_3P, Pt and I, but no Ph_3Ge groups.

16. $(n-Pr_3P)_2Pt(GePh_3)_2$ and magnesium iodide.

a). <u>Reaction time 2 days.</u>

The complex $(n-Pr_3P)_2Pt(GePh_3)_2$ (0·47 g.) in benzene (10 c.c.) was added to a filtered solution of magnesium iodide, prepared from iodine (0·5 g.) and magnesium in ether (100 c.c.). The mixture was stirred at room temperature for 46 hr. Hydrolysis with air-free water gave a cloudy organic extract from which the solvents were removed by distillation. Extraction with hot ethanol left a trace of hexaphenyldigermane undissolved. The ethanol solution yielded first <u>trans</u> $(n-Pr_3P)_2PtI_2$, m.p. 116-117° (220 mg., 68%) and then Ph_3GeI, m.p. 145-147° (70 mg., 20%). Sublimation of the residue (60°/10⁻⁴ mm.) gave an inseparable mixture of triphenylgermane ($\nu(Ge-H)$, 2034 cm.⁻¹) and a hydridoplatinum complex having $\nu(Pt-H)$ at 1731 cm.⁻¹ The residue from the sublimation consisted of a trace of hexaphenyldigermoxane.

b). <u>Reaction time 30 minutes.</u>

A similar experiment using $(n-Pr_3P)_2Pt(GePh_3)_2$ (0·42 g.) was hydrolysed after 30 minutes. The products at this stage included Ph_3GeH ($\nu(Ge-H)$, 2034 cm.⁻¹) and two hydridoplatinum complexes ($\nu(Pt-H)$, 2156 and 1731 cm.⁻¹). Normal work up gave hexaphenyldigermane (5 mg.) and, from

ethanol solution, bistri-n-propylphosphinetriphenylgermyliodoplatinum(II),
$(n-Pr_3P)_2Pt(I)GePh_3$ (36 mg.) as pale yellow crystals, m.p. 148-149°
(Found: C, 45.8; H, 6.3. $C_{36}H_{57}GeIP_2Pt$ (i.e. $(n-Pr_3P)_2Pt(GePh_3)I$)
requires C, 45.2; H, 6.1%). On further concentration in air, hexa=
phenyldigermoxane (120 mg., 51%) separated, and the filtrate was then
free from triphenylgermane. It appears that platinum complexes which were
also present catalyse the aerial oxidation of triphenylgermane. Sub-
limation of the residue gave a mixture of hydridoplatinum complexes
(ν(Pt-H) at 2165 and 1731 cm.$^{-1}$) which could not be separated.

17. Hydrogenolysis of $(R_3P)_2Pt(GePh_3)_2$

a). $(Et_3P)_2Pt(GePh_3)_2$

The complex (0.42 g.) in ethyl acetate (100 c.c.) was shaken with
hydrogen for 5 hr. at 1 atmosphere and 20°. The initial deep yellow
colour of the solution was completely discharged. Removal of the solvent
left an oily residue from which triphenylgermane (ν(Ge-H), 2034 cm.$^{-1}$)
was removed by extraction with light petroleum (b.p. 40-60°). The
residue of bistriethylphosphinetriphenylgermylhydridoplatinum(II)
separated from benzene solution as white crystals, m.p. 150° (dec.)
[Found: C, 48.5; H, 6.1; P, 7.5, 8.5%. M, 726. $C_{30}H_{46}GeP_2Pt$ (i.e.
$(Et_3P)_2Pt(H)GePh_3$) requires C, 48.9; H, 6.3; P, 8.4%; M, 736). A
crystalline specimen of this material was unchanged after 6 months in air.
Addition of Adam's catalyst to a similar reaction did not noticeably
accelerate the reaction and did not lead to cleavage of the second
Ge-Pt bond.

b). $(n-Pr_3P)_2Pt(GePh_3)_2$.

The complex (0·400 g., 0·36 mmole) in toluene (20 c.c.) was stirred magnetically in hydrogen (partial pressure 21 mm.) for 21 days. The deep yellow colour faded progressively over this period giving triphenylgermane (ν(Ge-H), 2034 cm.$^{-1}$; 'H n.m.r., (Ge)H, 4·2 in benzene solution) and <u>bistri-n-propylphosphinetriphenylgermylhydridoplatinum(II)</u>, $(n-Pr_3P)_2Pt(H)GePh_3$. (ν(Pt-H), 1957 cm.$^{-1}$; H_2 absorbed, 0·31 mmole. Calculated for the hydrogenolysis of one Ge-Pt bond, 0·36 mmole). Separation of the two reaction products was not possible due to their similar solubilities. Attempts to remove triphenylgermane from the mixture by sublimation led to the decomposition of the hydridoplatinum complex.

c). <u>Reaction rate measurements.</u>

In two experiments, $(n-Pr_3P)_2Pt(GePh_3)_2$ (302 mg.) in toluene (20 c.c.) was introduced into flasks equipped with break-seals, and, after thorough degassing, hydrogen was admitted to achieve essentially the same initial partial pressure of H_2 at 0° and 25°. The flasks were then sealed, and agitated vigorously for 24 hr. at 0° and 12 hr. at 25° respectively when excess hydrogen was measured.

<u>At 0°</u>   t = 0   P(H_2) = 186 mm.   V(H_2) = 37·7N c.c.

t = 24hr. P(H_2) = 170 mm.   V(H_2) = 34·4N c.c.

% Reaction = 54·8.

At 25°   t = 0 $P(H_2)$ = 181 mm. $V(H_2)$ = 33.56N c.c.

           t = 12hr. $P(H_2)$ = 155 mm. $V(H_2)$ = 28.73N c.c.

                         % Reaction = 80.1.

18. $(n\text{-}Pr_3P)_2Pt(GePh_3)_2$ and phenyl-lithium.

Etherial phenyl-lithium (40 c.c., 0.6 molar) and bistri-n-propyl phosphinebistriphenylgermylplatinum(II) (0.39 g.) in benzene (20 c.c.) were stirred at room temperature for 3 days. Hydrolysis and normal work up gave cis-bistri-n-propylphosphinediphenylplatinum(II), m.p. 151-153° (dec.) ex ethanol. (Found: C, 54.0; H, 7.8. $C_{30}H_{52}P_2Pt$ (i.e. $(n\text{-}Pr_3P)_2PtPh_2$) requires C, 53.8; H, 7.8%). Triphenylgermane was isolated from the ethanolic mother liquors by sublimation (55°/10⁻³ mm.) after removing the solvent. Experiments in which some bromobenzene was present (from the preparation of the PhLi) gave, in addition, tetra-phenylgermane by the reaction: $Ph_3GeLi + PhBr \longrightarrow Ph_4Ge$.

19. $(n\text{-}Pr_3P)_2Pt(GePh_3)_2$ and lithium aluminium hydride.

The complex (0.6 g.) in benzene (40 c.c.) was added to lithium aluminium hydride (1.0 g.) in ether (100 c.c.). The yellow solution deepened in colour over 2 days at 20°, when the ether was removed by distillation and replaced by benzene. Filtration gave a colourless solution containing only triphenylgermane (0.32 g., 98%) (ν(Ge-H), 2035 cm.⁻¹). Excess lithium aluminium hydride was removed from the residue by washing with dry ether. A yellow platinum complex, in-soluble in organic solvents, remained. This did not react with either bromobenzene or methyl iodide at 20°, and on exposure to air, it caught

fire. Treatment with aqueous ether at -78° resulted in some effervescence, and on warming to -20° platinum was deposited with further evolution of H_2, accompanied by a smell of tripropylphosphine. Addition of triphenyl-phosphine did not lead to a stable hydridoplatinum complex.

Reactions of the Germylhydridoplatinum complex, $(R_3P)_2Pt(GePh_3)H$

20. **Stability to alcohols, ketones and bases.**

Small samples of the complex $(Et_3P)_2Pt(H)GePh_3$ were dissolved in refluxing acetone, *iso*-propanol and ethanolic potassium hydroxide. In each case the material was recovered unaltered. A crystalline sample of this material was stored in air without change for six months.

21. **$(n-Pr_3P)_2Pt(H)GePh_3$ and diazomethane.**

The complex $(n-Pr_3P)_2Pt(GePh_3)_2$ (0.4 g., 0.36 mmole) was dissolved in a 1:1 benzene-toluene mixture (20 c.c.) and stirred with hydrogen (partial pressure approx. 20 mm.) in a vacuum apparatus. Uptake of hydrogen ceased after 3 weeks when 7.25N c.c. (91%) had been absorbed. To the products of the hydrogenation (an equimolar mixture of $(n-Pr_3P)_2Pt(H)GePh_3$ and Ph_3GeH) was added diazomethane (2 mmole) in ether (5.25 c.c.). After stirring the mixture for 24 hr. at room temperature the solvents were removed by continuous evacuation. The semi-solid residue was shown to contain only the two hydrides, indicating that diazomethane does not react with either the Pt-H or Ge-H bond.

22. **$(Et_3P)_2Pt(H)GePh_3$ and PEt_3.**

The complex $(Et_3P)_2Pt(H)GePh_3$ (10 mg.) in ethanol (10 c.c.) was

refluxed under nitrogen with triethylphosphine (1 drop). An infrared examination of the product after removal of the solvent indicated that most of the hydridoplatinum complex had survived unchanged, but weak bands at 2033 cm.$^{-1}$ (due to Ph_3GeH) and 859 cm.$^{-1}$ (due to $(Ph_3Ge)_2O$) indicated some cleavage of the Pt—Ge bond.

23. $(Et_3P)_2Pt(H)GePh_3$ and <u>trans</u> $(Et_3P)_2PtI_2$.

The complexes $(Et_3P)_2Pt(H)GePh_3$ (23 mg.) and $(Et_3P)_2PtI_2$ (5 mg.) were refluxed in ethanol (20 c.c.). On cooling, pure $(Et_3P)_2Pt(H)GePh_3$ crystallised. The mother liquors contained a trace of hexaphenyldiger-moxane (ν(Ge-O) 858 cm.$^{-1}$) as well as the two complexes.

Reactions of the Ethoxyplatinum complex, $(Et_3P)_2Pt(OEt)GePh_3$.

24. Et_3P and Ph_3P.

A sample of the ethoxyplatinum complex $(Et_3P)_2Pt(OEt)GePh_3$ (100 mg.) was recrystallised from ethanol to which a trace of Et_3P had been added. The complex was recovered unchanged, and no evidence indicating cleavage of Pt—Ge bonds was obtained.

In another experiment the complex (45 mg.) was dissolved in ethanol and triphenylphosphine (45 mg.) was added. On slow evaporation of the solvent, the two compounds crystallised separately, and no suggestion of phosphine exchange was found.

25. $(Et_3P)_2Pt(OEt)GePh_3$ and hydrogen.

Hydrogen gas was bubbled through a solution of the ethoxy complex (0.1 g.) in benzene (20 c.c.) for 18 hr. The $(Et_3P)_2Pt(OEt)GePh_3$ was

recovered unchanged. A similar result was obtained when the experiment was repeated using palladium-black catalyst.

26. $(Et_3P)_2Pt(OEt)GePh_3$ and iso-propanol.

The complex (50 mg.) was dissolved in hot iso-propanol. On cooling the solution yielded bistriethylphosphinetriphenylgermyl-iso-propoxy-platinum(II), m.p. 162-172° (dec.) after further recrystallising from iso-PrOH. (Found: C, 49.6; H, 6.5. $C_{33}H_{52}GeOP_2Pt$ (i.e. $(Et_3P)_2Pt-(OPr^i)GePh_3$) requires C, 49.9; H, 6.6%).

27. $(Et_3P)_2Pt(OEt)GePh_3$ and methanol.

In an experiment similar to above but using methanol, bistriethyl-phosphinetriphenylgermylmethoxyplatinum(II), m.p. 172-180° (dec.) was given (Found: C, 48.6; H, 6.36. $C_{31}H_{48}GeOP_2Pt$ (i.e. $(Et_3P)_2Pt(OMe)-GePh_3$) requires C, 48.6; H, 6.31%).

28. $(Et_3P)_2Pt(OEt)GePh_3$ and water.

The complex $(Et_3P)_2Pt(OEt)GePh_3$ (20 mg.) was dissolved in acetone (50 c.c.) and water was added dropwise until a precipitate began to form. The solution was heated and allowed to cool, when bistriethyl-phosphinetriphenylgermylhydroxyplatinum(II) was deposited as white needles, m.p. 153-156° (dec.). (Found: C, 47.6; H, 5.8. $C_{30}H_{46}GeOP_2Pt$ (i.e. $(Et_3P)_2Pt(OH)GePh_3$) requires C, 47.9; H, 6.2%). This complex shows a sharp band due to unassociated OH at 3630 cm.$^{-1}$ Heating at 100° in vacuo does not lead to dehydration, and treatment with ethanol re-generates the ethoxy complex.

Platinum(II) Grignard Reagents.

29. <u>Cis</u>$(Et_3P)_2PtBr_2$ and <u>cyclohexylmagnesium bromide</u>.

<u>Cyclohexylmagnesium bromide</u> was prepared from <u>cyclohexyl</u> bromide
(7.5 g.) and magnesium (1.2 g.) in ether (100 c.c.) and filtered from
excess magnesium through a grade 4 sintered disc. A 5 c.c. aliquot of
the solution was hydrolysed by water and v.p.c. analysis of the organic
part showed that it contained <u>cyclohexane</u>, but no <u>cyclohexene</u> or bi-
<u>cyclohexyl</u>. The remaining Grignard reagent was split into 2 parts and to
each <u>cis</u>$(Et_3P)_2PtBr_2$ (1.5 g.) was added. The two reaction mixtures were
stirred for $2\frac{1}{2}$ hr. at room temperature, during which time a black oil
was deposited.

The first reaction mixture was hydrolysed with de-aerated water.
After drying the ether extract ($MgSO_4$), v.p.c. examination of the
solvent revealed traces of <u>cyclohexene</u> and <u>bicyclohexyl</u> as well as <u>cyclo-</u>
hexane. Removal of the solvent left a residue (1 g.) consisting mainly
of <u>trans-bistriethylphosphine hydridobromplatinum(II)</u>, (ν(Pt-H) 2217 cm.$^{-1}$)
and some <u>trans</u>$(Et_3P)_2PtBr_2$ (m.p. 134-136°). The ether-insoluble tarry
residue (0.5 g.) also yielded a trace of <u>trans</u>$(Et_3P)_2PtBr_2$ by extracting
with methanol.

The second reaction mixture was hydrolysed with D_2O. The ether
soluble part this time gave at 2:1 mixture of $(Et_3P)_2Pt(D)Br$ and
$(Et_3P)_2Pt(H)Br$ (ν(Pt-H) 2217 cm.$^{-1}$; δ(Pt-H) 812 cm.$^{-1}$; ν(Pt-D) 1592 cm.$^{-1}$;
δ(Pt-D) 577 cm.$^{-1}$; m.p. 99-100°). Extraction of the tarry residue
(0.5 g.) with methanol again gave <u>trans</u>$(Et_3P)_2PtBr_2$.

A separate experiment showed that the deuteride was not formed by H-D exchange, since deuterolysis of $C_6H_{11}MgBr$ followed by addition of $(Et_3P)_2Pt(H)Br$ produced no absorption due to Pt-D. A separate experiment also established that bicyclohexyl was produced at 20° by the reaction between $C_6H_{11}Br$ and $C_6H_{11}MgBr$. An attempt to prepare the platinum Grignard reagent using only 20% excess cyclohexylmagnesium bromide (instead of a 10-fold excess as above) failed; no evidence for the presence of a Pt-H bond being found.

EXPERIMENTAL METHODS.

1. Nitrogen Supply.

All reactions and operations involving air sensitive compounds or intermediates were carried out in an atmosphere of pure, dry, oxygen-free nitrogen. Purification was effected by passing commercial "white spot" nitrogen through copper turnings at 450° to remove traces of oxygen, and then through a column of molecular sieve to remove water. In addition to this, for critical experiments, the nitrogen was then passed through a trap at -198° to remove final traces of moisture.

2. Infrared Spectra.

The region $2.5 - 25\mu$ was recorded on a Grubb-Parsons G.S.2A or Spectromaster Spectrophotometer. Solids were examined as pressed discs in KBr or KI or as nujol mulls: liquids were examined as thin films between KBr or KI plates. In special cases, infrared spectra were measured in solution, using an unreactive solvent which was transparent in the desired region. The region $22 - 50\mu$ was recorded on a Grubb-Parsons D.M.2/D.B.3 Spectrophotometer, solids being examined as nujol mulls between cesium iodide plates. Throughout this work the identity of known compounds was often confirmed by the complete superposition of their i.r. spectra.

3. Vapour-Phase Chromatography.

Vapour phase chromatograms were recorded on a Griffin and George Mk.IIB apparatus. The stationary phase was silicone elastomer on kieselguhr, and this was maintained at a temperature near the boiling point (at 1 atmosphere) of the least volatile compound to be examined. The carrier gas

was nitrogen at a flow rate of 1 litre/hr. and an internal excess pressure of 15 cm.

Identification of the components of a mixture was effected as follows. First a chromatogram of the mixture was obtained, and the retention times of various peaks was compared with those of the suspected compounds. When a close correspondence was found, a sample of the mixture, to which had been added a small amount of the authentic compound, was injected. The non-appearance of an extra peak and the strengthening of one already present established its identity.

The amount of sample injected varied from 2 drops (for pure compounds) to 1 c.c. (for dilute solutions).

4. Nuclear Magnetic Resonance Spectra.

'H nuclear magnetic resonance spectra were recorded on an A.E.I. R.S.2. instrument. Whore-ever possible pure liquids or solutions in CCl_4 were used. When CCl_4 proved too reactive (as in the case of germanium and platinum hydrides) C_6H_6 or C_6D_6 was used. Measurements relate to tetramethylsilane (τ = 10) as internal standard.

5. Solvents.

Benzene, toluene, petroleum (B.D.H. "analar grade") and diethyl ether were dried by standing over sodium wire for 1 week. 1,2-Dimethoxyethane and tetrahydrofuran were initially treated by standing over potassium hydroxide for 3 days. They were distilled under nitrogen immediately before use from potassium and benzophenone or from lithium aluminium hydride.

ANALYTICAL METHODS.

1. **Carbon** and **hydrogen** analyses were carried out in the analytical laboratory of this department under the direction of Mr. T. Holmes, and also by Drs. Weiler and Strauss of the micro-analytical laboratory, Oxford. A high temperature of combustion was required to achieve complete oxidation to CO_2 and H_2O.

2. **Germanium** was estimated in compounds which also contained only carbon, hydrogen and oxygen. The method employed was similar to that described by Rochow (9). The sample (0.3 g.) was decomposed in a 50 c.c. silica flask with a long neck (10 cm.) by the cautious addition of fuming nitric acid (10 c.c.) at 0°. The solution was allowed to warm to room temperature and ammonium persulphate (1 g.) and 6N sulphuric acid (2 c.c.) were added. After standing overnight the solution was evaporated to dryness on an electric heating mantle and the residue fumed with concentrated sulphuric acid. After this the flask, suspended by platinum wire from a glass beam, was ignited to constant weight, and the germanium estimated from the weight of oxide, GeO_2.

Considerable difficulty was experienced with compounds containing more than one methyl group bonded to germanium. For example all attempts to estimate Ge in $(PhCH_2)_2GeMe_2$ by this method failed. An attempt to measure the mixed oxides of silicon and germanium from $(PhCH_2)_3Ge \cdot SiMe_3$ also produced a low result. It was concluded that the germanium-methyl (and silicon-methyl) bonds in these compounds resisted oxidation long enough to escape as a volatile oxide during the fuming stages.

3. Molecular weights.

a) The majority of molecular weights were measured cryoscopically in benzene. The solvent used was B.D.H. "analar" benzene that had been dried over sodium and standardised with either biphenyl or triphenylphosphine. The method and apparatus are now well known but it is of note to mention the following points, as attention to them led to more consistent results.

i.   The cooling bath was maintained at about 7° below the freezing point of the solution.

ii.   A slow stream of nitrogen was passed over the solution, to which a piece of molecular sieve (grade 5A) had been added to remove traces of condensed water.

iii.   Care was taken to ensure that the stirrer did not interfere with the Bechmann thermometer.

b). A "Mechrolab Osmometer" was used to determine the molecular weights of some compounds. In this instrument a drop of pure solvent and a drop of the solution are suspended on two thermistor beads enclosed in an atmosphere saturated with solvent vapour. After a fixed time interval, the temperature difference between the two drops was read and the molecular weight found by referring to a calibration curve, drawn by performing measurements on known compounds (tetraphenylgermane and biphenyl were used at concentrations ranging from 0.003M. to 0.06M.). All measurements were made in benzene at 37°.

4. Platinum was estimated by weighing as the metal after degrading the compound (186). About 0.4 g. of the compound was placed in a 10 c.c. beaker and 2 c.c. of conc. HNO_3 were cautiously added. After 3 c.c. of

fuming nitric acid had been added, the solution was boiled until it became clear. Two successive aliquots of 2 c.c. of conc. HCl were then added, and after each the solution was boiled gently to remove germanium (as $GeCl_4$) and nitric oxide. The solution was transferred to a 500 c.c. round-bottom flask and diluted to 150 c.c. with water. After neutralising with NH_4OH, 10 c.c. of ammonium acetate solution (saturated) and 10 c.c. of formic acid were added. Platinum metal was given as a black precipitate on warming the mixture to 80° on a water bath. The precipitate co-agulated on boiling for 6 hr. and was collected on a no. 40 filter paper (ashless). After washing and drying at 100°, the paper and precipitate were ignited in a silica flask prior to weighing as metal.

PREPARATION OF STARTING MATERIALS AND REAGENTS.

1. <u>Phenyl-lithium</u> was prepared from lithium and bromobenzene in diethyl ether. A 10% molar excess of lithium was used in the form of shot, which was prepared by the standard method (187). Bromobenzene in ether was added at a rate sufficient to maintain refluxing in the ether suspension of the lithium shot. About 100 c.c. of ether was used for 0.1 mole, and the yield of phenyl-lithium (estimated by titration against 0.1N H_2SO_4 after hydrolysis) was about 95%. Filtration through glass wool removed the excess lithium shot.

2. <u>n-Butyl-lithium</u> was prepared from butyl bromide and lithium shot in ether as above. After initiation, however, the reaction was maintained at -10°, and estimation of the butyl-lithium was achieved by the double titration method of Gilman (188) using benzyl chloride.

3. <u>Benzyl-lithium</u> was prepared from $PhCH_2OCH_3$ and lithium shot in a tetrahydrofuran-ether mixture (185). Estimation was by double titration.

4. <u>Benzylmagnesium chloride</u> was prepared from benzyl chloride and magnesium turnings (10% molar excess) in diethyl ether (100 c.c. to 0.1 mole of Grignard reagent). The reaction was initiated by a crystal of iodine and the benzyl chloride in ether was added at a rate sufficient to maintain refluxing. The yield was not estimated as a large excess was always employed.

5. <u>n-Butylmagnesium bromide</u> was prepared similarly from butyl bromide and magnesium in ether.

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6. <u>Cyclohexylmagnesium bromide</u>, prepared as above from <u>cyclohexyl</u> bromide and magnesium in ether, was filtered through a grade 4 sintered disc to remove excess magnesium (for method see (183)). All operations on this and the preceding reagents were performed under nitrogen.

7. <u>Tetrabenzylgermane</u> was prepared by adding $GeCl_4$ (0·5 mole) to a solution of benzylmagnesium chloride (5 moles) in ether (3 lit.). Toluene (300 c.c.) was added to raise the boiling point and the mixture was refluxed for 6 hr. Hydrolysis and isolation in the usual way gave tetrabenzylgermane in about 95% yield, m.p. 110° from petroleum ether (b.p. 80-100°). The Grignard reagent was not filtered as it has been observed that magnesium does not cause coupling in this reaction (39).

8. <u>Tetrabutylgermane</u> was prepared as above using n-butylmagnesium bromide and germanium(IV) chloride. The product was isolated by vacuum distillation (90°/10⁻³ mm.), and its purity was checked by v.p.c.

9. <u>Hexaphenyldigermane</u> was prepared from the reaction between phenylmagnesium bromide and $GeCl_4$ in the presence of excess magnesium (39). Yields of 60% were obtained, and the product was recrystallised from chloroform by Soxhlet extraction (m.p. 352°).

10. <u>Triphenylgermane</u> was prepared by the reduction of triphenylbromgermane using lithium aluminium hydride (189). Bromine (21 g, 0·125 mole) was added dropwise to a refluxing solution of hexaphenyldigermane (76 g., 0·125 mole) in 1,2-dibromoethane (500 c.c.). Decolorisation of the bromine was rapid and the solvent was then distilled off. The product was dissolved in a 1:1 ether-benzene mixture (700 c.c.) and added slowly to

lithium aluminium hydride (30 g.) in ether (1 lit.). After refluxing for $2\frac{1}{2}$ hr. followed by cautious hydrolysis with 2N H_2SO_4, triphenylgermane was isolated in the usual way. Purification was by vacuum distillation ($140-146^\circ/10^{-3}$ mm.) followed by crystallisation from ethanol or petroleum ether (b.p. $40-60^\circ$).

11. **Triphenylgermyl-lithium** was prepared either by cleaving hexaphenyl-digermane by lithium in 1,2-dimethoxyethane (109) or by reacting tri-phenylgermane with one equivalent of n-butyl-lithium (35) in ether. The methods have been described in the introduction to this thesis (pages 27 and 28).

12. **Germanium(IV)iodide** was prepared by the reaction between constant boiling hydriodic acid and GeO_2 (190). The product was purified by sublimation ($100^\circ/10^{-3}$ mm.), giving orange-red crystals which were stored in the dark.

13. **Bistrialkylphosphineplatinum(II) halides** were prepared by adding two molecules of the phosphine to the platinum(II) halide in refluxing ethanol. The method of obtaining pure cis or trans isomers (which depends on whether an excess of the phosphine is present in the solution or not) has been described on pages 37 and 38.

14. **Diazomethane** was prepared from para-tolyl sulphonyl methylnitros-amide. A solution of potassium hydroxide (1·2 g.) in H_2O (1·5 c.c.) and EtOH(5 c.c.) was heated to $60-65^\circ$ on a water bath. The solution of p-tolyl sulphonyl methylnitrosamide (4·3 g.) in ether (20 c.c.) was added over about 5 min., and the yellow diazomethane-ether mixture which was

generated was condensed into a flask containing ether (25 c.c.) cooled to -78°. A further 5 c.c. of ether were added to the reaction vessel, when the condensing liquid became colourless. The distillation apparatus was flamed before use and rubber bungs rather than ground-glass joints were used to lessen the risk of explosion. The solution of diazomethane in ether was estimated by adding a 2 c.c. aliquot to 25 c.c. of 0·1N benzoic acid in ether, and titrating the excess acid against 0·1N NaOH.

DISCUSSION

PART A.   Benzyl Derivatives of Germanium.

Because of their synthetical importance, organogermanium alkali metal compounds have received almost continuous attention since the preparation of triphenylgermyl-sodium in 1927 (5).   The cleavage of germanium-germanium, germanium-carbon, and germanium-hydrogen bonds by alkali metals in liquid ammonia or ethylamine is now well known (1), but the utility of the reagents produced is limited by ready solvolysis reactions: for example, $Et_3GeLi + NH_3 \longrightarrow Et_3GeH + LiNH_2$.   More recently, however, triphenylgermyl-alkali metal compounds have been prepared by the cleavage of Ge-Ge, Ge-C, Ge-H and Ge-Br bonds by the alkali metal in strongly donating ether solvents such as tetrahydro-furan or 1,2-dimethoxyethane (109, 110, 111).   An even more satisfactory method for triphenylgermyl-lithium involves hydrogen-metal exchange in diethyl ether: $Ph_3GeH + RLi \longrightarrow Ph_3GeLi + RH$.

Attempts to prepare germyl-alkali metal compounds in ether solvents from organogermanes other than phenyl derivatives have been surprisingly unsuccessful.   Although in some cases, such as tetra-ethyl- and tetrabenzyl-germanes, coloured solutions have been obtained, no products indicative of a cleavage reaction were isolated, and evidence was produced that phenyl groups are more susceptible to cleavage than alkyl groups (112).   As a consequence, recent synthetical work requiring germyl-lithium reagents has been confined to the use of Ph_3GeLi.   For example carbonation leads to the acid $Ph_3GeCOOH$; reaction with benzophenone the carbinol $Ph_3GeC(OH)Ph_2$; organic halides usually form the unsymmetrical germane Ph_3GeR.   Compounds of the type

Ph_3GeMR_3, where M = C, Si, Ge, Sn, or Pb have been obtained by the general reaction: $Ph_3GeLi + R_3MX \longrightarrow Ph_3GeMR_3$, although a frequent complication is halogen-metal exchange leading to the symmetrical products, Ph_6Ge_2 and R_6M_2.

The present work is concerned with the cleavage by lithium and butyl-lithium of tetrabenzylgermane, hexabenzyldigermane, and tribenzyl-germane. Particular attention was paid to the possibility of finding a method of producing high yields of tribenzylgermyl-lithium in ether solvents.

Provided water and peroxides are rigorously excluded, tetrabenzyl-germane and lithium in ethylene glycol dimethyl ether undergo a rapid and exothermic reaction even more readily than tetraphenylgermane. The resulting deep brown solution contains mainly tribenzylgermyl-lithium, as evidenced by the isolation of tribenzylgermane after hydrolysis.

$$(PhCH_2)_4Ge + 2Li \longrightarrow (PhCH_2)_3GeLi + PhCH_2Li$$

$$(PhCH_2)_3GeLi + H_2O \longrightarrow (PhCH_2)_3GeH + LiOH$$
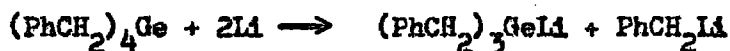
A number of simple reactions of tribenzylgermyl-lithium prepared in this way were examined but often considerable difficulty was ex-perienced in isolating pure products in high yield. Closer examination of the hydrolysis products revealed the presence of a small amount of dibenzylgermane, indicating that two benzyl groups can be cleaved from tetrabenzylgermane by lithium.

$$(PhCH_2)_4Ge \xrightarrow[0^\circ]{Li, C_4H_{10}O_2} (PhCH_2)_3GeLi + (PhCH_2)_2GeLi_2 + PhCH_2Li$$

$$(PhCH_2)_3GeLi \xrightarrow{H_2O} (PhCH_2)_3GeH \qquad (PhCH_2)_2GeLi_2 \xrightarrow{H_2O} (PhCH_2)_2GeH_2$$
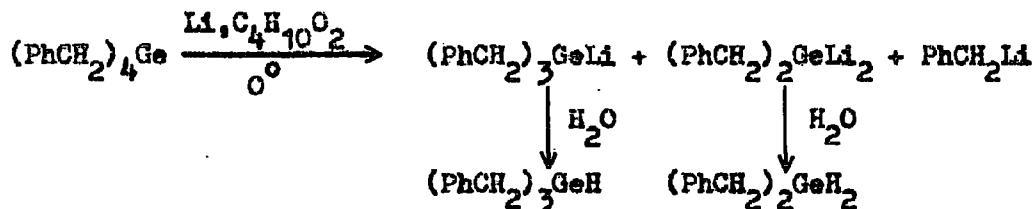
The dilithium compound may also be produced by cleavage of a second benzyl group by benzyl-lithium, which is also present in the reaction mixture. In support of this, bibenzyl is among the reaction products after hydrolysis. Moreover, the dilithio derivative is certainly formed in the reaction between tribenzylgermane and benzyl-lithium in a tetra-hydrofuran-ether solution, as dibenzyldimethylgermane is among the products isolated after treatment with methyl iodide.

$$(PhCH_2)_3GeH + PhCH_2Li \longrightarrow (PhCH_2)_4Ge + (PhCH_2)_3GeLi + (PhCH_2)_2GeLi_2 + LiH$$

$$(PhCH_2)_3GeLi + (PhCH_2)_2GeLi_2 \xrightarrow{MeI} (PhCH_2)_3GeMe + (PhCH_2)_2GeMe_2$$
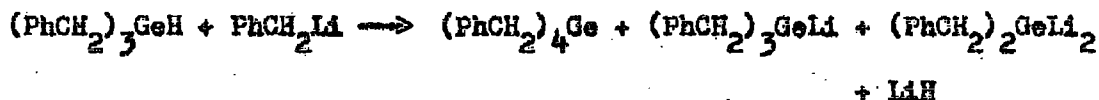
Apart from indirect evidence based on colour changes occurring when tetraphenylgermane or octaphenylcyclotetragermane react with sodium in liquid ammonia (5, 42), this is the first clear evidence for the existence of a di-alkali-metal derivative of an organogermane. There is no evidence that the reaction between tetraphenylgermane and lithium proceeds beyond Ph_3GeLi. This difference between tetrabenzylgermane and tetraphenylgermane is presumably a reflection of the weaker Ge-C bond strength in the benzyl derivative, since the solvated anion R_2Ge^{2-} would be more stable with R = phenyl, where delocalisation of charge is possible.

The cleavage of tetrabenzylgermane by lithium is strikingly de-
pendent on experimental conditions. The best results were obtained by
using a large excess of lithium (800%) and mixing the reactants to a
paste with the minimum of solvent. The reactions began after an induction
period of about 10 minutes. As with the cleavage of phenyl derivatives,
this time is rather erratic, varying from about 1 minute to several
hours. The highest yields of tribenzylgermyl-lithium (75%) were obtained
after about 1 hour at room temperature. After 48 hours at 0° no tetra-
benzylgermane remained, but appreciable conversion to the dilithium
compound occurred. Most reaction conditions gave a mixture of $(PhCH_2)_4Ge$,
$(PhCH_2)_3GeLi$ and $(PhCH_2)_2GeLi_2$.

Neither lithio derivative appears to react with the solvent during
24 hours at 0°. At reflux temperature, however, and with an excess of
lithium present, a progressive series of reactions takes place involving
demethylation of the ether followed by cleavage of another benzyl group
by lithium, giving, finally, benzyltrimethylgermane.

$$(PhCH_2)_3GeLi \xrightarrow{C_4H_{10}O_2} (PhCH_2)_3GeMe \xrightarrow{Li} (PhCH_2)_2GeMe \cdot Li \xrightarrow{C_4H_{10}O_2}$$

$$(PhCH_2)_2GeMe_2 \xrightarrow{Li} PhCH_2GeMe_2 \cdot Li \xrightarrow{C_4H_{10}O_2} PhCH_2GeMe_3$$
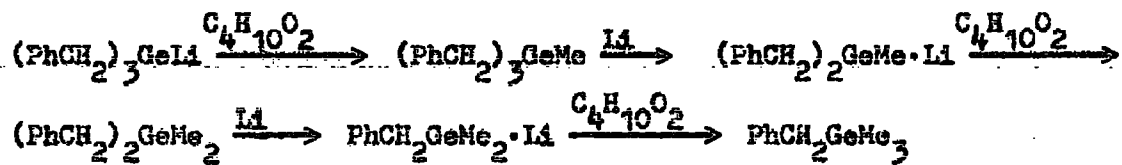
Tribenzylmethylgermane was isolated after refluxing for 4 hours, whilst
dibenzyldimethylgermane and benzyltrimethylgermane were present when the
reaction was continued for 19 hours. Benzyltrimethylgermane evidently
resists cleavage by lithium under these conditions, since no tetramethyl-
germane was produced after 6 days at reflux. Also, the germyl-lithium
intermediates appear to have a short life-time under these conditions,

as no germanium hydrides were detected after hydrolysis, indicating a negligible concentration of germyl-lithium compounds.

The fate of the benzyl-lithium produced in these cleavage reactions was also determined. Reaction with solvent occurs to give toluene (by hydrogen-metal exchange) and ethylbenzene (by methyl group abstraction). The metallated solvent reacts further by β-elimination of lithium methoxide to give methyl vinyl ether.

$$\text{PhCH}_2\text{Li} + \text{MeOCH}_2\text{CH}_2\text{OMe} \overset{90\%}{\underset{10\%}{\diagup\!\!\!\diagdown}} \begin{array}{l} \text{PhCH}_3 + \text{MeOCH(Li)CH}_2\text{OMe} \longrightarrow \text{LiOMe} + \text{CH}_2\text{:CHOMe} \\[2ex] \text{PhCH}_2\text{CH}_3 + \text{LiOCH}_2\text{CH}_2\text{OMe} \end{array}$$
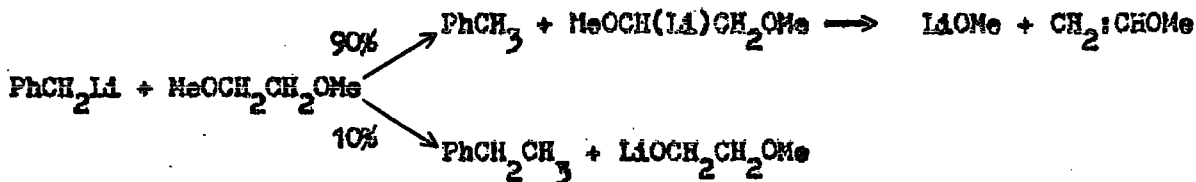
These reactions must be rapid even at 0°, since in many cases no derivatives of benzyl-lithium were detected.

The reactions of tribenzylgermyl-lithium are very similar to those of triphenylgermyl-lithium and normal substitution usually occurs. Thus deuterolysis produces tribenzyldeuterogermane; methyl iodide and ethyl bromide give tribenzylmethylgermane and tribenzylethylgermane respectively; trimethylchlorsilane leads to the formation of tribenzylgermyltrimethyl-silane. The reaction with trichlorsilane produced only an ill-defined, non-crystalline powder, however. This may have been due to the presence of the dilithio compound in the reaction mixture, leading to polymeric material. Halogen-metal exchange was not involved, as no hexabenzyl-digermane was given.

The products of the reaction between tribenzylgermyl-lithium and triethylbromgermane depended on the method of reaction. When the tri-benzylgermyl-lithium in 1,2-dimethoxyethane was added to pure triethyl-

brongermane, extensive halogen-metal exchange occurred and only the symmetrical digermanes, $(PhCH_2)_6Ge_2$ and Et_6Ge_2, were isolated. Reversing the addition, however, and adding the bromtriethylgermane in diethyl ether solution to the monoglyme solution of tribenzylgermyl-lithium, the unsymmetrical digermane, $(PhCH_2)_3Ge \cdot GeEt_3$, was produced, and there was no evidence for halogen-metal exchange.

Carbonation did not give a stable acid product. The products isolated from this reaction show that the tribenzylgermylcarboxylic acid formed decarbonylated during the working up process, even at room temperature, to give tribenzylgermanol. This immediately esterifies with either tribenzylgermylcarboxylic acid or phenylacetic acid (from $PhCH_2Li + CO_2$).

$$(PhCH_2)_3GeLi \xrightarrow{CO_2} (PhCH_2)_3GeCOOLi \xrightarrow{acid} (PhCH_2)_3GeCOOH$$

$$(PhCH_2)_3GeCOOH \longrightarrow (PhCH_2)_3GeOH$$

$$\xrightarrow{(PhCH_2)_3GeCOOH} (PhCH_2)_3GeOOCGe(CH_2Ph)_3$$

$$\xrightarrow[PhCH_2COOH]{} (PhCH_2)_3GeOOCCH_2Ph$$
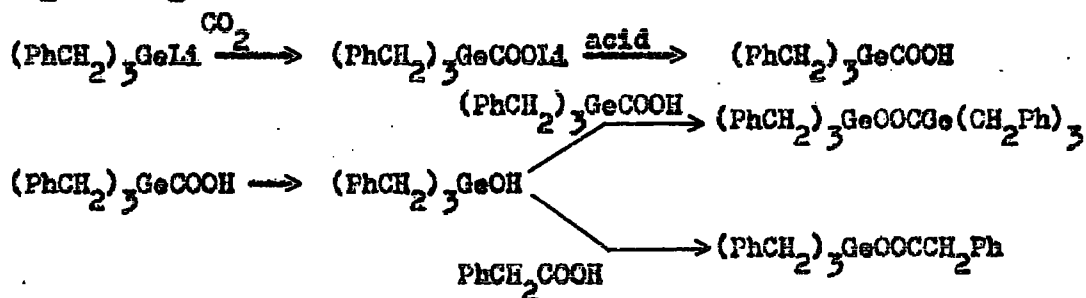
The reactions of tribenzylgermyl-lithium are summarised in the following table.

Reactions of tribenzylgermyl-lithium.

Reactant	Products	M.p. or b.p.
H_2O	$(PhCH_2)_3GeH$	$80-82^\circ$
D_2O	$(PhCH_2)_3GeD$	81°
MeI	$(PhCH_2)_3GeMe$	$82-85^\circ$
EtBr	$(PhCH_2)_3GeEt$	$34-35^\circ$
Me_3SiCl	$(PhCH_2)_3GeSiMe_3$	$63.5-64.5^\circ$
Et_3GeBr	$(PhCH_2)_6Ge_2 + Et_6Ge_2$	
	or $(PhCH_2)_3Ge \cdot GeEt_3$	$220-230^\circ/10^{-3}$ mm.
Cl_3SiH	Polymeric material	$35-45^\circ$
CO_2	$(PhCH_2)_3GeO \cdot CO \cdot CH_2Ph +$	$146-148^\circ$
	$(PhCH_2)_3GeO \cdot CO \cdot Ge(CH_2Ph)_3$	$77-80^\circ$

The reactions of tribenzylgermane and of hexabenzyldigermane with lithium in ethylene glycol dimethyl ether solution were examined as possible alternative routes to tribenzylgermyl-lithium, but both methods proved as complex as that already described. Tribenzylgermane and lithium react at 0° to give a black solution which, after adding excess methyl iodide, gives dibenzyldimethylgermane, $(PhCH_2)_2GeMe_2$, tribenzyl-methylgermane, $(PhCH_2)_3GeMe$, and, in small yield, a product slightly more volatile than dibenzyldimethylgermane which shows a strong Ge-H absorption at 2034 cm.$^{-1}$ and is probably dibenzylmethylgermane, $(PhCH_2)_2Ge(Me)H$. Thus not only are Ge-H and Ge-CH_2Ph bonds of comparable reactivity towards lithium, but some preferential cleavage of germanium-benzyl bonds also occurs. With hexabenzyldigermane the reaction was slow and incomplete

(50%) after 22 hours at 0°. The main product, $(PhCH_2)_3GeLi$, resulted from the cleavage of the germanium-germanium bond, but some cleavage of $Ge-CH_2Ph$ bonds was again indicated since toluene was isolated after hydrolysis.

The formation of R_3GeLi compounds by hydrogen-metal exchange with organo-lithium reagents has been investigated in a number of cases with varying results. It has been reported (35) that triphenylgermane is metallated almost quantitatively by n-butyl-lithium:

$$Ph_3GeH + BuLi \longrightarrow Ph_3GeLi + C_4H_{10}$$

Tristriphenylgermylgermane, $(Ph_3Ge)_3GeH$, and α-naphthylphenylmethylgermane also give good yields of the germyl-lithium compound with butyl-lithium in ether (43, 113). Triethylgermane is only partly metallated (10%) by butyl-lithium, however, and some alkylation has been reported in the reaction between triphenylgermane and phenyl-lithium or methyl-lithium (92, 35). Also, under more drastic conditions triphenylgermane and phenyl-lithium give tetraphenylgermane or hexaphenyldigermane, apparently depending on which reagent is present in excess (34). In the analagous reactions of silicon and tin compounds, alkylation takes place almost exclusively:

$$R_3MH + R'Li \longrightarrow R_3MR' + LiH. \quad (191, 192, 193).$$

Tribenzylgermane and butyl-lithium showed the same lack of selectivity already encountered in the cleavage reactions involving lithium metal. Alkylation, hydrogen-metal exchange, cleavage of $Ge-CH_2Ph$ bonds and coupling to give hexabenzyldigermane were all observed. The products isolated (after reaction with methyl iodide) depended partly on whether an

excess of butyl-lithium was present and on the temperature of reaction (room temperature or 0°).

Direct hydrogen-metal exchange accounts for the isolation of tribenzylmethylgermane and hexabenzyldigermane:

$$(PhCH_2)_3GeH + BuLi \longrightarrow (PhCH_2)_3GeLi \begin{cases} \xrightarrow{MeI} (PhCH_2)_3GeMe \\ \xrightarrow{(PhCH_2)_3GeH} (PhCH_2)_6Ge_2 + LiH \end{cases}$$
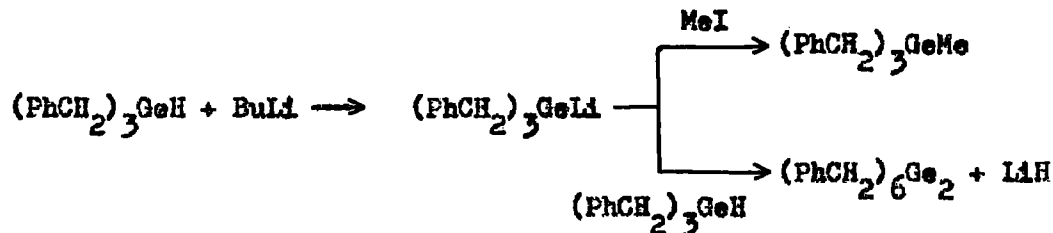
Formation of the other products may be interpreted in terms of nucleophilic attack by Bu^- on the polar hydride $(PhCH_2)_3\overset{\delta+}{Ge}-\overset{\delta-}{H}$ with displacement of either H^- or $PhCH_2^-$. Displacement of H^- gives tribenzylbutylgermane:

$$(PhCH_2)_3GeH + BuLi \longrightarrow (PhCH_2)_3GeBu + LiH$$

Displacement of $PhCH_2^=$ leads to the formation of dibenzylbutylgermane and benzyl-lithium, which can react with more tribenzylgermane to produce tetrabenzylgermane.

$$(PhCH_2)_3GeH + BuLi \longrightarrow (PhCH_2)_2Ge(Bu)H + PhCH_2Li$$
$$(PhCH_2)_3GeH + PhCH_2Li \longrightarrow (PhCH_2)_4Ge + LiH$$
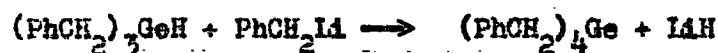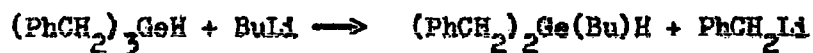
An independent experiment confirmed that tribenzylgermane and benzyl-lithium give, among other products, tetrabenzylgermane. Dibenzylbutylgermane still contains the Ge-H bond and is susceptible to further attack in the presence of excess butyl-lithium, giving dibenzyldibutylgermane and benzyldibutylgermane.

$$(PhCH_2)_2Ge(Bu)H + BuLi \begin{cases} \nearrow (PhCH_2)_2GeBu_2 + LiH \\ \searrow PhCH_2Ge(Bu)_2H \end{cases}$$
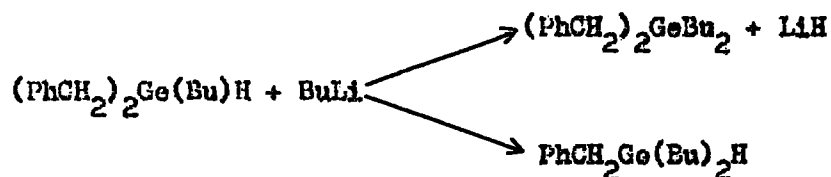
Similarly, benzyldibutylgermane can react further, giving, finally, benzyltributylgermane and tetrabutylgermane.

$$PhCH_2Ge(Bu_2)H + BuLi \left\langle \begin{array}{l} PhCH_2 \cdot GeBu_3 \\ Bu_3GeH \xrightarrow{BuLi} Bu_4Ge + LiH \end{array} \right.$$
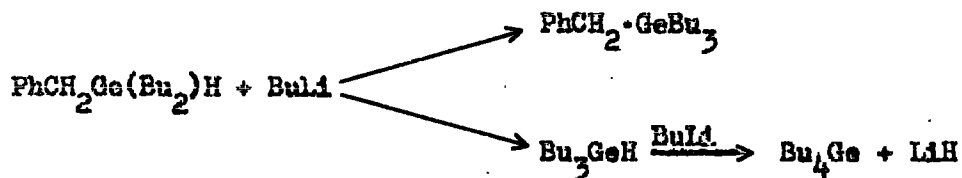
Hexabenzyldigermane, tetrabenzylgermane and the benzylbutylgermanes, $PhCH_2GeBu_3$ and $(PhCH_2)_2GeBu_2$, are unreactive towards butyl-lithium under these conditions. This may be because they lack the polar character of the hydrides, but they may also be subject to a large steric factor, as reported by Eaborn and his co-workers for nucleophilic attack by OH^- on benzyltrimethylgermane and related compounds (194).

The reaction between diphenylgermane, Ph_2GeH_2, and butyl-lithium was also examined with a view to obtaining further evidence for a dilithio derivative and to examine the selectivity of the reaction. With two equivalents of butyl-lithium and subsequent reaction with ethyl bromide there was evidence for the formation of Ph_2GeLi_2 (25) and a novel binuclear dilithium compound, $Ph_2Ge(Li)Ge(Li)Ph_2$. Cleavage of phenyl groups was not observed but otherwise the behaviour was similar to the reactions with tribenzylgermane. Metallation, alkylation and coupling reactions all take place.

$$Ph_2GeH_2 + 2BuLi$$

$$\downarrow$$

$$Ph_2GeLi_2 + Ph_2Ge(Bu)Li + Ph_2GeBu_2 + Ph_2Ge(Li)Ge(Li)Ph_2$$

$$\downarrow EtBr$$

$$Ph_2GeEt_2 + Ph_2GeBuEt + Ph_2GeBu_2 + Ph_2EtGe\cdot GeEtPh_2$$

| 2% | 20% | 12% | 28% |
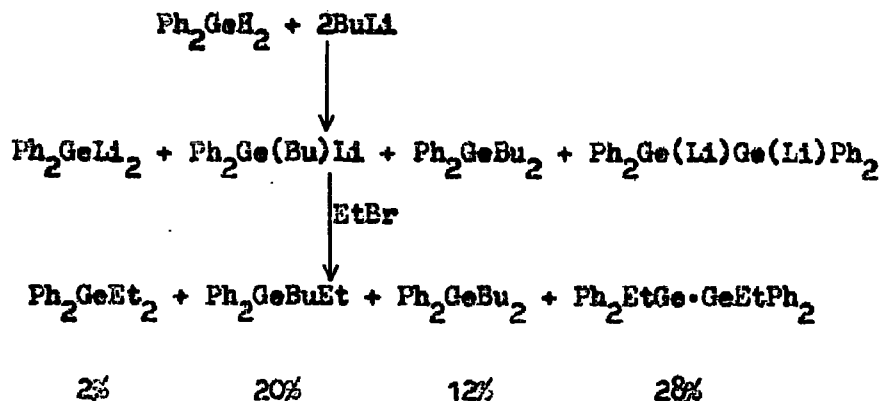
The fact that triphenylgermane resembles triphenylmethane by metallating on reacting with butyl-lithium, whereas triphenylsilane and triphenylstannane alkylate, has been cited as chemical evidence for an alternation in the electronegativity values of the group IVb elements (195). Although some disagreement exists over the actual values (2) such an alternation is consistent with chemical behaviour. The reactions with butyl-lithium might then be explained by changes in the polarity of the metal-hydrogen bond:

$$\overset{\delta+\,\delta-}{Ph_3Si\text{-}H} + BuLi \longrightarrow Ph_3SiBu + LiH$$

$$\overset{\delta-\,\delta+}{Ph_3Ge\text{-}H} + BuLi \longrightarrow Ph_3GeLi + C_4H_{10}$$
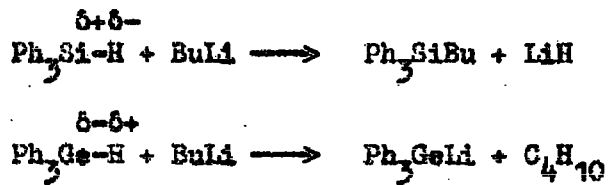
With triphenylgermane, however, changes in the experimental conditions or the use of different organo-lithium reagents leads to some alkylation. In the present work for example one reaction between butyl-lithium and triphenylgermane gave a small amount of triphenylbutylgermane, contrary to earlier reports (35). This probably indicates that the polar nature of the Ge-H bond is marginal and it would therefore be expected that in other germanium hydrides the nature of the groups attached to the

central germanium atom will have a noticeable effect on the course of this reaction. Electronegative groups attached to germanium should enhance the metallation reaction, and α-naphthylphenylmethylgermane and tristriphenylgermylgermane both react mainly by hydrogen-metal exchange (Chatt and Williams (196) have shown that the Group R$_3$Ge is capable of resonance and acts as an electron withdrawing group). Also, this work has established that the first hydrogen in diphenylgermane reacts with butyl-lithium largely by hydrogen-metal exchange. Conversely, ethyl groups can not accept a negative charge like phenyl groups, and triethylgermane is metallated only slightly (10%). Tribenzylgermane falls into the same category.

It also seems probable that alkylation of germanium hydrides will take place via attack of Bu⁻ at the germanium atom, whereas metallation will proceed via attack of Bu⁻ at the hydrogen. It is of interest that the metallation of α-naphthylphenylmethylgermane takes place with retention of configuration.

Attempts to cleave a germanium-benzyl bond by hydrogen failed. Hydrogen produced by the hydrolysis of lithium in the presence of tetra-benzylgermane or tribenzylgermane gave no reaction. Also, no reduction was observed when tetrabenzylgermane was shaken with hydrogen at atmospheric pressure in the presence of Adam's catalyst.

Triphenylgermane is known to disproportionate on heating (34): 2Ph$_3$GeH $\longrightarrow$ Ph$_2$GeH$_2$ + Ph$_4$Ge, and it seemed possible that this type of reaction could account for the production of dibenzylgermane from the reaction between tetrabenzylgermane and lithium, as the products were

isolated by vacuum distillation. Tribenzylgermane is, however, stable in vacuum at 240°, and only slight decomposition occurs at 370°. Above 390° decomposition is extensive, giving toluene, bibenzyl, trans-stilbene, a trace of a permanent gas (probably hydrogen), and a brown polymer having the approximate composition $Ge_3(CH_2Ph)_2$. No dibenzyl-germane was formed, and no germanium metal was deposited.

It was concluded that these reactions of the benzylgermanes are considerably more complex than those of the phenyl analogues owing to the similar reactivity of Ge-H and Ge-CH$_2$Ph towards nucleophilic attack, and the ease with which more than one benzyl group may be cleaved from tetrabenzylgermane. Although the reactions of tribenzylgermyl-lithium are very similar to those of triphenylgermyl-lithium, the latter reagent is more readily prepared in high yield. It also appears that the metallation reaction of triphenylgermane by butyl-lithium is not typical of all organogermanium hydrides.

PART B.   Triphenylgermylplatinum Complexes.

Organogermanium compounds in which the germanium atom is bonded to a non-transition metal have been known for many years (1,2). Among the group IVb elements compounds of the type $R_3Ge-MR'_3$ (where M = Si, Ge, Sn or Pb) are common, and compounds containing more than one metal-metal bond, including cyclic compounds, are known. The reactions of the hexa-organo-dimetal compounds are generally those expected for metals in oxidation level 3 and coordination number 4: the most reactive centre being the metal-metal bond. This can be cleaved by nucleophilic or electrophilic attack under mild conditions. Secondary reactions involving cleavage of metal-carbon bonds also occur, especially with lead compounds, but these are readily avoided with germanium.

Compounds containing germanium and boron are known (176, 177) and Russian workers are at present examining a series of compounds containing germanium bonded to group II elements (178, 179, 180). Little information is available concerning germanium-transition metal compounds. Germanium-manganese and germanium-iron compounds have been isolated (181, 182) but few reactions were reported. A more detailed examination of triphenyl-germyl complexes of copper, silver and gold has been made (119), but although quite a wide variety of compounds containing metal-metal bonds is known the general principles involved in the production of stable compounds have received little study (156).

This work is concerned with the formation of germanium-platinum complexes, $(R_3P)_2Pt(GePh_3)_2$, and an examination of a wide range of reactions of these compounds with a view to increasing knowledge of the stability

and reactivity of metal-metal bonds. Platinum was chosen for this initial study because of the high stability of platinum-carbon compounds and the extensive information which is available for comparison purposes, largely as a result of studies by Chatt and Shaw (123, 149). During the course of this work several publications on platinum-tin (169, 170, 171, 197, 198) and platinum-silicon systems (199) have appeared and these also afford some interesting comparisons.

Triphenylgermyl-lithium reacts readily with cis and trans $(Et_3P)_2PtCl_2$ and with trans $(n-Pr_3P)_2PtCl_2$ to give the bisgermylplatinum complexes, $(R_3P)_2Pt(GePh_3)_2$, in good yield.

$$(R_3P)_2PtCl_2 + 2Ph_3GeLi \longrightarrow (R_3P)_2Pt(GePh_3)_2 + 2LiCl$$
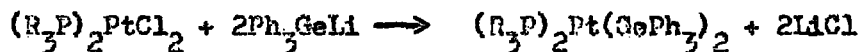
Both these yellow crystalline compounds decompose before melting at about 150°. They are stable even in solution to air, water, ethanol and ethanolic potassium hydroxide. The tri-n-propylphosphine complex is much more soluble in organic solvents than the triethylphosphine complex, and crystallisation from benzene gives the solvated complex, $(n-Pr_3P)_2Pt-(GePh_3)_2 \cdot C_6H_6$.

The preparation from trans $(Et_3P)_2PtCl_2$ gave a higher yield than that from the cis material, and as both products are largely identical, this suggests that the germyl-platinum complexes are produced in the trans form. Solutions of the complexes in different solvents vary greatly in the intensity of the yellow colour, however, and this is probably due to cis-trans interconversion. Dipole moment measurements on the bistri-n-propylphosphinebistriphenylgermylplatinum(II) complex in benzene solution gave a value of 2·4D, indicating that the trans isomer predominates.

The reaction between triphenylgermyl-lithium and the iodoplatinum complex, trans $(Et_3P)_2PtI_2$, was more complicated than with the chlorides. It was hoped that reactions with one equivalent of Ph_3GeLi would produce the complex, $(Et_3P)_2Pt(I)GePh_3$, but the main products were the bisgermyl compound, $(Et_3P)_2Pt(GePh_3)_2$, and unreacted starting material. Hexaphenyl-digermane, the hydrido complex trans $(Et_3P)_2Pt(H)I$, and, by crystallisation from ethanol, the ethoxyplatinum complex $(Et_3P)_2Pt(OEt)GePh_3$ were also given. Isolation of the hydridoplatinum halide is difficult to account for other than via a lithioplatinum intermediate formed by halogen-metal exchange.

$$(Et_3P)_2PtI_2 + Ph_3GeLi \longrightarrow (Et_3P)_2Pt(Li)I + Ph_3GeI$$

$$Ph_3GeI + Ph_3GeLi \longrightarrow Ph_6Ge_2$$

$$(Et_3P)_2Pt(Li)I + H_2O \longrightarrow (Et_3P)_2Pt(H)I.$$
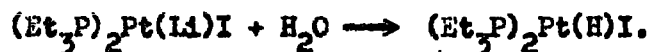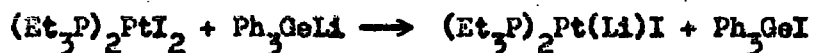
These exchange reactions become increasingly important when iodides rather than other halides are used. For example, during the work described in Part A of this thesis it was noted that the reaction between $GeCl_4$ and $PhCH_2MgCl$ gave only normal substitution, but when GeI_4 was employed some halogen-metal exchange occurred.

When two equivalents of triphenylgermyl-lithium were used, none of the hydridoiodide complex was produced, but instead the hydridogermyl complex bistriethylphosphinetriphenylgermylhydridoplatinum(II), $(Et_3P)_2Pt(H)GePh_3$, was isolated as colourless crystals. Also, treatment with ethanol did not give the ethoxy complex. This suggests that the ethoxy compound was originally produced from an intermediate iodo-

platinum complex $(Et_3P)_2Pt(I)GePh_3$, which reacts with ethanol probably after hydrolysis:

$$(Et_3P)_2Pt(I)GePh_3 \xrightarrow[\text{LiOH}]{\text{H}_2\text{O}} (Et_3P)_2Pt(OH)GePh_3 \xrightarrow{\text{EtOH}} (Et_3P)_2Pt(OEt)GePh_3$$

When sufficient Ph_3GeLi is present, however, this reacts with the intermediate by two paths, leaving none to form the ethoxide.

$$(Et_3P)_2Pt(I)GePh_3 + Ph_3GeLi \longrightarrow (Et_3P)_2Pt(Li)GePh_3 + (Et_3P)_2Pt(GePh_3)_2.$$

$$(Et_3P)_2Pt(Li)GePh_3 + H_2O \longrightarrow (Et_3P)_2Pt(H)GePh_3$$
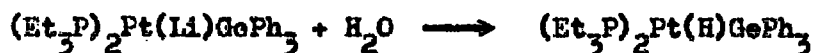
Reactions involving slightly less than two equivalents of triphenylgermyl-lithium gave the complete range of products, including the two hydrido-platinum complexes and, after treatment with ethanol, the ethoxyplatinum complex.

Lithioplatinum complexes have not previously been proposed, but this work indicates that they are readily formed as reaction inter-mediates, and that they survive in ether solution until hydrolysis. Evidence for the formation of related platinum-Grignard reagents is presented later.

Some free tertiary phosphine was liberated in all these reactions involving triphenylgermyl-lithium, but in no case was a phosphine-deficient platinum complex detected. The presence of the phosphine would allow the platinum halides to isomerise, which means that it is not possible to determine which species are responsible for the pre-ceeding reactions. The reactions with the iodides all gave a tarry residue, and treatment of this by sublimation at 100° <u>in vacuo</u> left residues containing Ph_4Ge and $(Et_3P)_2Pt(I)Ph$, strongly suggestive of a

radical decomposition process.

The reaction between triphenylgermyl-lithium and cis $(Ph_3P)_2PtBr_2$ failed to give any identifiable material apart from lithium bromide. Only an inhomogeneous powder or a red oil could be extracted from the reaction mixture. Halogen-metal exchange may again have been responsible for the complications, but steric reasons could also be involved.

An attempt to prepare $(Et_3P)_2Pt(GePh_3)_2$ from cis $(Et_3P)_2PtBr_2$ and triphenylgermane in the presence of triethylamine was unsuccessful; in refluxing benzene no reaction occurred. Also, no reaction took place between trans $(Et_3P)_2PtBr_2$ and Ph_3GeH in solution. When these compounds were sublimed together, however, extensive halogen-hydrogen exchange took place, and although no evidence for the formation of a platinum-germanium bond was obtained, triphenylbromgermane and 3 volatile platinum hydrides were produced. These had $v(Pt-H)$ at 2212, 2183 and 2004 cm.$^{-1}$ One of these (2183 cm.$^{-1}$) is close to the value expected for trans $(Et_3P)_2Pt(H)Br$ (140). A recent paper by Chalk and Harrod describes similar reactions using trialkylsilanes, and these authors propose a mechanism involving initial oxidation to a platinum(IV) intermediate (199). Only one platinum hydride was produced however.

$$\text{cis } (R_3P)_2PtCl_2 + R_3'SiH \longrightarrow \text{trans } (R_3P)_2Pt(H)Cl + R_3'SiCl$$
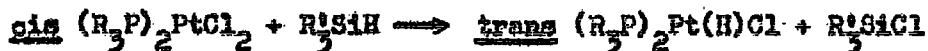
It is also of interest that this reaction did not proceed simply with the triphenylphosphine complex, a red polymer having approximate composition $Pt_2(Ph_3P)_4Cl$ being produced.

Although many reactions of the bisgermylplatinum(II) complexes

probably proceed via oxidation to platinum(IV) complexes, none of these intermediates were isolated. Also, the reaction between triphenylgermyl-lithium and trimethyliodoplatinum(IV) failed to give a stable germyl-platinum(IV) compound. The only isolable product was triphenylmethyl-germane, together with insoluble black pyrophoric material which showed no structure in the infrared.

Both the bisgermylplatinum complexes showed considerable thermal stability. The tri-n-propylphosphine compound began to decompose at 120° and the triethylphosphine compound at 155°. Pyrolysis of both complexes _in vacuo_, which was expected to follow a simple course in-volving cleavage of the metal-metal bonds to give $2R_3P + Pt + Ph_6Ge_2$, was more complicated and involved cleavage of germanium-carbon and phosphorus-carbon bonds as well. At 220° the triethylphosphine complex gave Ph_6Ge_2, Ph_4Ge, Et_3P, benzene and ethylene, leaving a black metallic-looking residue which gave a clear, brown, air-stable solution in benzene. Prolonged heating of this material _in vacuo_ resulted in further loss of Ph_4Ge and Ph_6Ge_2 when the product was no longer soluble but still retained some 20% carbon as both phenyl and ethyl groups. X-ray powder photographs showed that this residue was amorphous. $(n-Pr_3P)_2Pt(GePh_3)_2$ behaved similarly on pyrolysis, giving propylene in place of ethylene. Further evidence that the phosphine and germyl ligands are strongly bonded may be provided in that refluxing solutions with triphenylphosphine did not lead to any ligand exchange, although other factors may be involved here. Phenylacetylene and diazomethane also failed to react with the complexes.

The reactions with halogens, halogen acids, and certain organic and inorganic halides cause cleavage of the metal-metal bonds in the $(R_3P)_2Pt(GePh_3)_2$ complexes, often with interesting complications. Carbon tetrachloride is sufficiently reactive to cleave the germanium-platinum bonds giving triphenylchlorgermane and $(R_3P)_2PtCl_2$. The mechanism of this reaction was not determined, but it is known that CCl_4 reacts similarly with many other compounds, including $Ph_3PAu-GePh_3$ (200) and trans $(Et_3P)_2Pt(H)Cl$ (140). Also, during the present work it was noticed that CCl_4 slowly cleaved the Ge-H bonds in triphenylgermane and tribenzylgermane.

Iodine reacts with $(Et_3P)_2Pt(GePh_3)_2$ rapidly at room temperature, and even with equimolar ratios gives $(Et_3P)_2PtI_2$ and Ph_3GeI rather than the intermediate complex, $(Et_3P)_2Pt(I)GePh_3$.

$$(Et_3P)_2Pt(GePh_3)_2 + 2I_2 \longrightarrow (Et_3P)_2PtI_2 + 2Ph_3GeI.$$
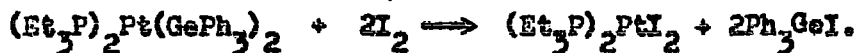
1,2-dibromethane reacts in a very characteristic manner, cleaving the Ge-Pt bonds and producing ethylene.

$$(R_3P)_2Pt(GePh_3)_2 + 2C_2H_4Br_2 \longrightarrow (R_3P)_2PtBr_2 + 2Ph_3GeBr + 2C_2H_4$$

The reaction is slower than with germanium-gold compounds (119), but was quantitative over 13 days at room temperature for the tri-n-propylphosphine complex and showed a definite decrease in rate after 1 mol. had reacted. The reaction between 1,2-dibromethane and $Ph_3PAu-GePh_3$ is thought to proceed via a 4-centre reaction intermediate (183) and it is likely that the Ge-Pt compounds behave similarly (although an alternative mechanism via oxidation to a platinum(IV) complex is possible in this

case). Bistriethylgermylmercury appears to react slightly differently to the gold and platinum compounds at first sight:

$$(Et_3Ge)_2Hg + C_2H_4Br_2 \longrightarrow 2Et_3GeBr + Hg + C_2H_4 \quad (201).$$

However, this reaction probably proceeds via cleavage of one Ge-Hg bond in the usual way, followed by loss of mercury from $Et_3GeHgBr$. This reaction with 1,2-dibromethane appears to be a useful diagnostic test for germanium-transition metal bonds, and may even be of analytical value when the ethylene produced can be accurately measured.

Hydrogen chloride also cleaves the Ge-Pt bonds, but the products isolated suggest that the initial step is addition of the reagent to give an octahedral platinum(IV) complex, $(R_3P)_2Pt(H)(Cl)(GePh_3)_2$. A direct cleavage reaction may compete with this mechanism, however.

$$(R_3P)_2Pt(GePh_3)_2 + HCl \nearrow Ph_3GeH + (R_3P)_2PtCl_2$$
$$\searrow (R_3P)_2Pt(H)(Cl)(GePh_3)_2 \longrightarrow Ph_3GeCl + (R_3P)_2Pt(H)GePh_3$$

$$(R_3P)_2Pt(H)GePh_3 + HCl \longrightarrow (R_3P)_2Pt(H)Cl + Ph_3GeH.$$
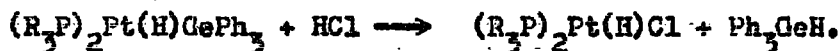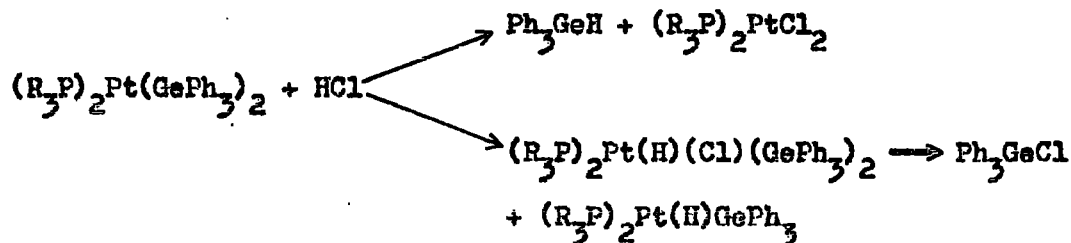
Moderately stable platinum(IV) hydridohalides have been described (e.g. $(Et_3P)_2Pt(H)_2Cl_2$ (140)) and the reaction between trialkylsilanes and cis $(R_3P)_2PtCl_2$ is reported to proceed via the intermediate $(R_3P)_2Pt(H)-(Cl)_2SiR_3'$ which then loses $R_3'SiCl$ (199). Under similar conditions, however, neither Ph_3GeH nor Ph_3GeBr showed any evidence of reaction with the germylplatinum complexes.

Methyl iodide similarly cleaves the Ge-Pt bonds, although this

reagent does not react with germanium-gold compounds (119). In a sealed tube at 110° both triphenyliodogermane and triphenylmethylgermane were given and it is probable that this reaction also proceeds via a Pt(IV) intermediate. The iodoplatinum complex $(R_3P)_2PtI_2$ was also given, and although no methylplatinum compounds were isolated, the presence of ethane indicated that they had probably been present but had decomposed. Methane was also produced, suggesting that radical intermediates were also involved. The binuclear complex, trans $(R_3P)_2Pt_2I_4$, was given in small yield but other products were not identified. Chatt has fully characterised a number of platinum(IV) compounds formed by addition of methyl iodide to platinum(II) complexes, and has shown that with prolonged heating the complex $(R_3P)_2Pt(Me)_2I_2$ decomposes to give ethane and $(R_3P)_2PtI_2$ (123).

Chatt (123) has also shown that dimethylplatinum(II) complexes react with magnesium iodide in what are probably a series of equilibrium reactions, giving $(R_3P)_2PtI_2$, $(R_3P)_2Pt(Me)I$ and MeMgI, and has produced evidence that the reactions proceed via platinum(IV) intermediates. Cleavage of the germylplatinum complexes by magnesium iodide produced a greater range of products than the methylplatinum analogues, and these provide evidence that platinum-Grignard reagents are formed, and exist in solution up to a hydrolysis stage. The Ge-Pt bond is cleaved to give both combinations of products: GeI + Pt(MgI) and Ge(MgI) + PtI. These may be produced via a platinum(IV) intermediate, $(R_3P)_2Pt(I)(MgI)(GePh_3)_2$, which then degrades to platinum(II) products. A maximum of 8 stable products after hydrolysis can result by this route (or 13, taking cis

and _trans_ isomers into account). Five products were isolated, and infra-
red evidence for two platinum hydrides was obtained.

Triphenylgermane and the iodoplatinum complexes, $(n\text{-}Pr_3P)_2PtI_2$
and $(n\text{-}Pr_3P)_2Pt(I)GePh_3$ were all isolated and probably resulted from
the following reactions:

$$(n\text{-}Pr_3P)_2Pt(GePh_3)_2 + MgI_2 \longrightarrow (n\text{-}Pr_3P)_2Pt(I)GePh_3 + Ph_3GeMgI$$

$$(n\text{-}Pr_3P)_2Pt(I)GePh_3 + MgI_2 \longrightarrow (n\text{-}Pr_3P)_2PtI_2 + Ph_3GeMgI$$

$$Ph_3GeMgI + H_2O \longrightarrow Ph_3GeH$$
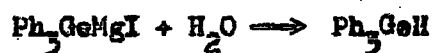
The ready hydrolysis of $(Et_3P)_2Pt(I)GePh_3$ discussed earlier is probably
due to the higher pH of that system. Alternately, the two iodogermyl-
platinum complexes may be different isomers. The other possible products
may be produced by the following reactions:

$$(n\text{-}Pr_3P)_2Pt(GePh_3)_2 + MgI_2 \longrightarrow (n\text{-}Pr_3P)_2Pt(MgI)GePh_3 + Ph_3GeI$$

$$(n\text{-}Pr_3P)_2Pt(I)GePh_3 + MgI_2 \longrightarrow (n\text{-}Pr_3P)_2Pt(I)MgI + Ph_3GeI$$

$$(n\text{-}Pr_3P)_2Pt(MgI)GePh_3 + MgI_2 \begin{cases} \longrightarrow (n\text{-}Pr_3P)_2Pt(I)MgI + Ph_3GeMgI \\ \longrightarrow (n\text{-}Pr_3P)_2Pt(MgI)_2 + Ph_3GeI \end{cases}$$

$$(n\text{-}Pr_3P)_2Pt(MgI)GePh_3 + H_2O \longrightarrow (n\text{-}Pr_3P)_2Pt(H)GePh_3$$

$$(n\text{-}Pr_3P)_2Pt(MgI)I + H_2O \longrightarrow (n\text{-}Pr_3P)_2Pt(H)I$$

$$(n\text{-}Pr_3P)_2Pt(MgI)_2 + H_2O \longrightarrow (n\text{-}Pr_3P)_2PtH_2$$

$$Ph_3GeMgI + Ph_3GeI \longrightarrow Ph_6Ge_2$$
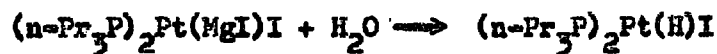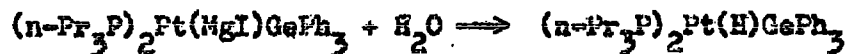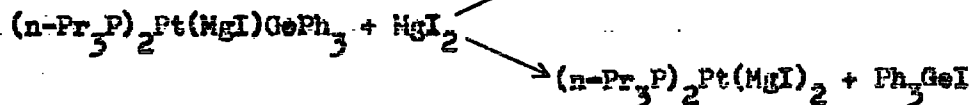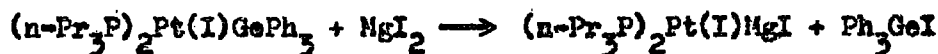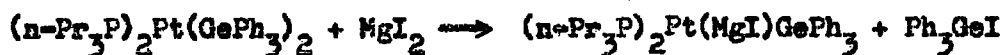
Other reaction paths, including halogen-metal exchange reactions among
the intermediates, would lead to the same products as above. Triphenyl-

Iodogermane, as well as hexaphenyldigermane, was isolated and this indicates that the coupling reaction between Ph_3GeI and Ph_3GeMgI is slow. The complex $(n-Pr_3P)_2Pt(H)GePh_3$ was not detected among the reaction products, so it is likely that the intermediate $(n-Pr_3P)_2Pt(MgI)GePh_3$ reacted further before hydrolysis. Two volatile platinum hydrides, having v(Pt-H) at 2165 cm.$^{-1}$ and 1731 cm.$^{-1}$, were given but they could not be separated. The former is close to the value expected for _trans_ $(n-Pr_3P)_2Pt(H)I$ (_trans_ $(Et_3P)_2Pt(H)I$ has v(Pt-H) at 2156 cm.$^{-1}$ (140)). The latter band is nearer the value given by Malatesta (151) for the dihydridoplatinum complex $(Ph_3P)_2PtH_2$ at 1670 cm.$^{-1}$, and may be due to the compound $(n-Pr_3P)_2PtH_2$, produced from the intermediate $(n-Pr_3P)_2Pt-(MgI)_2$.

Chatt and Shaw (149) reported that _cis_-bistriethylphosphineplatinum (II) bromide and _cyclohexylmagnesium_ bromide react to form the hydrido bromide _trans_ $(Et_3P)_2Pt(H)Br$ in 22% yield, and they suggested a mechanism independent of subsequent hydrolysis involving the production of _cyclohexene_ (which was not detected).

$$\textit{cis }(Et_3P)_2PtBr_2 + C_6H_{11}MgBr \xrightarrow{\;\;\;} \textit{trans }(Et_3P)_2Pt(H)Br + C_6H_{10} + MgBr_2$$

In view of the evidence supporting the formation of platinum(II) Grignard reagents, this reaction was re-examined and, using 10 mols of a filtered etherial solution of $C_6H_{11}MgBr$ per mol of _cis_ $(Et_3P)_2PtBr_2$, the hydrido-platinum complex was produced in about 50% yield. Two competing reaction paths appear to be involved. The method originally proposed accounts for 30% of the hydride produced. This is supported by two observations: deuterolysis still gives 15% of $(Et_3P)_2Pt(H)Br$, and _cyclohexene_ was

detected in the reaction mixture (the original Grignard reagent gave cyclohexane, but no cyclohexene on hydrolysis).

The remaining 70% of the platinum hydridobromide is produced by the hydrolysis of an intermediate platinum Grignard reagent.

$$\underline{\text{cis}}\ (Et_3P)_2PtBr_2 + C_6H_{11}MgBr \longrightarrow (Et_3P)_2Pt(MgBr)Br \begin{array}{c} \xrightarrow{H_2O} (Et_3P)_2Pt(H)Br \\ \xrightarrow{D_2O} (Et_3P)_2Pt(D)Br \end{array}$$
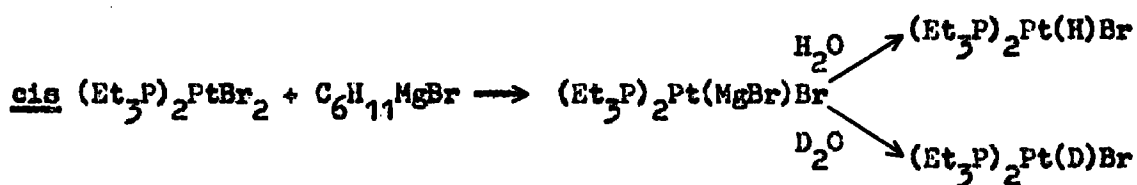
The evidence for this is based on the observation that deuterolysis gave a mixture of the hydrido- and deutero-platinum complexes, together with bicyclohexyl. The deuteride was not produced by H-D exchange since deuterolysis of $C_6H_{11}MgBr$ followed by addition of $(Et_3P)_2Pt(H)Br$ produced no absorption in the infrared due to $\nu(Pt-D)$. This reaction involves halogen-metal exchange, producing cyclohexyl bromide which reacts with excess Grignard reagent to give bicyclohexyl. Separate experiments established that this reaction does occur at room temperature, although the original Grignard solution was free from bicyclohexyl. Other products from the overall reaction include tarry material and the yellow trans $(Et_3P)_2PtBr_2$, which apparently is unreactive towards cyclohexylmagnesium bromide.

The reaction between β-styrylmagnesium bromide and cis $(Et_3P)_2PtCl_2$ has also been reported to give some trans $(Et_3P)_2Pt(H)Br$ (149) and this may also involve a platinum-Grignard intermediate. Without a large excess of $C_6H_{11}MgBr$, no platinum-Grignard reagent was produced so this reaction may be an equilibrium. Although they demonstrate the existence of Grignard reagents of platinum(II), neither this reaction nor the cleavage of $(R_3P)_2Pt(GePh_3)_2$ by MgI_2 are suitable for producing these

reagents for synthetical work.

One of the most remarkable reactions encountered in this work was the cleavage of one Ge-Pt bond in $(R_3P)_2Pt(GePh_3)_2$ by molecular hydrogen under extremely mild conditions. The metal-metal bond in $Mn_2(CO)_{10}$ can be cleaved by hydrogen, but far more drastic conditions are required (202). Closer analogies appear in the cleavage of certain metal-carbon bonds by hydrogen, notably cis $(Et_3P)_2Pt(Ph)Cl$ (140), $Li_3[CrPh_6]$ (203), and $MnPh_2$ (204).

When yellow solutions of $(Et_3P)_2Pt(GePh_3)_2$ were shaken with hydrogen at one atmosphere pressure and room temperature the colour faded progressively over 5 hours. Triphenylgermane and bistriethylphosphinetriphenylgermylhydridoplatinum(II) were readily isolated.

$$(Et_3P)_2Pt(GePh_3)_2 + H_2 \longrightarrow (Et_3P)_2Pt(H)GePh_3 + Ph_3GeH$$

The addition of Adam's catalyst did not noticeably accelerate the reaction, and did not lead to cleavage of the second Ge-Pt bond. The tri-n-propylphosphine complex was also cleaved by hydrogen under very mild conditions. Using a partial pressure of only 20 mm. of hydrogen at room temperature, the reaction proceeded to 92% in 20 days, when uptake of hydrogen ceased.

The tri-n-propylphosphine complex gave products of closely similar solubility properties, and separation was not achieved. An attempt to remove Ph_3GeH from the mixture by vacuum sublimation at 100° caused the slow decomposition of the platinum hydride, and neither Ph_3GeH nor $(n-Pr_3P)_2Pt(H)GePh_3$ was methylated by diazomethane.

The complex hydride $(Et_3P)_2Pt(H)GePh_3$ is a colourless crystalline solid, decomposing at 150°. It is stable to air, water, ketones,

alcohols and ethanolic potassium hydroxide. A sample remained unchanged in air after 6 months. Some cleavage of the Ge-Pt bond was observed when ethanolic solutions were heated in the presence of free triethylphosphine, or the iodoplatinum complex $(Et_3P)_2PtI_2$. The stereochemistry of the two platinum hydrides was not resolved, but the difference in the platinum-hydrogen stretching frequencies (2051 cm.$^{-1}$ for $(Et_3P)_2Pt(H)GePh_3$ and 1957 cm.$^{-1}$ for $(n-Pr_3P)_2Pt(H)GePh_3$) suggests that one is a _cis_ isomer and the other _trans_. These low values imply that the triphenylgermyl group has a very high _trans_ effect. It is known that the value of transition-metal-hydrogen stretching frequencies is affected by their environment, and it is of interest that a large shift in the value of $v(Pt-H)$ in $(Et_3P)_2Pt(H)GePh_3$ was observed depending on whether it was measured in benzene solution (2051 cm.$^{-1}$) or as a pressed disc in KBr (2042 cm.$^{-1}$).

A similar cleavage of platinum-tin bonds by hydrogen was reported in two short notes after the present work was completed (197,198). The value of $v(Pt-H)$ reported for _trans_ $(Et_3P)_2Pt(H)SnCl_3$ was 2105 cm.$^{-1}$ which indicates that the $SnCl_3$ group also has a high _trans_ effect, but not as great as the Ph_3Ge group.

A single rate determination on the hydrogenolysis of $(n-Pr_3P)_2Pt-(GePh_3)_2$ was made at 0° and 25° using a large (10-fold) excess of hydrogen at the same initial partial pressure. Vigorous agitation ensured that the toluene solution remained saturated throughout, and it was assumed that the solubility of hydrogen in toluene was essentially constant at 0° and 25° (205) and that the reaction is first-order with

respect to the platinum-germanium complex. A four-fold increase in rate
constant was obtained over this temperature range, corresponding to an
activation energy of about 9 kcals. The smallness of this value suggests
a radical chain mechanism, but this is unlikely since no byproducts such
as bibenzyl were detected for reactions carried out in toluene. This
favours a mechanism again involving an intermediate platinum(IV) complex
which gives the observed products by elimination of triphenylgermane. In
partial support of this view a trace of hexaphenyldigermane was detected
in some reactions, and this may be produced by a minor side-reaction from
the same intermediate.

$$(R_3P)_2Pt(GePh_3)_2 + H_2 \longrightarrow (R_3P)_2Pt(H)_2(GePh_3)_2 \xrightarrow{\begin{array}{c} > 90\% \\ \\ \sim 5\% \end{array}} \begin{array}{l} (R_3P)_2Pt(H)GePh_3 + Ph_3GeH \\ \\ (R_3P)_2PtH_2 + Ph_6Ge_2 \end{array}$$
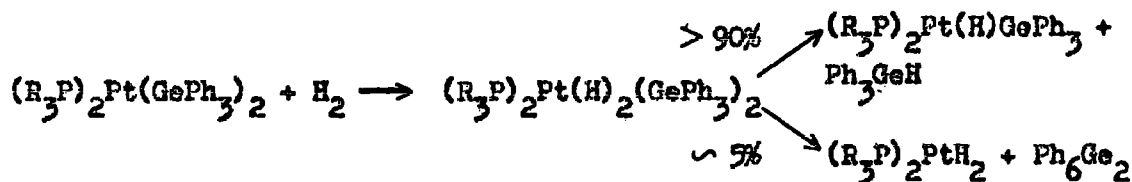
No platinum dihydride was detected, but it is possible that it de-
composed to hydrogen and a platinum (0) complex, which would account for
the apparent deficiency in hydrogen uptake.

The sparce knowledge available on platinum hydrides has limited the
deductions that can be made from the present work. No cis hydride-
platinum compounds have been characterised (140) and only one example
each of a binuclear hydride and a dihydride have been reported (147,151).
The platinum hydrides detected in the reaction between $(Et_3P)_2PtBr_2$ and
Ph_3GeH, and from the magnesium iodide reaction, almost certainly involve
some of these species, but no definite conclusions can be reached as no
information about them is at present available.

The oxidation by hydrogen of indium(I) to indium(III) complexes is known (206), and in this case the indium(III) hydrides are stable enough to be isolated. The low activation energy of the hydrogenolysis reaction in this view is a reflection of the facile oxidation of platinum(II) complexes to platinum(IV) intermediates, and it therefore seems reasonable to suspect that for many reactions catalysed homogeneously by platinum(II) compounds the initial step is the addition of a neutral molecule to give a platinum(IV) intermediate. A similar mechanism has been proposed for the "hydrosilation" of olefins catalysed by platinum(II) halides (199) and a reaction analogous to the hydrogenolysis of the Ge-Pt compound has been proposed to account for the isomerisation of olefins catalysed by platinum-tin complexes (207).

Nucleophilic attack by etherial phenyl-lithium on $(n-Pr_3P)_2Pt(GePh_3)_2$ was a slow reaction requiring a large excess of PhLi. This reaction gave no evidence of a platinum(IV) intermediate, and no lithioplatinum complex was detected. The reaction paralleled the cleavage of germanium-gold complexes by phenyl-lithium, but without the complication of further reaction by the triphenylgermyl-lithium produced.

$$(n-Pr_3P)_2Pt(GePh_3)_2 + 2PhLi \longrightarrow \underline{cis}(n-Pr_3P)_2PtPh_2 + 2Ph_3GeLi$$

In an attempt to produce a dilithioplatinum complex, and to obtain a trialkylphosphineplatinum dihydride by hydrolysis of this, a reaction between $(n-Pr_3P)_2Pt(GePh_3)_2$ and lithium aluminium hydride in ether was attempted. As with phenyl-lithium, this reaction was slow, requiring an excess of $LiAlH_4$. Both the triphenylgermyl groups were cleaved, giving Ph_3GeH as the only soluble product. The residue decomposed on hydrolysis

with evolution of hydrogen, and platinum black was subsequently isolated.

$$(n-Pr_3P)_2Pt(GePh_3)_2 + LiAlH_4 \longrightarrow 2Ph_3GeH + \text{Insoluble yellow Pt compound}$$

$$\downarrow H_2O$$

$$Pt + H_2$$
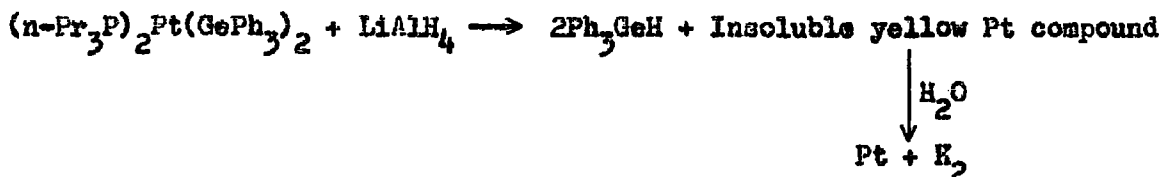
The insoluble platinum-containing material failed to give soluble phenyl- or methyl-platinum complexes on treatment with bromobenzene or methyl iodide, and is clearly not a straightforward lithioplatinum complex. Lithium hydride did not react with $(n-Pr_3P)_2Pt(GePh_3)_2$ under the same conditions, but this may be a reflection on its high insolubility.

Alkoxyplatinum halides have been shown to undergo spontaneous decomposition to hydridoplatinum halides (140).

$$\underline{Cis}\ (Et_3P)_2PtX_2 + EtOH + KOH \longrightarrow \underline{trans}\ (Et_3P)_2Pt(H)X + CH_3CHO$$

$$+ KX + H_2O$$
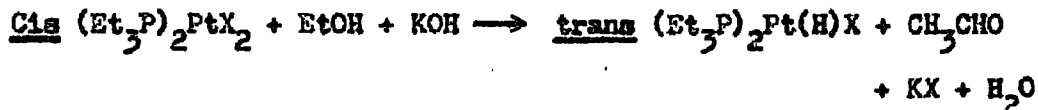
The stability of the ethoxyplatinum complex, $(Et_3P)_2Pt(OEt)GePh_3$, which was isolated from the reaction between triphenylgermyl-lithium and $(Et_3P)_2PtI_2$ after treatment with ethanol, is therefore remarkable. This colourless crystalline solid decomposes before melting at about 150°. It is stable to air and tertiary phosphines and does not react with molecular hydrogen. Ligand exchange reactions occur readily, however, and the hydroxy, methoxy and isopropoxy derivatives were obtained by treatment of the ethoxide with water, methanol and isopropanol respectively. These are almost certainly equilibria reactions as the ethoxide may be regenerated by treating the hydroxy complex with ethanol.

$$(Et_3P)_2Pt(OEt)GePh_3 + H_2O \rightleftharpoons (Et_3P)_2Pt(OH)GePh_3 + EtOH$$

$$(Et_3P)_2Pt(OEt)GePh_3 + MeOH \rightleftharpoons (Et_3P)_2Pt(OMe)GePh_3 + EtOH$$

$$(Et_3P)_2Pt(OEt)GePh_3 + Pr^iOH \rightleftharpoons (Et_3P)_2Pt(OPr^i)GePh_3 + EtOH$$
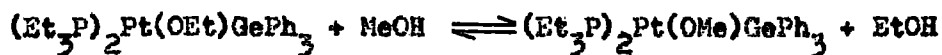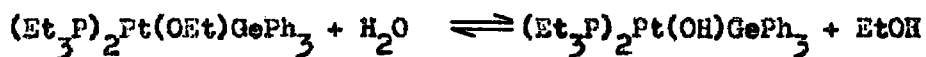
The hydroxy complex, $(Et_3P)_2Pt(OH)GePh_3$, shows a sharp band in the infrared at 3630 cm.$^{-1}$ characteristic of unassociated OH. This complex was not dehydrated at 100° in vacuo, further indicating that the hydroxy group is well shielded.

Dr. H.M.H. Shearer and Mr. C.B. Spencer of this department have made a partial X-ray study of the ethoxy complex, $(Et_3P)_2Pt(OEt)GePh_3$, and report its unit cell dimensions as a = 17.34, b = 11.16, c = 37.4Å, β = 108° 10', which contains 8 mononuclear units. The shortest platinum-platinum approach distance is 8.7Å, and the electron density arrangement around the platinum atom favours a trans configuration.

This investigation has shown that compounds containing germanium-platinum bonds can be prepared and that they have considerable thermal stability. Many reagents cleave the Ge-Pt bonds, but these reactions are complicated by oxidation reactions to platinum(IV) intermediates, and therefore may not give a true reflection of the character of the metal-metal bonds. The existence of platinum(II) lithio and Grignard reagents, and of stable alkoxyplatinum complexes, all hitherto unknown, has also emerged.

PART C. Infrared Spectra

Throughout this work infrared spectra have been invaluable as a means of identifying compounds. The identity of known compounds was confirmed by the superposition of their infrared spectra, and the recognition of new compounds was often facilitated by the observation of characteristic group frequencies. The infrared spectra of 90 organogermanes were examined in the region 2500-200 cm.$^{-1}$ with the main object of assigning these group frequencies to assist characterisation of similar compounds.

The assignments of many bands have been made by reference to work by other authors. Certain modes have not previously been observed in the infrared spectra of organogermanes, however, and these have been determined by comparisons with Raman spectra, and with the infrared spectra of related tin, lead and bromine derivatives. It is assumed that in the compounds examined the germanium atom is heavy enough to act as an "anchor", and that vibrations are not transmitted from one substituent to another. This assumption is not valid for heavier substituents, such as in bromides, iodides and transition-metal compounds. Never-the-less frequencies attributable to these groups have been observed, and, provided the limitations of a physical interpretation of the assignments are kept in mind, many useful correlations can be made. Abbreviations: w, weak; m, medium; s, strong; a, broad; c, complex; sh, shoulder; b, absent or extremely weak; d, region obscured; e, range not covered.

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Methyl derivatives

Complete assignments have been made for several methylgermanes, including tetramethylgermane (208), dimethyldiperfluorovinylgermane (209) and several methylgermanium oxides (210, 211) and chlorides (212, 213). Table 1 lists the useful methylgermanium bands found in the present work. The methyl rock is the strongest and most characteristic of these bands. The germanium-carbon stretch is generally stronger and at higher frequencies than for other alkylgermanes, with the exception of trans-butylgermanium compounds. In compounds with more than one type of alkyl group specific assignments are uncertain and in these cases all bands attributable to ν(Ge-C) are given.

Table 1

Characteristic Methylgermanium Bands

	δ asy CH₃	δ sym CH₃	ρ CH₃	ν Ge-C
MeGeI₃	b	1259 w	810 s	600 m
MeGePh₃	d	1235 w	788 m	586 m
MeGe(GePh₃)₃	d	d	787 w	559 w
MeGe(CH₂Ph)₃	d	d	800 s	573 m, 556 m, 542 w
MeGe(H)Ph₂	d	1239 w	797 s	594 m
[MeGe(CH₂Ph)₂]₂	d	d	801 m	576 w, 556 w
Me₂Ge(CH₂Ph)₂	1427 w	1227 m	802 s, 752 w	599 m, 576 m, 542 w sh
Me₃GeCH₂Ph	1422 w	1229 m	820 s, 744 m	595 s, 563 w
Me₃GeH (gas)	1429 w, 1408 w	1258 m, 1245 m	d	606 s, 595 s, 576 w sh

Ethyl derivatives

Although a complete assignment of ethylgermanium compounds is more difficult than for the methyl derivatives, a few compounds have been described (211, 214). Table 2 lists the compounds encountered in the present work. Methyl C-H deformations fall in the range expected for normal hydrocarbons (215), but the methylene C-H deformation bands are near the CH_3 bands of the methylgermanium compounds.

The absorption near 700 cm.$^{-1}$ is probably a methylene rocking mode, and the Ge-C stretch falls in the range 530-590 cm.$^{-1}$ Bands near 1020 cm.$^{-1}$ and 965 cm.$^{-1}$ are characteristic of ethylgermanium compounds, and these may involve 3 modes, since the high-frequency band is often of complex shape. Comparisons with the infrared (211) and Raman (216) spectra of other ethylgermanium compounds, and with the spectra of Et_4Sn and Et_4Pb (217) indicate that one of these bands is due to the C-C stretch. The assignment of the others, which involve C-H deformations, is less certain.

In the far infrared, two broad bands are usually observed and these are probably due to Ge-C-C deformations (C-Ge-C deformation modes will fall at a frequency lower than the range observed). These bands have not previously been observed, but they are known for ethyl-tin and ethyl-lead derivatives, and have been reported in the Raman spectra of ethylgermanium chlorides. Additional complications appeared in this region for phenylethylgermanes, and these are dealt with separately later.

TABLE 2

CHARACTERISTIC ETHYLGERMANIUM BANDS

	$\delta_{asym}(CH_3)$	$\delta_{asym}(CH_2)$	$\delta_{sym}(CH_3)$	$\delta_{sym}(CH_2)$				$\nu(Ge-C)$	
Ph₃GeEt	1456 w	d	d	d	1013 m	960 w	688 m	565 m	d
(PhCH₂)₃GeEt	d	d	d	d	1013 m	958 m	d	558 m, 552 sh w	297 m
(Ph₂EtGe)₂	1450 m	d	d	1209 w	1021 m, 1019 m	949 m	683 s	560 m	d
Ph₂GeEt₂	1460 m	d	d	1231 w	1019 c/oh	961 w	d	579 m, 553 m	d
PhGeEt₃	1462 m	d	d	1233 w	1021 oh	971 w	d	576 m, 540 w	d
Et₃GeBr	1458 s	1420 m	1377 m	1227 m	1025 s, 1010 s	971 m	707 a	581 s, 538 m	325 m, 298 m
(Et₃Ge)₂O	1451 m	1414 m	1374 w	1218 w	1016 oh	962 o/w	699 s	582 s, 536 w	323 m, 296 m
Et₄Ge	1460 m	1428 m	1374 m	1234 w	1029 s, 1005 m	968 m	703 s, 673 s	570 s	325 s, 294 m
Et₃GcBu	1462 s	1425 m	1376 m	1232 w	1017 c	962 m	699 m	570 s, 535 w	313 m
Et₃GePPh₃	1451 m	d	1372 m	1214 w	1020 s, 1009 s	966 m	d	569 m, 532 w	e
Et₃GeOP(O)Ph₃	1453 w	d	d	1220 w	d	d	725 s	578 s	e
(Et₃GePPh₃)AgI	1449 m	d	1368 w	1217 w	1008 s	966 m		590 m, 533 w	e
Et₃GeCH₂Ph	1460 m	1427 w	1379 w	1220 sh	1020 oh	971 w	730 m	573 m, 554 w, 535 w	321 m, 293 w
Ph₂Ge(Et)Bu	1456 c	d	d	1224 w	1014 m	962 w	d	565 m	e
(PhCH₂)₃GeGeEt₃	1460 sh	1425 w	1376 w	d	1012 m	968 w	d	d	327 m, 300 w

n-Butyl derivatives

In addition to the usual methyl and methylene deformations, two weak bands near 880 and 870 cm.$^{-1}$ are characteristic of n-butylgermanium compounds, and are of value as this region of the infrared is often transparent (Table 3). Most of the n-butylgermanes are liquids, and comparison with the spectra of n-propyl- and n-butyl-tin compounds (217, 218) and with n-propyl bromide (219) provides evidence for trans and gauche configurations (about the first C-C bond) having ν(Ge-C) near 645 and 550 cm.$^{-1}$ respectively. Triphenylbutylgermane is a crystalline solid, however, and as such it shows the stretching mode of the trans form only. In solution, or as a melt, it shows both trans and gauche forms. Absorption bands in the far infrared which are not attributable to phenyl, benzyl or ethyl groups are also given in Table 3. The lower frequency bands are probably due to Ge-C-C deformations, and the bands near 400 cm.$^{-1}$ may be C-C-C deformations.

Table 3

Characteristic n-Butylgermanium Bands

		v Ge-Bu trans	v Ge-C (including v Ge-Bu gauche)	
(PhCH₂)₃GeBu	882^sh w, 872 w	643 w	556^sh w, 549 w, 543^sh w	408 w
Ph₂Ge(Et)Bu	877 w, 867 w	645 w	Table 2	e
Ph₂Ge(H)Bu	881 vw, d	635 m	568 w	b
Ph₂GeBu₂	880 w, 870 w	647 w	565 m	e
(PhCH₂)₂GeBu₂	881 m, 872^sh m	645 w	549 w	405 w, 369^sh w, 288 w^a
PhCH₂GeBu₃	882 m, 870^sh m	645 w	550 w	415 w, 400^sh w, 374 w, 290m^a
Bu₄Ge	881 s, d	641 m	556 m	415 m, 400 m, 375 s, 294m^a
Et₃GeBu	917 w, 907 w	641 w	Table 2	e
Ph₃GeBu	888 w, 873 m	648 m	565 w (liquid only)	b
Bu₃GeOMe	879 w, 869^sh w	649^sh w	562^sh w	e
Bu₃GeOEt	881 m, 869^sh w	647 m	560^sh w	e
Bu₃GeOPr	884 w, 873^sh w	651 m	565 w	e

Isopropyl derivatives

The spectra available show a close similarity to isopropyl bromide, for which assignments have been made (220) (1466 s, 1385 w, 1370 w, 1160 w, 1082 w, 1006 $\frac{c}{m}$, 918 w, 878 m). Table 4 lists the bands typical of the germanium derivatives. The absorptions in the far infrared near 420 and 310 cm.$^{-1}$ are probably due to C-C-C and Ge-C-C deformations, respectively.

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Table 4

Characteristic Isopropylgermanium Bands

	$\delta\ Me_2C\text{-}H$	ν asy Ge-C	ν sym Ge-C	
iPr_3GeH	1211 w	565 m	556 m, sh	420 s, 313 s[a]
iPr_3GeD	1224 w	564 s	542 s	420 s, 311 s[a]
iPr_3GeCl	1224 m	562 s	521 w	421 m, 323 w[a]
$(iPr_2GeO)_n$	1215 w	578 m	545 w	e
iPr_4Ge	1224 w	557 m	544 m	e
iPr_6Ge_2	1224 m	544 s, 537 sh	505 m	413 s, 310 m[a], 305 m[a]

Benzyl derivatives

The spectra of these compounds are extremely complex, involving a monosubstituted benzene ring and a methylene group. (The bands due to $(PhCH_2)_3Ge$ in $(PhCH_2)_3GeCl$ are: 1949 w, 1869 w, 1805 w, 1745 w, 1595 s, 1577 w, 1488 s, 1447 s, 1404 w, 1333 w, 1314 w, 1282 w, 1250 w, 1218 w, 1203 m, 1181 w, 1155 w, 1145 w, 1055 m, 1026 w, 996 w, 980 w, 967 w, 901 m, 848 w, 813 w, 800 m, 781 m, 763 s, 694 s, 617 w, 557 w, 541 w, 461 m, 448 m, 337 w, 251 m cm.$^{-1}$). A number of bands are very characteristic of benzyl groups and can be used for characterisation purposes. Three bands, near 815, 805 and 775 cm.$^{-1}$, which probably include a CH_2 rocking mode, give a very characteristic pattern. The germanium-carbon stretch occurs near 550 cm.$^{-1}$, and is generally weaker than in the methyl-, ethyl-, and butyl-germanes. Two bands are usually observed for compounds having more than one benzyl group, and these are probably due to asymmetric and symmetric Ge-C stretch. Table 5 lists those bands, and the far infrared bands. For compounds of the type $(benzyl)_nGe(alkyl)_{4-n}$ it is not possible to distinguish between the different types of $\nu(Ge-C)$, and reference is made to earlier tables.

The far infrared spectra show two bands characteristic of the benzylgermanium group. Of these, the band at 245 ± 15 cm.$^{-1}$ is the most useful. Both this and the weak band near 335 cm.$^{-1}$ are present in benzyl bromide and are absent from methylene bromide.

Table 5

Characteristic Benzylgermanium Bands

	ν Ge–C	
$(PhCH_2)_3GeCl$	559 w, 540 w	337 w, 251 m
$(PhCH_2)_3GeBr$	557 w, 541 w	343 w, 256 s
$(PhCH_2)_3GeMe$	Table 1	340 w, 245 s
$(PhCH_2)_3GeEt$	Table 2	334 w, 251 w
$(PhCH_2)_3GeBu$	Table 3	333 w, 247 $\frac{c}{m}$
$(PhCH_2)_4Ge$	563 w, 550 m	336 w, 257 m, 237 m
$(PhCH_2)_6Ge_2$	556 w, 539 w	342 w, 238 m
$[(PhCH_2)_3Ge]_2O$	559 m, 544 w	b 260 s
$(PhCH_2)_3GeH$	541 w	334 $\frac{c}{w}$, 239 m
$(PhCH_2)_3GeD$	563 m, 541 w	334 $\frac{c}{w}$, 238 m
$(PhCH_2)_3Ge \cdot SiMe_3$	554 w	335 w, 261 m
$(PhCH_2)_3Ge \cdot GeEt_3$	d	d 267 m or 234 $\frac{a}{m}$
$(PhCH_2)_2GeMe_2$	Table 1	345 w, 249 m
$(PhCH_2)_2GeBu_2$	Table 3	334 w, 238 $\frac{a}{w}$
$(PhCH_2)_2GeH_2$	556 w, 532 w	e
$(PhCH_2)_2GeD_2$	564 w	e
$[(PhCH_2)_2MeGe]_2$	Table 1	334 w, 245 m
$PhCH_2GeBu_3$	Table 3	b b
$PhCH_2GeEt_3$	Table 2	d b
$PhCH_2GeMe_3$	Table 1	b b
$PhCH_2GePh_3$	562 w	d 245 w

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Phenyl derivatives

Recent papers on Ph_4M compounds (M = Si, Ge, Sn and Pb) (221), phenyl derivatives of tin (222) and triphenylgermyl azide (223) have established frequencies characteristic of phenylgermanium compounds. Most of the bands are identical with other monosubstituted benzene derivatives. The bands due to Ph_3Ge in Ph_3GeCl are at: 1965 w, 1894 w, 1826 w, 1770 w, 1653 w, 1582 w, 1484 m, 1429 s, 1381 w, 1335 w, 1305 m, 1266 w, 1183 w, 1159 w, 1092 s, 1063 w, 1026 w, 998 m, 971 w, 917 w, 855 w, 735 s, 694 s, 676 w, 613 w, 463 m, 453 m, 340 sh, 328 s, 275 m cm.$^{-1}$ The variations shown by certain bands have been the subject of much comment, and these bands have been noted in the present work. For example, the band at 1089 cm.$^{-1}$, one of Randle and Whiffen's "X-sensitive" bands (224), is stated to be constant for phenylgermanium compounds (221, 225). In the compounds examined, however, this strong, sharp band varies from 1073 cm.$^{-1}$ (in $(Ph_3Ge)_2Pt(PEt_3)_2$) to 1099 cm.$^{-1}$ (in hexaphenyldigermoxane) and can overlap the positions of the equivalent band in Ph-Si and Ph-Sn compounds. A similar observation has been reported for phenyltin compounds (222). The 1428 cm.$^{-1}$ band, however, is constant to within 5 cm.$^{-1}$ (221, 226).

Variations in the band near 695 cm.$^{-1}$ have been stated to depend on the electronegativity of the other substituents (221). Although variations in the position of this band were observed, they were too small to be of value. The band near 450 cm.$^{-1}$ has been reported as splitting in less symmetrical phenyl derivatives, especially in solids

(221, 227). In the compounds available this band fell in the range 482-448 cm.$^{-1}$, and in compounds containing more than one phenyl group splitting of the band does sometimes occur, but no pattern is obvious. For example, Ph$_3$GeCl and Ph$_3$GeBr both show two bands, whereas Ph$_3$GeI shows only one; in complexes having triphenylgermyl groups bonded to platinum, three bands are observed in this region.

Phenylgermanium compounds show two bands in the 350-200 cm.$^{-1}$ region. The stronger, near 325 cm.$^{-1}$ in Ph$_3$Ge compounds, is highly characteristic of this group (221) and for the analogous silicon compounds is stated to combine an in-plane ring deformation and the asymmetric M-phenyl stretch (227). This band falls at slightly lower frequencies (314-309 cm.$^{-1}$) in diphenylgermyl compounds. The weaker of these two bands probably involves the symmetric Ge-phenyl stretch. It is more variable (303-268 cm.$^{-1}$) and shows less splitting than has been reported for the silicon compounds (227). The band near 228 cm.$^{-1}$ in (Ph$_3$Ge)$_3$GeH and (Ph$_3$Ge)$_3$GeMe has been ascribed to the Ge-Ge stretch (43), and this mode may also involve some coupling with ring vibrations.

The far infrared bands and the band near 1089 cm.$^{-1}$ are given in Table 6. The phenylethylgermanes have more complex far infrared spectra and are presented separately (Table 7). Most of these compounds have 4 bands in this region, two of which are present in Et$_4$Ge. The band near 260 cm.$^{-1}$ is absent from most non-aromatic ethyl-germanium compounds other than Et$_3$GeBr. Triphenylgermyl-transition metal complexes and the phosphine compounds, Ph$_3$Ge-PPh$_2$ and Ph$_2$Ge(PPh$_2$)$_2$, also show additional

complexities in the far infrared, and are given in <u>Table 8</u>. The

additional bands may be due to the phosphine ligands and the Ge-M

stretch.

Table 6

Characteristic Phenylgermanium Bands

Ph$_4$Ge	1091		329 s		
Ph$_3$GeH	1093		323 s[a]	303 m	
Ph$_3$GeD	1093		322 s[a]	303 m	
Ph$_3$GeCl	1092	340 m,sh	328 s	275 m	
Ph$_3$GeBr	1090	340 m,sh	327 s	b	
Ph$_3$GeI	1089		335 s	d	
Ph$_3$GeMe	1092		319 s	289 m	
Ph$_3$GeBu	1092		326 s	307 m	
Ph$_3$GeCH$_2$Ph	1092		325 s	289 m	
(Ph$_3$Ge)$_2$	1086		322 s	268 s	
(Ph$_3$Ge)$_3$GeH	1086		329 s	b	228 s
(Ph$_3$Ge)$_3$GeMe	1087		328 s	b	228 m
(Ph$_3$Ge)$_2$O	1099	340 s	328 m	284 m	
Ph$_2$GeH$_2$	1094		312 s	292 m	
Ph$_2$GeBr$_2$	1089[c]		314 s,sh	b	
Ph$_2$Ge(H)Me	1093		309 s	292 m	254 w
Ph$_2$Ge(H)Bu	1093		314 s	301 m	
PhGeBr$_3$	1081		317 m		

Table 7

Ethylphenylgermanes

Et_4Ge	b	325 s		294 m̃		
Et_3GePh	1092	327 m̃	310 m	289 m̃	254 w	
Et_2GePh_2	1092	335 s	315 s	295 m	260 w	
$(Et(Ph_2)Ge)_2$	1083	321 s		294 s	260 m̃	226 w
$EtGePh_3$	1092	341 s	322 s	297 m	260 w	

Table 8

Germanium-Phosphorus and Germanium-Transition Metal Complexes

Ph_3GePPh_2	1086	327 s, 273 s, 254 w, 239 w, 221 w
$Ph_2Ge(PPh_2)_2$	1079	311 s, 288 s, 272 w, 257 s, 246 m, 235 w
$Ph_3Ge \cdot Ag(PPh_3)_3$	1094	323 w, 308 m, 296 m, 265 w
$Ph_3Ge \cdot AuPMe_3$	1083	345 w, 316 s, 309 s
$Ph_3Ge \cdot AuPPh_3$	1081	321 s, 307 s
$[(Ph_3Ge)_2Au]NEt_4$	1075	311 s
$(Ph_3Ge)_2Pt(PEt_3)_2$	1073	318 s, 305 s, 285 s, 242 m
$Ph_3GePt(H)(PEt_3)_2$	1074	326 s, 305 m, 292 s
$(Ph_3Ge)_2Pt(PPr_3)_2$	1076	317 s, 305 s, 287 s, 244 m
$Ph_3GePt(I)(PPr_3)_2$	d	329 s, 311 s, 298 m
$Ph_3GePt(OH)(PEt_3)_2$	1078	305 s [a], 291 m
$Ph_3GePt(OMe)(PEt_3)_2$	1079	334 s, 328 m, 310 s
$Ph_3GePt(OEt)(PEt_3)_2$	1083	333 s, 326 s, 313 s
$Ph_3GePt(OPr^i)(PEt_3)_2$	1080	309 s [a]

Tolyl derivatives.

Tolylgermanes (Table 9) contain two bands close to those found in phenylgermanes, near 320 and 290 cm.$^{-1}$, which may also involve the Ge-C stretch. The far infrared also contains bands which appear to be characteristic of ortho-, meta and para-substituents, but too few compounds are available to confirm this.

Table 9

Characteristic Tolylgermanium Bands

(o-Tolyl)$_3$GeBr	438 s	413 s	305 s	257 w
(o-Tolyl)$_3$GeH	438 s	403 m	304 s, 291 s	245 w
(o-Tolyl)$_6$Ge$_2$	446 s	407 m	307 m, 291 s, 286 s	253 w, 249 w
(m-Tolyl)$_3$GeH	426 s	379 m	316 s, 308 s	270 w
(m-Tolyl)$_4$Ge	430 s	388 m, 373 m	323 s, 303 s	261 w, 232 w
(m-Tolyl)$_6$Ge$_2$	426 s	373 m	312 s, 304 s	259 s
(p-Tolyl)$_4$Ge	437 s	373 m 367 s	328 s, 294 m	278 m
(p-Tolyl)$_6$Ge$_2$	484 s	362 m	316 s, 309 s	282 m, 237 m

FUNCTIONAL GROUPS

Organogermanium hydrides and deuterides.

Many organogermanium hydrides have been examined and, in addition to the Ge-H stretching frequency near 2050 cm.$^{-1}$, various deformation modes have been identified in simpler molecules (GeH$_2$ bend and wag near 860 and 780 cm.$^{-1}$ (184); GeH$_3$ rock near 600 cm.$^{-1}$ (228, 229)). The germanium-hydrogen stretch varies from 2175 cm.$^{-1}$ in GeH$_2$F$_2$ (184) to 1953 cm.$^{-1}$ in (Ph$_3$Ge)$_3$GeH (43), and for a series of organogermanes of similar structure, the Ge-H stretch has been related to the Taft electronegativity coefficients of the attached groups (230, 231). Table 10 lists the values of the Ge-H and Ge-D stretching frequencies found in the present work. Deformation modes are also given. Germanium-deuterium deformations occur in uncomplicated regions of the spectrum and are easily recognised. In contrast, for tribenzylgermane the Ge-H bend could not be identified, and in other cases only alternative assignments were possible. The spectrum of solid triphenylgermane showed remarkable complexities between 700 cm.$^{-1}$ and 500 cm.$^{-1}$, which were absent from solutions or the liquid melt, and may be connected with the α and β crystal forms. Diphenylgermane and dibenzylgermane, both of which are liquids, were also complicated in this region, and diphenylmethylgermane contained several bands additional to those expected.

Table 10

Characteristic Germanium-Hydrogen and Deuterium Bands

	Hydrides		Deuterides		
	ν Ge-H	Ge-H (deformations)		ν Ge-D	δ(Ge-D)
iPr₃GeH	1989 s	710 s	iPr₃GeD	1433 s	508 s
Ph₃GeH	2037 s	709 s	Ph₃GeD	1473 m	526 s
(o-Tolyl)₃GeH	2057 m	697 s			
(m-Tolyl)₃GeH	2034 m	719 s			
(p-Tolyl)₃GeH	2031 m	732 s or 688 s			
(mesityl)₃GeH	2053 m	707 m			
(PhCH₂)₃GeH	2034 m	-	(PhCH₂)₃GeD	1464 s	472 m
Ph₂(Me)GeH	2035 s	707 s			
Ph₂(Bu)GeH	2028 s	707 s	Ph₂(Bu)GeD	1465 s	525 s
(Ph₃Ge)₃GeH	1953 m	680 s			
Ph₂GeH₂	2051 s	866 s, (758 s or 723 s), 511 m			
(PhCH₂)₂GeH₂	2037 s	864 s (704 s?)	(PhCH₂)₂GeD₂	1466	615 m, 495 m
PhGeH₃	2062 s	870 m, 823 s, 583 m ᵃ			
Me₃GeH (gas)	2052 s / 2041 s / 2031 s	d			

Organogermanium halides

Some germanium-halogen stretching frequencies are given in Table 11. Raman spectra of several ethylgermanium chlorides show bands at 400 and 376 cm.$^{-1}$ ascribable to v_{asym}(Ge-Cl) and v_{sym}(Ge-Cl) respectively (214, 216). Similarly, the infrared spectrum of methyltrichlorgermane contains two bands at 430 and 403 cm.$^{-1}$ (212). The germanium-bromine stretching frequency covers a wide range and is difficult to assign in the phenylgermanes since it falls in the same region as the characteristic phenyl bands. In dibromdiphenylgermane the Ge-Br stretch and Ge-Ph stretch were not resolved. The wide range of values is to be expected, since with such heavy substituents the germanium atom will no-longer act as an "anchor" and the structure of the rest of the molecule will affect the vibration. As with silicon halides (227) the electronegativity of the other groups may affect the position of v(Ge-X) also.

Table 11

Germanium Halogen Stretching Frequencies

	ν Ge-Cl	ν Ge-Br	ν GeI
Ph_3GeCl	379 s		
$(PhCH_2)_3GeCl$	362 m		
Ph_3GeBr		313 s	
$(PhCH_2)_3GeBr$		251 s	
Et_3GeBr		269 m or 245 m	
Ph_2GeBr_2		315 m ^{ab}	
$PhGeBr_3$		327 s 228 w	
$GeBr_4$		330 s	
Ph_3GeI			283 s
$MeGeI_3$			256 m
GeI_4			263 s
$iso-Pr_3GeCl$	369 s		

Organogermanium oxides.

The frequencies attributable to germanium-oxygen stretch vary greatly depending on the other atom attached to the oxygen and on the structure of the molecule. Two bands, near 1040 and 680 cm.$^{-1}$, have been reported for the alkoxygermanes, $Ge(OR)_4$ (100). Only one band (near 850 cm.$^{-1}$) has been reported for diphenylgermanium oxide (98), but in dimethylgermanium oxide the position of the germanium-oxygen stretch varies depending on the degree of polymerisation (210, 95). This dependence on structure has also been reported for the corresponding silicon compounds (215) and a similar complexity is indicated for the isopropyl compound, (iso Pr_2GeO)n, in the present work. The bands due to germanium-oxygen are generally broad, and values are given in Table 12.

Table 12

Germanium Oxygen Stretching Frequencies

	ν Ge-O
$(Et_3Ge)_2O$	855 ^a_s
$(Ph_3Ge)_2O$	858 ^a_s
$[(PhCH_2)_3Ge]_2O$	926 ^a_s
$Et_3Ge \cdot OP(O)Ph_2$	954 ^a_s
$(iPr_2GeO)_n$	844 s, 789 s
$Ge(OMe)_4$	1033 s, 633 s

Other organogermanes.

$(PhCH_2)_3Ge-SiMe_3$ $\nu(Ge-Si)$ probably at 351 cm.$^{-1}$

$Et_3Ge-PPh_2$ $\nu(Ge-P)$ probably at 474 cm.$^{-1}$

$(p-Tolyl)_3GeCOOH$ $\nu(Ge-C)$ probably at 571 cm.$^{-1}$

PLATINUM ALKOXIDES.

Bands attributable to the OR radical in the alkoxides, $(Et_3P)_2Pt(OR)$-$GePh_3$, (described in Part B of this thesis) show a close similarity to the corresponding alcohols. These bands are given in Table 13. Although the band at 1033 cm.$^{-1}$ in the methoxide and 1060 cm.$^{-1}$ in the ethoxide can probably be assigned to the C-O stretch (232), the isopropoxide spectrum is too complex to assign this band with certainty. The medium intensity band which appears at 570 cm.$^{-1}$ in $(Et_3P)_2Pt(OH)GePh_3$, and 537 cm.$^{-1}$ in $(Et_3P)_2Pt(OMe)GePh_3$ is probably due to the Pt-O stretching mode. This band was not observed in the ethoxide or isopropoxide, however.

Table 13

MeOH	1031 s	$(Et_3P)_2Pt(OMe)GePh_3$	1033 s	$\nu(C-O)$
			539 m	$\nu(Pt-O)$
EtOH	1093 s	$(Et_3P)_2Pt(OEt)GePh_3$	1104 s	
	1050 s		1060 s	$\nu(C-O)$
	882 m		862 m	
isoPrOH	1164 m	$(Et_3P)_2Pt(OPr^i)GePh_3$	1157 w	
	1131 s		1121 s	
	1111 m		d	
	954 s		971 m	
	818 m		836 m	
		$(Et_3P)_2Pt(OH)GePh_3$	3630 m	$\nu(O-H)$
			570 s	$\nu(Pt-O)$

N.M.R. SPECTRA.

The 'H nuclear magnetic resonance spectra at 60 Mc/sec. of some organogermanes encountered in this work are given in Table 14. Chemical shifts relate to tetramethylsilane as an internal standard. Phenyl peaks were always complex.

Table 14

Compound	Solvent	Chemical Shift, γ			
		Ge→H	Ph	CH$_2$	Et
Ph_3GeH	25% in CCl_4	4.31	2.70	-	-
Ph_2GeH_2	-	4.91	2.77	-	-
$(PhCH_2)_2GeH_2$	-	5.98	3.06	7.87	-
$(PhCH_2)_3GeH$	25% in CCl_4	5.82	3.07	7.81	-
$(PhCH_2)_4Ge$	"		3.11	7.93	-
$(PhCH_2)_3Ge \cdot GeEt_3$	"		3.06	7.82	9.02

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