The oxidizing power of nickel(III) decreases upon adduct formation and the kinetic stability is greatly increased. This enhanced kinetic and thermodynamic stability of nickel(III) with five or more nitrogen donors suggests that nickel(III) could be expected to form in biological systems.[30] It is known[4] that $Ni^{II}(H_{-3}G_4)^{2-}$ will react with oxygen to give nickel(III) and we believe that bis(peptide)nickel(III) complexes would form readily to give a relatively stable reservoir of oxidizing power.

Acknowledgment. This investigation was supported by Public Health Service Grants No. GM-12152 and GM-19775 from the National Institute of General Medical Sciences.

Registry No. $Ni^{III}(H_{-2}G_3)$, 60165-86-8; $Ni^{III}(H_{-2}G_2his)$, 12170-35-3; $Ni^{III}(H_{-3}G_4)^-$, 34722-98-0; $Ni^{III}(H_{-3}G_5)^-$, 34740-00-6; $Ni^{III}(H_{-3}G_3a)$, 60108-87-4; $Ni^{III}(H_{-2}G_3a)(H_{-1}G_3a)$, 66172-40-5; $Ni^{III}(H_{-3}G_3a)NH_3$, 66172-39-2; $Ni^{III}(H_{-3}G_3a)(NH_3)_2$, 66172-44-9.

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Contribution from the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Carbon-13 Nuclear Magnetic Resonance, Infrared, and Equilibrium Studies of *cis*- and *trans*-W(CO)$_4$(CS)L Complexes

SCOTT S. WOODARD, ROBERT J. ANGELICI, and B. DUANE DOMBEK*[1]

Received September 13, 1977

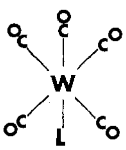
Complexes of the formula *trans*-$W(CO)_4(CS)L$, II, were prepared from *trans*-$W(CO)_4(CS)I^-$ by halide abstraction with silver(I) ion followed by addition of a ligand L (L = $P(OC_6H_5)_3$, $P(OCH_3)_3$, $P(C_6H_5)_3$, $P(4\text{-}CH_3C_6H_4)_3$, $P(n\text{-}C_4H_9)_3$, $4\text{-}CH_3C_5H_4N$, CNC_6H_{11}). Upon mild heating, the pure trans isomers were converted to equilibrium mixtures of *cis*-$W(CO)_4(CS)L$, III, and trans complexes. Equilibrium constants for these mixtures were determined by ^{13}C NMR and were found to be related to the π-acceptor capacity of L. Analysis of IR and ^{13}C NMR data collected from these complexes and their $W(CO)_5L$, I, analogues permits comparisons of bonding and spectroscopic properties of CO and CS. Correlations were found for k(CO) of II with k(cis CO) of I, k(CS) of II and III with k(cis CO) of I, k(cis CO) of I with δ(cis CO) of I, k(CO) of II with δ(CO) of II, k(CS) of III with δ(CS) of III, δ(CO's cis to L) and δ(CS) of III with δ(cis CO) of I, and δ(CO) of II with δ(cis CO) of I. The comparisons demonstrate the "charge-buffering effect" of CS, which in these complexes appears to be based largely on the strong π-acceptor capability of CS.

Introduction

A number of ^{13}C NMR studies of transition-metal carbonyl complexes have been recently published.[2,3] Results obtained on various substituted derivatives have been related to the charge-donor ability of substituent ligands and to M–CO σ and π bonding. However, there are few data in the literature on the ^{13}C NMR spectra of transition-metal thiocarbonyl complexes.[4,5] One purpose of this study was to gather ^{13}C NMR data on the CS group in a class of metal carbonyl compounds containing the CS ligand and another ligand which was systematically varied. Analysis of both δ(CS) and δ(CO) values, together with infrared results for the ν(CO) and ν(CS) modes, was expected to yield information about the bonding properties of the thiocarbonyl group.

Results and Discussion

A. Preparation and Characterization of Complexes. Thermal CO substitution in $W(CO)_5(CS)$ by PPh_3 has been previously found to afford mixtures of cis and trans isomers of $W(CO)_4(CS)(PPh_3)$ (II and III, L = PPh_3), which do not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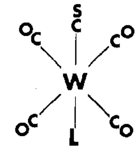
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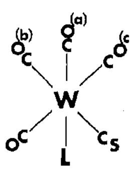

III

appear to be separable by fractional crystallization or column chromatography.[6] By use of silver(I) ion to abstract the halide ion from *trans*-$W(CO)_4(CS)I^-$ in a coordinating solvent, followed by addition of a ligand L, II is obtained[6,7] (eq 1).

$$trans\text{-}W(CO)_4(CS)I^- + Ag^+ \xrightarrow[-AgI]{L} trans\text{-}W(CO)_4(CS)L \tag{1}$$

This method has now been used with a variety of ligands to prepare pure trans products, which have been characterized by IR and ^{13}C NMR spectra (Tables I and III). For direct

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Table I. Infrared[a] and ^{13}C NMR[b] Data for W(CO)$_5$L and *trans*-W(CO)$_4$(CS)L Complexes

		W(CO)$_5$L					*trans*-W(CO)$_4$(CS)L				
	Ligand	Trans δ(CO)	Cis δ(CO)	$A_1{}^1$	$A_1{}^2$	E	δ(CS)	δ(CO)	A_1	E	ν(CS)
1	CO	191.0	191.0			1983 vs	298.7	192.4 (cis) 189.3 (trans)	2096 w 2007 m	1989 vs	1258 vs
2	P(OC$_6$H$_5$)$_3$	196.3	193.7	1967 m	2083 w	1956 vs	301.4	195.2	2069 w	1967 vs	1254 s
3	P(OCH$_3$)$_3$	197.4	194.8	1964 m	2080 w	1949 vs	302.8	196.4	2067 w	1959 vs	1248 s
4	P(4-CH$_3$C$_6$H$_4$)$_3$	199.1	197.0	1946 m[c]	2071 w	1941 vs	299.8	198.4	2058 w	1954 vs	1238 s
5	P(C$_6$H$_5$)$_3$	198.8	196.9	1948 m[c]	2071 w	1943 vs	299.6	198.1	2061 w	1956 vs	1241 s
6	P(*n*-C$_4$H$_9$)$_3$	199.1	197.1	1943 m	2068 w	1936 vs	300.0	198.1	2054 w	1947 vs	1236 s
7	4-CH$_3$C$_5$H$_4$N	202.1	198.4	1919 m	2070 w	1932 vs	302.7	199.6	2060 w	1949 vs	1226 s
8	CN–C$_6$H$_{11}$	196.1	193.9		2064 w	1953 vs	298.6	195.4	2061 w	1964 vs	1240 s
9	Cl$^-$ [d]	201.6	198.7	1840 m	2063 w	1919 vs	287.3	199.2	2064 w	1945 vs	1193 s
10	Br$^-$ [d]	201.6	197.7	1850 m	2063 w	1918 vs	287.4	198.5	2064 w	1947 vs	1193 s
11	I$^-$ [d]	201.6	196.3	1856 m	2064 w	1917 vs	285.7	196.5	2062 w	1947 vs	1195 s

[a] Recorded in *n*-hexane unless noted otherwise; cm^{-1}. [b] Recorded in CDCl$_3$, ppm downfield from Me$_4$Si. [c] Estimated values: see R. J. Angelici and M. D. Malone, *Inorg. Chem.*, 6, 1731 (1967). [d] Infrared spectra recorded in CH$_2$Cl$_2$.

Table II. Infrared[a] and ^{13}C NMR[b] Data for *cis*-W(CO)$_4$(CS)L Complexes

L[d]	ν(CO)				ν(CS)	δ(CS)	δ(CO)(a)	δ(CO)(b)	δ(CO)(c)
2	2062 m	1996 w	1968 vs	1973 m	1257 s	301.5	197.8	191.1	195.4
3	2060 m	1997 m	1958 vs	1971 s	1247 s	302.5	199.1	192.0	196.8
4	2050 m	1978 w	1952 vs		1238 s	306.4	200.9	193.9	198.9
5	2052 m	1981 w	1954 vs		1241 s	306.0	200.6	193.8	198.6
6	2047 m	1971 m	1946 vs	1954 m	1238 s	305.1	199.6	193.9	198.4
7[c]	2050 m	1969 m	1946 vs	1910 w	1239 s				
8	2049 m	1984 m	1954 s	1963 m	1240 s	302.7	198.2	191.4	195.8

[a] Recorded in *n*-hexane; cm^{-1}. [b] Recorded in CDCl$_3$, ppm downfield from Me$_4$Si. [c] Complex too unstable to obtain isomerized sample for ^{13}C NMR. [d] See Table I for ligand numbers.

Table III. $^2J(^{31}P-^{13}C)$ Coupling Constants (Hz) for Complexes[a]

	W(CO)$_5$L		*trans*-W(CO)$_4$(CS)L		*cis*-W(CO)$_4$(CS)L			
L[b]	Trans CO	Cis CO	Trans CS	Cis CO	Trans CO(a)	Cis CS	CO(b)	CO(c)
2	45.3	9.8	42.3	9.8	47.3	12.8	9.8	9.8
3	37.4	9.8	35.4	9.8	40.4	12.8	10.8	10.8
4	21.7	5.9	19.7	5.9	23.6	9.8	5.9	5.9
5	21.7	5.9	21.7	5.9	22.6	8.9	7.9	6.9
6	19.7	5.9	15.8	7.9	20.7	7.9	6.9	6.9

[a] Recorded in CDCl$_3$. [b] See Table I for ligand numbers.

Table IV. Force Constants for Complexes

	I			II			III
L	k_1	k_2	k_i	k(CO)	k_i	k(CS)	k(CS)
1	16.398[a]			16.495 (trans) 16.457 (cis)	0.241	8.135	8.135
2	15.851	16.065	0.308	16.176	0.277	8.083	8.122
3	15.817	15.970	0.315	16.081	0.293	8.006	7.993
4	15.503	15.843	0.315	15.978	0.281	7.878	7.878
5	15.531	15.865	0.310	16.016	0.284	7.917	7.917
6	15.471	15.772	0.318	15.882	0.288	7.852	7.878
7	15.076	15.749	0.338	15.937	0.299	7.726	7.891
8	15.582	15.944	0.271	16.100	0.263	7.904	7.904
9	13.826	15.592	0.360	15.917	0.321	7.316	
10	13.986	15.583	0.364	15.938	0.316	7.316	
11	14.077	15.556	0.358	15.927	0.310	7.341	

[a] H. Haas and R. K. Sheline, *J. Chem. Phys.*, 47, 2996 (1967).

comparison, the W(CO)$_5$L analogues (I) have also been prepared, and data from their spectra are also presented in the tables. Force constants in units of mdyn/Å calculated from the frequency data are presented in Table IV.

Complexes II exhibit the expected two bands in the carbonyl region of their IR spectra, corresponding to the A^1 and E stretching modes of the four equatorial carbonyls. A strong single band is observed for the thiocarbonyl stretching mode.

The ^{13}C NMR spectra of these derivatives have carbonyl carbon resonances, δ(CO), in the region of 190–200 ppm downfield from Me$_4$Si and thiocarbonyl carbon resonances, δ(CS), in the area of 300 ppm downfield from Me$_4$Si. These are singlets except when coupled through the metal to the ^{31}P nucleus of a coordinated phosphine ligand.

Isomerization of these trans derivatives to mixtures of trans (II) and cis (III) complexes occurred at slightly elevated temperatures (65 °C), except for the halo complexes, W(CO)$_4$(CS)X$^-$, which did not form the cis isomers even at higher temperatures. After equilibration, these mixtures were also examined by IR and ^{13}C NMR spectroscopy, and additional absorptions in the spectra were attributed to the *cis*-W(CO)$_4$(CS)L complexes (III) (Tables II and III). These cis complexes have the four predicted infrared carbonyl stretching bands and a single ν(CS) band. The ^{13}C NMR spectra show the δ(CS) resonance and three δ(CO) peaks in a ratio of 1:2:1. In all spectra the carbonyl trans to CS is the most shielded (i.e., occurs at highest field). In this respect the CS ligand differs from other noncarbonyl ligands in group 6B complexes, which all cause the trans carbonyl to be less shielded than the cis carbonyls.[2]

The thiocarbonyl ν(CS) values for corresponding trans (II) and cis (III) isomers are very similar in most cases. This represents a significant difference from the carbonyl ligand, since the stretching force constants of cis and trans carbonyls in W(CO)$_5$L complexes are generally quite different (see ref 2 for examples). Reactivities of the CS ligands in *cis*- and *trans*-W(CO)$_4$(CS)(PPh$_3$) have been shown to differ substantially, however.[8] This slight change in ν(CS) from cis to trans isomers may be the result of an interaction of CS π-bonding orbitals with metal d orbitals in combination with the normal d–π* back-bonding,[9] as previously discussed.[8] The two interactions would have opposing effects on the C–S bond strength upon changing from a cis to a trans position, thus keeping the overall C–S bond order approximately the same.

B. Equilibrium Constants. Previous studies[7] have shown that the isomerization of *trans*-W(CO)$_4$(^{13}CO)(CS) proceeds by a nondissociative process; however, it is not known whether or not the W(CO)$_4$(CS)L complexes reported in this study also

Table V. Bonding Parameters[a] for $W(CO)_5L$ Complexes Compared with Equilibrium Constants (65 °C) for $W(CO)_4(CS)L$

Ligand	$\Delta\sigma$	$\Delta\pi$	K^c
CS	0.029	0.702	
CO	0.008	0.664	4.00
$P(OCH_3)_3$	−0.267	0.511	2.63
$P(OC_6H_5)_3$	−0.111	0.450	1.42
$P(n\text{-}C_4H_9)_3$	−0.316	0.362	1.40
$P(C_6H_5)_3$	−0.191	0.330	0.74
$P(4\text{-}CH_3C_6H_4)_3$	−0.202	0.320	0.71
CNC_6H_{11}	−0.086	0.303	1.24
$NH_2C_6H_{11}$[b]	−0.000	0.000	
Cl^-	−1.102	−0.968	~0

[a] Reference 10. [b] Standard. $k_1 = 15.062$, $k_2 = 15.726$, $k_i = 0.342$. [c] K = cis/trans.

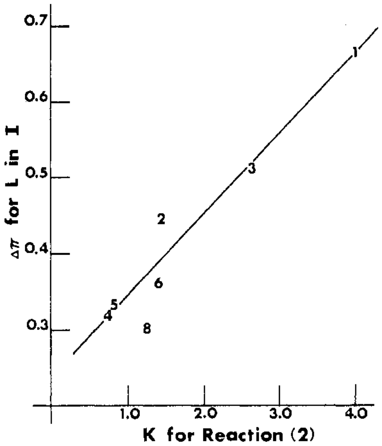
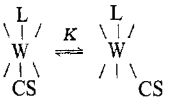


Figure 1. Plot of $\Delta\pi$ calculated for complexes I vs. K for complexes III/II. Slope = 0.106, r = 0.955.

isomerize by an intramolecular process. No disproportionation of the complexes is observed during equilibration, however.

Intensity measurements of CO and CS resonances in the ^{13}C NMR spectra of the equilibrated mixtures allowed equilibrium constants to be determined for eq 2 (Table V).



(2)

It might be expected that steric considerations could have an effect on the magnitude of K because of the greater covalent radius of sulfur in CS as compared to oxygen in CO. However, it is obvious that steric properties alone cannot account for the relative values of K.

It appears that a major factor which determines K is an anisotropic electronic effect transmitted through the metal between CS and L. Thus, the magnitude of K may be closely related to the π-bonding capacity of L. The more strongly π-accepting ligands may be less stable trans to the strongly π-bonding CS than trans to the weaker π-acceptor CO. Indeed, it can be seen in Table V that there is general agreement in the order of decreasing K with decreasing $\Delta\pi$, the Graham π-acceptor value[10] calculated from k(CO) values for $W(CO)_5L$ given in Table IV. This is shown graphically in Figure 1 for ligands other than X^-, and a good correlation (r, the linear correlation coefficient, is 0.955) is observed. Comparison of K with $\Delta\sigma$[10] gives a very poor correlation (r = 0.45).

C. Spectroscopic Correlations. Using the IR and ^{13}C NMR data for the three closely related series of compounds I, II, and III, it is informative to compare spectroscopic results for compounds in different series and also to look for correlations within each series. A number of good correlations were observed, and the most significant of them will be discussed here.

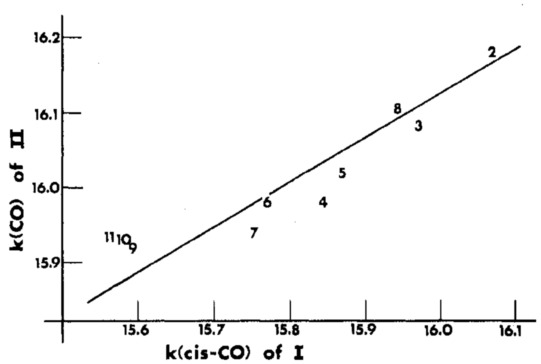


Figure 2. Plot of k(CO) of II vs. k(cis CO) of I. Slope = 0.63, r = 0.936.

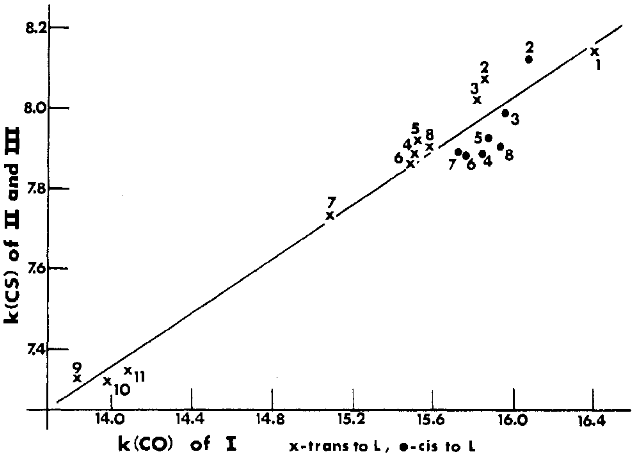


Figure 3. Plot of k(CS) of II and III vs. k(CO) for corresponding CO in I. Slope = 0.33, r = 0.974.

1. Force Constants vs. Force Constants. A plot of k(CO) for complexes II vs. k(cis CO) for complexes I is shown in Figure 2. A good linear correlation is observed, but the slope (0.63) is somewhat less than unity. This result suggests that the CS ligand in II is absorbing more of the electronic effects produced by the different L ligand than is the trans CO in I. Therefore k(CO) of II changes less than k(cis CO) of I. This might be explained by the stronger π-acceptor capability of CS relative to CO, which permits greater removal of electron density from the stronger donor L ligands. In particular, it is interesting to note that the force constants for the carbonyls in the *trans*-$W(CO)_4(CS)X^-$ halide complexes (**9**, **10**, and **11**) are significantly greater than might have been expected. The high electron density provided by the X^- ligands is apparently absorbed much more effectively by the CS than the CO group.

A correlation between thiocarbonyl stretching frequencies and CO force constants of analogous carbonyls has been previously reported.[11] We also observe that, in a plot of k(CS) in *cis*- or *trans*-$W(CO)_4(CS)L$ vs. k(CO) for the corresponding CO in I (Figure 3), there is a correlation of increasing k(CS) with increasing k(CO). Although direct comparison of changes in force constants for CO and CS may not be valid, it does appear that the CS force constant is far less sensitive to electronic changes than is k(CO), as was also observed for ν(CS) in *cis*- and *trans*-$W(CO)_4(CS)L$ complexes. A reason for this may again be the opposing effects on the C–S bond order of d–π^* back-bonding and the π–d interaction[9] with changing electron density.

2. Force Constants vs. δ(CO). It has been observed that for the $LW(CO)_5$ derivatives there is a reasonable correlation between the ^{13}C NMR chemical shift of the cis carbonyl

Table VI. Calculation of Predicted δ(CO) Values for *cis*- and *trans*-$W(CO)_4(CS)L$ Based on Additivity Effect

	Ligand								
	1	2	3	4	5	6	7	8	9
δ(CO) in II									
δ(CO) in $W(CO)_6$	191.0	191.0	191.0	191.0	191.0	191.0	191.0	191.0	191.0
δ(cis CO) in $W(CO)_5(CS)$ – δ(CO) in $W(CO)_6$	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
δ(cis CO) in I – δ(CO) in $W(CO)_6$	0.0	2.7	3.8	6.0	5.9	6.1	7.4	2.9	7.7
Calcd (total)	192.4	195.1	196.2	198.4	198.3	198.5	199.8	195.3	200.1
Exptl	192.4	195.2	196.4	198.4	198.1	198.1	199.6	195.4	199.2
δ(CO)(a) in III									
δ(CO) in $W(CO)_6$	191.0	191.0	191.0	191.0	191.0	191.0	191.0	191.0	
δ(cis CO) in $W(CO)_5(CS)$ – δ(CO) in $W(CO)_6$	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	
δ(trans CO) in I – δ(CO) in $W(CO)_6$	0.0	5.3	6.4	8.1	7.8	8.1	11.1	5.1	
Calcd (total)	192.4	197.7	198.5	200.5	200.2	200.5	203.5	197.5	
Exptl	192.4	197.8	199.1	200.9	200.6	199.6		198.2	
δ(CO)(b) in III									
δ(CO) in $W(CO)_6$	191.0	191.0	191.0	191.0	191.0	191.0	191.0	191.0	
δ(trans CO) in $W(CO)_5(CS)$ – δ(CO) in $W(CO)_6$	−1.7	−1.7	−1.7	−1.7	−1.7	−1.7	−1.7	−1.7	
δ(cis CO) in I – δ(CO) in $W(CO)_6$	0.0	2.7	3.8	6.0	5.9	6.1	7.4	2.9	
Calcd (total)	189.3	192.0	193.1	195.3	195.2	195.4	196.7	192.2	
Exptl	189.3	191.1	192.0	193.9	193.8	193.9		191.4	
δ(CO)(c) in III									
δ(CO) in $W(CO)_6$	191.0	191.0	191.0	191.0	191.0	191.0	191.0	191.0	
δ(cis CO) in $W(CO)_5(CS)$ – δ(CO) in $W(CO)_6$	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	
δ(cis CO) in I – δ(CO) in $W(CO)_6$	0.0	2.7	3.8	6.0	5.9	6.1	7.4	2.9	
Calcd (total)	192.4	195.4	196.2	198.4	198.3	198.5	199.8	195.3	
Exptl	192.4	195.4	196.8	198.9	198.6	198.4		195.8	

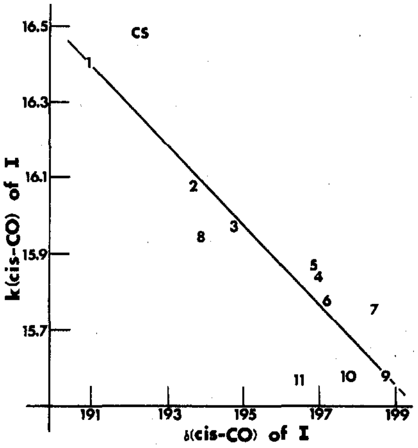


Figure 4. Plot of *k*(cis CO) of I vs. δ(cis CO) of I. Slope = −0.107, *r* = −0.894.

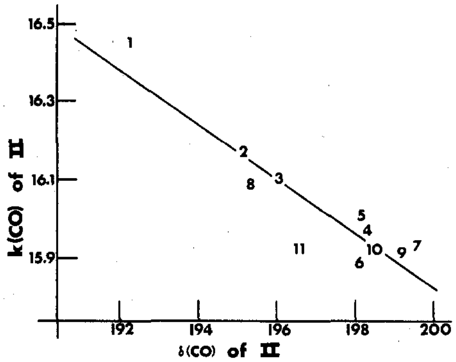


Figure 5. Plot of *k*(CO) of II vs. δ(CO) of II. Slope = −0.070, *r* = −0.900.

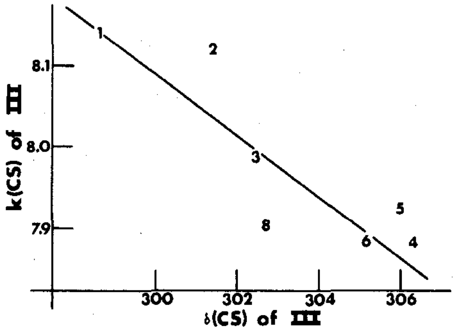


Figure 6. Plot of *k*(CS) of III vs. δ(CS) of III. Slope = −0.035, *r* = −0.865.

ligands and their infrared stretching force constants.[2] The correlation holds for the $LW(CO)_5$ complexes studied in this work (Figure 4), and an equally good correlation is also observed between *k*(CO) and δ(CO) for complexes II (Figure 5). A similar trend is seen in a plot of *k*(CS) vs. δ(CS) for complexes III (Figure 6), although there is a rather large amount of scatter. Nevertheless, this plot shows that a cis CS ligand is affected by changes in electron density in the same direction as is a cis carbonyl; i.e., an increase in the CS force constant is accompanied by shielding of the CS resonance.

Previous studies have shown that there is little correlation in a plot of *k*(CO) vs. δ(CO) for a carbonyl group trans to L.[2,3b] Similarly, we find poor correlations between δ(CS) of II with either *k*(trans CO) of I or *k*(CS) of II. It appears that individual properties of ligands (e.g., σ-donor and π-acceptor qualities) have unequal effects in determining *k*(CS) and δ(CS) of the thiocarbonyl ligand in this position.

3. δ(CO) vs. δ(CX) (X = O, S). Bodner[2,12] has observed that replacing carbonyl groups by other ligands has a nearly additive effect upon the chemical shifts of the remaining carbonyl carbon atoms. By application of this principle it should be possible to calculate the expected positions of each of the carbonyl carbon resonances in *cis*- and *trans*-$W(CO)_4(CS)L$ on the basis of chemical shift data from $W(CO)_6$, $W(CO)_5(CS)$, and $W(CO)_5L$. Listed in Table VI are the predicted and observed values; it is obvious that in most cases the agreement is excellent.

A consequence of this principle of additivity is that a plot of δ(CO) in $W(CO)_4(CS)L$ vs. δ(CO) for the corresponding CO ligand in $W(CO)_5L$ should be linear with a slope of unity.

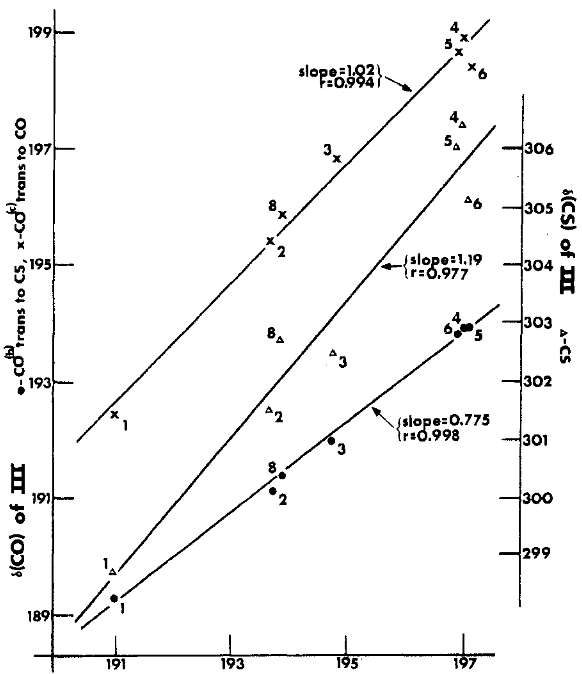


Figure 7. Plots of δ(CX), where X = O, S, for CO and CS groups cis to L in III vs. δ(cis CO) of I.

It is shown in Figure 7 that this is true for the two mutually trans carbonyls in III, i.e., those labeled (c). Similarly, δ(CO) for the carbonyl trans to L in III and the carbonyls in II also give good correlations when plotted against δ(CO) for analogous carbonyls in I (slopes of 0.985 and 0.950 and correlation coefficients of 0.984 and 0.998, respectively). However, the line for the carbonyl trans to CS in complexes III (Figure 7), which shows an excellent linear correlation, has a slope distinctly less than unity. This explains the rather poor predicted values for δ(CO) of these carbonyls (see Table VI).

The δ(CS) values for complexes III also correlate quite well with δ(CO) of cis carbonyls in II, and the slope of this line is significantly greater than unity (Figure 7). Although other factors could be involved, the greater sensitivity of δ(CS) to changes in L may be related to changes in electron density on the CS group. It has been observed that increased electron density on both carbonyl and thiocarbonyl ligands causes deshielding of the carbon resonance.[2,3] Thus, with increasing electron-donating power of the ligand L in III, the CS ligand may assume proportionately more of this charge (i.e., slope greater than 1) at the expense of charge density on the carbonyl trans to CS (i.e., slope less than 1). If this interpretation is correct, it provides another example of the "charge-buffering effect" of CS.[11] The highly anisotropic character of this effect indicates that in this series it is based largely on the strong π-acceptor capacity of CS.

Although δ(cis CO) in W(CO)$_5$L correlates well with δ(CS) in *cis*-W(CO)$_4$(CS)L, a very poor correlation exists between δ(trans CO) in I and δ(CS) in II. As noted above, δ(CS) in II also does not correlate well with CO or CS force constants. It appears that there is an unusual interaction between the CS ligand and the trans ligand which is manifested in the δ(CS) value.

4. ^{31}P–^{13}CX (X = O, S) Coupling Constants. Some interesting trends are observed in the $^2J(^{31}\text{P}-^{13}\text{C})$ coupling constants for complexes I–III (Table III). Previously[2] it was found that J(P–C) is larger when the phosphorus and CO ligands are trans rather than cis to each other in tungsten carbonyl complexes; the same result is observed (Table III) here for both CO and CS ligands. Likewise, the magnitude of J(P–C) for both CO and CS decreases as L becomes more electron donating, a trend observed in substituted tungsten carbonyl derivatives.[2]

Coupling constants for the trans CS in II are smaller than J(P–C) for the trans CO in I, while values for the carbonyl trans to L in III are consistently larger. However, the P–C coupling constants for the CS ligand cis to L in III are consistently larger than those of the cis carbonyls in I and II. Interpretation of these trends is unclear and further studies are required.

Conclusions. The cis–trans equilibrium constants for reaction 2 of the W(CO)$_4$(CS)L complexes have been shown to correlate remarkably well with Graham π-acceptor values of the ligands L. This suggests that the π-bonding capacity of CS strongly affects ligands bound trans to it. Further evidence is afforded by the ^{13}C NMR data, which show that δ(CO) of a carbonyl trans to a CS is somewhat buffered against change with varying ligands, while at the same time the δ(CS) value experiences a greater degree of change. A similar buffering effect is seen in the comparison of k(cis CO) values in W(CO)$_5$L and *trans*-W(CO)$_4$(CS)L. In the latter complex, the effect of L on k(cis CO) is substantially less than in W(CO)$_5$L, indicating that the CS ligand buffers the CO against electronic variations in L.

Experimental Section

Instrumentation. Infrared spectra were obtained on a Perkin-Elmer 337 grating infrared spectrophotometer with a Beckman 10-in. abscissa expander. Spectra in the ν(CO) region were calibrated with CO gas at 65 mmHg pressure and in the ν(CS) region with polystyrene film. Wavenumbers reported are believed to be accurate within ±1 cm^{-1}. Force constants for the CO groups in the complexes were calculated by the method of Cotton and Kraihanzel.[13] Although evidence suggests[11,14] that there is coupling between the ν(C–S) and ν(M–C) modes, the approximate k(CS) force constants were calculated assuming no coupling with the M–C mode.

Carbon-13 NMR spectra were obtained in deuterated chloroform solution containing the sample and 35 mg of tris(acetylacetonato)chromium(III) on a Bruker Fourier transform pulsed NMR spectrometer (HX-90) equipped with an internal deuterium lock and operating at 22.636 MHz. Chemical shifts are believed to be accurate within ±0.1 ppm.

Materials. W(CO)$_6$ was purchased from the Pressure Chemical Co. and used without further purification. All ligands were used as obtained from commercial sources without further purification with the exception of 4-picoline which was fractionally distilled. Tetrahydrofuran was distilled from lithium aluminum hydride before use. All solutions and solvents were maintained under a dry nitrogen atmosphere unless indicated otherwise. The complexes W(CO)$_5$X$^-$ (X = Cl, Br, I),[15] *trans*-W(CO)$_4$(CS)X$^-$ (X = Cl, Br, I),[6] and W(CO)$_5$(CS)[6] were prepared by methods described in the literature.

W(CO)$_5$L (L = P(OCH$_3$)$_3$, P(OC$_6$H$_5$)$_3$, P(C$_6$H$_5$)$_3$, P(4-CH$_3$C$_6$H$_4$)$_3$, P(n-C$_4$H$_9$)$_3$, CNC$_6$H$_{11}$, 4-CH$_3$C$_5$H$_4$N). To 1.87 mmol of AgOSO$_2$CF$_3$ or AgBF$_4$ (0.48 g or 0.36 g, respectively) dissolved in 10 mL of acetone was added a solution of 1.87 mmol (1.00 g) of [Et$_4$N]W(CO)$_5$Br in 50 mL of acetone. The mixture was stirred for 10 min, and then ~1 g of Celite was added and the mixture filtered to remove the AgBr precipitate. After addition of 2.24 mmol of the ligand, the solution was stirred for 30 min. At this point the product had been formed and the nitrogen atmosphere was no longer necessary. The solution was evaporated under reduced pressure to an oil, then dissolved in hot hexanes (~65 °C), filtered, and evaporated to dryness (or an oil). The product was then dissolved in hexanes (~5 mL) and passed through a Florisil chromatography column (2 × 20 cm) with hexane as the eluent. The product fraction was isolated and evaporated to dryness (or to a liquid with L = P(OMe)$_3$, P(n-Bu)$_3$) and used for the spectroscopic studies without further purification (~80% yield).

***trans*-W(CO)$_4$(CS)L (L = P(OCH$_3$)$_3$, P(OC$_6$H$_5$)$_3$, P(C$_6$H$_5$)$_3$, P(4-CH$_3$C$_6$H$_4$)$_3$, P(n-C$_4$H$_9$), CNC$_6$H$_{11}$, 4-CH$_3$C$_5$H$_4$N).** To 2.82 mmol of AgOSO$_2$CF$_3$ or AgBF$_4$ (0.72 g or 0.55 g, respectively) dissolved in 10 mL of acetone was added a 50 mL acetone solution of 2.82 mmol (2.00 g) of Bu$_4$N[W(CO)$_4$(CS)I]. After the mixture was stirred for 10 min, ~1.5 g of Celite was added, and the mixture was filtered to remove the AgI precipitate. After 3.38 mmol of the ligand was added, the solution was stirred for 30 min. At this point the product had been formed and a nitrogen atmosphere was no longer maintained. The solution was evaporated under reduced pressure to an oil, 40 mL of hot hexanes (~65 °C) was added, and the solution was filtered and evaporated to dryness (or an oil). The product was then dissolved in ~5 mL of pentanes and passed through a Florisil chromatography column (2 × 20 cm) using pentanes as the eluent. The product fraction was isolated and evaporated to dryness (or an oil), dissolved in carbon disulfide (~5 mL) and passed through a small Florisil chromatography column (0.5 × 7 cm) to remove the excess phosphorus ligands which adhere to the Florisil when CS_2 is the eluent. The product fraction was isolated and evaporated to dryness (L = $P(OMe)_3$, $P(n\text{-}Bu)_3$ gave liquids) with an average yield of ~80%. These products were identified by comparison of their IR spectra with known[6] *trans*-$W(CO)_4(CS)L$ derivatives. The x-ray structural determination of the *trans*-$W(CO)_4(CS)(CNC_6H_{11})$ has been reported.[16]

***cis*-$W(CO)_4(CS)L$ (L = $P(OCH_3)_3$, $P(OC_6H_5)_3$, $P(C_6H_5)_3$, $P(4\text{-}CH_3C_6H_4)_3$, $P(n\text{-}C_4H_9)_3$, CNC_6H_{11}, 4-$CH_3C_5H_4N$).** The *cis*-$W(CO)_4(CS)L$ complexes were formed by heating the trans isomer in cyclohexane (1.5 mM) at 65.0 ± 0.1 °C until the infrared carbonyl stretching spectrum no longer changed (25–70 h), indicating the cis–trans mixture was at equilibrium. The solution was then passed through a Florisil chromatography column (2 × 5 cm) using pentanes as the eluent. The *cis*-$W(CO)_4(CS)L$–*trans*-$W(CO)_4(CS)L$ product fraction was evaporated to dryness and used in the IR and ^{13}C NMR studies. To ensure that no isomerization occurred on the Florisil column, the cis/trans ratio of $W(CO)_4(CS)[P(C_6H_5)_3]$, determined by ^{13}C NMR, was found to be the same within experimental error (±~10%) before and after chromatography on the Florisil column.

Acknowledgment. We thank the National Science Foundation (Grant CHE75-15147) and the NATO Research Grants Program for partial support of this research. We also thank Dr. Martyn Poliakoff, University of Newcastle upon Tyne, for calculating some of the $k(CO)$ values.

Registry No. I (L = **1**), 14040-11-0; I (L = **2**), 23306-41-4; I (L = **3**), 23306-42-5; I (L = **4**), 17000-16-7; I (L = **5**), 15444-65-2; I (L = **6**), 17000-19-0; I (L = **7**), 17000-14-5; I (L = **8**), 15603-77-7; I (L = **9**), 14911-74-1; I (L = **10**), 15131-04-1; I (L = **11**), 14911-58-1; II (L = **1**), 50358-92-4; II (L = **2**), 66007-56-5; II (L = **3**), 65969-64-4; II (L = **4**), 65969-63-3; II (L = **5**), 50358-94-6; II (L = **6**), 65969-62-2; II (L = **7**), 65969-61-1; II (L = **8**), 61509-59-9; II (L = **9**), 58569-44-1; II (L = **10**), 58569-42-9; II (L = **11**), 56030-99-0; III (L = **2**), 65969-60-0; III (L = **3**), 66007-60-1; III (L = **4**), 66007-59-8; III (L = **5**), 58617-28-0; III (L = **6**), 66007-58-7; III (L = **7**), 65969-65-5; III (L = **8**), 66007-57-6; $[Et_4N]W(CO)_5Br$, 14780-94-0; $Bu_4N[W(CO)_4(CS)I]$, 56031-00-6; ^{13}C, 14762-74-4.

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Contribution from the Chemistry Division, Naval Research Laboratory,
Washington, D.C. 20375

Investigation of the Hydride Impurity of $(SN)_x$. Formation of $(SN)_x$ in the Presence of Water

R. D. SMITH,[1] J. R. WYATT, D. C. WEBER, J. J. DECORPO,* and F. E. SAALFELD

Received September 16, 1977

An investigation of the origin and the nature of the hydride species of $(SN)_x$ is described. The vapor-phase hydride species has a molecular weight of 220 ± 12 and results from a reaction involving water during the synthesis of $(SN)_x$. Reaction with water occurs following S_2N_2 crystal formation and prior to $(SN)_x$ sublimation. The hydride species has been found to comprise up to 20% of the vapor species in some $(SN)_x$ samples, with more typical values being 5–10%. Experimental results are presented which suggest that formation of the hydride species may be the first step of a hydrolysis process.

Introduction

Polymeric sulfur nitride (polythiazyl), $(SN)_x$, has attracted considerable interest due to its characterization as a strongly anisotropic metal.[1-6] Recently, Smith et al.[5] have studied the vapor-phase species produced upon sublimation of $(SN)_x$ and determined the principal component of the vapors to be an $(SN)_4$ species, probably having a linear, bent-chain structure.[5b] These mass spectrometric studies also revealed the presence of a hydride impurity which has an estimated concentration on the order of 1–4 atom % hydrogen.[5] All other detectable impurities[7] were due to surface-related processes and were negligible after heating under vacuum for a few hours.[5]

The magnitude of the hydrogen concentration of $(SN)_x$ is rather surprising, especially since $(SN)_x$ crystals have often been reported to be "analytically pure". This finding, which has since been confirmed by other workers,[8] immediately gave rise to questions concerning the effect of the hydride impurity on the conductivity of $(SN)_x$ and the temperature at which $(SN)_x$ becomes a superconductor. For example, a hydride impurity might be expected to lower the temperature at which the highly anisotropic $(SN)_x$ crystals become superconducting if hydrogen acts as an $(SN)_x$ chain-terminator. Alternately, the hydride impurity might raise the superconducting temperature of $(SN)_x$. Indeed, the absorption of hydrogen into certain metals (e.g., Pt) is known to increase the superconducting temperature. It has also been recently reported that the addition of bromine to $(SN)_x$ decreases the hydride impurity to less than one-tenth its normal level in this material.[10] Additionally, the hydride impurity, or its precursor, may play a role in the solid-state polymerization of S_2N_2 to $(SN)_x$. For these reasons, and the possible implications for experimental measurements of electronic properties of $(SN)_x$, a further study of this hydride impurity has become imperative.

In the present report we detail our efforts, using a variety of mass spectrometric techniques, to identify the origin and nature of the hydride species detected in the $(SN)_x$ vapors. In the course of this study we have examined $(SN)_x$ samples prepared in this laboratory, as well as at two other laboratories