group is being weakened without assistance from the entering group.

Caution should be exercised in accepting an I_d mechanism for a substitution reaction of a square-planar complex, when all other such reactions go by the A mechanism. The I_d mechanism can be expected to occur, if at all, only in cases of the most extreme steric hindrance to the approach of the entering group.

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Arsenic–Sulfur Polydentate Ligands. I. Palladium(II) Complexes of Bis[phenyl(*o*-thiomethylphenyl)arsino]propane and Bis[phenyl(*o*-thiomethylphenyl)arsino]ethane

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Syntheses of two potentially quadridentate arsenic–sulfur ligands, 1,3-bis[phenyl(*o*-thiomethylphenyl)arsino]propane (C_3) and 1,2-bis[phenyl(*o*-thiomethylphenyl)arsino]ethane (C_2) are described. A variety of palladium(II) complexes of these two ligands have been prepared and structural assignments have been made on the basis of synthetic reactions, conductance, electronic spectra, molecular weight, and pmr data. The isolated complexes are of the following types: (1) $Pd(C_n)X_2$ (n = 3; X = Cl, Br, I, SCN; n = 2; X = Cl, Br, I) exist in nonpolar solvents with two anions and two arsenic atoms coordinated to palladium(II); (2) $Pd_2(C_n)X_4$ (n = 2, 3; X = Cl, I) have two halides, one thiomethyl group, and one arsenic atom (attached to the same benzene ring) coordinated to each palladium(II); (3) $Pd_2(C_n)_2X_2^{2+}$ are dimeric bi-univalent electrolytes in polar solvents and have two arsenic and one exchanging $-SCH_3$ group coordinated to palladium(II) along with a halide ion; (4) $Pd_2(C_n)_2^{4+}$ (n = 2, 3) are obtained as perchlorate salts and are square planar with the ligands functioning as bridging quadridentates. The complexes $Pd(C_3)Cl_2$ and $Pd(C_2)Cl_2$ undergo S-demethylation in hot dimethylformamide or hot dimethylformamide–butanol media, giving dimeric [Pd(demethylated C_3 or C_2)]$_2$. The demethylated complexes can be alkylated with methyl iodide to provide $Pd(C_3)I_2$ and $Pd(C_2)I_2$. Several new palladium(II) complexes with the ligands 1,2-bis(diphenylarsino)ethane (dias), (*o*-methylthiophenyl)diphenylphosphine (SP), and bis(*o*-methylthiophenyl)phenylphosphine (DSP) have been prepared and studied in order to provide standards for comparison. These complexes are $Pd(dias)I_2$, $Pd(SP)I_2$, and $Pd(DSP)I_2$.

Introduction

Polydentate ligands containing phosphorus–sulfur,[2–6] arsenic–sulfur,[5,7–9] nitrogen–sulfur,[2,7] nitrogen–phosphorus,[2,10–12] arsenic–phosphorus,[13] and nitrogen–arsenic[2,9,14] mixed donors, along with polydentate phosphorus[15,16] and arsenic[17–19] ligands, are of considerable current interest. Several such ligands have been reported to give rise to less familiar coordination environments around the central transition metals, which include five-coordinate nickel(II), palladium(II), and platinum(II) with trigonal-bipyramidal or square-pyramidal geometries. The supposedly good π-acceptor properties of sulfur, arsenic, or phosphorus donors are thought to promote pentacoordination. It appears that the flexidentate character of such multidentate ligands has not been effectively exposed in earlier studies.

We describe herein the syntheses of two quadridentate ligands (structure I) containing soft arsenic and sulfur donors, namely, 1,3-bis[phenyl(*o*-thiomethylphenyl)arsino]propane (C_3) and 1,2-bis[phenyl(*o*-thiomethylphenyl)arsino]ethane (C_2), and a study of their palladium(II) complexes. Earlier studies related to palladium(II) complexes of dimethyl(*o*-methylthiophenyl)arsine (chel, structure II),[8] 1,2-bis(*o*-diphenylarsinophenylthio)ethane (SAS, structure III),[7] and tris(*o*-methylthiophenyl)arsine (TSA)[5] have been made. Whereas chel, a close analog to the present series of ligands, can function in a bidentate fashion, our ligands are potentially quadrifunctional. Our experiences with these ligands reveal that the nature of the bridging

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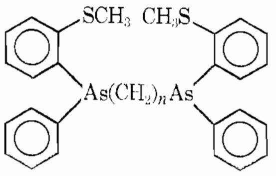
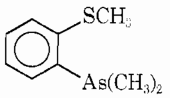
backbone, affinity of the anions for coordination sites, and the role of solvents are factors which govern the flexidentate behavior of the ligands, leading to the isolation of a variety of palladium(II) complexes.

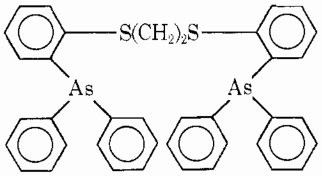
These new compounds provided the opportunity to extend investigations of S-dealkylation and S-alkylation reactions of metal chelates[20-22] containing the coordinated thioether and mercapto groups. Attempts were also made to initiate a cyclization reaction on the demethylated complexes so as to provide arsenic–sulfur macrocycles.



C_2, $n = 2$
C_3, $n = 3$
I



chel
II



SAS
III

Experimental Section

Reagents.—1,3-Dibromopropane, 1,2-dibromoethane, 2-aminobenzenethiol (Aldrich Chemical Co.), and phenyldichloroarsine (Strem Chemicals) were used as received.

Nitromethane (Matheson Coleman and Bell) was washed three times with 5% aqueous sulfuric acid and three times with 5% sodium bicarbonate, dried over fused calcium chloride, and distilled (100.5–101.5°). Thus obtained, nitromethane has a specific conductance[23] of the order of 10^{-7} ohm^{-1}. Tetrahydrofuran was refluxed over lithium aluminum hydride and distilled prior to use. Dichloromethane, chloroform, dimethyl sulfoxide, and dimethylformamide (Baker's Analyzed grade) were used without further purification. Acetonitrile (Fischer Certified grade) was distilled over P_4O_{10} (81.5–82.0°) and had a specific conductance of the order of 10^{-7} ohm^{-1}.

Synthesis of 1,3-Bis[phenyl(*o*-thiomethylphenyl)arsino]propane. 1,3-Propanebis(phenylarsonic acid).—Phenyldichloroarsine (64 g) was added dropwise over 1 hr to a well-cooled (5–8°) and efficiently stirred sodium hydroxide solution (50 g in 140 ml of water), such that the temperature did not rise beyond 13–15°. Some heavy white precipitate tends to separate toward the end of the addition of the phenyldichloroarsine.

1,3-Dibromopropane (30 g) was added dropwise to the above material over a period of 1 hr while the temperature was maintained at *ca.* 10–15°. The mixture was heated at reflux for 5 hr. After every 2 hr, more 1,3-dibromopropane (4 ml) was added to the refluxing solution. The reaction mixture was left overnight, filtered, and cooled to 5°. The solution was carefully acidified with concentrated hydrochloric acid to a distinct change from red to blue of Congo red paper (pH $\simeq$3.5–4.0). Stirring was continued and the soft precipitate of 1,3-propanebis(phenylarsonic acid) was allowed to stand for 1 day. The material was finally filtered, washed with dilute HCl, and dried in a desiccator. The dried material was recrystallized from a hot 2:1 water–ethanol solvent as snow white crystals; yield 20–22 g; mp 159–160°. *Anal.* Calcd for 1,3-propanebis(phenylarsonic acid): C, 43.69; H, 4.40; As, 36.35; O, 15.56. Found: C, 43.52; H, 4.61; As, 35.46; O (by difference), 15.44.

1,3-Propanebis(phenylchloroarsine).—The dry 1,3-propanebis(phenylarsonic acid) (20–22 g) was suspended in water (150 ml), and concentrated hydrochloric acid (180 ml) was added, followed by more water (250 ml). The solution was cooled to 5° and treated with potassium iodide (1 g in 10 ml of water), and the reduction was carried out by a flow of gaseous sulfur dioxide at 0–5° for 1.5 hr. The resulting thick oil was separated after 2 days, washed with 4 *M* HCl, and finally dried over potassium hydroxide and then Drierite; yield 18–20 g.

1,3-Bis[phenyl(*o*-thiomethylphenyl)arsino]propane.—2-Bromothioanisole (14 g) (prepared from 2-aminobenzenethiol)[24] and anhydrous ether (80 ml) were run into a three-necked flask fitted with an efficient mechanical stirrer, a nitrogen inlet, and a dropping funnel. With dry nitrogen flushing the system, the reaction flask was cooled to 0–5° with an acetone–Dry Ice bath. *n*-Butyllithium in hexane (1.6 *N*; 45 ml) was added to the bromothioanisole over a period of 1 hr. Toward the end of the addition, some of the lithio derivative separates from solution. After an additional 0.5 hr of stirring, 1,3-propanebis(phenylchloroarsine) (14 g) in freshly distilled tetrahydrofuran (20 ml) was added dropwise over another period of 1 hr. After 0.5 hr of stirring, dilute HCl (1 ml in 84 ml of water) was added dropwise and the precipitate of lithium chloride dissolved. Without separating the two layers, the ethereal layer was reduced in volume under a stream of air, the walls of the container were scratched, and the solution was allowed to stand in the refrigerator overnight. The resulting colorless material was filtered, washed with a little water, and dried. The crude product was further crystallized from hot acetone to give shining, colorless crystals; yield 10 g; mp 98–99°. *Anal.* Calcd for 1,3-Bis[phenyl(*o*-thiomethylphenyl)arsino]propane: C, 58.83; H, 5.10; As, 25.31; S, 10.83. Found: C, 58.98; H, 5.11; As, 25.18; S, 10.80.

The ligand 1,2-bis[phenyl(*o*-thiomethylphenyl)arsino]ethane was also obtained by following essentially the same steps.

1,2-Ethanebis(phenylarsonic acid) was obtained according to a published procedure;[25] mp 210–212° (lit.[25] mp 210–211°). *Anal.* Calcd for 1,2-ethanebis(phenylarsonic acid): C, 42.23; H, 4.05. Found: C, 42.21; H, 3.92.

1,2-Ethanebis(phenylchloroarsine) was also prepared by a published[25] method; mp 90–91° (lit.[25] mp 91–93°). *Anal.* Calcd for 1,2-ethanebis(phenylchloroarsine): C, 41.72; H, 3.50. Found: C, 41.45; H, 3.56.

1,2-Bis[phenyl(*o*-thiomethylphenyl)arsino]ethane.—The yield of the crude material was 13–15 g. This was purified from a hot 1:1 ethanol–acetone solvent, mp 102–104°. *Anal.* Calcd for 1,2-bis[phenyl(*o*-thiomethylphenyl)arsino]ethane: C, 58.15; H, 4.88; As, 25.91; S, 11.09. Found: C, 58.23; H, 4.71; As, 25.69; S, 11.24.

Preparation of Complexes. Chloropalladate Solution.—$PdCl_2$ (1.8 g) and LiCl (1.0 g) in 1-butanol (50 ml) were heated with magnetic stirring until a nearly clear solution was formed; the solution was then filtered.

$Pd(C_3)Cl_2$.—The chloropalladate solution (5 ml, 0.001 mol) was added with stirring to a warm acetone (15 ml) solution of the C_3 ligand (0.6 g, 0.001 mol). Light orange-yellow crystals separated and were crystallized from hot ethanol.

$[Pd(C_3)Cl]ClO_4$.—The chloropalladate solution (5 ml, 0.001 mol) was treated with a hot 1-butanol (20 ml) solution of lithium perchlorate (0.5 g) and was added to an acetone solution of the ligand (0.6 g, 0.001 mol). The mixture was warmed and filtered, and the filtrate was allowed to stand at around 5°. The fine orange-yellow crystals were collected, washed with ethanol, and dried.

$[Pd(C_3)Cl][B(C_6H_5)_4]$.—The chloro complex $Pd(C_3)Cl_2$ (0.3 g) was dissolved in boiling ethanol (50 ml) and then filtered. The

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filtrate was treated with an ethanol solution of sodium tetraphenylborate. The flocculent precipitate was collected and washed with ethanol.

$[Pd(C_3)Cl](BF_4)$.—This compound was obtained by the addition of a boiling ethanol (20 ml) solution (with a few drops of water) of $NaBF_4$ to an ethanol solution of $Pd(C_3)Cl_2$. On standing overnight, shining yellow crystals separated, which were further purified by recrystallization from boiling ethanol.

$Pd(C_3)Br_2$.—The chloropalladate solution (2.5 ml, 0.0005 mol) was heated with LiBr (1.5 g) in ethanol and was filtered into a warm 1:1 ethanol–acetone solution of the ligand (0.3 g, 0.0005 mol). The product was recrystallized from boiling ethanol.

$[Pd(C_3)Br][(BC_6H_5)_4]$.—This was obtained by the action of ethanolic sodium tetraphenylborate on the above bromo complex dissolved in ethanol.

$Pd(C_3)I_2$.—The ligand solution was treated with lithium iodide and the chloropalladate solution was added dropwise. The resulting deep orange-red crystals were recrystallized from a dichloromethane–ethanol medium.

$[Pd(C_3)I][B(C_6H_5)_4]$.—The complex $Pd(C_3)I_2$ was dissolved in acetonitrile under reflux, sodium tetraphenylborate (1 g) was added, and the solution was filtered. The filtrate was concentrated to 10–15 ml, ethanol (30 ml) was added, and the solution was allowed to stand. The orange-red crystals were collected and dried.

$Pd(C_3)(SCN)_2$.—The C_3 ligand (0.3 g, 0.0005 mol) was dissolved in hot acetone–ethanol (10 ml) and treated with ethanolic sodium thiocyanate. Chloropalladate (2.5 ml, 0.0005 mol) was added, and the solution was stirred and filtered. The filtrate deposited yellow crystals.

$[Pd(C_3)](ClO_4)_2$.—$Pd(C_3)Cl_2$ (0.25 g, 0.00033 mol) was dissolved in dichloromethane (30 ml) and was stirred with an acetone solution of silver perchlorate (0.14 g, 0.00066 mol). The yellowish precipitate was filtered and the filtrate was concentrated to a small volume and allowed to stand, whereupon light yellow crystals were deposited.

$Pd_2(C_3)Cl_4$.—The C_3 ligand (0.3 g, 0.0005 mol) and the chloropalladate solution (2.5 ml, 0.0005 mol) were heated together until a clear solution formed and then treated with a further amount (2.5 ml, 0.0005 mol) of the chloropalladate solution. The yellow crystalline precipitate was digested with hot ethanol to remove any $Pd(C_3)Cl_2$. The complex was then dissolved in a large volume of chloroform, concentrated, and treated with ethanol to recover the yellow crystalline product.

$Pd_2(C_3)I_4$.—The C_3 ligand (0.3 g, 0.0005 mol), lithium iodide, and chloropalladate (2.5 ml, 0.0005 mol) were combined to obtain $Pd(C_3)I_2$. This was dissolved in dichloromethane and treated with more lithium iodide and chloropalladate solution (2.5 ml). The dark red solution was concentrated and the dark red solid was purified by two recrystallizations from dichloromethane.

The palladium(II) complexes of the C_2 ligand were all obtained by following procedures similar to those for the C_3 complexes, with some slight modifications.

$[Pd(C_2)Cl][B(C_6H_5)_4]$.—This was obtained by treating $Pd(C_2)Cl_2$ in refluxing acetonitrile with sodium tetraphenylborate.

$Pd_2(C_2)Cl_4$.—The C_2 ligand (0.3 g, 0.0005 mol) and chloropalladate (5 ml, 0.001 mol) were mixed in an acetone–ethanol solution. Dichloromethane (100 ml) was added to dissolve the crystalline precipitate of $Pd(C_2)Cl_2$. On standing, this solution deposited yellow crystals of $Pd_2(C_2)Cl_4$.

S-Demethylated Complexes. Pd(demethylated C_3).—The chloro complex $Pd(C_3)Cl_2$ (0.3 g) was dissolved in a mixture of 1-butanol (10 ml) and dimethylformamide (DMF) (10 ml). The solution was heated at the reflux temperature for 5 hr. (Often some demethylated complex began to crystallize after 2 hr.) Most of the solvent was removed by evaporation and the remaining sticky mass was treated with ethanol. The product was further recrystallized from chloroform or dichloromethane. Pd(demethylated C_2) was also obtained by a similar procedure.

S-Alkylation Reactions.—The Pd(demethylated C_3) complex was dissolved in dichloromethane and mixed with 2 equiv of methyl iodide. After the reaction sat overnight the solvent was removed and the complex $Pd(C_3)I_2$ was precipitated with ethanol.

$[Pd(C_3)I_2]\cdot CH_3I$.—Pd(demethylated C_3) dissolved readily in a few milliters of CH_3I and crystals quickly separated. These were washed with ethanol and dried. The extra methyl iodide was, however, lost on crystallization from dichloromethane–ethanol medium.

S-Alkylation reactions with the C_2 complexes were accomplished by similar procedures.

Attempted Cyclization Reactions.—The Pd(demethylated C_3) complex (0.34 g, 0.0005 mol) was dissolved in chloroform and stirred for 24 hr with *o,o'*-xylyl dibromide (0.13 g, 0.0005 mol). The solvent was almost all removed and precipitation was initiated by adding ethanol. Dissolution in dichloromethane and precipitation with ethanol was repeated several times. *Anal.* Calcd for $[Pd(C_{35}H_{32}As_2S_2)]Br_2$: C, 45.16; H, 3.40; S, 6.85; Br, 17.23. Found: C, 42.20; H, 3.19; S, 7.34; Br, 16.15. Several modifications in reaction conditions were made but a pure product has yet to be isolated.

The similar reaction with Pd(demethylated C_2) complex and *o,o'*-xylyl dibromide also provided an impure product. *Anal.* Calcd for $[Pd(C_{34}H_{30}As_2S_2)]Br_2$: C, 44.44; H, 3.29; S, 6.98; Br, 17.39. Found: C, 41.87; H, 3.37; S, 6.28; Br, 18.75.

$Pd(SP)I_2$.—(*o*-Methylthiophenyl)diphenylphosphine[4] (SP) (0.61 g, 0.002 mol) was dissolved in hot butanol (60–70 ml) and treated with chloropalladate solution (10 ml, 0.002 mol). After 1 hr the greenish yellow $Pd(SP)Cl_2$ material was filtered, dissolved in dichloromethane (20 ml), and treated with an ethanol (10 ml) solution of lithium iodide (0.5 g). The blood red solution was concentrated. The vermillion red crystals were filtered and purified further by recrystallization from dichloromethane–ethanol.

Pd(demethylated SP)$_2$.—SP ligand (0.61 g, 0.002 mol) was dissolved in hot ethanol (40 ml), NaI (1 g) and chloropalladate solution (5 ml, 0.001 mol) were added, and the solution was warmed for 30 min after which it was allowed to stand overnight. Most of the solvent was removed and the product was purified by recrystallizing twice from dichloromethane.

$Pd(DSP)I_2$.—Bis(*o*-methylthiophenyl)phenylphosphine[4] (DSP) (0.18 g, 0.0005 mol) was dissolved in hot ethanol (60 ml), and lithium iodide (2 g) was added, followed by dropwise addition of chloropalladate (2.5 ml, 0.0005 mol) solution. The deep maroon-red product was recrystallized from dichloromethane.

$Pd(dias)I_2$.—1,2-Bis(diphenylarsino)ethane (dias) (0.25 g, 0.0005 mol) was dissolved in a mixture of dichloromethane (5 ml) and ethanol (10 ml) and the solution was treated with an ethanol solution of excess lithium iodide. On dropwise addition of the chloropalladate solution (2.5 ml, 0.0005 mol), dark orange-red crystals separated.

Analyses.—Analyses were performed by Galbraith microanalytical laboratories and by Alfred Bernhardt laboratories. A few carbon and hydrogen analyses were done by Mr. P. Kovi in our laboratory. The iodide contents in $Pd(DSP)I_2$ and $Pd(SP)I_2$ were determined gravimetrically as AgI after dissolving the complexes in dichloromethane and treating with silver perchlorate in acetone.

Electrical Conductance.—Conductivities were measured using an Industrial Instruments Model RC-16B conductivity bridge. Measurements were all made around 25° at a frequency of 1000 cps for the electrolytes and at 50 cps for the nonelectrolytes with a cell of constant 2.12. The specific conductances of the solvents were determined as a check on their purities. Dilution studies were carried out in acetonitrile in the concentration range 1.4×10^{-3} to 4.0×10^{-4} *N*, the choice being dictated by the solubility of a particular complex species.

Infrared Spectra.—The infrared spectra were obtained with a Perkin-Elmer Model 337 spectrophotometer. Nujol mull and KBr pellet techniques were employed. The spectra of *o*-aminothioanisole and *o*-bromothioanisole were run as liquids pressed between KBr plates. A polystyrene spectrum was used for calibration.

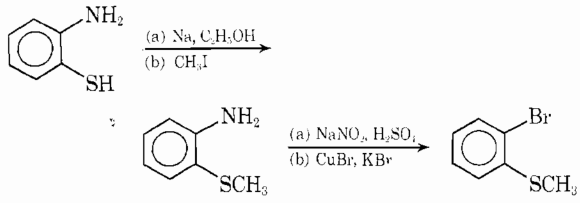
Electronic Spectra.—The visible spectra were run with a Cary 14 recording spectrophotometer with 1-cm matched cells in the range 300–700 mμ. Spectral runs were taken for most of the complexes in the solid state as halocarbon oil mulls, in polar solvents (acetonitrile, nitromethane, dimethyl sulfoxide, and dimethylformamide), and in nonpolar solvents (dichloromethane and chloroform). Volumes of 10 or 25 ml of (1–2) × 10^{-4} *M* concentration were prepared for such purposes by weighing the requisite amount of solute on a Sartorius microbalance. For the purpose of spectrophotometric titrations, 2-ml aliquots of 0.0005 *M* solutions of $[Pd(C_3)](ClO_4)_2$ and $[Pd(C_2)](ClO_4)_2$ in acetonitrile were transferred to a series of 10-ml flasks. Varying quantities of a 0.0005 *M* solution of tetrabutylammonium iodide (also in acetonitrile) were added and the spectra were taken. Optical densities at 400 and at 440 mμ, respectively, were plotted against moles of added iodide.

Molecular Weights.—Molecular weights were obtained in chloroform at 37° with a Mechrolab vapor pressure osmometer, Model 301A, calibrated with benzil. Determinations were made at two concentrations for most samples and at several concentrations where a concentration dependence was suspected.

Nmr Spectra.—These were run in Varian Associates HA-60 and HA-60A spectrometers. Tetramethylsilane was used as an internal standard in deuteriochloroform as solvent.

Results and Discussion

Syntheses of the Ligands.—The quadridentate arsenic–sulfur ligands were prepared by the reaction sequences



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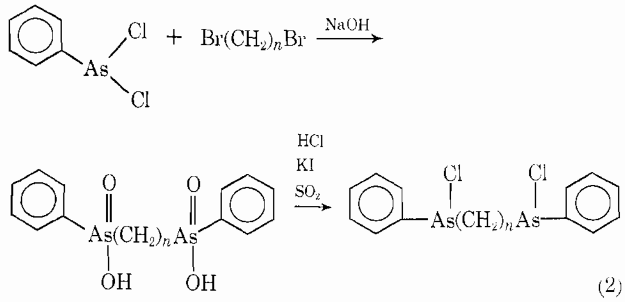

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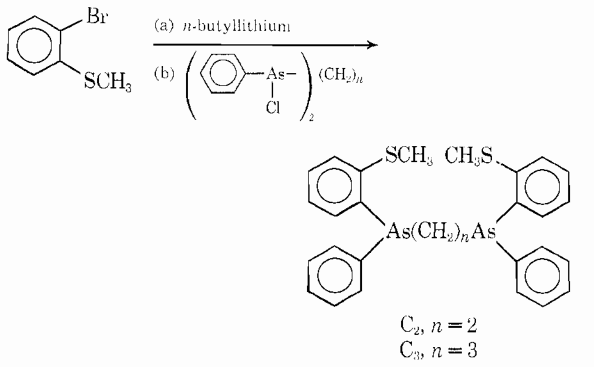


(3)

o-Aminothioanisole was prepared from 2-aminobenzenethiol by following Livingstone's procedure.[24] Phenyldichloroarsine was combined with 1,3-dibromopropane as recommended for 1,2-dibromoethane, giving the 1,3-propanebis(phenylarsonic acid). The acidification step must be done cautiously; otherwise a soft and sticky material spearates from solution. The 1,3-propanebis(phenylarsonic acid) is reduced to the trivalent arsenic compound 1,3-propanebis(phenylchloroarsine) by sulfur dioxide. The infrared spectrum of the chloroarsine shows the absence of the As=O band around 900 cm^{-1}, indicating that reduction of arsenic(V) to arsenic(III) has occurred. The oily material was dried and used directly in the last step of the synthesis. The ligands are finally obtained as glistening, snow white crystals from acetone or an acetone–ethanol medium and are stable to the usual atmospheric conditions.

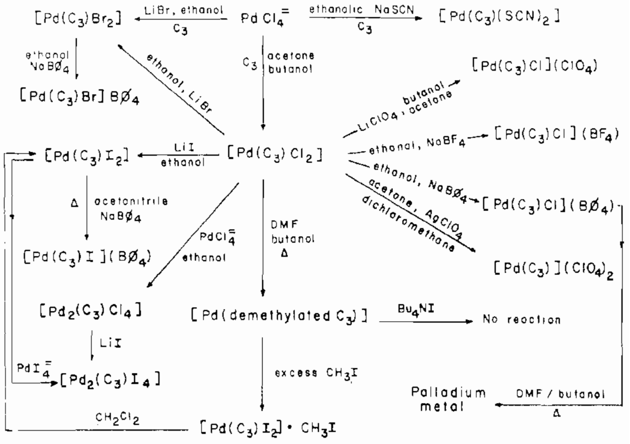


Figure 1.—Methods of preparation of the palladium(II) complexes of 1,3-bis[phenyl(*o*-thiomethylphenyl)arsino]propane.

Syntheses of Palladium(II) Complexes of the Neutral Ligands.—The chloro complex $Pd(C_3)Cl_2$ responds to a series of metathetical reactions with salts of several large, noncoordinating anions (perchlorate, tetraphenylborate, fluoroborate, etc.) leading to the loss of one of the two chloride ions: $Pd(C_3)Cl_2$ + excess X^- → $[Pd(C_3)Cl]X + Cl^-$. Reaction of $Pd(C_3)Br_2$ and $Pd(C_3)I_2$ with sodium tetraphenylborate also causes replacement of only one of the two halides. The chloro complex reacts with 2 mol of silver perchlorate to give the diperchlorate salt $[Pd(C_3)](ClO_4)_2$. $Pd(C_3)Cl_2$ and $Pd(C_3)I_2$ react with additional amounts of $PdCl_4^{2-}$ or PdI_4^{2-}, respectively, to provide the complexes $Pd_2(C_3)Cl_4$ or $Pd_2(C_3)I_4$.

The C_2 ligand readily forms the corresponding complexes $Pd(C_2)X_2$ (X = Cl, Br, I). Under forcing conditions (such as refluxing acetonitrile as solvent) $Pd(C_2)Cl_2$ reacts with sodium tetraphenylborate to form $[Pd(C_2)Cl][B(C_6H_5)_4]$. Silver perchlorate converts $Pd(C_2)Cl_2$ to $[Pd(C_2)](ClO_4)_2$. Like the $Pd(C_3)X_2$ complexes, the $Pd(C_2)X_2$ (X = Cl, I) complexes also react with additional PdX_4^{2-} (X = Cl, I) to furnish $Pd_2(C_2)X_4$ complexes. The preparative schemes are summarized in Figures 1 and 2 and the analytical data on the complexes appear in Table I.

In general, the complexes of the C_2 ligand are much less soluble in common solvents than are those of the C_3 ligand, with the exception of $Pd(C_2)I_2$, which is more soluble than $Pd(C_3)I_2$ in common organic solvents.

A range of physical measurements has been applied in the study of these compounds. The results are

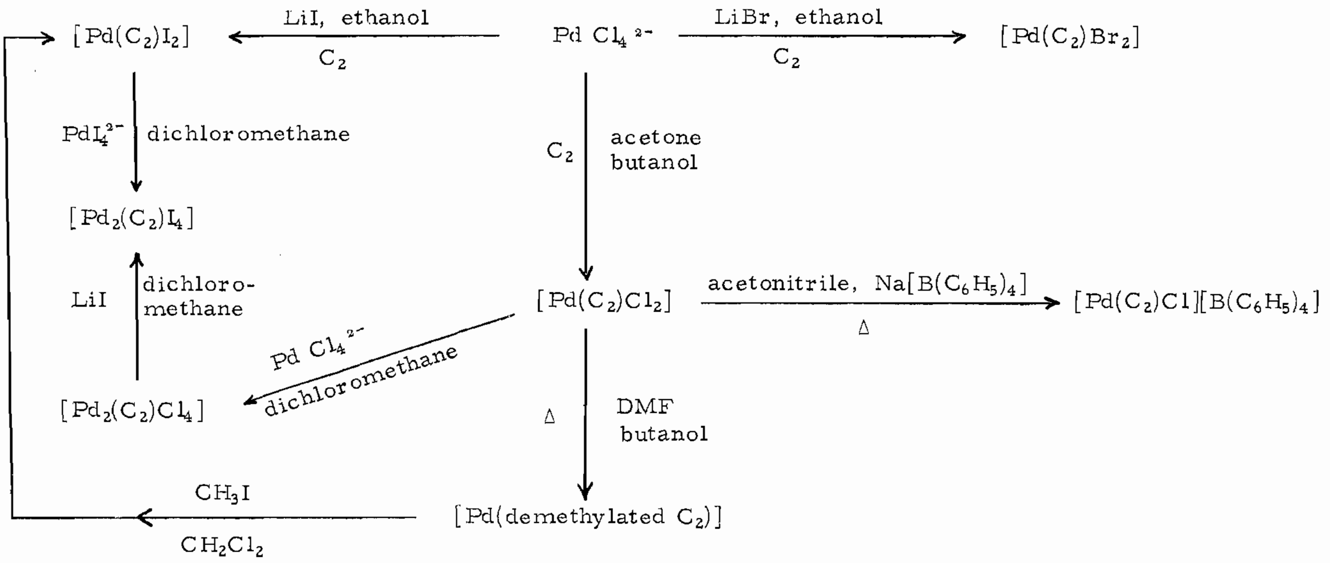


Figure 2.—Methods of preparation of the palladium(II) complexes of 1,2-bis[phenyl(*o*-thiomethylphenyl)arsino]ethane.

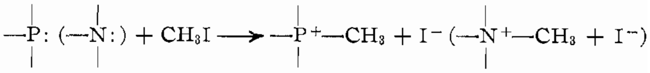
TABLE I

ANALYTICAL DATA FOR THE NEW PALLADIUM(II) COMPLEXES

Compound (empirical compn)	% C		% H		% halide		% S		% As	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
$Pd(C_3)Cl_2$	45.26	45.27	3.92	4.01	9.25	9.21	8.35	8.33		
$[Pd(C_3)Cl]ClO_4$	41.99	41.79	3.99	3.63	8.50	8.49	7.95	7.70	18.60	18.00
$[Pd(C_3)Cl][B(C_6H_5)_4]$	60.70	60.45	4.95	4.79	3.52	3.37				
$[Pd(C_3)Cl]BF_4$	42.51	42.39	3.36	3.60	4.27	4.31				
$Pd(C_3)Br_2$	40.48	40.56	3.65	3.52	18.63	18.61			17.33	17.45
$[Pd(C_3)Br][B(C_6H_5)_4]$	57.85	57.97	4.63	4.59	7.25	7.27				
$Pd(C_3)I_2$	36.40	36.50	3.12	3.15	26.85	26.60				
$[Pd(C_3)I][B(C_6H_5)_4]$	54.87	55.59	4.42	4.40	10.84	11.08				
$Pd(C_3)(SCN)_2$	45.51	45.71	3.84	3.71	3.31 (N)	3.44 (N)				
$[Pd(C_3)](ClO_4)_2$	38.59	38.78	3.48	3.36	7.76	7.90				
$Pd_2(C_3)Cl_4$	36.51	36.79	3.07	3.19	15.20	14.98				
$Pd_2(C_3)I_4$	27.03	26.54	2.57	2.30	38.15	38.68				
$Pd(C_2)Cl_2$	44.61	44.45	3.82	3.74	9.31	9.42	8.54	8.41		
$[Pd(C_2)Cl][B(C_6H_5)_4]$	60.28	60.07	4.59	4.65	3.13	3.41				
$Pd(C_2)Br_2$	39.59	39.81	3.34	3.34	18.70	18.92	7.76	7.59	17.91	17.74
$Pd(C_2)I_2$	35.82	35.78	3.05	2.96	27.61	27.58	6.83	7.03		
$[Pd(C_2)](ClO_4)_2$	37.97	38.04	3.37	3.19	7.93	8.03				
$Pd_2(C_2)Cl_4$	35.76	36.04	3.08	3.24	15.24	15.19				
$Pd_2(C_2)I_4$	25.64	25.89	2.16	2.17	38.86	39.08				
Pd(demethylated C_3)	48.41	48.51	3.82	3.62			9.33	9.33	22.34	22.34
Pd(demethylated C_2)	48.05	47.82	3.42	3.48			9.85	10.04	23.03	22.89
$Pd(C_3)I_2$ (by alkylation)	36.50	36.38	3.15	3.25	26.60	26.73				
$[Pd(C_3)I_2]\cdot CH_3I$	32.45	32.90	2.98	3.01	35.51	34.92				
$Pd(C_2)I_2$ (by alkylation)	35.04	35.78	2.95	2.96	28.02	27.58				
$Pd(SP)I_2$	35.02	34.12	2.68	2.56	37.28	37.98	4.98	4.78		
$Pd(DSP)_2$	34.05	33.65	2.91	2.65	35.86	35.60				
$Pd(dias)I_2$	37.28	37.08	2.68	2.86	30.25	30.02				
Pd(demethylated SP)$_2$	61.48	62.40	3.98	4.10	Nil	Nil				

summarized in a number of tables and these are discussed as the characterizations are presented for the various classes of compounds.[26]

Recently, several groups[6,11,12,27] of researchers have attempted to identify uncoordinated nitrogen, phosphorus, or sulfur donor functions by the use of the alkylation reaction that should occur upon addition of methyl iodide



$$\text{—P: (—N:)} + CH_3I \longrightarrow \text{—P}^+\text{—}CH_3 + I^- \text{ (—N}^+\text{—}CH_3 + I^-)$$

Such reactions have been performed in nitrobenzene, nitromethane, and acetonitrile over varying periods of time. We have examined this reaction in considerable detail using a representative group of related sulfur, phosphorus and arsenic donor ligands and their complexes. The results indicate that often even the free ligands, particularly those containing sulfur, do not

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(26) There was no infrared spectral evidence to support the supposition that either of the two ligands or any of their complexes have undergone oxidation to arsenic(V) *via* the addition of =O groups. Some phosphine or arsine derivatives are known to exhibit oxidation to phosphine oxides or arsine oxides during the syntheses of their complexes: F. A. Hartman and J. E. Newbery, *J. Inorg. Nucl. Chem.*, **28**, 1334 (1966).

(27) G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 4433 (1961).

Table II

Conductometric Studies on Methyl Iodide Reaction in Nitromethane[a]

Reactant	Molar conductance (Λ_M, ohm^{-1} cm^2 mol^{-1}) Without CH_3I	With CH_3I 30 min	With CH_3I 24 hr[b]	Change in electrolyte type (after 24 hr)
Ligand C_3	10.0	34	175	0 → 2:1
Ligand C_2	12.0	27	132	0 → 2:1
Ligand SP	6.0	84	88	0 → 1:1
Ligand DSP	6.0	55	65	0 → 1:1
Ligand dias	10.0	13	92	0 → 1:1
$Pd(C_3)I_2$	74	74	76	1:1 → 1:1
$Pd(C_2)I_2$	10	10	10	0 → 0
$Pd(SP)I_2$	6	6	6	0 → 0
$Pd(DSP)I_2$	8	8	9	0 → 0

[a] [Ligand or complex] = 0.0002 *M;* [CH_3I] = 0.32 *M.* [b] Conductance values remained virtually unchanged at the end of 24 hr.

alkylate at all the available functional groups under the usual conditions of the experiment. For example, both the ligands SP and dias have two potential centers for alkylation but the conductance values (Table II) indicate quaternization at only one point. Similarly quaternization at room temperature does not seem to occur at all the functional groups in the ligands DSP, C_2, or C_3. Results with the complexes $Pd(SP)I_2$, $Pd(DSP)I_2$, $Pd(C_2)I_2$, and $Pd(C_3)I_2$ are also not conclusive as to the number of uncoordinated donor atoms. We conclude, therefore, that the technique is not generally useful.

Classification of the Complexes.—For a discussion and comprehensive appreciation of the varieties of structures involved, the complexes are grouped under the following headings: I, $Pd(C_n)X_2$ ($n = 2$; X = Cl, Br, I; $n = 3$; X = Cl, Br, I, SCN); II, $Pd_2(C_n)X_4$ ($n = 2$; X = Cl, I; $n = 3$; X = Cl, I); III, $Pd_2(C_n)_2X_2^{2+}$ ($n = 2$; X = Cl; $n = 3$; X = Cl, Br, I); IV, $Pd_2(C_n)_2^{4+}$ (n = 2, 3). To avoid some difficulties in the presentation of the experimental data, the monomeric, empirical formulas have been retained in all tables and figures.

Table III

Molar Conductivities of the Complexes $Pd(C_n)X_2$ and $Pd_2(C_n)X_4$

Complex	Molar conductance (Λ_M, ohm^{-1} cm^2 mol^{-1}) Nitromethane[a]	Acetonitrile[b]	Dimethylformamide[c]	Dichloromethane[d]
$Pd(C_3)Cl_2$	78	110		5
$Pd(C_2)Cl_2$	10	20[e]		5
$Pd(C_3)Br_2$	75	130[e]		7
$Pd(C_2)Br_2$	10	. . .		5
$Pd(C_3)I_2$	74	130[e]		7
$Pd(C_2)I_2$	10	20		3
$Pd(C_3)(SCN)_2$	90			
$Pd_2(C_3)Cl_4$			10[e]	
$Pd_2(C_2)Cl_4$			11[e]	
$Pd_2(C_3)I_4$			12[e]	
$Pd_2(C_2)I_4$			12[e]	

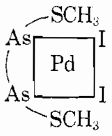
[a] Values reported for 1:1 and 2:1 electrolytes in nitromethane are 80–95 and 160–190, respectively: T. D. DuBois and D. W. Meek, *Inorg. Chem.*, **8,** 146 (1969). [b] Values reported for 1:1 and 2:1 electrolytes in acetonitrile are 135–155 and 250–310, respectively: M. Ciampolini and P. Paoletti, *Inorg. Chem.*, **6,** 1261 (1967). [c] Values reported for 1:1 and 2:1 electrolytes in dimethylformamide are 70–90 and 140–150, respectively: R. A. Robinson and R. H. Stokes, "Electrolytic Solutions," 2nd ed, Academic Press, New York, N. Y., 1959, p 162. [d] A 1:1 electrolyte has a value of 78 in dichloromethane. [e] Concentrations are (2–2.5) × 10^{-4} *M;* all other concentrations are ≃5.0 × 10^{-4} to 1.0 × 10^{-3} *M.*

Table IV

Molecular Weights of $Pd(C_n)X_2$ and $Pd_2(C_n)X_4$ Complexes in Chloroform

Complex	Concn, g/l.	Mol wt (found)	Empirical formula wt
$Pd(C_3)Cl_2$	2.15	770	769
	5.25	820	
$Pd(C_3)I_2$	2.0	870	954
	2.55	940	
$Pd(C_2)I_2$	2.35	904	939
	2.95	922	
$Pd_2(C_3)I_4$	1.58	1316	1312
$Pd(SP)I_2$	5.385	640	668
	8.02	668	
$Pd(DSP)I_2$	7.15	660	714
	10.75	685	

I. Complexes of the Type $Pd(C_n)X_2$.—The key compound in this class is $Pd(C_2)I_2$. This complex is essentially a nonelectrolyte in a wide variety of solvents, for example, dichloromethane, nitromethane, and acetonitrile (Table III). In chloroform, the complex has a monomer molecular weight that confirms the monomeric formulation (Table IV). Consistent with the conductance behavior, the complex exhibits the same electronic spectra (λ_{max} ≃440 mμ) irrespective of the polar nature of the solvent (Table V). The pmr spectrum of the compound does not show an absorption downfield from the position of the thiomethyl resonance of the free ligand. Such a shift would signal the presence of coordinated $-SCH_3$ groups.[11,12,28] The accumulated evidence suggests that, in this complex, the ligand C_2 is coordinated to the Pd(II) through its two arsenic atoms and that two coordinated iodide ions are also present (structure IV). For the sake of comparison, the complex $Pd(dias)I_2$ was synthesized and its properties were studied.



IV

The electronic spectrum of the nonionic $Pd(dias)I_2$ is closely similar to that of $Pd(C_2)I_2$ (Tables V and VI). It must be recognized, however, that the electronic spectrum of $Pd(chel)I_2$ (as reported in the literature[8]) is also similar to that of $Pd(C_2)I_2$. Further, in the complexes of type II (below), we have authentic examples of compounds within which the palladium is coordinated to two iodide ions, one arsenic atom, and one thiomethyl group and the spectra of the latter compounds are different from those of $Pd(dias)I_2$ and $Pd(C_2)I_2$.

The complex $Pd(C_3)I_2$, a monomer in chloroform (Table IV), is also believed to assume structure IV

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(28) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Am. Chem. Soc.*, **90,** 6938 (1968).

TABLE V

ELECTRONIC SPECTRA OF THE COMPLEXES $Pd(C_n)X_2$ AND $Pd_2(C_n)X_4$

(λ_{max} IN mμ; EXTINCTION COEFFICIENTS IN PARENTHESES)

Complex	Halocarbon oil mull	Dichloromethane	Chloroform	Nitromethane	Acetonitrile	DMSO	DMF
$Pd(C_3)Cl_2$	360	365 (4200)	360 (4700)	...	345 (5000)	345 (6000)	...
$Pd(C_2)Cl_2$	350	366 (4700)	370 (4300)	...	365 (4500)	365 (5000)	...
$Pd(C_3)Br_2$	...	370 (3900)	370 (3700)	...	360 (4200)	357 (5200)	...
$Pd(C_2)Br_2$	360–390	390 (4650)	392 (4400)	...	385 (4400)	...	...
		350 sh	350 sh	...	355 sh	...	...
$Pd(C_3)I_2$	453	455 (3900)	455 (3400)	395 (3300)	395 (3300)	395 (3400)	...
$Pd(C_2)I_2$	440	440 (5300)	442 (5500)	436 (5000)	437 (5500)	436 (5200)	...
$Pd_2(C_3)Cl_4$	365	370 (4600)	...	...	...	370 (4500)	370 (4500)
$Pd_2(C_2)Cl_4$	370	372 (4500)	...	...	...	372 (5200)	370 (5000)
$Pd_2(C_3)I_4$	...	460 (5200)	460 (5500)	...	455 (4000)	...	454 (7000)
$Pd_2(C_2)I_4$	...	460 (5500)	460 (6500)	...	452 (6500)	...	454 (6500)
$Pd(C_3)(SCN)_2$	...	415 sh (1700)	415 sh (1700)	...	390 sh (1500)	...	...

TABLE VI

CONDUCTANCE AND ELECTRONIC SPECTRA OF REFERENCE COMPOUNDS $Pd(L)I_2$

Complex	Molar conductance in nitromethane[a] (Λ_M, ohm^{-1} cm^2 mol^{-1})	Solvent	λ_{max}, mμ (ε)
$Pd(SP)I_2$	6	Dichloromethane	450 (3100)
		Chloroform	450 (3100)
		Nitromethane	440 (2900)
		Acetonitrile	440 (2900)
		Halocarbon mull	445
$Pd(DSP)I_2$	8	Dichloromethane	455 (4200)
		Chloroform	455 (4000)
		Nitromethane	450 (3800)
		Acetonitrile	450 (3800)
		Halocarbon mull	450
$Pd(dias)I_2$	3	Dichloromethane	440 (4600)
		Chloroform	440 (4700)
		Acetonitrile	436 (4500)
		Halocarbon mull	440
$Pd(dias)Cl_2$	12[b]	DMSO	362 (4200)
		Halocarbon mull	350

[a] Concentration is 2.0×10^{-4} M. [b] In dimethylformamide.

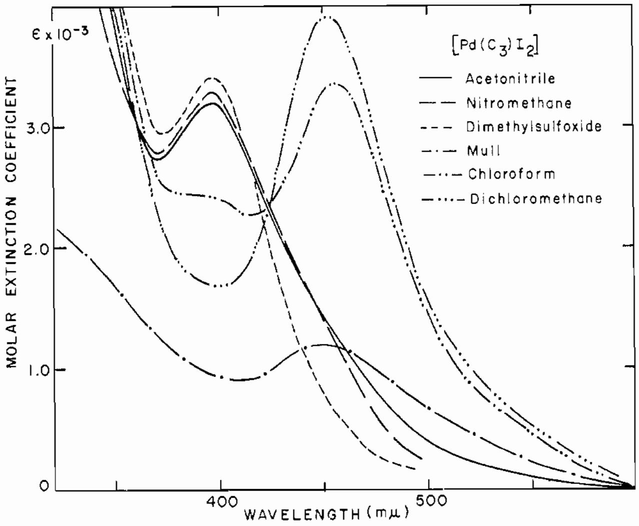

Figure 3.—Electronic absorption spectra of $Pd(C_3)I_2$ in different states: —, acetonitrile; – –, nitromethane; - - -, dimethyl sulfoxide; –·–, halocarbon mull; –··–, chloroform; –···–, dichloromethane.

when dissolved in nonpolar solvents. The differences in the electronic spectra of $Pd(C_2)I_2$ and $Pd(C_3)I_2$ in nonpolar solvents are minimal. When viewed from this standpoint, the behavior of $Pd(C_3)I_2$ in polar solvents is somewhat remarkable (Figure 3; Table V). Whereas $Pd(C_3)I_2$ and $Pd(C_2)I_2$ give comparable nonionic conductance values ($\Lambda_M \simeq 5$ mhos) in low dielectric constant solvents, such as dichloromethane, $Pd(C_3)I_2$ appears to exist as a 1:1 electrolyte in nitromethane and acetonitrile. In these solvents, the complex almost certainly assumes a structure closely related to those of the complexes of type III, *e.g.*, $[Pd(C_3)Cl]_2(ClO_4)_2$. As shown below, dilution studies show the type III complexes to be dimeric. The distinction in conductance behavior between the C_2 and C_3 derivatives in polar solvents is accompanied by substantial modifications in their electronic spectra, the maximum ($\simeq$455 mμ) in nonpolar solvents shifting to $\simeq$395 mμ in polar media for $Pd(C_3)I_2$. The similarity of the spectrum of this substance in polar solvents with that of $[Pd(C_3)I][B(C_6H_5)_4]$ in both polar and nonpolar solvents is striking. Additional evidence in support of the different structural types present in polar solvents for $Pd(C_2)I_2$ and $Pd(C_3)I_2$ is found in the spectrophotometric titrations[6,29,30] of $[Pd(C_n)](ClO_4)_2$ (n = 2, 3) with tetrabutylammonium iodide in acetonitrile. For the C_3 complex a definite break is observed at 1:1 complex:iodide ratio, whereas that for the C_2 compound occurs at 1:2 ratio (Figure 4).

The foregoing discussion may now be extended to other members of the series (X = Cl, Br). The conductance behavior of $Pd(C_2)X_2$ in polar solvents may, on first inspection, be interpreted to mean that in these compounds halide ions are never displaced by the competing thiomethyl groups. Although this situation obviously prevails under the conditions used for our conductance measurements, the process can be forced. Thus, $Pd(C_2)Cl_2$ does react with sodium tetraphenylborate in refluxing acetonitrile, forming $[Pd(C_2)Cl][B(C_6H_5)_4]$, a complex of type III.

$Pd(C_3)(SCN)_2$ also belongs to category I. Its infrared spectrum shows two bands at 2100 and 2080

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(29) J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

(30) R. L. Dutta, D. De, and A. Syamal, *J. Indian Chem. Soc.*, **45**, 663 (1968).

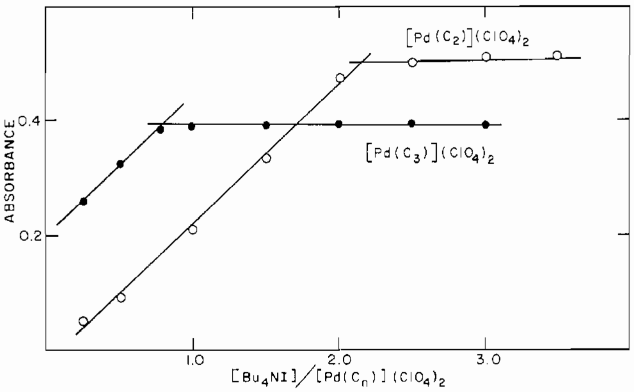
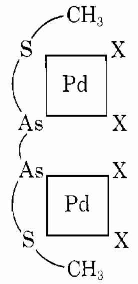


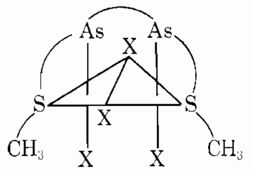
Figure 4.—Spectrophotometric titrations of $[Pd(C_3)](ClO_4)_2$ and $[Pd(C_2)](ClO_4)_2$ against tetrabutylammonium iodide in acetonitrile: ●, $[Pd(C_3)](ClO_4)_2$ at 400 mμ; ○, $[Pd(C_2)](ClO_4)_2$ at 440 mμ.

cm^{-1} in the C≡N stretching region.[31] Unfortunately the NCS bending region and the CS stretching regions are obscured by strong interfering absorbances of the C_3 ligand. The electronic spectrum of this complex has its lowest energy absorption band as a shoulder around 415 mμ in nonpolar solvents and around 390 mμ in polar media. The distinct shift of the spectra in a given solvent toward lower energy, compared to $Pd(C_3)Cl_2$ and even $Pd(C_3)Br_2$, indicates a weak contribution to the ligand field by the thiocyanate group.[32] We thus ascribe sulfur bonding to the –SCN group in the complex. Unfavorable solubility did not permit an infrared intensity measurement.[33]

II. Complexes of the Type $Pd_2(C_n)X_4$.—This series of complexes results when compounds of the type $Pd(C_n)X_2$ are treated with a second mole of PdX_4^{2-}. The chloro and the iodo series have been isolated and characterized. An alternative formulation $[Pd(C_n)][PdX_4]$ is not acceptable on the basis of the nonionic natures of these substances in dimethylformamide. The molecular weight of $Pd_2(C_3)I_4$ corresponds to the dimeric formula weight (Table IV). The electronic spectra of the $Pd_2(C_n)X_4$ complexes show little differences between polar and nonpolar solvents. These complexes are almost certainly examples of structures in which one arsenic and one thiomethyl group from the same benzene moiety are coordinated to one palladium(II) ion. We do not have experimental evidence that will distinguish between the four-coordinate and five-coordinate alternative structures (V and VI).



V



VI

III. Complexes of the Type $Pd_2(C_n)_2X_2^{2+}$.—These species are formed from $Pd(C_n)X_2$ upon displacement (in polar solvents) of a coordinated halide ion by a competing thiomethyl group. The displacement process is accompanied by dimerization of the complex. Although such compounds provide normal 1:1 electrolyte molar conductance values in nitromethane or acetonitrile solutions (Table VII), dilution conductance measurements (Table VIII; Figure 5) in the latter solvent give values for the Onsager slope A in the range typical of bi-univalent electrolytes.[34-39] These results strongly suggest that in polar solvents the actual cation is a dipositive ion. The conductance data are consistent with a five-coordinated structure in solution in which all four ligand donor centers are coordinated to palladium(II) in addition to a halide (structure VII). A second possibility is a four-coordinate, planar structure in which one halide and three of the four ligand donor atoms are coordinated. The electronic spectra of these complexes are not comparable to those of the known trigonal-bypyramidal $Pd\{As(o\text{-}C_6H_4As(C_6H_5)_2)_3\}X^+$ and $Pd\{P(o\text{-}C_6H_4P(C_6H_5)_2)_3\}X^+$ complexes.[40] The

Table VII

Molar Conductivities of $[Pd(C_n)X]Y$ and $[Pd(C_n)](ClO_4)_2$

	Molar conductance[a] (Λ_M, ohm^{-1} cm^2 mol^{-1})		
Complex	Nitromethane	Acetonitrile	Dichloromethane
$[Pd(C_3)Cl]ClO_4$	85	118	36
$[Pd(C_3)Cl][B(C_6H_5)_4]$[b]	60	97	38
$[Pd(C_3)Br][B(C_6H_5)_4]$[b]	56	96	48
$[Pd(C_3)I][B(C_6H_5)_4]$[b]	56	80	44
$[Pd(C_2)Cl][B(C_6H_5)_4]$[b]	56	89	30
$[Pd(C_3)](ClO_4)_2$	188	326	. . .
$[Pd(C_2)](ClO_4)_2$	187	314	. . .

[a] Concentration 5.0×10^{-4} to 1.0×10^{-3} M. [b] These low values are consistent with earlier reports and suggest ion pairing: G. A. Pneumaticakis, *Chem. Ind.* (London), 770 (1968); T. Tarantelli and C. Furlani, *J. Chem. Soc., A*, 1717 (1968).

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(34) It is becoming increasingly clear that molar conductance values measured at one concentration do not distinguish between a monomeric uni-univalent complex [ML]X and the corresponding bi-univalent dimer $[M_2L_2]X_2$. According to the Onsager limiting law $\Lambda_0 - \Lambda_e = A\sqrt{c}$, the equivalent conductivity (Λ_e) varies linearly with $\sqrt{c}$ (c is the equivalent concentration). The slope of this plot (A) may be calculated[35] using an experimentally determined Λ_0 and constants α^* and β^* appropriate to the conditions of the experiment and making assumptions with regard to the ionic composition of the complex species: $A = \alpha^*\Lambda_0 + \beta^*$. For such dilution studies acetonitrile is preferred over nitromethane because of its higher dielectric constant and lower viscosity. The choice of acetonitrile for our studies was also based on the greater solubilities of the complexes of interest in that solvent. The complexes $[Pd(C_3)X]ClO_4$ (X = Cl), $[Pd(C_3)X][B(C_6H_5)_4]$ (X = Cl, Br), $[Pd(C_2)X][B(C_6H_5)_4]$ (X = Cl), $[Pd(C_2)](ClO_4)_2$, and $[Pd(C_3)](ClO_4)_2$ were investigated in detail. Below a concentration range of 4×10^{-4} N most of the complexes tended to produce nonlinear $(\Lambda_0 - \Lambda_e)$ *vs.* $\sqrt{c}$ plots, which we ascribe to solvolytic displacement of the coordinated halides. The slopes A (580–800) for the halide-coordinated complexes $Pd(C_n)X^+$ indicate the compounds to be dimeric 2:1 electrolytes; whereas those (1250, 1310) for the perchlorate salts indicate an even higher electrolyte type.

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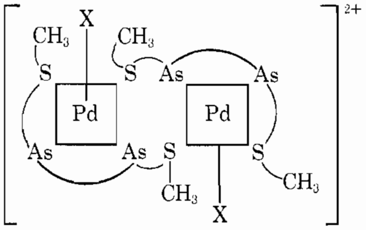
TABLE VIII

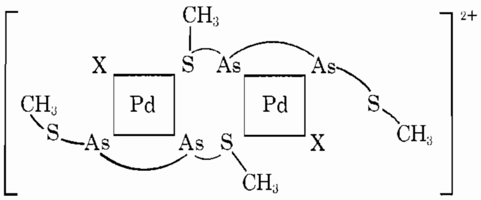
DILUTION CONDUCTANCE RESULTS IN ACETONITRILE[a]

Complex	Concn × 10^3, equiv/l.	Λ_e	Λ_0	Exptl slope A
$[Pd(C_3)Cl]ClO_4$	1.4	115	144	800
$[Pd(C_3)Cl][B(C_6H_5)_4]$	1.0	97	123	800
$[Pd(C_3)Br][B(C_6H_5)_4]$	1.0	96	118	700
$[Pd(C_3)](ClO_4)_2$	1.0	163	201	1250
$[Pd(C_2)Cl][B(C_6H_5)_4]$	1.0	88	106	580
$[Pd(C_2)](ClO_4)_2$	1.2	153	198	1310

[a] The theoretical values of the slopes A have been calculated from the equivalent conductivities at infinite dilution (Λ_0) and the individual ionic conductivities and constants appropriate for acetonitrile. The values thus obtained are in the range 306–376 for 1:1 electrolytes and in the range 829–1038 for 2:1 electrolytes. In the calculation of the theoretical slopes, the following values have been used: viscosity 0.003449 P, dielectric constant 36.01 at 25°, ionic conductivity for ClO_4^- 103.4 and for $B(C_6H_5)_4^-$ 57.7: G. J. Janz, F. J. Kelly, and H. V. Venkatasetty, "A Survey of Nonaqueous Conductance Data," Rensselaer Polytechnic Institute, Troy, N. Y., 1962; J. F. Coetzee and G. P. Cunningham, *J. Am. Chem. Soc.*, **87,** 2529 (1965).



VII



VIII

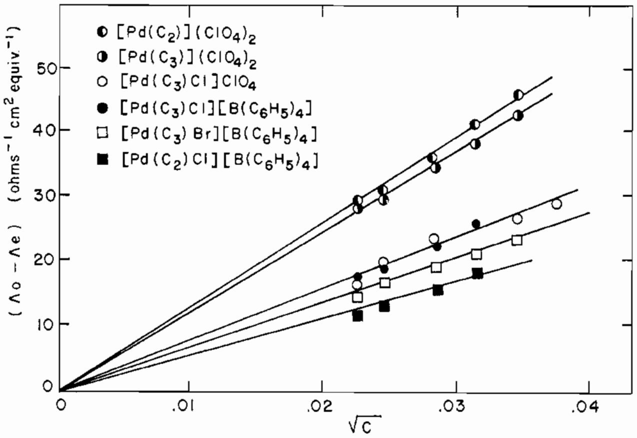


Figure 5.—Plots of $\Lambda_0 - \Lambda_e$ *vs.* $\sqrt{c}$ for complexes in acetonitrile: ■, $[Pd(C_2)Cl][B(C_6H_5)_4]$; □, $[Pd(C_3)Br][B(C_6H_5)_4]$; ●, $[Pd(C_3)Cl][B(C_6H_5)_4]$; ○, $[Pd(C_3)Cl]ClO_4$; ◑, $[Pd(C_3)](ClO_4)_2$; ◐, $[Pd(C_2)](ClO_4)_2$.

TABLE IX

PROTON MAGNETIC RESONANCE DATA FOR SOME LIGANDS AND THEIR COMPLEXES IN $CDCl_3$

Compound	Chemical shift of protons, τ: CH_3 of free thioether group	CH_3 of coordinated thioether group	$-CH_2-$
SP	7.64[a]	...	...
DSP	7.61[a]	...	...
$Pd(SP)I_2$	...	6.95	...
$Pd(DSP)I_2$	...	7.25	...
C_2	7.75[c,d]	...	7.8[d]
C_3	7.65[d]	...	7.85,[d] 7.95,[d] 8.1[d]
$Pd(C_2)I_2$	7.75 (3)	...	8.9 (2)
$[Pd(C_3)Cl][B(C_6H_5)_4]$	...	7.48[b] (3)	8.05[b] (3)
$[Pd(C_3)I][B(C_6H_5)_4]$	...	7.30,[b] 7.50[b] (total 3)	7.85[b] (3)

[a] W. S. Tsang, D. W. Meek, and A. Wojcicki, *Inorg. Chem.*, **7,** 1263 (1968). [b] Broad. [c] Doublet. [d] The total area under $-SCH_3$ and $-CH_2$ protons gives a good proton count against the aromatic protons in the multiplet centered around τ 2.8. Approximate relative intensities in parentheses.

TABLE X

MOLECULAR WEIGHT OF THE COMPLEXES $Pd(C_n)X^+$ IN CHLOROFORM SOLVENT

Complex (monomer formula)	Concn, g/l.	Mol wt (found)	Monomer wt
$[Pd(C_3)Cl]ClO_4$	3.0	882	833
	4.14	940	
	8.165	1070	
	10.975	1100	
	17.20	1230	
	20.15	1380	
$[Pd(C_3)Cl][B(C_6H_5)_4]$	9.25	930	1053
	13.95	1000	
$[Pd(C_3)Br][B(C_6H_5)_4]$	5.05	1052	1098
	7.35	1010	
$[Pd(C_3)I][B(C_6H_5)_4]$	5.90	1080	1144

pmr spectrum (Table IX) of $[Pd_2(C_3)_2Cl_2][B(C_6H_5)_4]_2$ (empirical formula $[Pd(C_3)Cl][B(C_6H_5)_4]$) in deuteriochloroform shows an absorption at τ 7.48 ($-CH_3$ protons) and a broader envelope at τ 8.05 ($-CH_2$ protons). The iodo complex $[Pd_2(C_3)_2I_2][B(C_6H_5)_4]_2$ (empirical formula $[Pd(C_3)I][B(C_6H_5)_4]$) shows resonances at τ 7.30, 7.50, and 7.85. In this context, we wish to refer to two phosphorus–sulfur-containing palladium(II) complexes. The complex $Pd(SP)I_2$, a nonelectrolyte that is monomeric in chloroform, gives a sharp single resonance at τ 6.95 in agreement with a square-planar diiodo structure within which both ligand functions are bound. On the other hand, $Pd(DSP)I_2$ is also a nonelectrolyte and monomeric in chloroform, and its pmr spectrum also shows a single resonance, but at τ 7.25, thereby indicating two equivalent thiomethyl groups. In this second case, the $S-CH_3$ resonance position is the exact time-averaged position between that for coordinated $-SCH_3$ (τ 6.85 from $Pd(SP)I_2$) and that for free $-SCH_3$ (τ 7.61 for DSP). This intermediate resonance position indicates a rapid exchange process by which the two thiomethyl groups become equivalent. In order to test the exchange hypothesis, the pmr spectra of $Pd(DSP)I_2$ in $CDCl_3$ was studied down to −50°. The sharp signal at room temperature decreased much in height and showed considerable broad-

Table XI

Electronic Spectra of $[Pd(C_n)X]Y$ and $[Pd(C_n)](ClO_4)_2$

(λ_{max} in mμ; Extinction Coefficients in Parentheses)

Complex	Halocarbon oil mull	Dichloromethane	Chloroform	Nitromethane	Acetonitrile	DMSO
$[Pd(C_3)Cl]ClO_4$	345	355 (6700)	350 (6000)	...	348 (5700)	346 (6700)
$[Pd(C_3)Cl][B(C_6H_5)_4]$	345	355 (6700)	350 (6000)	...	348 (5700)	346 (6700)
$[Pd(C_3)I][B(C_6H_5)_4]$	360–390	395 (3800)	390 (4300)	390 (3000)	390 (3600)	387 (3600)
$[Pd(C_2)Cl][B(C_6H_5)_4]$	360–380	365 (4900)	366 (4500)	...	368 (4700)	...
$[Pd(C_3)](ClO_4)_2$	320	...	...	...	No band up to 310 mμ	No band up to 310 mμ
$[Pd(C_2)](ClO_4)_2$	320	...	...	...	No band up to 310 mμ	No band up to 310 mμ

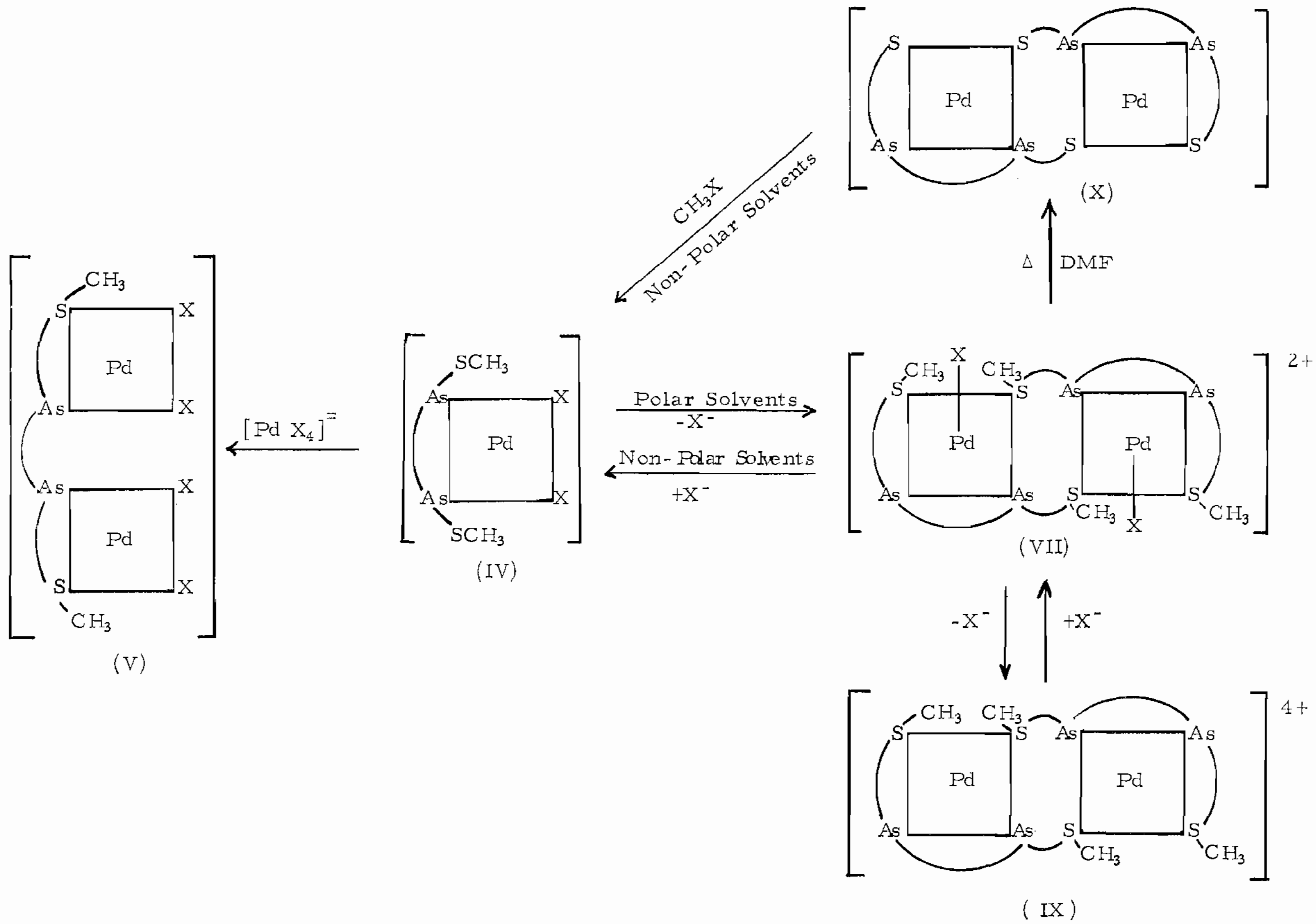


Figure 6.—Diagrammatic representation of relationships between different structural types of the palladium(II) complexes of the ligands C_3 and C_2.

ening at −50°, although distinct splitting into two resonances did not occur at this limiting low temperature. In the light of these results, it seems reasonable to argue that the $-SCH_3$ groups in the $Pd(C_3)X^+$ complexes are also undergoing exchange between coordinated and uncoordinated positions (Table IX).

An appraisal of the molecular weight data (Table X) obtained in chloroform would indicate that these are also consistent with our proposed model. The complexes $Pd_2(C_n)_2X_2^{2+}$ (empirical formula $Pd(C_n)X^+$) have a substantial conductance even in low-polarity solvents such as dichloromethane, though ion association is also indicated. Consequently, instead of an ideal value of one-third the dimeric formula weight, the molecular weights are consistently high, and, in the case of the perchlorate, a concentration dependence has been observed. These observations are interpretable in terms of an outer-sphere association of the complexes. The several evidences presented favor assignment of structure VIII to these complexes.

IV. Complexes of the Type $Pd_2(C_n)_2^{4+}$.—These compounds are obtained from $Pd(C_n)X_2$ or $Pd_2(C_n)_2X_2^{2+}$ by removal of all the halide ion with silver perchlorate. Square-planar coordination is indicated by the movement of the first band in the electronic spectra of these complexes far to higher energy (≃310 mμ, Table XI). Conductance measurements in nitromethane or acetonitrile fall in the range usually found for 2:1 electrolytes but the values of the slope A (1250, 1310) in acetonitrile are far greater than those for 2:1 electrolytes. Indeed on removing the coordinated halides from the dimeric bi-univalent electrolyte $Pd_2(C_n)_2X_2^{2+}$, a 4:1 electrolyte should be formed (structure IX, Figure 6).

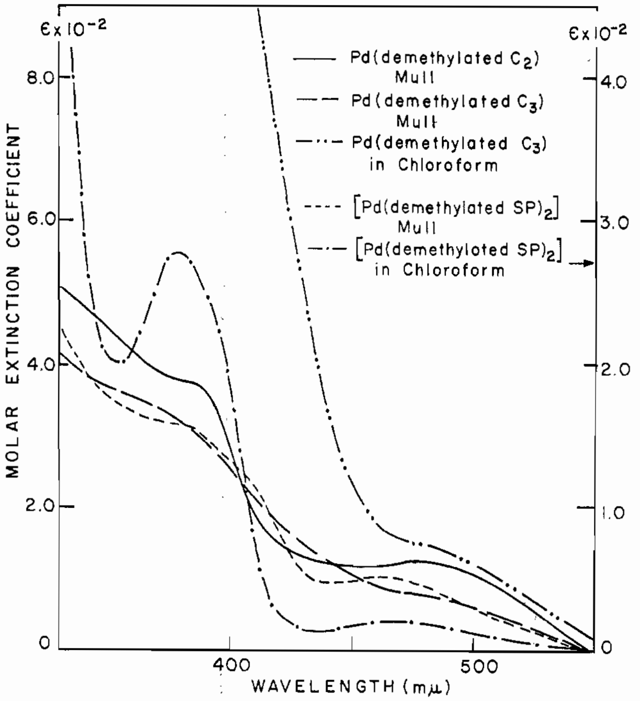


Figure 7.—Electronic absorption spectra of demethylated complexes: Pd(demethylated C_2): —, halocarbon mull; Pd(demethylated C_3): – –, halocarbon mull; – · · –, chloroform; Pd(demethylated $SP)_2$: - - - -, halocarbon mull; —·—, chloroform (read right-hand ordinate scale).

The infrared spectra, as expected, do not show coordinated perchlorate. The bands around 1100 and 625 cm^{-1} show no splitting.[41–43]

A schematic diagram (Figure 6) shows the interrelations among the different types of complexes.

Demethylation Reactions.—The first report[44] of S-demethylation related to the action of platinum(II) on dimethyl sulfide. Subsequently, sodium tetrachloroaurate has been shown to cause the demethylation of 8-methylthioquinoline leading to the formation of dichloro(8-methylthioquinolinato)gold(III).[45] Palladium(II) and platinum(II) complexes of chel (structure II), $Pd(chel)_2X_2$ (X = Cl, Br), and $M(chel)X_2$ (M = Pd, X = Cl, Br, I; M = Pt, X = I) are reported to undergo demethylation in boiling DMF, producing nonionic μ-thiolo complexes.[20] S-Demethylation of a tridentate SNN type of Schiff base has also been reported in boiling 1-butanol in the presence of nickel(II) iodide.[22] S-Demethylation of some metal chelates of *o*-methylthioaniline and SP has also been published.[46]

The complexes $Pd(C_3)Cl_2$ and $Pd(C_2)Cl_2$ undergo S-demethylation quite readily in hot DMF or in a mixed 1-butanol–DMF solvent. Attempts to force demethylation of the $[Pd(C_n)Cl][B(C_6H_5)_4]$ complexes resulted in reduction to metallic palladium. The demethylated complexes are yellow-orange nonelectrolytes in DMF and their electronic spectra (Figure 7; Table XII) show a band of weak intensity around 480–490 mμ and a shoulder at higher energy. The low intensity of the first band is characteristic of a square-planar species.[47] The weak ligand field strength of the mercaptide form of the ligands is thus indicated. A molecular weight determination in chloroform (found: 1285, 1320, 1290; monomer value 668) supports formulation of the compound as the dimeric complex Pd_2(demethylated $C_3)_2$ (structure X, Figure 6). The absence of bridging thiolo groups is suggested by their easy S-alkylation. For example Pd_2(demethylated $C_3)_2$ readily added four methyl iodide molecules. The resistance toward S-alkylation of bridging mercaptide groups had previously been reported[48] and confirmed.[20]

TABLE XII

ELECTRONIC SPECTRA OF Pd(DEMETHYLATED C_n) AND Pd(DEMETHYLATED $SP)_2$ COMPLEXES

Complex	Solvent	λ_{max} (ε)
Pd(demethylated C_3)	Dichloromethane	480 (150)
	Chloroform	480 (155)
	Halocarbon mull	470 360 sh
Pd(demethylated C_2)	Dichloromethane	485 (140)
	Halocarbon mull	480 380
Pd(demethylated $SP)_2$	Dichloromethane	465 (200) 380 (2750)
	Chloroform	465 (200) 380 (2750)
	Halocarbon mull	460 380

In order to test whether the demethylated complexes have any tendency to add on a fifth ligand, we made a spectrophotometric study of the influence of tetrabutylammonium iodide on Pd_2(demethylated $C_3)_2$ in chloroform. The spectral profile remained unaltered in the region 330–560 mμ over the range of mole ratios 1:0.50 to 1:10.

In an attempt to obtain the complex $Pd(SP)_2I_2$, we found that the ligand readily undergoes demethylation to give Pd(demethylated $SP)_2$. A square-planar structure is indicated by the presence of an electronic absorption band of low extinction coefficient at ~460 mμ. Compared to the demethylation reaction conditions prevailing in the originally reported[46] syntheses, the process reported here occurs under quite mild conditions (see Experimental Section).

S-Alkylation Reactions.—The palladium(II) chelate of β-mercaptoethylamine undergoes an S-alkylation with alkyl halides in chloroform. Similar reactions with square-planar, diamagnetic bis(β-mercaptoethylamine)nickel(II) led to the isolation of octahedral, paramagnetic dihalobis(β-thioalkylethylamine)nickel(II).[49] Reactions with chloroacetate led to octa-

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hedral nickel(II) complexes.[21] S-Alkylation reactions with the *o,o'*-xylyl dibromide of the nickel complex of the Schiff base of 2,3-pentanedione and β-mercaptoethylamine have been utilized to synthesize macrocyclic complexes.[50] An extension of these reactions[39] has recently been made to mercaptoaniline. S-Alkylation of the complexes[20] of the type $M(AsS)_2$ (M = Pd, Pt) has also been accomplished: $M(AsS)_2 + 2RX \rightarrow M(AsSR)X_2 + AsSR$ (M = Pd, RX = CH_3I, *n*-C_3H_7Br, $C_6H_5CH_2Cl$, *p*-$NO_2C_6H_4CH_2Br$; M = Pt, RX = CH_3I).

The demethylated complexes described in this article readily react with alkyl iodide, such as methyl iodide to regenerate the complexes $Pd(C_3)I_2$ and $Pd(C_3)I_2$. The identity of the S-alkylated products was established by elemental analyses, electronic spectra, and conductance measurements.

In several attempts to obtain a macrocyclic complex, the demethylated complex was allowed to react with *o,o'*-xylyl dibromide under varied conditions but a pure homogeneous product has not been isolated to date. This behavior is not inconsistent with the probable dimeric structure of the reactants (Figure 6).

Acknowledgment.—We are grateful for the support of the U. S. Public Health Service (Grant GM 10040-08, National Institute of General Medical Sciences) and of the National Science Foundation (Grant No. GP 8365).

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The Preparation and Nuclear Magnetic Resonance Spectra of Some Cationic Methylplatinum(II) Complexes

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Methods are described for the preparation of a wide range of cationic methylplatinum(II) complexes, *trans*-$Pt(CH_3)LQ_2^+$, where Q is dimethylphenylphosphine and L is a neutral ligand. Their nmr spectra are discussed and compared with those of other platinum(II) complexes. The nmr data for some platinum(II) complexes in liquid sulfur dioxide are interpreted in terms of octahedral solvate formation.

Introduction

Several types of cationic platinum(II) complexes have been described recently,[1-3] and some aspects of their chemistry have been explored.[4] These complexes are generally stabilized by tertiary phosphines or arsines, the other ligands about platinum(II) frequently being a halide and carbon monoxide. Methylplatinum(II) complexes show interesting chemical[5,6] and nmr spectroscopic[6] behavior; thus the nmr spectra of complexes of the type *cis*- or *trans*-$PtXCH_3\{P(C_2H_5)_3\}_2$ have recently been studied in detail,[7] and the methyl resonance patterns of some of the corresponding $P(CH_3)_2(C_6H_5)$ and $P(CH_3)(C_6H_5)_2$ complexes have also been reported.[6] A study of the hydride resonances of cationic complexes of the type *trans*-$PtHL\{P(C_2H_5)_3\}_2^+$ has shown[2] that there is a correlation between *J*(Pt–H) and the *trans* influence of the neutral ligand L, although such a relationship does not always hold[8] for neutral complexes $PtHX\{P(C_2H_5)_3\}_2$. We now describe the preparation and methyl resonance patterns of cationic complexes of the type *trans*-$PtCH_3LQ_2^+$ where Q = $P(CH_3)_2C_6H_5$ and L = neutral ligand.

Results and Discussion

Preparation of the Complexes.—The chloride ligand in *trans*-$PtCl(CH_3)Q_2$ (I) is labile and can readily be replaced by another ligand L in a polar solvent such as methanol or acetone. Addition of 1 molar equivalent of a strongly bonding ligand L, such as a tertiary phosphine, to a suspension of I in methanol causes the solid to give a cationic species which can be precipitated out by addition of a large anion such as PF_6^- or $B(C_6H_5)_4^-$. If L is not strong enough to displace Cl, an alternative procedure may be used: the chloride ion is removed by addition of 1 molar equivalent of silver tetrafluoroborate, to give presumably $[PtCH_3(CH_3OH)Q_2]BF_4$. This reacts readily with L (or in some cases L can be used as reaction solvent in place of methanol) to give the required cationic complex, which can be precipitated out by addition of a large anion. However, addition of $B(C_6H_5)_4^-$ to solutions of $Pt(CH_3)(CH_3OH)Q_2^+$ or solutions presumably containing (by analogy with the above complexes) $Pt(CH_3)L'Q_2^+$ where L' is a very weakly held ligand, *e.g.*, an olefin, gives *trans*-

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