1008. *Triphenylgermylplatinum Complexes*

By R. J. CROSS and F. GLOCKLING

The complexes $(R_3P)_2Pt(GePh_3)_2$ (R = Et or Pr^n), which are formed from *cis*- or *trans*-$(R_3P)_2PtCl_2$ and Ph_3GeLi, are stable to air and water and decompose at about 150° with cleavage of Ge–Pt, Ph–Ge, and R–P bonds. Iodine, hydrogen chloride, methyl iodide, 1,2-dibromoethane, phenyllithium, magnesium iodide, and lithium aluminium hydride all cleave the Ge–Pt bonds; in some cases at least (hydrogen chloride, methyl iodide, magnesium iodide) cleavage probably proceeds *via* Pt^{IV} intermediates. Hydrogenolysis of one of the Ge–Pt bonds takes place under extremely mild conditions, the activation energy being of the order of 9 kcal., and this reaction is also considered to involve a Pt^{IV} intermediate, $(R_3P)_2Pt(H)_2(GePh_3)_2$. The iodide, $(R_3P)_2PtI_2$, and Ph_3GeLi react partly by halogen–metal exchange, giving $(R_3P)_2Pt(Li)I$, $(R_3P)_2Pt(Li)GePh_3$ and the iodo-complex, $(R_3P)_2Pt(I)GePh_3$, from which stable alkoxy-derivatives, $(R_3P)_2Pt(OR)GePh_3$ may be obtained.

ORGANOMETALLIC compounds involving metal–metal bonds are well known among the Group IV elements, silicon, germanium, tin, and lead. Most are of the type, $R_3M{-}M'R_3$, but cyclic compounds, $[R_2M]_n$, are known in which the metal is in oxidation level 2, but retains its co-ordination number 4.[1] The reactions of hexa-alkyl (or aryl) dimetal compounds are, for the most part, those expected for a metal in oxidation level 3 and co-ordination number 4; the most reactive centre being the metal–metal bond. Many electrophilic and nucleophilic reagents cleave the M–M bond under mild conditions, but secondary reactions also occur, especially with lead, due to attack on the metal–carbon bonds. Organo-digermanes show considerable thermal stability, and some cleavage of Ge–C bonds often accompanies metal–metal cleavage reactions. For example, mild bromination of

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[1] C. A. Kraus and C. L. Brown, *J. Amer. Chem. Soc.*, 1930, **52**, 4031; W. P. Neumann, *Angew. Chem. Internat. Ed.*, 1963, **2**, 555.

hexaphenyldigermane gives mainly bromotriphenylgermane, but some bromobenzene is also formed;[2] hexabenzyldigermane is cleaved by lithium to tribenzylgermyl-lithium, but some selective cleavage of benzyl–germanium bonds also occurs.[3] Hexaisopropyldigermane is extremely resistant to attack by lithium, even in boiling monoglyme.[4]

Since 1941, an increasing number of organometallic compounds have been described which involve bonding between Group IV and transition metals; observations on the stability and reactions of such molecules are often rather surprising, and of potential importance as the role of metal–metal complexes in catalytic processes becomes more apparent.[5] With few exceptions {*e.g.*, $Et_4N[Au(GePh_3)_2]$}[6] stable compounds are formed only when the transition metal is simultaneously bonded to π-bonding ligands such as carbon monoxide[7] [as in $(Ph_3Pb)_2Fe(CO)_4$, $Ph_3Si{\cdot}Mn(CO)_5$, $R_3Sn{\cdot}Mn(CO)_5$] or tertiary phosphines[6] [as in $Ph_3Ge{\cdot}AuPPh_3$, $Ph_3Ge{\cdot}Cu(PPh_3)_3$]. Related compounds involving two transition metals are also known, *e.g.*, $Ph_3PAu{\cdot}Mn(CO)_5$,[8] $(C_5H_5)(CO)_3Mo{\cdot}W(CO)_3(C_5H_5)$.[9]

Factors affecting the stability and reactivity of the metal–metal bonds have received relatively little study. Mn–Sn compounds have greater stability than Mn–Pb analogues, as judged by the temperature at which loss of carbon monoxide occurs.[7] Neutral-ligand replacements have been studied, leading to complexes typified by $Ph_3Sn{\cdot}Mn(CO)_4AsPh_3$. The effect of different ligands has been examined for the series[6] $Ph_3Ge{\cdot}M(PR_3)_n$, where M = Cu, Ag, or Au. For example, the triphenylphosphine gold complex, $Ph_3Ge{\cdot}AuPPh_3$ is more thermally stable and less reactive towards air and water than the corresponding trimethylphosphine complex, $Ph_3Ge{\cdot}AuPMe_3$. This difference could be partly accounted for by the crystal lattice stabilisation for the more symmetrical triphenylphosphine complex, but probably of greater importance is the more effective π-bonding in the triphenylphosphine complex, with greater removal of negative charge from gold to the aromatic rings. The copper and silver complexes are much less stable and only isolable with three co-ordinated phosphines, $(Ph_3P)_3M{\cdot}GePh_3$. 1,2-Dibromoethane and phenyl-lithium both cleaved the metal–metal bond in this series of compounds. In contrast, electrophilic attack (Cl_2 or Br_2) on $Ph_3Sn{\cdot}Mn(CO)_5$ cleaves the phenyl groups, giving $X_3Sn{\cdot}Mn(CO)_5$.[7]

The present 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 complexes with a view to increasing our knowledge of the stability and reactivity of the metal–metal bonds. Platinum was selected 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.[10,11]

Triphenylgermyl-lithium reacts smoothly with the trialkylphosphineplatinum dichlorides, *cis*- or *trans*-$(Et_3P)_2PtCl_2$ and *trans*-$(Pr^n{}_3P)_2PtCl_2$, to give high yields of the bistriphenylgermyl derivatives (although some free tertiary phosphine is always liberated).

$$\textit{cis-}\text{ or }\textit{trans-}(R_3P)_2PtCl_2 + 2Ph_3GeLi \longrightarrow (R_3P)_2Pt(GePh_3)_2 \quad \text{(I)}$$

In contrast, the triphenylphosphine complex, $(Ph_3P)_2PtBr_2$, gave only coloured, ill-defined polymeric material, possibly owing to halogen–metal exchange. Both of these yellow crystalline complexes were stable to air, water, ethanol, and ethanolic potassium hydroxide. Their ultraviolet (u.v.) spectra in cyclohexane solution were almost identical, showing two main bands at 2075 Å (log ε 5·0) and 3005 Å (log ε 4·36). The tri-n-propylphosphine

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[2] F. Glockling and K. A. Hooton, *J.*, 1963, 1849.
[3] R. J. Cross and F. Glockling, *J.*, 1964, 4125.
[4] A. Carrick and F. Glockling, unpublished observations.
[5] G. C. Bond and M. Hellier, *Chem. and Ind.*, 1965, 35.
[6] F. Glockling and K. A. Hooton, *J.*, 1962, 2658.
[7] R. D. Gorsich, *J. Amer. Chem. Soc.*, 1962, **84**, 2486.
[8] C. E. Coffey, J. Lewis, and R. S. Nyholm, *J.*, 1964, 1741.
[9] E. W. Abel, A. Singh, and G. Wilkinson, *J.*, 1960, 1321.
[10] J. Chatt and B. L. Shaw, *J.*, 1959, 705.
[11] J. Chatt and B. L. Shaw, *J.*, 1959, 4020.

complex was much more soluble in organic solvents than the triethylphosphine compound, and solutions in different solvents varied greatly in the intensity of the yellow colour, probably due to *cis–trans* interconversion in solution. Dipole-moment measurements on the tri-n-propylphosphine complex in benzene solution gave a value of 2·4 D (assuming atom polarisation to be 15% of the electron polarisation), indicating that the *trans*-isomer predominates. An attempt to prepare the complex (I) from triphenylgermane and the halide, *cis*-$(Et_3P)_2PtBr_2$, in the presence of triethylamine was unsuccessful; in refluxing benzene no reaction occurred.

Both complexes showed considerable thermal stability, decomposing at about 150°. The phosphine ligands are strongly bonded, since refluxing solutions with triphenylphosphine did not result in ligand exchange. Pyrolysis of both complexes *in vacuo*, which was confidently expected to follow a simple course giving $2R_3P + Pt + Ph_6Ge_2$, by cleavage of the Ge–Pt bonds, was more complex, and involved cleavage of both germanium–carbon and phosphorus–carbon bonds. At 220° the triethylphosphine complex gave hexaphenyldigermane, tetraphenylgermane, triethylphosphine, benzene, ethylene, and a black metallic-looking residue which formed 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 contained some 20% carbon as both phenyl and ethyl groups. *X*-Ray powder photographs showed that the residue was essentially amorphous, like freshly prepared platinum black. The tri-n-propylphosphine complex behaved similarly on pyrolysis, giving propene in place of ethylene.

The reactions with halogens, halogen acids, and organic halides showed some interesting complications. Carbon tetrachloride is sufficiently reactive to cleave the Ge–Pt bonds, giving Ph_3GeCl and $(R_3P)_2PtCl_2$. Iodine likewise reacts immediately at room temperature and, even with equimolar ratios, gave $(R_3P)_2PtI_2 + Ph_3GeI$ rather than the intermediate complex, $(R_3P)_2Pt(I)GePh_3$. 1,2-Dibromoethane reacts in a very characteristic manner which may be used as a diagnostic test for germanium–transition-metal bonds.

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

We have previously suggested[12] that this reaction proceeds *via* a four-centred transition intermediate. The reaction is quantitative over 13 days at 20° for the tri-n-propylphosphine complex, and showed a definite decrease in rate after one mol. of 1,2-dibromomethane had reacted.

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, although this could be in competition with direct cleavage.

$$\begin{tikzcd}
(\mathrm{I};\ R = Et) + HCl \arrow[r] \arrow[d] & Ph_3GeH + \textit{trans}\text{-}(Et_3P)_2PtCl_2 \\
(Et_3P)_2Pt(H)(Cl)(GePh_3)_2 \arrow[r] & Ph_3GeCl + (Et_3P)_2Pt(H)GePh_3 \arrow[d, "HCl"] \\
 & (Et_3P)_2Pt(H)Cl + Ph_3GeH
\end{tikzcd}$$

Methyl iodide, in a sealed tube at 110°, reacted similarly, giving iodotriphenylgermane and methyltriphenylgermane, but radical intermediates were also involved, since methane and ethane were isolated, and the mixture of platinum products proved difficult to separate. Chatt has fully characterised a numer of Pt^{IV} complexes formed by the addition of methyl iodide to Pt^{II} compounds,[10] and has also obtained good evidence that hydrogen chloride can give Pt^{IV} adducts of moderate stability,[13] *e.g.*, $(Et_3P)_2Pt(H)_2(Cl)_2$.

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[12] R. J. Cross and F. Glockling, *Proc. Chem. Soc.*, 1964, 143.

[13] J. Chatt and B. L. Shaw, *J.*, 1962, 5075.

Nucleophilic cleavage by phenyl-lithium was a slow reaction requiring a large excess of phenyl-lithium, but gave no evidence of a lithio–platinum(IV) intermediate, and paralleled the same reaction with germanium–gold complexes.

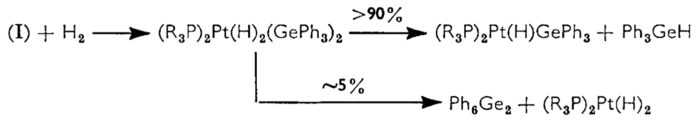
$$\text{(I)} + \mathrm{PhLi} \longrightarrow cis\text{-}(\mathrm{R_3P})_2\mathrm{PtPh_2} + \mathrm{Ph_3GeLi}$$

One of the most remarkable reactions encountered in this work was the cleavage of *one* Ge–Pt bond by molecular hydrogen under extremely mild conditions. We can find no parallel for this reaction in other compounds containing metal–metal bonds. Metal carbonyls such as $Mn_2(CO)_{10}$ require far more drastic conditions,[14] but close analogies appear in the cleavage of some transition-metal–carbon bonds, notably *cis*-$(Et_3P)_2Pt(Ph)Cl$,[13] $Li_3[CrPh_6]$,[15] and $MnPh_2$.[16] When yellow solutions of the complexes $(R_3P)_2Pt(GePh_3)_2$ are shaken with hydrogen at atmospheric pressure and room temperature the colour fades progressively over 5 hours, but the reaction is not quantitative. Using a partial pressure of 20 mm. hydrogen at room temperature, the reaction proceeded to 92% in 20 days, when uptake of hydrogen ceased. From the triethylphosphine complex both triphenylgermane and hydrobistriethylphosphinetriphenylgermylplatinum(II) are readily isolated.

$$\text{(I; R = Et)} + \mathrm{H_2} \longrightarrow (\mathrm{Et_3P})_2\mathrm{Pt(H)GePh_3} + \mathrm{Ph_3GeH}$$

The tri-n-propylphosphine complex gave products of closely similar solubility properties, and separation was not achieved. Neither hydrobistri-n-propylphosphinetriphenylgermylplatinum(II) nor triphenylgermane was methylated by diazomethane.

A single rate determination 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. Assuming the solubility of hydrogen in toluene to be essentially constant [17] at 0 and 25°, and that the reaction is first-order with respect to the platinum–germanium complex, we obtain a four-fold increase in rate constant over this temperature range, corresponding to an activation energy of about 9 kcal. The smallness of this value is suggestive of a radical chain mechanism but, against this, for reactions carried out in toluene we failed to detect any by-products such as bibenzyl. This favours a mechanism again involving an intermediate octahedral platinum(IV) complex which, by elimination of triphenylgermane, gives the observed products, and in partial support of this view, about 5% of hexaphenyldigermane is also formed.



$$\begin{tikzcd}
\text{(I)} + \mathrm{H_2} \arrow[r] & (\mathrm{R_3P})_2\mathrm{Pt(H)_2(GePh_3)_2} \arrow[r, ">90\%"] \arrow[dr, "\sim 5\%"'] & (\mathrm{R_3P})_2\mathrm{Pt(H)GePh_3} + \mathrm{Ph_3GeH} \\
 & & \mathrm{Ph_6Ge_2} + (\mathrm{R_3P})_2\mathrm{Pt(H)_2}
\end{tikzcd}$$

The dihydroplatinum complex, $(Ph_3P)_2Pt(H)_2$, has been fully characterised,[18] but it is possible that, with trialkylphosphines attached to platinum, any dihydride would decompose slowly to hydrogen and a platinum(0)–phosphine complex, which would account for the apparent deficiency in hydrogen uptake. Further evidence for a *trans*-dihydroplatinum complex is discussed later. The low activation energy of the hydrogenolysis reaction on this view is a reflection of the facile oxidation of platinum(II) complexes to platinum(IV) intermediates. The stereochemistry of the two hydro-complexes, $(R_3P)_2Pt(H)GePh_3$, has not been resolved, but the differences in the platinum–hydrogen stretching frequencies [2051 cm.$^{-1}$ for $(Et_3P)_2Pt(H)GePh_3$ and 1957 cm.$^{-1}$ for $(Pr^n{}_3P)_2Pt(H)GePh_3$] suggest that one is a *cis*- and the other a *trans*-complex. These low values imply that the triphenylgermyl group has a very high *trans* effect. The complex $(Et_3P)_2Pt(H)GePh_3$ is stable to air,

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[14] W. Hieber and G. Wagner, *Z. Naturforsch.*, 1958, **13**b, 399.

[15] F. Hein and R. Weiss, *Z. anorg. Chem.*, 1958, **295**, 145.

[16] K. Clauss and H. Bestian, *Annalen*, 1962, **654**, 8.

[17] M. W. Cook, University of California Radiation Laboratory, no. 2459, p. 74.

[18] L. Malatesta and R. Ugo, *J.*, 1963, 2080.

water, ketones, ethanol, and ethanolic potassium hydroxide. Some cleavage of the Ge–Pt bond was observed when solutions in ethanol were heated either with free phosphine, or with the platinum iodide complex, $(Et_3P)_2PtI_2$.

In attempts to resolve problems connected with the reaction between magnesium iodide and the complex, $(Pr^n{}_3P)_2Pt(GePh_3)_2$, discussed below, we tried to prepare the germylplatinum halide complex, $(Et_3P)_2Pt(I)GePh_3$, by the action of one equivalent of triphenylgermyl-lithium on *trans*-$(Et_3P)_2PtI_2$. None of the desired product was isolated but, after hydrolysis, $(Et_3P)_2Pt(GePh_3)_2$, Ph_6Ge_2, and $(Et_3P)_2Pt(H)I$ were obtained. Crystallisation from ethanol gave a stable, crystalline compound, originally thought to involve a Pt–Pt bond,[19] but which has now been characterised as the ethoxyplatinum complex, $(Et_3P)_2Pt(OEt)GePh_3$. Isolation of the hydroplatinum halide is difficult to account for except *via* a lithioplatinum intermediate formed by halogen–metal exchange. These exchange reactions become increasingly important when iodides rather than other halides are involved. Evidence for related platinum–Grignard reagents, $(Et_3P)_2Pt(MgX)X$ has been presented elsewhere.[19]

$$(Et_3P)_2PtI_2 + Ph_3GeLi \longrightarrow (Et_3P)_2Pt(I)Li + Ph_3GeI$$
$$Ph_3GeI + Ph_3GeLi \longrightarrow Ph_6Ge_2$$
$$(Et_3P)_2Pt(I)Li + H_2O \longrightarrow (Et_3P)_2Pt(H)I$$

With more than two equivalents of triphenylgermyl-lithium the platinum iodide complex gave none of the hydroiodide, but rather the same hydrogermylplatinum compound that was obtained from the hydrogenolysis reaction. Furthermore, treatment with ethanol did not give the ethoxy-complex, $(Et_3P)_2Pt(OEt)GePh_3$. These observations are compatible with an intermediate iodo-compound, $(Et_3P)_2Pt(I)GePh_3$, reacting with further triphenylgermyl-lithium by two paths.

$$(Et_3P)_2Pt(I)GePh_3 + Ph_3GeLi \longrightarrow (Et_3P)_2Pt(GePh_3)_2 + (Et_3P)_2Pt(Li)GePh_3$$
$$(Et_3P)_2Pt(Li)GePh_3 + H_2O \longrightarrow (Et_3P)_2Pt(H)GePh_3$$

Reactions involving slightly less than two equivalents of triphenylgermyl-lithium gave the complete range of products including both hydroplatinum complexes and, after treatment with ethanol, the ethoxyplatinum complex. All these reactions gave some tarry materials, and sublimation at 100° *in vacuo* left residues containing tetraphenylgermane and $(Et_3P)_2Pt(I)Ph$, strongly suggestive of radical decomposition processes.

The ethoxyplatinum complex, isolated in about 10% yield, is most probably formed by hydrolysis of the germylplatinum iodide:

$$(Et_3P)_2Pt(I)GePh_3 \xrightarrow[LiOH]{H_2O} (Et_3P)_2Pt(OH)GePh_3 \underset{H_2O}{\overset{EtOH}{\rightleftharpoons}} (Et_3P)_2Pt(OEt)GePh_3$$

The stability of this compound is remarkable in relation to the spontaneous decomposition of alkoxyplatinum halides to hydroplatinum halides:[13] *cis*-$(R_3P)_2PtX_2 + EtOH + KOH \longrightarrow$ *trans*-$(R_3P)_2Pt(H)X + CH_3CHO + KX$. It is unaffected by air, hydrogen, or tertiary phosphines, but ligand-exchange reactions occurred readily. For example, the hydroxy-, methoxy-, and isopropoxy-derivatives were obtained by treatment of the ethoxide with water, methanol, and propan-2-ol, respectively. These are certainly equilibria, since the ethoxide may be regenerated by treating the hydroxy-complex with ethanol.

Dr. H. M. M. Shearer and Mr. C. B. Spencer have made a partial *X*-ray study of the ethoxy-complex, $(Et_3P)_2Pt(OEt)GePh_3$, and report as follows: "Buerger precession photographs gave the unit-cell dimensions as $a = 17{\cdot}34$; $b = 11{\cdot}16$; $c = 37{\cdot}41$; $\beta = 108° \, 10'$. The space group was $P2_1/C$ with $Z = 8$ (mononuclear units). The Patterson function was calculated in the (100) and (010) projections, and co-ordinates were assigned to the two platinum atoms in the asymmetric unit which account for the major features of this function. In projection along *b* the shortest platinum–platinum approach distance

[19] R. J. Cross and F. Glockling, *J. Organometallic Chem.*, 1965, **3**, 253.

was 8·7 Å. Structure factors calculated using the co-ordinates found for the Pt atoms gave $R(010) = 0{\cdot}27$; $R(100) = 0{\cdot}35$. The peaks surrounding the platinum atoms in the (010) projection suggest a square planar configuration, and their heights have a slight bias towards a *trans*-configuration."

The reaction between $(\text{Pr}^n_3\text{P})_2\text{Pt}(\text{GePh}_3)_2$ and magnesium iodide also leads to the conclusion that platinum–Grignard reagents exist, and are sufficiently stable in solution to survive up to a hydrolysis stage. Chatt [10] has shown that dimethylplatinum(II) complexes react with magnesium iodide in what are probably a series of equilibria, giving $(\text{R}_3\text{P})_2\text{PtI}_2$, $(\text{R}_3\text{P})_2\text{Pt(I)Me}$, and MeMgI, and has produced evidence that the reactions proceed *via* a Pt^{IV} intermediate. Cleavage of the germylplatinum complexes by magnesium iodide produced a greater range of products than the methylplatinum analogues. These may be rationalised either by considering that each Ge–Pt bond is cleaved by magnesium iodide to give both combinations of groups, [GeI + Pt(MgI)] and [Ge(MgI) + PtI], or that the reaction proceeds *via* a platinum(IV) intermediate, $(\text{R}_3\text{P})_2\text{Pt(I)(MgI)}(\text{GePh}_3)_2$, which then degrades to platinum(II) products. In either case, a maximum of 8 stable products can result after hydrolysis, or 13 taking *cis–trans*-isomers into account. Experimentally we have isolated 5 products, and have some evidence (infrared spectra) for 2 hydroplatinum complexes.

$$\begin{tikzcd}
\underset{(\text{I};\ \text{R} = \text{Pr}^n)}{(\text{Pr}^n_3\text{P})_2\text{Pt}(\text{GePh}_3)_2 + \text{MgI}_2} \arrow[r] & \underset{(\text{II})}{(\text{Pr}^n_3\text{P})_2\text{Pt(I)GePh}_3} \arrow[d, "\text{MgI}_2"] & + & \text{Ph}_3\text{GeMgI} \arrow[d, "\text{H}_2\text{O}"] \\
& (\text{Pr}^n_3\text{P})_2\text{PtI}_2\ (\text{III}) & & \text{Ph}_3\text{GeH}
\end{tikzcd}$$

Triphenylgermane and the complexes (II) and (III) were all isolated. It is of interest that the iodogermylplatinum complex, (II), was not obtained by treating (I) with 1 mol. of iodine. The ready hydrolysis of the complex $(\text{Et}_3\text{P})_2\text{Pt(I)GePh}_3$, discussed earlier, could be due to the higher pH or to the presence of a more reactive isomer.

$$\begin{tikzcd}
(\text{I};\ \text{R} = \text{Pr}^n) + \text{MgI}_2 \text{ or } (\text{II}) + \text{Ph}_3\text{GeMgI} \arrow[r] & (\text{Pr}^n_3\text{P})_2\text{Pt(MgI)GePh}_3 \arrow[d, "\text{H}_2\text{O}"] & + & \text{Ph}_3\text{GeI} \arrow[d, "\text{Ph}_3\text{GeMgI}"] \\
& \underset{(\text{IV})}{(\text{Pr}^n_3\text{P})_2\text{Pt(H)GePh}_3} & & \text{Ph}_6\text{Ge}_2
\end{tikzcd}$$

Hexaphenyldigermane was isolated and, since all the platinum hydrides present sublimed at low temperature, we conclude either that (IV) was absent or that it decomposed in the presence of other reaction products.

$$\begin{tikzcd}
(\text{II}) + \text{MgI}_2 \text{ or } (\text{III}) + \text{Ph}_3\text{GeMgI} \arrow[r] & (\text{Pr}^n_3\text{P})_2\text{Pt(I)MgI} \arrow[d, "\text{H}_2\text{O}"] & + \text{Ph}_3\text{GeI} + & (\text{Pr}^n_3\text{P})_2\text{Pt(MgI)}_2 \arrow[d, "\text{H}_2\text{O}"] \\
& (\text{Pr}^n_3\text{P})_2\text{Pt(I)H}\ (\text{V}) & & (\text{Pr}^n_3\text{P})_2\text{Pt(H)}_2\ (\text{VI})
\end{tikzcd}$$

Iodotriphenylgermane was isolated, together with two hydroplatinum complexes which could not be separated. These showed absorption due to the platinum–hydrogen stretch at 2165 and 1731 cm.$^{-1}$. The former is close to the expected value for (V), *i.e.*, *trans*-$(\text{Pr}_3{}^n\text{P})_2\text{Pt(I)H}$; [*trans*-$(\text{Et}_3\text{P})_2\text{Pt(I)H}$ has ν(Pt–H) at 2156 cm.$^{-1}$ in hexane].[13] The band at 1731 cm.$^{-1}$ is well outside the range given by Chatt for 20 complexes (2265—2005 cm.$^{-1}$), but is closer to Malatesta's [18] dihydroplatinum complex $(\text{Ph}_3\text{P})_2\text{Pt(H)}_2$ at 1670 cm.$^{-1}$, for which the assignment is certain since the expected shift is observed on deuteration.[20] We tentatively suggest that the magnesium iodide reaction gives dihydrobistri-n-propylphosphineplatinum (VI), which is likely to be the *trans*-isomer because of the large infrared

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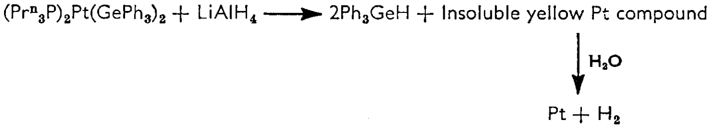
[20] L. Malatesta, private communication.

shift. The *cis*-isomer would probably be similar to the complex, $[Et_3P(H)Pt{\cdot}PPh_2]_2$[21] having ν(Pt–H) at 2005 cm.$^{-1}$, in which bridging Ph_2P groups are *trans* to hydrogen.

We have examined the reaction between triphenylgermane and *trans*-$(Et_3P)_2PtBr_2$ with a view to obtaining an alternative explanation of the 1731-cm.$^{-1}$ Pt–H band, but no reaction occurs in solution, even on the addition of triethylamine. When sublimed together, three bands attributable to Pt–H stretch appear, all in the " normal " region (2212, 2183, and 2004 cm.$^{-1}$). In an attempt to produce the dihydride (VI), and at the same time obtain more direct evidence for a dilithioplatinum compound, we treated $(Pr^n_3P)_2Pt(GePh_3)_2$ with an excess of lithium aluminium hydride in ether. Both triphenylgermyl groups were cleaved, giving triphenylgermane as the only soluble product, but the residue on hydrolysis decomposed with evolution of hydrogen, and platinum black was subsequently isolated.



$$(Pr^n_3P)_2Pt(GePh_3)_2 + LiAlH_4 \longrightarrow 2Ph_3GeH + \text{Insoluble yellow Pt compound} \xrightarrow{H_2O} Pt + H_2$$

The insoluble platinum-containing compound failed to give soluble phenyl- or methylplatinum complexes on treatment with bromobenzene or methyl iodide, and is clearly *not* a straightforward dilithio-complex, $(Pr_3^nP)_2PtLi_2$.

The reaction between trimethylplatinum(IV) iodide and triphenylgermyl-lithium was also examined, but the only isolable product was methyltriphenylgermane, together with insoluble black pyrophoric material which showed no structure in the infrared region.

The hydridic proton resonance in *trans*-platinum complexes of the type $(R_3P)_2Pt(H)X$ shows large chemical shifts.[22] The combined effect of the two equivalent ^{31}P and the ^{195}Pt nuclei is to split the proton resonance into three separate triplets. The complex $(Et_3P)_2Pt(H)GePh_3$ was too insoluble for effective examination, but the tri-n-propylphosphine analogue, as an equimolar mixture with triphenylgermane, failed to show a detectable signal attributable to the Pt–H resonance, whereas the GeH resonance (τ, 4·2) was just observable. If this complex has a *cis*-configuration even greater splitting is to be expected, since the effect of the two ^{31}P nuclei on the hydridic proton would then be non-equivalent, with even greater reduction in peak intensity.

Infrared Spectra.—Bands attributable to the OR radical in the alkoxides, $(Et_3P)_2Pt(OR)GePh_3$, show a close similarity to the corresponding alcohols (see Table). 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,[23] 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 539 cm.$^{-1}$ in $(Et_3P)_2Pt(OMe)GePh_3$, is probably due to the Pt–O stretch. This band is either absent or extremely weak in the ethoxide and isopropoxide.

MeOH	1031s cm.$^{-1}$	$(Et_3P)_2Pt(OMe)GePh_3$	1033s cm.$^{-1}$	ν(C–O)
			539m	ν(Pt–O)
EtOH	1093s	$(Et_3P)_2Pt(OEt)GePh_3$	1104s	
	1050s		1060s	ν(C–O)
	882m		862m	
Pr^iOH	1164m	$(Et_3P)_2Pt(OPr^i)GePh_3$	1157w	
	1131s		1121s	
	1111m		Obscured	
	954s		971m	
	818m		836m	
		$(Et_3P)_2Pt(OH)GePh_3$	3630m	ν(O–H)
			570s	ν(Pt–O)

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[21] J. Chatt and J. M. Davidson, *J.*, 1964, 2433.

[22] J. Chatt, *Proc. Chem. Soc.*, 1962, 318.

[23] F. K. Butcher, W. Gerrard, E. F. Mooney, R. G. Rees, and H. A. Willis, *Spectrochim. Acta*, 1964, **20**, 51.

The far-infrared spectra of compounds $(Et_3P)_2Pt(GePh_3)_2$, $(Pr^n_3P)_2Pt(GePh_3)_2$, and $(Et_3P)_2Pt(H)GePh_3$ show several strong bands in the region of the Ge–Ph stretch.[24] Three related compounds show similar bands: $(Pr^n_3P)_2Pt(I)GePh_3$ (329s, 311s, 298m); $(Et_3P)_2Pt(OMe)GePh_3$ (334s, 328m, 310s); $(Et_3P)_2Pt(OEt)GePh_3$ (333s, 326s, 313s). In the isopropoxy-complex, $(Et_3P)_2Pt(OPr^i)GePh_3$, these bands were obscured by a strong broad absorption at 309 cm.$^{-1}$, which is probably a skeletal deformation of the isopropoxy-group.

EXPERIMENTAL

Operations on air-sensitive substances were carried out in pure dry nitrogen. The identities of the known compounds formed as reaction products were verified by comparison of their infrared (i.r.) spectra with those of the authentic materials, unless otherwise stated. N.m.r. data (chemical shifts) are related to tetramethylsilane.

Bistriethylphosphinebistriphenylgermylplatinum(II).—Triphenylgermyl-lithium, from n-butyl-lithium (20·4 mmoles) and triphenylgermane (6·2 g., 20·4 mmoles) in ether (120 c.c.) was added dropwise to a solution of *trans*-bistriethylphosphineplatinum(II) chloride (5·0 g., 10 mmoles) in ether (100 c.c.). 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 the *complex* $(Et_3P)_2Pt(GePh_3)_2$, (9·5 g., 91%), as pale yellow needles from methylcyclohexane, m. p. 160° (decomp.) (Found: C, 55·9; H, 5·8; Pt, 19·5; *M* (freezing benzene), 1004. $C_{48}H_{60}Ge_2P_2Pt$ requires: C, 55·9; H, 5·8; Pt, 18·8%; *M*, 1039). This germylplatinum complex is stable to air and water, and only sparingly soluble in common organic solvents. The same complex was isolated in 65% yield starting from the *cis*-bistriethylphosphineplatinum(II) chloride.

Bistri-n-propylphosphinebistriphenylgermylplatinum(II).—A reaction similar to that described above using *trans*-bistri-n-propylphosphineplatinum(II) chloride (9·0 g., 15·4 mmoles) gave the *complex*, $(Pr^n_3P)_2Pt(GePh_3)_2$ (17 g., 98%). Purification from benzene gave the *solvate* 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.*, $(Pr^n_3P)_2Pt(GePh_3)_2,C_6H_6$ requires: C, 60·0; H, 6·5; C_6H_6, 7·0%). The *unsolvated complex* is obtained by heating at 40° *in vacuo* (Found: C, 57·5; H, 6·5; P, 5·45. $C_{54}H_{72}Ge_2P_2Pt$ requires: C, 57·7; H, 6·5; P, 5·5%).

Pyrolysis of Bistri-n-propylphosphinebistriphenylgermylplatinum(II).—The complex (0·332 g.) decomposed *in vacuo* at 120°, and at 175° collapsed to a black tar. Fractional sublimation (250° for 1 hr.) gave tetraphenylgermane (35 mg., m. p. 227—235°) and hexaphenyldigermane (25 mg., m. p. 351—353°), together with benzene, propene, 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 benzene-insoluble (Found: C, 20·0; H, 2·2%). Its i.r. spectrum showed bands associated with phenyl and propyl groups.

Pyrolysis of Bistriethylphosphinebistriphenylgermylplatinum(II).—The complex (0·203 g.) darkened *in vacuo* at 155°, and at 180° a white sublimate of tetraphenylgermane formed. At 193° the compound collapsed to a black liquid, which became increasingly viscous as the temperature was held at 230° for 30 min. Tetraphenylgermane (41 mg.), hexaphenyldigermane (15 mg.), and a black, benzene-soluble residue (87 mg.) were isolated as previously described, together with benzene, ethylene, and triethylphosphine.

Reactions of the Germylplatinum Compexes.—Bistriethylphosphinebistriphenylgermylplatinum(II) *and carbon tetrachloride*. A few crystals of the germylplatinum complex were boiled for 5 min. with carbon tetrachloride; chlorotriphenylgermane $\nu_{max.}$ 379 (Ge–Cl stretch), 328 cm.$^{-1}$ (Ge–Ph stretch) with a characteristic band[24] at 257 cm.$^{-1}$ and *trans*-bistriethylphosphineplatinum(II) chloride, $\nu_{max.}$ 415 (Pt–P stretch), 340 cm.$^{-1}$ (Pt–Cl stretch), were produced.

Bistriethylphosphinebistriphenylgermylplatinum(II) *and iodine*. Dropwise addition of iodine (89 mg., 0·35 mmole) in benzene (13·8 c.c.) to the complex (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 light petroleum (b. p. 60—80°), giving starting material (0·15 g.)

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[24] R. J. Cross and F. Glockling, *J. Organometallic Chem.*, 1965, **3**, 146.

as the insoluble fraction. Sublimation of the petroleum-soluble material, followed by crystallisation from ethanol, gave iodotriphenylgermane, m. p. 149—154°, and *trans*-bistriethylphosphineplatinum(II) iodide, m. p. 133—135° (Found: C, 21·2; H, 4·5. Calc. for $C_{12}H_{30}I_2P_2Pt$: C, 21·0; H, 4·4%). A trace of hexaphenyldigermoxane was isolated.

Bistrialkylphosphinebistriphenylgermylplatinum(II) *and* 1,2-*dibromoethane*. Bistriethylphosphinebistriphenylgermylplatinum(II) (0·4 g.) and 1,2-dibromoethane (20 c.c.) were heated under reflux in a slow stream of nitrogen for 20 hr., the emergent gases being passed through traps maintained at −78 and −198°. Ethylene (9·84 N.* c.c.; 57%) was isolated from the liquid-nitrogen trap. Sublimation of the residue (100°/10^{-3} mm.), after removal of excess of 1,2-dibromoethane, gave *trans*-bistriethylphosphineplatinum(II) bromide, $(Et_3P)_2PtBr_2$, m. p. 128—133° (from ethanol), and bromotriphenylgermane, Ph_3GeBr, m. p. 135—137° (from ethanol), in a combined yield of 0·25 g. The residue from the sublimation (0·17 g.) gave *cis*-bistriethylphosphineplatinum(II) bromide, m. p. 200—202° (from ethanol), and hexaphenyldigermoxane, $(Ph_3Ge)_2O$, m. p. 176—179°. The latter is presumably formed by the hydrolysis of bromotriphenylgermane in the working-up process.

The tri-n-propylphosphine complex, $(Pr^n_3P)_2Pt(GePh_3)_2$ (49 mg.), with 1,2-dibromoethane (10 c.c.) in a vacuum apparatus, gave ethylene (1·95 N * c.c., 99·6%) over 12 days at room temperature.

Bistrialkylphosphinebistriphenylgermylplatinum(II) *and hydrogen chloride*. The triethylphosphine complex (0·22 g.) in benzene (20 c.c.) was treated with an excess of dry hydrogen chloride. The yellow solution rapidly became colourless. Sublimation of the products (90°/10^{-4} mm.) left a trace of hexaphenyldigermoxane as residue. The oily sublimate contained triphenylgermane, $\nu_{max.}$ 2036 cm.$^{-1}$ (Ge–H stretch), ^{1}H n.m.r. τ (Ge)H 4·2; chlorotriphenylgermane, $\nu_{max.}$ 379 cm.$^{-1}$ (Ge–Cl stretch); *trans*-hydrobistriethylphosphineplatinum(II) chloride $\nu_{max.}$ 2185 cm.$^{-1}$ (Pt–H stretch), τ (Pt)H 26·7; and *trans*-bistriethylphosphineplatinum(II) chloride, $\nu_{max.}$ 341 (Pt–Cl stretch) and 412 cm.$^{-1}$ (Pt–P stretch).

An analogous experiment using the tri-n-propylphosphine complex gave similar products, and in this case *cis*-bistri-n-propylphosphineplatinum(II) chloride, m. p. 145—150°, was isolated by fractional crystallisation from methanol.

Bistri-n-propylphosphinebistriphenylgermylplatinum(II) *and methyl iodide*. 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 (3·56 N * c.c.; 0·16 mmole) and ethane (6·02 N * c.c.; 0·27 mmole) were isolated when the tube was opened to a vacuum system. Removal of the excess of methyl iodide left a complex mixture (0·53 g.) which yielded, by fractional crystallisation first from acetone and then from ethanol, iodotriphenylgermane, m. p. 144—147°; *trans*-bistri-n-propylphosphineplatinum(II) iodide, m. p. 112—114° and, in low yield, red crystals of the diplatinum iodide complex, *trans*-$(Pr^n_3P)_2Pt_2I_4$, m. p. 198—201° (Found: C, 18·0; H, 3·5. Calc. for $C_{18}H_{42}I_4P_2Pt_2$: 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 methyltriphenylgermane as the only volatile component, m. p. 68—69° from methanol (Found: C, 70·9; H, 5·6. Calc. for $C_{19}H_{18}Ge$: C, 71·5; H, 5·7%).

Bistriethylphosphinebistriphenylgermylplatinum(II) *and methyl iodide*. As in the preceding experiment this reaction gave, as main products, the iodides Ph_3GeI and *trans*-$(Et_3P)_2PtI_2$, m. p. 133—135°, together with trace quantities of methyltriphenylgermane and unidentified white and red compounds, both containing Et_3P, Pt, and I.

Bistri-n-propylphosphinebistriphenylgermylplatinum(II) *and phenyl-lithium*. Ethereal phenyl-lithium (40 c.c., 0·6M) and the complex (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° (decomp.) from ethanol (Found: C, 54·0; H, 7·8. Calc. for $C_{30}H_{52}P_2Pt$, C, 53·8; H, 7·8%). Triphenylgermane was isolated from the ethanolic mother-liquors by sublimation (55°/10^{-3} mm.). Experiments in which some bromobenzene (from the preparation of phenyl-lithium) was present gave, in addition, tetraphenylgermane by the reaction: $Ph_3GeLi + PhBr \longrightarrow Ph_4Ge$.

Hydrogenolysis of bistriethylphosphinebistriphenylgermylplatinum(II). The complex (0·42 g.) in ethyl acetate (100 c.c.) was hydrogenated for 5 hr. at 1 atm., when the initial deep yellow colour of the solution was completely discharged. Removal of solvent left an oily residue

* Measured at N.T.P.

from which triphenylgermane was separated by extraction with light petroleum (b. p. 40—60°). The residue of *hydrobistriethylphosphinetriphenylgermylplatinum*(II), $(Et_3P)_2Pt(H)GePh_3$, separated from benzene as white crystals, $\nu_{max.}$ (C_6H_6 soln.) 2051 cm.$^{-1}$ (Pt–H stretch), m. p. 150° (decomp.) (Found: C, 48·5; H, 6·1; P, 7·5, 8·5%; *M*, 726. $C_{30}H_{46}GeP_2Pt$ 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.

Hydrogenolysis of bistri-n-propylphosphinebistriphenylgermylplatinum(II). The complex (0·400 g., 0·36 mmole) in toluene (20 c.c.) was stirred magnetically in hydrogen (partial pressure 20 mm.) for 21 days. The deep yellow colour faded progressively to colourless over this period, giving triphenylgermane, ν_{max} 2034 cm.$^{-1}$ (Ge–H stretch); H n.m.r., τ (Ge)H, 4·2 (in C_6H_6 soln.) and *hydrobistri-n-propylphosphinetriphenylgermylplatinum*(II), $(Pr_3{}^nP)_2Pt(H)GePh_3$, $\nu_{max.}$ 1957 cm.$^{-1}$ (Pt–H stretch). H_2 absorbed; 0·31 mmole. (Calc. for the hydrogenolysis of one Pt–Ge bond, 0·36 mmole.) Their similar solubilities rendered separation of the two reaction products impossible.

Reaction Rate Measurements.—In two experiments $(Pr_3{}^nP)_2Pt(GePh_3)_2$ (302 mg.) in toluene (20 c.c.) was introduced into flasks equipped with break-seals, and, after thorough degassing, hydrogen was admitted so as 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 the excess hydrogen was measured.

At 0°	$t = 0$	$P_{H_2} = 186$ mm.	$V_{H_2} = 37{\cdot}7$ N* c.c.
	$t = 24$ hr.	$P_{H_2} = 170$ mm.	$V_{H_2} = 34{\cdot}4$ N* c.c.
		% Reaction = 54·8.	
At 25°	$t = 0$	$P_{H_2} = 181$ mm.	$V_{H_2} = 33{\cdot}56$ N* c.c.
	$t = 12$ hr.	$P_{H_2} = 155$ mm.	$V_{H_2} = 28{\cdot}73$ N* c.c.
		% Reaction = 80·1	

trans-*Bistriethylphosphineplatinum*(II) *Iodide and Triphenylgermyl-lithium.*—(*a*) *Using 2 equivalents of triphenylgermyl-lithium.* A filtered solution of triphenylgermyl-lithium, prepared from hexaphenyldigermane (5 g.) and lithium shot (1·5 g.) in 1,2-dimethoxyethane (20 c.c.), was added dropwise to the iodide (4·4 g.) 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 1½ 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 light petroleum (50 c.c.; b. p. 40—60°) removed a small amount of tarry material. The residue was extracted with hot propan-2-ol (150 c.c.), leaving $(Et_3P)_2Pt(GePh_3)_2$ (3·9 g., 54%) undissolved. The propan-2-ol solution yielded hydrobistriethylphosphinetriphenylgermylplatinum(II) (0·3 g.), as colourless plates (Found: C, 49·3; H, 6·2. Calc. for $C_{30}H_{46}GeP_2Pt$ 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 ($\nu_{max.}$ 2042 cm.$^{-1}$) compared with the value in benzene solution ($\nu_{max.}$ 2051 cm.$^{-1}$).

(*b*) *Using less than 2 equivalents of triphenylgermyl-lithium.* In a similar experiment triphenylgermyl-lithium prepared from hexaphenyldigermane (6 g.) in monoglyme (15 c.c.) was added to the iodide (5·5 g.) in a 2 : 1 ether–benzene solution (100 c.c.). Hydrolysis, after 3 hr. under reflux, gave hexaphenyldigermane (1·5 g., 25%). Infrared examination of the organic residue showed *trans*-$(Et_3P)_2Pt(H)I$, $\nu_{max.}$ 2163 cm.$^{-1}$ (Pt–H) and $(Et_3P)_2Pt(H)GePh_3$, $\nu_{max.}$ 2042 cm.$^{-1}$ (Pt–H). Extraction with hot ethanol (150 c.c.) left $(Et_3P)_2Pt(GePh_3)_2$ (2·8 g., 33%) undissolved. The ethanol solution yielded *bistriethylphosphinetriphenylgermylethoxyplatinum*(II), $(Et_3P)_2Pt(OEt)GePh_3$ (0·4 g.), as colourless plates, m. p. 160—170° (decomp.) [Found: C, 49·3; H, 6·35; P, 7·8, 7·2%; *M* (*X*-ray), 772 (density 1·48). $C_{32}H_{50}GeOP_2Pt$ requires C, 49·25; H, 6·5; P, 7·9%; *M*, 780]. The ^1H n.m.r. spectrum of this complex at 60 Mc./sec. showed a quartet at τ 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. $(Et_3P)_2Pt(OEt)GePh_3$ requires 1 : 16·5. The ethanolic mother-liquors gave a brown tar from which *trans*-$(Et_3P)_2Pt(H)I$ (0·5 g.), $\nu_{max.}$ 2163 cm.$^{-1}$ (Pt–H), ^1H n.m.r. (in C_6D_6) (Pt)H τ 22·8, was isolated by sublimation (100°/10^{-4} mm.). Chromatography of the non-volatile residue on alkaline alumina [eluent 1 : 1 benzene–light petroleum (b. p. 40—60°)] gave a trace of $(Et_3P)_2PtI_2$ (Found: C, 21·0;

H, 4·8. Calc. for $C_{12}H_{30}I_2P_2Pt$: C, 21·0; H, 4·4%), tetraphenylgermane and *bistriethylphosphineiodophenylplatinum*(II), $(Et_3P)_2Pt(I)Ph$ (0·22 g.), m. p. 101—102° from methanol (Found: C, 34·0; H, 5·5. $C_{18}H_{35}IP_2Pt$ 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, $(Et_3P)_2Pt(OEt)GePh_3$ (0·5 g.), and unreacted $(Et_3P)_2PtI_2$ (2 g., 36%). The tarry residue (1·5 g.) again contained *trans*-$(Et_3P)_2Pt(H)I$.

Ligand Exchange Reactions of Bistriethylphosphinetriphenylgermylethoxyplatinum(II).—*Isopropoxide*. The ethoxide (0·05 g.) was heated under reflux with propan-2-ol (10 c.c.) for 5 min. *Bistriethylphosphinetriphenylgermylisopropoxyplatinum*(II), $(Et_3P)_2Pt(OPr^i)GePh_3$, m. p. 162—172° (decomp.), separated on cooling (Found: C, 49·6; H, 6·5. $C_{33}H_{52}GeOP_2Pt$ requires C, 49·9; H, 6·6%).

Methoxide. Similarly, using methanol gave *bistriethylphosphinetriphenylgermylmethoxyplatinum*(II), $(Et_3P)_2Pt(OMe)GePh_3$, m. p. 172—180° (decomp.) (Found: C, 48·6; H, 6·35. $C_{31}H_{48}GeOP_2Pt$ requires C, 48·6; H, 6·3%).

Hydroxide. *Bistriethylphosphinetriphenylgermylhydroxyplatinum*(II), $(Et_3P)_2Pt(OH)GePh_3$, m. p. 153—156° (decomp.), crystallised from 1 : 1 aqueous acetone (30 mg. in 25 c.c.) (Found: C, 47·6; H, 5·8. $C_{30}H_{46}GeOP_2Pt$ requires C, 47·9; H, 6·2%). Its i.r. spectrum showed a sharp band at 3630 cm.$^{-1}$, characteristic of unassociated OH. The ethoxy-complex was regenerated from this compound in ethanol.

Bistri-n-propylphosphinebistriphenylgermylplatinum(II) *and Magnesium Iodide*.—The complex (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.), and the mixture stirred at 20° for 46 hr. Hydrolysis of the turbid solution with air-free water, gave an 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 *trans*-$(Pr^n_3P)_2PtI_2$, m. p. 116—117° (220 mg., 68%), and then iodotriphenylgermane, m. p. 145—147° (70 mg., 20%). Sublimation of the residue (60°/10^{-4} mm.) gave an inseparable mixture of triphenylgermane [ν (Ge–H), 2034 cm.$^{-1}$] and a hydroplatinum complex having ν(Pt–H) 1731 cm.$^{-1}$. The residue from the sublimation consisted of a trace of hexaphenyldigermoxane.

A similar experiment, using $(Pr^n_3P)_2Pt(GePh_3)_2$ (0·42 g.), with hydrolysis after 30 min. and normal work-up, gave hexaphenyldigermane (5 mg.) and, from ethanol solution, *bistri-n-propylphosphinetriphenylgermyliodoplatinum*(II), $(Pr^n_3P)_2Pt(I)GePh_3$ (36 mg.) as pale yellow crystals, m. p. 148—149° (Found: C, 45·8; H, 6·3. $C_{36}H_{57}GeIP_2Pt$ requires C, 45·2; H, 6·1%). The ethanol mother-liquors at this stage contained triphenylgermane but, on further concentration in air, hexaphenyldigermoxane (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. Sublimation of the residue gave a mixture of hydroplatinum complexes [ν(Pt–H) 2165 and 1731 cm.$^{-1}$], which could not be separated.

Bistri-n-propylphosphinebistriphenylgermylplatinum(II) *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°, after which the ether was separated by distillation and replaced by benzene. Filtration gave a colourless filtrate containing only triphenylgermane (0·32 g., 98%). The residue, a yellow platinum complex, which was insoluble in organic solvents, took fire in air, and did not react with either bromobenzene or methyl iodide at 20°. Treatment with aqueous ether at −78° resulted in some effervescence and, on warming to −20°, platinum was deposited with further evolution of hydrogen. Addition of triphenylphosphine did not lead to a stable hydroplatinum complex.

Iodotrimethylplatinum(IV) *and Triphenylgermyl-lithium*.—Triphenylgermyl-lithium, from hexaphenyldigermane (1·3 g.) and lithium (1·0 g.) in 1,2-dimethoxyethane (20 c.c.), was added slowly to the complex (1·25 g.) in 2 : 1 benzene–ether (100 c.c.). A black precipitate formed over 18 hr. The soluble fraction yielded methyltriphenylgermane [ρ(CH_3–Ge) 788; ν(Ge–CH_3) 586 cm.$^{-1}$]. The black residue (1·1 g.) which showed no i.r. bands, ignited in air.

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