X = Br, I) anions with neutral ligands, provides a convenient route to a variety of seven-coordinate complexes. In terms of yields and experimental simplicity this method is to be rated equal to that involving halogen oxidation of molybdenum(0)- and tungsten(0)-substituted carbonyls for mono-, bi-, and tridentate ligands. However, it is the only known synthetic procedure for seven-coordinate complexes containing tetradentate ligands that do not form the dicarbonyls $M(CO)_2(L\text{-}L)_3$ (M = Mo, W).

Infrared Spectra.—The infrared carbonyl stretching frequencies of the complexes, recorded in solution and in the solid, exhibit several rational trends. Accordingly, for the same ligands, the molybdenum compounds absorb at higher wave numbers than the tungsten analogs. Other factors being equal, complexes containing the more polarizable iodide give rise to carbonyl absorptions at lower wave numbers than those containing coordinated bromide. Further, the anions $M(CO)_3I_3P(C_6H_5)_3^-$ (M = Mo, W) show lower carbonyl stretching frequencies than the neutral tricarbonyls.

Unfortunately, little can be said about the structures of these seven-coordinate complexes from the spectral data. For all of the dicarbonyls in CH_2Cl_2 solution, the symmetric CO stretching frequency is of higher intensity than the asymmetric one, suggesting that the OC–M–CO angle is less than 90°.[28,29] However, there are several structures in which such a bond angle is to be expected, and therefore extensive speculation at this time is inappropriate.

Acknowledgment.—The authors thank the National Science Foundation for financial support of this research through Grants GP-5729 (to D. W. M.) and GP-5466 (to A. W.).

---

(28) A. Reckziegel and M. Bigorgne, *J. Organometal. Chem.* (Amsterdam), **3**, 341 (1965).

(29) W. Beck, A. Melnikoff, and R. Stahl, *Angew. Chem.*, **77**, 719 (1965).

Contribution from the McPherson and Evans Chemical Laboratories,
The Ohio State University, Columbus, Ohio 143210

Linkage Isomerism in Carbonyl-π-cyclopentadienyl(thiocyanato)metal Complexes[1]

By THOMAS E. SLOAN[2] AND ANDREW WOJCICKI

Received March 28, 1968

Both sulfur- and nitrogen-bonded thiocyanato linkage isomers of dicarbonyl-π-cyclopentadienyliron and tricarbonyl-π-cyclopentadienylmolybdenum have been prepared by air oxidation of dicarbonyldi-μ-carbonyldiπ-cyclopentadienyldiiron in the presence of potassium thiocyanate and hexafluorophosphoric acid and by the reaction of tricarbonyl-π-cyclopentadienylhydromolybdenum with thiocyanogen. The isomers are readily separable by chromatography. The thiocyanato-S complex of iron does not undergo linkage isomerization in chloroform at 36°, in bis(2-methoxyethyl) ether at 50°, and in refluxing acetonitrile but converts readily to the thiocyanato-N form in the solid at 35–40°. Isomerization of tricarbonyl-π-cyclopentadienyl(thiocyanato)molybdenum to the corresponding isothiocyanate either in chloroform or in acetonitrile at 35° is essentially complete in 5 hr. The reaction of tricarbonyl-π-cyclopentadienylhydrotungsten with thiocyanogen affords only the sulfur-bonded thiocyanate, which is stable with respect to linkage isomerization. The previously synthesized π-cyclopentadienyldinitrosyl(isothiocyanato)chromium was shown by infrared spectroscopy, a technique employed throughout this study, to contain a chromium–nitrogen linkage for the thiocyanate. The results of this and of other investigations on thiocyanatocarbonyls are compared.

Introduction

The synthesis of a number of thiocyanatocarbonyl complexes of manganese(I),[3,4] chromium(0),[5] chromium(I),[6] molybdenum(0),[5] tungsten(0),[5] and rhodium(I)[7] has been reported recently. Interestingly, whereas for pentacarbonyl(thiocyanato)manganese both the S- and the N-bonded linkage isomers were detected, the former being the stable species in the solid,[3] the isoelectronic $Cr(CO)_5(NCS)^-$ was found always to contain a Cr–NCS attachment.[5] On the basis of these and some related observations Farona and Wojcicki[4] suggested that in complexes containing strongly π-bonding ligands, higher oxidation states of the metal promote M–SCN bonding, and lower oxidation states favor M–NCS bonding. In order to test this hypothesis over a wider range of oxidation states the synthesis of $Fe(CO)_4(CNS)_2$,[8] expected to contain Fe–SCN linkages, was attempted, albeit unsuccessfully.[3]

Inasmuch as the complexes $C_5H_5M(CO)_xX$ (X = Cl, Br, I) may be formally regarded as containing metal in the +2 oxidation state, we have now prepared several corresponding derivatives with X = NCS and SCN. Reported here are the results of our investigation on the synthesis and on the nature of metal–thiocyanate

---

(1) Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 10–14, 1967.

(2) Based on the M.S. thesis submitted by T. E. S. to The Ohio State University, 1968.

(3) M. F. Farona and A. Wojcicki, *Inorg. Chem.*, **4**, 857 (1965).

(4) M. F. Farona and A. Wojcicki, *ibid.*, **4**, 1402 (1965).

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

(6) H. Behrens and D. Herrmann, *Z. Naturforsch.*, **21b**, 1236 (1966).

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

(8) In this paper NCS designates M–NCS bonding, SCN designates M–SCN bonding, and CNS designates either that the bonding is not known or that both isomers are present.

bonding in $C_5H_5M(CO)_x(CNS)$ (M = Fe, x = 2; M = Mo, W; x = 3) as well as some proton magnetic resonance and infrared spectral data on these and the analogous halogeno derivatives.

Experimental Section

Materials.—Hexafluorophosphoric acid (65%), dicarbonyldi-μ-carbonyldi-π-cyclopentadienyldiiron, nickel tetracarbonyl, and dicarbonyl-π-cyclopentadienylcobalt were purchased from Alfa Inorganics, Inc. Hexacarbonyldi-π-cyclopentadienyldimolybdenum was obtained from Pressure Chemical Co., whereas tungsten hexacarbonyl was a gift from Climax Molybdenum Co. Carbon tetrabromide was purchased from Matheson Coleman and Bell, and nickelocene was obtained from Arapahoe Chemicals, Inc. They were used without further purification.

All solvents, with the exception of hexane and pentane, were reagent grade. Tetrahydrofuran and bis(2-methoxyethyl) ether were distilled from lithium aluminum hydride immediately before use. Fisher Florisil (60–100 mesh) was used in chromatography.

Solutions of thiocyanogen in hexane were prepared by the oxidation of suspended lead thiocyanate with pure bromine under scrupulously dry conditions.[9] They were filtered and used immediately for subsequent reactions.

The compounds $C_5H_5Fe(CO)_2Cl$,[10] $C_5H_5Fe(CO)_2I$,[11] $C_5H_5Mo(CO)_3H$,[12] $C_5H_5Mo(CO)_3X$[12] (X = Cl, Br), $C_5H_5W(CO)_3H$,[12] $C_5H_5W(CO)_3Cl$,[13] $C_5H_5Cr(NO)_2Cl$,[14] $C_5H_5Cr(NO)_2(NCS)$,[11] and $[C_5H_5Ni(CO)]_2$[15] were synthesized as described in the literature. The bromide $C_5H_5Fe(CO)_2Br$ was obtained (1.5 g, 52% yield) by air oxidation of an absolute ethyl alcohol solution (300 ml) of $[C_5H_5Fe(CO)_2]_2$ (2.0 g, 5.6 mmol), KBr (4.0 g, 31 mmol), and 65% HPF_6 (6 ml) for 3 hr at 25°. The complexes $C_5H_5Cr(NO)_2X$[11] (X = Br, I) were prepared by treating aqueous $C_5H_5Cr(NO)_2Cl$ with $AgNO_3$ and then adding 20% excess NH_4Br or KI to the resulting solutions.

Two new cyclopentadienyltungsten carbonyl halides were prepared as follows. They were characterized only by their nmr and infrared spectra (Table I).

(a) **$C_5H_5W(CO)_3Br$.**—A solution of $C_5H_5W(CO)_3H$ (2.0 g, 6.0 mmol) and CBr_4 (2.2 g, 6.5 mmol) in 75 ml of ether was heated at 32° under nitrogen for *ca.* 10 min. After the solvent was evaporated off, sublimable material was removed at 40° (0.1 mm). The residue was dissolved in 5 ml of $CHCl_3$ and the product crystallized upon addition of pentane (50 ml). The red crystals were collected on a filter and washed with three 5-ml portions of pentane; yield 2.0 g (81%).

(b) **$C_5H_5W(CO)_3I$.**—Iodine (0.84 g, 3.3 mmol) was added to a solution of $C_5H_5W(CO)_3H$ (2.0 g, 6.0 mmol) in 75 ml of ether under nitrogen. An immediate color change to deep red took place. The solution was treated with two 50-ml portions of 0.1 *M* aqueous $Na_2S_2O_3$ to remove excess iodine, and then the ether layer was dried over $MgSO_4$ for *ca.* 8 hr. The mixture was filtered, the ether was evaporated off, and sublimable material was removed at 40° (0.1 mm). The residue was dissolved in 5 ml of $CHCl_3$ and the product crystallized upon addition of pentane (50 ml). The red crystals were collected on a filter and washed with three 15-ml portions of pentane; yield 2.4 g (87%).

Preparation of Carbonyl-π-cyclopentadienyl(thiocyanato)metal Complexes. (a) $C_5H_5Fe(CO)_2(SCN)$ and $C_5H_5Fe(CO)_2(NCS)$.—Hexafluorophosphoric acid (6 ml) and KSCN (7.0 g, 72 mmol) were added to $[C_5H_5Fe(CO)_2]_2$ (3.5 g, 9.9 mmol) in absolute ethyl alcohol (300 ml). Air was bubbled through and the solution was stirred magnetically at 25° for 1 hr. Solvent was then removed under reduced pressure (~20 mm) and the residue was extracted with 200 ml of distilled water. The solution was filtered and the residual solid was washed with dichloromethane until the final wash was colorless (*ca.* 75 ml). The aqueous phase was extracted with CH_2Cl_2, the extracts were combined with the dichloromethane wash, and the solution was dried over 5 g of $MgSO_4$ for 24 hr. It was then filtered and concentrated to approximately 10 ml. Chromatography of this solution in two equal portions on Florisil columns (3 × 35 cm), eluting with CH_2Cl_2, resulted in the appearance of two bands, yellow and red. The yellow bands were eluted off, the solutions were combined, their volume was reduced to *ca.* 5 ml, and 50 ml of pentane was added. Golden-yellow crystals were collected on a filter and washed with three 15-ml portions of pentane;[16] yield 0.86 g (18.5%); mp 119–121° dec. *Anal.* Calcd for $C_8H_5O_2NSFe$ (isomer A): C, 40.9; H, 2.13; N, 5.97; S, 13.7; mol wt, 235. Found: C, 41.2; H, 2.4; N, 5.8; S, 13.43; mol wt, 247.

TABLE I

INFRARED (CM^{-1}) AND PROTON MAGNETIC RESONANCE (τ) SPECTRAL DATA FOR THE COMPLEXES[n]

Compound	CO or NO str[a]	CN str[a]	A(CN) × 10^{-4}	CS str[b]	Chem shift[c]
$C_5H_5Fe(CO)_2Cl$	2061 vs, 2019 vs[d]				4.94[e]
$C_5H_5Fe(CO)_2Br$	2057 vs, 2015 vs				*f*
$C_5H_5Fe(CO)_2I$	2043 vs, 2005 vs[g]				4.96
$C_5H_5Fe(CO)_2(NCS)$	2072 vs, 2035 vs	2123 s	6.70	830 m	4.86
$C_5H_5Fe(CO)_2(SCN)$	2056 vs, 2013 vs	2118 m	1.64	698 w	4.94
$C_5H_5Mo(CO)_3Cl$	2063 vs, 1990 vs, br[h]				4.28
$C_5H_5Mo(CO)_3Br$	2055 vs, 1983 vs, br[i]				4.38
$C_5H_5Mo(CO)_3I$	2040 vs, 1968 vs, 1955 sh[j]				*f*
$C_5H_5Mo(CO)_3(NCS)$	2068 vs, 1997 vs, br	2099 s	9.80	*k*	4.33
$C_5H_5Mo(CO)_3(SCN)$	2056 vs, 1988 vs, 1974 vs	2114 m–s	2.19	699 w	4.33
$C_5H_5W(CO)_3Cl$	2052 vs, 1968 vs, br				4.23
$C_5H_5W(CO)_3Br$	2048 vs, 1966 vs, br				4.26
$C_5H_5W(CO)_3I$	2040 vs, 1961 vs, br				4.30
$C_5H_5W(CO)_3(SCN)$	2050 vs, 1975 vs, 1959 vs	2127 m	1.54	695 w	4.21
$C_5H_5Cr(NO)_2Cl$	1821 vs, 1717 vs[l]				4.28
$C_5H_5Cr(NO)_2Br$	1823 vs, 1720 vs				*f*
$C_5H_5Cr(NO)_2I$	1822 vs, 1722 vs				*f*
$C_5H_5Cr(NO)_2(NCS)$	1828 vs, 1728 vs[m]	2103 s[m]	10.5	*k*	4.17

[a] Chloroform solution. [b] Nujol mull. [c] All peaks are singlets. [d] Lit.[10] 2050 vs, 2010 vs. [e] Measured at concentrations of 1.05, 2.92 × 10^{-1}, and 1.70 × 10^{-1} *M* with the same result. [f] Not measured. [g] Lit.[11] 2044 vs, 2000 vs. [h] Lit.[12] 2055 vs, 1980 vs, 1960 vs. [i] Lit.[12] 2049 vs, 1977 vs, 1958 vs. [j] From ref 12. [k] Masked by other absorptions. [l] Lit.[11] 1823 vs, 1715 vs. [m] Lit.[11] 1827 vs, 1723 vs, (NO), 2094 vs (CN). [n] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder.

After the red band had moved down each column, the top 4 cm of Florisil was removed mechanically to separate the adsorbed impurities. The bands were then eluted from their respective columns with acetone. The solutions were combined and the acetone was removed (~20 mm) to leave a red oil. This was dissolved in 50 ml of ethyl ether, and the volume of the solution was reduced to 10 ml in a stream of nitrogen. Addition of 50 ml of pentane afforded dark red crystals, which were collected on a filter and washed with three 15-ml portions of cold (0°) pentane;[16] yield 1.8 g (39%); mp 36–40° (isomerization). *Anal.* Calcd for $C_8H_5O_2NSFe$ (isomer B): C, 40.9; H, 2.13; N, 5.97; mol wt, 235. Found: C, 41.6; H, 2.56; N, 6.05; mol wt, 253.

Both A and B are soluble in acetone, acetonitrile, chloroform, and methanol, moderately soluble in benzene and ethyl ether, and sparingly soluble in saturated hydrocarbons. When isomer

---

[9] R. G. R. Bacon and R. S. Irwin, *J. Chem. Soc.*, 778 (1958).

[10] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

[11] T. S. Piper and G. Wilkinson, *ibid.*, **2**, 38 (1956).

[12] T. S. Piper and G. Wilkinson, *ibid.*, **3**, 104 (1956).

[13] E. O. Fischer and K. Fichtel, *Chem. Ber.*, **94**, 1200 (1961).

[14] R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press Inc., N. Y., 1965, pp 161–163.

[15] See ref 14, pp 119–121.

[16] Another chromatography is sometimes necessary to achieve complete separation of the two isomers.

B is heated at *ca.* 40°, it changes to an oil with a concomitant conversion to isomer A.

Attempts were also made to synthesize $C_5H_5Fe(CO)_2(CNS)$ from the corresponding chloride and iodide. The reaction of $C_5H_5Fe(CO)_2Cl$ (1.0 g, 4.7 mmol) in 150 ml of 50% aqueous methanol with 10 ml of 1 *M* aqueous $AgNO_3$ and 5 ml of 1 *M* HNO_3 resulted in the precipitation of AgCl. After filtration, the solution was treated with 25 ml of 1 *M* KSCN, filtered again, and extracted with 75 ml of $CHCl_3$. The red extract was dried over $MgSO_4$ for 24 hr, filtered, and concentrated to 10 ml. Chromatography using chloroform eluent gave one large red band with extensive trailing. Infrared spectra of various collected fractions showed them to be mixtures of the unreacted chloride and the thiocyanate. No efficient separation could be effected on repeated chromatographies. When $C_5H_5Fe(CO)_2I$ was used in place of the chloride, predominantly the unreacted iodide and a trace of red material, presumably $C_5H_5Fe(CO)_2(CNS)$, were isolated.

A mixture of $C_5H_5Fe(CO)_2I$ (1.0 g, 3.3 mmol), KSCN (0.6 g, 6.0 mmol), and HPF_6 (1 ml) in methanol (50 ml) was refluxed for 3 hr under nitrogen. The solvent was removed, the residue was extracted with 15 ml of CH_2Cl_2, and the extracts were chromatographed using dichloromethane eluent. Only the starting dicarbonyl was obtained. The chloride, $C_5H_5Fe(CO)_2Cl$, gave the same result.

(b) **$C_5H_5Mo(CO)_3(SCN)$ and $C_5H_5Mo(CO)_3(NCS)$.**—Thiocyanogen (*ca.* 8.4 mmol) in 40 ml of hexane was added slowly with stirring to 2.0 g (8.1 mmol) of $C_5H_5Mo(CO)_3H$ in 50 ml of tetrahydrofuran at 0° and under nitrogen. The light yellow tetrahydrofuran solution turned red. After 1.5 hr of reaction time the solution was evaporated to dryness (~20 mm), the residue was extracted with three 5-ml portions of dichloromethane, and the extracts were chromatographed on a 3 × 35 cm column eluting with dichloromethane. Two bands, yellow and red, developed on the column. The yellow band was eluted off, the volume of the solution was reduced to *ca.* 5 ml (~20 mm), and pentane (50 ml) was added. The resulting red crystals were collected on a filter and washed with three 5-ml portions of pentane; yield 0.31 g (13%); mp 117–120° (chars). *Anal.* Calcd for $C_9H_5O_3NSMo$ (isomer A): C, 35.6; H, 1.65; N, 4.62; S, 10.57; mol wt, 303. Found: C, 35.46; H, 1.68; N, 4.8; S, 10.32; mol wt, 344.

After the red band was eluted to the bottom of the column, the top 4 cm of Florisil was removed mechanically to separate the adsorbed impurities. The band was then removed with acetone and the solvent was evaporated off. The light red residue was dissolved in 5 ml of CH_2Cl_2 and filtered; addition of 50 ml of pentane yielded crystals which were collected on a filter and washed with three 15-ml portions of pentane; yield 0.59 g (24%); mp 90–93° dec. *Anal.* Calcd for $C_9H_5C_3NSMo$ (isomer B): C, 35.6; H, 1.65; N, 4.62; S, 10.57; mol wt, 303. Found: C, 34.95; H, 1.33; N, 4.53; S, 10.35; mol wt, 293.

Both A and B are soluble in acetone, acetonitrile, and chloroform, but insoluble in saturated hydrocarbons.

(c) **$C_5H_5W(CO)_3(SCN)$.**—This compound was prepared from $C_5H_5W(CO)_3H$ (2.8 g, 8.4 mmol) and thiocyanogen (*ca.* 8.4 mmol) using a procedure similar to that described above for $C_5H_5Mo(CO)_3(CNS)$. On chromatographing, only one band, red, appeared on the column. It was eluted off with acetone, after the top 4 cm of Florisil had been removed mechanically from the column. The yield of light orange crystals was 0.4 g (12%); mp 119–120° dec. *Anal.* Calcd for $C_9H_5O_3NSW$: C, 27.6; H, 1.28; N, 3.59; S, 8.19; mol wt, 391. Found: C, 27.85; H, 1.40; N, 3.70; S, 8.08; mol wt, 371. The complex is soluble in polar organic solvents and insoluble in saturated hydrocarbons.

Attempted Preparation of Other Carbonyl-π-cyclopentadienyl(thiocyanato)metal Complexes. (a) **$C_5H_5Ni(CO)(CNS)$.**—A solution of thiocyanogen (*ca.* 8.4 mmol) in 40 ml of hexane was added with stirring to $[C_5H_5Ni(CO)]_2$ (1.5 g, 4.9 mmol) in 75 ml of hexane at *ca.* −10° and under nitrogen. Immediately, a black, amorphous precipitate, insoluble also in dichloromethane, was deposited. It was shown to contain no carbonyl groups (infrared spectroscopy).

When thiocyanogen in hexane was added to $[C_5H_5Ni(CO)]_2$ in tetrahydrofuran and the resulting solution was evaporated to dryness, chromatography of the residue, eluting with CH_2Cl_2, gave only one band, containing the unreacted carbonyl.

(b) **$C_5H_5Co(CO)(CNS)_2$.**—Mixing of hexane solutions containing 0.72 g (4.5 mmol) of $C_5H_5Co(CO)_2$ and 8.4 mmol of $(SCN)_2$ resulted in an immediate gas evolution and formation of a dark precipitate. This material, insoluble in dichloromethane and only very sparingly soluble in acetone, contained no carbonyl groups (infrared spectroscopy).

Infrared Spectra.—All spectra, except that of $C_5H_5Fe(CO)_2(SCN)$, were recorded on a Beckman Model IR-9 spectrophotometer. The spectrum of $C_5H_5Fe(CO)_2(SCN)$ in the region 1200–400 cm^{-1} was measured using a Perkin-Elmer Model 337 spectrophotometer. Solids were examined in Nujol suspensions between KBr plates; solutions were placed in a 0.05-mm KBr cell, with a matched reference cell being used at all times. The integrated absorption intensities, A (M^{-1} cm^{-2}), of the CN stretching bands were determined by Ramsey's method of direct integration.[17]

Proton Magnetic Resonance Spectra.—Nmr spectra were obtained in $CDCl_3$ solutions using a Varian Associates A-60 spectrometer. Tetramethylsilane was employed as an internal standard.

Molecular Weights.—Measurements were made on 1×10^{-2} to 2×10^{-2} *M* chloroform solutions with a Mechrolab Model 301-A osmometer.

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed in these laboratories by Mr. P. J. Kovi using a Coleman Model 29 analyzer and commercially by Galbraith Laboratories, Inc., Knoxville, Tenn., and Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Sulfur was determined by Galbraith and Pascher.

Results and Discussion

Synthesis and Characterization of Thiocyanato Complexes.—The two thiocyanato linkage isomers of dicarbonyl-π-cyclopentadienyliron were synthesized using a modified procedure of Piper, *et al.*,[10] for the preparation of $C_5H_5Fe(CO)_2Cl$. The method involved air oxidation of dicarbonyldi-μ-carbonyldi-π-cyclopentadienyldiiron in the presence of potassium thiocyanate and a strong acid containing a noncoordinating anion, hexafluorophosphoric acid. Metathetical reactions involving $C_5H_5Fe(CO)_2Cl$ or $C_5H_5Fe(CO)_2I$ and thiocyanate ion proved either unsuccessful or impractical because of the difficulties encountered in a complete removal of the unreacted carbonyl from the desired product.

Thiocyanatocarbonyl complexes of π-cyclopentadienylmolybdenum and -tungsten may be obtained from the reaction of their respective hydrides, $C_5H_5M(CO)_3H$ (M = Mo, W), with thiocyanogen. With molybdenum, both linkage isomers are formed, whereas, with tungsten, only the S-bonded thiocyanate is isolated. This synthetic procedure is somewhat analogous to that employed previously for the preparation of $C_5H_5Mo(CO)_3I$ from $C_5H_5Mo(CO)_3CH_3$ and iodine.[12]

Attempts to prepare $C_5H_5Ni(CO)(CNS)$ and $C_5H_5Co(CO)(CNS)_2$ by the interaction of $[C_5H_5Ni(CO)]_2$ and $C_5H_5Co(CO)_2$, respectively, with thiocyanogen resulted only in the formation of amorphous, noncarbonyl solids. This behavior contrasts that of the two car-

---

(17) D. A. Ramsey, *J. Am. Chem. Soc.*, **74**, 72 (1952).

bonyls toward iodine; in the latter reactions, $C_5H_5Ni(CO)I$[18] and $C_5H_5Co(CO)I_2$[19,20] are isolable.

Structural assignments for all of the thiocyanato complexes prepared in this study have been made on the basis of one or both of the following infrared spectral criteria: (a) position of the CS stretching frequency and (b) the integrated absorption intensity of the CN stretching band. All of the NCS bending absorptions for these complexes are masked by other peaks in the spectra. The pertinent data are listed in Table I and the complete spectra of $C_5H_5Mo(CO)_3(SCN)$ and $C_5H_5Mo(CO)_3(NCS)$ are shown in Figures 1 and 2, respectively.

The CS stretching frequencies of $C_5H_5Fe(CO)_2(SCN)$ (isomer B), $C_5H_5Mo(CO)_3(SCN)$ (isomer B), and $C_5H_5W(CO)_3(SCN)$ lie in the region 700–695 cm^{-1}, thus reflecting a common mode of M–SCN attachment therein.[21,22] This is supported by the values of the integrated absorption intensities of the CN stretching bands, which are in the range 1.54×10^4 to $2.19 \times 10^4\ M^{-1}\ cm^{-2}$.[23–25]

For $C_5H_5Fe(CO)_2(NCS)$ (isomer A), the CS stretching frequency indicates an Fe–NCS linkage;[21] however, for $C_5H_5Mo(CO)_3(NCS)$ (isomer A) and $C_5H_5Cr(NO)_2(NCS)$ the corresponding absorptions are masked by other, stronger bands in the spectra. Nevertheless, these complexes are assigned thiocyanato-N structures on the basis of the integrated intensities of their CN stretching absorption peaks, which fall in the range 6.70×10^4 to $10.5 \times 10^4\ M^{-1}\ cm^{-2}$, diagnostic of the isothiocyanates.[23]

The positions of the CN stretching bands are in concert with the foregoing conclusion,[26,27] the S-bonded thiocyanates absorbing at *ca.* 2120 cm^{-1} and the N-bonded thiocyanates at about 2100 cm^{-1}. One notable exception is provided by the linkage isomers of $C_5H_5Fe(CO)_2(CNS)$. There, the thiocyanate exhibits a lower stretching frequency (2118 cm^{-1}) than the isothiocyanate (2123 cm^{-1}). A similar reversal of the expected order was reported earlier by Schmidtke for complexes containing the ions $M(NH_3)_5(CNS)^{2+}$ (M = Rh, Ir).[28]

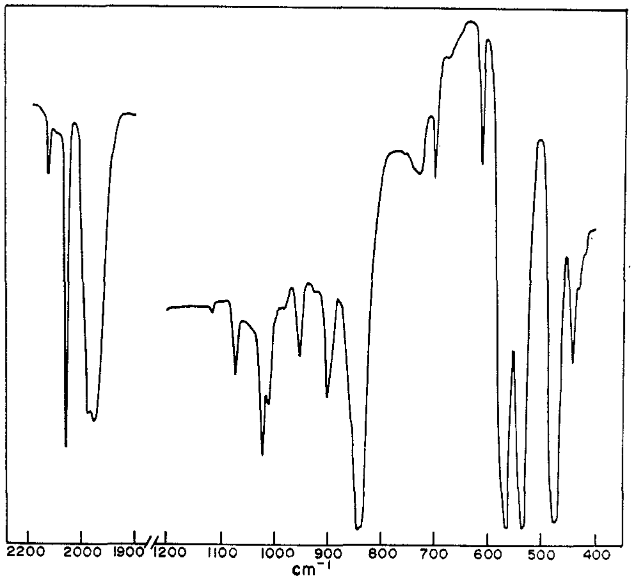


Figure 1.—The infrared spectrum of $C_5H_5Mo(CO)_3(SCN)$: 2200–1900 cm^{-1}, in chloroform solution; 1200–400 cm^{-1}, in Nujol mull.

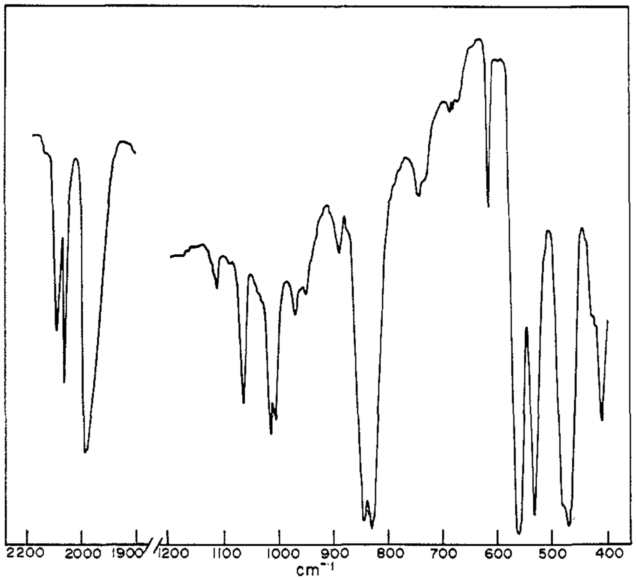


Figure 2.—The infrared spectrum of $C_5H_5Mo(CO)_3(NCS)$: 2200–1900 cm^{-1}, in chloroform solution; 1200–400 cm^{-1}, in Nujol mull.

Linkage Isomerization.—The formation of linkage isomers of both $C_5H_5Fe(CO)_2(CNS)$ and $C_5H_5Mo(CO)_3(CNS)$ and their facile and clean separation represent only the second example of such comparatively high kinetic stability with respect to isomerization of any pair of thiocyanato-S and -N species. Previously it was communicated that the reaction of $M(NH_3)_5(H_2O)^{3+}$ (M = Rh, Ir) with sodium thiocyanate yields a mixture of the S- and N-bonded $M(NH_3)_5(CNS)^{2+}$, each of which is stable under the experimental conditions.[28]

In order to elucidate the conditions necessary for linkage isomerization, a 0.033 *M* solution of $C_5H_5Mo(CO)_3(SCN)$ in acetonitrile was maintained at 35° under nitrogen. Infrared spectra in the carbonyl stretching frequency region were recorded periodically and are shown in Figure 3. It may be seen that the intensity of the CN stretching band at 2125 cm^{-1} of the S-bonded

---

(18) E. O. Fischer and C. Palm, *Chem. Ber.*, **91**, 1725 (1958).

(19) R. B. King, *Z. Naturforsch.*, **19b**, 1160 (1964).

(20) R. F. Heck, *Inorg. Chem.*, **4**, 855 (1965).

(21) Turco and Pecile[22] give the following ranges for the CS stretching frequencies: M–SCN, 720–690 cm^{-1}; M–NCS, 860–780 cm^{-1}. The position of this band was determined in each case by comparing the spectrum in the 860–660-cm^{-1} range of the thiocyanato derivative with that of a corresponding halogeno complex.

(22) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

(23) Pecile[24] reports the following ranges for the integrated intensities of the CN stretching absorption bands (*A*): M–SCN, 0.8–2.3 $\times 10^4\ M^{-1}\ cm^{-2}$; M–NCS, 9–12 $\times 10^4\ M^{-1}\ cm^{-2}$. For the organic thiocyanates and isothiocyanates, R–SCN and R–NCS, $A \sim 0.8 \times 10^4$ and 4–16 $\times 10^4\ M^{-1}\ cm^{-2}$, respectively.[25]

(24) C. Pecile, *Inorg. Chem.*, **5**, 210 (1966).

(25) C. Pecile and T. Tarantelli, *Ann. Chim.* (Rome), **52**, 75 (1962), and references therein.

(26) The CN stretching frequencies for M–SCN (>2100 cm^{-1}) are usually higher than those for M–NCS ($\leq$2100 cm^{-1}).[27]

(27) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

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

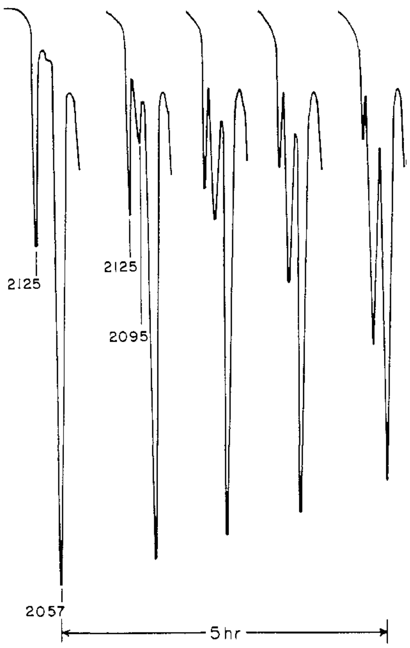


Figure 3.—Changes in the infrared spectrum in the carbonyl stretching region showing thiocyanato-S to thiocyanato-N linkage isomerization of $C_5H_5Mo(CO)_3(SCN)$ in an acetonitrile solution at 35°.

isomer diminishes as the CN stretching band at 2095 cm^{-1}, due to the N-bonded isomer, emerges and grows in intensity. The isomerization is accompanied by some decomposition, as evidenced by the deposition of an insoluble material from the solution and by a continuous diminution of intensity of the carbonyl band at *ca.* 2057 cm^{-1}.[29] Because of this complication, the system is not amenable to a kinetic study. After a period of 5 hr, most of the original S-bonded species disappears. The identity of the isothiocyanate is further confirmed by evaporation of the solvent, chromatography of the residue on Florisil using CH_2Cl_2 eluent, and comparison of the infrared spectrum of the eluted band with that of the authentic $C_5H_5Mo(CO)_3$-(NCS). Similar results were obtained using chloroform solutions at 35°.

By way of contrast, the infrared spectra of acetonitrile solutions of $C_5H_5W(CO)_3(SCN)$ thermostated at 50° under nitrogen revealed no new absorption bands in the carbonyl stretching region even after 8 hr. Some decomposition with the formation of an insoluble material was observed.

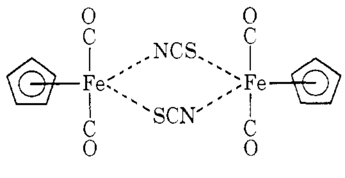
After $C_5H_5W(CO)_3(SCN)$ in bis(2-methoxyethyl) ether (*ca.* 0.025 *M*) was heated for 6 hr at 85° under nitrogen, the infrared spectrum of the solution revealed a new absorption peak at 2096 cm^{-1}. Extensive decomposition was also noted. Removal of the solvent, followed by chromatography on Florisil using dichloromethane eluent, gave a yellow band. The recovered solid showed infrared peaks at 2095 (m–s), 2057 (vs), and 1977 (vs, br) cm^{-1} ($CHCl_3$ solution), but analyzed neither as the N-bonded thiocyanate nor as the cyanide, $C_5H_5W(CO)_3(CN)$.[30] Its small yield precluded further attempts at characterization.

The behavior of $C_5H_5Fe(CO)_2(SCN)$ with respect to linkage isomerization is most unusual. Solutions of this S-bonded complex in chloroform maintained at 36° up to 40 min gave no evidence of linkage rearrangement, only of some decomposition. A similar result is obtained after 4 hr using bis(2-methoxyethyl) ether as solvent at 50°.

When a solution of the thiocyanate in acetonitrile is heated at 82° for 6 hr under nitrogen, the infrared spectrum reveals no new absorption bands in the carbonyl stretching region. Removal of the solvent and chromatography on Florisil using CH_2Cl_2 eluent give a single band. The solid recovered therefrom was shown by infrared spectroscopy to be ferrocene[31] (*ca.* 30% yield).

Although there is negative evidence for the formation of $C_5H_5Fe(CO)_2(NCS)$ from $C_5H_5Fe(CO)_2(SCN)$ in solution,[32] the isomerization can be effected, in good yields, using suspensions of the solid[33] thiocyanate at 35°. It was followed by placing a Nujol mull of the S-bonded complex in the beam of an infrared spectrophotometer. A decrease in intensity of the CS stretching frequency band of $C_5H_5Fe(CO)_2(SCN)$ at 698 cm^{-1} and a concomitant increase in intensity of the corresponding absorption of $C_5H_5Fe(CO)_2(NCS)$ at 830 cm^{-1} are shown in Figure 4. The process is virtually complete in 10 min. Similarly, $C_5H_5Fe(CO)_2(SCN)$ in the crystal undergoes conversion to the thiocyanato-N isomer at *ca.* 40°. To our knowledge this behavior represents the only reported example of linkage isomerization taking place solely in the solid phase.[34]

The occurrence of the above phenomenon raises an interesting question concerning its origin. Undoubtedly, the mechanism of isomerization involves some process which, by virtue of its requirement of an ordered and close arrangement of the molecules, ceases to play an important role in solution. It is inviting to suggest that an activated complex composed of two C_5H_5Fe-$(CO)_2(CNS)$ units



may be responsible for the rearrangement of the coordinated thiocyanate. In this context, it is of interest to note that the formation of a similar species was in-

---

[29] Although chloroform solutions of $C_5H_5Mo(CO)_3(SCN)$ and C_5H_5Mo-$(CO)_3(NCS)$ separately show the highest frequency carbonyl stretching band at 2056 and 2068 cm^{-1}, respectively, for a mixture of the two isomers in the more polar acetonitrile the two peaks are apparently superposed at *ca.* 2057 cm^{-1}.

[30] *Anal.* Calcd for $C_5H_5W(CO)_3(NCS)$: C, 27.6; H, 1.28; S, 8.19. Calcd for $C_5H_5W(CO)_3(CN)$: C, 30.1; H, 1.40; S, 0.00. Found: C, 33.28; H, 4.33; S, 5.54.

[31] E. R. Lippincott and R. D. Nelson, *J. Chem. Phys.*, **21**, 1307 (1953).

[32] We have shown that $C_5H_5Fe(CO)_2(NCS)$ is reasonably stable under the conditions of isomerization experiments, thus ruling out its initial formation from $C_5H_5Fe(CO)_2(SCN)$ and a subsequent, rapid decomposition.

[33] Although $C_5H_5Fe(CO)_2(SCN)$ is a solid up to *ca.* 36°, the linkage isomerization which commences at approximately this temperature results in the formation of an oily mixture. Consequently, the word "solid" is used in a rather loose sense.

[34] Linkage isomerizations known to proceed in the solid state also occur in solution; see, for example, F. Basolo, W. H. Baddley, and K. J. Weidenbaum, *J. Am. Chem. Soc.*, **88**, 1576 (1966).

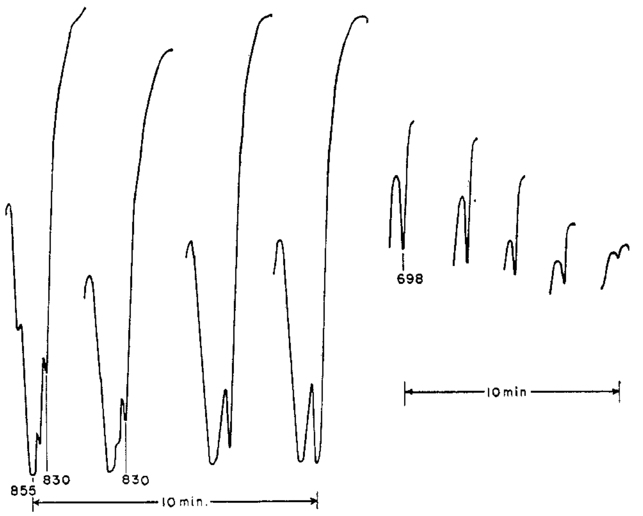
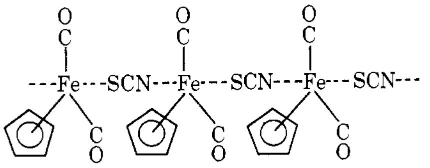


Figure 4.—Changes in the infrared spectrum in the CS stretching region showing thiocyanato-S to thiocyanato-N linkage isomerization of $C_5H_5Fe(CO)_2(SCN)$ in a Nujol mull at 35°.

voked to rationalize second-order dependence on $C_5H_5Fe(CO)_2Cl$ concentration of the rate of radiochloride exchange therein.[35] However, an alternative path, involving a single SCN bridge such as



is equally compatible with our observations in this study.

The incidence of thiocyanato-S derivatives of π-cyclopentadienylmetal carbonyls is in agreement with the earlier suggestion[4] that sulfur bonding should become more prevalent relative to nitrogen bonding as the oxidation state of the metal increases. The compounds $C_5H_5Fe(CO)_2(CNS)$ and $C_5H_5Cr(NO)_2(NCS)$ support this point most convincingly. In the latter, the formal oxidation state of chromium is 0; in the former, the formal oxidation state of iron is +2. In accord with this difference, the iron system yields both the S- and the N-bonded linkage isomer, whereas chromium affords only the N-bonded form.

Infrared and Nmr Spectra of Halogeno and Thiocyanato Complexes.—A comparison of the carbonyl stretching frequencies for a number of $C_5H_5M(CO)_xX$ complexes (Table I) reveals that they increase as a function of X in the order $I < Br \sim SCN < Cl < NCS$. This sequence parallels a decrease in polarizability of the anions which diminishes the electron density at the metal, thus reducing the extent of M=CO π bonding. Clearly, if both thiocyanato linkage isomers are known, the above criterion permits unambiguous differentiation between them. In contrast, however, there is no rational trend among the nmr chemical shifts of the cyclopentadienyl protons in the complexes studied.

Acknowledgment.—This work was supported by a grant from the National Science Foundation (GP-5466). T. E. S. wishes to acknowledge the cooperation of Chemical Abstracts Service in this study. Thanks are also due to the Climax Molybdenum Co. for a generous gift of tungsten hexacarbonyl.

(35) A. Wojcicki and F. Basolo, *J. Inorg. Nucl. Chem.*, **17**, 77 (1961).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN 53706

Electronic Structure and Bonding in $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$ [1a]

BY KENNETH G. CAULTON[1b] AND RICHARD F. FENSKE

Received November 20, 1967

The nature of the bonding of the isoelectronic series $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$ is investigated by means of semiempirical molecular orbital (MO) calculations. As a preliminary to the calculations on the transition metal complexes, MO calculations are performed on the free ligand CO, and good agreement is found with SCF calculations. The ease of oxidation of $V(CO)_6^-$ to $V(CO)_6$ is explained, and the first nine ionization potentials of $Cr(CO)_6$ are calculated with an average accuracy of 5%. Changes in the charge density in the carbon–oxygen internuclear region are examined along the isoelectronic series, and these changes are correlated with infrared stretching frequencies. All such changes occur in the π-bonding orbitals, the C–O σ framework being invariant. The unusual *decrease* observed in metal–carbon stretching frequency upon increasing the metal oxidation state is explained on the basis of decreased interaction between the metal $3d_\pi$ orbital and the ligand antibonding 2π orbital. On the basis of net atomic charges, a number of reactions between hexacarbonyls and nucleophiles are rationalized, and several kinetic predictions are made.

Introduction

In recent years molecular orbital theory has gained tremendous popularity as a means of interpreting properties of transition metal complexes. This is due in part to an increasing interest in compounds whose properties defy a crystal field interpretation, but it is also the result of the formulation of a number of procedures which allow actual calculation of molecular

(1) (a) Abstracted in part from the Ph.D. thesis of K. G. Caulton, University of Wisconsin, Jan 1968. (b) National Science Foundation Graduate Fellow.