whereas AP forms chelate complexes with copper(I) halides. The shift in C=C stretching frequency on complexing, $\Delta\nu$(C=C), which provides a rough measure of metal–olefin bond strength, is approximately 50 cm^{-1} for AgNO$_3$·AA and approximately 80 cm^{-1} for [CuX·AP]$_2$. Previous results[2,5,15,18,19] indicate, as would be expected, that olefin complexes of copper(I) and silver(I) are formed more readily if poorly coordinating anions, such as BF$_4^-$, ClO$_4^-$, or NO$_3^-$, are present in place of halide ions. It is surprising, therefore, that AA, but not AP, forms a chelate complex with silver nitrate, since in the case of the copper halides discussed above, and in the case of palladium(II),[9] AP is clearly the better chelate ligand. Preliminary attemps to prepare chelate complexes of AP with AgBF$_4$ have also been unsuccessful. Experiments using a range of related olefinic tertiary phosphines and arsines will be required to provide an answer to this problem.

Acknowledgments.—We thank Dr. R. Bramley for recording and analyzing the nmr spectra and the Science Research Council for the award of a studentship to W. R. K.

Contribution from the William Ramsay and Ralph Forster Laboratories,
University College, London W.C.1, England

Metal Complexes of Unsaturated Tertiary Phosphines and Arsines. VII.[1] Chelate Monoolefin Complexes of Platinum(II) and Palladium(II)

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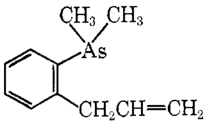
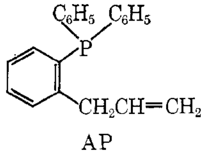
Received June 29, 1967

The ligands *o*-allylphenyldimethylarsine (AA), *o*-CH$_2$=CHCH$_2$C$_6$H$_4$As(CH$_3$)$_2$, and *o*-allylphenyldiphenylphosphine (AP), *o*-CH$_2$=CHCH$_2$C$_6$H$_4$P(C$_6$H$_5$)$_2$, form chelate complexes of formula MX$_2$(ligand) (M = Pt, Pd; X = Cl, Br), in which both the group V atom and the double bond are coordinated to the metal. The reactions of these compounds with iodide ion and with thiocyanate ion lead to a variety of compounds in which the double bond may or may not be coordinated to the metal. These studies, together with the infrared spectra of the complexes, suggest that metal–olefin bonding is stronger for platinum(II) than for palladium(II), in agreement with previous work. The phosphine AP forms chelate complexes more readily than does the arsine AA.

Introduction

Olefinic tertiary phosphines and arsines containing the 4-pentenyl group, of general formula CH$_2$=CH(CH$_2$)$_3$P(As)R$_2$ (R = CH$_3$ or C$_6$H$_5$), form chelate, monomeric monoolefin complexes with platinum(II) of formula PtX$_2$(ligand) (X = Cl, Br, or I), but with palladium(II) dimeric complexes exemplified by [PdCl$_2$(ligand)]$_2$ are formed, in which the double bond is not coordinated to the metal.[2] We have previously briefly reported the preparation of chelate derivatives of formula PtBr$_2$(ligand) with *o*-allylphenyldimethylarsine (AA)[3] and *o*-allylphenyldiphenylphosphine (AP),[4] and now we compare the chelating tendencies of these two ligands with platinum(II) and palladium(II).


AA


AP

Experimental Section

Starting Materials.—Tetrahydrofuran was distilled from sodium–benzophenone and stored over sodium. All other solvents and chemicals were of reagent grade quality and were used without purification.

o-Allylphenyldimethylarsine (AA) and *o*-allylphenyldiphenylphosphine (AP) were prepared as described previously.[3,4] They are referred to as "the arsine" and "the phosphine" throughout the Experimental Section.

Measurements.—Infrared spectra, proton nmr spectra, melting points, molecular weights, conductances, and X-ray powder data were measured as described previously.[1] Magnetic susceptibilities were measured at room temperature on powdered samples using the Gouy method, following the procedure of Figgis.[5] Ultraviolet and visible spectra were recorded on a Unicam SP 800 spectrophotometer using 1-cm silica cells.

Microanalyses were carried out by the microanalytical laboratory of this department, by Messrs Weiler and Strauss, Oxford, and by Alfred Bernhardt, Max Planck Institut für Kohlenforschung, Mülheim, Germany. Platinum and palladium in the tertiary arsine complexes were determined by ignition to the metal after moistening with a few drops of concentrated sulfuric acid.

Dichloro(*o*-allylphenyldiphenylphosphine)platinum(II), PtCl$_2$AP.—A solution of the phosphine (2.5 g, 8.3 mmoles) in 40 ml of chloroform was added slowly (1 hr) to a stirred suspension of anhydrous platinum(II) chloride (2.2 g, 8.3 mmoles) in 30 ml of chloroform at room temperature. The mixture was refluxed

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for 30 min and filtered; the filtrate was concentrated to *ca.* 5 ml (15 mm) and 10 ml of hexane was added. The white solid, a chloroform solvate of formula $PtCl_2AP \cdot 0.5CHCl_3$ was filtered off and recrystallized from ethanol to give white crystals, $PtCl_2AP$ (4 g, 75%).

The complexes $PtBr_2AP$, $PtCl_2AA$, and $PtBr_2AA$ were prepared similarly from the platinum(II) halide and the ligand.

Diiodo(*o*-allylphenyldiphenylphosphine)platinum(II), PtI_2AP.—A solution of the complex $PtCl_2AP$ (1 g, 1.75 mmoles) in 80 ml of acetone was treated with sodium iodide (3 g, 20 mmoles). The mixture was stirred at room temperature for 30 min and refluxed for a further 30 min. The yellow solution was evaporated to dryness at 15 mm, and the residue was extracted with four 30-ml portions of chloroform. The combined extracts were evaporated to dryness (15 mm), and the yellow residue (0.8 g, 60%) was recrystallized from ethanol to give yellow plates, PtI_2AP.

The complexes $Pt(NCS)_2AP$, PtI_2AA, and $Pt(NCS)_2(AA)_2$ were prepared similarly from $PtCl_2$(ligand) and the appropriate sodium halide.

Dichloro(*o*-allylphenyldiphenylphosphine)palladium(II), $PdCl_2AP$.—A solution of the phosphine (4.7 g, 15.6 mmoles) in 50 ml of chloroform was added slowly (1 hr) to a solution of dichlorobis(benzonitrile)palladium(II)[6] (6 g, 15.6 mmoles) in 40 ml of chloroform at room temperature. The solution was refluxed for 1 hr, filtered while still hot, and evaporated to *ca.* 5 ml at 15 mm. The yellow solid (5.8 g, 70%) was filtered off, washed with benzene, and recrystallized from ethanol, to give pure $PdCl_2AP$.

The complex $PdCl_2AA$ was prepared similarly.

Dibromo(*o*-allylphenyldiphenylphosphine)palladium(II), $PdBr_2AP$.—A solution of the complex $PdCl_2AP$ (1 g, 2.1 mmoles) in 70 ml of acetone was treated with lithium bromide (3.5 g, 40 mmoles). The mixture was worked up as described for PtI_2AP, and the product was recrystallized from ethanol to give pure $PdBr_2AP$ (0.84 g, 70%).

The complexes PdI_2AP, $Pd(NCS)_2(AP)_2$, $PdBr_2AA$, $[PdI_2AA]_2$, and $Pd(NCS)_2(AA)_2$ were prepared similarly from $PdCl_2$(ligand) and the appropriate lithium or sodium halide.

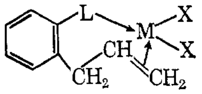
The analytical and molecular weight data for the complexes, together with their colors and C=C stretching frequencies, are summarized in Table I.

Results and Discussion

The ligands AA and AP form diamagnetic, monomeric, colorless, or pale yellow complexes of general formula MX_2(ligand) (M = Pt, Pd; X = Cl, Br) which are nonconducting in nitrobenzene. The infrared spectra of the platinum(II) complexes show a band at *ca.* 1500 cm^{-1}, which is absent from the spectrum of the ligands; the band at 1640 cm^{-1} due to a C=C stretching frequency in the spectra of the ligands is absent from the spectra of the complexes. The band at *ca.* 1500 cm^{-1} is assigned to a C=C stretching frequency modified by coordination to platinum(II), in agreement with previous assignments for platinum(II)–olefin complexes,[7-9] and the chelate structure I (M = Pt; X = Cl or Br) is assigned to the complexes. The palladium(II) complexes evidently have the same structure, since their infrared spectra show a band at *ca.* 1530 cm^{-1} characteristic of a C=C stretching frequency modified by coordination to palladium(II).[9,10] In view of the similar molecular structures, it is interesting that only the following pairs of compounds are mutually isomorphous as shown by their X-ray powder patterns: $PdCl_2AA$ and $PdBr_2AA$; $PdCl_2AP$ and $PdBr_2AP$. Especially noteworthy is the lack of isomorphism of, for example, $PtCl_2AA$ with $PtBr_2AA$ or of $PtCl_2AA$ with $PdCl_2AA$.

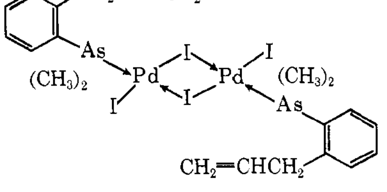
Since palladium(II) and platinum(II) salts are known to catalyze the isomerization of terminal olefins,[11] it seemed possible that the chelate complexes could contain the isomeric *o*-propenyl-substituted ligands *o*-$CH_3CH{=}CHC_6H_4L$ [L = $As(CH_3)_2$, $P(C_6H_5)_2$]. A facile isomerization of this type with the ligand AP has been observed in the presence of group VI hexacarbonyls.[4] It was not possible to obtain well-resolved proton nmr spectra of the platinum(II) and palladium(II) chelate complexes, owing to their limited solubility in organic solvents. However, the 100-Mc ^1H nmr spectrum of $PdCl_2AP$ in deuteriochloroform shows signals similar to those of the free ligand, and there are no signals due to methyl groups, showing that no isomerization has occurred in this case. Also, the original ligand is displaced unchanged by treatment of $PtBr_2AP$ with potassium cyanide.[4]

On heating $PtCl_2AA$ and $PtCl_2AP$ with an excess of sodium iodide, the yellow chelate complexes PtI_2AA and PtI_2AP are obtained [ν(C=C) *ca.* 1500 cm^{-1}]. Under the same conditions, starting from $PdCl_2AA$, a black, diamagnetic complex of formula PdI_2AA is obtained, the infrared spectrum of which has a band at 1640 cm^{-1}, showing that the double bond is not coordinated. The complex is dimeric in chloroform, but is essentially monomeric in acetone. These observations support the formulation of PdI_2AA as an iodo-bridged dimer (structure II). It is likely that the iodine bridges are broken in acetone, giving a monomeric species $PdI_2(AA)(CH_3COCH_3)$; similar behavior has been observed with dimeric chloro-bridged complexes of platinum(II).[12] Dark red or black iodo-bridged complexes, such as $Pd_2I_4(PR_3)_2$ (R = *n*-C_3H_7 or *n*-C_4H_9), have been prepared previously.[13,14]

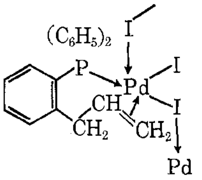


I

L = $As(CH_3)_2$ or $P(C_6H_5)_2$
M = Pd or Pt
X = Cl or Br



II



III

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TABLE I

ANALYTICAL DATA, COLORS, MELTING POINTS, MOLECULAR WEIGHTS, AND C═C STRETCHING FREQUENCIES (CM^{-1}) OF COMPLEXES OF AA AND AP

	Color	% C		% H		% P(As)		% halogen		% metal		Calcd	Mol wt in $CHCl_3$		Mol wt in acetone		ν(C═C),
Compound	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	mol wt	Molarity	Found	Molarity	Found	cm^{-1}
$PdCl_2AA$	Yellow 193–194	33.0	33.1	3.8	3.8	18.8	18.6	17.8	17.8	26.7	26.9	400	0.0049 0.0103	429 445			1527
$PdBr_2AA$	Orange 195–196	27.0	27.0	3.1	3.0	15.3	15.3	32.8	32.1	21.8	22.0	488	0.0050 0.0089	588 625	0.0050	504	1527
$[PdI_2AA]_2$	Dark red 180–182	22.6	22.7	2.6	2.7	12.8	12.8	43.6	42.9	18.3	19.1	1165	0.0021 0.0191 0.0391	1100 1080 1093	0.0032 0.0047	618 735	1640
$Pd(NCS)_2(AA)_2$	Orange 132–134	43.2	43.0	4.5	4.6	22.5	22.4	4.2 9.6	4.2 (N) 9.5 (S)	16.0	16.0	667	0.0209 0.0400	680 672			1640
$PtCl_2AA$	White 243–244	27.0	27.0	3.1	3.3	15.4	15.8	14.5	14.6	40.0	39.7	488	0.0048 0.0206 0.0424	505 535 550	0.0049 0.0100	442 495	1504
$PtBr_2AA$	Cream 250–251	22.9	23.0	2.6	2.5	13.0	12.8	27.7	28.4	33.8	33.3	577	0.0208 0.0408	625 660	0.0054 0.0089	507 565	1496
PtI_2AA	Yellow 242–243	19.7	19.8	2.2	2.2	11.2	11.0	37.9	38.0			671	0.0047 0.0206	753 768	0.0049	632	1493
$Pt(NCS)_2(AA)_2$	Yellow 123–125	38.2	38.3	4.0	4.1	19.8	19.8	3.7 8.5	3.6 (N) 8.2 (S)	25.8	25.6	755			0.0104 0.0411	687 805	1640
$PdCl_2AP$	Yellow 190–191	52.5	52.7	4.0	4.1	6.5	6.4	14.8	14.7			480	0.0104 0.0334	517 565			1530
$PdBr_2AP$	Orange 214–215	44.3	44.5	3.4	3.4	5.5	5.6	28.1	27.8			569	0.0100 0.0314	570 608			1527
PdI_2AP	Black 196	38.1	37.9	2.9	3.2	4.7	4.4	38.3	38.9			663	0.0109 0.0349	716 832			1535
$Pd(NCS)_2(AA)_2$	Orange 174–175	63.8	63.5	4.6	4.4	3.4	3.3	7.8	7.6			828					1640
$PtCl_2AP$	White 256 257	44.4	44.6	3.4	3.3	5.4	5.4	12.5	12.3			568	0.0108 0.0348	632 672			1497
$PtBr_2AP$	Fawn 253–254	38.4	38.3	2.9	2.8	4.7	4.7	24.3	25.3			657	0.0103 0.0311	755 771			1497
PtI_2AP	Orange 244–245	33.6	33.8	2.6	2.7	4.1	4.6	33.8	33.5			751	0.0101	783			1499
$Pt(NCS)_2AP$	Cream 210–211	45.0	44.9	3.1	3.4	5.1	4.8	10.6 4.4	10.4 (S) 4.4 (N)			614	0.0313 0.0109	834 656			1508

TABLE II

ABSORPTION MAXIMA IN THE VISIBLE AND ULTRAVIOLET SPECTRA OF SOME IODOPALLADIUM(II) COMPLEXES

Complex	λ, mμ (ε)	λ, mμ (ε)	λ, mμ (ε)
$[PdI_2AA]_2$[a]	*Ca.* 285 (15,000)[b]	325 (13,500)	465 (3,000)
PdI_2AP[a]	*Ca.* 290 (14,000)[b]	335 (14,000)	460 (2,600)
PdI_2QAS[c]	292 (19,600)[b]	384 (7,500)	535 (6,300)
PdI_2TAS[d]	306 (24,500)	403 (3,750)	465 (1,800)

[a] Measured in methanol solution. [b] Shoulder on absorption increasing into ultraviolet region. [c] Taken from ref 15; measured in benzene solution. QAS = tris(*o*-diphenylarsinophenyl)arsine; complex is five-coordinate trigonal bipyramid. [d] Taken from ref 15; measured in benzene solution. TAS = bis(*o*-diphenylarsinophenyl)phenylarsine; complex is four-coordinate and square- [lanarpPDI(TAS)]$^+$I$^-$.

A red-black complex PdI_2AP is obtained by heating $PdCl_2AP$ with sodium iodide. It is similar in appearance, both in the solid state and in solution, to PdI_2AA, and the electronic absorption spectra of the two compounds (Table II) in methanol solution are almost identical. However, the solid-state infrared spectrum of PdI_2AP shows a band due to a coordinated C=C stretching frequency at 1535 cm^{-1}, and shows no band at 1640 cm^{-1}. Attempts to measure the molecular weight of the complex in acetone have been frustrated by the poor solubility in this solvent, but in chloroform, PdI_2AP, unlike PdI_2AA, is monomeric. It has been observed previously that iodopalladium(II) complexes are deep red or violet when bridging iodine atoms are present,[13,14] when iodine atoms are bound to each palladium atom in a five-coordinate structure,[15] or when both features are present.[16] Square-planar *trans*-diiodo complexes of palladium(II) are usually orange or orange-red. In the solid state, therefore, it seems likely that PdI_2AP is an infinite polymer held together by single iodine bridges, with each palladium atom being surrounded by three iodine atoms and the chelate ligand (structure III). This structure resembles that found by X-ray study of the red polymorph of *trans*-$PdI_2\{P(CH_3)_2C_6H_5\}_2$.[16] In solution, the iodine bridges are broken to give either the monomeric chelate complex PdI_2AP or the solvated nonchelate complex $PdI_2(AP)$(solvent), analogous to $PdI_2(AA)$(solvent). The former possibility seems less probable on account of the deep red color of PdI_2AP in solution. The question could, in principle, be resolved by locating the position of the C=C stretching frequency of PdI_2AP in solution, but the poor solubility of the complex and the weakness of the band have prevented this being done. As shown in Table II, the electronic spectra of $[PdI_2AA]_2$ and PdI_2AP in solution more closely resemble those of a square-planar palladium(II) complex than of a five-coordinate trigonal-bipyramidal complex.

Considering the lack of isomorphism of the presumably isostructural platinum(II) and palladium(II) chloro and bromo complexes discussed above, it is remarkable that the X-ray powder patterns of PtI_2AP and PdI_2AP are virtually superimposable. Presumably the large iodine atoms play a larger part in determining the crystal packing than bromine atoms, and it is possible that there is weak iodine bridging in PtI_2AP.

Both chelate complexes $PdCl_2AA$ and $PdCl_2AP$ react with an excess of potassium thiocyanate to give complexes of the type Pd(ligand)$_2$(CNS)$_2$, in which the double bonds are uncoordinated. These complexes are probably formed by a disproportionation reaction

$$2PdCl_2(\text{ligand}) + 6CNS^- \longrightarrow Pd(CNS)_2(\text{ligand})_2 + Pd(SCN)_4^{2-} + 4Cl^-$$

The initial product is probably a bridging thiocyanato complex of the type (SCN)(ligand)Pd(NCS)$_2$-Pd(ligand)NCS, which is then readily split by excess thiocyanate ion to give the observed product.[17]

Surprisingly, a similar disproportionation giving $Pt(CNS)_2(AA)_2$ occurs when $PtCl_2AA$ is heated with potassium thiocyanate, and no intermediate bridged complex can be isolated. This contrasts with the behavior of the chelate complex $PtCl_2\{P(C_6H_5)_2C_5H_9\}$ under the same conditions, which gives the dimeric, nonchelate complex $[Pt(NCS)_2\{P(C_6H_5)_2C_5H_9\}]_2$[2] ($C_5H_9$ = 4-pentenyl). However, when $PtCl_2AP$ is heated with excess potassium thiocyanate, a chelate, monomeric dithiocyanate $Pt(CNS)_2AP$ is obtained, which is nonconducting in nitrobenzene {I, L = $P(C_6H_5)_2$; X = CNS}. The solid-state spectrum shows a band due to C=C stretching at 1508 cm^{-1}, and two strong, sharp bands due to C—N stretching at 2134 and 2123 cm^{-1}, characteristic of thiocyanate ion S-bonded to platinum(II) or palladium(II).[18–20] There is strong ligand absorption in the C–S stretching and NCS deformation regions of the infrared spectrum, which can also be used to distinguish between N- and S-bonded thiocyanate.[18–21] The complexes $M(CNS)_2(AA)_2$ (M = Pt, Pd) show a single rather broad band due to C—N stretching at 2120 and 2110 cm^{-1}, respectively, and they show no absorption in the 690–720-cm^{-1} region characteristic of the C—S stretching mode of S-bonded thiocyanate.[18–21] It is concluded that these complexes contain N-bonded thiocyanate. A weak to medium band at 860 cm^{-1} in the spectra of both compounds can then be assigned to the C=S stretching frequency. Unfortunately the characteristic NCS bending regions (400–440 cm^{-1} for S bonding and 450–490 cm^{-1} for N bonding)[18–21] are masked by ligand absorption. The complex $Pd(CNS)_2(AP)_2$ shows bands at 2085 cm^{-1} (s, b) and 860 cm^{-1} (m) and probably also contains N-bonded thiocyanate, but in this case, both the 690–720-cm^{-1} regions and the 400–490-cm^{-1} regions are masked by ligand absorption.

The ligands AA and AP are better chelating agents than tertiary phosphines and arsines containing the 4-pentenyl group,[2] since the former, but not the latter, give stable, chelate, monoolefin complexes of palladium(II). This can be attributed to more severe steric constraint on the double bond in AA and AP. The formation of $[PdI_2AA]_2$ (double bond uncoordinated) and PdI_2AP (double bond coordinated) suggests that the phosphine is the better chelate group. The same conclusion can be drawn from the formation of $Pt(SCN)_2AP$ (double bond coordinated) and $Pt(NCS)_2(AA)_2$ (double bond uncoordinated), and is also evident from a comparison of the reactions of the two ligands with copper(I) halides.[1] For both ligands, the tendency to form chelate complexes is greater for platinum(II) than for palladium(II), which may be correlated with the weaker metal–olefin bonding for the latter element. This is also evidenced by a comparison

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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]

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Some Syntheses of Platinum–Germanium Complexes

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Received August 28, 1967

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.

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