are simply not understood. Another unusual aspect is that plots of $\Delta H°$ vs. $\Delta S°$ are linear according to $\Delta S° = (2.9 \times 10^{-3})\Delta H° + 13$. The equation $\Delta G° = \Delta H° - T\Delta S$, upon substituting $\Delta G° = -RT \ln K$, may be arranged into the same form: $\Delta S° = (\Delta H°/T) + R \ln K$. The constants in the experimental equation are therefore related to $1/T$ and $R \ln K$. Thus $T = 344°K$ or $71°C$ and $K = 660$. This means that all of the reactions will have the same equilibrium constant (660) at 71°. This unusual relationship

between $\Delta H°$ and $\Delta S°$ has also been observed in a few other quite different systems[14,15] and has been discussed from a theoretical standpoint.[16]

(14) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **77**, 2164 (1955).
(15) G. Briegleb, "Elektronen-Donator-Acceptor Komplexe," Springer-Verlag, Berlin, 1961.
(16) W. B. Person, *J. Am. Chem. Soc.*, **84**, 536 (1962). We thank a referee for calling this reference to our attention.

# The Chemistry of Dinuclear Carbonyl Anions. IV.[1] Thiocyanate- and Cyanide-Bridged Complexes

By J. K. RUFF

The reaction of either cyanide or thiocyanate ions with $M(CO)_6$ (where $M = Cr$ or W) produced, in addition to the mononuclear anions $M(CO)_5X^-$, dinuclear anions of the type $M_2(CO)_{10}X^-$. Extension of this reaction to $Fe(CO)_5$ resulted in the preparation of the anions $Fe(CO)_4NCS^-$, $Fe(CO)_4CN^-$, and $Fe_2(CO)_8CN^-$. The spectra of these materials are discussed in relation to their structure.

The previous paper in this series[1] described the preparation of halogen-containing dinuclear carbonyl anions of the type $M_2(CO)_{10}X^-$ (where $X = I$, Br, or Cl). Their preparation was believed to occur in the stepwise manner

$$M(CO)_6 + X^- \longrightarrow M(CO)_5X^- + CO$$
$$M(CO)_5X^- + M(CO)_6 \longrightarrow M_2(CO)_{10}X^-$$
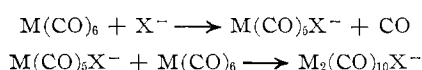
These reactions have now been extended to include the pseudohalides, CN^- and SCN^-. Both the mononuclear and the dinuclear species could be isolated when either chromium or tungsten hexacarbonyl was employed. Furthermore, treatment of iron pentacarbonyl under the same conditions led to the formation of the new anions $Fe(CO)_4CN^-$, $Fe_2(CO)_8CN^-$, and $Fe(CO)_4NCS^-$. The reaction of cyanide ion with iron pentacarbonyl appeared to be unique since no dinuclear iron carbonyl thiocyanate derivative could be isolated.

Experimental Section

The analytical data for the compounds prepared are summarized in Table I.

Materials.—The cyanide and thiocyanate salts of the bis-(triphenylphosphine)imminium cation (hereafter abbreviated as PPN) were prepared by reaction of the chloride with a large (50 times) excess of potassium cyanide or thiocyanate in aqueous solution. The metal carbonyls were obtained from commercial sources.

Preparation of (PPN)Fe(CO)₄NCS.—A mixture of 0.6 ml of Fe(CO)₅ and 1.19 g of (PPN)SCN in 50 ml of CH₂Cl₂ was irradiated with a uv flood lamp until 75 cm³ of gas (STP) was evolved. The solvent was removed from the mixture at room temperature. The residue was dissolved in 20 ml of CH₂Cl₂, and 120 ml of ether was added. The mixture was filtered, and pentane was added to the filtrate. A 0.55-g sample of product was obtained.

Preparation of (PPN)Fe(CO)₄CN and (PPN)Fe₂(CO)₈CN.—A mixture of 1.17 g of (PPN)CN and 0.6 ml of Fe(CO)₅ in 50 ml of CH₂Cl₂ was treated as described above. After irradiation was complete, the solvent was removed under vacuum. The residue was extracted three times with 50 ml of ether. Pentane was added to the combined extracts and a 0.21-g sample of (PPN)Fe₂(CO)₈CN was obtained. The residue from the extraction was dissolved in 10 ml of CH₂Cl₂ and 75 ml of ether was added. The mixture was filtered, and pentane was added to the filtrate. A 0.29-g sample of (PPN)Fe(CO)₄CN was obtained.

Preparation of (PPN)M(CO)₅NCS (Where M = Cr or W).—The preparations of both the chromium and tungsten derivatives were performed in analogous manners. A mixture of 1.0 g of Cr(CO)₆ and 1.25 g of (PPN)SCN in 30 ml of CH₂Cl₂ was irradiated with a uv flood lamp until 50 cm³ of gas (STP) was evolved. The solvent was removed from the mixture and the excess metal carbonyl was sublimed away. The residue was dissolved in 15 ml of CH₂Cl₂, and 50 ml of ether was added. The mixture was filtered, and pentane was added to the filtrate. The product crystallized on cooling.

Preparation of (PPN)M₂(CO)₁₀SCN (Where M = Cr or W).—The preparations of both the chromium and tungsten derivatives were carried out in analogous manners. A mixture of 0.69 g of (PPN)SCN and 1.0 g of Cr(CO)₆ in 50 ml of THF was irradiated until approximately 80 cm³ of gas had been evolved. The solvent was removed under vacuum. The residue was extracted with 25 ml of ether. Another 25-ml portion of ether was added to the extract, followed by pentane. The product crystallized on cooling and was recrystallized from ether and pentane.

The Preparation of (PPN)₂M(CO)₄(CN)₂ and (PPN)M(CO)₅CN (Where M = Cr or W).—The reaction was performed similarly for both the metal carbonyl derivatives. A mixture of 0.52 g of Cr(CO)₆ and 1.03 g of (PPN)CN in 50 ml of CH₂Cl₂

(1) Part III: J. K. Ruff, *Inorg. Chem.*, **7**, 1821 (1968).

<div align="center">

TABLE I

ANALYTICAL DATA FOR THE ANIONS PREPARED

</div>

Anion	% yield	Mp, °C	Calcd C	H	N	M	O or S	Found C	H	N	M	O or S
Fe(CO)₄CN⁻	22	132–134	67.8	4.10	3.82	7.7	8.7(O)	67.3	4.24	3.92	7.6	8.5(O)
Fe₂(CO)₈CN⁻	42	107–108	60.0	3.33	3.17	12.4	14.2(O)	59.6	3.34	3.23	12.1	13.9(O)
Fe(CO)₄NCS⁻	37	117–112	64.5	3.93	3.66	7.3	4.19(S)	64.4	4.18	3.80	7.2	4.07(S)
Cr(CO)₅CN⁻	77	148–150	66.7	3.97	3.70	6.9	8.9(O)	66.4	4.02	3.77	6.8	8.8(O)
Cr(CO)₄(CN)₂²⁻	64	253–255	4.64	4.33	3.25	4.02	5.0(O)	72.2	4.77	3.55	3.8	5.0(O)
Cr₂(CO)₁₀CN⁻	24	113–115	59.5	3.16	2.95	11.0	16.9(O)	59.4	3.14	3.15	10.7	16.7(O)
W(CO)₅CN⁻	13	127–129	56.8	3.38	3.15	20.7	9.0(O)	56.8	3.30	2.95	...	8.9(O)
W(CO)₄(CN)₂²⁻	62	267–270	65.3	4.21	3.93	12.9	4.5(O)	65.4	4.17	3.89	...	4.4(O)
W₂(CO)₁₀CN⁻	23	132–134	46.6	2.48	2.31	30.4	13.2(O)	46.5	2.52	2.33	...	13.3(O)
Cr(CO)₅NCS⁻	36	119–120	64.0	3.81	3.55	6.0	4.06(S)	63.9	3.85	3.75	5.4	3.92(S)
Cr₂(CO)₁₀SCN⁻	78	90–91	57.6	3.06	2.85	10.6	3.26(S)	57.5	3.00	2.77	10.5	3.15(S)
W(CO)₅NCS⁻	32	137–139	54.8	3.26	3.04	20.0	8.7(O)	54.8	3.30	3.11	...	8.5(O)
W₂(CO)₁₀SCN⁻	63	99–100	45.4	2.41	2.25	29.6	12.9(O)	45.3	2.51	2.32	...	12.7(O)

was irradiated until 52 cm³ (STP) of gas had been evolved. The solvent was removed *in vacuo* and the residue was dissolved in 10 ml of CH_2Cl_2. Ether (20 ml) was added to precipitate 0.62 g of $(PPN)_2Cr(CO)_4(CN)_2$. It was recrystallized from a mixture of 15 ml of CH_2Cl_2 and 10 ml of ether. Ether (40 ml) was added to the filtrate from above and the mixture was filtered. Pentane was added to the filtrate. A 0.12-g sample of $(PPN)Cr(CO)_5CN$ was obtained. The yields given in Table I for the tungsten derivatives are those obtained by this method. A better way to make $(PPN)Cr(CO)_5CN$ is described below. A 0.26-g sample of $Cr(CO)_6$ in 50 ml of THF was irradiated until 41 cm³ of gas (STP) had been evolved. Then a 0.87-g sample of (PPN)CN was added to the mixture. After stirring for 10 min, the solvent was removed under reduced pressure. The residue was dissolved in 50 ml of CH_2Cl_2, and 60 ml of ether was added. The mixture was filtered and a 0.37-g sample of (PPN)CN was recovered. Pentane was added to the filtrate. A 0.52-g sample of (PPN)-$Cr(CO)_5CN$ was obtained.

The disubstituted cyanide derivative can also be made by a thermal method. A mixture of 1.12 g of (PPN)CN and 0.6 g of $Cr(CO)_6$ was carefully mixed in 50 ml of Ansul ether 121. The mixture was refluxed 3 hr during which time the product crystallized. A 0.75-g sample of $(PPN)_2Cr(CO)_4(CN)_2$ was obtained by filtering the warm reaction mixture. It was recrystallized from CH_2Cl_2 and ether.

Preparation of $(PPN)M_2(CO)_{10}CN$ (Where M = Cr or W).— The reaction was carried out similarly for both of the derivatives. A mixture of 0.71 g of (PPN)CN and 1.0 g of $Cr(CO)_6$ in 50 ml of THF was irradiated until 75 cm³ of gas (STP) had been evolved. The solvent was removed from the mixture under vacuum. The residue was extracted with 25 ml of ether, and 25 ml of ether was added to the extract. The addition of pentane resulted in the precipitation of the impure product. It was recrystallized from ether and pentane.
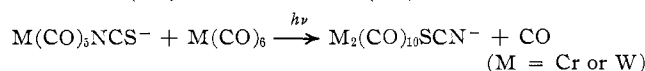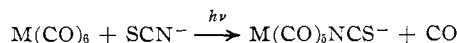
Infrared Spectra.—The infrared spectra in the carbonyl stretching region of the compounds prepared were obtained on solutions of approximately 0.010 g/ml in CH_2Cl_2 unless noted otherwise. The instrument, a Perkin-Elmer Model 521 spectrometer, was calibrated with indene. Table II tabulates the bands observed in the carbonyl region. The spectrum of (PPN)-$Fe(CO)_4NCS$ was obtained in CH_3CN, CH_2Cl_2, and THF solutions. No changes were observed in the spectrum and little or no shift in frequency of the CN and CO stretching modes occurred as a function of either time or solvent. The solid-state spectra were obtained on Nujol mulls using KBr plates.

Conductivity Measurements.—The conductivity of all of the compounds prepared was determined on solutions approximately 10^{-3} M in nitromethane using equipment previously described.[2] The specific conductivity of the nitromethane employed was 5.82×10^{-7} ohm⁻¹ cm⁻¹. The anion, concentration (M), and molar conductance (cm⁻²/ohm equiv) are: $Fe(CO)_4NCS^-$,
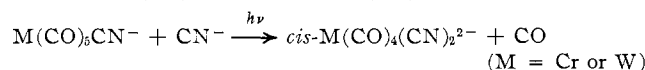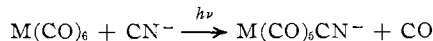
1.042×10^{-3}, 75.9; $Fe(CO)_4CN^-$, 1.029×10^{-3}, 73.4; Fe_2-$(CO)_8CN^-$, 1.000×10^{-3}, 63.3; $Cr_2(CO)_{10}SCN^-$, 1.000×10^{-3}, 60.1; $Cr_2(CO)_{10}CN^-$, 1.042×10^{-3}, 57.2; $W_2(CO)_{10}SCN^-$, 1.042×10^{-3}, 57.9; $W_2(CO)_{10}CN^-$, 1.007×10^{-3}, 59.2; Cr-$(CO)_4(CN)_2^{2-}$, 0.985×10^{-3}, 155.5; $W(CO)_4(CN)_2^{2-}$, 1.028×10^{-3}, 154.6.

Results and Discussion

The reaction of halide ions with the group VI metal carbonyls using photolytic activation has recently been shown[1] to be a two-step process yielding both mononuclear and dinuclear species. This reaction has now been extended to include the cyanide and thiocyanate ions. Thiocyanate behaved similarly to iodide and by employing the appropriate experimental

$$M(CO)_6 + SCN^- \xrightarrow{h\nu} M(CO)_5NCS^- + CO$$
$$M(CO)_5NCS^- + M(CO)_6 \xrightarrow{h\nu} M_2(CO)_{10}SCN^- + CO$$
$$(M = Cr \text{ or } W)$$

conditions either the mononuclear or the dinuclear anions could be isolated in moderate yield. The reaction of cyanide ion with the group VI metal carbonyls was more complicated. Photolysis of mixtures of cyanide ion and the group VI metal carbonyl under conditions which normally lead to the formation of the mononuclear species produced two products. The

$$M(CO)_6 + CN^- \xrightarrow{h\nu} M(CO)_5CN^- + CO$$
$$M(CO)_5CN^- + CN^- \xrightarrow{h\nu} cis\text{-}M(CO)_4(CN)_2^{2-} + CO$$
$$(M = Cr \text{ or } W)$$

disubstituted derivative predominated over the mono-substituted by a ratio of about 4:1 even when an excess of carbonyl was used. It appears that a cyanide group labilizes a *cis*-carbonyl group for further photochemical substitution. This does not seem to occur to such a great extent when thermal activation is used. In order to obtain the monosubstituted derivative in decent yield, it was necessary first to prepare a solution containing $Cr(CO)_5 \cdot$ THF (THF = tetrahydrofuran)[3] by photolysis before adding the cyanide ion. However, by using THF as a solvent and a large excess of

$$Cr(CO)_6 + THF \xrightarrow{h\nu} Cr(CO)_5 \cdot THF + CO$$
$$Cr(CO)_5 \cdot THF + CN^- \longrightarrow Cr(CO)_5CN^- + THF$$
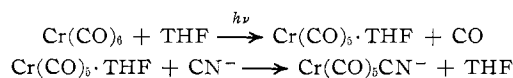
(2) J. K. Ruff, *Inorg. Chem.*, **2**, 813 (1963).

(3) W. Strohmeier, *Angew Chem. Intern. Ed. Engl.*, **3**, 730 (1964).

the metal hexacarbonyl, it was possible to isolate dinuclear derivatives in moderate yield.

The preparation of three iron anionic derivatives has recently been reported.[4,5] No evidence was found for the formation of dinuclear species in either study under both photolytic and thermal conditions. This was also found to be true for the reaction of thiocyanate ion with iron pentacarbonyl. However, two products

$$Fe(CO)_5 + SCN^- \xrightarrow{h\nu} Fe(CO)_4NCS^- + CO$$
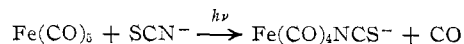
were obtained when cyanide was employed. The solvent used did not seem to affect the product distribution as it did in the case of the group VI derivatives.

$$Fe(CO)_5 + CN^- \xrightarrow{h\nu} Fe(CO)_4CN^- + CO$$

$$Fe(CO)_4CN^- + Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_8CN^- + CO$$
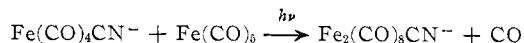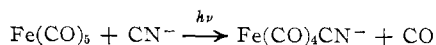
The dinuclear derivative was obtained in higher yield than the mononuclear species and efforts to increase the yield of the latter were not successful. This is the first example of an anionic dinuclear derivative containing groups other than CO or hydrogen. Since this compound is isoelectronic with $Fe_2(CO)_9$, the question of structural similarities becomes vital (see discussion later). All of the anions were isolated as the bis(triphenylphosphine)imminium salts.[6]

The group VI metal carbonyl derivatives prepared in this study appear to be stable in air in the solid state although they are slowly oxidized in solution. The iron derivatives are more reactive toward oxygen than the others. All the salts are soluble in polar organic solvents such as CH_2Cl_2, CH_3CN, CH_3NO_2, and THF. The dinuclear species are also soluble in ether. The iron derivatives are yellow to orange and the group VI derivatives are yellow. Proton nmr measurements showed that no hydridic hydrogen or paramagnetic impurities were present in these compounds. The molar conductivity of approximately 10^{-3} M nitromethane solutions was in the range attributed to 1:1 electrolytes for all of the salts except the two disubstituted cyano derivatives.[7] These salts had a molar conductance approximately twice that of the monosubstituted cyano derivatives as expected.

The infrared spectra (see Table II) of the mononuclear thiocyanate derivatives of chromium and tungsten are identical with those of the same compounds prepared in a thermal reaction.[8] The presence of a CS stretching band in the 790–810-cm^{-1} region indicates that the thiocyanate group is bonded through nitrogen. Thus, the room-temperature preparation of these materials produced the same isomer that was obtained at 100°.

Both the monosubstituted and disubstituted cyano

TABLE II
INFRARED SPECTRA OF THE ANIONS (CM^{-1})

Anion	ν_{CN}	ν_{CO}			ν_{CS}
Fe(CO)₄NCS[a]	2118 w	2045 m, 1948 w, sh			
Fe(CO)₄NCS[b]	2115 w	2043 m, 1946 w, sh, 1930 vs, doublet			809 w
Fe(CO)₄CN⁻	2100 w	2034 m, 1946 w, sh, 1927 s			
Fe₂(CO)₈CN⁻	2152 w	2036 m, 1938 s, 1900 w, sh			
Cr(CO)₅NCS	2112 w	2066 w, 1988 w, sh, 1933 s, 1872 m			795 w[b]
Cr₂(CO)₁₀NCS[a]	2143 w	2070 vw, 2058 w, 1975 sh, 1940 s, 1923 m, sh, 1872 ms			762 w[b]
Cr(CO)₅CN	2094 w	2051 w, 1966 w, sh, 1921 s, 1879 m			
Cr(CO)₄(CN)₂	2080 w, sh	2071 w, 1980 mw, 1867 s, 1841 m, sh, 1791 m			
Cr₂(CO)₁₀CN	2131 vw	2054 w, 1971 w, sh, 1946 s, 1894 m, 1873 m			
W(CO)₅NCS	2101 w	2062 vw, 1965 w, sh, 1919 vs, 1872 m			805 w[b]
W₂(CO)₁₀NCS[a]	2138 w	2070 vw, sh, 2061 w, 1972 w, 1934 s, 1917 m, sh, 1879 m			765 w[b]
W(CO)₅CN	2098 w	2056 w, 1961 w, sh, 1914 s, 1879 m, sh			
W(CO)₄(CN)₂	2088 vw, sh	2080 w, 1983 w, 1861 s, 1842 m, sh, 1790 m			
W₂(CO)₁₀CN[a]	2121 vw	2056 w, 1965 w, sh, 1929 s, 1895 m, 1873 m			

[a] Taken on THF solutions. [b] Taken on the solid state as a Nujol mull.

derivatives of chromium have been reported.[9,10] They were prepared by the reaction of cyanide ion with the pentacarbonylchromate(2−) ion. The photolytic preparation is much simpler and uses much more readily available starting materials. The infrared spectrum of the monocyano derivative, while not identical with published spectra, is in reasonable agreement with them.[11] The difference may be due to solvent effects. The infrared spectrum of the Cr(CO)₄(CN)₂²⁻ ion does not agree with the reported spectra[10] and appears to contain carbonyl bands which are shifted to lower frequency. The spectrum, however, is consistent with the *cis* substitution since two ν_{CN} frequencies may be assigned (2080 and 2071 cm^{-1}) and four carbonyl frequencies are observed as required for C_{2v} symmetry. One of the carbonyl frequencies is in the region normally attributed to bridging carbonyls. However, this is believed to arise from the presence of the negative charges on the ion which results in a shift to lower frequencies. Both the mono- and disubstituted derivatives of tungsten appear to be similar to the corresponding chromium compounds.

The structure of the dinuclear species is not known, but some information is available from the infrared spectra of the complex ions. No bands were observed in the region attributed to bridging carbonyl groups as was found for the analogous dinuclear halide species.[1] Behrens and his coworkers prepared both the cyano and thiocyanato[12] dinuclear chromium derivatives by a complicated procedure and have studied their infrared spectra.[11] They also found no evidence for bridging carbonyl groups. In addition to the ν_{CN} stretching band, they observed four bands attributable to carbonyl stretches. On this basis they concluded that the ions had D_{4d} symmetry with linear bridging cyanide or thiocyanate groups even though only three active infrared frequencies are predicted for this symmetry. However this symmetry is inappropriate for these ions

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(5) E. W. Abel, I. S. Butler, and C. R. Jenkins, *J. Organometal. Chem.* (Amsterdam), **8**, 382 (1967).

(6) R. Appel and A. Huass, *Z. Anorg. Allgem. Chem.*, **311**, 290 (1961).

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

(9) H. Behrens and J. Kohler, *Z. Naturforsch.*, **14b**, 462 (1959).

(10) H. Behrens and J. Kohler, *Z. Anorg. Allgem. Chem.*, **306**, 94 (1960).

(11) E. Lindner and H. Behrens, *Spectrochim. Acta*, **23A**, 3025 (1967).

(12) H. Behrens and D. Herrman, *Z. Naturforsch.*, **21b**, 1234 (1966).

even if a linear bridge is present because of the asymmetry of the bridging groups.

Strong evidence for the presence of bridging cyano and thiocyanato groups in these complexes is the increase in the CN stretching frequency over that in the $Cr(CO)_5CN^-$ and $Cr(CO)_5NCS^-$ ions. This increase has been observed in several other cases where bridging cyanide or thiocyanate groups are present.[13-15] It would be expected that the cyano-bridged complexes would be linear and have C_{4v} symmetry, and thus six infrared-active bands would be expected. Five are observed. It is not possible to determine whether the bridge in the thiocyanate complexes is linear (C_{4v}) or bent (C_{2v}) since either six or eight carbonyl bands would be predicted. Six are observed, but the possibility that some of the bands are degenerate cannot be ruled out.

The iron carbonyl cyanide derivatives appear to be analogous, in part, to the chromium or tungsten derivatives. The infrared spectrum of the mononuclear species is typical of a monosubstituted derivative iron pentacarbonyl.[16] The presence of one band attributable to ν_{CN} stretch and three bands in the carbonyl stretching region is compatible with C_{3v} symmetry. The cyanide band and, to a lesser extent, the carbonyl bands are shifted to lower frequencies when compared to the neutral methyl isocyanide complex, $CH_3N \equiv CFe(CO)_4$.[16] This again reflects the increased iron–carbon interaction due to the negative charge on the iron. The infrared spectrum of the dinuclear species indicates that there are no bridging carbonyl groups present. Thus, this material cannot have a structure similar to diiron enneacarbonyl. Since the ν_{CN} has increased over that found in the spectrum of the mononuclear species, the cyanide group most likely forms a linear bridge between the two irons.[13-15] The simplicity of the spectrum in the carbonyl region can be attributed to a lack of coupling of the carbon–oxygen stretching modes or to poor resolution.

The infrared spectrum of the $Fe(CO)_4NCS^-$ ion in the carbonyl stretching region appears to be typical of a monosubstituted iron pentacarbonyl derivative and is quite similar to the mononuclear iron carbonyl cyanide derivative (see Table II). Thus, it is likely that the thiocyanate group is bonded to the apical position of a trigonal bipyramid (C_{3v} symmetry) as are most of the monosubstituted iron pentacarbonyl compounds.[16] However, the question of linkage isomerization of the thiocyanate group must be raised. Recent work on thiocyanate derivatives of the transition metals has demonstrated that in a few cases the exchange from an S-bonded thiocyanate group to an N-bonded thiocyanate group is sufficiently slow so that both isomers may be identified.[17-20] The isomer identification is based primarily on the position of the C–S stretching frequency in the infrared region and to lesser extent on the position of the C–N stretching frequency. Only one isomer, $Fe(CO)_4NCS^-$, could be isolated in this study. Since the infrared spectrum of this compound contained a band at 809 cm^{-1}, it was assigned the N-bonded configuration. This band was present both in the solid state and in solution. Thus, isomerization to the S-bonded isomer was not observed. This is in contrast to the results reported for the compound $C_5H_5Fe(CO)_2SCN$ where both the S- and N-bonded isomers could be isolated.[20] However, it has been suggested that bonding of the thiocyanate group through sulfur would be favored by a higher oxidation state of iron so it is perhaps not unexpected that in the $Fe(CO)_4NCS^-$ ion the N-bonded form would predominate since the formal oxidation state of iron in the anion is -1 while it is $+2$ in the cyclopentadiene derivative.

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

(19) M. A. Jennings and A. Wojcicki, *Inorg. Chem.*, **6**, 1854 (1967).

(20) T. E. Sloan and A. Wojcicki, *ibid.*, **7**, 1268 (1968).