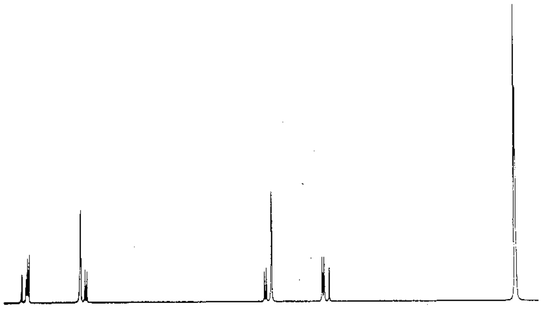

Figure 6. Calculated ^{31}P NMR spectrum for the ^{195}Pt satellite portion of Figure 4. The intensities are not scaled to accommodate the isotopic abundance of ^{195}Pt.

an accidental coincidence of the ^{195}Pt satellite multiplet. For the complex $Pt[OP(OMe)_2]_2dppe$ this coincidence is not observed and the satellite multiplet observed (Figure 3). Nevertheless even in this latter case the ^{195}Pt satellite portion of the spectrum is not symmetric, and second-order effects between ^{31}P and ^{195}Pt are apparent.

The complex $Pt[OP(OMe)_2]_2(diars)$ is structurally analogous. No second-order effects due to the arsenic quadrupole are observed, and the methoxy groups give rise to a single resonance at $\delta = 61.6$, $^1J(PPt) = 4753$ Hz.

Experimental Section

Complexes $PtH[OPPh_2][QOPPh_2]PMePh_2$ (Q = H, BF_2),[6] $PtCl[OP(OMe)_2][QOP(OMe)_2]L$ (Q = H, BF_2, L = PEt_3; Q = H, L = PPh_3),[5,9] $\{PtCl[OP(OMe)_2]_2PEt_3\}_4Th$,[9] $Pt[OPPh_2]_2[HOPPh_2]_2$,[4c,d] and $Pt[OP(OMe)_2]_2[HOP(OMe)_2]_2$[22] were prepared as previously described. Nuclear magnetic resonance spectra were measured as solutions in $CDCl_3$. ^1H NMR spectra were measured in 5-mm sample tubes with hexamethyldisiloxane ($\delta = 0.02$) as internal reference on a Jeol MH-100 spectrometer. ^{31}P NMR spectra were measured in 10-mm spinning sample tubes with 85% H_3PO_4 as external reference on a Bruker WH-90 Fourier transform spectrometer. Broad-band decoupling of ^1H was employed and the nucleus resonated at 36.450 MHz in a multinuclear tunable probe. Preliminary calculations were made with a Nicolet NMRCAL program on the WH-90 computer, and final iterative fits were achieved using a LAOCOON III program.

Acknowledgment. We thank Dr. J. N. Shoolery of Varian Associates for measuring the spectra shown in Figure 2 on a Varian XL-100 spectrometer. We thank Dr. J. A. Magnuson, Mr. R. Lyon, and Mr. J. Boehme for assistance with the ^{31}P NMR spectra. Thanks are due to Washington State University, University of Idaho, and the National Science Foundation for funds to purchase the Bruker WH-90 spectrometer. This research was supported by the National Science Foundation.

Registry No. $\{PtCl[OP(OMe)_2]_2PEt_3\}H$, 63264-38-0; $\{PtCl[OP(OMe)_2]_2PEt_3\}BF_2$, 63678-34-2; $\{PtCl[OP(OMe)_2]_2PEt_3\}_2UO_2$, 63239-09-8; $\{PtCl[OP(OMe)_2]_2PEt_3\}_4Th$, 66454-95-3; $\{PtCl[OP(OMe)_2]_2PEt_3\}_2Zn$, 66322-92-7; $\{PtCl[OP(OMe)_2]_2PPh_3\}H$, 63292-78-4; $\{PtCl[OP(OMe)_2]_2PPh_3\}_4Th$, 63310-65-6; $Pt[OP(OMe)_2]_2dppe$, 21657-30-7; $[\{Pt[OP(OMe)_2]_2dppe\}_2Zn][ClO_4]_2$, 63280-74-0; $Pt[OP(OMe)_2]_2diars$, 63264-39-1; $\{PtH[OPPh_2]_2PPh_2Me\}H$, 55012-58-3; $\{PtH[OPPh_2]_2PPh_2Me\}BF_2$, 55012-60-7; $\{PtCl[OP(OPh)_2]_2PEt_3\}H$, 63292-77-3; $Pt[OP(OMe)_2]_2[HOP(OMe)_2]_2$, 21794-30-9.

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

Kinetic Study of Carbonyl Dissociation in $W(CO)_3(CS)(o\text{-phen})$. Labilization by the Thiocarbonyl Ligand

Ruth A. Pickering and Robert J. Angelici*

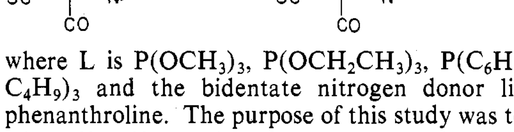
Received October 27, 1977

In 1967 Graham and Angelici[1] reported kinetic studies of substitution reactions of an *o*-phenanthroline complex

$$W(CO)_4(o\text{-phen}) + L \rightarrow cis\text{-}W(CO)_3(L)(o\text{-phen}) + CO \qquad (1)$$

where L was $P(n\text{-}C_4H_9)_3$, $P(OC_2H_5)_3$, $P(OCH_2)_3CCH_3$, or $P(C_6H_5)_3$. With all L ligands, the reaction proceeded by a dissociative pathway. With the more nucleophilic ligands, an associative mechanism was also detected.

We now report results of a kinetic study of the reaction of the analogous thiocarbonyl complex



(2)

where L is $P(OCH_3)_3$, $P(OCH_2CH_3)_3$, $P(C_6H_5)_3$, or $P(n\text{-}C_4H_9)_3$ and the bidentate nitrogen donor ligand is *o*-phenanthroline. The purpose of this study was to determine what effect if any, the CS group has on the mechanism and rate of reaction (eq 2) as compared to that of the carbonyl analogue (eq 1).

Experimental Section

Preparation and Purification of Materials. Preparation of $W(CO)_3(CS)$(*o*-phen). To a solution of 0.0992 g (0.14 mmol) of $Bu_4N[W(CO)_4(CS)I]^2$ in 15 mL of acetone was added dropwise 0.145 mL of a 1.01 M solution of $AgBF_4$ in acetone at room temperature. A yellow precipitate of AgI formed. Then a solution of 0.0287 g (0.16 mmol) of *o*-phenanthroline in 3 mL of acetone was added, yielding a red solution. The solution was allowed to stir for approximately 2 h at room temperature. It was then filtered through Celite and evaporated to dryness. The residue was dissolved in CH_2Cl_2 and eluted on a Florisil column (1.5 × 30 cm) with methylene chloride. A deep red solution was collected. The solution was concentrated under reduced pressure, diluted with hexanes, and cooled to −20 °C. Dark red crystals were obtained in a yield of 40%. IR(CS_2): ν(CO) at 2005 (w), 1917 (s), and 1890 (m); ν(CS) at 1212 (m) cm^{-1}. Anal. Calcd for $W(CO)_3(CS)$(*o*-phen): C, 39.04; H, 1.64. Found: C, 39.05; H, 1.91.

The chlorobenzene solvent for the kinetic studies was purified by distillation from P_2O_5 onto molecular sieves. $P(OCH_3)_3$ was fractionally distilled onto molecular sieves. $P(OCH_2CH_3)_3$ and $P(n\text{-}C_4H_9)_3$ were fractionally distilled under reduced pressure, and the $P(C_6H_5)_3$ was crystallized from methylene chloride with hexanes.

Determination of Reaction Rates. The rates of reaction were determined by following the disappearance of the high-frequency CO stretching absorption of $W(CO)_3(CS)$(*o*-phen) at 2005 cm^{-1}, on a Beckman IR-8 or a Perkin-Elmer 237B infrared spectrophotometer. Solutions were approximately 1.3×10^{-2} M in $W(CO)_3(CS)$(*o*-phen); and infrared cells of 0.5-mm path length were used. The $W(CO)_3(CS)$(*o*-phen) was placed in a dry 10-mL volumetric flask. The flask was flushed with N_2 and then wrapped in aluminum foil. Four milliliters of chlorobenzene flushed with N_2 was pipetted into the flask. The flask was then fitted with a septum and again flushed with N_2. The flask was submerged in an oil bath and allowed to reach thermal equilibrium. Prethermostated $P(OCH_3)_3$ was added, by syringe, through the septum, and aliquots were periodically withdrawn with a syringe. The absorbance at 2005 cm^{-1} was determined for each aliquot. The slopes of plots of ln $(A - A_\infty)$ vs. time, where A is the absorbance at time t and A_∞ is the absorbance at the completion of the reaction, gave first-order rate constants, k_{obsd}. The plots were linear for at least the first 80% of reaction. During the time that the reaction with $P(OCH_3)_3$ would have been complete, about 10% of the $W(CO)_3(CS)$(*o*-phen) decomposed in the absence of $P(OCH_3)_3$. This decomposition was accompanied by black precipitate formation, which was not observed during the substitution reactions, except with $P(n\text{-}C_4H_9)_3$, as noted below.

Product Identification. The product of the reaction of $W(CO)_3(CS)$(*o*-phen) with $P(OCH_3)_3$ was identified by its infrared spectrum in chlorobenzene which consisted of two bands of equal intensity at 1920 and 1842 cm^{-1}. It was never isolated from the experimental solutions; however, it was isolated from a preparative-scale reaction. To a solution of $W(CO)_3(CS)$(*o*-phen) (15.4 mg, 0.031 mmol) in 2.5 mL of 1,2-dichloroethane under N_2 was added $P(OCH_3)_3$ (5.7 mg, 0.046 mmol). The reaction mixture was heated to 85 °C and allowed to react for 1.8 h. It was then cooled to −20 °C whereupon black crystals of the product precipitated. IR(CS_2): ν(CO) at 1932 (s) and 1855 (s); ν(CS) at 1179 (s) cm^{-1}. Anal. Calcd for $W(CO)_2[P(OCH_3)_3](CS)$(*o*-phen): C, 36.75; H, 2.92. Found: C, 36.62; H, 2.95.

Results

The starting complex, $W(CO)_3(CS)$(*o*-phen), was prepared by a method used previously[2] for $W(CO)_3(CS)$(bpy). Like the bipyridyl complex, $W(CO)_3(CS)$(*o*-phen) is assigned the C_s geometry shown in eq 2 on the basis of relative intensities of the ν(CO) absorptions in its infrared spectrum. The weak band at 2005 cm^{-1} may be assigned to the symmetric (A′) stretch of the trans CO groups, while the strong 1917-cm^{-1} band would be the antisymmetric (A″) stretching mode. The low-frequency, medium-intensity absorption is then the unique CO trans to the nitrogen.

The infrared spectrum of the product, $W(CO)_2(L)(CS)$(*o*-phen), shows two ν(CO) bands of equal intensity. The absence of a weak ν(CO) absorption eliminates a structure in which the CO groups are mutually trans. Of the three possible remaining structures, that with both CO groups trans to the N donors should have ν(CO) frequencies similar to those (1828 and 1787 cm^{-1})[3] of $W(CO)_3[P(OC_2H_5)_3]$(*o*-phen), in which all CO's are mutually cis. The observed high values of 1932 and 1855 cm^{-1} are inconsistent with this structure. The structure in which L is trans to an N donor would be expected to be less stable than one where the N donors and L were all trans to CO or CS groups. These arguments, although not unequivocal, suggest that the most likely structure for the product is that shown in eq 2. Therefore, the geometries of the reactant and product are probably the same as those in eq 1, except that one of the CO groups trans to a nitrogen donor is replaced by a CS.

Table I. Rate Constants for the Reaction (eq 2) of $W(CO)_3(CS)$(*o*-phen) with L in Chlorobenzene Solvent

L	Temp, °C	[L], M	10^4k_{obsd}, s^{-1}
$P(OCH_3)_3$	64.9	1.34×10^{-1}	1.54
		1.34×10^{-1}	1.55
		6.57×10^{-1}	1.71
		6.57×10^{-1}	1.91
		1.34	1.89
	73.9	1.34×10^{-1}	4.14
		1.38×10^{-1}	4.31
		6.57×10^{-1}	4.74
		6.57×10^{-1}	4.55
		1.31	5.17
		1.34	4.53
		1.34	4.92
	83.8	1.34×10^{-1}	12.2
		1.36×10^{-1}	13.2
		6.57×10^{-1}	13.2
		1.34	11.2
$P(OCH_2CH_3)_3$	83.8	9.13×10^{-2}	12.1
		9.13×10^{-1}	12.2
		1.48	12.0
$P(C_6H_5)_3$	83.8	1.33×10^{-1}	13.0
		1.01	10.5

Table II. Activation Parameters for CO Dissociation in Analogous Carbonyl–Thiocarbonyl Complexes

Complex	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
$W(CO)_4$(*o*-phen)[a,b]	33.4 ± 1.0	−10.6 ± 3.0
$W(CO)_3(CS)$(*o*-phen)[b]	25.8 ± 0.1	0.1 ± 0.4
$W(CO)_6$[c,d]	39.9 ± 1.6	13.8 ± 3.7
$W(CO)_5(CS)$[d,e]	31.5 ± 1	3.1 ± 3

[a] Reference 1. [b] In chlorobenzene solvent. [c] Reference 5. [d] In decalin solvent. [e] Reference 2.

The rate of reaction 2 follows a general two-term rate expression in which $k_{obsd} = k_1 + k_2[L]$:

$$\text{rate} = (k_1 + k_2[L])[W(CO)_3(CS)(o\text{-phen})] \qquad (3)$$

At the highest temperature (83.8 °C), the k_1 term predominates and k_{obsd} is independent of the concentration and the nature of the L ligand; an average k_{obsd} gives k_1 as 12.2×10^{-4} s^{-1}. At the lower temperatures (64.9 and 73.9 °C), the rate shows a small but significant dependence on the $P(OCH_3)_3$ concentration. A least-squares fit of the data to eq 3 gave the following k_1 and k_2 values, respectively: 1.51×10^{-4} s^{-1} and 2.89×10^{-5} s^{-1} M^{-1} at 64.9 °C and 4.16×10^{-4} s^{-1} and 6.83×10^{-5} s^{-1} M^{-1} at 73.9 °C. The decreasing importance of the k_2 term to the overall rate at higher temperatures indicates that the enthalpy of activation is smaller for the k_2 than the k_1 pathway. Activation parameters and their associated standard deviations (Table II) for the k_1 term of the reaction with $P(OCH_3)_3$ were determined from a least-squares evaluation of the slope and intercept of a plot of ln (k/T) vs. $1/T$.

Of the ligands tried in reaction 1,[1] $P(n\text{-}C_4H_9)_3$ gave the largest k_2 term. In an attempt to determine k_2 values for reaction 2 with $P(n\text{-}C_4H_9)_3$, reactions at 73.9 °C at various $P(n\text{-}C_4H_9)_3$ concentrations were studied. The k_{obsd} values obtained at the phosphine concentrations given in parentheses were 5.84×10^{-4} (0.181 M), 6.14×10^{-4} (0.502 M), 6.33×10^{-4} (0.903 M), and 8.05×10^{-4} s^{-1} (1.33 M). However, plots from which these k_{obsd} values were obtained deviated from linearity especially at the lowest phosphine concentrations. In addition, a precipitate formed during these reactions. While the rate of the reaction does show a substantial $P(n\text{-}C_4H_9)_3$ concentration dependence, it is doubtful that the calculated k_1 and k_2 values (5.28×10^{-4} s^{-1} and 1.87×10^{-4} s^{-1} M^{-1}) are reliable in view of the above-mentioned complications.

Discussion

The two terms in the rate law (eq 3) suggest that reaction 2 proceeds by both dissociative and associative pathways. The dissociative mechanism presumably involves rate-determining dissociation of one of the two mutually trans CO groups, as was observed previously for $Cr(CO)_4$(*o*-phen).[4] The associative pathway with $P(OCH_3)_3$ is negligible at the highest temperature studied (83.8 °C) but becomes measurable at the lower temperatures. Although the k_2 rate constants are too small to give accurate activation parameters, the decreasing contribution of the associative mechanism at higher temperatures indicates that the activation energy for the associative mechanism is less than that of the dissociative pathway, as was found for reaction 1.[1]

A direct comparison of the rates of the dissociative pathways for reactions 1 and 2 may be made by extrapolating the rate constant for the thiocarbonyl reaction to 114 °C. This yields a k_1 value of 2.3×10^{-2} s^{-1} for reaction 2 which is approximately 140 times larger than that (1.63×10^{-4} s^{-1}) for reaction 1 under the same conditions (114 °C, in chlorobenzene solvent).[1] Thus, the thiocarbonyl ligand has clearly increased the rate of CO dissociation as compared to the carbonyl analogue.

Activation parameters for the dissociative pathways of reactions 1 and 2 are given in Table II. These results show that the increased rate for the thiocarbonyl complex is primarily due to a decrease of 7.6 kcal/mol in the activation energy. A decrease (8.4 kcal/mol, Table II) in $\Delta H^\ddagger$ was also observed for the dissociation of the trans CO from $W(CO)_5(CS)$[2] as compared to $W(CO)_6$.[5] This result could be interpreted as indicating that the CS group weakens the W–CO bond thereby reducing the activation energy. The kinetic results support other evidence[6-9] which suggests that CS is a better π^*-bonding ligand than CO. Its stronger π^*-bonding ability would reduce π bonding to the CO groups, hence weakening the W–CO bonds and facilitating CO dissociation.

To our knowledge only one other kinetic comparison of CO and CS has been reported. In that case the rate of cyclooctene dissociation from $(C_5H_5)Mn(CO)(CS)(C_8H_{14})$[10] was found to be approximately 4 times faster than from $(C_5H_5)Mn(CO)_2(C_8H_{14})$,[11] and the activation energy was also lower for the thiocarbonyl complex. The increased lability of the cyclooctene group was also attributed to the greater π^*-bonding ability of the CS ligand.

Acknowledgment. We are grateful to the National Science Foundation for partial support of this research.

Registry No. $W(CO)_3(CS)$(*o*-phen), 66523-88-4; $P(OCH_3)_3$, 121-45-9; $P(OCH_2CH_3)_3$, 122-52-1; $P(C_6H_5)_3$, 603-35-0; $P(n\text{-}C_4H_9)_3$, 998-40-3; $W(CO)_2[P(OCH_3)_3](CS)$(*o*-phen), 66523-89-5; $Bu_4N[W(CO)_4(CS)I]$, 56031-00-6.

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Correspondence

Metal Ion Specificity in the Oxidation of the Coordinated Mercapto Group

Sir:

There are many examples of metalloproteins which contain a coordinated sulfur.[1,2] A large fraction of these metalloproteins are involved in electron-transfer reactions. Because of these biological implications there have been many studies on suitable model systems.[3-10]

All the systems previously studied are cobalt(III)–mercapto complexes. The cobalt(III) can be reduced via electron transfer through the coordinated mercapto group or by direct electron transfer.[3-11] However, the coordinated mercapto group is a good electron donor and it can be oxidized to either a disulfide group,[12] a sulfinato,[3,4,8-10] or a sulfenato group.[3] The mole ratio of oxidizing agent per mercapto group and the type of oxidizing agent employed determine in part the nature of the oxidized product.

All the complexes employed in the above studies, except one,[8-10] contained only one mercapto group bonded to the cobalt(III). We have been studying the reactions of various metal ions with tris(2-mercaptoethylamine)cobalt(III) (CoL_3).[11] CoL_3 is slightly soluble in water and insoluble in other solvents. This complex, CoL_3, can function as a tridentate ligand and coordinate to such metal ions as Ni^{2+}, Co^{3+}, Fe^{3+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} using the coordinated mercapto groups as the donor atoms.[13-15] However, the reactions of CoL_3 in the presence of reducing metal ions such as chromium(II) or iron(II) or oxidizing metal ions such as chromium(III) or UO_2^{2+} resulted in the isolation of the product $Co(CoL_3)_2X_3$. A mechanism involving several oxidation–reduction reactions has been suggested.[11] In these previous studies we have not been able to isolate the oxidized sulfur ligand coordinated to the cobalt(III).

The reactions of $[Ni(CoL_3)_2]Br_2$[13] or $[Pb(CoL_3)_2](NO_3)_2$ with large excesses of H_2O_2 resulted in the formation of a yellow precipitate which analyzed for $Co(NH_2CH_2CH_2SO_2)_3(CoL_3O_6)$. This yellow precipitate is slightly soluble in water. Evidence that CoL_3O_6 contains three coordinated sulfinato groups includes the observation of bands at 1173 and 1187 cm^{-1} in the infrared spectra which did not appear in the complex CoL_3 and also a sharp band at 1098 cm^{-1}. (The S-coordinated sulfenato group usually has one asymmetric stretch in the 1250–1100-cm^{-1} range and another symmetric stretch at 1000–1000 cm^{-1}.[3,4,16]) Since two bands instead of one were observed in the 1250–1100-cm^{-1} region of the in-