No such change in the spectrum was found so the slow step is looked at as the interaction of the two species.

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Coordination Complexes of Diphenyl(*o*-diphenylarsinophenyl)phosphine Sulfide and Diphenyl(*o*-diphenylarsinophenyl)phosphine[1,2]

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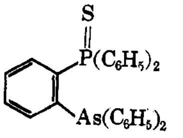
Diphenyl(*o*-diphenylarsinophenyl)phosphine sulfide (I) forms stable complexes with palladium(II), platinum(II), gold(I), and copper(I). Ligand I forms a chelate by coordinating both the thiophosphoryl and arsino groups to palladium(II), platinum(II), and copper(I), whereas it is bonded only through the arsenic atom in the gold(I) chloride complex. Electronic absorption spectra of the palladium(II) complexes indicate that the phosphine sulfide, I, exerts a weaker ligand field than the corresponding phosphine, II. The yellow palladium thiocyanate complex of diphenyl(*o*-diphenylarsinophenyl)phosphine, $[Pd(C_{30}H_{24}AsP)(NCS)(SCN)]$, is an example of an unusual type of thiocyanate complex because it contains one N-bonded and also one S-bonded thiocyanate ion in the same molecular complex.

Introduction

In contrast to numerous metal complexes of phosphine oxides[4] and arsine oxides,[5] few phosphine sulfide complexes had been reported before 1965.[6,7] Recently, we[8] have been investigating the coordination properties of tertiary phosphine sulfides toward transition metal ions. In spite of the limited results of previous investigators,[6,7] our results indicate that tertiary phosphine sulfides form numerous stable complexes with metals which normally bond to easily polarized donor atoms, *e.g.*, "class b" or "soft" metals, using the designations of Ahrland, Chatt, and Davies[9] and Pearson,[10] respectively.

The ligand diphenyl(*o*-diphenylarsinophenyl)phosphine sulfide (I), which potentially could function as a chelating ligand, was synthesized to ascertain if introduction of the P=S group into a chelate ring would materially increase the coordination tendency of the thiophosphoryl group and facilitate isolation of "class a" metal complexes. Also, by comparing the electronic absorption spectra of palladium(II) complexes of ligand I with analogous complexes of diphenyl(*o*-diphenylarsinophenyl)phosphine (II), one can determine the position of the P=S group in the spectrochemical series, relative to the parent phosphine.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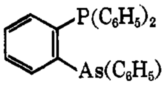
II

Experimental Section

Materials.—Sodium tetrachloroaurate(III) (Alfa), sodium tetrachloroplatinate(II) (Platinum Chemicals Co.), palladium nitrate (Alfa), sodium tetrachloropalladate(II) (Engelhard), and 1-butyllithium (Foote Mineral) were reagent grade chemicals and were used without further purification. Diphenylchlorophosphine was fractionated before use, bp 170–172° (10 mm). Dimethylformamide (DMF) was dried for 2 days over anhydrous barium oxide and then distilled, bp 55° (20 mm), from fresh BaO. Diphenylthiophosphoryl chloride, $(C_6H_5)_2P(S)Cl$, bp 183–184° (3 mm), was prepared in 96% yield from diphenylchlorophosphine (93.9 g, 0.425 mole) and elemental sulfur (13.6 g, 0.425 g-atom) in 100 ml of refluxing toluene.

Preparation of Diphenyl(*o*-diphenylarsinophenyl)phosphine Sulfide.—To a stirred solution (0–5°) of diphenyl(*o*-bromophenyl)arsine[11] (24.8 g, 0.0644 mole) in 200 ml of anhydrous diethyl ether was added 0.064 mole of 1-butyllithium over a period of 1.5 hr. The mixture was stirred for 1 hr more at 0–5° and then diphenylthiophosphoryl chloride, $(C_6H_5)_2P(S)Cl$ (16.2 g, 0.064 mole), in 50 ml of ether was added over a period of 45 min. The mixture was stirred for 2 hr at room temperature and then hydrolyzed with 0.2 N HCl. The insoluble material was collected by filtration and washed successively with water, ethanol, and ether. The crude product (19.2 g, mp 186–190°) was recrystallized from 375 ml of hot 1-butanol; yield 15.3 g

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[2] Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965; Abstracts, p O-13.

[3] Public Health Service Predoctoral Fellow (No. 5-Fl-GM-25), 1965–1966.

[4] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961); E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 1878, 2276 (1960).

[5] D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961); D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 2298, 3735 (1961).

[6] E. Bannister and F. A. Cotton, *ibid.*, 1959 (1960).

[7] J. Philip and C. Curran, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 28L.

[8] D. W. Meek and P. Nicpon, *J. Am. Chem. Soc.*, **87**, 4951 (1965).

[9] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

[10] R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

[11] W. Cochran, R. A. Hart, and F. G. Mann, *J. Chem. Soc.*, 2816 (1957).

(46%); mp 190–192°. *Anal.* Calcd for $C_{30}H_{24}AsPS$: C, 68.96; H, 4.63; S, 6.14. Found: C, 68.19; H, 4.64; S, 6.22.

Preparation of Diphenyl(*o*-diphenylarsinophenyl)phosphine.—This compound was prepared by the same procedure as the above phosphine sulfide, except that diphenylchlorophosphine was used in the last step. The resulting material, when recrystallized from hot 1-butanol, gave 15.8 g (50% yield) of the product, mp 190.5–192.5°.[12] *Anal.* Calcd for $C_{30}H_{24}AsP$: C, 73.47; H, 4.93. Found: C, 73.59; H, 5.13.

Preparation of Complexes.—Specific directions are presented for the phosphine sulfide complexes. Analogous complexes of the phosphine ligand, II, were prepared and recrystallized in a similar manner.

$[Pd(C_{30}H_{24}AsPS)_2](NO_3)_2$.—The phosphine sulfide ligand (1.57 g, 3 mmoles) in 20 ml of DMF was added with stirring to a filtered solution of palladium(II) nitrate (0.345 g, 1.5 mmoles) in 30 ml of DMF. The solution was stirred for 1 hr and then the complex was precipitated by adding 150 ml of diethyl ether. Recrystallization was effected by dissolving the complex in 25 ml of warm DMF, filtering, and precipitating by slow addition of ether while stirring.

$[Pd(C_{30}H_{24}AsPS)Cl_2]$.—Ligand I (1.57 g, 3 mmoles) in 75 ml of hot 1-butanol was added to a stirred solution of sodium tetrachloropalladate(II) (0.88 g, 3 mmoles) in 75 ml of absolute ethanol. The yellow precipitate, which formed immediately, was collected on a filter and then recrystallized by dissolving it in 20 ml of hot DMF, filtering, and reprecipitating the compound by slow addition of absolute ethanol.

$[Pd(C_{30}H_{24}AsPS)X_2]$ (Where X = Br, I, SCN, and SeCN).—These complexes were prepared in a manner analogous to $[Pd(C_{30}H_{24}AsPS)Cl_2]$ except that the ethanol solution of sodium tetrachloropalladate(II) was treated with an ethanol solution of the appropriate lithium or sodium salt before adding the ligand.

$[Pt(C_{30}H_{24}AsPS)Cl_2]$.—This complex was prepared in the same manner only employing sodium tetrachloroplatinate(II). Two recrystallizations were necessary, one from DMF–ethanol as above and a second from dichloromethane–hexane.

$[Au(C_{30}H_{24}AsPS)Cl]$.—Sodium tetrachloroaurate(III) (0.25 g, 0.69 mmole) dissolved in 5 ml of absolute ethanol was mixed with 0.73 g (1.4 mmoles) of the phosphine sulfide ligand in 25 ml of hot 1-butanol. An orange precipitate formed immediately but redissolved within a few minutes as the solution became colorless. A white precipitate began forming after several minutes. The reaction mixture was stirred for 2 hr, cooled, and then filtered. The solid material was dissolved in 10 ml of dichloromethane and filtered. Addition of 45 ml of *n*-hexane and subsequent cooling to 5° for 12 hr produced white crystals. These were collected on a filter, washed with hexane, and dried *in vacuo*.

$[Cu(C_{30}H_{24}AsPS)_2]ClO_4$.—To 0.56 g (1.5 mmoles) of copper(II) perchlorate in 15 ml of absolute ethanol was added 1.57 g (3 mmoles) of ligand I in 50 ml of hot 1-butanol. The solution became light green, and a colorless complex precipitated upon cooling. It was isolated by filtration, washed with ethanol and ether, and dried over P_4O_{10} *in vacuo*.

Attempted Preparation of Manganese(II), Iron(II), Cobalt(II), and Nickel(II) Complexes of the Phosphine Sulfide.—No complexes of ligand I were isolated from the reactions with anhydrous halides of cobalt(II) and nickel(II) or perchlorates of manganese(II), iron(II), cobalt(II), and nickel(II) in several nonaqueous solvents. Slight color changes were observed in solution, but all attempts to isolate a complex resulted in crystallization of free ligand.

Diphenyl(*o*-diphenylarsinophenyl)phosphine Complexes.—The corresponding phosphine complexes were prepared in a manner analogous to the preparation of phosphine sulfide complexes. Cobalt and nickel complexes of this ligand will be reported in future papers.

Spectra.—Infrared spectra were obtained with a Perkin-Elmer Model 337 grating spectrophotometer and a high-resolution Beckman IR-9 spectrophotometer using Nujol mulls between KBr plates. Visible and ultraviolet spectra of the complexes in solution were taken with a Cary Model 14 recording spectrophotometer using a set of matched 1-cm quartz cells. The spectra of the complexes in the solid state were obtained with the same instrument by use of Nujol mulls supported on filter paper.[13]

Conductance Measurements.—The measurements were performed with an Industrial Instruments Model RC-16B conductivity bridge on approximately 10^{-3} *M* acetonitrile solutions. (See Table I.)

Discussion

One of the interesting features of diphenyl(*o*-diphenylarsinophenyl)phosphine sulfide, I, is whether it will form a chelate by coordination of both the diphenylarsino and diphenylthiophosphoryl groups to the same metal. Coordination of the thiophosphoryl group may be detected by infrared spectra, that is, if the P═S group bonds to positive ions, the phosphorus–sulfur bond order will decrease and the P═S stretching frequency will occur at lower energy than in the free ligand.[8,14] By comparing the infrared spectrum of I with the analogous phosphine, II, the P═S stretching frequency is assigned unambiguously at 638 cm^{-1}. This value is consistent with the P═S vibration (637 cm^{-1}) of triphenylphosphine sulfide.[15] In all complexes, except the gold(I) chloride complex, the strong 638-cm^{-1} absorption of the free ligand is absent, and a very strong band appears in the 593–609-cm^{-1} region (Table II, Figure 1). Thus, the shift of the P═S band to lower energy, when coupled with the electronic spectral data, demonstrates that I functions as a bidentate ligand in all but one of the complexes. The P═S vibration (Table II) in the $(C_{30}H_{24}AsPS)AuCl$ complex indicates that I acts as a monodentate ligand in this case, coordinating *via* arsenic.

The possibility that factors such as coupling might offset the lowering of the bond order in the gold(I) chloride complex can be excluded on the basis of the behavior of several phosphine sulfides which we have investigated.[16] In each case, coordination of a phosphine sulfide ligand to a metallic ion causes the infrared P═S band to shift 25–40 cm^{-1} to lower energy, even with univalent ions such as Cu^+ and Ag^+. Since triphenylphospine sulfide complexes of both Au(I) and Au(III) have been isolated recently,[17–19] the uncoordinated P═S group in $(C_{30}H_{24}AsPS)AuCl$ most probably is due to the linear character of gold(I) complexes and to the preference for arsenic donors.

In the presence of coordinating anions, both ligands I and II form nonelectrolyte complexes of composition $Pd(ligand)X_2$, whereas palladium(II) nitrate forms the square-planar, di-univalent complexes $[Pd(C_{30}H_{24}AsPS)_2](NO_3)_2$ and $[Pd(C_{30}H_{24}AsP)_2](NO_3)_2$. Only one sharp phosphorus–sulfur stretching vibration was

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[12] Although both ligands melt at nearly the same temperature, their analyses and infrared spectra are different.

[13] R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **3**, 1278 (1964).

[14] F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

[15] K. A. Jensen and P. H. Nielson, *Acta Chem. Scand.*, **17**, 1875 (1963).

[16] P. Nicpon and D. W. Meek, data to be published.

[17] P. Nicpon, Ph.D. Thesis, The Ohio State University, 1966.

[18] I. M. Keen, *J. Chem. Soc.*, 5751 (1965).

[19] R. A. Potts and A. L. Allred, *J. Inorg. Nucl. Chem.*, **28**, 1479 (1966).

TABLE I

ANALYTICAL AND CONDUCTANCE DATA ON THE DIPHENYL(*o*-DIPHENYLARSINOPHENYL)PHOSPHINE SULFIDE AND DIPHENYL(*o*-DIPHENYLARSINOPHENYL)PHOSPHINE COMPLEXES

		Λ_M,[a]		Analyses,[b] %									
		cm²/ohm		C		H		S		N		Halogen	
Complex	Color	mole	Yield	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Pd(C_{30}H_{24}AsPS)Cl_2]$	Yellow	<2	69	51.49	51.38	3.46	3.60	4.58	4.73			10.13	9.98
$[Pd(C_{30}H_{24}AsPS)Br_2]$	Orange	<2	85	46.68	46.63	3.07	3.23	4.06	4.22			20.26	20.07
$[Pd(C_{30}H_{24}AsPS)(SCN)_2]$	Orange	<1	79	51.59	51.64	3.24	3.40	12.89	13.00	3.76	3.55		
$[Pd(C_{30}H_{24}AsPS)(SeCN)_2]$	Red-orange	<1	80	45.82	45.65	2.88	3.00			3.34	3.20		
$[Pd(C_{30}H_{24}AsPS)I_2]$	Purple	<2	90	40.82	41.00	2.74	2.95	3.63	3.80			28.76	28.48
$[Pd(C_{30}H_{24}AsPS)_2](NO_3)_2$	Yellow	281	66	56.51	56.34	3.79	3.90	5.02	4.82	2.19	1.97		
$[Pt(C_{30}H_{24}AsPS)Cl_2]$	Yellow	<1	34	45.70	45.54	3.07	3.07	4.07	3.95			8.99	9.20
$[Pt(C_{30}H_{24}AsPS)Br_2]$	Yellow	<1	27	41.07	41.30	2.76	3.00						
$[Au(C_{30}H_{24}AsPS)Cl]$	Colorless	12.1	29	47.73	47.49	3.20	3.04					4.70	4.95
$[Cu(C_{30}H_{24}AsPS)_2](ClO_4)$	Colorless	142	80	59.66	59.53	4.01	4.07	5.31	5.08			2.93	3.18
$[Pd(C_{30}H_{24}AsP)Cl_2]$	Pale yellow	*c*	24	53.96	53.88	3.62	3.80					10.62	10.55
$[Pd(C_{30}H_{24}AsP)Br_2]$	Light yellow	*c*	43	47.62	47.82	3.20	3.48					21.12	20.84
$[Pd(C_{30}H_{24}AsP)(CNS)_2]$	Yellow	8.3	45	53.91	53.61	3.39	3.20	8.99	8.72	3.93	3.74		
$[Pd(C_{30}H_{24}AsP)_2][Pd(SCN)_4]$	Orange	*c*	77	53.91	54.10	3.39	3.49	8.99	8.79	3.93	3.91		
$[Pd(C_{30}H_{24}AsP)(SeCN)_2]$	Yellow	3.7	79	45.82	45.65	2.88	3.00			3.34	3.20		
$[Pd(C_{30}H_{24}AsP)I_2]$	Orange	3.9	75	42.36	42.55	2.84	3.03					29.84	29.56
$[Pd(C_{30}H_{24}AsP)_2](NO_3)_2$	Pale yellow	277	52	59.51	59.58	3.99	4.12			2.31	2.50		
$[Pt(C_{30}H_{24}AsP)Cl_2]$	Colorless	*c*	34	47.63	47.71	3.20	3.40					9.37	9.58

[a] Molar conductance on approximately 10^{-3} *M* solutions in acetonitrile at 25°. Uni- and di-univalent electrolytes will have values in the ranges 135–150 and 270–300, respectively. [b] Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., except that nitrogen analyses were done in this laboratory with a Coleman nitrogen analyzer. [c] Insoluble.

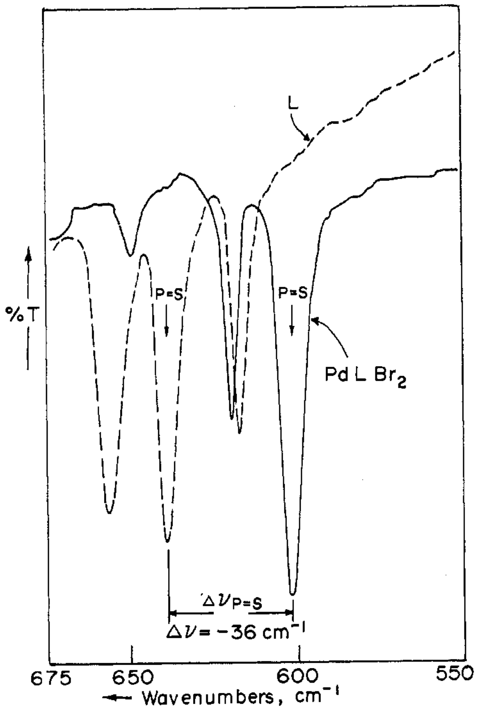

Figure 1.—The phosphorus-sulfur stretching region in the infrared spectra of (– – – –) $C_{30}H_{24}AsPS$ and (———) $[Pd(C_{30}H_{24}AsPS)Br_2]$ in Nujol mulls.

observed in $[Pd(C_{30}H_{24}AsPS)_2](NO_3)_2$, indicating that the P=S groups are *trans* to each other (Table II). Two bands would be expected if the P=S groups were in a *cis* configuration. The available data do not permit an assignment of either the *cis* or *trans* arrangement of ligands in the $[Pd(C_{30}H_{24}AsP)_2](NO_3)_2$ complex. We have seen no evidence for a second compound in this synthesis.

When first isolated, the Pt(II) complexes of I are very insoluble in solvents such as dichloromethane, and they exhibit complicated infrared spectra in the 590–610-cm⁻¹ region (P=S stretching region.) If the compounds are dissolved in hot dimethylformamide and then precipitated carefully by adding absolute ethanol, crystalline yellow complexes are obtained. After recrystallization these yellow $[Pt(C_{30}H_{24}AsPS)X_2]$ complexes are quite soluble in dichloromethane and each exhibits one sharp P=S vibration. The original materials probably can be formulated as Magnus-type salts, *i.e.*, $[Pt(C_{30}H_{24}AsPS)_2][PtX_4]$, which undergo rearrangements to nonelectrolyte $[Pt(C_{30}H_{24}AsPS)X_2]$ complexes on heating in DMF. The complex infrared spectra may result from both *cis* and *trans* isomers in the cation of the Magnus salts or a mixture of only one isomer and some monomeric $[Pt(C_{30}H_{24}AsPS)X_2]$.

TABLE II

PHOSPHORUS–SULFUR STRETCHING FREQUENCY IN THE PHOSPHINE SULFIDE COMPLEXES

Compound[a]	$\nu_{P=S}$, cm⁻¹ [b]	Compound[a]	$\nu_{P=S}$, cm⁻¹ [b]
L	638 s	$[PdL_2](NO_3)_2$	593 vs
$PdLCl_2$	603 vs	$PtLCl_2$	609 vs
$PdLBr_2$	602 vs	$PtLBr_2$	602 vs
$PdLI_2$	603 vs		
$PdL(SCN)_2$	602 s	AuLCl	637 s
$PdL(SeCN)_2$	603 vs	$[CuL_2]ClO_4$	609 vs

[a] L corresponds to diphenyl(*o*-diphenylarsinophenyl)phosphine sulfide, $C_{30}H_{24}AsPS$. [b] s, strong; vs, very strong.

Thiocyanate and Selenocyanate Bonding.—Both electronic and steric factors from the other ligands present in complexes containing coordinated thiocyanate appear to provide a delicate balance as to whether the thiocyanate ion bonds *via* nitrogen or sulfur.[20–22] Burmeister and Basolo[21] observed that *trans*-$[Pd((C_6H_5)_3P)_2(NCS)_2]$ contained only N-bonded

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(20) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

(21) J. L. Burmeister and F. Basolo, *Inorg. Chem.*, **3**, 1587 (1964).

(22) M. F. Farona and A. Wojcicki, *ibid.*, **4**, 1402 (1965).

thiocyanate whereas both N- and S-bonded isomers were isolated for the analogous triphenylarsine complex; therefore, it was of interest to determine if SCN^- was N or S bonded in the square-planar palladium complexes of ligands I and II, where each SCN^- ion must, of necessity, be *trans* to a different donor atom.

The C≡N stretching frequency of $[Pd(C_{30}H_{24}AsPS)(SCN)_2]$ occurred as two sharp, closely spaced peaks, indicating sulfur-bonded *cis*-thiocyanate groups (Table III).[21,23] Unfortunately, intense ligand vibrations obscure the two other diagnostic SCN^- regions at 690–860 and 400–480 cm^{-1}.[23] However, confirmation of Pd–SCN bonding is provided by the electronic spectrum. The energy of the first electronic transition (Table IV) for the $[Pd(C_{30}H_{24}AsPS)X_2]$ complexes produces the following spectrochemical series: $Cl^- > Br^- > SCN^- > SeCN^- > I^-$. If the thiocyanate ion had been bonded through nitrogen, then the ligand field strength would have been greater than for chloride.[24]

TABLE III

INFRARED ABSORPTION OF SELECTED COMPOUNDS IN THE 2000–2200-Cm^{-1} REGION

Compound	$\nu_{C\equiv N}$, cm^{-1} [a]
$[Pd(C_{30}H_{24}AsPS)(SCN)_2]$	2110 s, vsp
	2119 m, vsp
$[Pd(C_{30}H_{24}AsPS)(SeCN)_2]$	2117 m
	2128 w, sp
$[Pd(C_{30}H_{24}AsP)_2][Pd(SCN)_4]$	2102 s, sp
(orange isomer)	
$[Pd(C_{30}H_{24}AsP)(SCN)(NCS)]$	2117 s, vsp
(yellow isomer)	2058 s, b
$[Pd(C_{30}H_{24}AsP)(SeCN)_2]$	2126 s vsp
	2120 s, vsp

[a] s, m, and w refer to strong, medium, and weak intensity, respectively; vsp, sp, and b refer to very sharp, sharp, and broad bands, respectively.

TABLE IV

ELECTRONIC ABSORPTION SPECTRA OF PALLADIUM(II) COMPLEXES

Complex[a]	E_{max}, cm^{-1} (ϵ) (CH_2Cl_2 solution)	E_{max},[b] cm^{-1} (Nujol mull)
$PdLCl_2$	26,000 (1630)	26,300 sh[c]
$PdLBr_2$	25,800 (2460)	25,600 sh
$PdL(SCN)_2$	22,700 (980)	22,000
$PdL(SeCN)_2$	21,100 (820)	20,950
$PdLI_2$	20,400 (3400)	20,000
	23,300 (~2000) sh	
$PdL'Cl_2$	28,400 (5200)	28,600 sh
$PdL'Br_2$	26,700 (5500)	27,000
	29,400 (~4060) sh	29,800 sh
$[PdL'_2][Pd(SCN)_4]$	... ...	20,000
(orange isomer)		25,000
		28,600 sh
$[PdL'(SCN)(NCS)]$	~25,000 sh	25,000 sh
(yellow isomer)	~30,000 sh	30,250 sh
$PdL(SeCN)_2$	23,500 (1140)	23,800 sh
$PdLI_2$	20,000 sh	20,800 sh
	23,200 (14,000)	23,800 sh
$[PdL'_2](NO_3)_2$	...	29,000

[a] L and L′ correspond to diphenyl(*o*-diphenylarsinophenyl)phosphine sulfide, $C_{30}H_{24}AsPS$, and diphenyl(*o*-diphenylarsinophenyl)phosphine, $C_{30}H_{24}AsP$, respectively. [b] Spectral samples prepared according to ref 13. [c] sh, shoulder on a stronger absorption band.

In contrast to the thiocyanate case discussed below, diphenyl(*o*-diphenylarsinophenyl)phosphine, II, forms only the selenium-bonded complex $[Pd(C_{30}H_{24}AsP)(SeCN)_2]$ with palladium selenocyanate. The infrared spectrum exhibits two sharp peaks at 2126 and 2120 cm^{-1}, indicative of the *cis*-Pd–SeCN linkage.[23] This is confirmed by the electronic spectrum, which places the selenocyanate ion at a comparable energy with that of iodide.

When II is mixed with an ethanolic solution of $Na_2Pd(SCN)_4$, an orange product, which is insoluble in a variety of solvents such as acetonitrile, chloroform, and dichloromethane, is precipitated immediately. The solubility properties of this compound differ markedly from the palladium halide complexes and suggest the possibility of a Magnus-type compound, *i.e.*, $[Pd(C_{30}H_{24}AsP)_2][Pd(SCN)_4]$. This formulation is supported by both the infrared spectrum and the electronic absorption spectrum (Table IV). The reflectance spectrum of the orange compound is a composite of the spectra of the $[Pd(C_{30}H_{24}AsP)_2]^{2+}$ and $[Pd(SCN)_4]^{2-}$ ions.[21] The infrared spectrum has a weak, sharp peak at 2128 cm^{-1} and an intense, rather broad absorption in the C≡N region at 2102 cm^{-1}, consistent with the $[Pd(SCN)_4]^{2-}$ ion (Figure 2). The insolubility of the orange compound in a variety of nonpolar solvents precludes a molecular weight determination, and it undergoes isomerization in polar solvents. The compound turns yellow in a melting point capillary at approximately 220°, and it finally melts at 253.5–254.5° to a red-orange liquid. Differential thermal analysis showed that the orange compound undergoes a strong exothermic rearrangement at 216 ± 1° and infrared spectra showed that the product is the yellow isomer described below.

Orange $[Pd(C_{30}H_{24}AsP)_2][Pd(SCN)_4]$ dissolves slowly in hot DMF to give a yellow solution, and a yellow compound of identical composition can be obtained by addition of ethanol. The yellow isomer is a nonconductor in acetonitrile and a monomer in chloroform (calcd mol wt for $[Pd(C_{30}H_{24}AsP(CNS)_2]$, 713; found, 716); it melts to a red-orange liquid at 253–253.5°. The infrared spectrum (Nujol mull) of this yellow isomer shows a strong, sharp absorption at 2117 cm^{-1}, consistent with S-bonded thiocyanate,[21,23] and also a strong, broader peak at 2058 cm^{-1}, indicative of N-bonded thiocyanate (Figure 2). The splitting is too large to be due to *cis*-SCN^- groups; also, it is not caused by the crystal lattice since a dichloromethane solution of the compound also exhibits two peaks at 2122 and 2085 cm^{-1}. We have shown that if both thiocyanate groups are N bonded, the λ_{max} and ϵ_{max} are greater than those of the corresponding palladium chloride complex.[16] The yellow isomer, on the other hand, has comparable λ_{max} and ϵ_{max} values with $[Pd(C_{30}H_{24}AsP)Br_2]$. Thus, both the infrared and elec-

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(23) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).

(24) C. Schäffer, "International Conference on Coordination Chemistry," The Chemical Society, London, 1959, p 153.

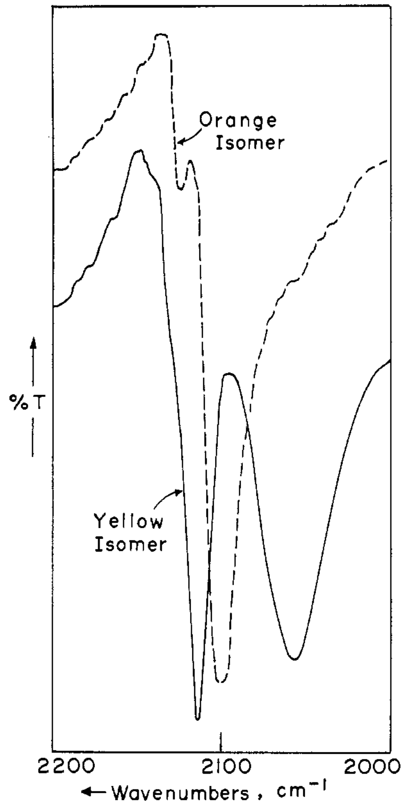

Figure 2.—The $C\equiv N$ region in the infrared spectra of the (———) yellow and (– – – –) orange palladium thiocyanate complexes of diphenyl(*o*-diphenylarsinophenyl)phosphine in Nujol mulls.

tronic spectra suggest that one thiocyanate ion is N bonded and one is S bonded in the yellow isomer, *i.e.*, $[Pd(C_{30}H_{24}AsP)(SCN)(NCS)]$.

The yellow isomer represents an unusual case among thiocyanate complexes because it is one of only two (or perhaps three) molecular complexes which contain both N- and S-bonded thiocyanate groups.[25] It is the only example where the type of thiocyanate bonding is controlled by use of a chelating ligand containing two different donor atoms. The compound can be prepared either by recrystallizing the orange compound from DMF–ethanol or by heating the solid at 220° for 45 min. The infrared spectra of the compounds which result from the two preparative routes are identical. We are currently studying palladium(II) thiocyanate complexes of other "mixed" donor atom bidentate ligands to determine which thiocyanate group is *trans* to phosphorus.

Summary.—These palladium(II), platinum(II), gold(I), and copper(I) complexes demonstrate that I functions as a chelating ligand involving coordination of the P=S group. "Class b" metals form stable complexes, whereas no complexes of "class a" metals were obtained. A comparison of the electronic absorption spectra of palladium(II) complexes of the phosphine sulfide, I, and phosphine, II, shows that the ligand field strength of II is greater than that of I.

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[25] After this study was completed, Raymond and Basolo [*Inorg. Chem.*, **5**, 1632 (1966)] reported a copper complex which contains both S- and N-bonded thiocyanate groups, and Bertini and Sabatini [*ibid.*, **5**, 1025 (1966)] suggest this possibility for a palladium complex.

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Five-Coordination. III. Trigonal-Bipyramidal Nickel(II) Complexes with a Phosphorus–Selenium Tetradentate Ligand[1-4]

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The new tetradentate ligand, tris(*o*-methylselenophenyl)phosphine, TSeP, IV, has been synthesized, and the resulting series of five-coordinate, trigonal-bipyramidal nickel(II) complexes has been characterized. The intensely blue complexes are diamagnetic and uni-univalent electrolytes, consistent with the formula $[Ni(TSeP)X]ClO_4$, when the fifth ligand is an anion, and di-univalent electrolytes when the fifth ligand is a neutral molecule. A comparison of the electronic absorption spectra of these complexes with those of similar trigonal-bipyramidal nickel(II) complexes containing sulfur, arsenic, or phosphorus atoms gives a spectrochemical series for the donor groups. A different order of the first spectral band intensity is obtained.

Introduction

One of the most interesting recent developments in the field of coordination chemistry has been the investigation of the unusual structures and the stereochemistries which occur among complexes of polydentate ligands. For example, several series of the previously unusual five-coordinate nickel(II) complexes have been obtained by use of polydentate ligands during the

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[2] Presented at the Anniversary Meeting of The Chemical Society (London), Oxford, England, March 1966.

[3] Part I of this series: G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, **3**, 1544 (1964).

[4] Part II: G. Dyer and D. W. Meek, *ibid.*, **4**, 1398 (1965).