of the C=C frequencies modified by coordination to platinum(II) (*ca.* 1500 cm^{-1}) and palladium(II) (*ca.* 1530 cm^{-1}). For both elements, using both ligands, the tendency to form chelate complexes is affected by the anion present; iodide and especially thiocyanate ion tend to displace the coordinated double bond. This parallels the affinity of various anions for platinum(II) as derived from an equilibrium study of their reaction with Zeise's anion $[C_2H_4PtCl_3]^-$, *viz.*, $F \ll Cl < Br < I \ll NCS$.[22]

[22] I. Leden and J. Chatt, *J. Chem. Soc.*, 2936 (1955).

CONTRIBUTION FROM THE RICHARD BENBRIDGE WETHERILL LABORATORY,
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Some Syntheses of Platinum–Germanium Complexes

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A new series of compounds containing platinum–germanium bonds has been prepared from solutions of trichlorogermane in concentrated hydrochloric acid. The tetramethylammonium salt of hydridopentakis(trichlorogermyl)platinate(II), $[(CH_3)_4N]_2HPt(GeCl_3)_5$, and the yellow isomer of the tetramethylammonium salt of dichlorobis(trichlorogermyl)platinate(II), $[(CH_3)_4N]_2Cl_2Pt(GeCl_3)_2$, can be precipitated from such solutions under different conditions. The red isomer of tetramethylammonium dichlorobis(trichlorogermyl)platinate(II) is precipitated from a nitrobenzene solution of the tetramethylammonium hydridopentakis(trichlorogermyl)platinate(II) by the addition of diethyl ether. Various phosphonium salts and phosphine complexes also can be prepared from the hydrochloric acid solutions. Triphenylphosphonium tetrachlorobis(trichlorogermyl)platinate(IV), $[(C_6H_5)_3PH]_2Cl_4Pt(GeCl_3)_2$, and a yellow complex, chloro(trichlorogermyl)bis(triphenylphosphine)platinum(II), $[(C_6H_5)_3P]_2ClPt(GeCl_3)$, are formed under different conditions. Triphenylphosphonium tetrachlorobis(trichlorogermyl)platinate(IV) loses hydrogen chloride reversibly to form a different yellow complex, dichlorobis(trichlorogermyl)bis(triphenylphosphine)platinum(IV), $[(C_6H_5)_3P]_2Cl_2Pt(GeCl_3)_2$. A white solid, trichloro(trichlorogermyl)bis(triphenylphosphine)platinum(IV), $[(C_6H_5)_3P]_2Cl_3Pt(GeCl_3)$, is precipitated from a solution of *cis*-dichlorobis(triphenylphosphine)platinum(II) in acetone–diethyl ether by the addition of trichlorogermane. Direct treatment of $(Cl_3PPtCl_2)_2$ with trichlorosilane gives $(Cl_3PPtSiCl_3)_x$; treatment with trichlorogermane gives $(Cl_3PPtGeCl_3)_x$. There is some evidence for the formation of a Ni–Ge complex in the reaction of trichlorogermane with nickel(II) chloride in nitromethane solution.

Introduction

The chemistry of compounds containing group IVb elements bonded to platinum has been studied extensively in the past several years. A recent review by Cross[2] summarizes σ-bonded compounds of this type. In most cases the structure of these compounds is square-planar and platinum formally is in the +2 oxidation state. Complexes of the type $(R_3M)Pt(M'R_3)_nX_{2-n}$ (where $n = 1, 2$; R = alkyl, aryl; M = Sb, As, P; and M' = Si, Ge, Sn, Pb) generally are prepared from Grignard reagents or from lithium or sodium salts of $(R_3M')^-$ and the platinum halide. Species such as $(R_3P)_2Pt(SnCl_3)H$ are prepared from $(R_3P)_2PtClH$ and $SnCl_2$. Nyholm[3] used a novel synthetic method to prepare $[(C_6H_5)_3P]_2Pt(Cl)Sn(C_6H_5)_3$ from $[(C_6H_5)_3P]_4Pt$ and $ClSn(C_6H_5)_3$. Another method commonly used to prepare compounds containing transition metal–tin bonds is the displacement of carbon monoxide from metal carbonyls with stannous chloride. Thus, the treatment of $Pt(CO)_2Cl_2$ with stannous chloride is reported to yield a red platinum–tin complex which has not been characterized fully.[4]

Notable exceptions to the usual square-planar complexes are found among the tin–platinum-bonded compounds. In these cases pentacoordinated platinum and metal clusters are reported.

Since the first report of the red solutions produced by platinum salts and stannous chloride in 1835 there has been an interest in their composition.[5]

Numerous workers have attempted to explain the complexes present in these red solutions. Shukla[6] has reviewed this subject recently as have Meyers and Ayers.[7]

Two different research groups, headed by Lindsay[8] and Wilkinson,[4,9] reported the isolation and characterization of salts of several Pt–Sn complexes of which $[(CH_3)_4N]_2Cl_2Pt(SnCl_3)_2$ is representative.

Although Young, Gillard, and Wilkinson[4] suggested a complex with a tin:platinum ratio of 5:1, it took elegant and meticulous research by Lindsay,

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[1] (a) The work herein reported fulfilled in part the requirements for the degree of Doctor of Philosophy for J. K. Wittle at Purdue University, Jan 1968; (b) to whom inquiries concerning this publication should be addressed.

[2] R. J. Cross, *Organometal. Chem. Rev.*, **2**, 97 (1967).

[3] A. J. Layton, R. S. Nyholm, G. A. Pneumaticakis, and M. L. Tobe, *Chem. Ind.* (London), 465 (1967).

[4] J. F. Young, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 5176 (1964).

[5] R. J. Kane, *Phil. Mag.*, **7**, 399 (1835).

[6] S. K. Shukla, *Ann. Chim.* (Paris), [13] **6**, 1383 (1961).

[7] A. O. Meyers, Jr., and G. H. Ayers, *J. Am. Chem. Soc.*, **86**, 2671 (1964).

[8] R. D. Cramer, E. L. Jenner, R. V. Lindsay, Jr., and U. G. Stolberg, *ibid.*, **85**, 1691 (1963).

[9] A. G. Davies, G. Wilkinson, and J. F. Young, *ibid.*, **85**, 1692 (1963).

et al.,[10] to isolate and characterize the red complex ion $[Pt(SnCl_3)_5]^{3-}$. This pentacoordinate complex ion has the rare gas electronic configuration expected for platinum(II) but seldom found.

The unique bimetallic cage complex ion, $[Pt_3Sn_8Cl_{20}]^{4-}$, and the closely related neutral 1,5-cyclooctadiene complex, $Pt_3(SnCl_3)_2(C_8H_{12})_3$, also were isolated and characterized.[11]

The ability of $SnCl_2$ to reduce platinum to a zerovalent state probably contributes to the range of compounds in which $SnCl^{3-}$ appears as a ligand and possibly accounts for the formation of cage ion as in eq 1.

$$3[Cl_2Pt(SnCl_3)_2]^{2-} + 5SnCl_2 + 4Cl^- \longrightarrow [Pt_3Sn_8Cl_{20}]^{4-} + 3SnCl_6^{2-} \quad (1)$$

Only one transition metal complex has been reported in which $GeCl_3^-$ appears as a ligand. Nesmeyanov isolated $Cl_3GeMn(CO)_5$ from the products of the reaction of $(CO)_{10}Mn_2$ with trichlorogermane.[12]

There appears to be little reason why $GeCl_3^-$ should not form complexes analogous to the Pt–Sn examples previously discussed, since the bonding of the two ligands appears to be quite similar and the species differ only slightly in Lewis basicity.

In two papers published recently we find evidence that the ions MCl_3^- (M = Ge, Sn) do not differ greatly as ligands. Shriver, Shriver, and Johnson[13] have investigated the preparation and structures of $Cl_3Ge–BCl_3^-$ and $Cl_3Sn–BCl_3^-$. It is probable that these are simple σ-bonded complexes. There is no evidence of a measurable difference in the Lewis base strength of $GeCl_3^-$ and $SnCl_3^-$. The report of Jetz and Graham[14] on the force constants of the carbonyl stretch in the compounds $Cl_3MMn(CO)_5$ (M = Si, Ge, Sn) would indicate that all three ligands have a similar Lewis basicity.

We have prepared and characterized several germanium complexes of platinum which are analogous to the tin complexes. We have also found new types not reported among the Pt–Sn complexes. The +4 oxidation state of platinum is apparently stable in the presence of $GeCl_3^-$. Also, as a consequence of the somewhat smaller steric requirements of the $GeCl_3^-$ ligand, hexacoordinate complexes are quite common in this series although they are quite rare among the platinum–tin complexes.

The inability of $GeCl_2$ to reduce platinum suggested the possibility of forming $Ni–GeCl_3$ complexes analogous to the $Pt–SnCl_3$ and $Pt–GeCl_3$ complexes. We have obtained some evidence for the formation of such complexes but these are not yet characterized.

Discussion

When trichlorogermane is added to potassium tetrachloroplatinate(II) in concentrated hydrochloric acid to make a solution in which the ratio of germanium to platinum is 5:1, a deep red solution is obtained. Addition of tetramethylammonium chloride to this red solution results in the precipitation of a cream-colored solid. This solid has been identified as the tetramethylammonium salt of a new platinum–germanium complex ion, hydridopentakis(trichlorogermyl)platinate(II). The formula of this novel salt has been established, by the determination of its elemental composition, as $[(CH_3)_4N]_2HPt(GeCl_3)_5$. The ion, hydridopentakis(trichlorogermyl)platinate(II), probably has platinum in a hexacoordinate state with five $GeCl_3^-$ ligands and the H attached to the platinum. The infrared spectrum of the compound exhibits a band at 2083 cm^{-1} in the region typical of the Pt–H stretching frequency[15] consistent with that expected from the proposed structure.

We have assigned an oxidation number of IV to the platinum in this salt because of its close relationship to other salts we have prepared. The hydrogen is protonic, however, since treatment of the salt with trimethylamine vapor changes its color from cream to yellow and removes the infrared band ascribed to the Pt–H stretch. In this reaction almost 2 moles of trimethylamine may be taken up by the complex.

Among the analogous Pt–Sn complexes there appear to be no examples where the platinum is hexacoordinate. In the present Pt–Ge complexes, analysis rules out a −3 ion which seems to be the rule in pentacoordinate $[Pt(SnCl_3)_5]^{3-}$. Thus, some $GeCl_3^-$ complexes differ significantly from known Pt–Sn examples.

Platinum(IV) complexes of $SnCl_3^-$ apparently do not form as readily as the analogous $GeCl_3^-$ complexes. The only example of such a Pt–Sn complex previously reported was prepared with stannic chloride.[16]

We found several reactions in which a Pt(IV) complex is formed using Ge(II). One occurs when a solution of *cis*-dichlorobis(triphenylphosphine)platinum(II) is treated with trichlorogermane. This immediately precipitates an orange solid which rapidly redissolves and after several hours a different solid precipitates. The new white solid has a composition which best fits the formula $[(C_6H_5)_3P]_2Cl_3Pt(GeCl_3)$. It proved impossible to purify this complex but the analysis clearly rules out chloro(trichlorogermyl)bis(triphenylphosphine)platinum(II). The infrared spectrum displays no bands attributed to the triphenylphosphonium ion. Thus, all facts would support the formulation of the Pt(IV) complex given.

Other platinum(IV) complexes are formed when a solution of trichlorogermane and potassium tetrachloroplatinate(II) in concentrated hydrochloric acid, with a ratio of Ge:Pt of 5:1, is treated with tri-

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[10] R. D. Cramer, R. V. Lindsay, Jr., C. T. Prewitt, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965).

[11] R. V. Lindsay, Jr., G. W. Parshall, and U. G. Stolberg, *Inorg. Chem.*, **5**, 109 (1966).

[12] A. N. Nesmeyanov, K. N. Ansimov, N. E. Kolobova, and A. B. Antonova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1284 (1965).

[13] M. P. Johnson, D. F. Shriver, and S. A. Shriver, *J. Am. Chem. Soc.*, **88**, 1588 (1966).

[14] W. Jetz and W. A. G. Graham, *ibid.*, **89**, 2773 (1967).

[15] Literature values for the Pt–H stretching frequency are reported at: 2072 (s) cm^{-1}, 2052 (sh) cm^{-1} in $[(CH_3)_4N]_2HPt(SnCl_3)_5$; 2100 cm^{-1} in *trans*-$[(C_6H_5)_3P]_2Pt(SnCl_3)H$; 2103 cm^{-1} in *trans*-$[(C_2H_5)_3P]_2Pt(SnCl_3)H$; and 2205 cm^{-1} in $HPt[Si(CH_3)(C_6H_5)_2][P(CH_3)(C_6H_5)_2]$ (see ref 2 in this paper).

[16] M. C. Baird, *J. Inorg. Nucl. Chem.*, **29**, 367 (1967).

phenylphosphine. In this case, the orange-red phosphonium salt, $[(C_6H_5)_3PH]_2Cl_4Pt(GeCl_3)_2$, precipitates from solution. Both are complexes of platinum(IV). The phosphonium salt, $[(C_6H_5)_3PH]_2Cl_4Pt(GeCl_3)_2$, readily loses hydrogen chloride when heated at 130° *in vacuo*. This loss of hydrogen chloride proceeds until the phosphonium salt is completely converted to the yellow phosphine complex, $[(C_6H_5)_3P]_2Cl_2Pt(GeCl_3)_2$. This reaction is reversible and it is possible to convert $[(C_6H_5)_3P]_2Cl_2Pt(GeCl_3)_2$ to reasonably pure $[(C_6H_5)_3PH]_2Cl_4Pt(GeCl_3)_2$ by allowing the phosphine complex to stand in contact with hydrogen chloride for several days at room temperature (eq 2). At room temperature the equilibrium apparently favors the phosphonium salt. The product represents the equilibrated mixture under the conditions of the preparation. This impure phosphonium salt also can be converted to a reasonably pure state by treatment with hydrogen chloride at room temperature. The same equilibrium mixture of $[(C_6H_5)_3PH]_2Cl_4Pt(GeCl_3)_2$ and $[(C_6H_5)_3P]Cl_2Pt(GeCl_3)_2$ may be precipitated from a 1:5 molar ratio mixture of potassium hexachloroplatinate(IV) and trichlorogermane in hydrochloric acid by the addition of triphenylphosphine. The orange-red solid, $[(C_6H_5)_3PH]_2Cl_4Pt(GeCl_3)_2$, melts to a deep red liquid. The infrared spectrum is consistent with the phosphonium formulation. Infrared bands which may be attributed to the phosphonium cation are seen in the salt and disappear with the loss of hydrogen chloride.

$$[(C_6H_5)_3P]_2Cl_2Pt(GeCl_3)_2 + 2HCl \rightleftharpoons [(C_6H_5)_3PH]_2Cl_4Pt(GeCl_3)_2 \quad (2)$$

Meticulous assignments of infrared frequencies of some phosphonium salts have been made by Sheldon and Tyree[17] and by van den Akker and Jellinek.[18] These workers agree that the band at 2380 cm^{-1} is attributable to the P–H stretching mode, that at about 900 cm^{-1} to a bending mode, and the 1100 and 720 cm^{-1} bands are frequencies which are found in many tetracoordinated phosphorus compounds. All of these bands are found in the platinum–germanium complex phosphonium salts prepared in the present work.

Reaction of potassium hexachloroplatinate(IV) with stannous chloride[8] in hydrochloric acid, where the reactants are in similar ratios, produces the orange phosphine complex, $[(C_6H_5)_3P]_2Pt(SnCl_3)_2$. Thus, two differences are apparent in platinum–germanium chemistry. Namely, the greater tendency for forming phosphonium salts and the ease of formation of Pt(IV) complexes.

Other Pt–Ge complexes have been prepared in the present work which are completely analogous to Pt–Sn complexes. For example, when potassium tetrachloroplatinate(II) in hydrochloric acid is mixed with trichlorogermane in a germanium-to-platinum ratio of 2:1, a light red solution is formed which changes to a light yellow after 20–30 min at room temperature. Addition of triphenylphosphine, dissolved in ethanol, to this yellow solution produces a copious light yellow precipitate, $[(C_6H_5)_3P]_2ClPt(GeCl_3)$. The analogous tin compound $[(C_6H_5)_3P]_2ClPt(SnCl_3)$ can be prepared in a similar fashion.[4]

The complex ion $Cl_2Pt(SnCl_3)_2^{2-}$ has been prepared in a red form and a yellow form. The red form has been classified tentatively as the *trans* and the yellow as the *cis* form by Wilkinson.[4]

Similar red and yellow isomers of the analogous complex ion, $Cl_2Pt(GeCl_3)_2^{2-}$, can be isolated. The yellow isomer is formed when trichlorogermane is added to a concentrated hydrochloric acid solution of potassium tetrachloroplatinate(II) (germanium to platinum molar ratio of 2:1). The initial deep red solution becomes light yellow. Tetramethylammonium chloride precipitates a yellow compound, $[(CH_3)_4N]_2Cl_2Pt(GeCl_3)_2$, from this yellow solution. The red isomer is prepared by adding diethyl ether to bright red acetone solutions of tetramethylammonium hydridopentakis(trichlorogermyl)platinate(II).

We cannot assign definite configurations to the red and yellow forms. The yellow form is more soluble in polar solvents than the red. The yellow complex has an electronic absorption in the ultraviolet spectrum at 285 mμ while the absorption for the red complex is at 235 mμ.

The solubility would favor assigning the yellow form the *cis* configuration while the ultraviolet spectrum would argue for the opposite assignment.

All of the complexes containing a $GeCl_3$ group have a broad infrared band in the CsBr region at about 360–380 cm^{-1}. This is possibly a combination band of Pt–Cl stretching and $GeCl_3$ stretching modes.[19]

When an acetone solution of $[(CH_3)_4N]_2Cl_2Pt(SnCl_3)_2$ is treated with stannous chloride the platinum is reduced to the zerovalent state and an interesting cage species results. Treatment of the yellow isomer, $[(CH_3)_4N]_2Cl_2Pt(GeCl_3)_2$, with trichlorogermane failed to produce an analogous compound. The dichlorobis(trichlorogermyl)platinate(II) ion apparently is resistant to reduction by trichlorogermane in acetone. The same ion, however, can be reduced by stannous chloride since a red solution and deep red solid are formed upon the treatment of an acetone solution of $[(CH_3)_4N]_2Cl_2Pt(GeCl_3)_2$ with stannous chloride. This red solid may be the tetramethylammonium salt of the cage ion, $[Pt_3Sn_8Cl_{20}]^{4-}$, or it may contain germanium. It will be studied further.

While $SnCl_3^-$ apparently is not a σ donor to nickel(II),[20] it is possible that $GeCl_3^-$ may be since when trichlorogermane is added to $NiCl_2 \cdot 2H_2O$ in nitromethane or acetone a deep purple solution forms which fades during several hours. Formation of a colored solution suggests that a σ complex of the type formed in platinum chemistry may be present in this solution.

In the exploration of the analogous chemistry of

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[17] J. C. Sheldon and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **80**, 2117 (1958).

[18] M. van den Akker and F. Jellinek, *Rec. Trav. Chim. Pays-Bas*, **86**, 275 (1967).

[19] M. Delwaulle and F. Francois, *Compt. Rend.*, **227**, 1229 (1948).

[20] One salt, $[(C_5H_5)Ni((C_6H_5)_3P)_2]SnCl_3$, has been synthesized under conditions where M–Sn bonds are normally produced [P. A. McArdle and A. R. Manning, *Chem. Commun.*, 417 (1967)].

group IVb, we have studied reactions of platinum compounds with trichlorosilane under conditions which produce platinum–germanium complexes but have failed to isolate any platinum complexes.

Other workers have reported similar failures.[16] Treatment of *trans*-$PtHCl[(C_6H_5)_3P]_2$ with silicon tetrachloride, trichlorosilane, or germanium tetrachloride results only in the slow chlorination of the platinum hydride. Chalk and Harrod,[21] while studying hydrosilations of olefins, investigated the reactions between silanes and triorganophosphine–platinum complexes. They found that no reaction occurred when most silanes were used. When trialkyl- or triarylsilanes were used, however, metathetic exchanges were observed as shown in eq 3. In other cases they reported brown solids, having compositions corresponding approximatately to $Pt_2[(C_6H_5)_3P]_4Cl$. There was no evidence for silicon–platinum bond formation in the systems studied.

$$(R_3P)_2PtCl_2 + R'_3SiH \longrightarrow (R_3P)_2PtClH + R'_3SiCl \quad (3)$$

While we did not find silicon compounds analogous to the Pt–Ge complexes, we did observe several interesting reactions involving silanes. For example, potassium tetrachloroplatinate(II) induces disproportionation of Si_2Cl_6 to Si_5Cl_{12} according to eq 4. On the other hand, potassium hexachloroplatinate(IV) did not have such a catalytic effect.

$$4Si_2Cl_6 \xrightarrow{K_2PtCl_4} Si_5Cl_{12} + 3SiCl_4 \quad (4)$$

Perhaps a more interesting reaction is that in which a novel compound, containing both Si and Pt, is obtained from the treatment of $[Cl_3PPtCl_2]_2$ with trichlorosilane. The product, $[Cl_3PPtSiCl_3]_x$, is a dark brown solid. It is very easily hydrolyzed in moist air and can be recrystallized from dry benzene. The reaction may be effected in benzene or in the absence of a solvent. When no solvent is used other products are hydrogen, hydrogen chloride, and silicon tetrachloride. In benzene solution only trace amounts of hydrogen are formed. A material balance is achieved by assuming hydrogenation of benzene. The solubility of the brown solid in benzene is not sufficiently high to determine a meaningful molecular weight, nor is the infrared spectrum helpful in assigning any structure to this substance.

When $[Cl_3PPtSiCl_3]_x$ is pyrolyzed at 182°, silicon tetrachloride, phosphorus trichloride, and chlorine are evolved leaving a residue of platinum contaminated with a small amount of phosphorus.

A similar product is formed when trichlorogermane is used in place of trichlorosilane in the reactions with $[Cl_3PPtCl_2]_2$. In this case the brown solid product has the composition $[Cl_3PPtGeCl_3]_x$.

Experimental Section

Apparatus and Reagents.—All purifications of materials volatile at room temperature were carried out in a vacuum apparatus. Reactions in this investigation mainly were carried out in the absence of air and moisture.

Benzene, Spectroquality, was dried over lithium aluminum hydride and purified by distillation through U tubes maintained at −23, −45, and −196° until the fraction retained in the −45° U tube exhibited vapor tension of 25 mm at 0°.

cis-**Dichlorobis(triphenylphosphine)platinum(II)** was prepared by the method described by Jensen.[22]

Disilicon hexachloride, obtained from Stauffer Chemical Co., Weston, Mich., was distilled through traps maintained at 0, −23, and −79°. The fraction retained at −23° had a vapor tension of 3.0 mm at 0°.

Potassium hexachloroplatinate(IV), prepared from platinum wire as described in the literature,[23] was recrystallized from water.

Potassium tetrachloroplatinate(II) was prepared by the hydrazine dihydrochloride reduction of potassium hexachloroplatinate(IV).[24]

Trichlorogermane was prepared from germanium metal and hydrogen chloride at 450° by a method previously described.[25] It was purified by distillation at 77° (750 mm). The purity was verified by its infrared spectrum.

Di-μ-chloro-dichlorobis(trichlorophosphine)diplatinum(II) was prepared by the method described by Arbuzov.[26] Platinum wire was substituted for the platinum black used in the reported preparation.

Trichlorosilane, obtained from Matheson Coleman and Bell, Norwood, Ohio, was purified by distillation through traps maintained at −79, −95, and −196° until the fraction retained in the −95° trap exhibited a vapor tension of 217 mm at 0°.

Triphenylphosphine secured from the Carlisle Chemical Works, Inc., Reading, Ohio, was used as received.

Analytical Methods.—Carbon, hydrogen, chloride, phosphorus, and nitrogen were determined by standard microanalytical methods by the Purdue Microanalytical Labs. Germanium and platinum were determined gravimetrically as platinum metal and germanium dioxide. The sample was treated with 0.5 ml of ammonium hydroxide and heated to dryness. Several drops of 30% hydrogen peroxide were added and the crucible was ignited at about 900° to constant weight. The residue of platinum metal and germanium dioxide was treated repeatedly with concentrated hydrochloric acid and $GeCl_4$ and H_2O were volatilized by heating to dryness. The crucible again was ignited at 900° to constant weight. This residue gave the percentage of platinum in the original sample. The difference between the platinum residue and combined residue of platinum and germanium dioxide gave the percentage of germanium in the original sample.

The amounts of sample used in this analysis generally were not greater than 0.02 g. We found in the analyses of the tetramethylammonium salts that both the platinum and germanium contents were low. In the analyses of the phosphonium salts and phosphine complexes both elements gave high results. In all cases the ratio of platinum to germanium was in good agreement with the formulas given.

In most cases deviations from perfect material balances reflected these difficulties encountered in obtaining good platinum and germanium values.

Silicon and platinum were determined in a similar manner. In this case the residue was platinum metal and silicon dioxide. Silicon dioxide was volatized as SiF_4 by repeated treatment with 48% HF.

Infrared spectra were recorded in the 2–15 μ region on a Perkin-Elmer Model 221 infrared spectrometer. Samples were prepared as KBr pellets. The infrared region from 11 to 35 μ was recorded on a Beckman IR-5A spectrometer equipped with cesium bromide optics operated as a single-beam instrument. Samples were prepared as Nujol mulls.

The ultraviolet spectra were obtained using a Cary Model 14

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[21] A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 16 (1965).

[22] K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **229**, 242 (1936).

[23] R. N. Keller, *Inorg. Syn.*, **2**, 247 (1946).

[24] W. E. Cooley and D. H. Busch, *ibid.*, **7**, 208 (1957).

[25] A. K. Petrov, V. F. Mironiv, and N. G. Dzhuinsdaya, *Dokl. Akad. Nauk*, **128**, 739 (1959).

[26] A. E. Arbuzov and V. M. Zoroastrova, *Bull. Acad. Sci., USSR, Div. Chem. Sci.*, 737 (1952).

operated in the region of 200–650 mμ. Samples were dissolved in concentrated hydrochloric acid placed in 1-cm quartz cells.

Preparation of Tetramethylammonium Salt of Hydridopentakis(trichlorogermyl)platinate(II), $[(CH_3)_4N]HPt(GeCl_3)_5$.—In a typical experiment, 0.4082 g of potassium tetrachloroplatinate(II) (0.98 mmol), partially dissolved in 25 ml of concentrated HCl, was placed in a dry bag and swept with nitrogen. Trichlorogermane, 0.700 cc (7.32 mmol), was syringed into the red reaction mixture, when all of the solid had dissolved. Tetramethylammonium chloride, 0.323 g (2.97 mmol), dissolved in 25 ml of concentrated hydrochloric acid then was added to the red solution. Immediately, a cream-colored solid precipitated. This mixture stood at room temperature for 3 hr. Then the solid was filtered and washed, first with 10 ml of concentrated hydrochloric acid then with 5 ml of cyclopentane. The washed solid was dried over phosphorus pentoxide *in vacuo*. Before analysis, the sample was dried further for several hours at 90° *in vacuo*. This dried solid melted with decomposition at 257–263°. Attempts to purify this substance by recrystallization from acetone, methylene chloride, or nitromethane resulted in chemical change to a different salt discussed later. The purity of the solid, even without recrystallization, appeared from the analytical data to be quite good.

Anal. Calcd for $C_8H_{25}N_2Cl_{15}PtGe_5$: C, 7.82; H, 2.02; Cl, 42.92; Pt, 15.75; Ge, 29.29; N, 2.26. Found: C, 7.63; H, 2.09; Cl, 43.00; Pt, 14.6; Ge, 27.8; N, 2.22.

The infrared spectrum is listed in Table I. The ultraviolet spectrum showed three absorption maxima at 290, 253, and 235 mμ.

Treatment of Tetramethylammonium Hydridopentakis(trichlorogermyl)platinate(II) with Trimethylamine.—Tetramethylammonium hydridopentakis(trichlorogermyl)platinate(II), 0.0554 g (4.47×10^{-2} mmol), was weighed into a reaction tube A. This was attached to the apparatus shown in Figure 1. Bulb B, containing trimethylamine vapor at approximately atmospheric pressure, was weighed and attached to the other leg of the apparatus. The entire assembly, shown in Figure 1, was attached to the vacuum apparatus, evacuated, and the constriction at C sealed off. Tube A was cooled to −79°, the stopcock on bulb B opened, and the trimethylamine in bulb B condensed onto the solid in tube A. After 24 hr at −79° the tetramethylammonium hydridopentakis(trichlorogermyl)platinate(II) in tube A turned yellow. Tube A was warmed to room temperature and bulb B cooled to −196°. Excess trimethylamine condensed in bulb B then was isolated by closing the stopcock on bulb B. The constriction at D was sealed off and the entire apparatus disassembled. Bulb B containing unreacted trimethylamine was weighed again. The difference in weights showed that 0.00487 g of trimethylamine (8.255×10^{-2} mmol) was consumed in this reaction. Tube A was weighed and the solid was found to have gained 0.00488 g.

The Pt–H frequency at 2080 cm^{-1}, observed in the hydride complex, is no longer found in the infrared spectrum. The hydrogen in this complex thus appears to be acidic. Since the trimethylamine absorbed by $[(CH_3)_4N]_2HPt(GeCl_3)_5$ was 1.8:1 and greater than 1:1, it is possible that the additional trimethylamine occupies the coordination position vacated by the protonic hydrogen. No other observable changes in the infrared spectrum could be seen.

The Reaction of *cis*-Dichlorobis(triphenylphosphine)platinum(II) and Trichlorogermane in Ether and Acetone.—When trichlorogermane, 0.2 cc (2.16 mmol), was syringed into a solution of *cis*-dichlorobis(triphenylphosphine)platinum(II), 0.3442 g (0.438 mmol), in 5 ml of acetone and 3 ml of diethyl ether, a yellow-orange solid formed but redissolved before a filtration could be effected. A white solid precipitated from the resulting clear, light yellow solution during 6 hr. The solid was filtered, washed with ether, and dried *in vacuo*. Analysis indicates this solid is trichloro(trichlorogermyl)bis(triphenylphosphine)platinum(IV), $[(C_6H_5)_3P]_2Cl_3Pt(GeCl_3)$. This compound melted sharply at 240° without decomposition. The infrared spectrum displayed no bands attributable to a phosphonium salt.

TABLE I

INFRARED DATA (CM^{-1})[a]

1. $[(CH_3)_4N]_2HPt(GeCl_3)_5$

3500 w, 3050 w, 2950 vw, 2085 m, 1620 w, 1490 vs, 1460 m, 1420 w 1285 w, 950 s, 720 w, 680 m, 630 m, 430 sh, band 430–340 vs

2. $[(C_6H_5)_3P]_2Cl_3Pt(GeCl_3)$

3450 m, 3090 w, 2925 w, 1480 m, 1450 sh, 1440 s, 1185 m, 1150 w, 1190 m, 740 m, 695 s, 540 md, 515 s, 495 m, 392 s, band 380–340 with 370 d

3. $[(C_6H_5)_3PH]_2Cl_4Pt(GeCl_3)_2$

3500 w, 3100 w, 2950 vw, 2380 w, 1600 w, 1480 w, 1450 s, 1330 wd, 1190 w, 1160 w, 1120 s, 1030 wb, 890 mb, 740 s, 725 s, 685 s, 535 sh, 500 sb, 460 w, 390 sh, band 400–310 s

4. $[(C_6H_5)_3P]_2Cl_2Pt(GeCl_3)_2$

3500 w, 3100 w, 2950 w, 1480 m, 1440 s, 1310 w, 1190 w, 1160 w, 1110 sh, 1100 s, 1025 w, 740 s, 690 s, 535 s, 515 sb, 497 sh, 460 w, 445 w, 405 sh, 392 s, band 384–330 s

5. $[(C_6H_5)_3P]_2ClPt(GeCl_3)$

3500 w, 3100 w, 2950 vw, 1490 m, 1450 s, 1310 w, 1190 w, 1160 w, 1100 w, 1030 w, 740 s, 695 s, 545 m, 570 s, 500 s, 380 s, 355 vbd

6. $[(CH_3)_4N]_2Cl_2Pt(GeCl_3)_2$ (yellow)

3450 m, 3050 w, 2925 w, 1490 s, 1450 w, 1410 w, 945 s, 750 wb, 694 m, 405 s, band 400–330 s, 345 sh, 316 sb, 285 sb

7. $[(CH_3)_4N]_2Cl_2Pt(GeCl_3)_2$ (red)

3450 m, 3050 w, 2950 w, 1490 s, 1450 w, 1420 w, 945 s, 750 wb, 694 m, 545 wb, band 400–310 s, 340 sh

8. $[Cl_3PPtSiCl_3]_x$

band 3500 vs, band 1650 vb, band 1100 vb, band 900 vb, band 550 vb

[a] s, strong; m, medium; w, weak; sh, shoulder; d, doublet; b, broad.

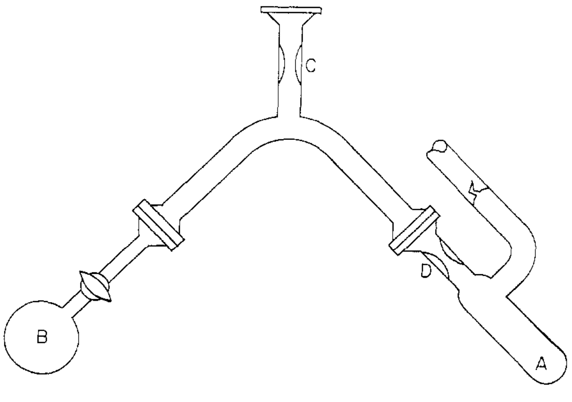

Figure 1.—Apparatus for the treatment of the tetramethylammonium salt of hydridopentakis(trichlorogermyl)platinate(II) with trimethylamine.

Anal. Calcd for $C_{36}H_{30}P_2Cl_6GePt$: C, 43.0; H, 3.01; Cl, 21.16; Ge, 7.22; Pt, 19.4. Found: C, 42.2; H, 3.27; Cl, 19.76; Ge, 7.04; Pt, 23.12.

The infrared spectrum is tabulated in Table I.

Preparation of the Triphenylphosphonium Salt of Tetrachlorobis(trichlorogermyl)platinate(IV), $[(C_6H_5)_3PH]_2Cl_4Pt(GeCl_3)_2$.—Trichlorogermane, 1 ml (10.7 mmol), was added to a flask containing potassium tetrachloroplatinate(II), 0.48 g (1.15 mmol), dissolved in 20 ml of concentrated hydrochloric acid. The red solution which resulted was stirred under nitrogen for 1.5 hr. Addition of a hot ethanol solution of triphenylphosphine, 0.60 g (2.3 mmol), precipitated an orange solid. After filtration, the orange precipitate was washed with ethanol. The filtration and subsequent washings all were effected in an inert atmosphere.

The solid was dried *in vacuo* and stored in a vacuum desiccator over phosphorus pentoxide. Attempts to purify this orange solid by recrystallization from nitromethane, ethanol, or benzene gave red or yellow oils.

When the orange solid was heated to the melting point under nitrogen a red melt was obtained at 172°.

The infrared spectrum has peaks atrributable to $(C_6H_5)_3PH$ at 2380, 1120, 890, and 720 cm^{-1}. Analysis of the material indicates that the phosphonium salt is contaminated with $[(C_6H_5)_3P]_2Cl_2Pt(GeCl_3)_2$. All purification methods failed to give a pure product.

Anal. Calcd for $C_{36}H_{32}P_2Cl_{10}Ge_2Pt$: C, 35.40; H, 2.68; P, 5.08; Cl, 29.03; Ge, 11.89; Pt, 15.98. Found: C, 31.99; H, 2.58; P, 4.65; Cl, 24.25; Ge, 13.6; Pt, 18.3.

If a sample of the mixed complex is placed under an atmosphere of hydrogen chloride for several days the composition more closely agrees with the formula given.

Anal. Calcd for $C_{36}H_{32}P_2Cl_{10}Ge_2Pt$: C, 35.40; H, 2.68; P, 5.08; Cl, 29.03; Ge, 11.89; Pt, 15.98. Found: C, 31.68; H, 2.55; P, 4.57; Cl, 27.99; Ge, 13.36; Pt, 17.98.

When the phosphonium salt is heated to 130° *in vacuo* hydrogen chloride is evolved, along with small amounts of sublimable white and yellow solids. The solid remaining in the bulb is now yellow in color and melts over the range 247–253°. The analysis of the solid residue identified it as dichlorobis(trichlorogermyl)-bis(triphenylphosphine)platinum(IV), $[(C_6H_5)_3P]Cl_2Pt(GeCl_3)_2$.

Anal. Calcd for $C_{36}H_{30}P_2Cl_8Ge_2Pt$: C, 37.59; H, 2.60; P, 5.38; Cl, 24.66; Ge, 12.62; Pt, 16.97. Found: C, 37.92; H, 2.79; P, 5.85; Cl, 24.60; Ge, 12.93; Pt. 18.2.

The infrared spectrum confirmed the change from a phosphonium salt to the phosphine complex. The infrared spectrum for this complex is presented in Table I.

The triphenylphosphonium salt of tetrachlorobis(trichlorogermyl)platinate(II) also can be prepared from potassium hexachloroplatinate(IV) using a method similar to that described using potassium tetrachloroplatinate(II). The product is an orange solid having a melting point of 172° and a composition and infrared spectrum which indicate that the product is the same as that found in the previous case. The product melts under nitrogen to yield a red liquid and when heated *in vacuo* loses hydrogen chloride to give a yellow solid with a melting range of 245–249° and an infrared spectrum identical with that of the yellow solid identified as $[(C_6H_5)_3P]_2Cl_2Pt(GeCl_3)_2$.

When $[(C_6H_5)_3P]_2Cl_2Pt(GeCl_3)_2$ is heated *in vacuo* to temperatures in excess of 130° a yellow solid sublimes and the residue has a higher germanium content.

Preparation of Chloro(trichlorogermyl)bis(triphenylphosphine)-platinum(II), $[(C_6H_5)_3P]_2ClPt(GeCl_3)$.—Potassium tetrachloroplatinate(II) 0.9285 g (2.237 mmol), was dissolved in 10 ml of distilled water. (This was necessary to ensure complete dissolution of the salt due its lack of ready solubility in concentrated hydrochloric acid.) Trichlorogermane, 0.4149 cc (4.474 mmol), dissolved in concentrated hydrochloric acid, was added to the tetrachloroplatinite solution under nitrogen. Initially a red solution results, but, upon stirring, the color fades finally to yellow. Triphenylphosphine, 1.168 g (0.4474 mmol), dissolved in 10 ml of hot ethanol, precipitates a light yellow solid.

The light yellow solid was washed with several portions of cyclopentane and dried *in vacuo*. The new compound melted over a temperature range of 253–254°.

The infrared spectrum is presented in Table I. No bands attributable to triphenylphosphonium salt are observable in this spectrum.

Anal. Calcd for $C_{36}H_{80}P_2Cl_4GePt$: C, 46.28; H, 3.23; P, 6.63; Cl, 15.17; Ge, 7.75; Pt, 20.89. Found: C, 45.79; H, 3.20; P, 6.85; Cl, 15.50; Ge, 9.7; Pt, 25.2.

Preparation of the Yellow Isomeric Form of Tetramethylammonium Dichlorobis(trichlorogermyl)platinate(II), $[(CH_3)_4N]_2Cl_2Pt(GeCl_3)_2$.—Potassium tetrachloroplatinate(II), 0.4322 g (1.118 mmol), was dissolved in 10 ml of distilled water and 30 ml of concentrated hydrochloric acid was added. The flask was swept with nitrogen and placed in a dry bag. Trichlorogermane, 0.2074 cc (2.237 mmol), was syringed into the reaction vessel. The reaction mixture was stirred for 1 hr. Initially, the reaction mixture turned a deep red. After a few minutes the color faded to a clear yellow. Addition of tetramethylammonium chloride, 0.244 g (2.237 mmol), in 10 ml of hydrochloric acid, precipitated a yellow solid. The solid was filtered and washed with 10 ml of hydrochloric acid, followed by 5 ml of diethyl ether. The compound was purified further by dissolving it in nitromethane and reprecipitating with ether. After washing this yellow solid with ether, it was dried *in vacuo* at 100° and stored in a vacuum desiccator over phosphorus pentoxide. The dried solid melted to a dark liquid over the range of 260–266°.

Anal. Calcd for $C_8H_{24}N_2Cl_8PtGe_2$: C, 12.48; H, 3.13; Cl, 36.73; Ge, 18.73; Pt, 25.27; N, 3.64. Found: C, 12.53; H, 3.12; Cl, 36.74; Ge, 16.2; Pt, 23.8; N, 3.68.

The infrared spectrum is tabulated in Table I. The ultraviolet spectrum showed an absorption maximum at 285 mμ.

Preparation of the Red Isomeric Form of Tetramethylammonium Dichlorobis(trichlorogermyl)platinate(II); $[(CH_3)_4N]_2Cl_2Pt(GeCl_3)_2$.—The red form of tetramethylammonium dichlorobis(trichlorogermyl)platinate(II) is prepared by dissolving tetramethylammonium hydridopentakis(trichlorogermyl)platinate(II) in sufficient nitromethane to obtain a clear solution, then adding diethyl ether to this solution to precipitate the red-orange solid. The red-orange crystals, washed with diethyl ether and dried *in vacuo*, melted over the range 207–210°. Analysis established the composition as $[(CH_3)_4N]_2Cl_2Pt(GeCl_3)_2$.

Anal. Calcd for $C_8H_{24}N_2Cl_8PtGe_2$: C, 12.44; H, 3.13; Cl, 36.73; Ge, 18.73; Pt, 25.2; N, 3.64. Found: C, 12.77; H, 3.34; Cl, 36.90; Ge, 17.2; Pt, 22.2; N, 3.92.

The infrared spectrum is summarized in Table I. The ultraviolet spectrum in concentrated hydrochloric acid displayed one absorption maximum at 235 mμ

The Reaction between Nickel Chloride and Trichlorogermane.—When a concentrated hydrochloric acid solution of nickel(II) chloride is treated with trichlorogermane a deep purple solution is obtained, but the intense color fades in a few seconds. When trichlorogermane is added to a suspension of nickel(II) chloride in acetone or nitromethane a similar deep purple solution is formed in which the color persists for several hours. Several attempts to isolate phosphine complexes or tetramethylammonium salts of the soluble colored species failed to produce precipitates.

The Disproportionation of Hexachlorodisilane in the Presence of Potassium Tetrachloroplatinate(II).—In contact with K_2PtCl_4, hexachlorodisilane disproportionates to silicon tetrachloride and a higher polysilane. Potassium tetrachloroplatinate(II), 0.0331 g (0.08 mmol), was weighed into a reaction tube which was evacuated and cooled to −79°. A sample of Si_2Cl_6, weighing 0.8455 g (3.15 mmol), was condensed into the reaction bulb and sealed off. The resulting mixture was heated slowly and held at 160° for 24 hr, then cooled to 0°. A white solid rapidly formed at this temperature. The red K_2PtCl_4 had darkened to a black residue. The reaction tube was attached to a sublimation apparatus and evacuated. The tube was opened and all volatile materials were removed. The white solid sublimed at 70–75°. A $SiCl_4$ titration[27] indicated a molecular weight of 563.4 (calculated for Si_5Cl_{12}, 565.8).

The volatile material was separated by repeated fractional condensation through U tubes maintained at −63, −79, and −196°. Three fractions were isolated. A trace of volatile material, possibly HCl, was condensed in the −196° U tube. Silicon tetrachloride (2.52 mmol) condensed in the −79° U tube and was identified by its vapor tension at 0° (found, 76 mm; reported, 76 mm). The fraction retained by the −63° U tube was identified as unchanged Si_2Cl_6 (0.029 mmol) by its 0° vapor tension (found, 1.5 mm; reported, 1.5 mm).

According to eq 5, the amount of $SiCl_4$ which should have been

$$5Si_2Cl_6 \longrightarrow 3SiCl_4 + Si_5Cl_{12} \qquad (5)$$

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[27] A. Kaczmarczyk, M. Millard, J. W. Nuss, and G. Urry, *J. Inorg. Nucl. Chem.*, **26**, 421 (1964).

formed was calculated to be 2.35 mmol. The excess $SiCl_4$ may be due to oxidation of Si_2Cl_6 by K_2PtCl_4.

In a similar experiment as outlined above, K_2PtCl_6 was substituted for K_2PtCl_4. Under identical reaction conditions no disproportionation of the Si_2Cl_6 was observed.

The Preparation of $[Cl_3PPtSiCl_3]_x$.—Under a nitrogen atmosphere, $[Cl_3PPtCl_2]_2$, 0.5772 g (0.715 mmol), was placed in a reaction vessel which was attached to the vacuum apparatus and evacuated. The evacuated vessel than was cooled to −196° and 9.802 mmol of trichlorosilane condensed upon the $[Cl_2PPtCl_2]_2$. The resulting mixture was warmed to room temperature and stirred for about 40 min. After this period, a reaction ensued as indicated by the fact that the orange solid $[Cl_3PPtCl_2]_2$ changed to a dark brown solid and a noncondensable gas was evolved. The gas was collected with a Toepler pump through two U tubes maintained at −196°. The materials retained by these traps were separated by distillation through U tubes maintained at −63, −95, and −196°. The trichlorosilane condensed in the −95° U tube was returned to the reaction vessel and this new mixture allowed to stand at room temperature an additional 24 hr. Again the volatile materials were condensed and the noncondensable gas transferred. The total amount of noncondensable gas produced a pressure of 70.9 mm in a volume of 524.4 cc at 27.4° (1.971 mmol). This noncondensable material was identified as hydrogen by combustion over CuO. The condensable materials were separated by the usual fractional condensation methods. Distillation through a series of U tube traps maintained at −23, −45, −63, −79, −95, and −126° into one at −196° yielded three fractions. The material which condensed in the −196° trap was shown to be hydrogen chloride (0.834 mmol) by vapor density and vapor tension measurements. The fractions in the −79 through −126° traps were shown by infrared spectrum to be a mixture of trichlorosilane and silicon tetrachloride. The total quantity of these combined fractions was found to be 9.802 mmol from a *PVT* measurement. To determine the composition of this mixture an aliquot was hydrolyzed with ethanol and potassium hydroxide. Hydrolysis of trichlorosilane to form H_2 under these conditions is quantitative.[28]

A 2.771-mmol sample of the silane mixture yielded 1.771 mmol of hydrogen corresponding to 63.9% trichlorosilane and 36.1% silicon tetrachloride and a recovery of 5.007 mmol of trichlorosilane and 2.830 mmol of silicon tetrachloride. Additional silane, 0.186 mmol of trichlorosilane, and 0.260 mmol of silicon tetrachloride evolved slowly from the brown solid for several days. The reaction bulb was attached to a vacuum filtration apparatus. The entire assembly was evacuated and cooled to −79°. Benzene then was condensed into the apparatus. The filtration apparatus was sealed off and a brown benzene solution filtered from the insoluble residue. Removal of the solvent from this solution left a crystalline brown solid which is soluble in acetone, nitromethane, and other organic solvents but is hydrolyzed in H_2O. Thus, the solid recovered from aqueous solution contains a larger percentage of platinum than the original material.

Anal. Calcd for Cl_6SiPPt: Cl, 44.2; Si, 6.15; P, 6.78; Pt, 42.9. Found: Cl, 44.15; Si, 6.60; P, 7.55; Pt, 42.7.

The compound $(Cl_3PPtSiCl_3)_x$ is very easily hydrolyzed as evidenced by the fact that a sample stored in air loses Cl^-. The molecular weight was not obtainable due to the low solubility of the complex in benzene or acetone. The infrared spectrum is summarized in Table I.

Pyrolysis of $[Cl_3PPtSiCl_3]_x$.—A sample of $[Cl_3PPtSiCl_3]_x$ (0.4154 g) was placed in a reaction vessel and heated to 180°, at which temperature a measurable pressure was observed over the solid $[Cl_3PPtSiCl_3]_x$. After 12 hr at 320° the reaction tube was opened to the vacuum apparatus and the material volatile at 320° removed. This pyrolysis yielded a trace of noncondensable gas, identified as H_2 by combustion over CuO at 350°. The amount formed was determined to be $0.6 \pm 0.1 \times 10^{-2}$ mmol by a *PVT* measurement. The condensable pyrolysis products were separated by fractional condensation. Distillation through U tubes maintained at −53, −63, −79, and −196° yielded three fractions. These were identified as (a) chlorine (0.255 mmol) by vapor tension and vapor density measurements, (b) silicon tetrachloride (0.981 mmol) by its vapor tension, and (c) trichlorophosphine (0.282 mmol) by vapor tension and vapor density.

The residue in the pyrolysis vessel weighed 0.1883 g and consisted of 3.72% P and 96.28% Pt. The total amount of Pt in the compound before pyrolysis is calculated to be 42.5%. The total composition based on pyrolysis products, therefore, is: Cl, 45.11; P, 3.79; Si, 6.61; Pt, 42.5; and 0.7% of an unidentified volatile solid. The calculated composition of $[Cl_3PPtSiCl_3]_x$ is: Cl, 44.2; P, 6.78; Si, 6.15; Pt, 42.9. Some loss of phosphorus in the vacuum apparatus apparently occurred during the pyrolysis. Reduction with mercury is a possible explanation of this loss.

The Preparation of $[Cl_3PPtGeCl_3]_x$.—The compound $[Cl_3PPtGeCl_3]_x$ analogous to the silicon compound was prepared by the treatment of di-μ-chloro-dichlorobis(trichlorophosphine)-diplatinum(II) with trichlorogermane. Under a nitrogen atmosphere, $[Cl_3PPtCl_2]_2$, 0.4964 g (0.6345 mmol), was placed in the reaction vessel which was attached to the vacuum apparatus, evacuated, and cooled to −196°. Dry benzene, 5 ml, and 0.12 ml (1.270 mmol) of trichlorogermane were condensed upon the $[Cl_3PPtCl_2]_2$. The resulting mixture was warmed to room temperature and stirred for 5 hr. During this time the reaction mixture turned to a deep brown color and a noncondensable gas was evolved. The gas was collected with a Toepler pump through two U tubes maintained at −196°. The noncondensable gas produced a pressure of 71.0 mm in a volume of 16.6 cc at 24.0° (0.0637 mmol). This noncondensable material was identified as pure hydrogen by combustion over CuO. The condensable materials were separated by fractional condensation. Distillation through U tube traps maintained at −45, −79, and −196° yielded two fractions. The fraction which condensed in the −196° bath was shown to be hydrogen chloride (0.303 mmol) by vapor density measurements. The other fraction consisted of benzene, trichlorogermane, and germanium tetrachloride. Since the volatilities of benzene, trichlorogermane, and germanium tetrachloride are similar they could not be separated in the vacuum apparatus. The amount of germanium in this mixture was determined by precipitating it from the benzene solution as the sulfide. Concentrated sulfuric acid (5 ml) and thioacetamide were added to the solution and the germanium was precipitated as GeS_2. The germanium disulfide was ignited to a germanium dioxide residue weighing 0.02095 g (0.2014 mmol). The brown residue in the reaction bulb was attached to a vacuum filtration apparatus by the break-off seal and evacuated. The apparatus was cooled to −79° and several milliliters of dry benzene was condensed into the apparatus. The filtration apparatus was sealed off and the break-off seal to the sample was broken by means of a magnetic hammer. A brown benzene-soluble material was extracted from the reaction residue. The filtration apparatus again was attached to the vacuum apparatus and opened, and the benzene was removed. The brown benzene-soluble material was analyzed and found to fit the formulation $[Cl_3PPtGeCl_3]_x$ moderately well.

Anal. Calcd for Cl_6GePPt: Cl, 40.5; Ge, 14.5; Pt, 39.2. Found: Cl, 40.0; Ge, 14.1; Pt, 34.2.

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(28) F. P. Price, *J. Am. Chem. Soc.*, **69**, 2600 (1947).