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Organogermyl Complexes of Platinum and Palladium

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Received November 14, 1967

cis-*Triphenylgermylplatinum complexes of the type (phosphine)$_2$Pt(GePh$_3$)$_2$ are reported, and dipole moment measuremenst indicate extensive isomerisation in solution. Ligand exchange reactions with Ph$_2$PC$_2$H$_4$PPh$_2$ and CN$^-$ either lead to new Ge–Pt complexes or result in cleavage of the Pt–Ge bonds. Factors affecting the stability of the complexes and the mechanism of bond cleavage by H$_2$ and HCl are discussed. Mass spectra of the new complexes are reported.*

Introduction

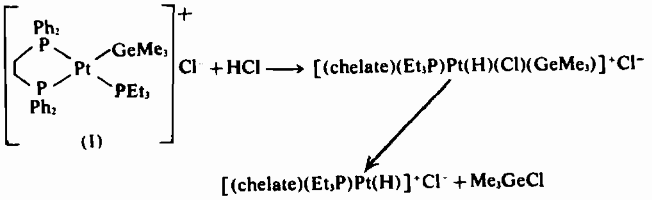
The formation, stability and reactions of a variety of compounds containing germanium bonded to transition metals have been described, and of these platinum complexes are the most fully investigated.[1,2] Preparative methods are illustrated below:

$$(R_3P)_2PtCl_2 + 2Ph_3GeLi \rightarrow (R_3P)_2Pt(GePh_3)_2 + 2LiCl$$

$$(Et_3P)_2PtCl_2 + (Me_3Ge)_2Hg \rightarrow$$
$$(Et_3P)_2Pt(Cl)GeMe_3 + Me_3GeCl + Hg$$

$$(R_3P)_2Pt(H)Cl + R'_3GeH \rightleftharpoons (R_3P)_2Pt(Cl)GeR'_3 + H_2$$

The greater thermal stability of germylplatinum complexes over their palladium analogues corresponds to the situation with their organo derivatives.[3] In all these complexes the centre of reactivity is the transition metal and the majority of reactions have been interpreted in terms of primary addition to Pt^{II} followed by an elimination reaction from an octahedral Pt^{IV} intermediate. In only one case, however, has a platinum(IV) intermediate been isolated:[4]



This paper is concerned with the factors influencing the stability and reactivity of Ge–Pt and Ge–Pd complexes. They include *a* the coordination number, stereochemistry and oxidation state of the transition metal, *b* the charge on the complex, *c* the groups attached to the germanium atom and *d* the nature of the remaining ligands.

Results and Discussion

It is probable that all Pd–Ge complexes so far described are *trans* isomers; attempts to prepare *cis* complexes of the type (phosphine)$_2$Pd(GePh$_3$)$_2$ have been unsuccessful. With platinum, however, several *cis* isomers have been isolated containing one or two triphenylgermyl groups, and these are quite stable in solution. Thus triphenylgermyl-lithium and the *cis*-chelating complex (Ph$_2$PC$_2$H$_4$PPh$_2$)PtI$_2$ form the *cis* compound (Ph$_2$PC$_2$H$_4$PPh$_2$)Pt(GePh$_3$)$_2$ as a white solid. Similarly the reaction between Ph$_3$GeLi and *cis*-(Et$_3$P)$_2$PtBr$_2$ gives the colourless *cis*-complex, (Et$_3$P)$_2$-Pt(GePh$_3$)$_2$. Dipole moment measurements on these two compounds provide evidence for *cis-trans* interconversion in benzene solution. Whereas the chelate complex has a moment of 8.85 D., *cis*-(Et$_3$P)$_2$Pt(GePh$_3$)$_2$ gives, after a few hours, an apparent moment of 4.45 D. and the solution becomes progressively more yellow with time. The pure *trans* isomer, which is pale yellow in the solid state, likewise isomerises in solution since it gives a net moment of 2.4 D.[1] Presumably, given sufficient time, the same resultant moment would be obtained from both forms. Earlier studies on organoplatinum derivatives suggests that isomerisation only occurs *via* ionic intermediates,[3] but such a mechanism is unlikely in this case, since the complexes are quite stable in solution. Further evidence that an alternative process can operate is found in the thermal rearrangement of *cis*-(Ph$_3$P)$_2$Pt(C$_6$F$_5$)$_2$.[5] Possibly under the influence of solvent or high temperatures a ligand can alter position (via one of the vacant coordination sites) without being completely detached from the metal.

Varying the groups attached to germanium can affect the stability and reactivity of the complex since the *trans* effect of the R$_3$Ge moiety will vary. Also elimination reactions within the R$_3$Ge group may be possible. The extremely high *trans* effect of the Me$_3$Ge group is shown by the low Pt–Cl stretching frequency[2] in the complex *trans*-(Et$_3$P)$_2$Pt(Cl)GeMe$_3$. Our attempts to prepare the bistrimethylgermyl complex by the reaction of either *cis*-(Et$_3$P)$_2$PtCl$_2$ or *trans*-(Et$_3$P)$_2$Pt(Cl)-

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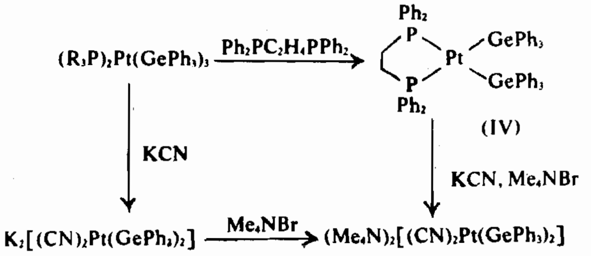
(1) R. J. Cross and F. Glockling, *J. Chem. Soc.*, 5422 (1965).
(2) F. Glockling and K. A. Hooton, *J. Chem. Soc.*, (A), 1066 (1967).
(3) R. J. Cross, *Organometallic Chem. Rev.*, *2*, 97 (1967).
(4) F. Glockling and K. A. Hooton, *J. Chem. Soc.*, (A), in the press.
(5) D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc.*, 5275 (1965).

$GeMe_3$ with trimethylgermyl-lithium have led to coloured decomposition products together with evidence for halogen-metal exchange. Thus the complex, $(Et_3P)_2Pt(GeMe_3)_2$ is probably inherently unstable at room temperature. Similarly, the hydrido complex, $(Et_3P)_2Pt(H)GeMe_3$, obtained as a liquid mixture of isomers by the reaction between $(Et_3P)_2Pt(H)Cl$ and trimethylgermyl-lithium, is only marginally stable.

Attempts to prepare a Me_3Ge–Pd complex from the reaction between $(Et_3P)_2PdX_2$ and $(Me_3Ge)_2Hg$ have been unsuccessful. We have also attempted the formation of similar complexes with the grouping H_3Ge–Pt. Germyl-lithium or -potassium does not react with *cis*-$(Et_3P)_2PtCl_2$ at room temperature in benzene. At 50° reaction occurs but is accompanied by extensive decomposition from which only a black tar has been isolated. Once again this instability could be due to the *trans* activating effect of H_3Ge groups, but hydrogen or hydrogen chloride elimination reactions are also possible with this group.

The effect of other ligands attached to platinum on the stability and reactivity of the Ge–Pt bond can be quite marked. Ligand exchange reactions in which triethylphosphine or tri-n-propylphosphine in the complex $(R_3P)_2Pt(GePh_3)_2$ is replaced by cyanide or chelating phosphine readily occur.



(II) (III)

Rather surprisingly ligand exchange was not observed with triphenylphosphine, bipyridyl or thiocyanate. With excess of cyanide, the replacement proceeds slowly beyond $K_2[(CN)_2Pt(GePh_3)_2]$ to give, eventually, $K_2Pt(CN)_4$ and hexaphenyldigermane.

The cyanide complexes (II) and (III) show only a single cyanide stretching frequency (2076 cm^{-1}) and are therefore probably the *trans* isomers. Their thermal stability is considerably greater than that of the neutral phosphine complexes; decomposition occurs above 260° and they are stable to air and water. This enhanced stability may be a crystal lattice effect, although the palladium complex $(Me_4N)_2[(CN)_2Pd(GePh_3)_2]$ also shows an increased stability in solution.[6]

The reaction between 1,2-bisdiphenylphosphinoethane and the hydride, $(Et_3P)_2Pt(H)GePh_3$ proceeds differently. Triphenylgermane is eliminated with the formation of a platinum(O) complex.

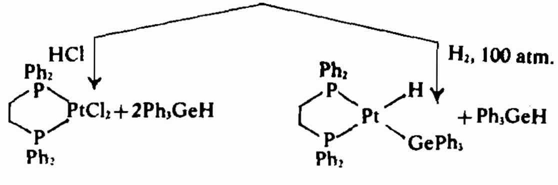
$$2Ph_2PC_2H_4PPh_2 + (Et_3P)_2Pt(H)GePh_3 \longrightarrow [Ph_2PC_2H_4PPh_2]_2Pt + 2Et_3P + Ph_3GeH$$

This reaction closely resembles that of the chelating phosphine with the complex *trans*-$(Et_3P)_2Pt(Cl)GeMe_3$, where triethylphosphine and a chloride ion are eliminated so that the final product is the salt(I).

The *cis* complex (IV) shows a greater thermal stability and a lower reactivity than its bis-triethylphosphine analogue. By contrast to the triethylphosphine complex hydrogenolysis of one Pt–Ge bond proceeds only under pressure, and this reduced reactivity has also been observed with other *cis* Pt–Ge and Pt–Si compounds.[2] The platinum hydride (V), a sparingly soluble white solid, shows ν(Pt–H) at 1998 cm^{-1}.

With excess hydrogen chloride in benzene both Pt–Ge bonds are cleaved to give exclusively the platinum dichloride complex and triphenylgermane. With one or two equivalents of hydrogen chloride in ether, however, no reaction occurred over 20 days at 20°

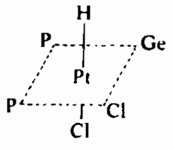
(IV)



(V)

trans Complexes differ in their cleavage by hydrogen chloride in that the second group is removed as R_3MCl. Hydrogen chloride reacts with benzene solutions of $(Et_3P)_2Pt(GePh_3)_2$ to give both $(Et_3P)_2Pt(H)Cl$ and $(Et_3P)_2PtCl_2$,[1] and these solutions are now known to contain both *cis* and *trans* germyl complexes.

There is considerable evidence that these and related hydrogen chloride cleavage reactions involving platinum(II) complexes proceed by an addition-elimination mechanism.[7] If we assume that only *cis* elimination reactions from an octahedral Pt^{IV} intermediate are possible, then the differences in behavior of *cis* and *trans* complexes may be interpreted in terms of the stereochemistry of the 6-coordinate intermediate. Cleavage of the first Ge–Pt bond resulting in elimination of R_3GeH must be governed by kinetic factors since one R_3Ge group is *cis* to both H and Cl. If the phosphine ligands are mutually *cis* then the second germanium group is most likely to be *cis* to hydrogen as in (VI) and elimination of R_3GeH again occurs. If, however, the phosphine ligands are *trans* then the germyl group may be *trans* to hydrogen as in the intermediate (VII) when *cis* elimination of R_3GeCl will occur.



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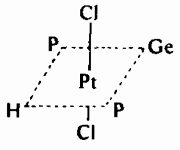

(VII)

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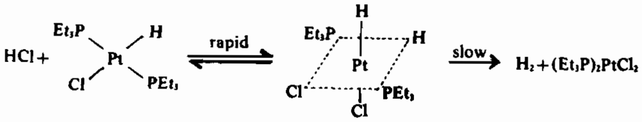
(6) E. H. Brooks and F. Glockling, *J. Chem. Soc.*, (A), 1241 (1966).

(7) U. Belluco, M. Giustiniani, and M. Graziani, Chemical Society Meeting, Durham, England (1967); U. Belluco, U. Croatto, P. Uguagliati, and R. Pietropaolo, *Inorg. Chem.*, *6*, 718 (1967).

The reversible addition of hydrogen chloride to $(Et_3P)_2Pt(H)Cl$ is well known[3] and, on prolonged heating in a sealed system, the octahedral addition product slowly eliminates hydrogen. Belluco and co-workers[7] have also observed this reaction. The infrared Pt–H stretching frequencies of $(Et_3P)_2Pt(H)_2Cl_2$ suggest that the hydrogen atoms are mutually *cis*, hence this reaction may be represented as:



The reaction between $(Et_3P)_2Pt(H)GePh_3$ and hydrogen chloride also results in elimination of hydrogen.

The complex (IV) reacts with carbon monoxide under pressure to give a yellow solid product, stable to air and water, but this could not be purified. It showed one carbonyl frequency (2058 cm^{-1}) in the i.r. and evolved carbon monoxide on treatment with cyanide. The palladium complex, $(Et_3P)_2Pd(GePh_3)_2$ also reacts with carbon monoxide to give hexaphenyldigermane and an unstable red oil which showed five bands ascribable to carbonyl groups.

The reactions between triphenylgermyl-lithium and the platinum halide complexes $(py)_2PtCl_2$, $(PhCN)_2PtCl_2$, (1,5-cyclooctadiene)$PtCl_2$ and $(Et_3P)_2Pt_2Cl_4$ failed to produce stable Pt–Ge compounds. This is somewhat surprising as organo-platinum and -palladium derivatives have been isolated using these and similar ligands. Possibly the decomposition results from the method of preparation, rather than from an inherent instability of the complexes.

Mass Spectra. Low resolution mass spectra of $(Ph_2PC_2H_4PPh_2)Pt(GePh_3)_2$, $(Ph_2PC_2H_4PPh_2)Pt(H)GePh_3$, $(Ph_2PC_2H_4PPh_2)Pt(Me)GePh_3$ and $(Ph_2PC_2H_4PPh_2)_2Pt$ have been examined. Molecular ions were observed for each complex, with the exception of (IV), and the platinum(O) complex also showed and extremely strong doubly charged molecular ion, $(Ph_2PC_2H_4PPh_2)_2Pt^{2+}$, reflecting the removal of two non-bonding electrons. The main features of the fragmentation are progressive loss of phenyl radicals from both phosphorus and germanium. The ion $(Ph_2PC_2H_4PPh_2)Pt^+$ readily loses ethylene. All four spectra provide evidence for a transfer of phenyl groups from germanium or phosphorus to platinum as has been observed in the mass spectra of other metal-metal bonded compounds,[8] and by thermal migration in Pt–$SnPh_3$ complexes.[9]

Experimental Section

All operations on air-sensitive materials were carried out under an atmosphere of pure, dry nitrogen. Mass spectra were recorded on an A.E.I. M.S. 9 mass spectrometer.

cis-*Bistriethylphosphinebistriphenylgermylplatinum(II), cis-$(Et_3P)_2Pt(GePh_3)_2$.* Triphenylgermyl-lithium, prepared from hexaphenyldigermane (9 g.) and lithium shot (3 g.) in 1,2-dimethoxyethane (20 c.c.), was added slowly to a colourless suspension of *cis*-$(Et_3P)_2PtBr_2$ (5.5 g.) in ether (100 c.c.). A yellow precipitate and brown solution were produced, and the emergent nitrogen stream smelt of triethylphosphine. After stirring overnight and refluxing for 1 hour, the mixture was hydrolysed with deaerated water. Distillation of solvents gave, by extraction with light petroleum (B.pt. 40-60°), some triphenylgermane (ν(Ge–H), 2035 cm^{-1}) formed by hydrolysis of unreacted Ph_3GeLi and a trace of $(Et_3P)_2PtH(GePh_3)$ (ν(Pt–H), 2041 cm^{-1}). Extraction of the residue with hot ethanol (150 c.c.) left *cis*-$(Et_3P)_2Pt(GePh_3)_2$ (6.5 g., 58%) undissolved. The pure complex was obtained by Soxhlet extraction with petroleum (B.pt. 40-60°) as a white solid which decomposed at 175-180°. (Found: C, 55.8; H, 6.15; P, 6.0. $C_{48}H_{60}Ge_2P_2Pt$ requires C, 56.0; H, 5.8; P, 6.0%). The ethanol solution gave a brown tar from which Ph_4Ge and Ph_6Ge_2O were obtained by alumina chromatography. A small amount of platinum metal was also produced.

The infrared spectra of *cis*-$(Et_3P)_2Pt(GePh_3)_2$ differs from that of the *trans* complex only below 400 cm^{-1}. (316 m, 302 s, 279 s, 224 m, 222 m). Solutions of the complex in benzene turn yellow and have a dipole moment of 4.45 D.

cis-*1,2-Bisdiphenylphosphinoethanebistriphenylgermylplatinum(II).* Triphenylgermyl-lithium, prepared from Ph_6Ge_2 (5.7 g.) and lithium shot (1.5 g.) in monoglyme (20 c.c.), was added slowly to a suspension of $(Ph_2PC_2H_4PPh_2)PtI_2$ in a 1:1 ether-benzene mixture (150 c.c.). The reaction was exothermic and a yellow colour developed. After refluxing for 2 hours and stirring overnight, the mixture was hydrolysed with deaerated water. Removal of solvents from the organic part, and extraction with light petroleum (B.pt. 40-60°) left *cis*-$(Ph_2PC_2H_4PPh_2)Pt(GePh_3)_2$ as a white powder (6.6 g., 98%), m.p. 260-280° *ex* isopropanol (Found: C, 61.5; H, 4.6; P, 5.8. $C_{62}H_{54}Ge_2P_2Pt$ requires C, 61.5; H, 4.5; P, 5.9%). The petroleum solution contained some Ph_3GeH (from Ph_3GeLi).

$(Ph_2PC_2H_4PPh_2)Pt(GePh_3)_2$ is a colourless crystalline solid, stable to air and water. Its benzene solutions are colourless, and give a dipole moment of 8.85 D.

The same complex was obtained when 1,2-bis-diphenylphosphinoethane (225 mg.), *cis*-$(Et_3P)_2Pt(GePh_3)_2$ (0.5 g.) and benzene (50 c.c.) were refluxed for 24 hours. Volatile material was removed under vacuum and condensed onto methyl iodide giving triethylmethylphosphonium iodide (0.2 g., 93%). The non-volatile product consisted of $(Ph_2PC_2H_4PPh_2)Pt(GePh_3)_2$ (0.55 g., 95%), obtained above. A similar reaction using *trans*-$(Et_3P)_2Pt(GePh_3)_2$ gave the same products.

cis-*$(Et_3P)_2Pt(GePh_3)_2$ and KCN.* To a suspension of *cis*-$(Et_3P)_2Pt(GePh_3)_2$ (0.6 g.) in ethanol (50 c.c.) was added a solution of potassium cyanide (38 mg.) in water (1 c.c.). A strong smell of triethylphosphine was noticed in the emergent nitrogen stream. The mixture was refluxed for 30 min. when the product, *dipotassium dicyano-bis-triphenylgermylplatinite*, $K_2[(CN)_2Pt(GePh_3)_2]$ was separated as a white crystalline

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(8) D. B. Chambers and F. Glockling, *J. Chem. Soc.*, (A), 735 (1968).
(9) M. C. Baird, *J. Inorg. Nucl. Chem.*, *29*, 367 (1967).

precipitate and washed with ethanol (0.3 g., 56%; decomp. without melting above 300°). (Found: C, 48.6; H. 3.8; N, 2.8%. ν(C N) 2076 cm^{-1} in Nujol $C_{38}H_{30}Ge_2K_2N_2Pt$ requires C, 48.9; H, 3.2; N, 3.0%).

The volatile part of the mother liquors with methyl iodide gave $[MeEt_3P]^+I^-$ (0.25 g., 84%). The residue could not be resolved, but contained several ir. bands due to ν(CN).

The potassium salt dissolves in acetone and addition of a methanol solution of $Me_4N^+Br^-$ yields *$(Me_4N)_2[(CN)_2Pt(GePh_3)_2]$* as a colourless crystalline precipitate. (Decomp. 260°. Found: C, 54.0; H, 5.7; N, 6.0%. ν(CN) 2079 cm^{-1} in KBr. $C_{46}H_{84}Ge_2N_4Pt$ requires C, 55.1; H, 5.4; N, 5.6%).

Both *trans*-$(Et_3P)_2Pt(GePh_3)_2$ and $(n\text{-}Pr_3P)_2Pt(GePh_3)_2$ reacted with KCN in a similar manner to give $K_2[(CN)_2Pt(GePh_3)_2]$.

A similar experiment using excess cyanide gave after 10 hours at 20° hexaphenyldigermane, m.pt. 335-337° as a white precipitate. Solvents and triethylphosphine were removed under vacuum, and the resulting pale yellow solid extracted with benzene. The infrared spectrum of the residue in methanol solution showed three major bands due to ν(CN). Two of these were ascribable to $K_2Pt(CN)_4$ (2137 cm^{-1}) and to KCN (2086 cm^{-1}). The third band at 2108 cm^{-1} is probably due to the complex $K_2[(CN)_3Pt(GePh_3)]$. In support of this, weak bands due to Ph_3Ge were also observed and the band at 1080 cm^{-1} is characteristic of Ph_3Ge–M complexes.[10]

$(Ph_2PCH_2CH_2PPh_2)Pt(GePh_3)_2$ and KCN. The complex (50 mg.) in acetone suspension (30 c.c.) was added to a solution of KCN (6 mg.) in water (0.2 c.c). The clear solution, with tetramethylammonium bromide (13 mg.) in methanol (1 c.c.), gave a crystalline precipitate of $(Me_4N)_2[(CN)_2Pt(GePh_3)_2]$ (14 mg.). (Found: C, 52.7; H, 6.1; N, 6.0%. ν(CN) 2080 cm^{-1} (KBr). $C_{46}H_{84}Ge_2N_4Pt$ requires C, 55.1; H, 5.4; N, 5.6%).

The mixed solvents were removed from the solution and the residue extracted in air by benzene. The benzene solution yielded the phosphine oxide $Ph_2P(O)C_2H_4P(O)Ph_2$ whilst the insoluble residue consisted of a mixture of cyanide complexes (ν(CN), 2132 w, 2114 sh, 2102 s and 2077 s cm^{-1} KBr).

$(Ph_2PC_2H_4PPh_2)Pt(GePh_3)_2$ and hydrogen chloride. Dry hydrogen chloride was passed through a solution of the complex (50 mg.) in benzene (50 c.c.) for 1 hour. Removal of the solvent and extraction with light petroleum (B.pt. 40-60°) left $(Ph_2PC_2H_4PPh_2)PtCl_2$ (dec. above 320°, *ex* ethanol. I.r. identical to authentic sample). The solution contained only triphenylgermane (ν(Ge–H) 2037 cm^{-1}).

When samples of $(Ph_2PC_2H_4PPh_2)Pt(GePh_3)_2$ were sealed with one and two equivalents of HCl in ether solvent, no reaction occurred after 20 days at 25°, the HCl being recovered quantitatively.

Hydrogenolysis of $(Ph_2PC_2H_4PPh_2)Pt(GePh_3)_2$. The complex (0.4 g.) in benzene (15 c.c.) was shaken with hydrogen for two days at 50° and 100 atmospheres. Removal of the solvent from the resulting clear solution left a white powder. Extraction with pentane gave triphenylgermane (0.15 g., ν(Ge–H) 2036 cm^{-1}). Recrystallisation of the residue from benzene gave the hydrido-complex *$(Ph_2PC_2H_4PPh_2)Pt(H)GePh_3$*, [M. pt. 221-223° dec. Found: C, 57.4; H, 4.38%; M (mass spec.), 898. $C_{44}H_{40}GeP_2Pt$ requires C, 58.7; H, 4.47%; Mol. wt (mass spectrum), 898 for ^{268}(PtGe)]. This compounds shows ν(Pt–H) at 1998 cm^{-1} (Nujol). $(Ph_2C_2H_4PPh_2)Pt(GePh_3)_2$ did not react with H_2 at 20° and one atmosphere pressure.

$(Et_3P)_2PtH(GePh_3)$ and $Ph_2PC_2H_4PPh_2$. To a solution of bistriethylphosphinetriphenylgermylhydridoplatinum(II) (347 mg., 0.47 mmoles) in benzene (20 c.c.) was added 1,2-bisdiphenylphosphinoethane (188 mg., 0.47 mmoles) in benzene (5 c.c.). The mixture turned yellow and was stirred for 3.5 hours at room temperature. The volatile part was removed under vacuum and condensed onto methyl iodide, giving methyltriethylphosphonium iodide (75 mg., 44%). Triphenylgermane (109 mg., 76%. ν(GeH) at 2036 cm^{-1}) was isolated by extraction of the residue with petroleum ether. Extraction with benzene gave starting material, $(Et_3P)_2PtH(GePh_3)$, (100 mg., 29%) whilst addition of petroleum ether (B.Pt. 40-60°) to the yellow solution precipitated $(Ph_2PC_2H_4PPh_2)_2Pt^0$ as a yellow solid (200 mg., 43%. Mol. wt. (mass spectrum) 991 for ^{195}Pt).

$(Et_3P)_2PtH(GePh_3)$ and hydrogen chloride. The complex (0.15 g., 0.204 mmoles), hydrogen chloride (4.56 c.c. at N.T.P., 0.204 mmoles) and ether (10 c.c.) were shaken in a sealed tube for 4 days at 20°. The tube was opened to a vacuum apparatus giving hydrogen (2.4 c.c. at N.T.P., 53%). No HCl was recovered. The involatile semi-solid residue was extracted with hexane and left a residue of starting material, $(Et_3P)_2PtH(GePh_3)$. Removal of hexane gave a semi-solid mixture containing $(Et_3P)_2PtHCl$ (ν(Pt–H) 2195 cm^{-1}) and Ph_3GeH (ν(Ge–H) 2045 cm^{-1}).

trans-*$(Et_3P)_2PtHCl$ and HCl.* The complex (0.43 g.), ether (15 c.c.) and excess hydrogen chloride (26 c.c. at N.T.P.) were heated in a sealed tube at 75° for ten days, when the temperature was briefly raised to 100°. Hydrogen (21.17 c.c. at N.T.P., 98%) was formed. The solid residue contained no Pt–H and consisted of *cis*-$(Et_3P)_2PtCl_2$ (m.pt. 188-191° *ex* EtOH), with a trace of *trans*-isomer.

Reaction of Ph_3GeLi with 1,5-cyclooctadieneplatinum(II)chloride. Triphenylgermyl-lithium, prepared from Ph_3GeH (7.3 g., 24 mmole) and n-butyllithium (27 mmole) in ether (50 c.c.) was added dropwise to a suspension of $(C_8H_{12})PtCl_2$ (4.0 g., 10.7 mmole) in benzene (100 c.c.). The exothermic reaction produced a brown colour, followed by a black precipitate. After stirring for 18 hours, solvents were removed under vacuum. The black residue contained no 1,5-cyclooctadiene, indicating complete decomposition, and no identifiable primary products were obtained.

Similar reactions between two equivalents of Ph_3GeLi and *cis*-$(py)_2PtCl_2$, $(Et_3P)_2Pt_2Cl_4$ and $(RhCN)_2PtCl_2$ also led to complete decomposition.

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(10) R. J. Cross and F. Glockling, *J. Organometallic Chem.*, 3, 146 (1965).

Trimethylgermyl-lithium and trans-*$(Et_3P)_2PtHCl$.* Trimethylgermyl-lithium, prepared from $(Me_3Ge)_2Hg$ (2.0 g.) and lithium (1.0 g.) in T.H.F. (40 c.c.), was added dropwise to a solution of $(Et_3P)_2PtHCl$ (3 g., 6.4 mmole) in T.H.F. (70 c.c.). The Me_3GeLi solution remained yellow-brown, but a precipitate formed. After stirring overnight, the mixture turned green. The solvent was removed under vacuum and the residue extracted with hexane giving unreacted $(Et_3P)_2PtHCl$ (0.8 g,. 27%) (i.r. identification). Removal of the hexane left $(Et_3P)_2PtH(GeMe_3)$ as a slightly impure oil. Its i.r. and n.m.r. spectra were identical to those previously reported[4] (ν(Pt–H) at 2037 and 1923 cm^{-1}).

A similar reaction between Me_3GeLi and $(Ph_3P)_2PtHCl$ produced an unstable solid which appeared to be $(Ph_3P)_2PtH(GeMe_3)$. This had ν(Pt–H) at 2055 cm^{-1}, and showed i.r. bands and n.m.r. absorptions typical of Me_3Ge and Ph_3P groups. Attempts to purify it by recrystallisation from petroleum at low temperatures failed.

Reaction of germylpotassium and germyl-lithium with cis-*$(Et_3P)_2PtCl_2$.* Germylpotassium was prepared as the grey powder $GeH_3K.2NH_3$ from the reaction between potassium (0.175 g., 4.5 mmoles) and germane (6.2 mmoles) in liquid ammonia, followed by removal of the solvent under vacuum. This was mixed with a suspension of *cis*-$(Et_3P)_2PtCl_2$ (1.1 g., 2.2 mmoles) in benzene (150 c.c.). No reaction took place at 40° but at 60°, decomposition began giving a black solution which was rapidly cooled but on normal work-up only an intractable black tar was obtained. A similar reaction with H_3GeLi led to extensive decomposition at 55°.

Bistriethylphosphinepalladiumdichloride and $(Me_3Ge)_2Hg$. A benzene solution of bistrimethylgermylmercury (0.9 g., 2.1 mmoles) was added dropwise to a solution of $(Et_3P)_2PdCl_2$ (0.85 g., 2.1 mmoles) in a 1:5 benzene-ether mixture (60 c.c.) at –10°. Mercury was deposited over 30 min. at room temperature, and was removed by filtration. On standing at –20°, the mixture slowly decomposed in solution. A trace of the binuclear complex $(Et_3P)_2PdCl_4$ was isolated (M.pt. 252°) from the grey deposit of palladium and brown tar.

In a similar reaction using $(Et_3P)_2PdBr_2$ instead of the chloride, 91% of the starting complex was recovered after 2 hours at –30°, although precipitation of mercury was observed.

Carbonylation reactions. 1,2-Bisdiphenylphosphinoethanebistriphenylgermylplatinum (232 mg.) in benzene (40 c.c.) was agitated with carbon monoxide (90 atm.) for 5 days at 20°. The solid product, which was unaffected by air or water, had ν(CO) at 2058 cm^{-1}, and showed i.r. bands characteristic of Ph–P and Ph–Ge groups. It softened at 50°, and decomposed with gas evolutions above 140°, but heating at 100° *in vacuo* failed to remove the CO. The compound could not be crystallised from benzene, hexane or ethanol, though the latter solvent yielded a trace of Ph_6Ge_2.

The remaining material was treated with KCN in acetone-methanol on a vacuum line. Carbon monoxide was evolved (i.r. identification), and the involatile residue showed i.r. bands due to CN and Ph.

$(Et_3P)_2Pd(GePh_3)_2$ (1.0 g.) in benzene (20 c.c.) was agitated at 20° for 3 days under carbon monoxide (70 atm.). Filtration gave hexaphenyldigermane (0.485 g., 80%). Removal of solvent from the red solution gave a brown oil which progressively decomposed. Its i.r. spectrum showed CO bands at 2040, 1960, 1923, 1852 and 1808 cm^{-1}. In hexane solution these degenerated into one broad complex band centered on 1820 cm^{-1}.

Acknowledgment. Two of us (E.H.B. and R.J.C.) wish to thank the Science Research Council for research awards.