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THE SYNTHESIS AND CHARACTERIZATION OF THIOCYANATE–ISOCYANIDE COMPLEXES OF PALLADIUM(II)*

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SUMMARY

The syntheses of the complexes $[Pd(CNR)_2(SCN)_2]$ (R = phenyl, cyclohexyl), $[Pd(CNR)\{P(C_6H_5)_3\}(SCN)_2]$ (R = phenyl, cyclohexyl, *p*-nitrophenyl), and $[Pd(CNC_6H_5)\{As(C_6H_5)_3\}(SCN)_2]$, via substitution reactions between the corresponding *cis*-dichloro and *trans*-diiodo derivatives and silver thiocyanate in chloroform solution, are described. Molecular weight, conductivity, near and far infrared (solid state and solution) and solution visible-ultraviolet data are presented for each of the complexes. The thiocyanate complexes were generally isolated as the *cis*-isomer in the solid state but isomerized completely to the *trans*-isomer in chloroform solution. The $[Pd(CNR)_2(SCN)_2]$ complexes contain only *S*-bonded thiocyanates, whereas the $[Pd(CNR)\{P(C_6H_5)_3\}(SCN)_2]$ complexes contain an appreciable number of *N*-bonded groups (most probably sterically induced), especially in the solid state. The decomposition of the complexes involves the formation of bridging thiocyanate groups. It is concluded that the isocyanides function primarily as σ-donors in these complexes, their *trans*-influence being insufficient to promote antisymbiotic behavior on the part of the thiocyanates.

INTRODUCTION

Of the several factors[1] which determine the bonding modes adopted by ambidentate ligands in coordination complexes, none has created greater controversy than the interplay between the electronic and steric effects of other ligands in the coordination sphere, especially those involving the coordinated thiocyanate ion. Turco and Pecile[2] originally ascribed the bonding difference in the complexes $[Pd(SCN)_4]^{2-}$ and *trans*-$[Pd\{P(C_2H_5)_3\}_2(NCS)_2]$ to the relative π-acidities of the phosphorus and sulfur atoms, since the complex *trans*-$[Pd(NH_3)_2(SCN)_2]$ was found to contain "normal" *S*-bonded groups. However, Basolo, *et al.*[3], demonstrated that steric factors alone were sufficient to initiate linkage isomerization of the coordinated thiocyanate group, *e.g.*, $[Pd(\text{diethylenetriamine})SCN]^+$ *vs.* $[Pd(1,1,7,7\text{-tetraethyldiethylenetriamine})NCS]^+$, and suggested that these steric factors could also be used[4] to explain the bonding pattern observed in palladium(II) and platinum(II) thiocyanate

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complexes containing phosphines, arsines, and stibines. Although two sets of palladium(II) complexes have subsequently been prepared wherein the bonding mode differences observed can be ascribed solely to electronic effects, *i.e.*, [Pd(2,2′-bipyridine)$(NCS)_2$][4] *vs.* [Pd(4,4′-dimethyl-2,2′-bipy)(SCN)(NCS)][5] and [Pd(1,10-phenanthroline) $(SCN)_2$][4] *vs.* [Pd(5-NO_2-1,10-phen) $(NCS)_2$][6], the results of more recent studies[7] involving palladium(II) thiocyanate complexes containing ligands with Group VA donor atoms have offered considerable support for a bonding mode rationale based predominantly on steric effects.

Two other observations have cast doubts upon Turco and Pecile's original π-acceptor hypothesis. Based on the results of molecular orbital calculations, Gutterman and Gray[8] have concluded that the thiocyanate ion functions only as a donor group when coordinated to the $Co(CN)_5^{2-}$ moiety, *i.e.*, as a $\sigma + \pi$ donor when *S*-bonded but only as a σ donor when *N*-bonded. This is completely in accord with the positions generally occupied by thiocyanate in the spectrochemical series: low in ligand field strength when *S*-bonded, intermediate when *N*-bonded. Secondly, there has been severe criticism[9-11] of the entire concept of considering trialkyl- and triarylphosphines to be π-acceptor ligands in platinum(II) complexes.

However, compelling evidence for a specific π-bonding effect on the bonding mode of the selenocyanate ion has been presented[12,13] in the comparison afforded by the complexes *trans*-$[Rh\{P(C_6H_5)_3\}_2(CO)NCSe]$ and *trans*-$[Pd\{P(C_6H_5)_3\}_2(SeCN)_2]$ (unfortunately, both of the corresponding thiocyanate complexes contain *N*-bonded groups). Indeed, this comparison serves as an excellent example of the general antisymbiotic *trans*-influence in class b complexes recently discussed by Pearson[14]. Since there is no reason to presuppose that the thiocyanate ion should be immune to this influence, we have sought to synthesize *cis* and *trans* palladium(II) thiocyanate complexes containing neutral ligands which have strong, generally accepted π-acidity, minimal steric requirements, and exert a strong *trans*-influence. The recently reported[15] palladium(II) isocyanide complexes of the types *cis*-$[Pd(CNR)_2Cl_2]$, *trans*-$[Pd(CNR)_2I_2]$, and *cis*-$[Pd(CNR)(L)Cl_2]$ appeared to provide an ideal set of substrates for this endeavor.

EXPERIMENTAL

Preparation of starting materials

The following starting materials, ligands, and complexes were prepared according to published procedures: potassium t-butoxide[16], phenyl isocyanide[17], *p*-nitroformanilide[18], *p*-nitrophenylisocyanide[17], *cis*-$[Pd(CNR)_2Cl_2]$[15], *trans*-$Pd(CNR)_2I_2]$[15] and *cis*-$[Pd(CNR)(L)Cl_2]$[15] [RNC $= C_6H_5NC$, $C_6H_{11}NC$, and *p*-$O_2NC_6H_4NC$; $L = P(C_6H_5)_3$ and $As(C_6H_5)_3$]. Satisfactory carbon and hydrogen analyses were obtained for the palladium(II) complexes. Cyclohexyl isocyanide was purchased from the Aldrich Chemical Co., Inc.

Preparation of $[Pd(CNR)_2(SCN)_2]$ and $[Pd(CNR)(L)(SCN)_2]$ complexes

One mmole of the appropriate $[Pd(CNR)_2Cl_2]$, $[Pd(CNR)_2I_2]$ or $[Pd(CNR)(L)Cl_2]$ complex was dissolved in 40 ml of Spectrograde chloroform. To this solution was added an excess of silver thiocyanate (slightly more than 2 mmoles for the chloro derivatives, 4 mmoles for the iodo derivatives). After stirring the mixture

(2 h for the chloro complexes, 13 h for the iodo complexes) the precipitated silver halide and excess silver thiocyanate were removed by filtration. The product was precipitated by adding at least 200 ml of petroleum ether to the clear yellow filtrates. The precipitate was allowed to settle for 15–30 min, isolated by filtration, washed with petroleum ether, and dried *in vacuo* over calcium chloride. The percent yields, colors, and melting points, as well as molecular weight, analytical and conductivity data for the resulting complexes are presented in Table 1. Of the thiocyanate complexes whose preparations were attempted, only $[Pd(p\text{-}O_2NC_6H_4NC)_2(SCN)_2]$ and $[Pd(p\text{-}O_2NC_6H_4NC)\{As(C_6H_5)_3\}(SCN)_2]$ failed to give satisfactory analytical results.

Physical measurements

Solid state survey spectra of all complexes in the 4000–400 cm^{-1} range were measured on a Perkin–Elmer Model 337 grating spectrophotometer. The complexes were held in a Nujol suspension between potassium bromide plates. High resolution solid state and chloroform solution spectra of the complexes were obtained with a Perkin–Elmer Model 180 spectrophotometer in a five-fold abscissa wave number scale expansion. For the solid state spectra, the Nujol mull technique was used with potassium bromide plates for the isocyanide and thiocyanate CN stretching range (2300–2000 cm^{-1}). Cesium iodide plates were used for measuring the spectra in the palladium halide and palladium thiocyanate stretching range (400–200 cm^{-1}). Matched 0.1 mm potassium bromide cells were used for the solution measurements. The integrated absorption intensities of the N–C stretching bands of the isocyanide and thiocyanate ligands in the complexes were determined by Ramsay's method of direct integration[19]. Visible-ultraviolet spectra of the complexes were measured as chloroform solutions on a Cary 14 spectrophotometer using 1 cm quartz cells.

Molar conductances of the complexes were determined with an Industrial Instruments, Inc., Model RC-16B2 conductivity bridge and a cell with platinized electrodes. Molecular weight determinations, as well as the carbon, hydrogen, and nitrogen microanalyses were carried out by the Alfred Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, West Germany. Melting points were determined with a Fisher–Johns melting point apparatus, and are uncorrected.

RESULTS

Near and far infrared solid state and chloroform solution data for the chloro, iodo, and thiocyanate complexes are shown in Tables 2–4. Visible-ultraviolet data for chloroform solutions of the complexes are given in Tables 5 and 6.

DISCUSSION

Geometric structure of the complexes

Dissociation of the thiocyanate complexes in nitrobenzene is minimal, as shown by the Λ_m values (Table 1), all of which are characteristic of non-electrolytes. Likewise, the results of the molecular weight determinations (Table 1) clearly show that, with the possible exception of $[Pd(p\text{-}O_2NC_6H_4NC)\{P(C_6H_5)_3\}(SCN)_2]$, there is no aggregation of the complexes in chloroform solution.

TABLE 1

PERCENT YIELDS, COLORS, MELTING POINTS, MOLECULAR WEIGHT, ANALYTICAL AND CONDUCTIVITY DATA FOR THE THIOCYANATE COMPLEXES

Complex	*Yield* (%)	*Color*	*M.p.* (°C)	*Mol. wt.*[f] *found* (*calcd.*)	*Analyses Found* (*calcd*) (%)			Λ_m[g] *ohm*$^{-1}$ *cm*^{2}·*mol*$^{-1}$
					C	*H*	*N*	
$[Pd(CNC_6H_5)_2(SCN)_2]$[a]	82	pale yellow	136	423 (429)	44.71 (44.82)	2.47 (2.35)	13.21 (13.06)	1.07
$[Pd(CNC_6H_5)_2(SCN)_2]$[b]	75	pale yellow	132	424 (429)	44.64 (44.82)	2.26 (2.35)	12.90 (13.06)	0.81
$[Pd(CNC_6H_5)\{P(C_6H_5)_3\}(SCN)_2]$[a]	76	yellow- orange	90[c]	589 (588)	54.97 (55.15)	3.55 (3.43)	7.34 (7.15)	1.03
$[Pd(CNC_6H_5)\{As(C_6H_5)_3\}(SCN)_2]$[a]	40	yellow- orange	95[d]	628 (632)	48.65 (51.32)	3.50 (3.19)	7.32 (6.65)	3.32
$[Pd(CNC_6H_{11})_2(SCN)_2]$[a]	52	pale yellow	74	431 (441)	43.50 (43.59)	4.89 (5.03)	12.55 (12.71)	0.82
$[Pd(CNC_6H_{11})_2(SCN)_2]$[b]	47	pale yellow	74	433 (441)	43.69 (43.59)	5.09 (5.03)	12.59 (12.71)	0.94
$[Pd(CNC_6H_{11})\{P(C_6H_5)_3\}(SCN)_2]$[a]	45	yellow	119	584 (594)	54.47 (54.59)	4.51 (4.41)	6.89 (7.07)	1.87
$[Pd(p\text{-}O_2NC_6H_4NC)\{P(C_6H_5)_3\}(SCN)_2]$[a]	72	yellow- orange	165[e]	672 (633)	51.13 (51.23)	3.14 (2.81)	9.02 (8.85)	0.51

[a] Prepared from chloro derivative. [b] Prepared from iodo derivative. [c] Darkening at 70°. [d] Darkening at 85° [e] Darkening at 120°. [f] Determined by osmometry, chloroform solution. [g] 10^{-3} *M* nitrobenzene solutions at 25°.

TABLE 2

SOLID STATE (NUJOL MULL) AND CHLOROFORM SOLUTION INFRARED DATA FOR THE $[Pd(CNR)_2X_2]$ AND $[Pd(CNR)(L)X_2]$ COMPLEXES

Compound	*Isocyanide N–C stretch, (cm^{-1})*		$A^a \times 10^{-4}$ $(M^{-1}\ cm^{-2})$
	Solid	*Solution*	
$[Pd(CNC_6H_5)_2Cl_2]$	2222	2215	1.6
	2240	2233	2.8
$[Pd(CNC_6H_5)_2I_2]$	2203	2201	5.9
$[Pd(CNC_6H_{11})_2Cl_2]$	2241	2234	2.1
	2258	2250	2.6
$[Pd(CNC_6H_{11})_2I_2]$	2219	2220	6.1
$[Pd(CNC_6H_5)\{P(C_6H_5)_3\}Cl_2]$	2210	2208	4.0
$[Pd(CNC_6H_5)\{As(C_6H_5)_3\}Cl_2]$	2202	2204	6.5
$[Pd(CNC_6H_{11})\{P(C_6H_5)_3\}Cl_2]$	2235	2228	4.6
$[Pd(p\text{-}O_2NC_6H_4NC)\{P(C_6H_5)_3\}Cl_2]$	2202	2200	4.2
C_6H_5NC	2124^b	2130	^{c}
$C_6H_{11}NC$	2135^b	2143	^{c}
$p\text{-}O_2NC_6H_4NC$	2116	2124	^{c}

[a] Integrated absorption intensity of N–C stretching band, calculated per mole of coordinated isocyanide [b] Liquid film [c] Not determined

The existence[15] of the $[Pd(CNR)_2X_2]$ complexes as *cis*-dichloro complexes and *trans*-diiodo complexes, both in the solid state and in solution, serves as yet another example of Pearson's antisymbiotic *trans*-influence principle, *i.e.*, two soft ligands in mutual *trans*-position will have a destabilizing effect on each other when attached to class b metal atoms, resulting in antisymbiotic behavior[14]. Thus, the relatively hard chloride ions preferentially bond *trans* to the strongly *trans*-directing isocyanide groups (doublet ν(NC) bands are found in both the solid state and solution infrared spectra, see Table 2). In the *trans*-diiodo complexes (note the singlet ν(NC) bands, Table 2), both ligands exert strong *trans*-influences, thereby negating the predictive value of the principle in this particular case. However, as predicted by the principle, the $[Pd(CNR)(L)Cl_2]$ complexes exhibit *cis*-geometry in the solid state, as evidenced by their doublet ν(Pd–Cl) bands[15]. It should be noted that steric interactions resulting from the larger size of the iodide ion may play a role in determining the *trans*-geometry observed for the diiodo complexes.

In this context, the behavior exhibited by the thiocyanate complexes is indeed surprising. Regardless of whether the *cis*-dichloro or *trans*-diiodo complexes were used as the substrates, the $[Pd(CNR)_2(SCN)_2]$ complexes isolated in the solid state exhibited predominantly *cis* geometry (doublet ν(NC), ν(CN), and ν(Pd–SCN) bands, see Tables 3 and 4), but isomerized completely to the *trans*-configuration in chloroform solution (singlet ν(NC) and ν(CN) bands, see Table 3. The $[Pd(CNC_6H_5)(L)(SCN)_2]$ complexes also exhibited *cis*-geometry in the solid state (doublet ν(Pd–SCN) bands, Table 4), whereas the remaining two $[Pd(CNR)\{P(C_6H_5)_3\}(SCN)_2]$ complexes apparently were isolated as the *trans*-isomers (singlet ν(Pd–SCN) bands, Table 4). Based on their singlet thiocyanate ν(CN) bands, (Table 3) all four complexes exist as the *trans*-isomer in chloroform solution. The source of the bands at ca. 2150 and < 2100 cm^{-1} in the infrared spectra of these complexes will be discussed below.

Different preparations of the $[Pd(CNC_6H_5)_2(SCN)_2]$ complex sometimes resulted in the isolation of a solid which contained varying amounts of the *trans* isomer. The slight differences in the data shown in Tables 3, 4 and 6 for the dithiocyanato complexes prepared from both dichloro and diiodo substrates are within experimental error, *i.e.*, the same dithiocyanato complexes were formed using either substrate. The existence of the *cis*-dithiocyanato complexes in the solid state may also be rationalized in terms of Pearson's antisymbiotic relationship. The isolation of a *cis*-$[PdL_2X_2]$ complex of any kind (where L is a monodentate ligand) under any circumstances is highly unusual [see, for example ref. 20.] However, the initial isolation of *cis*-$[PtL_2X_2]$ species, due to the kinetic *trans*-effects of the L ligands, followed by isomerization to the *trans*-isomer in solution (frequently under reflux) is not uncommon [see, for example ref. 21]. Significantly, those *cis*-$[PtL_2X_2]$ complexes which do not undergo subsequent *cis*→*trans* isomerization frequently involve ligands which exhibit a large difference in their hard/soft character, *e.g.*, *cis*-$[Pt(P(C_6H_5)_3)_2Cl_2]$.

TABLE 3

SOLID STATE (NUJOL MULL) AND CHLOROFORM SOLUTION INFRARED DATA FOR THE $[Pd(CNR)_2(SCN)_2]$ AND $[Pd(CNR)(L)(SCN)_2]$ COMPLEXES

Compound	*Isocyanide N–C stretch (cm^{-1})*		$A^a \times 10^{-4}$ $(M^{-1}\ cm^{-2})$	*Thiocyanate stretch C–N (cm^{-1})*		$A^b \times 10^{-4}$ $(M^{-1}\ cm^{-2})$
	Solid	*Solution*		*Solid*	*Solution*	
$[Pd(CNC_6H_5)_2(SCN)_2]^c$	2223 2235	2214	3.6	2128 2132^e	2120	2.0
$[Pd(CNC_6H_5)_2(SCN)_2]^d$	2223 2235	2214	3.8	2128	2120	2.1
$[Pd(CNC_6H_{11})_2(SCN)_2]^c$	2231 2255	2232	3.4	2092^e 2114^e 2121	2120	2.1
$[Pd(CNC_6H_{11})_2(SCN)_2]^d$	2232 2254	2232	3.6	2092^e 2113^e 2121	2120	2.3
$[Pd(CNC_6H_5)\{P(C_6H_5)_3\}(SCN)_2]^c$	2205 2150^f	2208 2152^f	g	2080^e 2108	2100^e 2112	g
$[Pd(CNC_6H_5)\{As(C_6H_5)_3\}(SCN)_2]^c$	2205 2145^f	2206 2154^f	g	2090^e 2110	2114	2.7
$[Pd(CNC_6H_{11})\{P(C_6H_5)_3\}(SCN)_2]^c$	2232	2230	3.4	2061 2115	2096^e 2113	g
$[Pd(p\text{-}O_2NC_6H_4NC)\{P(C_6H_5)_3\}(SCN)_2]^c$	2202 2146^f	2200 2150^f	g	2086^e 2110	2090^e 2113	g
KNCS	—	—	—	—	2060^h	4.4^h

[a] Integrated absorption intensity of N–C stretching band, calculated per mole of coordinated isocyanide [b] Integrated absorption intensity of C–N stretching band, calculated per mole of coordinated thiocyanate [c] Prepared from chloro derivative. [d] Prepared from iodo derivative. [e] Shoulder [f] Weak absorption band [g] Could not be determined [h] Butanone solution; data taken from ref. 27

TABLE 4

SOLID STATE (NUJOL MULL) FAR INFRARED DATA FOR THE [Pd(CNR)$_2$(SCN)$_2$] AND [Pd (CNR) (L) (SCN)$_2$] COMPLEXES

Complex	*Pd–S stretch* (*cm*$^{-1}$)
[Pd(CNC$_6$H$_5$)$_2$(SCN)$_2$][a]	289, 302
[Pd(CNC$_6$H$_5$)$_2$(SCN)$_2$][b]	290, 302
[Pd(CNC$_6$H$_{11}$)$_2$(SCN)$_2$][a]	292, 305
[Pd(CNC$_6$H$_{11}$)$_2$(SCN)$_2$][b]	292, 305
[Pd(CNC$_6$H$_5$) {P(C$_6$H$_5$)$_3$} (SCN)$_2$][a]	273, 302[c]
[Pd(CNC$_6$H$_5$) {As(C$_6$H$_5$)$_3$} (SCN)$_2$][a]	279, 303
[Pd(CNC$_6$H$_{11}$) {P(C$_6$H$_5$)$_3$} (SCN)$_2$][a]	277[d]
[Pd(*p*-O$_2$NC$_6$H$_4$NC) {P(C$_6$H$_5$)$_3$} (SCN)$_2$][a]	272

[a]Prepared from chloro derivative [b]Prepared from iodo derivative [c]Pd–N stretch at 343 cm^{-1} [d]Pd–N stretch at 330 cm^{-1}

The above band assignments were made by comparing the far infrared spectra of the thiocyanate complexes with those of the corresponding chloro and iodo complexes It should be noted, however, that definitive Pd–S stretching vibration assignments cannot be made in the presence of Pd–P bonds without appropriate isotopic substitutions.

TABLE 5

VISIBLE-ULTRAVIOLET SPECTRA FOR CHLOROFORM SOLUTIONS OF [Pd(CNR)$_2$X$_2$] AND [Pd(CNR) (L)X$_2$] COMPLEXES

Complex	λ_{max}(*nm*)	$\varepsilon_{max}\times10^{-3}$($M^{-1}$ *cm*$^{-1}$)
[Pd(CNC$_6$H$_5$)$_2$I$_2$]	5160(sh)	0.09
	4200(sh)	1.2
	3540	10.0
	3160(sh)	4.0
	2600(sh)	53
	2480	64
[Pd(CNC$_6$H$_{11}$)$_2$Cl$_2$]	3190	0.90
[Pd(CNC$_6$H$_{11}$)$_2$I$_2$]	4210(sh)	1.1
	3470	10.5
	2900(sh)	21.5
	2650	37
	2480	36
[Pd(CNC$_6$H$_5$) {P(C$_6$H$_5$)$_3$} Cl$_2$]	3350sh	4.2
	2800sh	15
[Pd(CNC$_6$H$_5$) {As(C$_6$H$_5$)$_3$} Cl$_2$]	3610sh	2.5
	2450	39.5
[Pd(CNC$_6$H$_{11}$) {P(C$_6$H$_5$)$_3$} Cl$_2$]	4460sh	0.06
	3270sh	5.0
	2730	12.7
	2380	16
[Pd(*p*-O$_2$NC$_6$H$_4$NC) {P(C$_6$H$_5$)$_3$} Cl$_2$]	3370sh	13.7
	2730	25

TABLE 6

VISIBLE-ULTRAVIOLET SPECTRA FOR CHLOROFORM SOLUTIONS OF [Pd(CNR)$_2$(SCN)$_2$] AND [Pd(CNR) (L) (SCN)$_2$] COMPLEXES

Complex	$\lambda_{max}(nm)$	$\varepsilon_{max} \times 10^{-3}$ $(M^{-1}\ cm^{-1})$
[Pd(CNC$_6$H$_5$)$_2$(SCN)$_2$][a]	4500(sh)	0.09
	3160	14.5
	2830	28
	2600(sh)	37
[Pd(CNC$_6$H$_5$)$_2$(SCN)$_2$][b]	4340(sh)	0.015
	3150	16
	2830	30.5
	2600(sh)	37
[Pd(CNC$_6$H$_{11}$)$_2$(SCN)$_2$][a]	4390(sh)	0.12
	3040	23
	2640	30
[Pd(CNC$_6$H$_{11}$)$_2$(SCN)$_2$][b]	4370(sh)	0.11
	3040	24.3
	2640	31
[Pd(CNC$_6$H$_5$) {P(C$_6$H$_5$)$_3$} (SCN)$_2$][a]	3150(sh)	14
	2780	31.5
[Pd(CNC$_6$H$_5$) {As(C$_6$H$_5$)$_3$} (SCN)$_2$][a]	3180(sh)	13
[Pd(CNC$_6$H$_{11}$) {P(C$_6$H$_5$)$_3$} (SCN)$_2$][a]	3650(sh)	3
	3090	13
[Pd(*p*-O$_2$NC$_6$H$_4$NC) {P(C$_6$H$_5$)$_3$} (SCN)$_2$][a]	2850	24.3

[a] Prepared from chloro derivative [b] Prepared from iodo derivative.

Bonding modes of the thiocyanate groups

There is little doubt that the [Pd(CNR)$_2$(SCN)$_2$] complexes contain predominantly *S*-bonded thiocyanates, both in the solid state and in solution. Evidence in support of this conclusion includes the following: the high frequency ($>2100\ cm^{-1}$) thiocyanate ν(CN) bands which exhibit integrated absorption intensities (Table 3) which are smaller than that of the free ion, the frequencies of the ν(Pd–SCN) bands (Table 4), and the low energy ligand field bands (see data for *N*- and *S*-bonded thiocyanates in ref. 22, 23 and 24, respectively) of the thiocyanate complexes (Table 6; compare with the visible-ultraviolet spectra of the chloro and iodo complexes in Table 5). The broad, weak shoulder at 2092 cm^{-1} (Table 3) in the solid state infrared spectrum of the [Pd(CNC$_6$H$_{11}$)$_2$(SCN)$_2$] complex suggests the presence of a trace amount of the *N*-isomer[22], which isomerizes upon dissolution in chloroform.

Significantly, the introduction of the bulkier triphenylphosphine ligand resulted in the formation of an appreciable number of *N*-bonded thiocyanate groups in the [Pd(CNR) {P(C$_6$H$_5$)$_3$}-(SCN)$_2$] complexes, both in the solid state and in solution, as evidenced[22,23] by the appearance of broad thiocyanate ν(CN) bands $\leqslant 2100$ cm^{-1} (Table 3) and higher frequency ν(Pd–NCS) bands (Table 4). Indeed the two solid state ν(CN) bands for these complexes have the appearance characteristic[7] of a mixed bonding mode complex, *i.e.*, [Pd(CNR) {P(C$_6$H$_5$)$_3$} (SCN)NCS]. The proportion of *N*-bonded groups diminished, however, to a great extent upon dissolution in chloroform.

Additional weak absorption bands were found at ca. 2150 cm^{-1} in the solid state and solution infrared spectra of most of the [Pd(CNR)(L)(SCN)$_2$] complexes. Since they do not coincide with the ν(NC) bands of any of the free isocyanides (see Table 2), their most logical source would appear to be the ν(CN) bands of bridging thiocyanates in complexes of the type:

The concentrations of these impurities are apparently too low to adversely affect the analytical results. Burmeister and Weleski[25] have reported a similar ν(CN) frequency of 2156 cm^{-1} for the bridging thiocyanates in the complex [Pd$_2${P(C$_6$H$_5$)$_3$}$_2$(SCN)$_2$Cl$_2$].

In an attempt to induce linkage isomerization, all of the complexes were heated at 56 or 100°, depending on their melting points (Table 1), in the solid state and in refluxing chloroform. In all cases, the solids or solutions darkened in color, the dominant change in the infrared spectra being the pronounced growth of bands at ca. 2150 cm^{-1}, indicating that the formation of thiocyanate bridges is involved in the decomposition of the complexes. No *N*-bonding was initiated by heating any of the complexes.

Overview of observed bonding pattern

In retrospect, the failure of the isocyanide ligands to induce a *cis*-geometry and/or *N*-bonding in the iodo and thiocyanate complexes must be traced to the inability of the isocyanides to exert their full π-acceptor capacity in these palladium(II) complexes. The fact that the ν(NC) frequencies of the complexed isocyanides are higher than those of the free ligands in all of these complexes (Tables 2 and 3), whereas the ν(NC) frequencies of isocyanides complexed to metals in lower oxidation states are lower than the free ligand values[26], indicates that the isocyanides are functioning primarily as σ-donor ligands in the present case. The resulting *trans*-influence is still strong enough to initiate the formation of *cis*-dichloro complexes, in accordance with Pearson's principle[14], but falls short in the diiodo and dithiocyanato complexes. (The isolation of the *cis*-dithiocyanato complexes in the solid state is undoubtedly a result of the lower solubility of this isomer in the chloroform/petroleum ether solvent mixture.) It should also be pointed out that the solvent effect of chloroform on palladium(II) thiocyanate complexes is to promote *N*-bonding[1]. Thus, one may safely conclude that there is little or no tendency toward *N*-bonding in the [Pd(CNR)$_2$(SCN)$_2$] complexes, and the partial *N*-bonding observed in the [Pd(CNR)(P(C$_6$H$_5$)$_3$)(SCN)$_2$] complexes is most probably sterically induced.

All of the complexes listed in Tables 2 and 3 exhibit decreasing isocyanide ν(NC) frequencies and $\Delta\nu$(NC) values (relative to the free isocyanides) in the order: cyclohexyl > phenyl > *p*-nitrophenyl. The frequency trend parallels that exhibited by the free isocyanides, and reflects the decreasing electron donor character of the substituent groups. Correspondingly, the $\Delta\nu$(NC) trend reflects decreasing σ-donation to the palladium(II). The thiocyanato and chloro complexes exhibit appreciably higher isocyanide ν(NC) frequencies and $\Delta\nu$(NC) values than the iodo complexes, in accord with the greater electronegativities of the former ligands, which create a higher effective positive charge on the palladium. This results in considerably higher integrated absorption intensities (see Tables 2 and 3) for the ν(NC) bands of the iodo complexes, *i.e.*, the weaker and, hence, longer NC bonds in the iodo complexes would give rise to greater changes in the dipole moments of the NC bonds as they vibrate and, hence, more intense ν(NC) bands.

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