

Ligand Effects on the Bonding Mode of the Selenocyanate
Ion in Palladium (II) Complexes. I.¹

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In an effort to ascertain the importance of Pd→Se π-bonding in [Pd(L)₂(selenocyanate)₂] complexes, the effects of a large number of ligands of varying π-bonding abilities and basicities on the Pd(II)-selenocyanate bonding mode have been studied. Unlike its homologue, the thiocyanate ion, the selenocyanate ion has been found to be relatively insensitive to changes in the character of the L ligand. Whereas the introduction into the Pd(II) coordination sphere of at least ten different π-bonding ligands has been observed to cause a switch in the preferred bonding mode of the remaining thiocyanates from Pd-SCN to Pd-NCS, only one such ligand, P(*n*-C₄H₉)₃, has thus far been found to be capable of initiating Pd-NCSe bonding, and this is most probably due to a steric effect. A correlation has been found between the stability of the complexes and the π-acceptor capability of pyridine-type ligands in [Pd(4-X-pyridine)₂(SeCN)₂] complexes. The synthesis of the linkage isomeric forms of [Pd(P(OCH₃)₃)₂(SCN)₂] is also discussed.

Introduction

In 1961, Turco and Pecile² observed that the reaction between K₂[M(SCN)₄] (M = palladium(II), platinum(II)) and triethylphosphine yields the disubstituted complexes [M(P(C₂H₅)₃)₂(NCS)₂], wherein the bonding mode of the remaining thiocyanates has been converted from M-SCN to M-NCS. Since that time, several other ligands possessing π-acceptor properties have been found which also initiate Pd-NCS and/or Pt-NCS bonding in such complexes, e.g., tri-*n*-propylphosphine,³ tri-*n*-butylphosphine,⁴ triphenylphosphine,⁴ triphenylarsine,^{4,5} 2,2'-bipyridine,^{4,5} 2,2',2''-tripyridine,⁴ 5-nitro-1,10-phenanthroline,⁶ 4,7-diphenyl-1,10-phenanthroline.⁷ The bonding mode has also been shown^{8,9} to be sensitive to steric factors as well, e.g. [(dien)Pd-SCN]⁺ versus [(Et₄dien)Pd-NCS]⁺ (dien =

= diethylenetriamine, Et₄dien = N,N,N',N'-tetraethyl-diethylenetriamine). Since both the thiocyanate and selenocyanate ions follow a M_(class a)-NCX, M_(class b)-XCN bonding pattern in complexes wherein they are the only ligands present,^{10,11,12} it was of great interest to determine whether the selenocyanate ion also exhibits a tendency to switch to a Pd-NCSe bonding mode when π-bonding or very bulky ligands such as the above are introduced into the palladium(II) coordination sphere, especially since the results of an earlier study¹³ had indicated radically different behavior.

Experimental Section

Preparation of Compounds. Potassium selenocyanate was prepared by the method given in *Inorganic Syntheses*.¹⁴ The [Pd(L)₂(selenocyanate)₂] complexes (L = ligands of varying π-acceptor capabilities) and their dichloro analogs were prepared according to the following methods:

(A) One mmole of palladium dichloride, 2 mmoles of potassium selenocyanate, and 45 ml. of methanol were stirred at room temperature for 0.5 hr., then filtered. To the dark red filtrate was added an alcoholic solution of 1 or 2 mmoles, respectively, of a bi- or monodentate ligand. The neutral complex, which precipitated immediately, was isolated by filtration, washed with water, ethanol, and ethyl ether, and dried *in vacuo* over P₂O₅.

(B) The tetrasubstituted species [PdL₄]²⁺ was first formed by the addition of excess L to an aqueous solution of K₂[PdCl₄]. The desired product was then obtained by the addition of a solution of potassium selenocyanate, dissolved in a minimum amount of water, and worked up as in (A).

(C) The dichloro complex, [Pd(L)₂Cl₂], was first prepared by adding an alcoholic solution of L to an aqueous solution of K₂[PdCl₄]. The diaquo complex was then prepared by warming an aqueous suspension of the dichloro complex with 2 equivalents of silver nitrate. The silver chloride which precipitated was

(1) Presented at the Sixteenth Delaware Science Symposium, Newark, Del., Jan. 21, 1967, and at the 153rd National Meeting of the American Chemical Society, Miami Beach, Florida, April 9-14, 1967.

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(9) F. Basolo, W. H. Baddley and K. J. Weidenbaum, *J. Am. Chem. Soc.*, **88**, 1576 (1966).

(10) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 1712 (1965).

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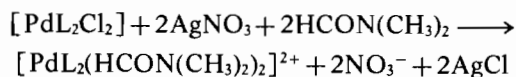
(12) J. L. Burmeister, *Coordin. Chem. Rev.*, **1**, 205 (1966).

(13) J. L. Burmeister and M. Y. Al-Janabi, *Inorg. Chem.*, **4**, 962 (1965).

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removed by filtration. To the filtrate, cooled in an ice-salt bath, was added 2 equivalents of potassium selenocyanate. The complex was then isolated as in (A).

(D) For the cases where none of the above methods gave the desired product, success was achieved by using *N,N*-dimethylformamide as the solvent in the reaction:



The insoluble silver chloride was removed by filtration and 2 equivalents of potassium selenocyanate was added to the filtrate. The color of the filtrate immediately changed following the addition of the potassium selenocyanate, but it was necessary to add the resulting solution to ca. 1 l. of cold ethyl ether to precipitate the desired product. In some cases, a bridged $[\text{Pd}_2\text{L}_2(\text{SeCN})_4]$ species was first isolated. This was converted to the desired product by stirring a suspension of the former in an ethanolic solution of 5 equivalents of L.

Reactions with Trifluorophosphine. Two mmoles of palladium dichloride and 4 mmoles of potassium thiocyanate were stirred in 60 ml. of methanol for 0.5 hr., whereupon the potassium chloride which precipitated was removed by filtration. Trifluorophosphine gas (purchased from Columbia Organic Chemicals Co.) was bubbled into the filtrate, which was pre-cooled to -78°

pyridine solution of the solid all showed the product to be $[\text{Pd}(\text{P}(\text{OCH}_3)_3)_2(\text{SCN})_2]$, rather than the desired $[\text{Pd}(\text{PF}_3)_2(\text{SCN})_2]$.

Anal. Calcd. for $[\text{Pd}(\text{P}(\text{OCH}_3)_3)_2(\text{SCN})_2]$: C, 20.39; N, 5.95; P, 13.16. Found: C, 20.82; N, 6.10; P, 13.19.

The preparation of the analogous selenocyanate complex was carried out in a similar manner. Two mmoles of palladium dichloride and 4 mmoles of potassium selenocyanate were stirred in 75 ml. of methanol for 0.5 hr. at room temperature. The solution was then filtered and trifluorophosphine gas was passed into the filtrate (pre-cooled to -78° in a Dry Ice-acetone bath) until the solution became red-orange in color. It was stirred at -78° for 2 hr., after which time a bright yellow solid was isolated by filtration. It was washed with ethanol and ethyl ether and dried *in vacuo* over P_2O_5 . The compound is stable if stored at -10° , but decomposes to an orange tar in 1 day at room temperature.

Anal. Calcd. for $[\text{Pd}(\text{P}(\text{OCH}_3)_3)_2(\text{SeCN})_2]$: C, 17.00; H, 3.21; N, 4.96. Found: C, 16.98; H, 3.25; N, 4.91.

Analyses. Carbon, hydrogen and nitrogen microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Mülheim, Germany. Percent phosphorus was determined by Micro-Analysis, Inc., Wilmington, Delaware. The results of the analyses and the preparative methods employed for the selenocyanate complexes are shown in Table I.

Table I. Analytical Data and Preparative Methods for the Palladium(II) - Selenocyanate Complexes

Complex, ^a (preparative method)	Theory			Analyses, %		
	C	H	N	C	H	N
$[\text{Pd}(\text{en})(\text{SeCN})_2]$, (C)	14.88	2.14	12.76	14.26	2.03	12.93
$[\text{Pd}(1,2\text{-diambz})(\text{SeCN})_2]$, (C)	22.63	1.90	13.20	22.55	2.17	13.12
$[\text{Pd}(\text{bipy})(\text{SeCN})_2]$, (A)	30.48	1.69	11.85	30.00	1.60	11.90
$[\text{Pd}(\text{phen})(\text{SeCN})_2]$, (A)	32.66	1.57	10.88	32.60	1.20	11.00
$[\text{Pd}(5\text{-NO}_2\text{-phen})(\text{SeCN})_2]$, (A)	31.05	1.30	12.91	31.08	1.60	13.27
$[\text{Pd}(\text{tripy})(\text{SeCN})_2]$, (A)	37.15	2.75	12.74	36.49	1.94	12.45
$[\text{Pd}(\text{NH}_3)_2(\text{SeCN})_2]$, (B)	6.80	1.71	15.86	6.94	1.82	15.86
$[\text{Pd}(4\text{-CH}_3\text{-py})(\text{SeCN})_2]$, (B)	33.45	2.81	11.15	33.75	3.15	11.60
$[\text{Pd}(4\text{-NH}_2\text{-py})(\text{SeCN})_2]$, (A)	28.56	2.40	16.65	28.49	2.48	16.16
$[\text{Pd}(\text{py})_2(\text{SeCN})_2]$, (B)	30.37	2.12	11.81	30.43	2.38	11.61
$[\text{Pd}(4\text{-acpy})(\text{SeCN})_2]$, (D)	40.04	3.36	6.67	40.66	3.59	6.62
$[\text{Pd}(\text{N,N-diphenyltu})_2(\text{SeCN})_2]$, (A)	43.50	3.13	10.87	45.95	3.16	10.35
$[\text{Pd}(\text{N,N'-diphenyltu})_2(\text{SeCN})_2]$, (A)	43.50	3.13	10.87	45.01	3.16	10.52
$[\text{Pd}(\text{P}(\text{n-C}_6\text{H}_5)_3)_2(\text{SeCN})_2]$, (A) ^b	43.29	7.55	3.89	43.59	7.62	3.95
$[\text{Pd}(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{SeCN})_2]$, (A) ^b	54.25	3.59	3.20	55.10	3.50	3.10
$[\text{Pd}_2(\text{As}(\text{C}_6\text{H}_5)_3)_2(\text{SeCN})_4]$, (D)	38.58	2.43	4.50	38.10	2.46	4.87

^a Abbreviations: en, ethylenediamine; 1,2-diambz, 1,2-diaminobenzene; bipy, 2,2'-bipyridine; phen, 1,10-phenanthroline; 5-NO₂-phen, 5-nitro-1,10-phenanthroline; tripy, 2,2',2''-tripyridine; 4-CH₃-py, 4-methylpyridine; 4-NH₂-py, 4-aminopyridine; py, pyridine; 4-acpy, 4-acetylpyridine; N,N-diphenyltu, N,N-diphenylthiourea. ^b Reaction carried out at -78° to prevent complete substitution of phosphines for selenocyanates (see ref. 13).

in a Dry Ice-acetone slurry, until the solution became yellow in color. This was quickly followed by the precipitation of a white solid, which was isolated by filtration, washed with ethanol and ethyl ether and dried *in vacuo* over P_2O_5 . The microanalytical results, the infrared spectrum of a hexachlorobutadiene mull, and the proton n.m.r. spectrum of a

Infrared Spectra. Infrared spectra, in the 4000-400 cm^{-1} range, of complexes held in Nujol suspension between KBr plates were measured on a Perkin-Elmer Model 421 recording spectrophotometer. The same instrument was used to record high resolution spectra of solutions of the complexes in the selenocyanate C-N stretching range (2200-2000 cm^{-1}). Matched 0.1-mm

NaCl cells were employed. The integrated absorption intensities, A ($M^{-1} \text{ cm}^{-2}$), of the C-N stretching bands were determined by Ramsay's method of direct integration,¹⁵

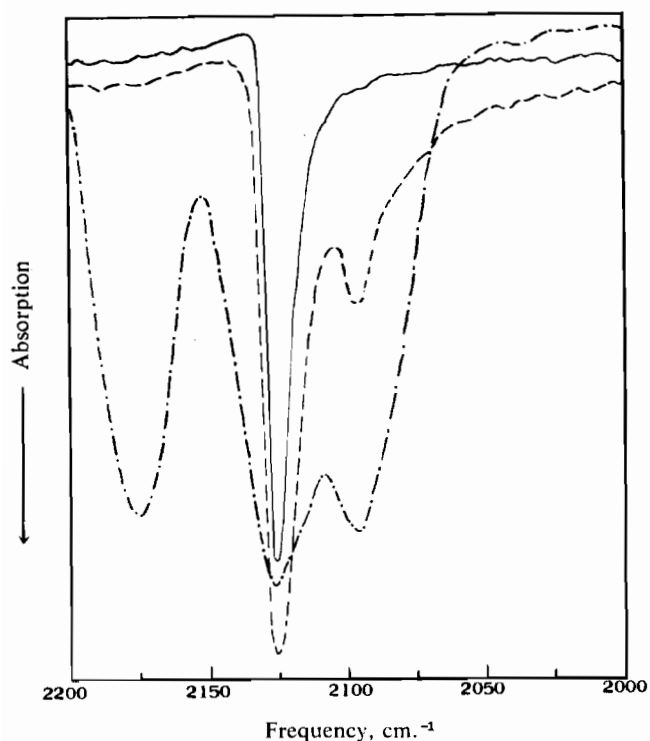


Figure 1. Infrared Spectra of the $[\text{Pd}(\text{P}(\text{C}_4\text{H}_9)_3)_2(\text{SeCN})_2]$ Complex. —: freshly prepared (at -80°) sample; ---: sample aged for four days at 0° ; - · - · -: sample aged overnight at 40° .

The bonding modes of the coordinated selenocyanate groups were determined on the basis of the previously elucidated^{11,16,17} behavior of the C-N and (where possible) C-Se stretching bands following Se- or N-coordination, i.e., M-SeCN: C-N stretch $> 2100 \text{ cm}^{-1}$, integrated absorption intensity $\cong 1 \times 10^4 M^{-1} \text{ cm}^{-2}$; C-Se stretch $< 558 \text{ cm}^{-1}$; M-NCSe: C-N stretch $\leq 2100 \text{ cm}^{-1}$, integrated absorption intensity $\cong 10 \times 10^4 M^{-1} \text{ cm}^{-2}$; C-Se stretch $> 558 \text{ cm}^{-1}$; M-SeCN-M: C-N stretch $> 2140 \text{ cm}^{-1}$. Analogous spectral behavior has been observed for the coordinated thiocyanate group.^{2,4,6,7,17} The infrared data for the new complexes are shown in Tables II and III; the spectrum of the $[\text{Pd}(\text{P}(\text{n-C}_4\text{H}_9)_3)_2(\text{SeCN})_2]$ complex (held in Nujol suspension) in the C-N stretching range is shown in Figure 1.

Conductance Measurements. Molar conductances, at 25° , of $10^{-3}M$ solutions of the complexes in *N,N*-dimethylformamide were measured with an Industrial Instruments, Inc. Model RC-16B2 conductivity bridge and a cell with platinized electrodes. The values obtained for the $[\text{Pd}(4\text{-X-pyridine})_2(\text{SeCN})_2]$ complexes are shown in Table IV.

Dielectric Constant Measurements. The ratio of the increment in dielectric constant produced to the solutions of $[\text{Pd}(\text{P}(\text{OCH}_3)_3)_2(\text{SeCN})_2]$ at 20° , was mole fraction of solute present, $\Delta\epsilon/f$, for benzene determined with a Wissenschaftlich Technische Werkstätten DMO1 «dipölmeter».

Proton Nuclear Magnetic Resonance Spectra. The proton n.m.r. spectrum of a pyridine solution of the $[\text{Pd}(\text{P}(\text{OCH}_3)_3)_2(\text{SeCN})_2]$ complex was measured with a Varian A60 nuclear magnetic resonance spectrometer.

Table II. Infrared Data for the Palladium(II) - Selenocyanate Complexes

Ligand	C-Se Stretch, ^a $\nu_1(\text{SeCN})$, (cm^{-1})	C-N Stretch, $\nu_1(\text{SeCN})$		
		Mull ^a (cm^{-1})	Solution ^b (cm^{-1})	$A^b \times 10^{-4}$ ($M^{-1} \text{ cm}^{-2}$)
<i>cis</i> - $[\text{Pd}(\text{L})(\text{SeCN})_2]$ complexes				
ethylenediamine	^c	2126, 2108	2112	0.65
1,2-diaminobenzene	^c	2122, 2102	2110	0.75
2,2'-bipyridine	528	2134, 2119	^d	^d
1,10-phenanthroline	530	2123, 2110	^e	^e
5-nitro-1,10-phenanthroline	525	2129, 2110	2111	0.79
2,2',2''-tripyrindine ^f	^c	2125, 2112	2110	0.50
<i>trans</i> - $[\text{Pd}(\text{L})_2(\text{SeCN})_2]$ complexes				
ammonia	528	2126	2111	0.93
4-methylpyridine	^c	2119	2112	1.0
4-aminopyridine	^c	2123	2119	0.90
pyridine	^c	2126	2109	1.0
4-acetylpyridine	531	2132	2115	1.0
<i>N,N</i> -diphenylthiourea	^c	2124	2115	0.97
<i>N,N'</i> -diphenylthiourea	^c	2121	2113	0.86
tri- <i>n</i> -butylphosphine	^c	2122	2125	0.76
triphenylphosphine	^c	2127	2122	0.61
$[\text{Pd}_2\text{L}_4(\text{SeCN})_4]$				
triphenylarsine	522	2150, 2128	^g	^g

^a Complex held in Nujol suspension. ^b *N,N*-dimethylformamide solution, $5 \times 10^{-2}M$ with respect to coordinated selenocyanate; A = integrated absorption intensity. ^c Band masked by absorption due to organic ligand. ^d Complex dissociates in DMF solution. ^e Complex insoluble in DMF. ^f In the solid complex, as has been found to be the case with its thiocyanate analog (ref. 4), the tripyridine is acting as a bidentate ligand, as evidenced by the two ring breathing vibrations at 1027 and 989 cm^{-1} and the absence of an ionic selenocyanate C-N stretching band. In DMF solution, the complex behaves as a 1:1 electrolyte, indicating the coordination of the third pyridine ring. ^g Not determined.

(15) D. A. Ramsay, *J. Am. Chem. Soc.*, 74, 72 (1952).

(16) A. Turco, C. Pecile and M. Nicolini, *J. Chem. Soc.*, 3008 (1962).

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

Table III. Infrared Data for the Palladium(II) - Trimethylphosphite Complexes

Complex	C-X Stretch, ^a	C-N Stretch, $\nu_3(\text{XCN})$	
	$\nu_1(\text{XCN}), (\text{cm}^{-1})$	Mull ^a (cm^{-1})	Solution (cm^{-1})
<i>trans</i> -[Pd(P(OCH ₃) ₃) ₂ (SCN) ₂]	710	2131	^c
<i>trans</i> -[Pd(P(OCH ₃) ₃) ₂ (NCS) ₂]	^d	2092	2099 ^e
<i>cis</i> -[Pd(P(OCH ₃) ₃) ₂ (SeCN) ₂]	^d	2135, 2126	2133 ^f
			$A^b \times 10^{-4} (M^{-1} \text{cm}^{-2})$
			^c
			11.0 ^e
			0.75 ^f

^a Complex held in Nujol suspension. ^b Integrated absorption intensity. ^c Complex isomerizes completely in DMF solution. ^d Band masked by absorption due to phosphine. ^e N,N-dimethylformamide solution, $5 \times 10^{-2} M$ with respect to coordinated thiocyanate. ^f Benzene solution, $5 \times 10^{-2} M$ with respect to coordinated selenocyanate. Dissolution probably results in isomerization to *trans*-geometry (*vide infra*).

Table IV. Molar Conductances of the [Pd(4-X-pyridine)₂(SeCN)₂] Complexes

X	Hammett substituent constant, σ_p^d	pK _a ^b	Λ_m^c ($\text{ohm}^{-1} \text{cm}^{-2} \text{mole}^{-1}$)
—CH ₃	—0.17	6.02	20.3
—NH ₂	—0.66	8.96	21.2
—H	0.00	5.17	22.3
—C—CH ₃	+0.52	—	25.0

^a Values taken from H. H. Jaffé, *Chem. Rev.*, 53, 191 (1953).

^b Values taken from H. C. Brown, D. H. McDaniel and O. Hafliger, in «Determination of Organic Structures by Physical Methods», E. A. Braude and F. C. Nachod, Ed., Academic Press, Inc., New York, p. 567 (1955). ^c Equilibrium values.

Discussion

Inspection of the data presented in Table II clearly shows that, unlike the bonding mode of its thiocyanate homologue, that of the selenocyanate is quite insensitive to changes in the nature of the L ligand. Indeed, all of the [Pd(L)₂(SeCN)₂] complexes prepared under the indicated reaction conditions involve Pd-SeCN bonding. Except for the tri-*n*-butylphosphine complex, no isomerization was observed to take place in the solid state with time or upon heating to elevated temperatures, despite the fact the several of the ligands used promote Pd-NCS bonding in the analogous thiocyanate complexes.

In the case of the tri-*n*-butylphosphine complex, however, the growth (see Figure 1) of a broad C-N stretching band at 2098 cm^{-1} , characteristic of an N-bonded species, was observed in the infrared spectra of aliquots taken from a sample of the original bright yellow complex which was kept $< 0^\circ$. This represents the first isomerization ever observed for an inorganic selenocyanate. Unfortunately, when the sample was heated to complete the isomerization, bridging, as evidenced by the appearance of a C-N stretching band at 2170 cm^{-1} , and eventual decomposition of the sample took place.

The question naturally arises, in the light of the π -bonding arguments previously advanced,^{2,4,6,7} as to whether the partial isomerization should be ascribed to the π -acceptor capability of the tri-*n*-butylphosphine, i.e., does it convert the normally soft palladium(II) coordination site into a hard site by withdrawing π -electron density from the metal? It would appear that the answer is no, since the complexes of triphenylphosphine and trimethylphosphite (Table III), both of

which have been shown¹⁸ to be stronger π -acceptors than tri-*n*-butylphosphine, both contain Se-bonded selenocyanates which do not undergo isomerization. This would suggest that the differing steric requirements of the ligands may be the determining factor. We are currently studying the effects of bulky, non- π -bonding ligands on the selenocyanate bonding mode in an effort to verify this possibility.

The ligands triphenylarsine, triphenylarsine oxide, triphenylphosphine oxide, and triphenylstibine all initially yielded polynuclear species involving selenocyanate bridging groups, as deduced from their infrared spectra. Only in the case of the triphenylarsine derivative did the microanalytical results correspond to a definite formulation, implying that the other products were mixtures of mono- and polynuclear species. However, the stability of the products derived from these four ligands was quite low, precluding further investigation.

In order to ascertain whether the varying π -bonding ability of the L ligand had any predictable effect on the stability of the palladium(II) complexes, the equilibrium molar conductances, in DMF, of the pyridine and 4-substituted pyridine complexes were determined. As shown in Table IV, the complex stability, as reflected in the increasing conductance values, does indeed decrease as the π -acceptor capability of the L ligand is increased in going from the 4-methylpyridine to the 4-acetylpyridine derivative (the 4-aminopyridine complex is out of line). It should be noted that the steric requirements of the ligands are essentially constant.

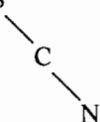
The inability of the selenocyanate ion to follow the pattern of behavior exhibited by the thiocyanate ion in these complexes adds yet another item to a list of puzzling questions which have arisen from the substantial amount of work carried out in this area within the past five years. For example, both [Pd(C₆H₅)₃]₂(NCS)₂⁴ and [Mn(CO)₅SCN]¹⁹ have been found to be stable with respect to isomerization in the solid state. The π -acceptor capability of triphenylphosphine has been used⁴ to explain the existence of the Pd-NCS bond in the former complex while the even greater π -acceptor capability of carbon monoxide has been used¹⁹ to explain the Mn-SCN bond in the latter complex.

The differing steric requirements of N- and S-bonded thiocyanates have been suggested⁸ to result primarily from the fact that the former bonding mode involves a linear (or nearly so) M-NCS linkage, whereas the latter

(18) W. D. Horrocks Jr. and R. C. Taylor, *Inorg. Chem.*, 2, 723 (1963).

(19) M. F. Farona and A. Wojcicki, *Inorg. Chem.*, 4, 857 (1965); 4, 1402 (1965).

mode involves a non-linear M—S linkage.



Decreased steric hindrance has been suggested^{4,8} as a possible explanation for the retention of the Pd-SCN linkage in $[\text{Pd}(\text{Sb}(\text{C}_6\text{H}_5)_3)_2(\text{SCN})_2]$ (as opposed to $[\text{Pd}(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{NCS})_2]$), whereas increased steric hindrance has been suggested¹⁹ to account for the switch to the Mn-SCN linkage in *cis*- $[\text{Mn}(\text{CO})_3(\text{Sb}(\text{C}_6\text{H}_5)_3)_2\text{SCN}]$ (as opposed to, for example, *cis*- $[\text{Mn}(\text{CO})_3(\text{py})_2\text{NCS}]$). The switch from N- to S-bonding in the pairs $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ versus $[\text{Co}(\text{CN})_5\text{SCN}]^{3-}$ ²⁰ and $[\text{Rh}(\text{NH}_3)_5\text{NCS}]^{2+}$ versus $[\text{Rh}(\text{SCN})_6]^{3-}$ ²¹ would appear to be nicely explained by the enhancement of the soft character of the metal ions resulting from the coordination of the soft ligands cyanide and S-thiocyanate. How, then, is one to explain, on this basis, the switch from S- to N-bonding in the complexes $[\text{Mn}(\text{CO})_5\text{SCN}]$ versus $[\text{Cr}(\text{CO})_5\text{NCS}]^-$,²² the latter coordination site being softer by virtue of its lower oxidation state?

One way of resolving the dilemma posed by the results obtained from the studies with palladium(II) and manganese(I) would involve the use, in palladium(II) complexes, of a ligand having a minimal steric requirement and a π -acceptor capability comparable to that of carbon monoxide. Trifluorophosphine is such a ligand. Since it is only slowly hydrolyzed by water at room temperature, it was anticipated that the low (-78°) temperature at which the reactions with $[\text{Pd}(\text{SCN})_4]^{2-}$ and $[\text{Pd}(\text{SeCN})_4]^{2-}$ were carried out would keep solvolysis to a minimum. Unfortunately, the solvolytic reaction with methanol was both rapid and complete, probably having been catalyzed by the coordination of trifluorophosphine to the palladium(II). This latter observation is in accord with those made by Gray²³ concerning the solvolysis of trihalogenophosphines coordinated to nickel(II).

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

(21) H.-H. Schmidtke, *J. Am. Chem. Soc.*, **87**, 2522 (1965).

(22) A. Wojcicki and M. F. Faron, *J. Inorg. Nucl. Chem.*, **26**, 2289 (1964).

(23) H. B. Gray, private communication.

Nonetheless, some interesting results (Table III) were obtained.

The white solid resulting from the reaction with $[\text{Pd}(\text{SCN})_4]^{2-}$ is a mixture of both the S- and N-bonded thiocyanate isomers of $[\text{Pd}(\text{P}(\text{OCH}_3)_3)_2(\text{SCN})_2]$ (both having *trans*-geometry) and represents the first known case of linkage isomerism of the thiocyanate ion in a palladium(II) complex containing a phosphine, only the N-bonded isomers having heretofore been observed. The ability of the trimethylphosphite to cause some of the thiocyanates to switch to N-bonding, even at -78° , is indicative of the ligand's relatively strong π -acceptor properties, in agreement with the conclusion of Horrocks and Taylor.¹⁸ Upon dissolution in N,N-dimethylformamide, the S-bonded component undergoes isomerization, and the pure pale yellow N-bonded isomer can be precipitated from the bright yellow solution by the addition of ethyl ether.

By way of contrast, the bright yellow $[\text{Pd}(\text{P}(\text{OCH}_3)_3)_2(\text{SeCN})_2]$ complex which results from the reaction with $[\text{Pd}(\text{SeCN})_4]^{2-}$ contains only Se-bonded selenocyanates and probably has *cis*-geometry, the latter being deduced from the splitting of the C-N stretching band (only in the case of the *cis*-isomer of a square planar complex are both the in-phase and out-of-phase vibrations theoretically infrared active.) The assignment of *cis*-geometry is not unequivocal, since the in-phase C-N stretching frequency of a *trans*-configuration in the solid state may be active if the site symmetry of the complex is not centrosymmetric. Dissolution in benzene results in considerable isomerization to the *trans*-configuration, as evidenced by the disappearance of one of the C-N stretching bands and a $\Delta\epsilon/f$ (change in dielectric constant/mole fraction solute) value of 55 (measured in benzene at 20°). According to Chatt and Wilkins,²⁴ the pure *cis*-isomer would exhibit a $\Delta\epsilon/f$ value of ca. 160.

Efforts to introduce trifluorophosphine into the palladium(II) coordination sphere are being continued.

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(24) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 70 (1953).