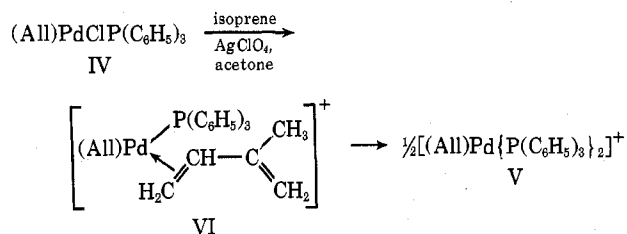


to phosphine. These features are consistent with the proposed structure of the cationic complexes III.

No assignment of protons other than those listed in Table II, such as H₁, H₃, and methylene protons of the side chain, has been made owing to the overlapping of each other or with solvent side bands. But, the 1-syn proton H₂ was clearly observed as a double doublet probably due to the coupling with meso proton H₁ and the geminal coupling with antiproton H₃ ($J_{12} = 7.0$ - 7.5 Hz, $J_{23} = 2$ Hz). The observed cis coupling ($J_{12} = 7$ Hz) is in the range of that for common π -allylic palladium complexes.¹²

Direct preparations of cationic species IIIb and IIIc by the reaction of monomeric chloro(π -allylic)triphenylphosphinepalladium(II) (IV) with isoprene in the presence of silver perchlorate gave only (π -allylic)-bis(triphenylphosphine)palladium(II) perchlorate (V), and no sign of insertion reaction of isoprene was observed. However, the π -crotyl derivative IVc gave

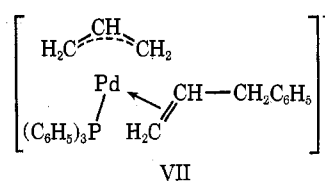


a, All = π -allyl; b, All = π -methyllyl; c, All = π -crotyl

(12) M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, **2**, 325 (1964).

partly the diene-inserted cationic complex, which had an infrared band at 1520 cm^{-1} due to a coordinated terminal vinyl group, but unfortunately the pure III-type complex could not be isolated. We cannot give a clear explanation for the different behavior between π -crotyl (IVc) and π -allyl (IVa) or π -methyllyl analogs (IVb). However, it seems possible that the intermediate VI (an intermolecular olefin-metal complex), which was formed from IV and a conjugated diene, is so unstable that it has a tendency to disproportionate to the cationic complex V. This finding also supports the view that a cationic olefin complex III obtained from II should have a chelated structure, namely, intramolecular coordination of the double bond to the palladium atom.

An attempt to isolate cationic complex VII by the reaction of complex IVa with allylbenzene in the presence of silver perchlorate or fluoroborate was also in vain, and the recovered olefin was found to be converted completely to propenylbenzene. It is interesting,



however, that the terminal olefin structure in complexes III was retained, although $[(\pi\text{-allylic})\text{PdP}(\text{C}_6\text{H}_5)_3]^+$ catalyzes olefin isomerization.

CONTRIBUTION FROM THE FACOLTÀ DI CHIMICA INDUSTRIALE, UNIVERSITY OF VENICE, VENICE, ITALY, AND LABORATORIO DEI COMPOSTI DEL CARBONIO CONTENENTI ETREATOMI DEL CNR, OZZANO E., BOLOGNA, ITALY

Some Reactions of Palladium(II)-Thiol Complexes with Organic Halides

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New palladium(II) complexes of 1,2-ethanedithiol and 1,3-propanedithiol are reported. These complexes, which are probably polymers with S bridges, react under relatively mild conditions with certain organic halides. The products of some of these reactions have been identified. Corresponding reactions of the known polymer $[\text{Pd}(\text{SPH})_2]_n$ have been carried out for comparison, and reasons for the varied reactivity of metal-thiol complexes are discussed.

Introduction

Considerable interest has been shown recently in the properties and reactions of metal complexes of ligands containing sulfur donors.²⁻⁹ Several complexes of palladium with aliphatic and aromatic monothiols (RSH) were prepared by Mann and Purdie,¹⁰ who considered them to be S-bridged high polymers of general

formula $[\text{Pd}(\text{SR})_2]_n$. A similar formulation was adopted by Jensen¹¹ for the corresponding nickel compounds. Hayter and Humiec¹² concluded that the palladium complexes of higher aliphatic thiols (e.g., for R = *n*-Pr) were probably S-bridged hexamers. Other examples of hexameric units in nickel- and palladium-thiol complexes have since been reported.^{13,14} The complexes of Pt and Pd with $\text{C}_6\text{F}_5\text{SH}$ also appear to be polymeric.¹⁵

A mercaptide ion often retains its tendency to form S bridges even in the presence of other groups capable of coordination, but in these cases the extent of polym-

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erization is often restricted to the formation of dimers.¹⁶⁻¹⁸ However, Busch, *et al.*,^{19,20} have prepared several monomeric Ni^{II} and Pd^{II} complexes of bidentate ligands containing both amine and thiol groups (*e.g.*, NH₂C₂H₄SH). Some of these complexes readily form S-bridged trinuclear species in the presence of free metal ions.^{21,22}

No complexes of Pd^{II} with the ligands HS(CH₂)_nSH appear to have been isolated, but studies of the equilibria²³ in mixtures of Ni²⁺ and HSC₂H₄SH have shown the existence of the species [Ni(SC₂H₄S)₂]²⁻ and [Ni₂(SC₂H₄S)₃]²⁻, the latter probably having a structure with S bridges.

One property of S bridges to which frequent reference has been made^{2,3,8,20} is that of low reactivity toward reagents such as *p*-toluidine (which readily cleaves chloride bridges) and certain organic halides (which often react readily with terminal thiol groups coordinated to metals). The S-alkylation reactions of many Ni^{II} and Pd^{II} amino thiols have been studied by Busch, *et al.*,^{20,24} but no similar reactions involving cleavage of sulfur bridges appear to have been reported since the early work of Hofmann and Rabe.²⁵ Livingstone²⁶ gives an example of cleavage of an S-bridged palladium complex by ammonia.

In the present work we report the preparation of new complexes of Pd^{II} with HS(CH₂)₂SH and HS(CH₂)₃SH and the reactions of these and of the palladium(II) benzenethiol complex with several organic halides. Some preliminary experiments on the reactions of these palladium-thiol complexes with ethylenediamine are also reported.

Experimental Section

Materials.—Allyl bromide, methyl iodide, 1,2-dibromoethane, 1,3-dibromopropane, 1,3-diiodopropane, 1,2-ethanedithiol, 1,3-propanedithiol, and benzenethiol were Fluka "purum" grade. All other reagents and solvents were reagent grade chemicals.

Preparation of Compounds.—Methods previously reported were used for the preparation of Na₂PdCl₄,²⁷ Pd(PhSCH₂CH₂SPh)₂ (X = Cl, Br, I),²⁸ and *trans*-Pd(PhCN)₂Cl₂.²⁹

In general the palladium-thiol complexes were prepared by mixing solutions of *trans*-Pd(PhCN)₂Cl₂ or Na₂PdCl₄ with solutions of the ligands or their sodium salts in methanol or aqueous methanol. A methanolic solution of the sodium salt of a ligand was obtained by adding the equivalent amount of sodium methoxide in methanol to a methanolic solution of the ligand. All solutions of the ligand and their sodium salts were kept and used under nitrogen. Details of the preparative methods are given below.

Method A.—A solution of the stoichiometric amount (*i.e.*, 1 mol of dithiol or 2 mol of monothiol per mole of palladium salt) of the sodium thiolate in 150 ml of methanol was added slowly with stirring to a solution of 0.76 g of *trans*-Pd(PhCN)₂Cl₂ in 300 ml of methanol. The product began to precipitate immediately

on adding the thiolate and was finally filtered, washed with water, methanol, and ether, and dried under vacuum.

Method B.—The procedure in method A was used except that a solution of 0.5 g of Na₂PdCl₄ in 80 ml of water diluted to 200 ml with methanol was used in place of the benzonitrile complex.

Method C.—Method B was followed except that a solution of the ligand in 100 ml of methanol was used in place of the sodium salt of the ligand.

Method D.—Method C was used except that the palladium solution was added to the thiol solution.

Reactions of the Palladium-Thiol Complexes with Organic Halides.—In general a sample (*ca.* 0.5 g) of the palladium complex was refluxed with 50 ml of the organic halide, for 4-6 hr in the case of the dithiol complexes and for 5-10 days in the case of the benzenethiol complex. In the reactions of the 1,2-ethanedithiol and benzenethiol complexes with allyl bromide, the reaction mixture was homogeneous after refluxing, but in all other cases some solid was present. The mixture was then either evaporated to dryness or mixed with pentane and filtered, and the solid residue was treated as detailed below. Each of the reactions 1-6 (below) was repeated with different samples of the palladium-thiol complexes. The different samples of a given complex gave the same products, as shown by comparing thin layer chromatograms and uv spectra of solutions. The separations on columns were effected by elution with chloroform and controlled by measurements of uv spectra. In the following sections the starting materials are named, and the description that follows refers to the treatment of the solid residue obtained from the reaction mixture by evaporation or precipitation.

1. Palladium-1,3-Propanedithiol Complex and Methyl Iodide.—The solid was extracted with chloroform until no more dissolved, and the residue was then dissolved in acetone. Compound I was precipitated from the acetone solution by adding chloroform. The chloroform solution, chromatographed on silica, showed the presence of three fractions, the first and third of which were very small. The middle fraction yielded compound II.

2. Palladium-1,3-Propanedithiol Complex with Allyl Bromide.—The solid residue was completely soluble in chloroform. Chromatography on a silica column showed only one fraction, compound III.

3. Palladium-1,3-Propanedithiol Complex with 1,3-Dibromopropane.—The solid residue was completely soluble in chloroform. Chromatography on a silica column showed two fractions; the first was very small. The second fraction yielded compound IV.

4. Palladium-1,2-Ethanedithiol Complex and Methyl Iodide.—The solid residue was dissolved completely in chloroform, and the solution was chromatographed on an alumina column. Two fractions in roughly equal amounts were obtained. The first yielded compound VIa and the second compound V. A sample of 100 mg of VIa was suspended in 10 ml of methanol and treated with the amount of silver nitrate required to react with all the iodine present. The precipitate of silver iodide was filtered off and a slight excess of aqueous sodium bromide solution added. The resulting precipitate was washed with water, methanol, and ether and dried under vacuum (compound VIb).

5. Palladium-1,2-Ethanedithiol Complex and Allyl Bromide.—The solid residue was dissolved in chloroform and chromatographed on a silica column. The first fraction was small and the second (about 90% of the total) yielded compound VII.

6. Palladium-Benzenethiol Complex and Allyl Bromide.—The chloroform solution of the residue was chromatographed on silica. About half of the product was strongly held and the other half was eluted to yield compound VIII.

Reactions of the Palladium-Thiol Complexes with Ethylenediamine.—About 0.5 g of palladium-thiol complex (sample C in each case) was mixed with 30 ml of ethylenediamine and allowed to stand several minutes at room temperature. The benzenethiol complex was almost completely soluble, but the palladium complexes of the dithiols were only partly soluble. In each case the mixture was filtered and the filtrate mixed with ether. A yellow amorphous precipitate was obtained in each case. The precipitate from the reaction of the palladium-benzenethiol complex with ethylenediamine was also obtained in crystalline form by adding a small quantity of ether to the ethylenediamine solution and allowing the mixture to stand for several hours. The yellow products were filtered, washed with ether, and dried under vacuum. Each one slowly turned red when free from excess ethylenediamine. One sample of the

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(17) J. Chatt and F. A. Hart, *ibid.*, 2363 (1953); 2807 (1960).

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(19) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 872 (1962).

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yellow product (compound IX) from the reaction of the benzenethiol complex was analyzed immediately after it was precipitated.

Reaction of [Pd(SPh)Cl]_n with Ethylenediamine.—A sample of [Pd(SPh)Cl]_n, supplied by Dr. T. Boschi, was mixed with ethylenediamine. Reaction occurred to give a yellow solution and a white residue (compound X) easily soluble in water. A yellow solid was precipitated from the solution by adding ether and was washed with water, methanol, and ether and dried under vacuum (compound XI). It slowly turned red on standing.

Instruments.—Physical measurements were carried out with the following instruments: infrared, Perkin-Elmer 337 and 621 spectrophotometers for the region 4000–400 cm⁻¹ and Beckman IR 11 spectrophotometer for the region 400–80 cm⁻¹; ultraviolet, Optica CF4R spectrophotometer; conductance, LKB 3216B bridge; molecular weight, Mecrolab thermoelectric osmometer; nmr, Perkin-Elmer 60; mass spectra, Hitachi Perkin-Elmer RMU-6D. Chromatographic separations were performed with a 60 × 2.5 cm column packed with silica or alumina. Ir measurements were carried out in Nujol or hexachlorobutadiene mulls and nmr measurements in chloroform solutions (TMS internal standard). Conditions for the mass spectra were electron energy, 60 eV; pressure, 1–3 × 10⁻⁶ Torr; source temperature, ca. 200°. Analyses were carried out by the microanalytical laboratory of the Institute of Organic Chemistry, University of Padova.

Results

Properties of the Palladium-Thiol Complexes.—The products in all cases were dark red or red-brown non-crystalline solids which were insoluble in common solvents and had decomposition temperatures above 280°. The composition of different samples varied slightly with variations in the method of preparation, as shown in Table I. Infrared spectra showed broad

TABLE I
ANALYSES OF SAMPLES OF PALLADIUM-THIOL COMPLEXES

Thiol	Method of prepn	Analyses, %			
		C	H	S	Cl
HS(CH ₂) ₈ SH	A	17.0	3.2	26.2	3.6
	B	16.9	2.8	26.0	Trace
	C	17.4	2.9	30.2	0
	D	17.5	2.9	30.3	0
Calcd for C ₈ H ₈ S ₂ Pd		16.98	2.83	30.19	0
HS(CH ₂) ₂ SH	A	11.5	2.0	25.0	Present
	C	12.4	2.2	32.5	0
Calcd for C ₂ H ₄ S ₂ Pd		12.12	2.02	32.32	0
C ₆ H ₅ SH	A	35.8	2.5	15.5	6.3
	C	43.0	3.0	19.6	Trace
Calcd for C ₁₂ H ₁₀ SPd		44.44	3.09	19.75	0

TABLE II
PROPERTIES OF COMPOUNDS I-IX

Compd	Description	Decomp temp, °C	Analyses, %				Uv spectrum, λ _{max} , nm
			C	H	S	Hal	
I	Black crystals	135	8.2	1.8	6.7	63.0	337
II	Orange-red crystals	264	13.4	2.6	18.6	34.7	305
		Calcd for C ₈ H ₁₈ S ₄ I ₂ Pd	13.56	2.54	18.08	35.88	
III	Yellow crystals	208	21.7	3.6	18.2	24.7	275–305 (sh)
		Calcd for C ₁₂ H ₂₂ S ₄ Br ₂ Pd ₂	21.62	3.30	19.22	24.02	
IV	Yellow	209	17.2	3.1	15.2	38.6	290
		Calcd for C ₁₂ H ₂₄ S ₄ Br ₄ Pd ₂	17.39	2.90	15.46	38.65	
V		212	9.8	2.1	13.6	51.4	284
		Calcd for C ₄ H ₁₀ S ₂ I ₂ Pd	9.96	2.07	13.28	52.70	
VIa	Red-violet	256	10.4	2.0	18.1	35.4	298, 244
		Calcd for C ₆ H ₁₄ S ₄ I ₂ Pd	10.59	2.06	18.82	37.35	
VIb	Orange-brown		13.2	2.4			
		Calcd for C ₆ H ₁₄ S ₄ Br ₂ Pd ₂	12.29	2.39			
VII	Yellow crystals	192	18.9	3.2	18.9	26.6	290
		Calcd for C ₁₅ H ₂₇ S ₆ Br ₃ Pd ₃	18.81	2.82	20.06	25.08	
VIII	Yellow crystals	119	37.7	3.4	11.1	28.1	
		Calcd for C ₁₈ H ₂₀ S ₂ Br ₂ Pd	38.16	3.53	11.31	28.27	
IX	Yellow		40.9	4.6	14.9	(N, 7.6)	
		Calcd for C ₁₄ H ₁₈ S ₂ N ₂ Pd	43.75	4.69	16.67	(N, 7.29)	

unresolved absorption in the region 400–80 cm⁻¹.

Properties of Compounds I-XI.—Some properties are collected in Table II. The uv spectra were measured in the region 270–420 nm with solutions in chloroform (acetone for compound I) containing 0.3–0.5 g/l. of the compound. The spectra showed one low intensity (absorbance 0.5–0.7) peak or shoulder in each case. Results of the infrared measurements are shown in Table III. In addition, the infrared spectrum in the region 3000–400 cm⁻¹ of each of the compounds III, VII, and VIII showed, among other absorptions, a peak at ca. 1628 cm⁻¹. A solution of 0.4 g/l. of compound I in acetone had a specific conductance 1.8 × 10⁻⁵ ohm⁻¹ cm⁻¹. Solutions of compounds II, III, VIa, and VII were nonconductors in chloroform.

Measurements of mass spectra of compounds II and VIa gave inconclusive results. Osmotic measurements on chloroform solutions gave the molecular weight of compound VII as 1000. Nmr measurements on chloroform solutions of compounds III and VII gave spectra that were not clearly resolved but showed absorption in the region τ 4–5 (TMS internal standard).

The analysis of a freshly precipitated sample of compound IX is given in Table II. Compounds IX and XI had practically identical infrared spectra in the region 4000–400 cm⁻¹, and the infrared spectrum of X in the same region was practically identical with that of a sample of [Pd(en)₂]Cl₂.

Miscellaneous Results.—On refluxing each of the three palladium-thiol complexes with Br(CH₂)₂Br or I(CH₂)₃I reaction occurred as judged by changes in the properties (analyses, infrared spectra) of the solid residues and by the presence in solution of products that could be precipitated with pentane. In all these cases, however, we were unable to separate and identify the products. Similar results were obtained in the reactions of the benzenethiol and 1,2-ethanedithiol complexes with Br(CH₂)₂Br and in the reaction of the benzenethiol complex with CH₃I. In the last reaction there was a significant difference in reactivity between samples A and C of the palladium complex. The reaction of sample A with CH₃I was complete after about 7 days whereas the reaction of sample C was not complete after 11 days.

TABLE III
INFRARED ABSORPTIONS (cm^{-1}) OF COMPOUNDS I-IX^a
AND THE COMPLEXES $\text{Pd}(\text{PhS}(\text{CH}_2)_2\text{SPh})\text{X}_2$
(X = Cl, Br, I) IN THE REGION 400-80 cm^{-1}

Compd	$\nu_{\text{Pd-X}}$	Other absorptions
I		218 vs, 142 m, 130 m, 124 m
II	165 vs, 136 vs	338 m, 312 vs, 262 w, 226 s, 214 sh
III	222 s, 185 s	360 w, 320 ms, 228 b
IV	220 m, 186 s	320 ms, 304 m, 293 w, 243 w
V	163 sh, 158 s	312, 290, 184 w, 97 ms
VIa	171 s, 142 s	368 m, 342 mw, 303 s, 279 s, 253 mw
VIb	212 sh, 196 s	366 w, 350 w, 308 ms, 283 m, 258 w
VII	200 vs, 182 sh	360 m, 315 m, 285 m, 226 w
VIII	277	202-212, ^a 152, 89
$\text{Pd}(\text{PhS}(\text{CH}_2)_2\text{SPh})\text{Cl}_2$	327 s, 313 s	274 s, 186 ms, 150 m, 120 m
$\text{Pd}(\text{PhS}(\text{CH}_2)_2\text{SPh})\text{Br}_2$	207 s, 199 sh	256 s, 243 m, 176 ms, 104 m
$\text{Pd}(\text{PhS}(\text{CH}_2)_2\text{SPh})\text{I}_2$	162 sb, 158 s	242 m, 94 ms

^a Not clearly resolved.

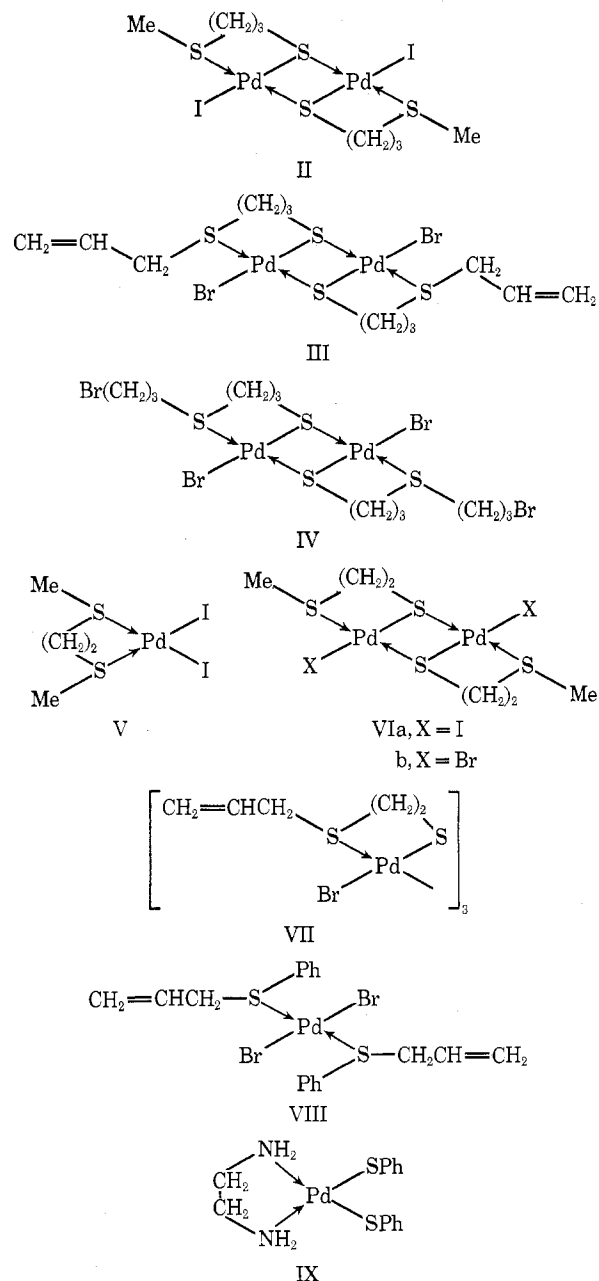
The reactions of the dithiol complexes with ethylenediamine also gave unidentified products. The residues remaining when these complexes were mixed with ethylenediamine and the yellow products obtained by adding ether to the solutions all contained nitrogen (that was not removed by washing with ether) and had infrared spectra different from those of the starting materials.

Discussion

The palladium complexes of 1,2-ethanedithiol and 1,3-propanedithiol reported here are new. In their general properties (noncrystalline solids with high decomposition temperatures, insoluble in common solvents, unresolved ir spectra), they closely resemble the palladium complex of benzenethiol first prepared by Mann and Purdie.¹⁰ The variations in composition of different samples of a given complex (Table I) are as expected for highly insoluble substances of this type (*cf.* Nyholm, *et al.*¹⁵), but, in general, the composition corresponds well with the empirical formulas $\text{Pd}[\text{S}(\text{CH}_2)_2\text{S}]$ and $\text{Pd}[\text{S}(\text{CH}_2)_3\text{S}]$ for the complexes with 1,2-ethanedithiol and 1,3-ethanedithiol, respectively. The palladium complex of benzenethiol has previously been formulated as a polymer with sulfur bridges, and this formulation seems to be generally accepted.^{2,3} In view of their general similarity to $[\text{Pd}(\text{SPh})_2]_n$, it is reasonable to regard the new compounds as polymers with sulfur bridges. However, contrary to the previous experience of the reactions of S-bridged compounds,²⁰ we find that the present compounds react with certain organic halides under relatively mild conditions—comparable conditions, for example, to those employed in the reactions of methyl iodide with complexes containing terminal thiol groups.^{20,24a} Chatt and Mingos⁹ have also recently reported that the sulfide bridged complex $\text{Pt}_2\text{S}_2(\text{PMe}_2\text{Ph})_4$ reacts with benzyl bromide under very mild conditions to give an S-benzyl derivative. Our preliminary experiments also show that the present polymers (and also $[\text{Pd}(\text{SPh})_2]_n$) react readily with ethylenediamine.

Before considering the implications of these general

results, we discuss the nature of the products of the reactions reported here. The structures suggested for compounds II-IX are given below. Those containing more than one Pd atom are considered to be nonplanar.



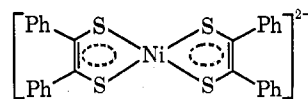
In all cases the compounds are the types of products expected by analogy with known S-alkylation reactions of complexes containing thiol ligands.²⁰ In each case the formula corresponds to the analyses reported and, where measured, to the zero conductance in chloroform. Each of the compounds III, VII, and VIII has a peak at 1628 cm^{-1} (characteristic of a free C=C bond in its infrared spectrum). The nmr spectra of compounds III and VII also confirm the presence of a free allyl group. The assignments of $\nu_{\text{Pd-X}}$ in the infrared spectra in the region 400-80 cm^{-1} are consistent among themselves and are reasonable by comparison with the spectra of the compounds $\text{Pd}(\text{PhS}(\text{CH}_2)_2\text{SPh})\text{X}_2$ and with previously reported values.³⁰

(30) "Spectroscopic Properties of Inorganic and Organometallic Compounds," Vol. I, The Chemical Society, London, 1968.

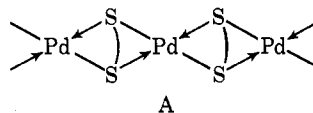
A comparison of the infrared absorption for compounds VIa and VIb also identifies $\nu_{\text{Pd-I}}$ and $\nu_{\text{Pd-Br}}$. The remaining absorptions are difficult to interpret but, again, show consistency for the group of compounds taken together. For example, common peaks are found for the group of compounds II, III, and IV and for VIa, VIb, and VII. The trimeric structure for VII is based upon a molecular weight determination. Lindoy, *et al.*,³¹ have also found evidence for trimers in Pd and Pt complexes of dimethyl-*o*-methylthiophenylarsine. Conclusive molecular weight determinations were not possible with the other compounds, and these are given by the simplest structures consistent with their empirical formulas. The structures of the dimers correspond to those proposed by Livingstone^{18b} for some very similar complexes. The polymers $[\text{Pd}(\text{S}(\text{CH}_2)_3\text{S})_n]$ and $[\text{Pd}(\text{S}(\text{CH}_2)_2\text{S})_n]$ might have been expected to undergo very similar reactions with CH_3I . In fact the products II and VIa from the respective reactions are analogous, but I differs markedly from V (and from the products of the other reactions) in its insolubility in chloroform, in its conductance, and in its ir and uv spectra. We are unable at the moment to suggest any reasonable formulation for I.

With regard to the products of the reactions of $[\text{Pd}(\text{SPh})_2]_n$ with ethylenediamine we suggest that compound IX is $\text{Pd}(\text{en})(\text{SPh})_2$. Compound XI is similar to its general properties and has practically identical ir spectrum. As XI is presumably formed by further reaction of the S-bridged intermediate⁸ $[(\text{en})\text{Pd}(\text{SPh})_2\text{Pd}(\text{en})]^{2+}$ with ethylenediamine, it is probably the same as IX. The other product, X, of the last reaction should then be $[\text{Pd}(\text{en})_2]\text{Cl}_2$. This view is supported by the ir data.

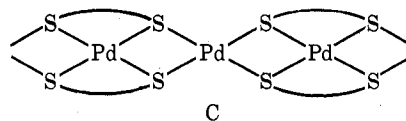
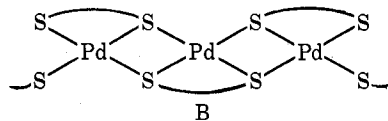
An important result of the present work is that it demonstrates an unexpectedly high reactivity of certain S-bridged compounds toward organic halides and ethylenediamine. Many compounds with sulfur bridges are known to have very low reactivity toward organic halides.²⁰ In this category we may include some of the compounds reported here (II, III, IV, VIa, VIb, VII) and also $[\text{Pd}(\text{SPh})_2]_n$, the reactivity of which is low compared with that of the two dithiol polymers. It has been suggested²⁰ that reactivity toward electrophiles may be used to distinguish bridged from terminal mercapto groups, and, where a direct comparison can be made, it appears that terminal thiol groups are more reactive than S bridges. For example, the reaction of the dimeric Ni^{II} complex of *N*-methyl-2,2'-dimercaptodiethylamine with CH_3I results in methylation of only the terminal sulfur.²⁰ However, the reactivities of complexes containing terminal mercapto groups are rather variable. For example, Lindoy and Livingstone³² find that S-methylation occurs when bis(2-aminobenzenethiolo)nickel(II) is treated with CH_3I , but that the complex is unreactive toward 2-chloromethylpyridine and benzyl chloride. Similarly, Schrauzer and Rabinowitz report³³ that whereas the anion reacts with CH_3I , the corresponding anion with a single negative charge does not. Considering all these results and the present ones, it seems that a wide range of



reactivity is shown both by complexes containing terminal thiols and by those containing S bridges. Owing to the lack of quantitative information, the reasons for these differences are not obvious. Steric effects could be important. For example, if the palladium-dithiol polymers have structures such as A



(where S—S represents $\text{S}(\text{CH}_2)_n\text{S}$), their reactivity could arise from the strain present in such an arrangement. Similarly, the low reactivity of $[\text{Pd}(\text{SPh})_2]_n$ could be due to steric hindrance of the phenyl groups. However, such explanations are capable of accounting for only a limited number of cases, and electronic distributions appear to be much more important than steric effects. Reactions of thiol complexes with organic halides (RX) probably involve important contributions from both nucleophilic attack by X on the metal^{24d} and electrophilic attack by R on the sulfur atom. This means that the negative charge residing on the sulfur atom is an important factor in determining the reactivity of the system, whether or not the sulfur atom is bridged or terminal. For terminal sulfur atoms this seems to be nicely demonstrated by the results of Schrauzer and Rabinowitz³³ quoted above. Most of the S-bridged complexes that are known to be unreactive toward organic halides are similar to the S-bridged products of the present reactions in that they contain halogen ligands which could compete for strongly negative charge. The sulfur atoms in the unreactive compound $[\text{Pd}(\text{SPh})_2]_n$ are attached to electron-withdrawing phenyl groups. The above factors are absent from the compounds $[\text{Pd}(\text{S}(\text{CH}_2)_3\text{S})_n]$, $[\text{Pd}(\text{S}(\text{CH}_2)_2\text{S})_n]$, and $\text{Pt}_2\text{S}_2(\text{PMe}_2\text{Ph})_4$,⁹ all of which readily undergo S-addition reactions. The structures of the present palladium polymers could then be of type B or C.



It could be objected that the apparent low reactivity of $[\text{Pd}(\text{SET})_2]_n$ toward CH_3I (Hofmann and Rabe²⁵) argues against the above views. However, this reaction (or the corresponding one with $[\text{Pd}(\text{SET})_2]_n$) requires further investigation. Hofmann and Rabe obtained the product $\text{Pt}(\text{MeSET})_2\text{I}_2$ after heating the reagents at 70–80° for 2 days in a sealed tube. It is possible that isolable intermediates are formed in this reaction. In our reaction of $[\text{Pd}(\text{SPh})_2]_n$ with allyl bromide, for instance, compound VIII represents only about half of the total product. The other half was not identified.

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The reaction of $[\text{Pd}(\text{SPh})_2]_n$ with ethylenediamine reveals an unexpectedly high reactivity for the polymer. The isolation of IX shows that the ethylenediamine is not merely acting as a solvent (*cf.* Hunter and Krause).³⁴ Its high reactivity in this reaction contrasts with its behavior toward organic halides and suggests that steric effects of the phenyl groups may not be very important. The reactions with ethylene-

diamine are nucleophilic substitutions and have no electrophilic component as in the reactions with RX. We are unable to estimate at present the relative reactivities of the palladium polymers toward ethylenediamine, but work on this type of reaction is continuing.

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Polytertiary Phosphines and Arsines. VII. Zerovalent Platinum Complexes of Arylated Polytertiary Phosphines and Arsines¹

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Zerovalent platinum complexes of polytertiary phosphines and phosphine-arsines can be prepared by reaction of a mixture of K_2PtCl_4 and the ligand with sodium borohydride in aqueous ethanol. The chelating bidentate ligands (*m*- $\text{CH}_2\text{C}_6\text{H}_4$)₂- $\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$, $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{As}(\text{C}_6\text{H}_5)_2$, and *cis*-(C_6H_5)₂ $\text{PCH}=\text{CHP}(\text{C}_6\text{H}_5)_2$ form yellow to orange derivatives of the type (bidentate)₂Pt. The nonchelating ditertiary phosphines *trans*-(C_6H_5)₂ $\text{PCH}=\text{CHP}(\text{C}_6\text{H}_5)_2$ and $(\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CP}(\text{C}_6\text{H}_5)_2$ form three-coordinate yellow [*trans*-(C_6H_5)₂ $\text{PCH}=\text{CHP}(\text{C}_6\text{H}_5)_2$]₃Pt and two-coordinate yellow [$(\text{C}_6\text{H}_5$)₂ $\text{PC}\equiv\text{CP}(\text{C}_6\text{H}_5)_2$]₂Pt, respectively. The potentially tridentate ligands [$(\text{C}_6\text{H}_5$)₂ PCH_2CH_2]₂ PC_6H_5 and [$(\text{C}_6\text{H}_5$)₂ AsCH_2CH_2]₂ PC_6H_5 form the polymetallic derivatives $\{[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2]_2\text{PC}_6\text{H}_5\}_4\text{Pt}_3$ and $\{[(\text{C}_6\text{H}_5)_2\text{AsCH}_2\text{CH}_2]_2\text{PC}_6\text{H}_5\}_3\text{Pt}_2$, respectively. The tetra-tertiary phosphines [$(\text{C}_6\text{H}_5$)₂ PCH_2CH_2]₃P and $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ form the yellow derivatives [$(\text{C}_6\text{H}_5$)₂ PCH_2CH_2]₃Pt and [$(\text{C}_6\text{H}_5$)₂ $\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$]₂Pt₂, respectively. The new platinum(II) derivatives [*cis*-(C_6H_5)₂ $\text{PCH}=\text{CHP}(\text{C}_6\text{H}_5)_2$]₂PtCl₂ and $\{[\text{trans}-(\text{C}_6\text{H}_5)_2\text{PCH}=\text{CHP}(\text{C}_6\text{H}_5)_2]_4\text{Pt}_2\}[\text{PF}_6]_4$ are also described.

Introduction

Zerovalent platinum derivatives of the type $(\text{R}_3\text{P})_4\text{Pt}$,³ particularly the triphenylphosphine derivative, form novel derivatives with small molecules of interest such as oxygen,⁴ carbon monoxide,⁵ carbon disulfide,⁶ hexafluoroacetone,⁷ and various alkynes.⁸ This paper describes the preparation and properties of related zerovalent platinum derivatives of polytertiary phosphines and phosphine-arsines, particularly of the ligands made available by preparative techniques recently developed in this laboratory.^{9,10}

Experimental Section

Potassium tetrachloroplatinate(II) (46.6% platinum), K_2PtCl_4 , was purchased from Engelhard Industries, Newark, N. J. The ligands *cis*-bis(1,2-diphenylphosphino)ethylene, *cis*-(C_6H_5)₂- $\text{PCH}=\text{CHP}(\text{C}_6\text{H}_5)_2$ (abbreviated as *cPf*=*Pf*),¹¹ *trans*-bis(1,2-

diphenylphosphino)ethylene, *trans*-(C_6H_5)₂ $\text{PCH}=\text{CHP}(\text{C}_6\text{H}_5)_2$ - (abbreviated as *tPf*=*Pf*),¹⁰ bis(1,2-diphenylphosphino)acetylene, $(\text{C}_6\text{H}_5)_2\text{P}\equiv\text{CP}(\text{C}_6\text{H}_5)_2$ (abbreviated as *Pf*≡*Pf*),¹² 1-diphenylphosphino-2-diphenylarsinoethane, $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{As}(\text{C}_6\text{H}_5)_2$ (abbreviated as *Asf*-*Pf*),¹⁰ bis(2-diphenylphosphinoethyl)phenylphosphine, [$(\text{C}_6\text{H}_5$)₂ PCH_2CH_2]₂ PC_6H_5 (abbreviated as *Pf*-*Pf*),¹⁰ bis(2-diphenylarsinoethyl)phenylphosphine, [$(\text{C}_6\text{H}_5$)₂ AsCH_2CH_2]₂ PC_6H_5 (abbreviated as *Asf*-*Pf*-*Asf*),¹⁰ tris(2-diphenylphosphinoethyl)phosphine, [$(\text{C}_6\text{H}_5$)₂ PCH_2CH_2]₃P [abbreviated as *P*-(*Pf*)₃],¹³ and 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane, $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (abbreviated as *Pf*-*Pf*-*Pf*-*Pf*),¹⁰ were prepared by the cited published procedures.

Preparation of 1-Diphenylphosphino-2-di-*m*-tolylphosphinoethane.—The preparation of the ligand 1-diphenylphosphino-2-di-*m*-tolylphosphinoethane (abbreviated as *Pmt*-*Pf*) is given in detail here since it has not been previously described.

A mixture of 4.0 g (18.9 mmol) of diphenylvinylphosphine, 4.0 g (18.7 mmol) of di-*m*-tolylphosphine (from Pressure Chemical Corp., Pittsburgh, Pa.), 0.4 g (3.57 mmol) of potassium *tert*-butoxide, and 100 ml of redistilled tetrahydrofuran was boiled under reflux for 16 hr in a nitrogen atmosphere. Solvent was then removed at 25° (25 mm). The resulting brown oil was triturated with 100 ml of methanol, whereupon it solidified to give a white solid. This solid was filtered and crystallized from a mixture of benzene and methanol to give 7.6 g (95% yield) of white (*m*- $\text{CH}_2\text{C}_6\text{H}_4$)₂ $\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$, mp 95°. *Anal.* Calcd for $\text{C}_{28}\text{H}_{28}\text{P}_2$: C, 78.8; H, 6.6; P, 14.5; mol wt, 426. Found: C, 78.6; H, 6.8; P, 14.5; mol wt, 422 (osmometer in benzene).

Preparations of the Zerovalent Platinum Derivatives (Table I).—The indicated quantity (Table I) of potassium tetrachloroplatinate(II), water (about 20 ml for each gram of K_2PtCl_4), the indicated quantity (Table I) of the polytertiary phosphine or

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