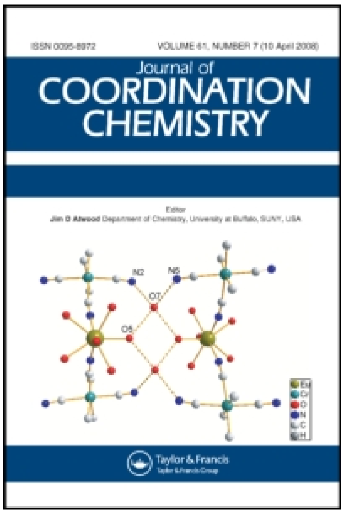

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Henry J. Gysling[a]; Louis J. Gerenser[a]; M. Gary Mason[a]
[a] Research Laboratories, Eastman Kodak Company, Rochester, New York

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AN N-BONDED Cu(I) THIOCYANATE COMPLEX: ISOTHIOCYANATO-(1,1,1,-TRIS(DIPHENYL-PHOSPHINOMETHYL)ETHANE) COPPER(I)

HENRY J. GYSLING, LOUIS J. GERENSER, and M. GARY MASON

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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The complex $[Cu(((C_6H_5)_2PCH_2)_3CCH_3)(NCS)]$ has been prepared and characterized by infrared, PMR, and X-ray photoelectron spectroscopy. It has been formulated as a mixture of N- and S-bonded isomers in the solid state, the ratio of the isomers depending on the conditions of isolation of the complex as well as the sampling technique used for the infrared spectral measurements (i.e., mull vs. KBr pellet). In $CHCl_3$ solution the complex exists exclusively as the N-bonded isomer, although PMR spectroscopy indicates that a rapid exchange of the phosphorus sites of the ligand occurs at room temperature.

The complex $[Cu(P(C_6H_5)_3)_2SCN]_2$, in contrast, is formulated as a dimeric species in the solid state with two bridging thiocyanates. In $CHCl_3$ solution, however, the bridges cleave to give exclusively the N-bonded monomeric three-coordinate complex.

INTRODUCTION

Although a large number of thiocyanate complexes of transition metals and lanthanides have been prepared and characterized with respect to the bonding mode of the ambidentate pseudohalide ligand,[1] relatively few such complexes of Cu(1) have been reported.[2] In those cases where the bonding mode of the thiocyanate ligand has been proposed on the basis of infrared spectroscopy, dimeric structures with bridging thiocyanate ligands have generally been formulated. Unlike the wide variety of halo complexes formed with organophosphine ligands (i.e., $[(CuX)_aP_b]$; $a = 1, b = 1–3; a = 2, b = 3$),[3] cuprous thiocyanate has a marked tendency to form thiocyanate-bridged dimeric complexes even when excess phosphine is used in the synthesis (i.e., $[P_2Cu(\mu\text{-}SCN)_2CuP_2]$).[2c] An apparent exception to this bonding pattern is the complex $[(CuSCN)_2((C_6H_5)_2PC{\equiv}CP(C_6H_5)_2)_3]$[2j] formulated as a dimer with three bridging phosphine ligands and terminal thiocyanates which on the basis of infrared spectroscopy (i.e., $\nu_{CN} = 2060\ cm^{-1}$; $\nu_{CS} = 798\ cm^{-1}$ *w*, $805\ cm^{-1}$, *w*) have been assigned Cu–NCS bonding modes.

A single-crystal X-ray structural determination has been reported for only one Cu(1) thiocyanate complex, $[Cu(P(C_6H_5)_2CH_3)_2SCN]_2$.[2k] This complex was shown to be dimeric with two thiocyanate bridges. The Cu–S distances were, however, rather long (2.46 ± 0.01 Å vs. 2.39 Å for the sum of the covalent radii, whereas the Cu–N distances (2.02 ± 0.02 Å) were typical of a normal Cu–N single bond.† Indeed the ν_{CN} of this complex in the solid state was found at a value ($2103\ cm^{-1}$) characteristic of a terminal thiocyanate rather than at a higher value generally found for such bridged complexes (e.g., $(CuSCN)_n$,[5] $2175\ cm^{-1}$; $[Cu(methylisonicotinate)SCN]_2$,[2g] 2132 vs. $2085\ cm^{-1}$, m; $[Co(NCS)_4Hg]$,[6] $2145\ cm^{-1}$). Molecular weight measurements in $CHCl_3$, a solvent of low dielectric constant ($\epsilon = 4.79$), further support the weak nature of the thiocyanate bridges, a monomeric complex being found. The sharp ν_{CN} observed in the solid state for this complex splits into a broad doublet (2084, $2112\ cm^{-1}$) in $CHCl_3$, and this has been suggested to indicate the presence of both N- and S-bonded monomeric isomers in such solutions.[2k]

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† A single-crystal X-ray diffraction study of CuSCN has also been recently reported.[4] The structure consists of a three-dimensional skeleton of mutually interacting, nearly linear CuSCN units in which the copper is tetrahedrally coordinated by three sulfur atoms and a nitrogen atom. Here both the Cu–N (1.93 Å) and the Cu–S (2.34–2.37 Å) bond distances are slightly less than the single bond values.

In our studies of Cu(I) complexes, we have found a marked tendency to form three- and four-coordinate complexes‡ by dimer formation with the anions acting as bridging ligands (i.e., $[L_aCu(\mu\text{-}X)_2CuL_a]$ (L = monodentate phosphines and phosphites; $a = 1, 2$; X = Cl, Br, I, SCN, SeCN, BH_3CN).[9]

EXPERIMENTAL

Reagents

Cuprous thiocyanate,[2m] $[Cu(P(C_6H_5)_3)_2NO_3]$[10,11] and $K_2[Pd(SCN)_4]$[12] were prepared as previously described. The ligand 1,1,1-tris-(diphenylphosphinomethyl)ethane (p_3; Orgmet, Inc.), triphenylphosphine (Eastman Organic Chemicals), and $Eu(fod)_3\text{-}d_{27}$ (fod = 1,1,1,2,2,3,3-heptafluorooctane-4,6-dionatoeuropium(III); Stohler Isotope Chemicals) were obtained from the indicated commercial sources and used as received.

$[Cu(P(C_6H_5)_3)_2SCN]_2$

To a solution of $[Cu(P(C_6H_5)_3)_2NO_3]$ (6.5 g, 10 mmole) in 300 mL of $CHCl_3$ was added a solution of NaSCN (0.8 g, 10 mmole) dissolved in 75 mL of methanol. The solution was stirred at room temperature for 0.5 hr and filtered through a fine porosity glass frit. The filtrate was concentrated to dryness and the residue recrystallized from 1 : 1 $CHCl_3/CH_3OH$ (4.5 g; 70%); mp 235°C. *Anal.* Calcd. for $C_{37}H_{30}CuNP_2S$: C, 68.71; H, 4.68; N, 2.17; Cu, 9.83. Found: C, 68.5; H, 4.5; N, 2.3; Cu, 9.7.

$[Cu(p_3)NO_3]$

To a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (2.4 g, 10 mmole) in 250 mL of hot methanol was added p_3 (8.1 g, 13 mmole) as a solid. The resulting suspension was refluxed for 15 min and cooled to room temperature, and the white precipitate was filtered. After the crude product was washed with methanol and ether, it was recrystallized from 500 mL of hot CH_2Cl_2. Concentration of the filtered recrystallization solution gave 4 g (53%) of white microcrystals; mp 295°C (dec). *Anal.* Calcd. for $C_{41}H_{39}CuNO_3P_3$: C, 65.64; H, 5.24; N, 1.87; Cu, 8.47; P, 12.39. Found: C, 65.7; H, 5.1; N, 2.1; Cu, 8.3; P, 12.1.

$[Pd(p_3)(NCS)_2]$

To a solution of $K_2[Pd(SCN)_4]$ (0.83 g, 2 mmole) in 75 mL of methanol was added a solution of p_3 (1.25 g, 2 mmole) dissolved in 25 mL of CH_2Cl_2. The reaction solution was stirred at room temperature for 15 min, and the yellow precipitate was filtered, washed with small volumes of methanol and ether, and vacuum dried to give an essentially quantitative yield of the complex. *Anal.* calcd. for $C_{43}H_{39}N_2P_3PdS_2$: C, 60.96; H, 4.64; N, 3.31; Pd, 12.56. Found: C, 60.7; H, 5.0; N, 3.7; Pd, 12.3.

$[Cu(p_3)NCS]$

To a solution of $[Cu(p_3)NO_3]$ (1.5 g, 2 mmole) in 800 mL of $CHCl_3$ was added a solution of NaSCN (0.24 g, 3 mmole) dissolved in 75 mL of methanol, and the resulting solution was stirred at room temperature for 0.5 hr and filtered through a fine-porosity glass frit. The filtrate was concentrated to dryness and the residue recrystallized by dissolving in 250 mL of hot CH_2Cl_2, adding 500 mL of CH_3OH to the filtered solution, and cooling in a freezer compartment overnight to give 1.7 g (80.5%) of white microcrystals; mp 310° (dec). *Anal.* calcd. for $C_{42}H_{39}CuNP_3S$: C, 67.59; H, 5.27; N, 1.88; Cu, 8.51; P, 12.45. Found: C, 67.7; H, 5.1; N, 2.0; Cu, 8.8; P, 12.1.

Physical Measurements

Infrared spectra were recorded on a Nicolet series 7000 Fourier transform infrared spectrometer. Solution spectra were recorded using a 0.1-mm NaCl cell, the background due to the solvent being subtracted instrumentally. Solution integrated absorption intensities of the ν_{CN} bands were determined by Ramsay's method of direct integration.[1,13] Solid state intensity measurements were made using salicylic acid (i.e., the $\nu_{C=O}$ at 1654 cm^{-1}) as the internal reference.[14]

PMR spectra were recorded on a Bruker model HX-100 spectrometer. The spectra of solutions containing the europium shift reagent $Eu(fod)_3\text{-}d_{27}$ were recorded using a 0.5 molar ratio of shift reagent/thiocyanate complex.[15] DSC scans were recorded in a nitrogen atmosphere with a Du Pont model 990 thermal analyzer. Molecular weights were measured with a Hewlett-Packard model 302B

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‡Although the most common coordination number of Cu(I) is four,[3] several three-coordinate complexes have been reported[6-7] and a recent paper[8] has described the first well-established, five-coordinate Cu(I) complex.

osmometer. Benzil solutions were used for calibration. The photoelectron spectra were recorded on a Hewlett-Packard 5950A ESCA spectrometer at room temperature. The C_{1S} line of the ligand was used as a reference and assigned a binding energy of 284.6 eV. Sample charging was minimized through use of a low-energy electron-flood gun. All samples were stable with time and showed no evidence of decomposition in the X-ray beam.

RESULTS AND DISCUSSION

One approach to inducing N-bonding in a copper(1) thiocyanate complex is to incorporate a soft tridentate ligand in the coordination sphere, leaving only one vacant coordination site available for bonding to a terminal thiocyanate ligand. The one established case of a five-coordinate Cu(1) complex[8] involves the weak coordination of CO in the axial position of a square pyramidal geometry, the basal coordination sites being occupied by a tetradentate ligand. Thus, one would not expect five-coordination (i.e., dimer formation with two bridging thiocyanates and terminal tridentate phosphines) to occur under the conditions used here. The ligand chosen was 1,1,1-tris(diphenylphosphinomethyl)ethane (p_3) and the thiocyanate complex was prepared from either the corresponding chloride or nitrate complex:

$$[Cu(p_3)X] + NaSCN \xrightarrow{CH_2Cl_2/CH_3OH} [Cu(p_3)NCS]$$

$X = Cl, NO_3$ (1)

The chloro complex was prepared in the usual manner by reacting CuCl with one equivalent of the ligand in $CHCl_3$,[9b] and the nitrate complex was prepared by a ligand reduction reaction between $Cu(NO_3)_2 \cdot 3H_2O$ and 1.5 equivalents of the phosphine.[11] Unidentate coordination of the nitrate ligand in the solid state for this complex is suggested by infrared spectroscopy.[16,17] Although the local symmetry of complexes with monodentate and bidentate bonding modes is the same (C_{2v}),[16] the difference between the symmetric and asymmetric stretching frequencies for the nitrate ligand is significantly greater for bidentate coordination (i.e., $\Delta > 150\ cm^{-1}$; $[Cu(P(C_6H_5)_3)_2NO_3]$, $\Delta = 200\ cm^{-1}$)[16] than for monodentate coordination (i.e., $\Delta < 125\ cm^{-1}$; $[Cu(P(C_6H_5)_3)_3NO_3]$, $\Delta = 120\ cm^{-1}$).[10] The corresponding bands for $[Cu(p_3)NO_3]$ occur at 1295 cm^{-1} and 1388 cm^{-1} ($\Delta = 93\ cm^{-1}$).

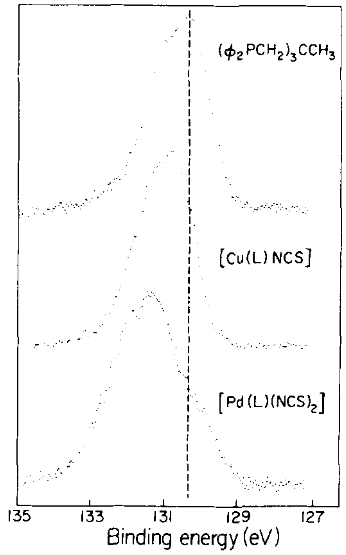
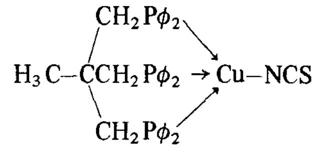
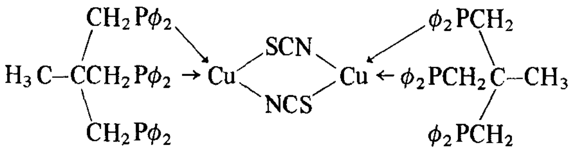


FIGURE 1 P 2p Binding Energies of $(\phi_2PCH_2)_3CCH_3$ and its Cu(I) and Pd(II) Thiocyanate Complexes.

Concentration of the reaction solution to dryness and recrystallization of the residue from 1:2 CH_2Cl_2/CH_3OH gave a crop of white crystals of the desired complex.

The X-ray photoelectron spectrum of the complex (Figure 1) indicates the presence of only one type of phosphorus site in the complex, precluding a solid-state structure involving bidentate coordination of the phosphine ligand†(B):


(A)


(B)

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†Both tridentate and bidentate bonding modes of this tri(tertiary) phosphine ligand have been established by single-crystal X-ray diffraction studies (i.e., $[(p_3)NiSNi(p_3)]B\phi_4$ (Ref. 18) and $[PtMe_2(P_2)P]$ (Ref. 19).

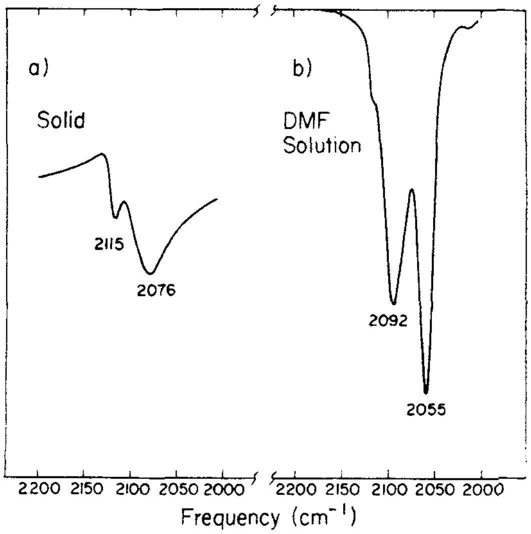

FIGURE 2 Infrared Spectra of [Pd(NCS)(SCN)(($\phi_2PCH_2)_3CCH_3$)] in the Solid State and DMF Solution.

TABLE I
Thiocyanate binding energies[a]

Compound	C 1s – S 2p	N 1s – C 1s
[Cu(p$_3$)(NCS)]	122.2	113.1
(CuSCN)$_n$	122.5	112.9
[Cu(P(C$_6$H$_5$)$_3$)$_2$SCN]$_2$	122.2	113.7

[a] Reference is neutral carbon at 284.6 eV.

Comparison of the P 2p spectra of the copper thiocyanate complex, the free ligand, and [Pd(p$_3$)(NCS)$_2$] (in which the phosphine functions as a bidentate ligand) indicates that the phosphine coordinates via all three donor sites in the copper complex (Figure 1).

The formulation of a bidentate bonding mode of the tri(tertiary) phosphine ligand in the Pd(II) complex is based on infrared spectroscopy. The solid-state spectrum of the complex in the ν_{CN} region (2076 (Pd–NCS), 2115 cm^{-1} (Pd–SCN)) supports a cis arrangement of two thiocyanate ligands and therefore a bidentate coordination mode of the phosphine (Figure 2). The spectrum of the complex in DMF indicates that the phosphine assumes a tridentate coordination mode with expulsion of one of the thiocyanates from the coordination sphere (i.e., ν_{CN} = 2092 (Pd–NCS), 2055 cm^{-1} (ionic SCN$^-$) (Figure 2)). A similar pseudohalide expulsion reaction has been previously observed for analogous complexes with 2,2′,2″-terpyridine.[21]

The P 2p spectrum of the copper complex gives the unresolved spin doublet with a full width at half maximum (fwhm) of 1.8 eV, identical to that of the free ligand but shifted to higher binding energy by 0.4 eV (Figure 1). On the basis of this result, one can assume that all three phosphorus atoms are nearly equivalent in the copper complex. In comparison, the P 2p spectrum of the Pd complex is shifted to higher binding energy by 1.0 eV relative to the free ligand and has a definite shoulder at lower binding energy. Through use of the Du Pont 310 curve resolver, this spectrum can be resolved into two components separated by 1.0 eV with an intensity ratio of 2:1. The higher binding energy component corresponds to the two phosphorus atoms bonded to Pd, and the shoulder at lower binding energy corresponds to the uncomplexed phosphorus atom. The binding energy of this shoulder is identical to that of the free ligand.

The possibility of thermal dimerization reaction for [Cu(p$_3$)(CNS)] (i.e., A $\xrightarrow{\Delta}$ B) or a linkage isomerization (i.e., Cu–NCS $\xrightarrow{\Delta}$ Cu–SCN) was precluded by DSC analysis. Since no evidence for any significant reaction was observed before the melting point (310°C), the photoelectron spectrum at high temperature was not measured.

The use of photoelectron spectroscopy to determine the bonding mode of thiocyanate ligands has been reported,[22] the C 1s line of the thiocyanate being used as an internal reference with the bonding assignment being made on the basis of the difference in binding energies of the reference and the N and S atoms. A subsequent paper[23] pointed out the limitations of such measurements as diagnostic criteria of thiocyanate bonding modes. Indeed, measurements of the binding energies of [Cu(p$_3$)NCS], (CuSCN)$_n$, [Cu(P(C$_6$H$_5$)$_3$)$_2$SCN]$_2$ (Table I) show little difference between terminal Cu–NCS and thiocyanate bridging for these Cu(I) complexes.

The ν_{CN} band of the recrystallized complex appeared as a strong absorption at ca 2100 cm^{-1} which on examination under high resolution was shown to consist of two overlapping bands, a sharp band at 2099 cm^{-1} and a broader band at 2083 cm^{-1} (Figure 3). The position and shapes of these bands are consistent with the presence of an isomeric mixture of Cu(p$_3$)SCN (i.e., 2099 cm^{-1} sharp) and Cu(p$_3$)NCS (i.e., 2083 cm^{-1}, broad). Attempts to obtain the pure isomers in the solid state gave only mixtures of various proportions of both isomers. In the recrystallization procedure described above, the complex was dissolved in hot CH$_2$Cl$_2$, filtered, and, after dilution with a twofold excess of methanol,

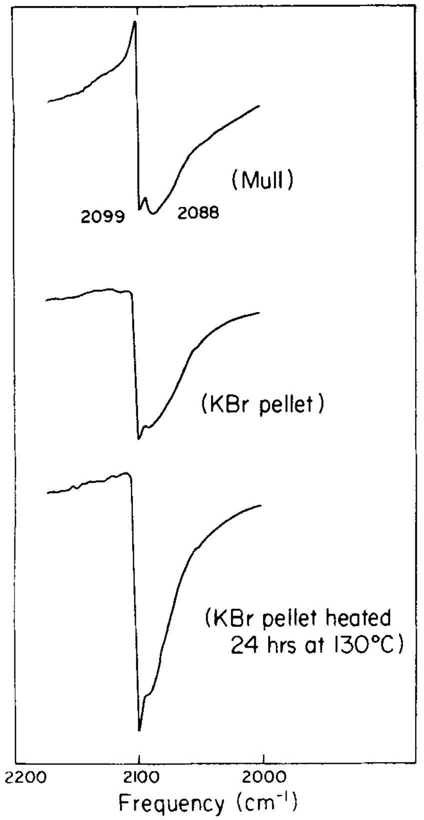

FIGURE 3 Infrared Spectra of $[Cu((\phi_2PCH_2)_3CCH_3)NCS]$ in the Solid State.

cooled in a freezer compartment overnight. The resulting product was rich in the N-bonded isomer (Figure 3). The solid-state intensity of the ν_{CN} band (using the internal-standard-ratio method of Bailey et al.[14]) was 2.3, supporting the formulation of the recrystallized material as primarily the N-bonded isomer. The ratio of the isomers was somewhat dependent on the method of isolation of the complex as well as on the infrared sampling technique. The crude complex, obtained by concentrating the reaction solution to dryness at room temperature, and the material obtained by concentrating a CH_2Cl_2 solution of recrystallized complex to dryness at room temperature were both rich in the S-bonded isomer. The proportion of S-bonded isomer was also enhanced in a KBr pellet of the recrystallized material vs. a mineral oil mull (Figure 3). The ratio of S-bonded isomer was also increased by heating the isomeric mixture. We did not, however, obtain a sample of either pure isomer in the solid state.

The solution structure of the complex was studied by qualitative and quantitative infrared spectroscopy[1] and PMR spectroscopy.[15] The molecular weight in chloroform (728 vs. a theoretical value of 746.3) indicates a monomeric formulation with possibly a slight amount of thiocyanate dissociation. The insolubility of the complex in other solvents precluded such measurements in more polar solvents.

The ν_{CN} stretching frequency in $CHCl_3$ (Figure 4)

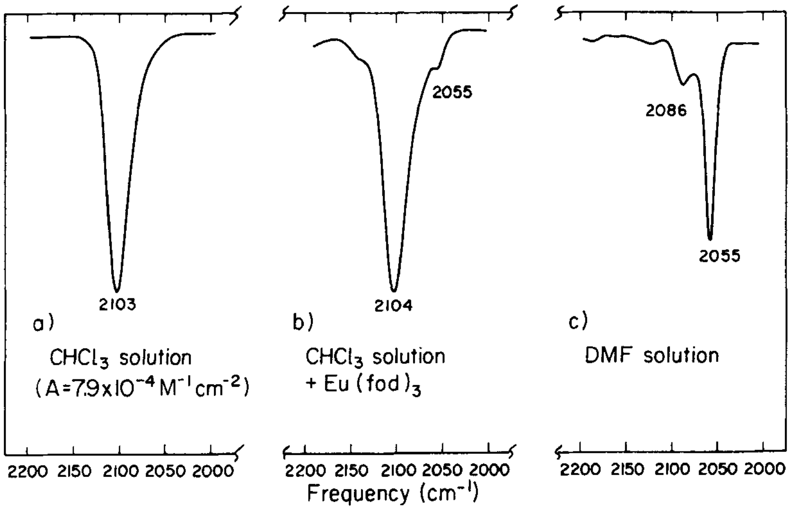

FIGURE 4 Infrared Spectra of $[Cu((\phi_2PCH_2)_3CCH_3)NCS]$ in Solution.

occurred at 2103 cm^{-1} with an integrated intensity value of 7.9 x 10^{4} M^{-1}cm^{-2}, characteristic of M–NCS bonding.[1] In DMF the complex undergoes extensive dissociation of the thiocyanate, as evidenced by the appearance of a strong ν_{CN} band due to ionic thiocyanate at 2055 cm^{-1} (Figure 4). The weak band at 2084 cm^{-1} is most reasonably assigned to a terminal Cu–NCS species. The shift of this band from 2103 cm^{-1} in $CHCl_3$ is too great to be due to a solvation effect. It has previously been shown that for analogous complexes the change in position of the ν_{CN} in going from the solid state or a solution in a nonpolar solvent such as $CHCl_3$ to DMF is negligible (assuming no linkage isomerism), whereas for M–SCN complexes hydrogen bonding can result in shifts to lower energy of 5–10 cm^{-1}. The position of the ν_{CN} bands of this complex in DMF and the large shift (19 cm^{-1}) of the band for the coordinated thiocyanate are, however, consistent with dissociation of one of the phosphorus atoms of the phosphine ligand to give a complex containing bidentate phosphine. The spectrum of the related complex $[Cu(P(C_6H_5)_2(CH_3))_2SCN]_2$ in $CHCl_3$ exhibits bands at 2084 and 2112 cm^{-1} which have been assigned to Cu–NCS and Cu–SCN isomers of the monomeric three-coordinate complex.[2k]

The complex $[Cu(P(C_6H_5)_3)_2SCN]_2$, prepared by reaction of CuSCN with excess phosphine or by a metathetical reaction between the nitrate analog and NaSCN, can be formulated, on the basis of infrared spectroscopy, as a dimer with thiocyanate bridges. In the solid state this complex has a single sharp ν_{CN} at 2097 cm^{-1}, and in $CHCl_3$ solution the band shifts to 2071 cm^{-1} and has an integrated intensity of 10.66 x 10^{-4}M^{-1}cm^{-2}. The position and intensity of this band are typical of N-bonded thiocyanates.[1] Unlike the $P(C_6H_5)_2CH_3$ analog[2k] there is no evidence for a mixture of Cu–NCS and Cu–SCN isomers in solution. Both steric and electronic factors, however, favor Cu–NCS bonding in the $P(C_6H_5)_3$ derivative compared to the less bulky and weaker acceptor $P(C_6H_5)_2CH_3$.

The solution bonding mode of the thiocyanate in $[Cu(p_3)NCS]$ is also supported by PMR spectroscopy using the shift reagent $Eu(fod)_3\text{-}d_{27}$ (Figure 5). The negligible shifts of the resonances of the ligand when the spectrum is recorded in a solution containing 0.5 equivalent of the shift reagent are indicative of coordination of the hard nitrogen end of the ambidentate thiocyanate ligand.[1 5]

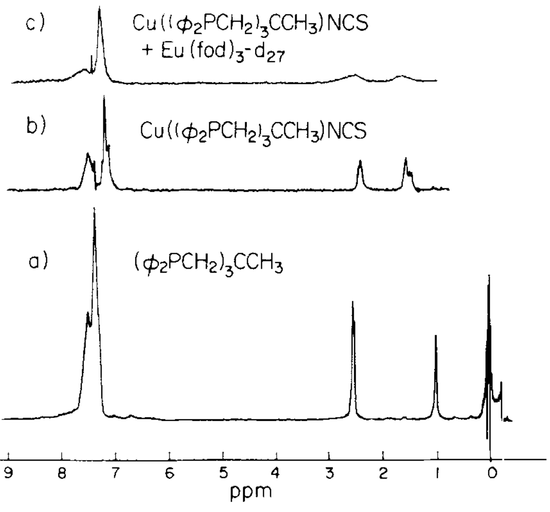

FIGURE 5 PMR Spectra of $(\phi_2PCH_2)_3CCH_3$ and its CuSCN Complex.

The failure to observe splitting of the methylene resonance for the copper complex by the phosphorus (Figure 5b) indicates that a rapid exchange process is occurring with the phosphorus sites (i.e., $J_{3\,{}^1P-{}^1H}$ = 2 Hz for the free ligand; Figure 5a). Such exchange processes in organophosphine complexes of cuprous halides have been reported.[24]

The bonding of the ambidentate thiocyanate ligand in this Cu(I) complex and, indeed, the pronounced tendency of this anion to act as a bridging ligand in a wide variety of Cu(I) complexes suggest that the energy difference between the two bonding modes (i.e., Cu–NCS vs. Cu–SCN) is quite small. We are currently studying $Cu(p_3)NCS$ by single-crystal X-ray diffraction and continuing our studies of the various factors (e.g., other ligands in the Cu(I) coordination sphere and external factors such as temperature, solvent, and pressure) which influence the bonding mode of the ambidentate thiocyanate ligand in Cu(I) coordination complexes.

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