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

Reactions of Tungsten Thiocarbonyl Complexes with Nucleophiles

B. DUANE DOMBEK and ROBERT J. ANGELICI*

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Primary amines react with $W(CO)_5(CS)$ to afford the corresponding isocyanide complexes $W(CO)_5(CNR)$ in high yields. Secondary amines are found to give lower yields of thioformamide complexes, $W(CO)_5(S{=}C(H)NR_2)$. Kinetic studies of these reactions show a second-order dependence in amine concentration. It is suggested that the rate-determining step is the addition of a hydrogen-bonded amine to the thiocarbonyl carbon atom. The phosphine-substituted analogues, *cis*- and *trans*-$W(CO)_4(CS)(PPh_3)$, react much slower, presumably due to increased electron density at the thiocarbonyl ligand. Azide ion reacts rapidly with $W(CO)_5(CS)$, forming cleanly the known $W(CO)_5(NCS)^-$. A number of weaker nucleophiles, including H_2O, alcohols, hydrazine, aniline, NH_3, CH_3SH, and Ph_3PO, do not react with $W(CO)_5(CS)$. Stronger nucleophiles such as CH_3Li, R_2NLi, and RO^- appear to add to the CS ligand, although the reactions are not straightforward.

Introduction

A study of the reactions of an iron thiocarbonyl complex, $(\eta\text{-}C_5H_5)Fe(CO)_2(CS)^+$, with nucleophiles showed that attack occurs at the carbon atom of the CS ligand rather than at the carbon of the CO ligands in this complex.[1] In contrast, it has been reported that $Ir(CO)_2(CS)(PPh_3)_2^+$ undergoes nucleophilic addition with CH_3O^- only at a carbonyl ligand, giving $Ir(CO)(CS)(PPh_3)_2(CO_2CH_3)$.[2] It has recently been found that *trans*-$PtCl(CS)(PPh_3)_2^+$ reacts readily with H_2O to form $PtCl(CO)(PPh_3)_2^+$.[3] All of these thiocarbonyl complexes are cationic and thus, might be expected to react readily with nucleophiles.

The availability of $W(CO)_5(CS)$ prompted an investigation of reactions of this neutral complex with nucleophilic reagents. The parent $W(CO)_6$ complex undergoes attack at a carbonyl carbon atom only with very strong nucleophiles such as lithium dialkylamide or alkyllithium compounds[4] and is not affected by water, alcohols, alkoxides, or amines. It was, therefore, of interest to determine the site of nucleophilic attack in $W(CO)_5(CS)$, the nucleophilic strength necessary for reaction to occur, and the products of the reactions.

Results and Discussion

Synthetic Studies. Reactions were attempted between $W(CO)_5(CS)$ (**1**) and a number of nucleophilic reagents. Water and alcohols were observed not to react at room temperature. Methanethiol, propylene oxide, triphenylphosphine oxide, and dicyclohexylcarbodiimide also showed no evidence of reaction. Many primary and secondary amines do react with **1**, and these are discussed below. Aniline, hydrazine, and ammonia, however, did not give any reaction at room temperature. Stronger nucleophiles react rapidly and appear to attack exclusively the thiocarbonyl ligand. Thus, azide ion, which reacts with $W(CO)_6$ to yield $W(CO)_5(NCO)^-$,[5] forms $W(CO)_5(NCS)^-$ upon reaction with $W(CO)_5(CS)$

$$W(CO)_5(CS) + N_3^- \rightarrow W(CO)_5(NCS)^- + N_2 \quad (1)$$

The identical complex was prepared by reaction of NCS^- with $W(CO)_6$, as reported in the literature.[6] The reaction of *trans*-$(^{13}CO)W(CO)_4(CS)$ with N_3^- to give *trans*-$(^{13}CO)W(CO)_4(NCS)^-$ occurs with retention of the specific trans label.[7]

Alkoxide ions also react with **1**, but attempts to characterize the product by reaction with $[(C_2H_5)_3O]BF_4$ gave several products, none of which was isolated or identified. The addition of CH_3Li to **1** followed by $[(CH_3)_3O]PF_6$ gave several products in low yields. One of these was isolated and found to be $W(CO)_5[S(CH_3)_2]$. The mechanism for the formation of this complex is unknown. Similar reactions with dialkylamide ions also gave several uncharacterized products in low yields.

Primary amines were found to react readily with the $M(CO)_5(CS)$ complexes (M = Cr, Mo, W) to give isocyanide complexes, $M(CO)_5(CNR)$; e.g., reactions with methylamine yield the methyl isocyanide complexes[8] (eq 2). This reaction

$$M(CO)_5(CS) + CH_3NH_2 \rightarrow M(CO)_5(C{\equiv}N{-}CH_3) + H_2S \quad (2)$$

differs from that of $[CpFe(CO)_2(CS)]^+$ with CH_3NH_2, which gives mainly $CpFe(CO)_2[C(=S)NHCH_3]$.[1] However, small amounts of $[CpFe(CO)_2(CNCH_3)]^+$ have also been observed in this reaction.[9]

Reactions between **1** and a number of other primary amines, RNH_2, were also observed to produce the corresponding isocyanide complexes, $(CO)_5W{-}C{\equiv}N{-}R$. Such isocyanide complexes were identified in reactions with cyclohexylamine, benzylamine, *n*-butylamine, and *tert*-butylamine. The reaction with glycine methyl ester, $H_2NCH_2CO_2CH_3$, proceeded to the $(CO)_5W(CNCH_2CO_2CH_3)$ product. As expected, *trans*-$W(CO)_4(^{13}CO)(CS)$ reacts with primary amines to give *trans*-$W(CO)_4(^{13}CO)(CNR)$ complexes; the stereochemistry at the metal center is unchanged.[7]

Secondary amines also react with **1** in a process which involves rearrangement, to give thioformamide complexes in 20–40% yields (eq 3). Identical products were obtained from

$$W(CO)_5(CS) + R_2NH \rightarrow (CO)_5W{\leftarrow}S{=}C(H){-}NR_2 \quad (3)$$

the photochemical substitution of a CO group in $W(CO)_6$ by a thioformamide, i.e.

$$W(CO)_6 + H{-}C(=S){-}NR_2 \xrightarrow{h\nu} W(CO)_5{\leftarrow}S{=}C(H){-}NR_2 + CO \quad (4)$$

Our earlier report[8] that the products of reaction 3 are aminothiocarbene complexes, $(CO)_5W{-}C(SH)(NR_2)$, is therefore in error; the isolated thioformamide products are perhaps formed by the rearrangement of such an intermediate.

Tertiary amines, including pyridine, triethylamine, and Dabco (1,4-diazabicyclo[2.2.2]octane), did not cause any changes in the ir spectrum of **1** over long periods of time.

Kinetic Studies. A kinetic study of the reaction of amines with **1** was undertaken to gain information about the mechanism of this process. The reactions were carried out at 25.0 °C in *n*-hexane solvent using at least a tenfold excess of the amine. The primary monoamines were found to react according to an overall third-order rate expression (eq 5).

$$-d[\mathbf{1}]/dt = k_1[\mathbf{1}][\text{amine}]^2 \quad (5)$$

Sample data for the reaction between **1** and cyclohexylamine

Table I. Kinetic Data for the Reaction between $W(CO)_5(CS)$ and Cyclohexylamine at 25.0 °C in *n*-Hexane[a]

10^2[cyclohexylamine], M	$10^4 k_{obsd}$, s^{-1}	10^2[cyclohexylamine], M	$10^4 k_{obsd}$, s^{-1}
3.053	0.555	9.081	5.00
5.079	1.56	11.11	7.60
7.051	2.95	13.12	10.8

[a] $k_1 = 6.1 \times 10^{-2}$ M^{-2} s^{-1}

Table II. Data for the Reaction between $W(CO)_5(CS)$ and *n*-Butylamine in *n*-Hexane at Different Temperatures[a]

Temp, °C	10^2[*n*-$BuNH_2$], M	$10^4 k_{obsd}$, s^{-1}
25.0[b]	11.75	2.92
	13.07	3.75
	13.77	4.08
	15.64	5.64
35.0[c]	7.178	1.67
	8.548	2.58
	9.521	3.10
	11.92	5.00
	14.82	7.63
45.0[d]	6.808	2.25
	8.384	3.33
	9.877	4.25
	12.73	8.00

[a] $\Delta H^{\ddagger} = 7.0 \pm 1$ kcal/mol; $\Delta S^{\ddagger} = -39.0 \pm 3$ eu. [b] $k_1 = 1.35 \times 10^{-1}$ M^{-2} s^{-1}. [c] $k_1 = 2.15 \times 10^{-1}$ M^{-2} s^{-1}. [d] $k_1 = 3.05 \times 10^{-1}$ M^{-2} s^{-1}.

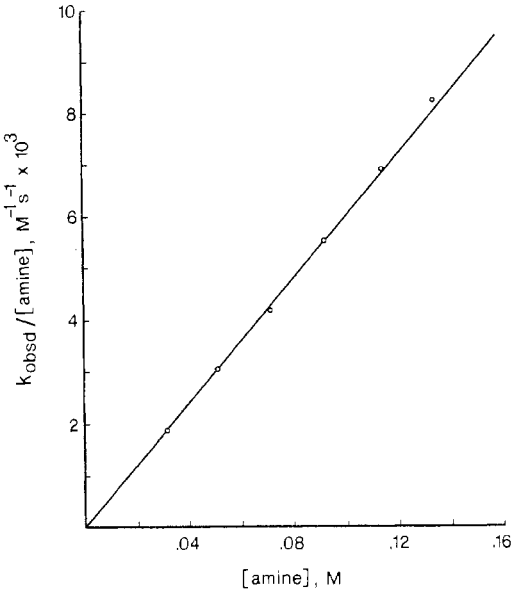


Figure 1. Plot of k_{obsd}/[amine] vs. [amine] for the reaction between $W(CO)_5(CS)$ and cyclohexylamine at 25.0 °C in *n*-hexane. The slope gives the rate constant for the term second order in amine; the zero intercept shows that there is no term first order in amine.

are shown in Table I. A plot of ln k_{obsd} vs. ln [amine] gives a straight line of slope 2.00 showing the second-order dependence on the amine concentration. Furthermore, a plot of k_{obsd}/[amine] vs. [amine] (Figure 1) shows that there is no reaction first order in amine. A straight line of slope k_1 with a zero intercept is seen.

The reaction of *n*-butylamine with **1** was studied at several temperatures, and the activation parameters are given in Table II. The rate constants for reactions of **1** with several amines at 25 °C are listed in Table III. These rate constants appear to decrease with decreasing basicity and increasing steric hindrance of the amines. The secondary amines diethylamine and piperidine also exhibit second-order dependence and give

Table III. Rate Constants of Reactions between $W(CO)_5(CS)$ and Amines at 25.0 °C in *n*-Hexane[a]

Amine	k_1
N,N-Dimethyl-1,3-diaminopropane	1.9×10^{-1} M^{-1} s^{-1}
n-Butylamine	1.35×10^{-1} M^{-2} s^{-1}
Piperidine	1.1×10^{-1} M^{-2} s^{-1}
Cyclohexylamine	6.1×10^{-2} M^{-2} s^{-1}
Benzylamine	5.1×10^{-2} M^{-2} s^{-1}
Diethylamine	3.65×10^{-3} M^{-2} s^{-1}
tert-Butylamine	1.4×10^{-4} M^{-2} s^{-1} [b]

[a] Each rate constant was determined from at least three runs at different amine concentrations. [b] ±10%.

Table IV. Kinetic Data for the Reactions of *cis*- and *trans*-$W(CO)_4(CS)(PPh_3)$ with *n*-Butylamine at 25.0 °C in *n*-Hexane

[*n*-$BuNH_2$], M	$10^4 k_{obsd}$ (cis),[a] s^{-1}	$10^6 k_{obsd}$ (trans),[b] s^{-1}
0.5188	1.58	
0.5460	1.80	
0.6821	2.82	
0.8205	4.00	4.44
1.103	7.01	7.94

[a] k_1(cis) = 6.0×10^{-4} M^{-2} s^{-1} (±5%). [b] k_1(trans) ≤ 6.6×10^{-6} M^{-2} s^{-1}.

Table V. Rate Constants for the Pyridine-Catalyzed Reactions of $W(CO)_5(CS)$ with Amines[a]

Amine	k_2, M^{-2} s^{-1}	k_1/k_2
n-Butylamine	1.5×10^{-1}	0.91
Benzylamine	7.0×10^{-2}	0.73
Cyclohexylamine	5.7×10^{-2}	1.08
Diethylamine	3.8×10^{-3}	0.96
tert-Butylamine	1.8×10^{-4} [b]	0.78

[a] Rate constants are averages of at least three runs at different pyridine concentrations (±10%). [b] ±20%

rate constants similar to those of primary amines, even though the products differ from those of the primary amine reactions. The diamine *N,N*-dimethyl-1,3-diaminopropane showed a first-order dependence, but the tertiary amine end of the molecule is presumably also involved in the reaction.

The kinetics of reactions with *cis*- and *trans*-$W(CO)_4(CS)(PPh_3)$ and *n*-butylamine were also studied and found to have the same rate expression as that in eq 5. Mixtures of the two isomers were reacted with the amine and the rate of disappearance of each isomer was recorded. The cis isomer reacts approximately 200 times more slowly with *n*-butylamine than does **1**, yielding *cis*-$W(CO)_4(PPh_3)(CNC_4H_9)$. This product was identified by comparison of its infrared spectrum with that of isolated *cis*-$W(CO)_4(PPh_3)(CNCH_3)$ (see Experimental Section). The reaction of *n*-butylamine with *trans*-$W(CO)_4(CS)(PPh_3)$ proceeds much more slowly, more than 20 000 times slower than with **1**. Due to the slowness of this reaction, the accuracy of the rate constants is less than in the others; the constants in Table IV are upper limits. The product of this reaction is *trans*-$W(CO)_4(PPh_3)(CNC_4H_9)$, also identified by its ir spectrum.[10] Both *cis*- and *trans*-$W(CO)_4(CS)(PPh_3)$ have a ν(CS) band at the same position, 1241 ± 1 cm^{-1}. Thus, the ν(CS) frequencies do not reflect the observed difference in reactivities of the thiocarbonyl ligands in these isomers.

The rate equations for these amine reactions show that two molecules of the amine are involved in the transition state although only one amine is incorporated into the product. This suggests that one of the amines is acting as a catalyst. To show that these reactions are general base catalyzed, various amines were again reacted with **1**, this time in the presence of pyridine as a catalyst. The rate equation for these reactions comprised two terms (eq 6). Since k_1 had already been determined for

Table VI. Rate Constants for Base-Catalyzed Reactions of $W(CO)_5(CS)$ with Cyclohexylamine at 25.0 °C in *n*-Hexane[a]

Catalyst	K_a	k_2, M^{-2} s^{-1}
Tributylphosphine	2.3×10^{-9}	1.3×10^{-1}
4-Picoline	9.6×10^{-7}	1.0×10^{-1}
Dabco	5.0×10^{-9}	8.0×10^{-2} [b]
Cyclohexylamine	2.2×10^{-11}	6.2×10^{-2}
Pyridine	5.6×10^{-6}	5.7×10^{-2}
2-Picoline	1.1×10^{-6}	4.9×10^{-2}
tert-Butylamine	1.5×10^{-11}	3.9×10^{-2}
Triethyl phosphite	4×10^{-4}	3.0×10^{-2}
3-Bromopyridine	1.45×10^{-3}	2.2×10^{-2}
2,6-Lutidine	2.0×10^{-7}	2.2×10^{-2}
Tetrahydrofuran	1×10^{2}	1.9×10^{-2}
Benzyldimethylamine	1.2×10^{-9}	1.5×10^{-2}
Triethylamine	9.8×10^{-12}	3.3×10^{-3}
Diethyl ether	4×10^{3}	1.5×10^{-3}

[a] Each rate constant is an average of at least three runs at different base concentrations (±10%). [b] This value is obtained after correcting for the presence of two basic sites.

$$-d[\mathbf{1}]/dt = k_1[\mathbf{1}][\text{amine}]^2 + k_2[\mathbf{1}][\text{amine}][\text{pyridine}] \quad (6)$$

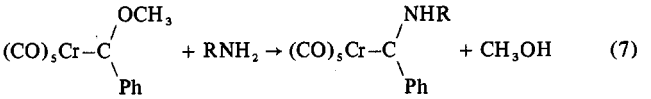
these amines, k_2 could be calculated (Table V) from k_{obsd} values, where $k_{obsd} = k_1[\text{amine}]^2 + k_2[\text{amine}][\text{pyridine}]$. The ratios of the rate constants, k_1/k_2, for the various amines are found to be almost invariant, even though the rate constants themselves vary by a factor of nearly 10^3. Although a different product is formed, a secondary amine, diethylamine, seems to fit well among the primary amines in this series also. Thus, it seems likely that primary and secondary amines go through the same type of transition state.

Pyridine appears to be a quite efficient catalyst for this reaction, slightly better in most cases than the amine itself. To determine the catalytic abilities of other bases, a series of reactions was performed using cyclohexylamine and a selection of catalysts (Table VI). These reactions show that remarkably weak bases such as tetrahydrofuran and ethyl ether are catalytically active. Indeed, the K_a values (in water) of the catalysts span a range of about 10^{14}, but the rate constants of the catalyzed reactions vary by less than a factor of 10^2. This indicates that if the catalyst is acting as a base (proton acceptor), then by the Bronsted relationship observed in other acid- and base-catalyzed reactions,[12] the transfer of the proton to the catalyst is only partially complete in the transition state.

Steric hindrance of the base appears to be an important factor in determining catalytic ability. Thus, a methyl group in the 4 position on the pyridine ring (4-picoline) enhances the catalytic activity as compared to pyridine, but a methyl group in the 2 position (2-picoline) lowers the activity. Methylation of both 2 positions (2,6-lutidine) lowers the activity still further. Triethylamine, a strong but highly hindered base, is a much poorer catalyst than Dabco, a bicyclic analogue.

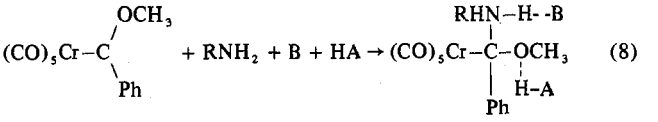
Reactions carried out in the presence of octanoic acid were decelerated to the extent expected if an equimolar quantity of the amine had been converted to a nonactive protonated form. Addition of methanol also retarded the rate, but to a lesser extent. Thus, the rate-determining step is base catalyzed but appears to be acid inhibited.

A kinetic study of a somewhat similar reaction, the aminolysis of a chromium methoxycarbene complex (eq 7), has



(7)

been reported.[13] This reaction was found to be catalyzed by both acids (HA) and bases (B). A transition state of the form shown in eq 8 was postulated. Similar carbene complexes have been observed to form fairly stable ylide complexes in the presence of a base such as a phosphine or tertiary amine (eq



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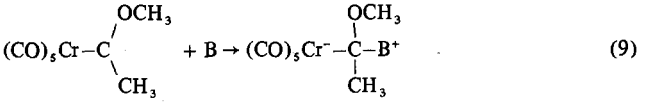
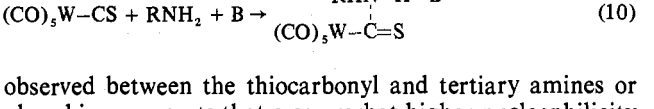


(9)

9).[14-16] Thus it is known that nucleophilic addition to the carbene carbon is a favorable process which could be involved in the initial step of the aminolysis.

A transition state similar to that proposed for the carbene aminolysis (eq 8) could be drawn for the thiocarbonyl reaction. However, the fact that the latter reaction is acid inhibited rules out such a structure and suggests that little negative charge has accumulated on the sulfur atom up to the transition state. A structure of the transition state which is consistent with the evidence is shown in eq 10. The fact that no interaction is

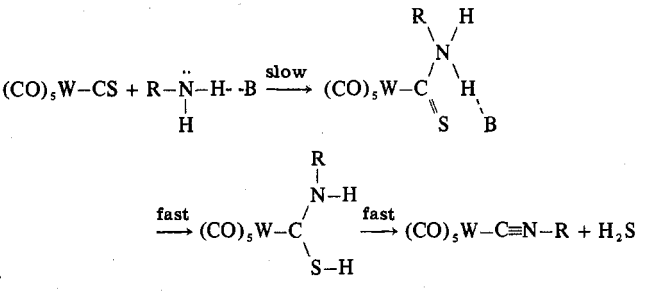


(10)

observed between the thiocarbonyl and tertiary amines or phosphines suggests that a somewhat higher nucleophilicity than that possessed by a free amine is necessary for addition to the thiocarbonyl to take place. The nucleophilicity of a primary or secondary amine, however, may be increased by hydrogen bonding of another base to the amine protons.[13] Such hydrogen-bonded amine dimers have been spectroscopically observed,[17-19] and even the weakly basic ethyl ether has been found to form hydrogen bonds with amine protons.[19] The relatively low enthalpy of activation found for the reaction between *n*-butylamine and **1** (7 kcal/mol) is readily accounted for by this model; the ΔH of a preequilibrium involving hydrogen bonding could, depending on the position of the equilibrium, be included in the value determined for $\Delta H^{\ddagger}$. This hydrogen-bonding ΔH is negative (−3 to −7 kcal/mol[20]) and, therefore, lowers the $\Delta H^{\ddagger}$ accordingly. In addition, very similar activation parameters ($\Delta H^{\ddagger}$ = 3.4 kcal/mol; $\Delta S^{\ddagger}$ = −45.6 cal/(deg mol)) were observed for the second-order amine term of the CH_3NH_2 aminolysis of phenyl acetate.[21]

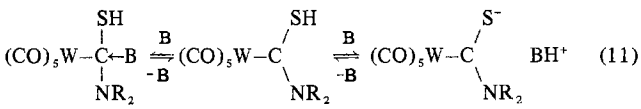
While mechanisms are possible involving the second mole of amine during or after attack at the CS carbon atom, we feel that the available evidence supports a rate-determining step in the reaction of **1** with primary and secondary amines as being the attack of a hydrogen-bonded amine complex RR′N–H---B on the thiocarbonyl carbon atom. A possible reaction sequence for the formation of an isocyanide complex in the reaction with primary amines is shown in Scheme I. The proposed aminothiocarbene intermediate, if actually formed, must proceed to the isocyanide product rapidly, since infrared spectra at various stages of these reactions show only **1** and the isocyanide product. Related aminothiocarbene complexes of platinum, *trans*-$Pt(Cl)[C(SH)NMe_2](PPh_3)_2^+$, are stable and have been isolated.[22]

Scheme I



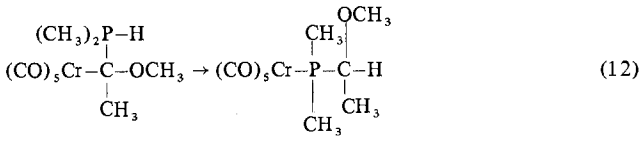
According to the sequence proposed in Scheme I, it is apparent that secondary amines could react similarly up to the stage where the aminothiocarbene complex is formed. The product finally isolated from these reactions in yields of 20–40% is the thioformamide complex, $(CO)_5W{\leftarrow}S{=}C(H)NR_2$. An approximately equal amount of the amine complex, $(CO)_5W(NHR_2)$, is also produced. Even though the disappearance of **1** is rapid on contact with secondary amines, the appearance of the thioformamide complex is very slow, which suggests that an intermediate forms in large quantities. Attempts to isolate this intermediate were not very successful; only an unstable gummy solid could be obtained which decomposed in several hours to yield some of the thioformamide complex. However, a partial characterization of the intermediate was possible. Reactions between equimolar **1** and piperidine in hexane rapidly gave a precipitate of this substance, but only about half of the total amount of **1** was consumed. A 2:1 molar ratio of the amine to **1** was required for all of **1** to react. A similar reaction carried out in hexane between **1** and equimolar piperidine with excess Dabco as a catalyst did give complete consumption of **1**. The intermediate precipitated in this reaction was investigated by NMR spectroscopy in $DCCl_3$. The ratio of areas of the 3- and 4-carbon alkyl protons (τ 8.25) of piperidine to the sharp singlet (τ 7.10) observed for Dabco shows that the two bases are present in approximately a 1:1 molar ratio. (The protons on the 2-carbons of the piperidine ring appear as a broad doublet at about τ 6.2. No other resonances were observed.) Extraction of the residue with hexane after evaporating this sample did not yield any free Dabco. The fact that only one sharp peak is observed for the Dabco protons, shifted downfield 0.15 ppm from the position in the free base, suggests that there is a rapid exchange of this base in solution. This was confirmed by adding excess Dabco to a solution of the intermediate; an upfield shift was observed. Addition of more Dabco caused a further shift. The chemical shift of the Dabco protons was unchanged when the base was added to a solution of $W(CO)_5[S{=}C(H)N(CH_3)_2]$.

This evidence suggests that an intermediate is produced which contains two amine molecules, one of which is involved in a rapid dissociation–association process in solution. A possible representation of this process is shown in eq 11. Since



(11)

there are several examples in the literature of the addition of tertiary amines or phosphines to similar carbene complexes,[14–16] it is possible that an ylide complex is formed by addition of the base to the carbene carbon. The base could also abstract the sulfur proton to give an anionic thiocarbamoyl complex. Any of the complexes proposed in eq 11 could be envisioned to rearrange to the observed $(OC)_5W{-}S{=}C(H)NR_2$ product.[23] An ylide complex somewhat similar to that in eq 11 has been reported to undergo a related rearrangement[14] (eq 12).



(12)

Conclusions

The thiocarbonyl ligand in $W(CO)_5(CS)$ is much more reactive toward nucleophiles than either the CO ligands in this complex or those in $W(CO)_6$. This difference in reactivity is especially obvious from the reactions with amines. The experimental and kinetic evidence supports a rate-determining step in these amine reactions which involves attack of a hydrogen-bonded amine molecule, RR′N–H---B, at the thiocarbonyl ligand. The base catalyst presumably increases the effective nucleophilicity of the attacking amine.

The high reactivity of the thiocarbonyl ligand may be rationalized by assuming that the nucleophile adds to the lowest energy unoccupied molecular orbital (LUMO) of the molecule, as suggested by Fenske and Lichtenberger.[24] Their molecular orbital calculations indicate that this LUMO is the CS π-antibonding orbital which is concentrated on the thiocarbonyl carbon atom. The attack is, in fact, observed to occur at this atom.

The reactivity of the thiocarbonyl ligand is greatly reduced in the *cis*- and *trans*-$W(CO)_4(CS)(PPh_3)$ complexes, presumably due to the electron-releasing effect on the phosphine relative to CO. This increases the electron density in the CS π-antibonding orbital and raises this LUMO to a higher energy, making attack by a nucleophile less favorable. The lower ν(CS) frequency (1241 cm^{-1}) in *cis*- and *trans*-$W(CO)_4(CS)(PPh_3)$ as compared to that (1258 cm^{-1}) in $W(CO)_5(CS)$ also seems to reflect the greater electron density on the thiocarbonyl ligand, analogous to observations on metal carbonyl ligands.[25,26]

That the *trans*-$W(CO)_4(CS)(PPh_3)$ isomer undergoes reaction much less rapidly than the cis complex suggests that more electron density is transmitted to the CS group when it is trans to the PPh_3 ligand. This greater electron transfer then must occur anisotropically, presumably through the metal d orbitals. The difference in reactivity of the CS ligands in *cis*- and *trans*-$W(CO)_4(CS)(PPh_3)$, however, is not manifest in their ν(CS) frequencies, which are the same (1241 cm^{-1}) for both isomers. The calculations performed by Fenske and Lichtenberger indicate that there is significant electron donation from the occupied *π-bonding* orbitals of CS to the metal d orbitals in thiocarbonyl complexes, as well as d–π^* backbonding from the metal to the unoccupied π-antibonding orbitals of the CS.[23] Going from *cis*-$W(CO)_4(CS)(PPh_3)$ to the trans isomer, the π-electron donation from the CS π-*bonding* orbital should diminish (increasing the C–S bond strength), while the metal to π^* donation is enhanced (decreasing the C–S bond strength). Thus, it is perhaps a balance between these two bonding effects which causes the ν(CS) value to be the same in the cis and trans isomers. Since nucleophilic attack presumably occurs at the CS π^* orbital, its higher energy in the trans isomer would lead to a slower rate, as is observed experimentally. This example illustrates the complexity of the metal–CS bond and the problems inherent in attempting to correlate reactivities or other properties with ν(CS) frequencies.

Experimental Section

General Information. Thiocarbonyl complexes were prepared as reported previously.[11] $[(PPh_3)_2N][N_3]$ was obtained by mixing aqueous solutions of $[(PPh_3)_2N]Cl$ and NaN_3, collecting the precipitated product, and drying under high vacuum. Tetrahydrofuran (THF) solvent was distilled before use from lithium aluminum hydride. Other reagent grade chemicals were used without further purification. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer equipped with an expanded-scale recorder calibrated with gaseous CO. Proton NMR spectra were recorded on a Perkin-Elmer Hitachi R-20B instrument, and ^{13}C NMR spectra were obtained with a Bruker HX-90 spectrometer operating in the Fourier-transform mode using solutions containing 0.05 M $Cr(acac)_3$.[27] Chemical shifts are downfield with respect to tetramethylsilane. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz.

Kinetic Experiments. Amines were fractionally distilled before use; Dabco was sublimed. Reactions were performed in reagent grade hexane solvent in foil-wrapped 50-ml volumetric flasks flushed with N_2 and capped with rubber septum stoppers. The concentration of thiocarbonyl complex was approximately 3×10^{-3} M. Amines were used in greater than a tenfold excess. Samples were withdrawn

periodically and ir absorbances of reactants (2096 cm^{-1} for $W(CO)_5(CS)$, 2052 cm^{-1} for *cis*-$W(CO)_4(CS)(PPh_3)$, and 1956 cm^{-1} for *trans*-$W(CO)_4(CS)(PPh_3)$) were measured. Plots of ln $(A - A_\infty)$ vs. t were linear with slopes of k_{obsd}, confirming pseudo-first-order kinetics. Identical reactions gave rate constants reproducible to within less than 5% except when indicated otherwise in the tables.

Reactions. Preparation of $W(CO)_5(NCS)^-$ from $W(CO)_5(CS)$. A mixture of $W(CO)_5(CS)$ (0.05 g, 0.136 mmol) and $[(Ph_3P)_2N][N_3]$ (0.08 g, 0.14 mmol) in a flask under N_2 was dissolved in 3 ml of THF. Gas evolution began immediately. After 45 min at room temperature, the ir spectrum showed that all of the $W(CO)_5(CS)$ had reacted. The complex was isolated by the addition of ethyl ether and cooling to −20 °C (0.10 g, 95%). The ir spectrum of this complex is identical with that of a sample prepared from $[(Ph_3P)_2N][NCS]$ according to the method of Wojcicki and Farona.[6] Ir (CH_2Cl_2) (cm^{-1}): ν(CN) 2102 (m), ν(CO) 2066 (w), 1921 (vs), 1862 (s).

An identical reaction with *trans*-$W(CO)_4(^{13}CO)(CS)$[7] gave [*trans*-$W(CO)_4(^{13}CO)(NCS)]^-$: Ir (CH_2Cl_2) ν(CN) 2102 (m), ν(CO) 2061 (w), 1921 (vs), 1822 (s) cm^{-1}.

Reaction of $W(CO)_5(CS)$ with CH_3Li and $[(CH_3)_3O]PF_6$. A solution of $W(CO)_5(CS)$ (1.0 g, 2.72 mmol) in 20 ml of THF was stirred at 0 °C while a 2.0 M ether solution of CH_3Li (1.35 ml, 2.70 mmol) was added dropwise. The mixture was stirred for 5 min and evaporated to dryness. The dark residue was dissolved in 10 ml of CH_2Cl_2 and added dropwise to $[(CH_3)_3O]PF_6$ (0.76 g, 3.7 mmol) in 10 ml of CH_2Cl_2. After the mixture was stirred 10 min, 5 g of Florisil was added, and the solution was evaporated to dryness. The Florisil was placed on top of a 1.5 × 35 cm Florisil–hexane column and washed with hexane. Developing with 2:1 hexane–CH_2Cl_2 brought off a broad yellow band containing several poorly separated fractions. The major fraction was collected and evaporated to an oil. Distillation under high vacuum at room temperature onto a water-cooled probe gave a yellow liquid (0.05 g). This was redistilled to yield pale yellow crystals, found to be $W(CO)_5[S(CH_3)_2]$: mp 25.5 °C; ir (hexane) 2075 (w), 1980 (vw), 1942 (vs), 1935 (m) cm^{-1}; NMR ($DCCl_3$) τ 7.38 (s); mass spectrum, parent ion, m/e calcd for $^{182}W(CO)_5[S(CH_3)_2]$[28] 383.9417, found 383.9432. Anal. Calcd for $W(CO)_5[S(CH_3)_2]$: C, 21.80; H, 1.55. Found: C, 21.84; H, 1.38.

Preparation of $W(CO)_5(CNCH_3)$ from $W(CO)_5(CS)$. A solution of $W(CO)_5(CS)$ (0.60 g, 1.67 mmol) in 50 ml of ethyl ether was saturated with CH_3NH_2. After 5 min the solution was evaporated to dryness. Sublimation of the residue at 35 °C under high vacuum gave 0.55 g of $W(CO)_5(CNCH_3)$ (92%): ir (hexane) ν(CN) 2177 (vw), ν(CO) 2069 (w), 1956 (vs) cm^{-1}; NMR ($DCCl_3$) τ 6.55 (s); mass spectrum, parent ion, m/e 365. Anal. Calcd for $W(CO)_5(CNCH_3)$: C, 23.60; H, 0.85. Found: C, 23.07; H, 0.73.

An identical reaction with *trans*-$W(CO)_4(^{13}CO)(CS)$[7] gave *trans*-$W(CO)_4(^{13}CO)(CNCH_3)$: ir (hexane) ν(CN) 2177 (w), ν(CO) 2064 (w), 1955 (vs), 1916 (m) cm^{-1}.

Preparation of $W(CO)_5(CNC_6H_{11})$ from $W(CO)_5(CS)$. A solution of $W(CO)_5(CS)$ (0.20 g, 0.56 mmol) and cyclohexylamine (0.065 g, 0.66 mmol) in 25 ml of pentane was allowed to stand at room temperature for 3 h. The mixture was evaporated, extracted with pentane, filtered, concentrated, and cooled to −20 °C. A yield of 0.22 g of $W(CO)_5(CNC_6H_{11})$ was collected (91%): ir (hexane) ν(CN) 2154 (w), ν(CO) 2065 (w), 1953 (vs) cm^{-1}; ^{13}C NMR ($DCCl_3$) δ(CO) −194.0 (cis), −196.2 (trans).

An identical preparation with *trans*-$W(CO)_4(^{13}CO)(CS)$[7] gave *trans*-$W(CO)_4(^{13}CO)(CNC_6H_{11})$: ir (hexane) ν(CN) 2154 (w), ν(CO) 2058 (w), 1953 (vs), 1912 (m) cm^{-1}.

Preparation of $W(CO)_5(CNCH_2CO_2CH_3)$ from $W(CO)_5(CS)$. A methanol solution of sodium methoxide was prepared by adding Na (0.10 g, 4.35 mmol) to 25 ml of methanol. To this solution was added glycine methyl ester hydrochloride (0.70 g, 5.6 mmol). This solution was added to a mixture of $W(CO)_5(CS)$ (0.70 g, 1.90 mmol) in 200 ml of methanol, and the solution was stirred for 12 h. Evaporation of the solvent, extraction of the residue into hexane, filtration, concentration to about 20 ml, and cooling to −20 °C gave 0.25 g (31%) of the product. The complex was recrystallized from hexane: ir (hexane) ν(CN) 2159 (vw), ν(CO) 2063 (w), 1957 (vs) cm^{-1}; NMR ($DCCl_3$) τ 5.60 (s, 2 H), 6.20 (s, 3 H); mass spectrum, parent ion, m/e 423. Anal. Calcd for $W(CO)_5(CNCH_2CO_2CH_3)$: C, 25.53; H, 1.18; N, 3.31. Found: C, 25.95; H, 1.14; N, 3.09.

Reaction of $W(CO)_5(CS)$ with Piperidine. A mixture[11] of $W(CO)_5(CS)$ and $W(CO)_6$ containing 2.0 g of $W(CO)_5(CS)$ (5.45 mmol) was dissolved in 200 ml of hexane. A solution of piperidine (0.514 g, 6.05 mmol) in 10 ml of hexane was added; the solution became cloudy immediately and a precipitate soon formed. The solution was stirred at room temperature for 5 days, but the ir spectrum showed that much $W(CO)_5(CS)$ was still present. More piperidine (0.35 g, 4.1 mmol) was added and the solution was stirred 1 day more. It was then evaporated to dryness, suspended in 1:1 CH_2Cl_2–hexane, and placed on a Florisil–hexane column. Washing with hexane removed the $W(CO)_6$. Developing with 1:1 CH_2Cl_2–hexane brought down a broad yellow band, the front of which was mainly $W(CO)_5(pip)$. This product was isolated and compared with a sample prepared by the reported method.[30] The remainder of the band, containing $W(CO)_5(SC(H)N(CH_2)_5)$, was collected, concentrated with warming, and cooled to −20 °C to yield 0.8 g (33%) of the thioformamide complex product: ir (hexane) 2070 (w), 1974 (vw), 1937 (s), 1929 (s), 1915 (m) cm^{-1}; NMR ($DCCl_3$) τ 1.1 (s, C–H), 6.15 (m, $-CH_2-$), 6.40 (m, $-CH_2-$), 8.28 (s, $-CH_2CH_2CH_2-$); mass spectrum, parent ion, m/e 453; ^{13}C NMR ($DCCl_3$) δ(trans CO) −201.79, δ(cis CO's) −198.60, δ(C=S) −188.60 (d, J_{H-C} = 172 Hz); other C resonances at δ −57.76, −47.75, −26.68, −24.98, −23.56. Anal. Calcd for $W(CO)_5(SC(H)N(CH_2)_5)$: C, 29.2; H, 2.43; S, 7.05. Found: C, 29.42; H, 2.13; S, 6,86.

Reaction of $W(CO)_5(CS)$ with Dimethylamine. A mixture of $W(CO)_5(CS)$ and $W(CO)_6$ containing 1.1 g of $W(CO)_5(CS)$ (3.0 mmol) was dissolved in 100 ml of hexane which was then saturated with dimethylamine. After standing 6 h at room temperature, the solution was stored at −20 °C overnight. The solution and precipitate were put on a 2 × 35 cm Florisil–hexane column and washed with hexane. Developing the column with 1:1 CH_2Cl_2–hexane brought down two yellow bands, the first of which was $W(CO)_5(NHMe_2)$.[30] The second band was collected, concentrated, and cooled to −20° to yield 0.20 g (16%) of $W(CO)_5(SC(H)NMe_2)$: ir (hexane) 2071 (w), 1975 (vw), 1938 (s), 1932 (s), 1916 (m) cm^{-1}; NMR ($DCCl_3$) τ 1.05 (s, C–H), 6.60 (s, $-CH_3$), 6.72 (s, $-CH_3$); mass spectrum, parent ion, m/e 413. Anal. Calcd for $W(CO)_5(SC(H)N(CH_3)_2)$: C, 23.2; H, 1.69; S, 7.75. Found: C, 22.89; H, 1.88; S, 7.40.

Preparation of $W(CO)_5(SC(H)N(CH_3)_2)$ from *N,N*-Dimethylthioformamide. A solution of $W(CO)_6$ (1.5 g, 4.25 mmol) and $SC(H)N(CH_3)_2$ (0.4 g, 4.5 mmol) in 40 ml of THF was stirred and irradiated with ultraviolet light for 7 h at 40–50 °C. The mixture was evaporated to dryness, dissolved in 1:2 CH_2Cl_2–hexane, placed on a 2 × 35 cm Florisil column, and washed with hexane. Developing with 1:1 CH_2Cl_2–hexane brought down a yellow band of the product (0.40 g, 23%). This complex had ir and NMR spectra identical with those of the complex prepared from $W(CO)_5(CS)$ and dimethylamine.

Reaction of $W(CO)_4(CS)(PPh_3)$ with CH_3NH_2. The mixture of cis and trans isomers of $W(CO)_4(CS)(PPh_3)$ which is obtained by the thermal preparation (0.30 g, 0.50 mmol)[11] was dissolved in 150 ml of hexane saturated with CH_3NH_2. After 5 h all of the cis isomer had reacted, so the solution was concentrated and placed on the top of a 1.5 × 35 cm Florisil–hexane column. After washing the mixture with hexane and developing with 1:1 CH_2Cl_2–hexane, a broad yellow band containing *trans*-$W(CO)_4(CS)(PPh_3)$ was eluted. Developing with CH_2Cl_2 brought down the isocyanide product, $W(CO)_4(CNCH_3)(PPh_3)$, which was mainly the cis isomer. Concentration, addition of hexane, and cooling to −20 °C gave crystals of the colorless product (0.044 g, 14.5%): ir (hexane) ν(CN) 2148 (w), ν(CO) 2018 (m), 1932 (m), 1913 (vs) cm^{-1}; NMR ($DCCl_3$) τ 2.70 (m, C_6H_5), 7.10 (d, $^5J_{P-H}$ = 1.5 Hz, $-CH_3$); mass spectrum, parent ion, m/e 599. Anal. Calcd for $W(CO)_4(CNCH_3)(PPh_3)$: C, 48.10; H, 3.00; N, 2.43. Found: C, 48.08; H, 3.01; N, 2.43.

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Registry No. $W(CO)_5(NCS)^-$, 45113-96-0; [*trans*-$W(CO)_4(^{13}CO)(NCS)]^-$, 59831-19-5; $W(CO)_5[S(CH_3)_2]$, 57550-26-2; $W(CO)_5(CNCH_3)$, 50298-27-6; *trans*-$W(CO)_4(^{13}CO)(CNCH_3)$, 59831-23-1; $W(CO)_5(CNC_6H_{11})$, 15603-77-7; *trans*-$W(CO)_4(^{13}CO)(CNC_6H_{11})$, 59831-24-2; $W(CO)_5(CNCH_2CO_2CH_3)$, 50298-28-7; $W(CO)_5(SC(H)N(CH_2)_5)$, 59831-20-8; $W(CO)_5$-

$(SC(H)NMe_2)$, 59831-21-9; $W(CO)_4(CNCH_3)(PPh_3)$, 59872-35-4; $W(CO)_5(CS)$, 50358-92-4; $[(Ph_3P)_2N][N_3]$, 38011-36-8; *trans*-$W(CO)_4(PPh_3)(CNCH_3)$, 50298-29-8; cyclohexylamine, 108-91-8; *n*-$BuNH_2$, 109-73-9; *N,N*-dimethyl-1,3-diaminopropane, 109-55-7; piperidine, 110-89-4; benzylamine, 100-46-9; diethylamine, 109-89-7; *tert*-butylamine, 75-64-9; *cis*-$W(CO)_4(CS)(PPh_3)$, 58617-28-0; *trans*-$W(CO)_4(CS)(PPh_3)$, 50358-94-6; tributylphosphine, 998-40-3; 4-picoline, 108-89-4; DABCO, 280-57-9; pyridine, 110-86-1; 2-picoline, 109-06-8; triethyl phosphite, 122-52-1; 3-bromopyridine, 626-55-1; 2,6-lutidine, 108-48-5; tetrahydrofuran, 109-99-9; benzyldimethylamine, 28262-13-7; triethylamine, 121-44-8; diethyl ether, 60-29-7; *cis*-$W(CO)_4(PPh_3)(CNC_4H_9)$, 59831-22-0; *trans*-$W(CO)_4(PPh_3)(CNC_4H_9)$, 59872-36-5; glycine methyl ester, 616-34-2; dimethylamine, 124-40-3; CH_3NH_2, 74-89-5.

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Contribution from the Department of Chemistry and the Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and the Department of Chemistry, Stanford University, Stanford, California 94305

Cadmium-113 Fourier Transform Nuclear Magnetic Resonance and Raman Spectroscopic Studies of Cadmium(II)–Sulfur Complexes, Including $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$

R. A. HABERKORN,[1a,b] L. QUE, Jr.,[1a] W. O. GILLUM,[1a,b] R. H. HOLM,*[1a,b] C. S. LIU,[1c] and R. C. LORD[1c]

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The ^{113}Cd Fourier transform NMR and Raman spectra (1700–100 cm^{-1}) of a series of Cd(II) chelate complexes (derived from dithiocarbamate, xanthate, dithiophosphinate, and dithiolate ligands), $Cd(SCH_2CH_2OH)_2$, and $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ have been determined. Cd–S stretching vibrations have been assigned to bands in the 220–144-cm^{-1} interval. ^{113}Cd chemical shifts of chelate complexes exhibited no trend in terms of the extent of sulfur ligation, but the nuclear deshielding sequence $Cd(SR)_2 < Cd(SR)_3 < Cd(SR)_4$ is indicated by measurements on the 1:2 cadmium(II)–glutathione complex and the decanuclear cation, which contains sites of the latter two types. The solution stability of $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ has been investigated by ^1H and ^{113}Cd NMR and Raman spectroscopy from −40 to +100°C. It is concluded that small structural differences may exist between the crystalline and solution phases, arising mainly from partial rupture of $\overline{CdSCH_2CH_2OH}$ chelate rings known to be present in the crystal, and that the solution structure approaches that in the crystal as solution temperatures are lowered below ca. 20–25 °C. From data obtained in this and previous studies a provisional ^{113}Cd chemical shift scale is presented in terms of the types of ligand atoms in the primary coordination sphere of Cd(II). A conspicuous feature of this scale is the marked deshielding effect of thiolate sulfur vs. oxygen, halide, and nitrogen ligands relative to the reference zero of chemical shift, 0.1 M aqueous $Cd(ClO_4)_2$ at 25 °C. Possible application of the deshielding sequence to investigation of cadmium–cysteinate binding in metallothionein proteins is suggested.

Introduction

In the past direct observation of the high-resolution NMR spectra of a number of the heavier nuclei[2,3] of the metallic elements has been hampered by their low natural-abundance sensitivity (S) at constant field (S = abundance × NMR sensitivity at constant field). The inherent sensitivities of nuclei (N) such as ^{27}Al, ^{59}Co, and ^{205}Tl, for which $S(N)/S(^{13}C) \simeq$ 1200, 1600, and 770,[4,5] respectively, do not normally present a problem of detection (excluding effects of quadrupolar line broadening) in conventional CW spectroscopy, accounting for the numerous NMR investigations of compounds containing these nuclei. However, reduction of the sensitivity ratio by ca. 10^2 or more renders the CW mode of detection impractical or at best possible only in large volumes of concentrated solutions. Recent developments in variable-frequency pulse Fourier transform techniques[4-7] now make practicable the

*To whom correspondence should be addressed at Stanford University.