Table IV. *E* and *C* Parameters[a]

Molecule	Acceptors E_A	C_A
p-t-$C_4H_9C_6H_4OH$	4.21	0.370
p-$CH_3C_6H_4OH$	4.20	0.379
C_6H_5OH	4.35	0.405
p-FC_6H_4OH	4.38	0.419
p-$Cl_6C_6H_4OH$	4.36	0.447
m-FC_6H_4OH	4.45	0.476
m-$CH_3C_6H_5OH$	4.50	0.493

Molecule	Donors E_B	C_B
$(C_2H_5)_2S$	0.380	7.40
$(C_2H_5)_2O$	1.02	3.08
$(CH_2)_4S$	0.375	7.96
$(CH_2)_4O$	0.973	4.36

[a] These *E* and *C* parameters were taken from a refined set of parameters soon to be published by the authors.

stants and infrared frequency shift have been reported for oxygen and nitrogen donors.[14]

In column 5 of Table III, the enthalpies predicted from eq 1 are listed. The *E* and *C* parameters reported in Table IV were used in eq 1 to calculate $-\Delta H$ and, within experimental error, the agreement between the last two columns is excellent.

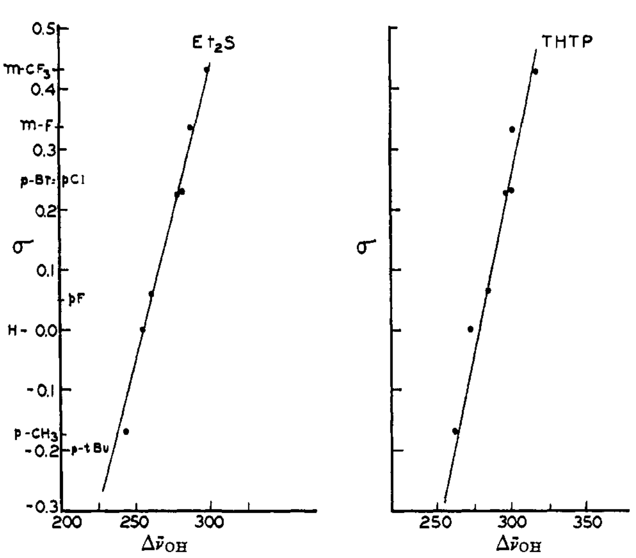


Figure 2. A plot of σ *vs.* $\Delta\bar{\nu}_{OH}$ (cm^{-1}) for substituted phenols reacting with diethyl sulfide and tetrahydrothiophene.

The new data are still consistent with the reversal[15] in donor strength toward iodine and phenol of analogous oxygen and sulfur donors. The C_BC_A product, which can be related to the "softness of interaction," dominates in the iodine interaction, and sulfur donors have a much larger C_B parameter than the oxygen donor. The E_BE_A product, which can be related to "hardness of interaction," is appreciable in the phenol interaction, and the parameters in Table IV indicate the oxygen donors are relatively much harder than analogous sulfur donors.

Acknowledgment. The authors acknowledge the generous support of the National Science Foundation through Grant No. GP5498 and the Paint Research Institute.

---

(14) C. Laurence and B. Bruno, *C. R. Acad. Sci.*, **264**, 1216 (1967).

(15) R. J. Niedzielski, R. S. Drago, and R. L. Middaugh, *J. Amer. Chem. Soc.*, **86**, 1694 (1964).

Mixed Thiocyanate Bonding in Palladium(II) Complexes of Bidentate Ligands[1,2]

Devon W. Meek, Philip E. Nicpon,[3] and Violet Imhof Meek

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received September 29, 1969*

Abstract: Several new [Pd(ligand)X_2] complexes have been prepared with bidentate ligands, most of which contain two different donor atoms. The spectrochemical position of the thiocyanate group in each [Pd(ligand)X_2] (X = Cl, Br, I, SCN) series and the integrated intensity of the infrared C≡N stretching frequency were measured to determine whether the thiocyanate ions are coordinated through the nitrogen or the sulfur atom. Stable *mixed* thiocyanate complexes of the type [Pd(ligand)(NCS)(SCN)], containing one Pd–SCN and one Pd–NCS linkage, were isolated with the bidentate ligands $(C_6H_5)_2P(o\text{-}C_6H_4As(C_6H_5)_2)$, $(C_6H_5)_2PCH_2CH_2N(CH_3)_2$, $(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2$, and $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. Bidentate ligands that contain two different donor atoms impose different electronic effects upon the thiocyanate ions that are *trans* to the two donors. The differentiation in the mode of thiocyanate bonding is discussed in terms of the steric and the *trans* electronic influences of the donor atoms.

Recent interest in ambidentate ligands—especially the thiocyanate ion, which can coordinate *via* the sulfur or the nitrogen atom, or both—probably results from two principal considerations. (1) Turco

---

(1) This research was supported financially by the National Science Foundation (Grants No. GP-5729 and GP-8365).

(2) Presented at the Great Lakes Regional Meeting of the American Chemical Society, Chicago, June 1966; this paper is based on part of the dissertation submitted by P. Nicpon to the Graduate School of The Ohio State University, Dec 1966, in partial fulfillment of the requirements for the Ph.D. degree.

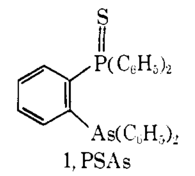
(3) Public Health Service Predoctoral Fellow (No. 5-F1-GM-25), 1965–1966.

and Pecile[4] were the first of several investigators[4-9] to point out that the presence of other ligands in a complex apparently affects the mode of thiocyanate coordination. (2) The ambidentate nature of SCN^- may be interpreted in terms of sulfur being a "soft" base and nitrogen being a "hard" base.[10,11] When the thiocyanate ion is the only ligand present in a complex, its mode of bonding generally follows the hard (M-NCS) or soft (M-SCN) pattern throughout the periodic table. However, the nature of other ligands in a complex may determine whether the metal functions as a hard ion, and forms isothiocyanato complexes, or as a soft ion, and forms thiocyanato complexes. For example, the pentaamminecobalt(III) ion forms the Co-NCS linkage,[4,12] whereas the pentacyanocobaltate(III) ion exhibits soft behavior in forming the Co-SCN bond.[13]

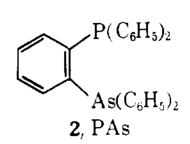
Steric factors in bulky ligands also may alter the nature of thiocyanate coordination.[14] For example, diethylenetriamine, $NH_2CH_2CH_2NHCH_2CH_2NH_2$, gives the stable S-bonded complex $[Pd(dien)SCN]^+$, whereas the N-bonded form is more stable with N,N,N′,N′-tetraethyldiethylenetriamine, $(C_2H_5)_2NCH_2CH_2NHCH_2CH_2N(C_2H_5)_2$, Et_4dien.[6,15] Both kinetic[16] and thermodynamic[17] evidence strongly support the steric effect in the Et_4dien complexes.

Burmeister and Basolo[5] used Turco and Pecile's[4] π-bonding explanation to synthesize the first thiocyanate linkage isomers. The S-bonded complex $[Pd(Ph_3As)_2(SCN)_2]$ is isolated at low temperature, but it is isomerized to the N-bonded species $[Pd(Ph_3As)_2(NCS)_2]$ when the solid is heated or dissolved.[5] These results were explained on the basis that triphenylarsine and the sulfur atom of SCN^- compete for π-bonding orbitals on palladium(II). Arsenic was considered more effective as a π-bonding ligand; consequently N-bonding of SCN^- was favored slightly.

In 1965 we noticed that both thiocyanate groups in the palladium complex of diphenyl(*o*-diphenylarsinophenyl)phosphine sulfide, **1**, were coordinated *via* sulfur; this result was unexpected on the basis of π-bonding considerations.[18] Moreover, our palladium thiocyanate complex of the parent phosphine-arsine, **2**, was only the second example known at that time that contained both N-bonded *and* S-bonded nonbridging thiocyanato groups.[19]



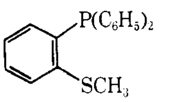
1, PSAs



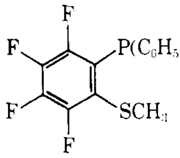
2, PAs

One major difference between the complexes of ligands **1** and **2** and those of triphenylphosphine and triphenylarsine is that the chelating ligands force the SCN^- ions to occupy *cis*-planar coordination sites, whereas the palladium complexes of the monodentate ligands contain *trans* SCN^- groups. In a complex of ligand **1**, the thiocyanate ions must, as a result of the planar geometry of palladium(II) complexes, *compete directly* with the P=S and As donors along the d_{xz} and d_{yz} orbitals.

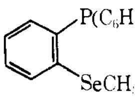
Our results with ligands **1** and **2** indicated that both the diphenylarsino and the diphenylphosphine sulfide groups dictate S bonding of a *trans* SCN^-, whereas the diphenylphosphino group apparently causes N bonding. Thus, additional studies were undertaken with chelating bidentate ligands, emphasizing ligands that contain two different donor atoms. Ligands such as



3, SP



4, FSP



5, SeP

$(C_6H_5)_2PCH_2CH_2N(CH_3)_2$
6, PC_2N

$(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2$
7, PC_3N

would be expected to exert different electronic influences on the thiocyanate groups that are *trans* to different types of ligand atoms, and they should permit a direct evaluation of the relative effectiveness of a given donor at promoting either Pd-NCS or Pd-SCN bonding.

This paper reports the characterization of several new series of palladium(II) complexes of bidentate ligands; in several instances these molecular complexes contain *both N- and S-bonded*, nonbridging thiocyanate groups.

Experimental Section

Syntheses of the Ligands. The preparations of ligands **1**, **2**, **3**, **4**, and **5** have been described previously.[18,20,21]

Synthesis of Diphenyl(2-dimethylaminoethyl)phosphine. $(C_6H_5)_2PCH_2CH_2N(CH_3)_2$, **6**. Lithium diphenylphosphide, $LiP(C_6H_5)_2$ (0.20 mol), was prepared according to Chatt and Hart's method[22] in 200 ml of purified tetrahydrofuran, and *t*-butyl chloride (19.1 g, 0.207 mol) was added to destroy the phenyllithium that was formed in the reaction.[23] The lithium diphenylphosphide solution was cooled to 0° and a solution (22.3 g, 0.207 mol, in 50 ml of tetrahydrofuran) of 2-chloroethyldimethylamine, $ClCH_2CH_2N(CH_3)_2$,[24]

---

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

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

(6) F. Basolo, W. J. Baddley, and J. L. Burmeister, *ibid.*, **3**, 1202 (1964).

(7) A. Sabatini and I. Bertini, *ibid.*, **4**, 959, 1665 (1965).

(8) H. H. Schmidtke, *J. Amer. Chem. Soc.*, **87**, 2522 (1965).

(9) H. H. Schmidtke, *Z. Phys. Chem.* (*Frankfurt am Main*), **45**, 305 (1965).

(10) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

(11) R. G. Pearson, *Science*, **151**, 172 (1966).

(12) M. M. Chamberlain and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 6412 (1959).

(13) J. L. Burmeister, *Inorg. Chem.*, **3**, 919 (1964).

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

(15) F. Basolo, W. H. Baddley, and K. Weidenbaum, *J. Amer. Chem. Soc.*, **88**, 1577 (1966).

(16) W. H. Baddley and F. Basolo, *ibid.*, **88**, 2994 (1966).

(17) D. J. Hewkin and A. J. Poe, *J. Chem. Soc. A*, 1884 (1967).

(18) (a) P. Nicpon, Ph.D. Dissertation, The Ohio State University, 1966; (b) P. Nicpon and D. W. Meek, *Inorg. Chem.*, **6**, 145 (1967).

(19) I. Bertini and A. Sabatini [*ibid.*, **5**, 1025 (1966)] reported solid-state infrared data in support of the mixed thiocyanate complex [Pd(4,4′-dimethylbipy)(NCS)(SCN)]. G. C. Kulasingam and W. R. McWhinnie [*Chem. Ind.* (*London*), 2200 (1966)] presented more convincing evidence for a mixed complex in [Cu(tri(2-pyridyl)amine)(NCS)(SCN)]. The copper thiocyanate complex of $N(CH_2CH_2NH_2)_3$, tren, which was originally reported as [Cu(tren)(NCS)(SCN)] [K. N. Raymond and F. Basolo, *Inorg. Chem.*, **5**, 1632 (1966)], has subsequently been shown by X-ray crystallography to be the five-coordinate [Cu(tren)(NCS)]SCN [P. C. Jain and E. C. Lingafelter, *J. Amer. Chem. Soc.*, **89**, 724, 6131 (1967)].

(20) G. Dyer and D. W. Meek, *ibid.*, **89**, 3983 (1967).

(21) P. G. Eller and D. W. Meek, *J. Organometal. Chem.*, **22**, 631 (1970).

(22) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1385 (1960).

(23) A. M. Aguiar, H. J. Greenberg, and K. E. Rubenstein, *J. Org. Chem.*, **28**, 2091 (1963).

Table I. Characterization Data for the Palladium(II) Complexes of the Bidentate Ligands

Compound	Color	Yield, %	Recrystallization solvents	Mol wt		Analyses, %: C		H		Halide or N[a]		Other	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Pd(C_{30}H_{24}AsP)Cl_2]$	Light yellow	24	DMF			53.96	53.88	3.62	3.80	10.62	10.55		
$[Pd(C_{30}H_{24}AsP)Br_2]$	Lemon yellow	43	CH_2Cl_2–*n*-hexane			47.62	47.82	3.20	3.48	21.12	20.84		
$[Pd(C_{30}H_{24}AsP)I_2]$	Light orange	75	CH_2Cl_2–*n*-hexane			42.36	42.55	2.84	3.03	29.84	29.56		
$[Pd(C_{30}H_{24}AsP)(SeCN)_2]$	Orange-red	79	CH_2Cl_2–*n*-hexane			45.82	45.65	2.88	3.00	3.34	3.20		
$[Pd(C_{26}H_{24}As_2)Cl_2]$	Light yellow	68	CH_2Cl_2–*n*-hexane			47.05	46.96	3.64	3.54	10.69	10.91		
$[Pd(C_{26}H_{24}As_2)Br_2]$	Yellow	40	CH_2Cl_2–*n*-hexane			41.50	41.63	3.21	3.17	21.24	20.96		
$[Pd(C_{26}H_{24}As_2)I_2]$	Orange-red	57	CH_2Cl_2–*n*-hexane	847	853	36.89	37.04	2.86	2.92	29.98	30.12		
$[Pd(C_{26}H_{24}As_2)(CNS)_2]^b$	Yellow	41	CH_2Cl_2–*n*-hexane			47.44	47.63	3.41	3.54	3.95	4.01	9.05	9.08 (S)
$[Pd(C_{26}H_{24}As_2)(SeCN)_2]$	Yellow-orange	42	CH_2Cl_2–*n*-hexane			41.90	42.00	3.01	3.14	3.49	3.22	19.67	19.87 (Se)
$[Pd(C_{26}H_{24}P_2)Cl_2]$	Light yellow	17	CH_2Cl_2–*n*-hexane			54.24	54.03	4.02	4.34	12.32	12.35		
$[Pd(C_{26}H_{24}P_2)Br_2]$	Yellow	72	CH_2Cl_2–*n*-hexane	665	676	46.98	47.69	3.64	3.86	24.05	22.94		
$[Pd(C_{26}H_{24}P_2)I_2]$	Deep yellow	81	CH_2Cl_2–*n*-hexane	759	776	41.16	40.92	3.19	3.37	33.46	33.86		
$[Pd(C_{26}H_{24}P_2)(NCS)(SCN)]^{b,c}$	Light yellow	59	CH_2Cl_2–*n*-hexane			54.15	54.01	3.89	3.85	4.51	4.32	10.33	10.58 (S)
$[Pd(C_{26}H_{24}P_2)_2][Pd(SCN)_4]$	Light orange	73				54.15	53.92	3.90	4.06	4.51	4.29	10.33	10.40 (S)
$[Pd(C_{26}H_{24}P_2)_2][Pd(SeCN)_4]$	Orange	70				47.05	47.24	3.38	3.50	3.92	3.79	22.09	22.30 (Se)
$[Pd(C_{16}H_{20}NP)Br_2]$	Yellow-brown	36		524	520	36.70	36.52	3.85	4.01	30.53	30.28		
$[Pd(C_{16}H_{20}NP)I_2]$	Red-brown	50				31.12	31.06	3.26	3.10	41.10	41.27		
$[Pd(C_{16}H_{20}NP)(NCS)(SCN)]$	Yellow	45	CH_2Cl_2–*n*-hexane	480	445	45.05	45.26	4.20	4.22	8.76	8.66	13.36	13.59 (S)
$[Pd(C_{19}H_{13}F_4PS)(SCN)_2]$	Yellow		CH_2Cl_2–C_2H_5OH			41.82	41.65	2.08	2.37	4.65	4.57	5.14	4.79 (P)
$[Pd(C_{19}H_{17}PS)(SCN)_2]$	Yellow	85	Acetone	531	554	47.52	47.29	3.22	3.15	5.28	5.04	18.12	18.20 (S)
$[Pd(C_{19}H_{17}PSe)(SCN)_2]$	Yellow	80	Acetone	578	598	43.66	43.25	2.97	3.12	4.85	5.13		

[a] Nitrogen analysis is reported for the thiocyanate and selenocyanate complexes; otherwise, the figures in the column correspond to the appropriate halogen. [b] The thiocyanate ion is written as CNS whenever a specific type of metal–thiocyanate coordination is not represented; $[ML(SCN)_2]$ is written for M–SCN linkages, whereas $[ML(NCS)_2]$ implies M–NCS bonding. [c] This compound was also prepared in a homogeneous reaction from $[Pd(C_{26}H_{24}P_2)(NO_3)_2]$ and NaSCN in hot DMF and recrystallized from methanol. The latter compound gave the following analytical data. Found: C, 53.94; H, 3.83; S, 10.42; mol wt, 545.

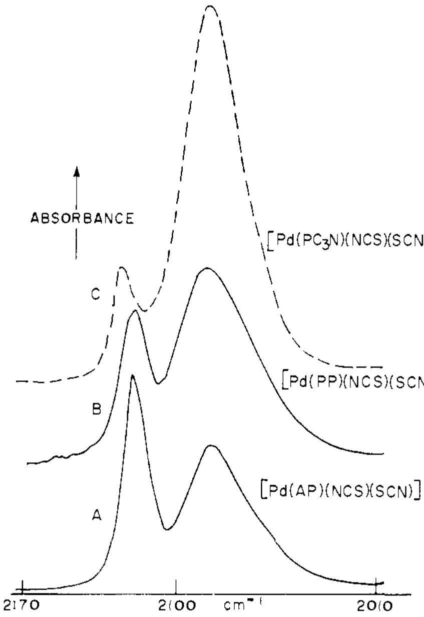


Figure 1. The expanded infrared spectra (dichloromethane solutions) used for integrated absorption calculations on (A) [Pd(AP)(NCS)(SCN)], (B) [Pd(PP)(NCS)(SCN)], and (C) [Pd(PC$_3$N)(NCS)(SCN)].[34]

was added over a period of 1 hr while stirring vigorously. The resulting mixture was refluxed 1 hr, cooled to room temperature, and hydrolyzed with 25 ml of methanol and then 150 ml of distilled water. The two liquid layers were separated, and the aqueous layer was washed with 100 ml of diethyl ether. The organic layers were combined and dried over sodium sulfate. After decanting the liquid, the solvent was removed by distillation under nitrogen, and then the light yellow material was vacuum distilled: bp, 179–181° (<1 Torr); yield, 13.0 g (25%).

Diphenyl(3-dimethylaminopropyl)phosphine. $(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2$, **7**. This compound was prepared from the hydrochloride of 3-chloropropyldimethylamine (Michigan Chemical Corp.) by the procedure that gave the above aminophosphine.

General Synthetic Procedure for the Complexes. A general preparation is given below for each series of complexes that was isolated with each ligand. For synthesis of the bromide, iodide, and pseudohalide derivatives, the $[PdX_4]^{2-}$ species were prepared *in situ* by mixing an ethanolic solution of sodium tetrachloropalladate(II), Na_2PdCl_4, with a tenfold excess of the appropriate lithium or sodium salt, except where potassium selenocyanate was used in a 4:1 mole ratio.[25] The recrystallization solvent for each compound is given in Table I.

Diphenyl(*o*-diphenylarsinophenyl)phosphine Complexes, $[Pd(C_{30}H_{24}AsP)X_2]$ (where X = Cl, Br, I, SCN, SeCN). A warm solution of ligand **2**, $C_{30}H_{24}AsP$ (1.96 g, 4 mmol, in 90 ml of absolute ethanol), was added to a magnetically stirred, filtered solution of $[PdX_4]^{2-}$ (4 mmol) in 100 ml of ethanol. A precipitate formed immediately, but the reaction mixture was stirred for 1 hr to promote homogeneity. The compound was collected on a sintered-glass filter funnel, washed with ethanol and ether, and then recrystallized.

1,2-Bis(diphenylarsino)ethane Complexes, $[Pd(C_{26}H_{24}As_2)X_2]$ (where X = Cl, Br, I, SCN, SeCN). To a filtered, stirred solution of $[PdX_4]^{2-}$ (2 mmol) in 75 ml of absolute ethanol was added a solution of 1,2-bis(diphenylarsino)ethane (0.96 g, 2 mmol, in 15 ml) in dichloromethane. The reaction mixture was magnetically stirred overnight and the precipitate was collected on a filter, washed with ethanol and ether, and then recrystallized.

1,2-Bis(diphenylphosphino)ethane Complexes, $[Pd(C_{26}H_{24}P_2)X_2]$ (where X = Cl, Br, I, SCN). The diphosphine complexes were prepared by the same general method as the above diarsine complexes.

$[Pd(C_{26}H_{24}P_2)_2][Pd(SCN)_4]$. This orange complex was isolated by carrying out the reaction with both the ethanolic solution of $[Pd(SCN)_4]^{2-}$ and the dichloromethane solution of the ligand cooled to 0°. After stirring the reaction mixture for 15 min at 0°, the product was isolated by filtration, washed with distilled water, ethanol, and ether, and then dried over P_4O_{10} for 48 hr *in vacuo*.

$[Pd(C_{26}H_{24}P_2)_2][Pd(SeCN)_4]$. The molecular complex $[Pd(C_{26}H_{24}P_2)(SeCN)_2]$, analogous to the halide and thiocyanate complexes above, was not obtained in a pure state by the general procedure. However, the orange Magnus salt, $[Pd(C_{26}H_{24}P_2)_2][Pd(SeCN)_4]$, was obtained by mixing an ethanolic solution of $[Pd(SeCN)_4]^{2-}$ with the ligand in boiling 1-butanol. The precipitate was collected on a filter, washed with distilled water, ethanol, and ether, and subsequently dried for 48 hr over P_4O_{10} *in vacuo*.

Diphenyl(2-dimethylaminoethyl)phosphine Complexes, $[Pd(C_{16}H_{20}NP)X_2]$ (where X = Cl, Br, I, SCN). The appropriate $[PdX_4]^{2-}$ solution (3 mmol in 100 ml of absolute ethanol) was treated with 0.67 ml (3 mmol) of ligand 6 dissolved in 10 ml of ethanol. The reaction mixture was stirred 1 hr and then the precipitate was collected, washed with distilled water, ethanol, and ether, and then recrystallized.

Dithiocyanato[diphenyl(*o*-methylthiophenyl)phosphine]palladium(II), $[Pd(C_{19}H_{17}PS)(SCN)_2]$. Ligand **3** (0.62 g, 2 mmol) was dissolved in hot 1-butanol and the resulting solution was mixed with a solution of Li_2PdCl_4[26] (2 mmol) in 1-butanol (10 ml). The resulting yellow powder was recrystallized from hot acetone and gave bright yellow needles.[27]

Dithiocyanato[diphenyl(*o*-methylselenophenyl)phosphine]palladium(II), $[Pd(C_{19}H_{17}PSe)(SCN)_2]$. This compound was prepared by the same procedure as the above complex of ligand **3** and recrystallized from hot acetone.[27]

Dithiocyanato[diphenyl(*o*-methylthio)tetrafluorophenyl)phosphine]palladium(II), $[Pd(C_{19}H_{13}F_4PS)(SCN)_2]$. To a warm solution of 0.295 g (1 mmol) of sodium tetrachloropalladate(II) in 20 ml of butanol was added a solution of 0.380 g (1 mmol) of ligand **4** in 5 ml of dichloromethane. The yellow precipitate, which formed on mixing the solutions, was recrystallized from a dichloromethane–ethanol mixture.[28]

Analyses. The microanalyses and molecular weight determinations were performed by Galbraith Laboratories, Knoxville, Tenn.

Conductivity and Electronic Spectral Measurements. These were obtained as described previously.[18,20]

Infrared Spectra. Routine characterization infrared spectra from 4000 to 400 cm^{-1} were obtained on a Perkin-Elmer Model 337 grating spectrophotometer with the samples mounted as potassium bromide pellets or as Nujol mulls between crystalline potassium bromide disks. The polystyrene spectrum was used for calibration. In order to aid in the assignment of the C–S stretching frequency and the NCS deformation frequency in the thiocyanate complexes, all of the organic ligand absorptions were determined from the spectra of the corresponding ligands and of the palladium halide complexes. Accurate peak positions and integrated absorptions of the C≡N bands for the thiocyanate complexes were obtained on a Beckman IR-9 spectrophotometer;[29] the peak maxima, which were read directly from the optical dial (and checked with the recorded spectrum), are accurate to ±1 cm^{-1} in the 400–900-cm^{-1} region and ±2 cm^{-1} in the 2100-cm^{-1} region. The Beckman IR-9 instrument was calibrated periodically with water and ammonia vapor.

For the integrated absorption measurements, spectroquality dichloromethane solutions of concentration $(0.9\text{–}6) \times 10^{-2}$ *M* were used whenever possible. In the cases of insufficient solubility in dichloromethane, spectroquality acetone or nitromethane was used. The scale on the frequency axis was expanded so that 10 in.

---

[24] The amine was isolated from the commercially available hydrochloride, $ClCH_2CH_2N(CH_3)_2 \cdot HCl$, using the procedure recommended in the Michigan Chemical Corp. brochure. *Caution!* The free amine is a type of nitrogen mustard and must be handled carefully in an efficient hood.

[25] Excess selenocyanate was avoided in the reactions with phosphine ligands because of the tendency for a chemical reaction between phosphines and the selenocyanate ion to produce phosphine selenides: P. E. Nicpon and D. W. Meek, *Inorg. Chem.*, **5**, 1297 (1966).

[26] A stable 1-butanol solution of Li_2PdCl_4 was prepared conveniently by dissolving $PdCl_2$ (1.77 g, 0.01 mol) and lithium chloride (0.95 g, 0.02 mol) in 50 ml of hot 1-butanol and then filtering the solution. No observable decomposition to palladium metal occurred when the solution was boiled for a few minutes, or when it was kept at room temperature for several months.

[27] The authors thank Dr. G. Dyer for preparing this compound.

[28] The authors thank P. G. Eller for the preparation and the data on this compound.

[29] The infrared spectrophotometer was purchased with an NSF instrument grant (No. GP-1719).

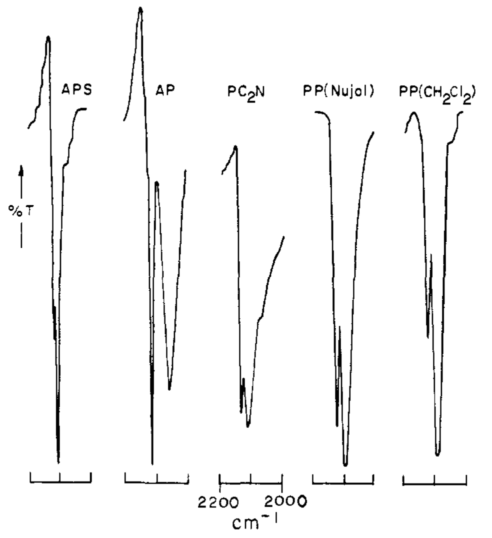


Figure 2. The C≡N stretching (2000–2200 cm^{-1}) region in the infrared spectra of palladium thiocyanate complexes of selected bidentate ligands. Note the relative half-band widths, which are usually in the ranges 12–18 and 30–40 cm^{-1} for S- and N-bonded thiocyanates, respectively. The abbreviations APS, AP, PC$_2$N, and PP correspond to the ligands $(C_6H_5)_2As(o\text{-}C_6H_4P(S)(C_6H_5)_2)$, **1**; $(C_6H_5)_2As(o\text{-}C_6H_4P(C_6H_5)_2)$, **2**; $(C_6H_5)_2PCH_2CH_2N(CH_3)_2$, **6**; and $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, respectively.

of chart paper corresponded to 200 cm^{-1}; the spectra were obtained in the absorption mode and were scanned at 8 cm^{-1}/min with the noise level adjusted to less than 2%; the programmed slit width was set at 0.5 mm at 2100 cm^{-1} for a resolution of 2 cm^{-1}; and the spectra were recorded using sealed, matched sets of potassium bromide cells of 0.205-, 0.504-, and 0.981-mm path length with a compensating cell containing pure solvent in the reference beam.

The Ramsay method[30] was used to calculate the C≡N integrated absorptions, since the band shape for both N- and S-bonded thiocyanate can be described by Lorenz functions, *i.e.*

$$A = K \ln (I_0/I_{\max})\Delta\nu_{1/2}{}^a/bc$$

where A is the integrated absorption, b is the cell thickness, c is the concentration of the solution, $\ln (I_0/I_{\max})$ is the apparent peak intensity, $\Delta\nu_{1/2}{}^a$ is the apparent half-band width at peak half-height, and K is the Ramsay constant (1.57 in this study). Probable errors in the integrated absorption values are about 2%. The expanded C≡N portion of the infrared spectra of [Pd(PP)(SCN)(NCS)], [Pd(ligand **2**)(NCS)(SCN)], and [Pd(PC$_3$N)(NCS)(SCN)] are given in Figure 1.

Results

The palladium thiocyanate complex of diphenyl(2-dimethylaminoethyl)phosphine, **6**, $C_{16}H_{20}NP$, is a non-electrolyte in both acetone [Λ_M = 1.2 cm^2/(ohm mol)] and DMF, and it is a monomer in DMF (calcd value, 480; found, 445). The infrared spectrum (Figure 2) (Nujol mull) of the solid displays a strong, sharp peak at 2126 cm^{-1} and a second, relatively broader peak at 2108 cm^{-1}, indicating the presence of two different types of coordinated thiocyanate ions. In dichloromethane solution the complex shows two distinct peaks at 2127 and 2087 cm^{-1}. From a comparison with the infrared spectrum of the palladium bromide complex, the weak absorption at 816 cm^{-1} in the spectrum of the thiocyanate complex is assigned to the C–S stretching frequency of an N-bonded thiocyanate (Figure 3). Intense absorptions of the organic ligand preclude location of the C–S stretching frequency of the S-bonded thiocyanate. However, the integrated absorption values of the two C≡N bands (Table II) confirm that one thiocyanate group is S-bonded and the other is N-bonded.[31,32] The intermediate position of this thiocyanate complex in the spectrochemical series (*i.e.*, Cl$^-$ > CNS$^-$ > Br$^-$ > I$^-$) also serves to confirm the [Pd($C_{16}H_{20}NP$)(SCN)(NCS)] formulation (Table III).[33]

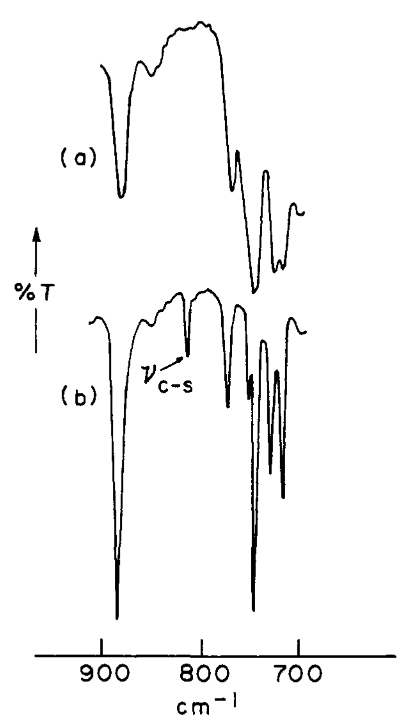


Figure 3. The 700–900-cm^{-1} region of the infrared spectra (Nujol mulls) of (a) [Pd(PC$_2$N)Br$_2$] and (b) [Pd(PC$_2$N)(NCS)(SCN)]; PC$_2$N is $(C_6H_5)_2PCH_2CH_2N(CH_3)_2$.

The diphenyl(3-dimethylaminopropyl)phosphine complex [Pd(PN)(SCN)(NCS)] is a non-electrolyte and a monomer in nitromethane [Λ_M = 4.2 cm^2/(ohm mol)]. The infrared spectrum of the solid (Nujol mull) has a very sharp peak at 2120 cm^{-1} and a relatively broader peak at ~2080 cm^{-1}, indicative of S- and N-bonded thiocyanate groups, respectively. The mixed mode of thiocyanate coordination is present in both the solid state and in solution. The evidence is: (1) the intermediate position of the thiocyanate complex in the ligand field spectrochemical series (*i.e.*, Cl$^-$ ≅ NCS$^-$ > Br > I); (2) the integrated absorption values, A, of the two infrared C≡N bands [*i.e.*, the spectrum of a dichloromethane solution of the compound shows a sharp peak at 2125 cm^{-1} ($\nu_{1/2}$ = 12 cm^{-1}, A = 1.50 × 10^4 cm^{-2} M^{-1}) and a broader peak at 2087 cm^{-1} ($\nu_{1/2}$ = 32 cm^{-1}, A = 11.5 × 10^4 cm^{-2} M^{-1})]; and (3) the three-dimensional X-ray structure of the crystalline complex.[34]

The diarsine ligand, $(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$, forms the S-bonded thiocyanate complex, [Pd($C_{26}H_{24}$-

---

(30) D. A. Ramsay, *J. Amer. Chem. Soc.*, **74**, 72 (1952).

(31) C. Pecile, *Inorg. Chem.*, **5**, 210 (1966).

(32) J. L. Burmeister, *Coord. Chem. Rev.*, **1**, 205 (1966), and references contained therein.

(33) Throughout this paper the thiocyanate ion is written as CNS whenever the specific type of bonding is unknown or is not to be represented; a formula written as [ML(SCN)$_2$] implies M–SCN linkages, whereas [ML(NCS)$_2$] implies M–NCS bonding.

(34) G. R. Clark, G. J. Palenik, and D. W. Meek, *J. Amer. Chem. Soc.*, **92**, 1077 (1970).

Table II. Infrared Spectral Data in the ν(C≡N) Region of the Palladium(II) Thiocyanate and Selenocyanate Complexes[a]

Compound[b]	ν(C≡N), cm^{-1} Nujol mull	Soln[c]	$\nu_{1/2}$, cm^{-1}	A/YCN × 10^{-4} cm^{-2} M^{-1}
[Pd(AsAs)(SeCN)$_2$]	2126	2123	12.6	1.00[f]
	2120			
[Pd(AsP)(SeCN)$_2$]	2122	2124	11.3	0.91[f]
[Pd(AsPS)(SeCN)$_2$]	2117	2122	12.8	0.98[f]
[Pd(AsPS)(SCN)$_2$]	2119	2116	15.2	1.63[g]
	2110			
[Pd(SeP)(SCN)$_2$]	2120	2121	21	1.63[g]
	2110	2111		
[Pd(FSP)(SCN)$_2$]	2123	2124	13	2.70[g]
	2110	2113	15	1.86[g]
[Pd(SP)(SCN)$_2$]	2122	2122	21	1.62[g]
	2111	2112		
[Pd(AsP)(SCN)(NCS)]	2117	2118	17.2	4.2[g]
	2985	2085	53.6	8.2[g]
[Pd(PC$_2$N)(SCN)(NCS)]	2126	2126	16	1.90[g]
	2108	2085	31	11.71[g]
[Pd(PC$_2$N)(SCN)(NCS)][d]	2126	2125	14	1.76[g]
	2108	2089	24	9.68[g]
[Pd(PP)(SCN)(NCS)]	2118	2121	14	2.5[g]
	2095	2086	41	10.7[g]
[Pd(PP)(SCN)(NCS)][d]	2118	2121	16	2.96[g]
	2095	2091	30	9.26[g]
[Pd(PP)(SCN)(NCS)][e]	2119	2123	16	3.28[g]
	2093	2090	35	10.15[g]
[Pd(PP)(SCN)(NCS)][d,e]	2119	2122	14	3.09[g]
	2093	2093	29	9.51[g]
[Pd(AsAs)(SCN)$_2$]	2116			
	2112			
[Pd(AsAs)(SCN)(NCS)]		2119	15	3.7[g]
		2086	33	11.5[g]

[a] The spectral parameters are defined in the Experimental Section. [b] The abbreviations for ligands are the coordinating atoms of the bidentate ligands listed in Table I and pictured in the introduction. [c] The solvent is dichloromethane unless specified otherwise. [d] The solvent is nitromethane. [e] This compound was prepared from [Pd(PP)(NO$_3$)$_2$] and NaSCN in hot DMF. [f] Y = Se. [g] Y = S.

Table III. Electronic Spectral Data for the [Pd($C_{16}H_{20}NP$)X$_2$], PC$_2$N, Complexes

X	Band maxima, cm^{-1} Solid[a]	CH$_2$Cl$_2$ soln (ϵ)[b,c]
Cl	20,800	20,800 sh (171)[d]
	28,600	28,600 (1965)
(NCS)(SCN)	25,000	24,400 sh (615)
	29,400	29,600 (5280)
Br	18,900	19,600 sh (328)
	23,600	
	27,800	27,800 (2740)
I	21,800	22,000 (2660)

[a] Transmission spectrum of a Nujol mull of the solid compound. [b] Molar extinction coefficient given in parentheses. [c] The lowest energy maximum for each complex is assigned to the "d–d" transition, and it is used for assignment of the spectrochemical series. [d] ϵ value is calculated from the absorption of a shoulder on a stronger peak; it has a higher value than would be observed if the band were resolved well enough to give a definite maximun.

Table IV. Electronic Spectral Data for the [Pd($C_{26}H_{24}As_2$)X$_2$] Complexes

X	Band maxima, cm^{-1} Solid[a]	CH$_2$Cl$_2$ soln (ϵ)[b]
Cl	27,000	27,200 (4450)
Br	25,600	25,800 (4920)
SCN	24,400	25,000 (1870)
SeCN	22,200	23,100 (1180)
	25,300	
I	19,200 sh	19,200 (1045)
	22,700	22,700 (5850)

[a] Transmission spectrum of a Nujol mull of the solid compound. [b] Molar extinction coefficient given in parentheses.

As$_2$)(SCN)$_2$], and the Se-bonded selenocyanate, [Pd($C_{26}H_{24}As_2$)(SeCN)$_2$] (Table II). Both compounds are nonelectrolytes in acetone (Λ_M = 1.6 and 0.8 cm^2/(ohm mol), respectively) and monomeric in chloroform. The lowest energy electronic transitions in the diarsine complexes (Table IV) produce the following spectrochemical series: Cl$^-$ > Br$^-$ > SCN$^-$ > SeCN$^-$ > I$^-$.

The infrared spectra (Nujol mull) of the solid thiocyanate and selenocyanate complexes show sharp absorptions above 2100 cm^{-1}, characteristic of S and Se bonding. Each infrared spectrum exhibits two closely spaced peaks (Table II); the splitting is attributed to the *cis* arrangement of the Pd–SCN groups. On the basis of the infrared spectra, the S-bonded species, [Pd($C_{26}H_{24}As_2$)(SCN)$_2$], is the only product obtained in the solid state from several different synthetic procedures. For example, one obtains the same product by mixing solutions of [Pd(SCN)$_4$]$^{2-}$ and the diarsine ligand at ~100° and then cooling the resulting solution rapidly to 0° as by performing the synthesis at room temperature. Also, an identical infrared spectrum of the solid is obtained when a sample of [Pd($C_{26}H_{24}As_2$)(SCN)$_2$] is dissolved in hot dimethylformamide (>100°) and recrystallized from a DMF–ethanol mixture. However, the integrated absorption data (Table II) indicate clearly that some [Pd($C_{26}H_{24}As_2$)(SCN)$_2$] isomerizes in dichloromethane solution so that both N- and S-bonded thiocyanate groups are present in solution. We cannot determine if the predominant species in dichloromethane is [Pd(diarsine)(SCN)(NCS)] or a mixture of [Pd(diarsine)(SCN)$_2$] and [Pd(diarsine)(NCS)$_2$]. On evaporation of the dichloromethane, however, only the S-bonded complex [Pd($C_{26}H_{24}As_2$)(SCN)$_2$] is obtained as a solid.

When a dichloromethane solution of 1,2-bis(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, is mixed with an ethanol solution of [Pd(SCN)$_4$]$^{2-}$, the orange Magnus salt [Pd($C_{26}H_{24}P_2$)$_2$][Pd(SCN)$_4$] precipitates immediately. Both the infrared and the electronic spectra of this orange compound are very similar to those of [Pd(SCN)$_4$]$^{2-}$.[5,18] Light yellow crystals of the same empirical formula are obtained when the Magnus salt is recrystallized from dimethylformamide. The latter compound is a nonconductor in acetone [Λ_M = 1.8 cm^2/(ohm mol)] and it is a monomer in chloroform (Table I). The spectrochemical series that is derived from the electronic spectra of the [Pd($C_{26}H_{24}P_2$)X$_2$] complexes is: Cl$^-$ ≈ CNS$^-$ > Br$^-$ > I$^-$ (Table V). The same monomeric complex [Pd($C_{26}H_{24}P_2$)(CNS)$_2$] was also prepared directly by mixing sodium thiocyanate with [Pd($C_{26}H_{24}P_2$)(NO$_3$)$_2$][35] in warm (~60°) dimethylformamide, DMF. The resulting DMF solution was heated at 100° for 30 min in order to promote any possible isomerization of the coordinated thiocyanate groups. The compound, which was isolated and recrystallized from methanol, was identical with

---

(35) D. Zatko and D. W. Meek, unpublished data.

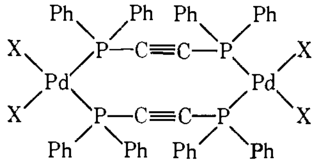
Table V. Electronic Spectral Data for the $[Pd(C_{26}H_{24}P_2)X_2]$ Complexes

X	Band maxima, cm^{-1}	
	Solid[a]	CH_2Cl_2 soln (ϵ)[b]
Cl	29,000	28,900 (6570)
(NCS)(SCN)		28,200 sh (4250)[c]
Br	28,400	28,000 (6060)
I	20,600 sh	20,600 sh (880)[c]
	24,300	24,500 (5800)

[a] Transmission spectrum of a Nujol mull of the solid compound. [b] Molar extinction coefficient given in parentheses. [c] ϵ value is calculated from the absorption of a shoulder on a stronger peak; it has a higher value than would be observed if the band were resolved well enough to give a definite maximum.

that obtained by recrystallization of $[Pd(C_{26}H_{24}P_2)_2][Pd(SCN)_4]$.

The infrared spectrum of the yellow, monomeric complex $[Pd(C_{26}H_{24}P_2)(CNS)_2]$, taken either as a Nujol mull of the solid or as a dichloromethane solution, shows two strong absorptions in the C≡N stretching region (Table II and Figure 2). One peak is very sharp ($\nu_{1/2}$ = ~16 cm^{-1}), typical of thiocyanato (M–SCN) coordination, and the other peak is broader ($\nu_{1/2}$= ~35 cm^{-1}), typical of isothiocyanato (M–NCS) coordination. The integrated absorption values of the infrared C≡N bands correspond to a stoichiometric 1:1 ratio of M–SCN and M–NCS linkages in dichloromethane solution. Since approximately the same ratio of intensities for the two infrared absorptions is observed regardless of the synthetic procedure, it is concluded that an equimolar mixture of the two linkage isomers $[Pd(C_{26}H_{24}P_2)(NCS)_2]$ and $[Pd(C_{26}H_{24}P_2)(SCN)_2]$ is unlikely. The large separation between the two C≡N infrared bands, their integrated intensities (Table II), and the energy of the electronic absorption (Table V) all signify the presence of both N- and S-bonded thiocyanate ions in the diphosphine complex.[35a] Carty and Efraty[36] recently reported a similar situation with two C≡N infrared peaks at 2118 and 2072 cm^{-1} in the complex $[Pd(DPPA)(CNS)_2]$ (**8**), which contains the linear, bridging ligand $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ and has the *cis* arrangement of diphenylphosphino groups. The electronic effects of the phosphorus atoms in **8** should be similar to those in $C_{26}H_{24}P_2$.



8

Ligands **3**, **4**, and **5** give the molecular thiocyanato complexes [Pd(ligand)$(SCN)_2$]. All three complexes exhibit two sharp, closely spaced infrared C≡N absorptions (Table II) that are typical of Pd–SCN bonding.

Jørgensen[37] has given the thiocyanate position in the spectrochemical series as M–SCN ≅ M–Cl < M–NCS; however, we find that when both thiocyanates are either N-bonded or S-bonded, the spectrochemical series is Pd–SCN < Pd–Cl < Pd–NCS. When both thiocyanate ions are S-bonded the spectrochemical position is less than or approximately equal to bromide, *i.e.*, Cl > Br ≥ –SCN > I (ref 18 and Table IV). When one N-bonded and one S-bonded thiocyanate are present, the average spectrochemical position is approximately equal to chloride (Tables III and V).

Discussion

Turco and Pecile[4] noted that the presence of other ligands in a complex apparently influenced whether the thiocyanate ion was N or S bonded. They suggested that phosphines, arsines, and similar donor atoms withdraw electron density from the metal through d_π–d_π (M→L) back-bonding, thereby reducing the relative tendency for the sulfur atom of SCN^- to participate in π bonding. As a consequence, when a SCN^- group is coordinated to a metal, along with strong π-acceptor ligands, it may be expected to bond preferentially *via* the nitrogen atom. On the basis of this explanation, isolation of the stable S-bonded complex of ligand **1** and the *mixed* N- and S-bonded complex of ligand **2** was quite unexpected. In ligand **1**, for example, one of the donors is effectively a triphenylarsine and the other is a soft phosphine sulfide group (capable of π bonding with palladium). Thus, both thiocyanate ions in $[Pd(C_{30}H_{24}AsPS)(SCN)_2]$ were expected to be N bonded; instead, both are S bonded.[18] In this complex the two thiocyanate ions must compete directly with the phosphine sulfide and arsenic donors along a d_{xz} or d_{yz} orbital for the d-orbital electron density on palladium. The π-acceptor ability of a ligand should be transmitted to the coordinated pseudohalide much more effectively when the ligand is *trans* to the pseudohalide (as in *cis*-PdL_2X_2) than when it is *cis* to the pseudohalide (as in *trans*-Pd L_2X_2). Thus, the S-bonded thiocyanates in [Pd(ligand **1**)$(SCN)_2$] indicate that both donor groups are weaker at π bonding than the sulfur atom of SCN^-, if the π-bonding explanation is utilized.

An electronic control on the mode of thiocyanate coordination may be deduced from the results of these chelating ligands, if one assumes that without steric hindrance arsenic and P=S donors are incapable of promoting N bonding. Thus, $(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$ and ligand **1** would form the S-bonded [Pd(ligand)$(SCN)_2$] complexes whereas ligand **2** would form the *mixed* [Pd(ligand **2**)(NCS)(SCN)] complex, in agreement with the experimental results. Phosphorus, on the other hand, by virtue of its stronger π-acceptor ability, can convert the *trans*-thiocyanate to the N-bonded case in the PAs, PC_2N, and PC_3N complexes.

However, the total picture is not so simple. On the basis of the above π-acceptor arguments, one would expect *one* N-bonded thiocyanate in the palladium(II) complexes of ligands **3**, **4**, and **5** and *two* N-bonded SCN^- groups with the diphosphines PP and DPPA. Instead, both thiocyanate ions are S bonded in the complexes of ligands **3**, **4**, and **5**, and the diphosphines PP and DPPA form complexes with one N-bonded and one S-bonded thiocyanate ion per palladium.

(35a) NOTE ADDED IN PROOF. The N- and S-bonded thiocyanate groups in this complex have been confirmed recently by X-ray crystallography. The crystal contains discrete $[Pd(C_{26}H_{24}P_2)(NCS)(SCN)]$ molecules, in which one thiocyanate group is S bonded and the other thiocyanate is N bonded. The S-bonded thiocyanate ion is bent away from one diphenylphosphino group in a manner similar to that shown in Figure 4: G. J. Palenik, personal communication, June 1970.

(36) A. J. Carty and A. Efraty, *Can. J. Chem.*, 47, 2573 (1968).

(37) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding," Pergamon Press, London, 1962, p 109.

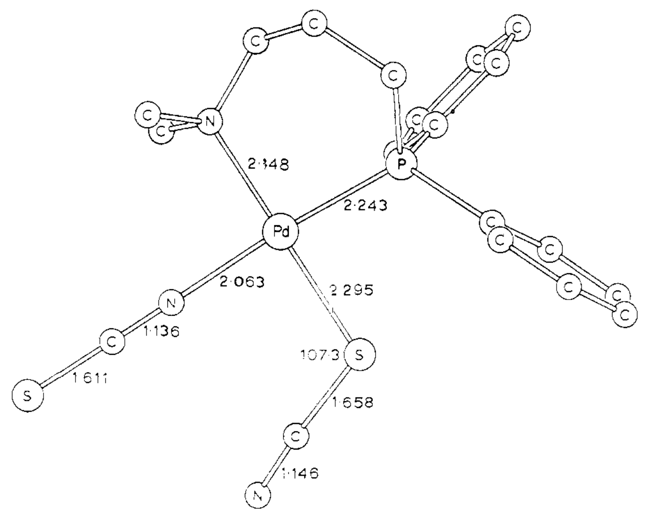
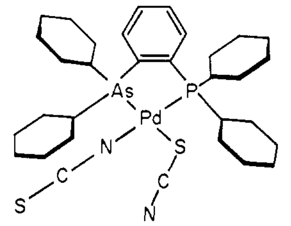


Figure 4. A view of the structure of [Pd(PC$_3$N)(SCN)(NCS)] normal to the plane of the four donor atoms.[34]

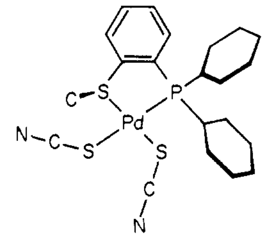
The latter results may be rationalized by invoking a steric interaction, in addition to the π-back-bonding electronic effect. The X-ray determination[34] of the structure of [Pd(PC$_3$N)(SCN)(NCS)] (PC$_3$N = (C$_6$H$_5$)$_2$-PCH$_2$CH$_2$CH$_2$N(CH$_3$)$_2$) provides some support for a steric hindrance by a *cis*-diphenylphosphino group. Figure 4 shows that one phenyl ring lies nearly parallel to the position that would be occupied by the thiocyanate group if it were N bonded. Such a linear Pd–NCS linkage would cause the filled π orbitals of the N≡C bond to experience a repulsive interaction with the phenyl π cloud. In the [Pd(PC$_3$N)(NCS)-(SCN)] complex, the thiocyanate group is bent away from the phenyl ring, perhaps to minimize the interaction of the π orbitals. The predictions of thiocyanate coordination based on the π bonding and on steric considerations lead to the same result in this case, namely, that the thiocyanate group *trans* to phosphorus will be N bonded and the one *trans* to nitrogen will be S bonded.

Although the donor groups are similar in each of the pairs (C$_6$H$_5$)$_3$As–(C$_6$H$_5$)$_2$AsCH$_2$CH$_2$As(C$_6$H$_5$)$_2$ and (C$_6$H$_5$)$_3$P–(C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$, a chelating ligand exhibits a smaller steric requirement than does a similar monodentate ligand in *trans*-[ML$_2$(CNS)$_2$] complexes. In such complexes each thiocyanate group is *cis* to *two* bulky ligands, whereas in the complexes of the bidentate ligands, each thiocyanate is *cis* to *only one* bulky ligand. Because of the shorter Pd–P bond distance, the steric effects of a *cis*-diphenylphosphino group will be larger than for a *cis*-diphenylarsino group. Thus, on the basis of steric hindrance, the most probable isomer for [Pd(PAs)(SCN)(NCS)] is **9**. Again, both steric and π-electronic considerations predict the same isomer. In the phosphine sulfide complex, [Pd(ligand **1**)(SCN)$_2$], steric factors should be minimized, since the phenyl groups on phosphorus are removed farther from the palladium and the thiocyanate ions; thus, the relative electronic properties of the ligand donor atoms should be reflected in the mode of bonding in the *trans*-thiocyanate ions. In this case, both thiocyanates are bonded *via* the soft sulfur atoms.



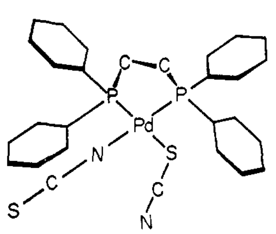
9

Ligands **3**, **4**, and **5** are unique among these bidentate ligands, since only one small substituent is attached to the sulfur and selenium atoms. Thus, these ligands should exhibit the least amount of steric hindrance and could easily accommodate two S-bonded thiocyanates (*e.g.*, **10**). This structural arrangement would allow the thiocyanate ion that is *cis* to the bulky diphenylphosphino group to bend away from phenyl ring in a manner similar to that observed in the complex [Pd-(PC$_3$N)(NCS)(SCN)]. The other angular thiocyanato group could bend either up or down, depending on the orientation of the S–CH$_3$ group.



10

The complexes of the diphosphines, (C$_6$H$_5$)$_2$PCH$_2$-CH$_2$P(C$_6$H$_5$)$_2$ and (C$_6$H$_5$)$_2$PC≡CP(C$_6$H$_5$)$_2$, and of the diarsine, (C$_6$H$_5$)$_2$AsCH$_2$CH$_2$As(C$_6$H$_5$)$_2$, illustrate the delicate balance of electronic and/or steric forces that govern whether a given thiocyanate group is N or S bonded. In the diarsine case, only S-bonded thiocyanate ions are present in the solid state; however, simply dissolving the compound in dichloromethane causes some isomerization to N bonding to occur. On evaporation of the solvent, the thiocyanate ion rearranges to the S-bonded form. The sensitivity to subtle changes in the physical environment of the complex or to changes in the ligand substituents provides a rational basis for the isolation of linkage isomers in the case of *trans*-Pd(AsPh$_3$)$_2$(CNS)$_2$ complexes,[5] whereas (C$_4$H$_9$)$_3$As forms only the S-bonded species in the solid.[7] However, even the (C$_4$H$_9$)$_3$As complex, [Pd-((C$_4$H$_9$)$_3$As)$_2$(SCN)$_2$], undergoes some isomerization to an N-bonded thiocyanate in the melt.[7] The isomerization in the melt has some analogy to the reversible isomerization of [Pd(C$_{26}$H$_{24}$As$_2$)(SCN)$_2$] in solution. In the diphosphine cases, coordination of one thiocyanate group apparently shifts the electronic and/or steric effect just sufficiently so that the second thiocyanate ion bonds in a different manner and gives the mixed complex [Pd(C$_{26}$H$_{24}$P$_2$)(NCS)(SCN)].[35a]



Conclusions. This study has produced several molecular palladium(II) complexes that contain both N- and S-bonded thiocyanate ions. With the ligands PAs, PC_2N, and PC_3N, it is impossible to ascertain definitively whether the mixed mode of thiocyanate coordination is due to steric hindrance or to the *trans* electronic influences of the donor atom, since the predicted results are the same, and in agreement with the observations. With the ligands PP, SP, FSP, and SeP, steric considerations alone favor *two* S-bonded thiocyanate ions. Isolation of the stable, mixed complex $[Pd(C_{26}H_{24}P_2)(SCN)(NCS)]$ and the reversible isomerization of $[Pd(C_{26}H_{24}As_2)(SCN)_2]$ in solution illustrate the delicate balance of electronic, steric, and solvent forces that influence the nature of thiocyanate coordination in a given complex.

Acknowledgments. The authors are grateful to Professor John Burmeister for several helpful suggestions on the original version of this paper, and to Professor G. J. Palenik for determining the structures of [Pd(PP)(NCS)(SCN)] and $[Pd(PC_3N)(SCN)(NCS)]$ by X-ray three-dimensional crystallography.

Photochemical Reactions of Oxalatobis(triphenylphosphine)platinum(II) and Related Complexes[1]

Daniel M. Blake and C. J. Nyman

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99163. *Received February 13, 1970*

Abstract: The oxalato complexes $ML_2C_2O_4$ (M = Pt or Pd, L = $P(C_6H_5)_3$ or $As(C_6H_5)_3$) and $Pt(diphos)C_2O_4$ (diphos = 1,2-bis(diphenylphosphino)ethane) have been prepared and characterized. Irradiation of these complexes with ultraviolet light gives carbon dioxide and reduced metal-containing species. Photochemical reactions of oxalatobis(triphenylphosphine)platinum(II) have been studied in detail. Photolysis of this complex in ethanol solution, under an inert atmosphere, yields a dimeric complex of formula $Pt_2[P(C_6H_5)_3]_4$; in the presence of triphenylphosphine the known compound $Pt[P(C_6H_5)_3]_4$ is obtained; with a disubstituted acetylene, compounds of the known type $Pt[P(C_6H_5)_3]_2$(acetylene) are obtained, whereas with phenylacetylene a diacetylide complex, $Pt[P(C_6H_5)_3]_2(C_2C_6H_5)_2$, is formed; reaction in a hydrogen atmosphere leads to partial reduction of the oxalate ion and formation of a new cluster compound of platinum, $Pt_4[P(C_6H_5)_3]_5(CO)_3$; and reaction with disubstituted acetylenes in an atmosphere of carbon monoxide gives new cluster compounds containing acetylenes, $Pt_3[P(C_6H_5)_3]_4(CO)_2$(acetylene). Physical properties, structures, and reactions of these products are discussed. Mechanisms for the photochemical reactions are discussed and the results are interpreted in terms of the formation of the coordinatively unsaturated species $Pt[P(C_6H_5)_3]_2$ in the initial decomposition of the oxalate complex. The reaction in the presence of hydrogen gas appears to be a special case in which $Pt[P(C_6H_5)_3]_2CO$ is the initial product.

Since their discovery in 1957 and 1958, tertiary phosphine complexes of palladium(0)[2] and platinum(0)[3] have proven to be versatile reagents for the synthesis of a wide variety of compounds.[4] Interest has been spurred by the reactivity of these compounds toward unsaturated molecules, reactivity in oxidative addition reactions, and use as homogeneous catalysts for oxidations by molecular oxygen. Reactions of the triphenylphosphine complexes of platinum have been the most extensively studied.[4] In many of these reactions there is evidence that a coordinatively unsaturated species having the formula $Pt[P(C_6H_5)_3]_2$ is a reactive intermediate.[4-6] A compound of this formula has been isolated.[7] More commonly, reactions are used which produce this species *in situ*. Some of these are: dissociation of $Pt[P(C_6H_5)_3]_3$;[5] dissociation of the ethylene adduct, $Pt[P(C_6H_5)_3]_2C_2H_4$;[5,8] reduction of $Pt[P(C_6H_5)_3]_2O_2$ with sodium borohydride;[8] reduction of *cis*-$Pt[P(C_6H_5)_3]_2Cl_2$ with hydrazine;[9] and deprotonation of platinum(II) hydride complexes with strong bases.[7,10] The use of $Pt[P(C_6H_5)_3]_2$ as a reactant would be advantageous because of the absence of free triphenylphosphine or other reagents that may compete for coordination sites on the platinum.

Another aspect of platinum(0) chemistry which has recently attracted interest is the synthesis and characterization of cluster compounds of platinum containing phosphines and carbon monoxide as ligands. While the number of such compounds of transition metals is rapidly growing, only a few compounds of this type are known that contain platinum.[11-13] Preliminary

---

(1) D. M. Blake and C. J. Nyman, *Chem. Commun.*, 483 (1969).

(2) L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1186 (1957).

(3) L. Malatesta and C. Cariello, *ibid.*, 2323 (1958).

(4) R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968).

(5) (a) J. P. Birk, J. Halpern, and A. L. Pickard, *Inorg. Chem.*, **7**, 2672 (1968); (b) J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, **90**, 4491 (1968).

(6) A. D. Allen and C. P. Cook, *Can. J. Chem.*, **42**, 1063 (1964).

(7) R. Ugo, F. Cariati, and G. La Monica, *Chem. Commun.*, 868 (1966).

(8) C. D. Cook, and G. S. Jauhal, *J. Amer. Chem. Soc.*, **90**, 1464 (1968).

(9) G. D. Dobinson, R. Mason, G. B. Robertson, R. Ugo, F. Conti, D. Morelli, S. Cenini, and F. Bonati, *Chem. Commun.*, 739 (1967).

(10) F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, **5**, 1128 (1966).

(11) (a) G. Booth, J. Chatt, and P. Chini, *Chem. Commun.*, 639 (1965); (b) G. Booth and J. Chatt, *J. Chem. Soc. A*, 2131 (1969).

(12) F. Cariati, and R. Ugo, *Chim. Ind.* (*Milan*), **48**, 1288 (1966); *Chem. Abstr.*, **66**, 65618*q* (1967).