portant contributor to optical activity in d–d transitions. Similar CD magnitudes observed for puckered, planar, and no chelate rings also suggest a low contribution from chelate ring puckering in the complexes discussed in this paper. Vicinal effects of substituents remain as the primary source of optical activity in ligand field bands of most tetragonal transition metal ion complexes displaying relatively weak CD.

The relative energies of the 4d orbitals in tetragonal palladium(II) are difficult to determine because they are closely spaced, and because electron-transfer transitions interfere at short wavelengths. A likely order of increasing energies for the 4d orbitals of palladium(II) in these systems is $z^2 < xz \sim yz < xy < x^2 - y^2$.[14] In the D_{4h} symmetry point group the above ordering is described by the representations $a_{1g} < e_g < b_{2g} < b_{1g}$. In d^8 palladium(II) the three spin-allowed one-electron d–d transitions in order of increasing energy are $b_{2g} \rightarrow b_{1g}$ ($A_{1g} \rightarrow A_{2g}$), $e_g \rightarrow b_{1g}$ ($A_{1g} \rightarrow E_g$), and $a_{1g} \rightarrow b_{1g}$ ($A_{1g} \rightarrow B_{1g}$). These transitions are designated A, E, and B, respectively. Of these three transitions only the highest energy one labeled B is magnetic dipole forbidden to the extent that D_{4h} microsymmetry is maintained. Application of the above ordering leads to the assignment of the E transition to the positive CD peak observed in most tripeptide palladium(II) complexes near 290 nm and the A transition to the negative peak near 335 nm. The CD of the tripeptide complexes of palladium(II) bears a sign pattern similar to that of the tetragonal nickel(II) complexes. Both display a consistently negative CD peak at a wavelength 35 nm or greater than the absorption maximum and occasionally a positive CD peak nearer the absorption maximum. The assignments suggested above are consistent with those already made for the tetragonal nickel(II) complexes where the B transition may be at relatively lower energy.[7] These assignments may also be applied to the other peptide, amide, and amino acid complexes of palladium(II).

[14] W. R. Mason and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5721 (1968).

Contribution from the Centro Chimica e Tecnologia Composti Metallorganici Elementi Transizione, C.N.R.,
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Polynuclear Complexes of Palladium(II) with Halogen and Sulfur Bridges

By T. BOSCHI, B. CROCIANI, L. TONIOLO, and U. BELLUCO

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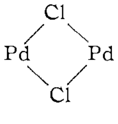
The reaction of $Na_2[PdCl_4]$ with diphenyl disulfide in methanol yields a polymeric compound of formula $[Pd(SC_6H_5)Cl]_n$ (I) containing alternating halogen and sulfur bridges. This compound is also formed by refluxing $[Pd((C_6H_5)_2S_2)Cl_2]_2$ in methanol. The characterization of I was based on its infrared spectra and on its bridge-splitting reactions. In the reaction of I with a neutral ligand L (L = pyridine, triphenylphosphine, triphenylarsine) S-bridged complexes of the type $[Pd(SC_6H_5)LCl]_2$ are formed. The reaction with ethylenediamine yields the cationic S-bridged complex $[Pd(SC_6H_5)(en)]_2Cl_2$, whereas with $[As(C_6H_5)_4]Cl$ the cationic complex $[Pd(SC_6H_5)Cl_2]_2[As(C_6H_5)_4]_2$ is formed. The above reactions involve only splitting of the



bridges. When I reacts either with 1,2-bis(diphenylphosphino)ethane or with an excess of phosphine, both the halogen and sulfur bridges are cleaved. The nature of the products in the bridge-splitting reactions has been determined on the basis of elemental analysis, ir spectra, conductivity, and molecular weight measurements, where possible.

Introduction

Palladium(II) has a great tendency to form thiolato-bridged complexes which are usually very resistant to cleavage by reactions with neutral ligands.[1] Polymeric structures with only sulfur bridges have been obtained in the reactions of $PdCl_4^{2-}$ with alkyl or aryl thiols.[2,3] The present work reports the synthesis and the bridge-splitting reactions of new polymeric complexes of palladium(II) containing alternating halogen and sulfur bridges, $[Pd(SC_6H_5)X]_n$. The aim was to study the course of the reaction between palladium(II) derivatives and diphenyl disulfide in order to investigate the cleavage of the sulfur–sulfur bond promoted by palladium(II) complexes and also to determine the nature of the reaction products in these reactions.

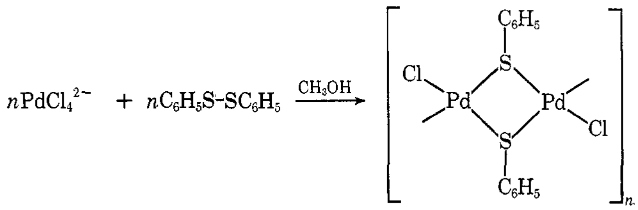
[1] L. F. Lindoy, *Coord. Chem. Rev.*, **4**, 41 (1969), and references therein.

[2] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1549 (1935).

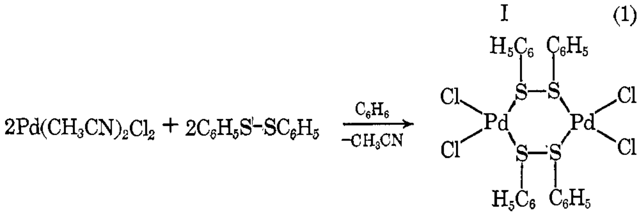
[3] R. G. Hayter and F. S. Humiec, *J. Inorg. Nucl. Chem.*, **26**, 807 (1964)

Results and Discussion

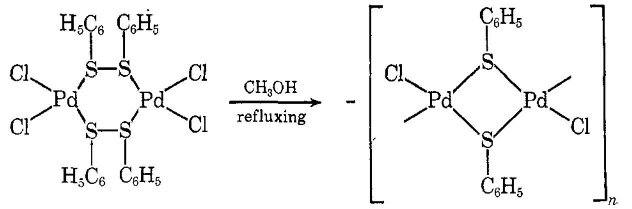
The reactions examined were



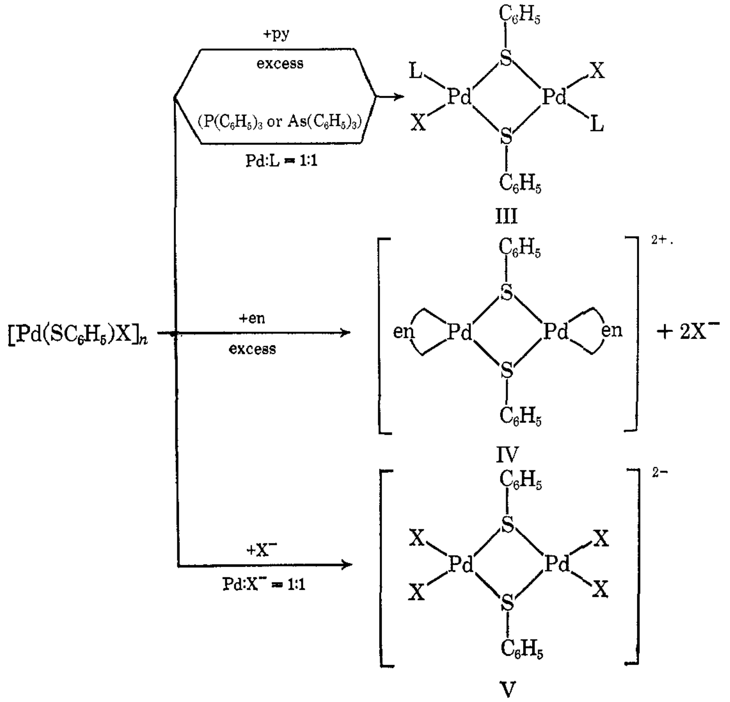
I (1)



II (2)



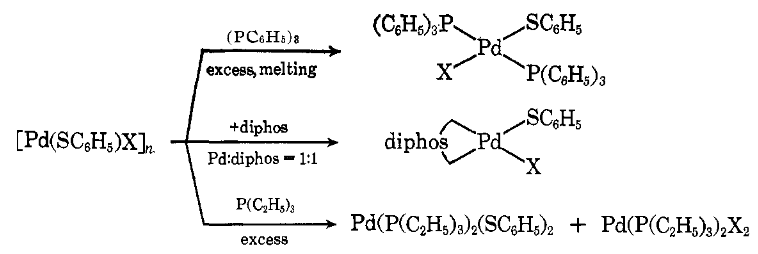
(3)



III (4a)

IV (4b)

V (4c)



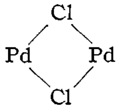
(5a)

(5b)

(5c)

Reaction 1.—The wine-colored product (I) obtained from this reaction is insoluble in most common organic solvents. Its elemental analysis corresponds to the empirical formula $Pd(SC_6H_5)Cl$ and its infrared spectrum in Nujol mull exhibits bands in the range 300–250 cm^{-1} typical of Pd^{II}–Cl bridging stretching frequencies[4,5] (see Table I). These findings are consistent with the structure given above for the products in eq 1.

Bridge-Splitting Reactions.—The full characterization of I was achieved by examining the bridge-splitting reactions shown in eq 4 and 5 [abbreviations: py, pyridine; en, ethylenediamine; diphos, 1,2-bis(diphenylphosphino)ethane; $X^- = Cl^-$ or Br^-]. The polymer I reacts readily with mono- and bidentate neutral ligands as well as with anionic ligands. Reactions with excess pyridine and with stoichiometric amounts of phosphine or arsine (eq 4a) afford complexes of formula $[Pd(SC_6H_5)LX]_2$, consistent with molecular weight measurements. The presence of S bridges in these complexes is supported by far-infrared and chemical evidences. As can be seen from the Table I ν(Pd–Cl) bands fall in the range 356–300 cm^{-1}, typical of terminal chloride: The chloro-bridged structures can be ruled out as the



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[4] (a) D. M. Adams and P. J. Chandler, *Chem. Commun.*, 69 (1966); (b) M. J. Grogan and K. Nakamoto, *J. Am. Chem. Soc.*, **90**, 918 (1968); (c) R. J. Goodfellow, P. L. Goggin, and L. M. Venanzi, *J. Chem. Soc., A*, 1897 (1967); (d) D. M. Adams and P. J. Chandler, *ibid.*, *A*, 588 (1969).

[5] (a) B. Crociani, P. Uguagliati, T. Boschi, and U. Belluco, *ibid.*, *A*, 2869 (1968); (b) B. Crociani, T. Boschi, and U. Belluco, *ibid.*, in press.

Table I

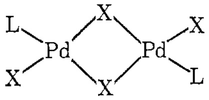
Metal–Halogen Stretching Frequencies

Complexes	ν(Pd–X),[a–c] cm^{-1}
$[Pd(C_6H_5S{-}SC_6H_5)Cl_2]_2$	367 ms, 355 s
$[Pd(SC_6H_5)Cl]_n$	300 m, 290 sh, 260 sh, 247 ms
$[Pd(SC_6H_5)Br]_n$	Not resolved, 205 ms
$[Pd(SC_6H_5)(py)Cl]_2$	356 s, 348 sh
$[Pd(SC_6H_5)(py)Br]_2$	203 sh, 197 s
$Pd(SC_6H_5)(P(C_6H_5)_3)_2Cl$	314 s
$Pd(SC_6H_5)(P(C_6H_5)_3)_2Br$	220 m
$[Pd(SC_6H_5)(P(C_6H_5)_3)Cl]_2$	320 sh, 307 s, 300 sh
$[Pd(S(C_6H_5)(P(C_6H_5)_3)Br]_2$	206 sh, 197 m
$[Pd(SC_6H_5)(As(C_6H_5)_3)Cl]_2$	310 s, 302 sh
$[Pd(SC_6H_5)(As(C_6H_5)_3)Br]_2$	208 sh, 197 s
$Pd(SC_6H_5)(diphos)Cl$	288 s
$\{[Pd(SC_6H_5)Cl_2]As(C_6H_5)_4\}_2$	330 m, 306 m, 286 vs
$\{[Pd(SC_6H_5)Br_2]As(C_6H_5)_4\}_2$	244 s, 212 s, 190 s
$\{[Pd(SC_6H_5)Cl_2]N(CH_3)_4\}_2$	335 m, 300 sh, 290 vs
$\{(Pd(SC_6H_5)Br_2]N(C_2H_5)_4\}_2$	244 s, 216 s, 194 ms, 182 ms
$\{[Pd(SC_6H_5)(diphos)]SnCl_3\}_2$	286 s, 260 s, 250 sh[d]

[a] The assignment is based on the shift caused by changing the halogen X. [b] The ν(Pd–S bridging) bands could not be located with certainty. Several spectra exhibit some weak bands in the region 380–330 cm^{-1} that might be related to such vibrations. [c] Abbreviations: m, medium; sh, shoulder; s, strong; vs, very strong. [d] ν(Sn–Cl).

unit shows two well-separated ν(Pd–Cl bridging) bands, one of which is always below 300 cm^{-1}.[4,5] Moreover it has been found that pyridine does not split sulfur bridges.[1]

Structure III with L in the *trans* position was assumed as the most probable one, at least in the solid state, on the basis of the structures of complexes of type $Pd_2L_2X_4$ (with L = neutral ligand and X = Cl, Br), for which X-ray investigations have shown the *trans* configuration[6]

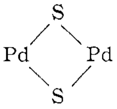


On the basis of the previous arguments the product of the reaction with ethylenediamine (en) (eq 4b) is assigned an S-bridged structure (IV). In fact en cannot split S bridges and in this sense is similar to *p*-toluidine.[1]

Moreover, far-ir spectra show no bands attributable to any Pd–X stretching frequencies. The coordination of en is proved by the values of ν(N–H) (3180 (s), 3144 (s), 3050 (s) cm^{-1}) and ν(Pd–en) (572 (m), 510 (m) cm^{-1}), which are in a good agreement with those reported for $[Pd(en)_2]Cl_2$[7] and $[Pd(C_{10}H_{12}OCH_3)(en)]Cl$.[8] Unfortunately the insolubility of this complex in most common solvents did not allow conductivity measurement. Reaction 4c yields anionic dimers of formula $[Pd(SC_6H_5)X_2]_2^{2-}$, which were assigned an S-bridged structure (V), since X^- is a poor bridge-splitting agent and it cannot cleave S bridges, which are stronger than halogen bridges. In fact many S-bridged compounds are obtained by metathetical reactions between the corresponding halogen-bridged compounds and mercaptides.[1] Moreover, in the reaction of $[Pd(SC_6H_5)X_2]_2^{2-}$ with pyridine, the same complex as from reaction 4a is obtained.

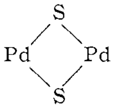
The molar conductivities of complexes V fall in the range 119–150 ohm^{-1} cm^2 mol^{-1} for 10^{-3} *M* solutions in nitromethane at 25°. This is consistent with uni-bivalent electrolytes.

Structure V may exhibit two different steric configurations: a planar one with all X, Pd, and S atoms lying in the same plane (highest symmetry possible D_{2h}) and a nonplanar one in which the unit

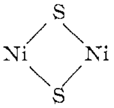


is bent along the line connecting the sulfur atoms (highest symmetry possible C_{2v}). For D_{2h} symmetry $\Gamma_{\nu(Pd-Cl)} = A_g + B_{1g} + B_{2u} + B_{3u}$, where Ag and B_{1g} are Raman active and B_{2u} and B_{3u} are infrared active. In the case of C_{2v} symmetry $\Gamma_{\nu(Pd-Cl)} = A_1 + A_2 + B_1 + B_2$, where A_2 is only Raman active and A_1, B_1, and B_2 are both Raman and infrared active.

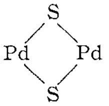
From Table I it can be seen that the anionic complexes $[Pd(SC_6H_5)X_2]_2^{2-}$ have at least three ν(Pd–X) bands, so that C_{2v} symmetry seems to be present. Only $\{[Pd(SC_6H_5)Br_2]N(C_2H_5)_4\}_2$ exhibits four bands attributable to ν(Pd–Br); this might be explained by a breakdown of the selection rules in the solid state. The occurrence of a bent



unit is not surprising, since an X-ray structure of an Ni^{II} complex with thiolato bridges[1] confirms the presence of bent



units. This finding can be reasonably extended to the other S-bridged complexes we have examined. If we consider the complexes of general formula $[Pd(SC_6H_5)LX]_2$, the highest symmetry possible in the presence of a bent



unit is C_2. This implies $\Gamma_{\nu(Pd-X)} = A + B$, where both A and B are Raman and infrared active. Therefore two ν(Pd–X) bands are to be expected in the spectra of these compounds. In fact the results in Table I show that two bands were observed, one of the two occurring as a shoulder.

Reactions 5 cause simultaneous cleavage of both

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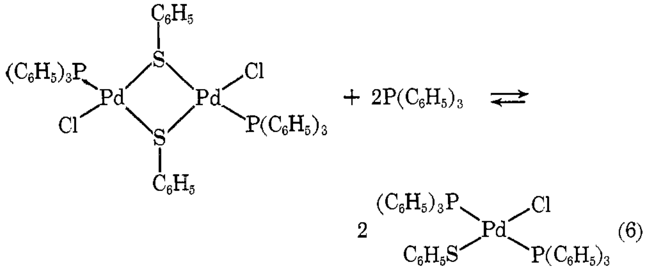
(6) (a) F. G. Mann and A. F. Wells, *J. Chem. Soc.*, 702 (1938); (b) A. F. Wells, *Proc. Roy. Soc.* (London), **A167**, 169 (1938); (c) J. N. Dempsey and N. C. Baenziger, *J. Am. Chem. Soc.*, **77**, 4984 (1955); (d) J. R. Holden and N. C. Baenziger, *ibid.*, **77**, 4987 (1955).

(7) (a) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **17**, 68 (1961); (b) G. W. Watt and D. S. Klett, *ibid.*, **20**, 1053 (1964).

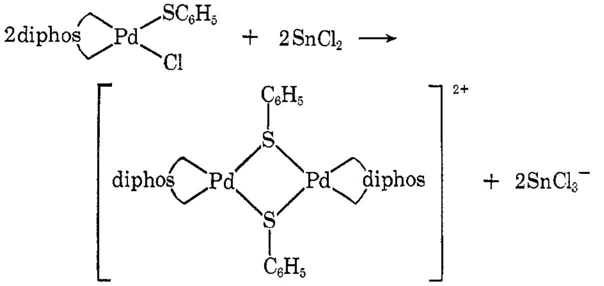
(8) P. Uguagliati, B. Crociani, and U. Belluco, *J. Chem. Soc.*, in press.

halogen and sulfur bridges. The reaction of I with molten triphenylphosphine gives *trans*-$Pd(SC_6H_5)(P(C_6H_5)_3)_2X$, which has been characterized by elemental analysis and infrared spectra (ν(Pd–Cl) = 314 cm^{-1} and ν(Pd–Br) = 220 cm^{-1}). The chloro derivative is also obtained by reaction of the dimer $[Pd(SC_6H_5)(P(C_6H_5)_3)Cl]_2$ with $P(C_6H_5)_3$ in 1,2-dichloroethane


(6)

The equilibrium is far to the left, so that is was impossible to isolate the pure monomer from the above reaction in solution. The presence of the monomer was monitored spectrophotometrically (λ_{max} 535 mμ for the monomer and λ_{max} 367 mμ for the dimer).

Reaction 5b yields the chelated complex $Pd(SC_6H_5)$(diphos)X, whose infrared spectrum exhibits ν(Pd–Cl) at 288 cm^{-1} consistent with a Cl *trans* to phosphine.[9] The complex is soluble in dichloromethane and in 1,2-dichloroethane and its molecular weight is consistent with the above formulation. From the reaction of this product with $SnCl_2$ in an alcohol–ether mixture a cationic S-bridged complex was probably obtained


(7)

Evidence in favor of this formulation is supported by elemental analysis and an infrared spectrum which reveals the presence in the solid state of the anion $SnCl_3^-$ (ν(Sn–Cl) = 286, 260, and 250 cm^{-1}). For a metal–$SnCl_3$ bond the ν(Sn–Cl) bands are expected to be >300 cm^{-1}.[10]

One single conductivity measurement of a saturated nitromethane solution (R = 100 ohms; cell constant = 0.00984 cm^{-1}) is indicative of the ionic nature of this product. A full conductivity study was prevented by the low solubility in most organic solvents.

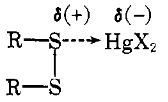
The only product of reaction 5c characterized was *trans*-$Pd(P(C_2H_5)_3)_2(SC_6H_5)_2$ which has an ir spectrum with only one band, ν(Pd–P) at 407 cm^{-1}. Its melting point is consistent with that of the product already reported in the literature.[3] As far as the S-bridge splitting reactions 5a and 6 are concerned, it is to be noted that triphenylarsine does not exhibit the same reactions as triphenylphosphine.

Reactions 2 and 3.—In order to investigate the course of reaction 1 we have examined the reaction of *trans*-$Pd(CH_3CN)_2Cl_2$ with $C_6H_5S–SC_6H_5$ in benzene. The initial palladium complex has two labile coordinated ligands, such as acetonitrile, and these are readily replaced by the entering disulfide without splitting of the S–S bond.

Molecular weight measurements in 1,2-dichloroethane suggest a structure with two $PdCl_2$ moieties bridged by two molecules of disulfide (compound II).

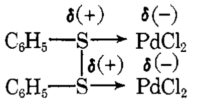
In view of the unshared pair of electrons on each S atom, a nonplanar six-membered ring $Pd(SS)_2Pd$ in the boat form with C_2 symmetry (due to *trans*-phenyl groups) is probable, as suggested also by models. However, a planar ring structure cannot be ruled out on the basis of infrared data. In fact, only two bands (ν (Pd–Cl) = 367 and 355 cm^{-1}) have been found, as expected for a D_{2h} symmetry.

Compound II undergoes S–S splitting by refluxing in methanol, yielding polymer I, $[Pd(SC_6H_5)Cl]_n$. Complex II is a reaction intermediate or a precursor to an intermediate in process 1. This points to a nucleophilic attack on the palladium(II) by a sulfur atom of the disulfide similar to the postulated initial stage of the S–S bond cleavage by HgX_2[11]

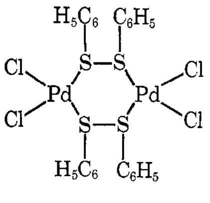


We wish to stress the importance of having isolated compound II. This strongly supports the mechanism which was previously a matter of speculation.

The following step of the reaction [*i.e.*, from II to I] requires the S–S bond fission which has to be related to the electrophilic character of the two sulfur atoms



The S–S bond fission should then occur by a nucleophilic attack on $S^{\delta(+)}$ by the oxygen of the methanol (reaction 3). In fact, reaction of *trans*-$Pd(CH_3CN)_2Cl_2$ with disulfide in benzene (reaction 2) affords the intermediate



which, when heated in the same solvent, undergoes complete decomposition, presumably because of the nucleophilic attack on $S^{\delta(+)}$ by the coordinated chloride.

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(9) G. E. Coates and C. Parkin, *J. Chem. Soc.*, 421 (1963).

(10) D. F. Shriver and M. P. Johnson, *Inorg. Chem.*, **6**, 1265 (1967).

(11) F. Challenger, "Aspects of the Organic Chemistry of Sulphur," Butterworth and Co. Ltd., London, 1959.

Consistently, only metallic palladium is obtained from the decomposition (and probably $C_6H_5S\text{–}Cl$). In other words in benzene palladium(II) oxidizes the disulfide to C_6H_5SCl, without formation of the polymer. The probable reaction is

$$[Pd(C_6H_5S\text{–}SC_6H_5)Cl_2]_2 \xrightarrow[\text{benzene}]{\text{reflux}} 2Pd + 4C_6H_5SCl$$

Formation of metallic palladium cannot be due to thermal decomposition of $[Pd(C_6H_5S\text{–}SC_6H_5)_2Cl_2]_2$ under the conditions of the conversion owing to the high thermal stability of this compound (dec pt 180°).

Experimental Section

All chemicals and solvents were reagent grade and were used without further purification. $Na_2[PdCl_4]$ and $Pd(CH_3CN)_2Cl_2$ were prepared according to standard literature methods.

$[Pd(C_6H_5S\text{–}SC_6H_5)Cl_2]_2$.—A 2-g sample of $Pd(CH_3CN)_2Cl_2$ dissolved in benzene was treated with a slight excess of disulfide under stirring. After a few minutes orange crystals appeared. The product was filtered off, washed with cold benzene and ether, and dried *in vacuo;* yield based on the starting palladium complex, 96%; mp 182° dec. *Anal.* Calcd for $C_{24}H_{20}Cl_4S_4Pd_2$: C, 36.43; H, 2.55; Cl, 17.92; S, 16.21. Found: C, 37.2; H, 2.6; Cl, 17.7; S, 15.8. Calcd formula wt, 791; mol wt found in 1,2-dichloroethane, 800.

$[Pd(SC_6H_5)Cl]_n$.—(a) A 2-g sample of Na_2PdCl_4 dissolved in 40 ml of CH_3OH was treated under stirring with an excess of disulfide. After 2 days a finely powdered wine red compound was obtained. It was filtered off, washed with water, methanol, and ether, and dried *in vacuo;* yield, 80%; mp >270°. No metallic palladium was found.

(b) A 1-g sample of $[Pd(C_6H_5S\text{–}SC_6H_5)Cl_2]_2$ was refluxed in 20 ml of methanol for 1 hr. The conversion into $[Pd(SC_6H_5)Cl]_n$ was quantitative; mp >270°. *Anal.* Calcd for C_6H_5ClSPd: C, 28.71; H, 2.01; Cl, 14.12; S, 12.77. Found: C, 28.6; H, 2.2; Cl, 14.9; S, 12.1.

(c) A 1-g sample of $[Pd(C_6H_5S\text{–}SC_6H_5)Cl_2]_2$ was refluxed in benzene for 1 hr. Metallic palladium in quantitative yield was recovered.

$[Pd(SC_6H_5)Br]_n$.—(a) A 1-g sample of Na_2PdCl_4 was dissolved in 40 ml of methanol and treated with an excess of LiBr and then with an excess of disulfide. After 2 days a wine red complex was precipitated from the red solution by diluting with water. The complex was washed with water, CH_3OH, and ether and dried *in vacuo;* yield, 60%; mp >270°.

(b) A 1-g sample of $[Pd(SC_6H_5)Cl]_n$ suspended in 40 ml of boiling acetone was treated with a large excess of LiBr. After 1 hr the complex was filtered off, washed with water, methanol, and ether, and dried *in vacuo;* yield, 85%; mp >270°. *Anal.* Calcd for C_6H_5BrSPd: C, 24.39; H, 1.70; Br, 27.04; S, 10.85. Found: C, 25.1; H, 1.8; Br, 26.5; S, 11.2.

$[Pd(SC_6H_5)(py)Cl]_2$.—A 200-mg sample of $[Pd(SC_6H_5)Cl]_n$ suspended in CH_2Cl_2 was treated with an excess of pyridine. The solution became orange and clear and the complex was precipitated by dilution with ether. The complex was washed with CH_2Cl_2 and ether and dried *in vacuo;* yield, 70%; mp 250° dec. *Anal.* Calcd for $C_{22}H_{20}N_2Cl_2S_2Pd_2$: C, 42.12; H, 2.95; N, 4.09; Cl, 10.36; S, 9.37. Found: C, 42.5; H, 3.1; N, 4.1; Cl, 10.8; S, 9.06.

$[Pd(SC_6H_5)(py)Br]_2$.—This red-orange complex was prepared in the same way as the chloride derivative starting from $[Pd(SC_6H_5)Br]_n$; yield, 65%; mp 250° dec. *Anal.* Calcd for $C_{22}H_{20}N_2Br_2S_2Pd_2$: C, 37.28; H, 2.61; N, 3.62; Br, 20.67; S, 8.29. Found: C, 36.8; H, 2.7; N, 3.41; Br, 20.3; S, 8.6.

$Pd(SC_6H_5)_2(P(C_2H_5)_3)_2$.—A 300-mg sample of $[Pd(SC_6H_5)Cl]_n$ suspended in 40 ml of CH_2Cl_2 was treated with an excess of $P(C_2H_5)_3$ under nitrogen. The wine red complex dissolved immediately; after 30 min the solution, reduced to small volume, was diluted with CH_3OH and yellow crystals precipitated. The precipitate was washed with methanol and ether and dried *in vacuo;* yield, 40%; mp 135°. *Anal.* Calcd for $C_{24}H_{40}P_2S_2Pd$: C, 51.38; H, 7.19; S, 11.43. Found: C, 51.5; H, 7.2; S, 11.3. Calcd formula wt, 561; mol wt found in 1,2-dichloroethane, 555.

$[Pd(SC_6H_5)(P(C_6H_5)_3)Cl]_2$.—A 300-mg sample of $[Pd(SC_6H_5)Cl]_n$, suspended in 40 ml of CH_2Cl_2, was treated with the stoichiometric amount of $P(C_6H_5)_3$ ($Pd:P(C_6H_5)_3 = 1:1$). The yellow precipitate obtained by dilution with ether–petroleum ether (1:1) was washed with CH_2Cl_2 and ether and then dried overnight at 100° until CH_2Cl_2 of crystallization was eliminated; yield, 75%; mp 257°. *Anal.* Calcd for $C_{48}H_{40}Cl_2S_2P_2Pd_2$: C, 56.16; H, 3.93; Cl, 6.91; S, 6.25. Found: C, 56.3; H, 3.8; Cl, 7.0; S, 6.3. Calcd formula wt, 1026; mol wt found in 1,2-dichloroethane, 1068.

$[Pd(SC_6H_5)(P(C_6H_5)_3Br]_2$.—This orange complex was prepared in the same way as the chloride derivative starting from $[Pd(SC_6H_5)Br]_n$; yield, 80%; mp 262° dec. *Anal.* Calcd for $C_{48}H_{40}Br_2S_2P_2Pd_2$: C, 51.68; H, 3.61; Br, 14.33; S, 5.75. Found: C, 51.6; H, 3.8; Br, 14.2; S, 5.8.

$Pd(SC_6H_5)(P(C_6H_5)_3)_2Cl$.—A 250-mg sample of $[Pd(SC_6H_5)Cl]_n$ was treated with an excess of molten $P(C_6H_5)_3$ for 10 min. The solid reaction mixture was finely ground in petroleum ether (bp 30–50°), filtered off, and washed with petroleum ether until complete dissolution of $P(C_6H_5)_3$. The violet complex formed was dried *in vacuo;* yield, 95%; mp 170°. *Anal.* Calcd for $C_{42}H_{35}ClSP_2Pd$: C, 65.04; H, 4.55; Cl, 4.57; S, 4.13. Found: C, 64.5; H, 4.6; Cl, 4.7; S, 4.2.

$Pd(SC_6H_5)(P(C_6H_5)_3)_2Br$.—This violet complex was prepared in the same way as the chloride derivative starting from $[Pd(SC_6H_5)Br]_n$; yield, 95%; mp 155°. *Anal.* Calcd for $C_{42}H_{36}BrSP_2Pd$: C, 61.51; H, 4.30; Br, 9.74; S, 3.91. Found: C, 61.7; H, 4.6; Br, 9.5; S, 4.0.

$[Pd(SC_6H_5)(As(C_6H_5)_3)Cl]_2$.—This orange compound was prepared in the same way as $[Pd(SC_6H_5)(P(C_6H_5)_3)Cl]_2$; yield, 80%; mp 263° dec. *Anal.* Calcd for $C_{48}H_{40}Cl_2S_2As_2Pd_2$: C, 51.73; H, 3.62; Cl, 6.36; S, 5.75. Found: C, 51.5; H, 3.6; Cl, 6.4; S, 5.5.

$[Pd(SC_6H_5)(As(C_6H_5)_3)Br]_2$.—This orange compound was prepared in the same way as $[Pd(SC_6H_5)(P(C_6H_5)_3)Br]_2$; yield, 80%; mp 262° dec. *Anal.* Calcd for $C_{48}H_{40}Br_2S_2As_2Pd_2$: C, 47.90; H, 3.35; Br, 13.28; S, 5.33. Found: C, 47.6; H, 3.2; Br, 13.3; S, 5.2.

$Pd(SC_6H_5)(diphos)Cl$.—A 250-mg sample of $[Pd(SC_6H_5)Cl]_n$ suspended in 40 ml of dichloromethane was treated with the stoichiometric amount of diphos (Pd:diphos = 1:1). A clear, orange solution was obtained; the red-orange complex was precipitated by diluting with ether. It was filtered off, washed several times with ether, and dried *in vacuo;* yield, 90%; mp 205° dec. *Anal.* Calcd for $C_{32}H_{29}ClSP_2Pd$: C, 59.18; H, 4.50; Cl, 5.46; S, 4.94. Found: C, 59.4; H, 4.3; Cl, 5.4; S, 5.0. Calcd formula wt, 649; mol wt found in 1,2-dichloroethane, 645. The complex is not conducting in dichloromethane solution.

$\{[Pd(SC_6H_5)(en)]Cl\}_2$.—A 250-mg sample of $[Pd(SC_6H_5)Cl]_n$, suspended in 40 ml of dichloromethane, was treated with an excess of ethylenediamine. A red precipitate was formed; after 30 min, it was filtered off, washed with methanol and ether, and dried *in vacuo*. This complex is insoluble in dichloromethane, nitromethane, and methanol; yield, 60%; mp >270°. *Anal.* Calcd for $C_{16}H_{26}N_4Cl_2S_2Pd_2$: C, 30.88; H, 4.21; N, 9.01; Cl, 11.39; S, 10.30. Found: C, 30.3; H, 4.2; N, 9.5; Cl, 11.9; S, 9.6.

$\{[Pd(SC_6H_5)(en)]Br\}_2$.—This red complex was prepared in the same way as the chloride derivative starting from $[Pd(SC_6H_5)Br]_n$. It is insoluble in the most common organic solvents; yield, 60%; mp >270°. *Anal.* Calcd for $C_{16}H_{26}N_4Br_2S_2Pd_2$: C, 27.02; H, 3.68; N, 7.88; Br, 22.47; S, 9.01. Found: C, 26.9; H, 3.6; N, 8.0; Br, 22.6; S, 8.8.

$\{[Pd(SC_6H_5)Cl_2]As(C_6H_5)_4\}_2$.—A 250-mg sample of $[Pd(SC_6H_5)Cl]_n$ was treated in dichloromethane with the stoichiometric amount of $As(C_6H_5)_4Cl$ ($Pd:As(C_6H_5)_4Cl = 1:1$) for 3 hr under stirring. The orange complex was filtered off, washed with dichloromethane and ether, and dried *in vacuo;* yield, 90%;

mp 241°. *Anal.* Calcd for $C_{60}H_{50}Cl_4S_2As_2Pd_2$: C, 53.79; H, 3.76; Cl, 10.58; S, 4.79. Found: C, 53.6; H, 3.6; Cl, 10.8; S, 4.8. Λ_M in nitromethane solution is 119 ohm^{-1} cm^2 mol^{-1} at 25° and a 10^{-3} *M* concentration.

$\{[Pd(SC_6H_5)Br_2]As(C_6H_5)_4\}_2$.—This complex was prepared by a metathetical reaction starting from the chloride analog in acetone with a large excess of LiBr. After 1 hr the red crystals were filtered off, washed with acetone, and dried; yield, 95%; mp 240°. *Anal.* Calcd for $C_{60}H_{50}Br_4S_2As_2Pd_2$: C, 47.49; H, 3.32; Br, 21.06; S, 4.22. Found: C, 47.6; H, 3.4; Br, 21.2; S, 4.2. Λ_M in nitromethane solution is 127 ohm^{-1} cm^2 mol^{-1} at 25° and a 10^{-3} *M* concentration.

$\{[Pd(SC_6H_5)Cl_2]N(CH_3)_4\}_2$.—This yellow-orange compound was prepared in the same way as $\{[Pd(SC_6H_5)Cl_2]As(C_6H_5)_4\}_2$ by reaction of $[Pd(SC_6H_5)Cl]_n$ with $N(CH_3)_4Cl$; yield, 80%; mp >270°. *Anal.* Calcd for $C_{20}H_{34}N_2Cl_4S_2Pd_2$: C, 33.30; H, 4.75; N, 3.88; Cl, 19.66; S, 8.89. Found: C, 33.2; H, 4.6; N, 4.0; Cl, 20.0; S, 9.1. Λ_M in nitromethane solution is 142 ohm^{-1} cm^2 mol^{-1} at 25° and a 10^{-3} *M* concentration.

$\{[Pd(SC_6H_5)Br_2]N(C_2H_5)_4\}_2$.—This red-orange compound was prepared in the same way as $\{[Pd(SC_6H_5)Cl_2]As(C_6H_5)_4\}_2$ by reaction of $[Pd(SC_6H_5)Br]_n$ with $N(C_2H_5)_4Br$; yield, 87%; mp >270°. *Anal.* Calcd for $C_{28}H_{50}N_2Br_4S_2Pd_2$: C, 33.25; H, 4.98; N, 2.77; Br, 31.60; S, 6.34. Found: C, 33.2; H, 4.6; N, 2.8; Br, 31.5; S, 6.2. Λ_M in nitromethane solution is 150 ohm^{-1} cm^2 mol^{-1} at 25° and a 10^{-3} *M* concentration.

$\{[Pd(SC_6H_5)(diphos)]SnCl_3\}_2$.—A 320-mg sample of $Pd(SC_6H_5)(diphos)Cl$ suspended in methanol–ether (1:1) was treated with an excess of $SnCl_2$ under stirring. Within 3 hr a yellow precipitate was formed. It was filtered off, washed with methanol and ether, and dried; yield, 85%; mp 215°. *Anal.* Calcd for $C_{64}H_{58}Cl_6S_2P_4Sn_2Pd_2$: C, 45.81; H, 3.48; Cl, 12.67; S, 3.82. Found: C, 45.3; H, 3.4; Cl, 12.9; S, 3.9.

For some of these compounds the analytical values are not in close enough agreement with calculated values owing to their difficult purification caused by their low solubility in most common organic solvents.

Molecular Weights and Conductivity Measurements.—A Mechrolab thermoelectric molecluar weight apparatus was used in all cases. An LKB Type 3216 B conductivity bridge was employed for conductivity measurements with a cell of $K = 0.0098$.

Infrared Spectra.—Infrared spectra were recorded in the region 4000–250 cm^{-1} with a Perkin-Elmer Model 621 instrument and with a Beckman IR-11 instrument in the region 400–140 cm^{-1}. From 4000 to 1300 cm^{-1} hexachlorobutadiene mulls and NaCl plates were used; from 1700 to 250 cm^{-1} Nujol mulls and CsI plates were used. Nujol mulls and thin polythene sheets were used from 400 to 140 cm^{-1}. Calibration was performed against either polystyrene film or a water vapor rotational spectrum. Accuracy is believed to be better than ±2 cm^{-1} in the range 4000–400 cm^{-1} and ±1 cm^{-1} in the range 400–150 cm^{-1}.

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Iodonium Salts of Complex Anions. I. The Self-Phenylation of Diphenyliodonium Salts of Bis(dithiooxalato)palladate(II) and -platinate(II)[1]

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The diphenyliodonium salts of the dithiooxalates of palladium(II) and platinum(II), $((C_6H_5)_2I)_2[M(S_2C_2O_2)_2]$, were isolated in a study of the phenylating effect of this cation on complex anions. This new ligand reaction was studied in both the solid state and in solution. At 150° in the solid state the products are the polymeric thiophenolates of palladium(II) and platinum(II), palladium also undergoing reduction to the metal to a considerable extent. These mercaptides were found to be soluble in molten triphenylphosphine and were briefly characterized in this solvent. In pyridine solution $(pyH)_2[Pd(S_2C_2O_2)_2]$ and 2-, 3-, and 4-phenylpyridines were the principal products while the platinum complex gave $[Pt(S_2C_2O_2)(py)_2]py$ and $(pyH)[Pt(S_2C_2O_2)(S_2C_2O_2C_6H_5)(py)_2]$. A radical mechanism is proposed for the reactions on the basis of the isolated products.

Introduction

The reactions of coordinated ligands have been a subject of considerable study in the last few years. Our interest in this area has prompted us to investigate the arylation of coordinated ligands by a new reagent for this field, the diphenyliodonium ion, $(C_6H_5)_2I^+$.

This cation has several interesting features which make it suited to such a study. Many of its salts are easily precipitated from aqueous solution and these salts have built-in reactivity; the cation is the attacking species, the complex anion is the substrate, and no solvent is required. The alternation of cation and anions in the crystal lattice ensures a precise stoichiometry and also eliminates the need for any other ions in the system. In addition, these salts are generally more soluble in organic solvents than are the corresponding alkali metal salts and so provide a wider range of possible reaction conditions for solution studies.

There have been a number of reports of arylation by the diphenyliodonium ion of simple nucleophiles like iodide[2] and chloride.[3] These reactions proceed *via* a nucleophilic substitution of iodobenzene by the simple

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[1] (a) Presented to the Graduate School of the University of Connecticut by G. E. H. in partial fulfillment of the requirements for the Ph.D. degree. (b) Presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

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