160 *Inorganic Chemistry, Vol. 15, No. 1, 1976*

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Organic Cyanate, Thiocyanate, and Selenocyanate Complexes of Chromium and Tungsten Carbonyls

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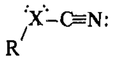
Received June 27, 1975

AIC50452E

The coordinating properties of various organic cyanates, isocyanates, thiocyanates, isothiocyanates, and selenocyanates toward the group 6B metal carbonyls have been examined. Twenty complexes of the type $M(CO)_5(R–XCN)$ (where M = Cr or W, X = O, S, or Se, and R = alkyl or aryl) have been prepared and characterized; no R–XCN derivatives of molybdenum carbonyl could be obtained. The infrared and ^1H and ^{13}C nuclear magnetic resonance spectra of the complexes indicate that these ligands coordinate through the cyano nitrogen rather than the X atom. Complexes of alkyl R–XCN ligands can be prepared by the reaction of the anions $[M(CO)_5NCX]^-$ with alkylating agents such as $MeOSO_2F$ or $[Et_3O][BF_4]$, but the yields are poor. Good yields of the complexes of phenyl cyanate and the alkyl and aryl thiocyanates are obtained by abstraction of iodide from the anions $[M(CO)_5I]^-$ by silver ion in acetone solution, followed by addition of the ligand. For the analogous selenocyanate complexes the yields obtained by this method are generally lower. Alkyl and aryl isocyanates and isothiocyanates do not form complexes with any of these metal carbonyls.

Introduction

Examples of all of the organic pseudohalides R–XCN and isopseudohalides R–NCX (where X = O, S, or Se) have been known for at least 10 years. The major resonance forms, structures I and II, indicate that these molecules should be interesting ligands, as various modes of coordination to a metal atom or ion can be visualized. It is therefore surprising that their coordination chemistry has not been more fully investigated.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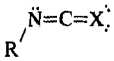

II

A number of aryl cyanates form rather unstable complexes with $AlCl_3$ and $SnCl_4$.[1] Apparently no examples of simple coordination complexes of isocyanates are known, but two iron carbonyl complexes which are proposed to contain bridging R–NCO ligands have been reported.[2,3] Several investigators have prepared adducts of a few alkyl thiocyanates with Lewis acids such as $TaCl_5$[4] and $TiBr_4$.[5] Methyl and ethyl isothiocyanates also form such adducts;[4,5] isothiocyanate complexes have also been obtained by oxidative addition reactions with $Pt(PPh_3)_3$ and $Rh(PPh_3)_3Cl$.[6] The bidentate ligand 1,2-dithiocyanatoethane forms complexes with halides of Co(II), Rh(III), and Ir(III),[7] and also Pt(II).[8] The dichloro complexes of Pd(II) and Pt(II) with the analogous ligand 1,2-diselenocyanatoethane are the only previously reported examples of the coordination of a selenocyanate.[9]

Our interest in substituted group 6B metal carbonyls led us to attempt the preparation of a series of $M(CO)_5(R–XCN)$ and $M(CO)_5(R–NCX)$ complexes. The monosubstituted derivatives were selected for the present study because the existence of various metal carbonyl anions $[M(CO)_5NCX]^-$ [10,11] suggested that one might obtain several R–XCN complexes by alkylation and because a simple method for the synthesis of other $M(CO)_5L$ complexes has been developed.[12] For those complexes which could be prepared, the infrared and NMR spectra were examined in order to determine the coordination mode of the ligands.

Experimental Section

Solvents and Reagents. Except where noted otherwise, solvents were reagent grade and were dried over anhydrous $CaSO_4$ or Baker type 4A molecular sieves before use. Technical grade bis(2-methoxyethyl) ether (diglyme) was dried over anhydrous $CaSO_4$ and then distilled from CaH_2. The 4-bromoaniline was purified by sublimation under high vacuum at 50–60°. Commercial $AgBF_4$ was dried over P_4O_{10} for 24 hr before use. Tetraethylammonium iodide ($[Et_4N]I$) was prepared by the reaction of Et_3N and EtI in refluxing ethanol; commercial $[Et_4N]Br$ was dried over P_4O_{10}. The azide and thiocyanate salts of the μ-nitrido-bis(triphenylphosphorus)(1+) cation ($[(Ph_3P)_2N]^+$, or $[PPN]^+$) were prepared from commercial [PPN]Cl as described by Ruff[13] and were recrystallized from acetone–ether. Potassium selenocyanate (KSeCN) was prepared by a literature method.[14] All other reagents were obtained from commercial sources and were used as received.

Intermediate Complexes. The salts $[Et_4N][M(CO)_5I]$ (M = Cr, Mo, W) were prepared essentially as described by Abel et al.[15] The anions $[W(CO)_5NCS]^-$ [10] and $[M(CO)_5NCO]^-$ [11] (M = Cr, W) were prepared by literature methods, except that $[PPN]^+$ was used as the counterion. The selenocyanate complex $[Et_4N][Cr(CO)_5NCSe]$ apparently has not been prepared before, so the method used is described here. To $[Et_4N][Cr(CO)_5I]$ (2.25 g, 5.0 mmol) dissolved in 15 ml of acetone at 0° was added dropwise a solution of $AgBF_4$ (0.98 g, 5.0 mmol) in 10 ml of acetone over a period of about 15 min. The reaction was carried out under prepurified nitrogen in a Schlenk tube, and the reaction mixture was stirred with a magnetic stirring bar. After all of the $AgBF_4$ had been added, the reaction mixture was stirred for 5 min more and was then filtered under nitrogen to remove the precipitated AgI. A solution of KSeCN (0.72 g, 5.0 mmol) in 5 ml of acetone was added to the clear orange filtrate, and the solution was stirred for 10 min. Solid $[Et_4N]Br$ (1.05 g, 5.0 mmol) was then added, and the reaction mixture was stirred for 2 hr; the resulting cloudy mixture was then filtered to separate precipitated KBr. The clear, golden yellow filtrate was evaporated under a stream of nitrogen; the residue was collected on a frit filter, washed five times with pentane, and dried in vacuo. The brownish yellow product thus obtained, a mixture of the pentacarbonyl selenocyanate complex and $[Et_4N][BF_4]$, was used immediately in the subsequent alkylation reaction (see below). The infrared spectrum of the product in CH_2Cl_2 solution showed bands at 2105 (weak, ν_{CN}), 2055 (weak), 1926 (strong), and 1878 (medium) cm^{-1}, in substantial agreement with reported spectra for this type of compound;[10,11] there was an additional weak band at 2067 cm^{-1}.

R–XCN and R–NCX Compounds. Phenyl cyanate (PhOCN) was prepared by the method of Grigat and Pütter.[16] The aryl thiocyanates 4-thiocyanatoaniline ($4\text{-}H_2NC_6H_4SCN$, or TA) and 4-thiocyanato-*N*,*N*-dimethylaniline ($4\text{-}Me_2NC_6H_4SCN$, or TDMA) were prepared by a literature method;[17] phenyl thiocyanate (PhSCN) was obtained from TA by a standard hypophosphorous acid reduction procedure.[18] Methyl selenocyanate (MeSeCN), ethyl selenocyanate (EtSeCN), and phenyl selenocyanate (PhSeCN) were prepared according to methods described in the literature,[19] as were 4-selenocyanatoaniline ($4\text{-}H_2NC_6H_4SeCN$, or SA) and 4-selenocyanato-*N*,*N*-dimethylaniline ($4\text{-}Me_2NC_6H_4SeCN$, or SDMA).[20] The remaining R–XCN and R–NCX compounds were obtained from commercial sources and were used as received.

Alkylation of $[M(CO)_5NCX]^-$. In the general procedure for these reactions, the $[Et_4N]^+$ or $[PPN]^+$ salt of $[M(CO)_5NCX]^-$ (5.0 mmol) was dissolved in 15 ml of CH_2Cl_2 at 0°; a cold (5–10°) solution of 5.0 mmol of the alkylating agent, methyl fluorosulfonate ($MeOSO_2F$) or triethyloxonium tetrafluoroborate ($[Et_3O][BF_4]$), in 10 ml of CH_2Cl_2 was added dropwise over a period of 10–15 min. The reaction was conducted under nitrogen in a Schlenk tube equipped with a magnetic stirring bar. When the addition was complete, the reaction mixture was evaporated to dryness under a rapid stream of nitrogen.

Table I. Physical and Analytical Data for $M(CO)_5(R{-}XCN)$ Complexes

					Analyses[d]		
R-XCN[a]	M	Color[b]	Mp,[c] °C	Yield, %	% C	% H	% N
PhOCN	Cr	Yel	80–85	73	46.32 (46.57)	1.62 (1.80)	4.50 (4.42)
	W	Yel	78–81	60	32.53 (32.81)	1.14 (1.30)	3.16 (3.36)
MeSCN	Cr	Yel	39–41	76	31.71 (31.77)	1.14 (1.04)	5.28 (5.26)
	W	Yel-gr	59–62	72	21.18 (21.43)	0.76 (0.80)	3.53 (3.63)
EtSCN	Cr	Yel	42–44	71	34.42 (34.11)	1.80 (1.73)	5.02 (5.00)
	W	Yel	71–74	73	23.38 (23.47)	1.23 (1.21)	3.41 (3.51)
PhSCN	Cr	Yel	50–52	75	44.04 (43.95)	1.58 (1.46)	4.28 (4.18)
	W	Yel-gr	68–71	68			
TA	Cr	Yel	80–83	71	42.11 (41.96)	1.74 (1.73)	8.21 (8.18)
	W	Yel-br	75–80	65			
TDMA	Cr	Yel	70–72	86	45.41 (45.61)	2.72 (2.49)	7.56 (7.73)
	W	Yel-br	86–89	84			
MeSeCN	Cr	Yel	56–58	33	26.94 (26.67)	0.97 (0.92)	4.49 (4.30)
	W	Yel-gr	65–70	39	18.94 (18.86)	0.68 (0.68)	3.16 (3.07)
EtSeCN	Cr	Yel-br	38–40	66	29.46 (28.95)	1.54 (1.68)	4.30 (4.35)
	W	Yel-gr	57–59	46	20.98 (20.86)	1.10 (1.04)	3.06 (2.95)
PhSeCN	Cr	Yel	45–48	54	38.52 (38.31)	1.35 (1.25)	3.74 (3.58)
SDMA	Cr	Yel-gr	75–80	63	40.30 (40.45)	2.42 (2.45)	6.71 (6.74)

[a] Abbreviations: Me, methyl; Et, ethyl; Ph, phenyl; TA, $4\text{-}H_2NC_6H_4SCN$; TDMA, $4\text{-}Me_2NC_6H_4SCN$; SDMA, $4\text{-}Me_2NC_6H_4SeCN$. [b] Abbreviations: yel, yellow; gr, green; br, brown. [c] All compounds melt with decomposition. [d] Found (calculated). Compounds for which no percentages are given were not analyzed.

The greenish brown residue was extracted with pentane, the extract was filtered, and the filtrate was evaporated under reduced pressure to give the complex as a yellow-green or yellow-brown powder. These products were not purified but were identified by their infrared and proton NMR spectra.

(a) $[PPN][M(CO)_5NCO]$ (M = Cr, W). The reaction of $[PPN][Cr(CO)_5NCO]$ with $[Et_3O][BF_4]$ gave a product which was identified as a mixture of $Cr(CO)_6$ and $Cr(CO)_5(EtOCN)$. The complex was rather unstable in solution and could not be purified; the yield was estimated by ir to be less than 10%. With $[PPN][W(CO)_5NCO]$, the reaction gave only $W(CO)_6$ and dark decomposition products; no evidence for the formation of $W(CO)_5(EtOCN)$ was found.

(b) $[PPN][W(CO)_5NCS]$. This compound with $MeOSO_2F$ and $[Et_3O][BF_4]$ gave low yields (about 10%) of the corresponding alkyl thiocyanate complexes $W(CO)_5(MeSCN)$ and $W(CO)_5(EtSCN)$.

(c) $[Et_4N][Cr(CO)_5NCSe]$. The complex $Cr(CO)_5(EtSeCN)$ was obtained in 19% yield from the reaction of this salt with $[Et_3O][BF_4]$.

Thiocyanate Complexes. The complex $W(CO)_5(MeSCN)$ was also prepared by the reaction of $[Et_4N][W(CO)_5I]$, $[Et_3O][BF_4]$, and MeSCN in CH_2Cl_2; this is the method introduced by Connor et al.[12] for the synthesis of other $M(CO)_5L$ compounds. However, with the thiocyanate ligand the yield was poor (~15%), so the modified procedure described here was developed for the preparation of the chromium and tungsten thiocyanate complexes. All reactions were carried out under prepurified nitrogen in Schlenk tubes, and the reaction mixtures were stirred with a magnetic stirring bar. A solution of $AgBF_4$ (0.98 g, 5.0 mmol) in 10 ml of acetone was added dropwise over a period of 15–20 min to a cold (0°) solution of $[Et_4N][M(CO)_5I]$ (5.0 mmol) and the alkyl or aryl thiocyanate (5.0 mmol) in 20 ml of acetone.

When the addition was complete, the reaction mixture was stirred for another 5 min and was then filtered to remove the precipitated AgI; the filtrate was evaporated to a moist residue under a rapid stream of nitrogen. The residue was extracted with 40 ml of a 6:1 mixture of pentane–acetone, the extract filtered to separate insoluble $[Et_4N][BF_4]$, and the yellow to yellow-orange filtrate evaporated under a nitrogen stream to give the product as a powder. Occasionally the extract acquired a green color, especially with tungsten complexes, in which case the solution was eluted through a 2-cm layer of Florisil (60–100 mesh) in a filter frit to obtain a yellow solution before the evaporation.

Recrystallization was accomplished by stirring the powdery product with 30 ml of pentane, adding acetone dropwise until all of the complex just dissolved, filtering off any insoluble material, and then cooling the solution to −20°. After several hours the crystals that formed were filtered off and dried in vacuo; the filtrate was evaporated to dryness, and the recrystallization procedure was repeated, using smaller amounts of solvent, to obtain a further yield of product. The yields, melting points, and analytical data for the compounds obtained by this method are given in Table I. The complexes were also characterized by their infrared and proton NMR spectra.

Although the above procedure indicates that the ligand was present when the $AgBF_4$ was added, it was found that the yield was unaffected if the ligand was introduced during or even after the addition of $AgBF_4$. Since the reactions were carried out in closed vessels, it was more convenient to have the ligand present initially. The rate of addition of the $AgBF_4$ was important, as the products were contaminated with appreciable amounts of $M(CO)_6$ if the silver salt was introduced too rapidly.

Phenyl Cyanate Complexes. The complexes $Cr(CO)_5(PhOCN)$ and $W(CO)_5(PhOCN)$ were obtained by the same method described above. Physical and analytical data for these compounds are also shown in Table I; the complexes were also characterized by their infrared and proton NMR spectra.

Selenocyanate Complexes. For the preparation of the $M(CO)_5(R{-}SeCN)$ compounds, a modification of the above procedure was necessary, since the alkyl and aryl selenocyanates decomposed fairly rapidly in acetone solutions of $AgBF_4$. These ligands were introduced *after* the $AgBF_4$ had been added and the AgI precipitate had been filtered off, as was done in the preparation of $[Et_4N][Cr(CO)_5NCSe]$ previously described. Additionally, all operations (except spectroscopic work) with the alkyl selenocyanates or their complexes were carried out on a vacuum line constructed inside a hood, as the revolting, tenacious odors of these compounds cannot be tolerated in the laboratory. The procedure for isolation and recrystallization of the selenocyanate complexes was the same as that for the thiocyanate analogs, except as noted below.

(a) MeSeCN. The chromium complex was initially obtained as an oil. The impure $Cr(CO)_5(MeSeCN)$ was passed twice through a 30-cm Florisil column, using 6:1 pentane–acetone as the eluent. After this treatment the compound could be crystallized.

(b) PhSeCN. The chromium complex was an oil initially. Chromatographic purification as in (a) gave $Cr(CO)_5(PhSeCN)$ as a crystalline solid. For tungsten, a solid product was obtained; this gave a satisfactory infrared spectrum, but the elemental analysis was very high for carbon and hydrogen, and very low for nitrogen. The impurity was isolated and identified by its melting point as diphenyl diselenide,[21] but during its separation the $W(CO)_5(PhSeCN)$ present decomposed completely.

(c) 4-Selenocyanatoaniline (SA). The reactions with SA gave only viscous, dark brown, pentane-insoluble oils for both chromium and tungsten. These decomposition products were not identified.

(d) 4-Selenocyanato-*N*,*N*-dimethylaniline (SDMA). The tungsten SDMA complex could not be obtained; extraction of the evaporated reaction mixture with a 3:1 pentane–acetone mixture gave an orange solid, the infrared spectrum of which contained no $C\equiv N$ or $C\equiv O$ absorptions. A carbon, hydrogen, and nitrogen analysis showed this compound to be the diselenide, $(4\text{-}Me_2NC_6H_4)_2Se_2$.

The yields, melting points, and analytical data for all complexes isolated by these methods are given in Table I.

Complexes of Other Ligands. The chromium and tungsten complexes of 4-bromoaniline,[22] acetonitrile,[23] phenylacetonitrile, propionitrile, and benzonitrile[23] were prepared by the $AgBF_4$ method described above for the thiocyanate complexes. Infrared and proton NMR spectra of these $M(CO)_5L$ complexes were recorded for comparison with the spectra of the $M(CO)_5(R-XCN)$ compounds.

Attempted Preparations. Attempts to obtain $M(CO)_5(R-NCX)$ complexes of several isocyanates (MeNCO, EtNCO) and isothiocyanates (MeNCS, EtNCS, PhNCS) by the same method used for the thiocyanates failed. Work-up of these reaction mixtures gave only dark residues consisting of decomposition products and unreacted ligands. No molybdenum complexes with any thiocyanate or isothiocyanate could be isolated.

Spectra. Infrared spectra in the 2400–1800-cm^{-1} region were recorded in pentane solution with a Perkin-Elmer 337 spectrophotometer. These spectra were calibrated using CO gas; band positions are believed accurate to within 1 cm^{-1}. For the thiocyanate complexes the spectra in the 750–600-cm^{-1} range were recorded in diethyl ether solution on the same instrument; band positions were determined using the 906.9- and 1028.3-cm^{-1} bands of polystyrene and should be accurate to within 2 cm^{-1}. Solution cells with NaCl windows and 1-mm path length were used for all infrared spectra. Proton NMR spectra were obtained in acetone-d_6 or chloroform-d_1 solution using a Varian A-60 spectrometer. Carbon-13 NMR spectra were recorded in acetone (70% d_6) solution on a Bruker HX-90 Fourier transform NMR spectrometer; proton decoupling was employed. Tetramethylsilane was used as an internal standard for all NMR spectra.

Results

Preparation and Properties. Organic thiocyanate derivatives of chromium and tungsten carbonyls were prepared in good yield by reaction 1. The method also gave good yields of the

$$[Et_4N][M(CO)_5I] + AgBF_4 + R\text{-}SCN \xrightarrow{\text{acetone}} M(CO)_5(R\text{-}SCN) + \underline{AgI} + Et_4NBF_4 \qquad (1)$$

analogous phenyl cyanate complexes. Alternatively, the silver salt could be added first to give the intermediate complex $M(CO)_5$(acetone), and the ligand could then be added to displace the solvent. For selenocyanates, which are decomposed by $AgBF_4$, the latter method was necessary. However, considerable decomposition of these ligands, apparently to the diselenides, occurred nevertheless. As a result, only two tungsten selenocyanate complexes were obtained in pure form, and the yield of every selenocyanate complex isolated was lower than that of the corresponding thiocyanate compound.

Chromium and tungsten complexes of a few alkyl R–XCN ligands were obtained by alkylation of the appropriate $[M(CO)_5NCX]^-$ compounds, but the yields were poor in all cases. This method was useful only for the preparation of $Cr(CO)_5(EtOCN)$, which could not be obtained by substitution methods because of difficulties encountered in the preparation of ethyl cyanate.

No molybdenum carbonyl complexes of the R–XCN ligands could be isolated; this result may be attributed to the lower stabilities generally observed for $Mo(CO)_5L$ derivatives.[24] The isomeric R–NCX compounds (X = O, S) failed to give complexes with any of these metal carbonyls. Since complexes of O-donor ligands with the group 6B carbonyls are usually too unstable to be isolated, the poor coordinating ability of the isocyanates is understandable. The failure of the isothiocyanates as ligands is more surprising, since $M(CO)_5L$ complexes are known for a number of C=S donor ligands, such as thioureas.[25] It is interesting that the thiocyanate ion in the anions $[M(CO)_5NCS]^-$ is exclusively N bonded;[10] perhaps this preference for the nitrogen end of the ion applies to its organic derivatives as well (see Discussion).

All of the $M(CO)_5(R-XCN)$ complexes are crystalline solids. Thiocyanate and selenocyanate complexes decompose if exposed to air for several hours at room temperature, but most appear to be indefinitely stable when stored in capped vials at 0° in the dark. Some decomposition of the phenyl cyanate complexes is evident after about 3 weeks, even if the compounds are kept at −20° in the dark (see below); the impure chromium ethyl cyanate complex decomposes even more rapidly under these conditions.

Table II. C–N and C–O Stretching Frequencies (cm^{-1}) for $M(CO)_5L$ in Pentane Solution

L[a]	M	ν_{CN}[b]	$\Delta\nu_{CN}$	ν_{CO}[c]		
				$A_1^{(2)}$	E	$A_1^{(1)}$
EtOCN	Cr[d]	2315 (2245)[e]	+70	2065	1948	1923
PhOCN	Cr	2308 (2278)	+30	2075	1949	1925
	W	2307	+29	2078	1943	1924
MeSCN	Cr	2176 (2162)	+14	2073	1953	1930
	W	2166	+4	2074	1948	1931
EtSCN	Cr	2172 (2159)	+13	2072	1952	1930
	W	2162	+3	2073	1948	1931
PhSCN	Cr	2170 (2161)	+9	2072	1953	1931
	W	2163	+2	2073	1948	1930
TA	Cr			2072	1952	1927
	W			2073	1946	1927
TDMA	Cr	2167 (2158)	+9	2072	1952	1926
	W			2072	1946	1925
MeSeCN	Cr	2170 (2156)	+14	2072	1953	1931
	W	2162	+6	2073	1947	1929
EtSeCN	Cr	2168 (2157)	+11	2072	1951	1928
	W	2162	+5	2074	1946	1928
PhSeCN	Cr	2168 (2158)	+10	2072	1953	1930
	W[d]	2160	+2	2073	1948	1930
SDMA	Cr	2166		2072	1952	1926
MeCN	Cr	2279		2076	1952	1928
	W	2275		2077	1946	1929
EtCN	Cr	2270 (2249)	+21	2072	1951	1927
	W	2263	+14	2075	1944	1926
$PhCH_2CN$	Cr	2272 (2253)	+19	2074	1951	1927
	W	2258	+5	2076	1945	1927
PhCN	Cr	2243 (2232)	+11	2074	1954	1931
	W	2238	+6	2075	1947	1930

[a] Abbreviations are the same as in Table I. [b] Concentration of solutions was ~2×10^{-2} *M*. Value in parentheses is for the free ligand in pentane. Where no value of ν_{CN} is given, the compound was not soluble enough in pentane to permit observation of this band. [c] Concentration of solutions was ~1×10^{-3} *M*. Relative band intensities: $A_1^{(2)}$ weak, E strong, $A_1^{(1)}$ medium. All bands are very sharp. [d] Impure compound. [e] Spectrum in CCl_4 solution; from ref 30.

All common organic solvents dissolve the $M(CO)_5(R-XCN)$ complexes to some extent. Concentrated solutions in CS_2 are orange, but all other solvents give yellow solutions. Carbon tetrachloride reacts rapidly to give a dark precipitate. The compounds are much more soluble and far more stable in donor solvents such as tetrahydrofuran and acetone; an exception is $Cr(CO)_5(EtOCN)$, which seems to be more stable in chloroform, as its NMR spectrum could not be obtained in acetone. The chromium complexes are slightly more stable in solution than those of tungsten; this probably explains the higher yields generally observed for the chromium compounds.

Spectra. Infrared spectra of the $M(CO)_5(R-XCN)$ complexes in the CO region (2100–1800 cm^{-1}) all show the three bands characteristic of monosubstituted group 6B metal carbonyls;[26] these C–O frequencies are given in Table II. For either metal, variations in the C–O stretching frequencies as the ligand is changed are small. Corresponding thiocyanate and selenocyanate complexes have nearly identical spectra, whereas for analogous cyanate complexes the $A_1^{(1)}$ and E bands occur at frequencies 4–6 cm^{-1} lower. The only significant difference between the carbonyl spectra of the chromium compounds and their tungsten analogs is in the frequency of the E mode, which is usually 5–6 cm^{-1} higher for chromium.

The C–N stretching frequencies for the R–XCN ligands and complexes are shown in Table II; these bands are much less intense than any of the C–O absorptions. For all pre-

Table III. C–S Frequencies (cm^{-1}) for Some $M(CO)_5(R{-}SCN)$ Complexes in Diethyl Ether Solution[a]

R-SCN	M	ν_{CS}[b,c]
MeSCN	Cr	740 s (704 m, 678 m–w, 642 w)
	W	740 s, 678 m
EtSCN	Cr	735 s, 628 m–w (689 w, 661 w, 633 m)
	W	735 s, 650 w, 624 m
PhSCN	Cr	748 vs, 692 s (746 vs, 692 s)
	W	752 vs, 690 s
TDMA	Cr	728 m, 709 w, 615 m (715 w, 679 m, 616 m–w)
	W	733 vw, 707 w

[a] Concentration of PhSCN and $M(CO)_5(PhSCN)$ solutions was ~0.1 *M*; the other solutions were ~0.5 *M*. [b] For M = Cr an intense Cr–C–O absorption obscures the 670–640-cm^{-1} region. ν_{CS} frequencies for the free ligands are given in parentheses. [c] Abbreviations: s, strong; m, medium; w, weak; v, very.

Table IV. ^1H Chemical Shifts for $M(CO)_5L$ Complexes in Acetone-d_6 Solution

L	M	δ(R)[a]			
CH_3CH_2OCN	Cr[b]	CH_2	4.58[c] (4.54)[d]		CH_3 1.57[c] (1.45)[d]
C_6H_5OCN	Cr	C_6H_5[e]	7.42 (7.38)		
	W		7.50		
CH_3SCN	Cr	CH_3	2.76 (2.65)		
	W		2.82; 2.73[c] (2.62)[c]		
CH_3CH_2SCN	Cr	CH_2	3.22 (3.06)[f]		CH_3 1.50 (1.45)[f]
	W		3.35		1.56
C_6H_5SCN	Cr	C_6H_5[e]	7.50 (7.45)		
	W		7.60		
4-$H_2NC_6H_4$-SCN	Cr	C_6H_4[e]	7.31 (7.32),	6.73 (6.73)	NH_2 5.20 (4.90)
	W		7.36	6.75	5.01
4-$(CH_3)_2NC_6$-H_4SCN	Cr	C_6H_4[e]	7.38 (7.36),	6.71 (6.69)	CH_3 2.96 (2.96)
	W		7.50	6.79	3.02
CH_3SeCN	Cr	CH_3	2.68 (2.56)		
	W		2.74		
CH_3CH_2-SeCN	Cr	CH_2	3.31 (3.13)		CH_3 1.68 (1.63)
	W		3.36		1.70
C_6H_5SeCN	Cr	C_6H_5[e]	7.72 (7.60),	7.53 (7.40)	
4-$(CH_3)_2NC_6$-H_4SeCN	Cr	C_6H_4[e]	7.46 (7.44),	6.71 (6.65)	CH_3 2.98 (2.93)
$(CH_3)_2S$	W	CH_3	2.62 (2.12)[c]		
4-$BrC_6H_4NH_2$	Cr	NH_2	5.39 (4.70)		
	W		6.37		

[a] In ppm downfield from TMS internal standard. δ values for free ligands are given in parentheses. [b] Impure compound (see text). [c] $CDCl_3$ solution. [d] Neat liquid; from ref 30. [e] Center of a multiplet. [f] J_{HCCH} = 7 Hz in the free ligand and its complexes.

Table V. Selected ^{13}C Chemical Shifts[a] of Some $M(CO)_5(R{-}SCN)$ Complexes in Acetone (70% d_6) Solution

R-SCN	M	δ(CO)		δ(SCN)[b]
		Trans	Cis	
CH_3SCN	Cr	219.7	214.5	124.6 (113.8)
	W	200.2	196.8	121.0
4-$H_2NC_6H_4SCN$	Cr	219.7	214.4	123.1 (112.9)
	W	200.2	196.7	121.8

[a] In ppm downfield from TMS internal standard. [b] δ values for the free ligands are shown in parentheses.

viously reported R–XCN complexes,[1-9] the ν_{CN} frequencies are higher for the coordinated ligands. This is also the case for the $M(CO)_5(R{-}XCN)$ compounds, but the $\Delta\nu_{CN}$ values are generally much smaller. The increase in ν_{CN} is always larger for the chromium complexes, and it is much larger for cyanates than for thiocyanates and selenocyanates.

When the cyanate complexes are stored, even at −20°, the sharp ν_{CN} band at about 2300 cm^{-1} gradually disappears and is replaced by a very broad, weak absorption at about 2100 cm^{-1}. This change indicates decomposition of the ligands as a result of coordination to the metal carbonyls, since the free cyanates are stable for longer periods under the same conditions.[16,27]

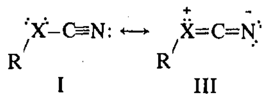
Table III shows the stretching frequencies in the C–S region (~740–600 cm^{-1})[28] for most of the organic thiocyanates and their Cr and W complexes. These spectra were determined in diethyl ether solution because of the rather high concentrations needed to observe these weak C–S bands. For chromium complexes the region is partially obscured by a very strong Cr–C–O vibration;[29] nevertheless, some changes in the C–S frequencies of the coordinated ligands can be seen for all of the complexes. In every case the highest frequency ν_{CS} band, which should correspond to the S–C stretch of the –SCN group,[28a] occurs at higher frequency in the complex than in the free ligand, though for the phenyl thiocyanate complexes this difference is small. For the alkyl thiocyanates the intensity of this band also appears to increase upon coordination.

The striking feature of the proton NMR spectra of the $M(CO)_5(R{-}XCN)$ complexes (Table IV) is the small effect of ligand coordination on the chemical shifts; the largest change is only about 0.3 ppm. Shifts upon coordination are toward lower field and are always larger for tungsten complexes than for the corresponding chromium compounds. Although the chromium ethyl cyanate complex was impure and rather unstable in solution, the chemical shifts clearly show the presence of the cyanate ligand.[30]

Carbon-13 NMR spectra were also determined for a few of the thiocyanate complexes (Table V). The carbonyl resonances give the typical pattern for $M(CO)_5L$ complexes,[31] the trans CO peaks occurring at lower field than the cis CO signals and the tungsten CO peaks appearing at higher field than the chromium CO resonances. The carbon resonance of the –SCN group is shifted downfield upon ligand coordination, this shift being slightly larger for chromium (~10 ppm) than for tungsten (7–9 ppm).

Discussion

The R–XCN ligands may be considered to be resonance hybrids of structures I and III



I III

Various studies[32-34] indicate that the more nonlinear structure (I) predominates, this form contributing about 74% for cyanates and about 90% for thiocyanates and selenocyanates. Thus, it is not unreasonable to regard these molecules as having two separate coordinating groups, an X atom and a cyano group. Intuitively, one might suppose that coordination through the cyano nitrogen lone pair would be more likely. This type of bonding is, in fact, proposed for several of the known R–XCN complexes,[1,4,7] but in other cases the ligands are reported to be X bound.[5,7-9] Therefore, in the present study it was necessary to determine which of the two possible modes of coordination occurs in the $M(CO)_5(R{-}XCN)$ complexes.

No distinction between N coordination and X coordination can be made on the basis of the C–N stretching frequencies. In the first instance, the increase in ν_{CN} could be attributed to an N-bound cyano group. This increase has been observed for complexes of other cyano groups such as nitriles,[35,36] cyanamides,[37] and cyanogen halides[38] and is believed to result from weak coupling of C–N and N–metal vibrations and an increase in the C–N stretching force constant.[35]

However, for an X-bound R–XCN ligand the increase in ν_{CN} could be the result of a larger contribution from resonance form I above, as is the case with, for example, an S-bound thiocyanate ion.[39] Further, in the previously reported R–XCN complexes the magnitude of $\Delta\nu_{CN}$ is subject to considerable variation, depending on the metal species and ligand as well as the bonding mode, and thus appears to be an unreliable sole criteron for assigning the mode of coordination of these ligands in new complexes.

The carbonyl frequencies (Table II) yield more significant information. It seems unlikely that the carbonyl spectra of corresponding thiocyanate and selenocyanate complexes would be almost identical if these ligands were coordinated through S and Se rather than the –CN group. Also shown in Table II are CO frequencies for several pentacarbonyl–nitrile complexes, and in most cases these are very similar to the carbonyl frequencies of the R–XCN complexes. It is also interesting that the changes in ν_{CN} are of similar magnitude for both $M(CO)_5(R{-}XCN)$ and $M(CO)_5(R{-}CN)$. These similarities suggest that the R–XCN ligands, like the nitriles, are N bound.

Coordination of a thiocyanate ligand through its sulfur atom should cause a weakening of the S–C bond of the –SCN group, owing to greater participation of the predominant resonance structure (I). A corresponding decrease in this C–S stretching frequency would be expected. The C–S frequencies given in Table III show that precisely the opposite effect is observed. A higher ν_{CS} frequency is more consistent with an increased contribution from resonance form III, as expected for an N-bound R–SCN ligand.

The very small differences between the proton NMR spectra (Table IV) of the coordinated and uncoordinated R–XCN ligands provide further evidence that the bonding in these complexes is most probably via the cyano nitrogen. For the two possible modes of coordination, the R group would be much nearer the perturbing influence of the metal species if the X atom were coordinated. It might be expected, for example, that the proton NMR shift of the R group of an alkyl thiocyanate would be affected in about the same way as the R groups of a coordinated dialkyl sulfide (R_2S), since these groups would be similarly located if both ligands were bound through sulfur. However, Table IV shows that the methyl resonance in the complex $W(CO)_5(Me_2S)$[40] is shifted 0.50 ppm downfield upon coordination, whereas the methyl signal of $W(CO)_5(MeSCN)$ is only 0.11 ppm lower than that of uncoordinated methyl thiocyanate. Thus, it appears that the thiocyanate methyl group must be more remote from the tungsten atom, as would be true if this ligand were N bound. Since the chemical shifts of the other R–XCN ligands are affected similarly by coordination, bonding through the cyano nitrogen evidently occurs in their complexes, also.

A final note of interest is the bonding of the ligand 4-thiocyanatoaniline (TA), which contains a second possible coordinating group. Comparison of the proton NMR spectra of the TA complexes with those of the 4-bromoaniline complexes (Table IV) shows that the TA amino group is slightly affected by coordination of the ligand, but much less so than the amino group of 4-bromoaniline. To obtain further evidence that no $-NH_2$ bonding occurs, the carbon-13 NMR spectra of the TA and methyl thiocyanate complexes (Table V) were examined. The similar downfield shift of the thiocyanate carbon resonances and the fact that the positions of the carbonyl peaks are almost the same with either ligand confirm coordination of TA via the –SCN rather than the $-NH_2$ group.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Institute of General Medical Sciences through PHS Research Grant No. GM-12626 for support of this research. The Bruker HX-90 spectrometer was purchased with funds provided by the National Science Foundation.

Registry No. $Cr(CO)_5(PhOCN)$, 57196-02-8; $W(CO)_5(PhOCN)$, 57196-04-0; $Cr(CO)_5(MeSCN)$, 57196-01-7; $W(CO)_5(MeSCN)$, 57196-05-1; $Cr(CO)_5(EtSCN)$, 57196-00-6; $W(CO)_5(EtSCN)$, 57196-06-2; $Cr(CO)_5(PhSCN)$, 57195-99-0; $W(CO)_5(PhSCN)$, 57196-07-3; $Cr(CO)_5(TA)$, 57195-98-9; $W(CO)_5(TA)$, 57196-08-4; $Cr(CO)_5(TDMA)$, 57195-97-8; $W(CO)_5(TDMA)$, 57196-09-5; $Cr(CO)_5(MeSeCN)$, 57195-96-7; $W(CO)_5(MeSeCN)$, 57196-10-8; $Cr(CO)_5(EtSeCN)$, 57196-03-9; $W(CO)_5(EtSeCN)$, 57196-11-9; $Cr(CO)_5(PhSeCN)$, 57196-12-0; $Cr(CO)_5(SDMA)$, 57196-13-1; $W(CO)_5(PhSeCN)$, 57196-14-2; $Cr(CO)_5(MeCN)$, 15228-38-3; $W(CO)_5(MeCN)$, 15096-68-1; $Cr(CO)_5(EtCN)$, 57196-15-3; $W(CO)_5(EtCN)$, 57196-16-4; $Cr(CO)_5(PhCH_2CN)$, 57196-17-5; $W(CO)_5(PhCH_2CN)$, 57196-18-6; $Cr(CO)_5(PhCN)$, 19706-01-5; $W(CO)_5(PhCN)$, 19705-90-9; $W(CO)_5[(CH_3)_2S]$, 31172-83-5; $Cr(CO)_5(4\text{-}BrC_6H_4NH_2)$, 57196-19-7; $W(CO)_5(4\text{-}BrC_6H_4NH_2)$, 16969-71-4; $[Et_4N][Cr(CO)_5I]$, 14780-98-4; $[Et_4N][W(CO)_5I]$, 14781-01-2; $[PPN][W(CO)_5NCS]$, 21948-45-8; $[PPN][Cr(CO)_5NCO]$, 57196-21-1; $[PPN][W(CO)_5NCO]$, 57196-22-2; $[Et_4N][Cr(CO)_5NCSe]$, 57196-24-4.

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