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The Effects of Geometric Isomerism on the Linkage Isomers Formed by Dithiocyanatobis(triphenylphosphine or -arsine)platinum(II) Complexes[1]

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The complexes cis-$\mathrm{[PtL_2(SCN)_2]}$*(L =* $\mathrm{P(C_6H_5)_3}$*, As* $\mathrm{(C_6H_5)_3}$*) have been observed to undergo exclusively cis S-bonded→cis N-bonded isomerizations in the solid phase on heating. Raising the temperature of the reactions between* $\mathrm{[Pd(SCN)_4]^{2-}}$ *and* $\mathrm{P(C_6H_5)_3}$ *or As* $\mathrm{(C_6H_5)_3}$ *in solution leads to the isolation of products which contain increasingly larger proportions of the trans N-bonded isomers, which are unaffected by heating in the solid phase. The results of νCN integrated absorption intensity ratio measurements indicate that the complexes cis-*$\mathrm{[PtL_2(SCN)Cl]}$ *(L = a variety of phosphines) and cis-*$\mathrm{[Pt(P(CH_3)_2C_6H_5)_2(CO)SCN]X}$ *(*$\mathrm{X^- = BF_4^-}$ $\mathrm{PF_6^-}$*), previously formulated by Cherwinski and Clark as containing S-bonded thiocyanate groups, actually involve N-bonding in the solid phase.*

Introduction

Cherwinski and Clark[2] recently reported the synthesis of the complexes *cis*-$\mathrm{[PtL_2(SCN)Cl]}$(L = P$\mathrm{(C_2H_5)_3}$, $\mathrm{P(CH_3)_2C_6H_5}$, $\mathrm{P(C_6H_5)_3}$) and *cis*-$\mathrm{[Pt(P(CH_3)_2C_6H_5)_2(CO)SCN]X}$ ($\mathrm{X^- = BF_4^-}$, $\mathrm{PF_6^-}$). They concluded that the thiocyanate groups in these complexes are S-bonded, since their νCN frequencies (Nujol mulls) were found to be $>2100\ \mathrm{cm^{-1}}$ (in the range $2105–2110\ \mathrm{cm^{-1}}$). We found these results to be intriguing, since Burmeister and Basolo[3] had shown that the *trans*-$\mathrm{[Pt(P(C_6H_5)_3)_2(NCS)_2]}$ complex contains N-bonded thiocyanates (νCN at $2097\ \mathrm{cm^{-1}}$, νCS at $859\ \mathrm{cm^{-1}}$, Nujol mull). This conclusion has been recently confirmed in our laboratory[4] by the results of integrated absorption intensity measurements on the νCN band for solutions of the complex in chloroform and dichloromethane. The *trans*-$\mathrm{[Pt(As(C_6H_5)_3)_2(NCS)_2]}$ complex was also found to contain N-bonded groups.[3] Thus, Cherwinski and Clark's conclusions, if correct, would offer further support for the argument that the formation of N-bonded thiocyanates in phosphine- and arsine-containing palladium(II) and platinum(II) complexes is sterically induced,[3,5] as opposed to the π-bonding electronic argument originally proposed by Turco and Pecile.[6] Steric hindrance to the formation of angular Pt–SCN linkages would be expected to be maximized in the *trans*-complex, since two bulky phosphines are adjacent to each thiocyanate, as opposed to only one in the *cis* isomer. On the other hand, the effects of π-withdrawal by the phosphines which, according to Turco and Pecile,[6] tend to promote N-bonded thiocyanates, would be expected to be maximized in the *cis*-complex, since two metal d_π orbitals would be shared by each phosphine/thiocyanate pair, as opposed to only one d_π orbital in the *trans*-isomer. We therefore have investigated the effects of geometric isomerism on the bonding modes adopted by the thiocyanate groups in the $\mathrm{[Pt(P(C_6H_5)_3)_2(CNS)_2]}$ and $\mathrm{[Pt(As(C_6H_5)_3)_2(CNS)_2]}$ complexes in the solid state.[7] The results of these studies indicate that Cherwinski and Clark's bonding mode assignments are incorrect.

Experimental Section

Preparation of Complexes

$\mathrm{[Pt(P(C_6H_5)_3)_2(CNS)_2]}$ and $\mathrm{[Pt(As(C_6H_5)_3)_2(CNS)_2]}$ were prepared at room temperature and at −78° according to the method of Burmeister and Basolo.[3] All four complexes gave satisfactory C, H, and N analyses.

The complex *cis*-$\mathrm{[Pt(P(C_6H_5)_3)_2Cl_2]}$ was prepared by Jensen's method,[8] and was subsequently used to prepare *cis*-$\mathrm{[Pt(P(C_6H_5)_3)_2(CNS)Cl]}$, as described by Cherwinski and Clark.[2] *Anal.* Calcd for $\mathrm{C_{37}H_{30}ClNP_2SPt}$: C, 54.7; H, 3.7. Found: C, 53.98; H, 3.41.

Physical Measurements

High resolution solid state (Nujol mull) infrared spectra of the complexes in the thiocyanate νCN range ($2300–2000\ \mathrm{cm^{-1}}$) were measured with a Perkin Elmer Model 180 spectrophotometer. Five-fold and ten-fold wave number scale expansions were employed. The relative integrated absorption intensity of the νCN band of the *cis*-$\mathrm{[Pt(P(C_6H_5)_3)_2(CNS)Cl]}$ complex in the solid state was determined by a modification of Bailey's method,[9,10] using salicylic acid as an internal standard. Weighed amounts of the complex, the standard, and KBr were thoroughly mixed. A sample of this mixture was pressed into a disk and used to record the infrared spectrum. The approximate areas of the νCN and standard bands were measured as the products of the band widths at half band height times the band heights at maximum absorbance. These areas were then corrected for concentration and expressed as a ratio, as follows:

$$\text{Ratio} = (A_{\text{sample}}/n)\,(mw_{\text{sample}}/x)/(A_{\text{standard}})\,(1000/y) \quad (1)$$

where A_{sample} = area under νCN of sample, A_{standard} = area under νCO of salicylic acid at 1612 cm^{-1}, n = number of moles of SCN^-/mole of sample, x = g of sample used in mixture, and y = g of salicylic acid used in mixture.

Carbon, hydrogen, and nitrogen microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Elbach–über–Engelskirchen, West Germany.

Results and Discussion

The –78° preparation of the $[Pt(P(C_6H_5)_3)_2(CNS)_2]$ complex yielded only the *cis* S-bonded isomer (sharp νCN doublet at 2120, 2122 cm^{-1}). The room temperature preparation of the complex yielded a solid which exhibited a broad, intense νCN band at 2094 cm^{-1}, with the 2120, 2122 cm^{-1} doublet present as a shoulder.

Heating the two samples in the solid state produced strikingly different results. The pure *cis* S-bonded sample, when heated at 132° for 1.5 h, isomerized to a complex which exhibited a broad νCN band at 2106 cm^{-1}. The sample prepared at room temperature was heated at 156° for 1 h. The νCN band at 2094 cm^{-1} initially present was essentially unaffected by this treatment, but the 2120, 2122 cm^{-1} νCN doublet was again replaced by the νCN band at 2106 cm^{-1}.

As mentioned above, the 2120, 2122 cm^{-1} νCN doublet is most certainly correctly assigned to the *cis* S-bonded isomer. On heating in the solid state, this isomerizes to the *cis* N-bonded isomer, to which the broad νCN band at 2106 cm^{-1} is assigned. The broad νCN band at 2094 cm^{-1} which is exhibited by the sample prepared at room temperature is therefore assigned to the *trans* N-bonded isomer, in agreement with our earlier studies.[3,4] Apparently, neither the *cis* S-bonded→*trans* N-bonded nor the *cis* N-bonded →*trans* N-bonded isomerizations occur to any noticeable degree in the solid state at the temperatures utilized in this study.

The behaviour of the $[Pt(As(C_6H_5)_3)_2(CNS)_2]$ complex differed only in degree, not in kind. The sample prepared at –78° exhibited a sharp νCN doublet at 2120, 2124 cm^{-1}, characteristic of the *cis* S-bonded isomer, plus an equally intense, broad νCN band at 2087 cm^{-1}. The solid isolated at room temperature exhibited a less intense 2120, 2124 cm^{-1} νCN doublet and a more intense 2087 νCN band. Much longer heating periods were required to create spectral changes comparable to those exhibited by the phosphine complex. In both samples, the 2087 cm^{-1} νCN band was unaffected by the heat treatment. The 2120, 2124 cm^{-1} νCN doublet in the spectrum of both samples was replaced by a strong, broad band at 2105 cm^{-1} after being heated at 156° for 42 h and 36 h, respectively, for the samples prepared at –78° and room temperature.

The νCN band at 2105 cm^{-1} is therefore assigned to the *cis* N-bonded isomer and that at 2087 cm^{-1} is assigned to the *trans* N-bonded isomer, in agreement with our earlier study.[3] As in the case of the phosphine complex, only a *cis* S-bonded→*cis* N-bonded isomerization was observed to take place in the solid state.

The initial formation of the *cis* isomer in solution in the reaction between $[Pd(SCN)_4]^{2-}$ and $P(C_6H_5)_3$ or $As(C_6H_5)_3$ is favored by the strong antisymbiotic *trans* effects[11] of the phosphine and arsine, with the former being the stronger of the two. Conversely, subsequent isomerization to the *trans* isomer in solution is promoted by the steric requirements of the bulky phosphine and arsine, with the latter being the greater of the two. Thus, it is not surprising that even the arsine complex isolated at –78° contains a large proportion of the *trans* isomer. In this context, it should be pointed out that the more labile $[PdL_2X_2]$ complexes are generally isolated as the *trans* isomer,[12] significant exceptions being found in the *cis*-$[Pd(As(CH_3)_3)_2X_2]$[12] and *cis*-$[Pd(CNR)_2Cl_2]$[13] complexes.

The slower rate of *cis* S-bonded→*cis* N-bonded isomerization observed for the arsine complex would be predicted on either steric[3,5] or electronic[3,6] grounds. Thus, it is possible to isolate a pure S-bonded *trans*-$[Pd(As(C_6H_5)_3)_2(SCN)_2]$ complex[3] at –78° (isomerization to the N-bonded isomer takes place in the solid state on heating[3]), whereas only N-bonded *trans*-$[Pd(P(C_6H_5)_3)_2(NCS)_2]$ can be isolated, even at –78°.[14]

In view of the fact that the νCN frequency exhibited by *cis*-$[Pt(P(C_6H_5)_3)_2(NCS)_2]$ (2106 cm^{-1}) falls precisely into the range observed by Cherwinski and Clark[2] for their *cis*-$[PtL_2(SCN)Cl]$ and *cis*-$[PtL_2(CO)SCN]^+$ complexes (2105–2110 cm^{-1}), their conclusion that the thiocyanates are S-bonded appeared to us to be questionable. Accordingly, we have determined the solid state integrated absorption intensity ratio of the νCN band at 2106 cm^{-1} in the infrared spectrum of *cis*-$[Pt(P(C_6H_5)_3(CNS)Cl]$. The value obtained (3.3), when compared with the ratio values for thiocyanate complexes of known bonding mode (see Table I) clearly shows that, in point of fact, the

TABLE I. Solid state integrated absorption intensity ratios[a] for the νCN bands of thiocyanate complexes.

Complex	νCN Integrated absorption Intensity Ratio	Bonding Mode of Thiocyanate
$K_2[Pt(SCN)_4]$	0.44	Pt–SCN
trans-$[Co(py)(dmg)_2SCN]$	0.60	Co–SCN
trans-$[Pd(As(C_6H_5)_3)_2(SCN)_2]$	0.73	Pd–SCN
trans-$[Pd(Sb(C_6H_5)_3)_2(SCN)_2]$	0.81	Pd–SCN
$[Pten(SCN)_2]$	0.87	Pt–SCN
$K_2[Pd(SCN)_4]$	0.92	Pd–SCN
$[Pden(SCN)_2]$	0.93	Pd–SCN
$Hg[Co(NCS)_4]$	1.3	Co–SCN–Hg
trans-$[Co(py)(dmg)_2NCS]$	2.6	Co–NCS
trans-$[Pd(P(C_6H_5)_3)_2(NCS)_2]$	3.0	Pd–NCS
cis-$[Pt(P(C_6H_5)_3)_2Cl(NCS)]$	3.3	Pt–NCS

[a] See Experimental Section for definition. Abbreviations: py = pyridine, dmg = dimethylglyoximate, en = ethylenediamine.

thiocyanate group is N-bonded in this complex, and is most probably N-bonded in the others as well.*

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* In response to questions raised by the referees, it should be pointed out that, although the *frequencies* of the νCS and δNCS bands of coordinated thiocyanates are generally better indicators of bond type than the νCN frequency,[10] their utility in this study was severely hampered by the presence of interfering absorption bands due to the triphenylphosphine and -arsine ligands. As seen in the infrared spectra of the corresponding chloro complexes, several bands are spread throughout the entire δNCS range (*ca.* 400–490 cm^{-1}), and the S-bonded νCS range (680–720 cm^{-1}) is obliterated by strong phenyl absorption. Only very weak interfering bands occur in the N-bonded νCS range, but the νCS bands that appear at *ca.* 860 cm^{-1} in the spectra of the $[Pt(Z(C_6H_5)_3)_2(NCS)_2]$ complexes[3] (Z = P, As) are rather weak and broad themselves, and are ill-suited for the observation of spectral changes accompanying the transformations discussed herein. Although the *cis*-splittings of the νCN bands observed in this study are very small, they are quite comparable to those observed for *cis*-$[Pt(Sb(C_6H_5)_3)_2(SCN)_2]$[3] ($\nu$CN at 2123, 2120 cm^{-1}), *cis*-$[Pd(CNC_6H_5)_2(SCN)_2]$ (νCN at 2132, 2128 cm^{-1}) [R.R. Cooke and J.L. Burmeister, *J. Organometal. Chem., 63,* 471 (1973)], and [Pd(2,2′-bipyridine)$(SeCN)_2$] (νCN at 2116, 2112 cm^{-1}) [J.L. Burmeister and M.Y. Al–Janabi, *Inorg. Chem., 4,* 962 (1965)], to cite but a few cases in point.