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Mechanism of Chelate Ring Opening in Metal Carbonyl Complexes

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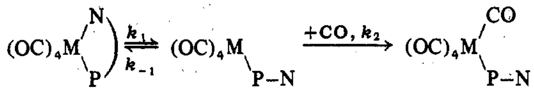
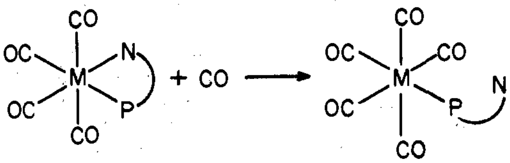
Carbon monoxide reacts with a series of $M(CO)_4(P–N)$ complexes, where M = Cr, Mo, and W and P–N is a phosphorus-nitrogen donor bidentate ligand, to give the monocoordinated ligand complex: $M(CO)_4(P–N) + CO \rightarrow M(CO)_5(P–N)$. Kinetic studies support the following mechanism for this chelate ring-opening reaction



The rate of the reaction is first order in CO concentration, but in the presence of a strong acid such as trifluoroacetic acid the uncoordinated N donor is immediately protonated preventing reclosure (k_{-1}) of the ring. Together with the rate data obtained in the absence of acid, the k_1 value obtained in the acid reactions allows the calculation of the rate ratio (k_{-1}/k_2) for ring closure (k_{-1}) to reaction with CO (k_2). Values of k_1 increase with the increasing bulkiness of the groups on the N-donor group of the ligand: $(C_6H_5)_2PCH_2CH_2NH_2 < (C_6H_5)_2PCH_2CH_2N(CH_3)_2 < (C_6H_5)_2PCH_2CH_2N(C_2H_5)_2$. For five- and six-membered chelate complexes, k_1 is much larger for the six-membered $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$ than for its five-membered analog, $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$. Since the k_{-1}/k_2 ratios were observed to be very similar for all of the complexes examined, the overall rates of reaction are primarily determined by the rates of N-donor dissociation (k_1).

Mechanistic studies of the replacement of monodentate ligands in metal carbonyl complexes by other ligands have been reported for a wide range of complexes.[2] In contrast, however, little is known about the mechanisms or rates of reactions involving replacement of only one donor group of a chelate ligand. Dobson and coworkers have studied bidentate ligand replacement in Cr, Mo, and W complexes $M(CO)_4(L–L)$, where L–L = $(CH_3)_2NCH_2CH_2N(CH_3)_2$,[3] $(CH_3)_2NCH_2CH_2CH_2N(CH_3)_2$,[4] $CH_3SCH_2CH_2SCH_3$,[5] $(CH_3)_3CSCH_2CH_2SC(CH_3)_3$,[6] $(CH_3)_3CSCH_2CH_2CH_2SC(CH_3)_3$,[4] and $(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$.[7] We have also examined similar reactions where L–L is 2,2′-dipyridyl[8] or $NH_2CH(CH_3)CH_2NH_2$.[9] In all cases, the bidentate ligands were completely displaced and there was no evidence for the ring-opened complex in which only one end of the ligand was bound to the metal. The kinetic results did, however, suggest that ring opening was rate determining, but the ring-opened intermediate rapidly lost the ligand to give the observed product.

The purpose of the present study was to examine chelate ring-opening reactions in which the reaction product was simply that containing the monocoordinated bidentate ligand and then to elucidate the mechanism and effects of chelate ligand structure on the rates of ring opening. Relative to phosphorus-donor ligands, nitrogen donors dissociate much faster[10,11] from carbonyl complexes of Cr, Mo, and W. For this reason, complexes of these metals with bidentate ligands containing a relatively inert phosphorus donor and a labile nitrogen-donor group were studied. The reactions may be represented as follows



(1)

where the P–N ligands are $(C_6H_5)_2PCH_2CH_2N(CH_3)_2$, $(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2$, $(C_6H_5)_2PCH_2CH_2NH_2$, and $(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2$.

Experimental Section

Materials. The P–N ligands and their $M(CO)_4(P–N)$ complexes were prepared and characterized as described elsewhere.[12] The complexes, *cis*-$Mo(CO)_4[P(C_6H_5)_3](NHC_5H_{10})$ and $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2NH_2]$, were kindly provided by Professors D. J. Darensbourg and G. R. Dobson, respectively. The piperidine complex, $Mo(CO)_5(NHC_5H_{10})$, was prepared by refluxing $Mo(CO)_6$ and $C_5H_{10}NH$ in heptane for 2 hr under a nitrogen atmosphere.[13] Carbon monoxide (99.5% minimum purity, Matheson Gas Products) was used without further purification. The solvent, 1,4-dichlorobutane, DCB (Aldrich Chemical Co.), was purified by shaking (24 hr, 25°) with concentrated H_2SO_4, washing with water, neutralizing with suspended solid Na_2CO_3, drying over $CaCl_2$, and finally distilling. The middle fraction was stored under a nitrogen atmosphere in the dark. On extended storage, it slowly decomposed to presumably give an acid (probably HCl), as evidenced by increased rates of reaction 1. The amines, $N(C_2H_5)_3$ and NHC_5H_{10}, and trifluoroacetic acid were fractionally distilled prior to use.

The solubilities of CO in 1,2-dichlorobutane (DCB) under the conditions of the kinetic studies are reported elsewhere.[14] The CO concentrations ranged up to approximately 6×10^{-3} *M*, where the CO pressure over the solution was 1 atm.

Kinetic Measurements. The kinetic studies were carried out in the apparatus diagrammed in Figure 1. This apparatus consisted of a 100-ml three-neck reaction flask which was fitted with a mercury thermometer, an adapter containing a stopcock and rubber septum for sample injection and withdrawal, and an adapter which connected to a Graham condenser and contained within it a length of glass tubing which projected down into the bottom of the reaction flask and dispersed CO into the reaction solution. The reaction flask was almost

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[1] Fellow of the Alfred P. Sloan Foundation, 1970–1972.

[2] For example, see R. J. Angelici, *Organometal. Chem. Rev.*, 3, 173 (1968).

[3] G. C. Faber, T. D. Walsh, and G. R. Dobson, *J. Amer. Chem. Soc.*, 90, 4178 (1968).

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[8] J. R. Graham and R. J. Angelici, *J. Amer. Chem. Soc.*, 87, 5590 (1965).

[9] J. R. Graham and R. J. Angelici, *Inorg. Chem.*, 6, 992 (1967).

[10] R. J. Dennenberg and D. J. Darensbourg, *Inorg. Chem.*, 11, 72 (1972).

[11] C. M. Ingemanson and R. J. Angelici, *Inorg. Chem.*, 7, 2646 (1968).

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[13] D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, 7, 959 (1968).

[14] W. J. Knebel and R. J. Angelici, *Inorg. Chem.*, 13, 632 (1974).

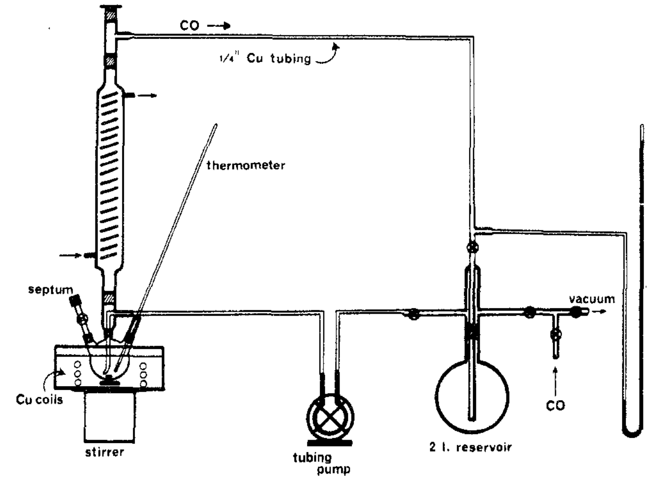

Figure 1. Apparatus used in the kinetic studies of reaction 1.

totally immersed in a thermostated mineral oil bath which, in turn, was temperature controlled by 0.25-in. copper coils which led ultimately from and to a Haake Constant Temperature Circulator (Model FE). The temperature of each kinetic experiment was maintained constant within ±0.05° during the run. Carbon monoxide was circulated continuously (60-90 ml/min) throughout the entire system, reaction solution, condenser, and gas bulb (2000-ml flask of volume 500 times that of CO uptake by the reactant) by a Cole-Parmer "Masterflex" Tubing Pump (Model Head 7015-"Viton" Tubing). A mercury manometer was attached to the unit for direct internal pressure readings.

A typical kinetic run was carried out in the following manner. The entire system was evacuated ($p < 0.03$ mm) and then filled with CO to a desired partial pressure. In studies in which the partial pressure of CO was required to be less than 1.0 atm, prepurified nitrogen served as the diluent and was added (after CO) until the total pressure within the system was 1.0 atm. Solvent (50.0 ml) was syringed into the reaction flask, and the system was allowed to equilibrate to the desired temperature. The pressure in the system was noted; it changed negligibly during a kinetic run.

A preweighed sample (0.05-0.08 g) of solid starting complex, $M(CO)_4(P\text{-}N)$, was placed in a syringe; after inserting the needle into the septum, the solid was washed into the solution by plunging. Temperature equilibrium was regained rapidly within several minutes. During each run the reaction solution was stirred vigorously with the magnetic stirrer while a steady stream of CO was circulated through the system. These conditions provided a constant saturated CO concentration in the solutions during the reactions.

During each run 10-12 samples (<0.5 ml volume) of solution were withdrawn periodically by syringe from the reaction vessel; the absorbance of the highest frequency $\nu(C{\equiv}O)$ (2013 ± 5 cm^{-1}) band was measured on a Beckman IR-8 infrared spectrophotometer using 1.0-mm NaCl cells. For reactions in acidic media the complex was introduced about 5 min prior to the addition of acid. In the case of the more rapid reactions ($t_{1/2} < 5$ min), aliquots were withdrawn every 15-20 sec. These solutions were immediately injected into test tubes chilled to −35° (liquid N_2-dichloroethane slush bath) to quench the reactions. The ir absorption measurements were made after all samples had been collected.

Plots of ln ($A_t - A_\infty$), where A_t is the absorbance at any time t and A_∞ (~0.05) is the absorbance at infinite time, *vs.* time were linear to at least 75% completion of reaction and gave slopes from which the pseudo-first-order rate constants (k_{obsd}) were calculated. Average deviations for these rate constants were less than 3%.

Several complexes were studied at varying CO concentrations. The results indicate a nearly linear relationship between k_{obsd} and [CO] for the more rapid reactions in nonacidic media. In the slower reactions, appreciable deviations from linearity were observed particularly at low CO concentrations ($<1.2 \times 10^{-3}$ *M*); this behavior was probably due to decomposition of the starting complex. This is supported by the appearance of a faint orange color which developed in reaction mixtures containing CO concentrations less than 3×10^{-3} *M*. It is also supported by the observation that k_{obsd} (7.67×10^{-5} sec^{-1}) for the decomposition of $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2]$ at 69.6° in the absence of CO (*i.e.*, in an N_2 atmosphere) is nearly the same as that (7.49×10^{-5} sec^{-1}) for reactions at low CO concentration (6.35×10^{-4} *M*). Thus, at low CO concentrations, decomposition becomes an increasingly important reaction path as compared to the reaction with CO (eq 1). For this reason rate constants obtained at high CO concentrations (usually above 5×10^{-3} *M*) are used in rate comparisons; under these conditions product band intensities indicated that less than 10% of the starting complex underwent decomposition.

Complete replacement of the P-N ligand from the initial P-bonded product, $Mo(CO)_5(P\text{-}N)$, occurred at rates ranging from approximately 8 to 500 times more slowly than those for initial N-donor replacement (eq 1). Evidence for this second conversion was the growth of the $Mo(CO)_6$ absorption at ~1980 cm^{-1}.

The rate of reaction of $Mo(CO)_5(NHC_5H_{10})$ with CO was followed by observing the decrease in intensity of the very strong 1933-cm^{-1} band of the reactant. The reaction of *cis*-$Mo(CO)_4[P(C_6H_5)_3](NHC_5H_{10})$ with CO to give $Mo(CO)_5[P(C_6H_5)_3]$ was followed by noting the disappearance of the medium intensity absorption of the reactant at 2015 cm^{-1}.

Identification of Reaction Products. The metal carbonyl product obtained initially from the reaction of the $Mo(CO)_4(P\text{-}N)$ complexes with CO in DCB exhibited four C-O stretching absorptions at 2072 (m), 1986 (w), 1954 (s), and 1941 (s) cm^{-1}. These frequences are the same as those observed for $Mo(CO)_5[P(C_6H_5)_3]$ in DCB. These are considerably different from those of the nitrogen ligand complex, $Mo(CO)_5(NHC_5H_{10})$, which has absorptions at 2070 (m), 1980 (w), 1933 (s), and 1893 (s) cm^{-1}. The $Mo(CO)_5(P\text{-}N)$ spectra are also very similar to that reported[15] for $Mo(CO)_5[(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2]$, a species that was identified as an intermediate in the reaction of $Mo(CO)_6$ with $(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2$. All of this evidence strongly supports dissociation of the N-donor end of the P-N ligand as shown in eq 1. Since the kinetic experiments were conducted in very dilute solutions (3×10^{-3} *M*), it was not possible to isolate the products from these solutions. However, the identities of two products were unequivocally established by preparing and derivatizing them in large quantities, as described below. The other products were assumed to be analogous because of their nearly identical infrared spectra.

Preparation of $\{Mo(CO)_5[(C_6H_5)_2PCH_2CH_2N(CH_3)(C_2H_5)_2]\}I$. Carbon monoxide was bubbled slowly through a solution of $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2]$ (0.740 g, 1.50 mmol) in chloroform (250 ml) under vigorous stirring at 51° for 12 hr. The system was then treated with a tenfold excess (0.93 ml) of methyl iodide and stirred at 51° for an additional 8 hr. After stripping off the solvent the light-brown residue was taken up in a minimal volume of $CHCl_3$, and the resulting solution was filtered. Addition of excess diethyl ether to the greenish-yellow filtrate precipitated pale yellow microcrystals of $\{Mo(CO)_5[(C_6H_5)_2PCH_2CH_2N(CH_3)(C_2H_5)_2]\}I$ (0.920 g, 92.5% yield) which was purified by recrystallization from acetone-ether; mp, 128-136° dec. The infrared spectrum (in $CHCl_3$) shows $\nu(C{\equiv}O)$ at 2071 (m), 1986 (w), 1952 (s), and 1940 (s) cm^{-1}. The pmr spectrum (in acetone-d_6) shows τ 2.43 (m, $P(C_6H_5)_2$), 6.24 (q, $J(CH_2\text{-}CH_3) = 7$ Hz, NCH_2CH_3), 6.63 (m, PCH_2CH_2N), 6.69 (s, NCH_3), and 8.80 (t, $J(CH_2\text{-}CH_3) = 7$ Hz, NCH_2CH_3). *Anal.* Calcd for $C_{24}H_{27}IMoNO_5P$: C, 43.5; H, 4.11; N, 2.11. Found: C, 43.4; H, 4.23; N, 2.25.

Preparation of $\{Mo(CO)_5[(C_6H_5)_2PCH_2CH_2N(H)(C_2H_5)_2]\}BF_4$. Carbon monoxide was bubbled slowly through a solution of $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2]$ (0.493 g, 1 mmol) in chloroform (180 ml) under vigorous stirring at 50° for 8 hr. The system was then treated with aqueous fluoroboric acid (3 ml), and the resulting suspension was agitated vigorously for an additional hour. The near-colorless chloroform layer was separated and evaporated to dryness. The residue was taken up in a minimal volume of acetone and the resulting solution was filtered. Addition of excess diethyl ether to the filtrate gave the white crystalline product $\{Mo(CO)_5[(C_6H_5)_2PCH_2CH_2N(H)(C_2H_5)_2]\}BF_4$ (0.465 g, 76.4% yield) which was purified by recrystallization from acetone-ether; mp 154-156° dec. The infrared spectrum (in $CHCl_3$) shows $\nu(N\text{-}H)$ at 3120 (w) cm^{-1}, $\nu(C{\equiv}O)$ at 2072 (m), 1988 (w), 1952 (s), and 1939 (s) cm^{-1}, and $\nu(B\text{-}F)$ at 1080 (vs) cm^{-1}. The pmr spectrum (in acetone-d_6) shows τ 2.43 (m, $P(C_6H_5)_2$), 6.53 (q, $J(CH_2\text{-}CH_3) = 7$ Hz, NCH_2CH_3), 6.72 (m, PCH_2CH_2N), and 8.77 (t, $J(CH_2\text{-}CH_3) = 7$ Hz, NCH_2CH_3). *Anal.* Calcd for $C_{23}H_{25}BF_4MoNO_5P$: C, 45.4; H, 4.15; N, 2.31. Found: C, 45.8; H, 4.68; N, 2.74.

Results

The complexes, $Mo(CO)_4(P\text{-}N)$, react with CO according to eq 1. Pseudo-first-order rate constants, k_{obsd}, for these

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[15] G. R. Dobson, R. C. Taylor, and T. D. Walsh, *Inorg. Chem.*, 6, 1929 (1967).

Table I. Rate Data for the Reactions of $M(CO)_4(P\text{-}N)^a$ with CO in DCB According to Eq 1

Temp, °C	10^3[CO], mol/l.	$10^3 k_{obsd}$/[CO], M^{-1} sec^{-1}
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2NH_2]$		
69.6	6.34	1.20
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]^f$		
69.6	6.34	6.32
80.0	6.41	8.48
90.0	6.52	13.5
100.0	6.67	31.0
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2]^g$		
60.0	6.11	13.6
69.6	6.28	36.5
69.6	6.35	37.5^b
69.6	4.74	36.9
69.6	3.16	40.5
69.6	1.58	46.5
69.6	0.635	118
69.6	0.00	c
80.0	6.38	96.3
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]^h$		
40.0	5.85	16.7
60.0	6.13	139
69.6	6.32	390
69.6	6.36	381^d
69.6	4.65	383
69.6	3.14	376
69.6	1.56	403
69.6	0.00	e
$Cr(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$		
69.6	6.30	1.63
69.6	3.23	1.79
$W(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$		
69.6	6.32	0.305
69.6	2.53	0.385

[a] Initial complex concentrations ranged from 3.23×10^{-3} to 4.42×10^{-3} M. [b] With 2.79×10^{-1} M $N(C_2H_5)_3$ added. [c] $k_{obsd} = 7.67 \times 10^{-5}$ sec^{-1}. [d] With 1.53×10^{-1} M $N(C_2H_5)_3$ added. [e] $k_{obsd} = 2.18 \times 10^{-4}$ sec^{-1}. [f] $\Delta H^* = 12.7 \pm 4.1$ kcal/mol; $\Delta S^* = -31.7 \pm 12.0$ eu. [g] $\Delta H^* = 22.2 \pm 0.2$ kcal/mol; $\Delta S^* = -0.6 \pm 0.5$ eu. [h] $\Delta H^* = 21.5 \pm 1.1$ kcal/mol; $\Delta S^* = 2.4 \pm 3.4$ eu.

reactions under varying conditions are given in Table I. Except at low CO concentrations where decomposition of the complex becomes significant, the rate of reaction follows the expression

$$\text{rate} = k[M(CO)_4(P\text{-}N)][CO] \qquad (2)$$

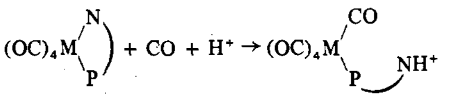
where $k_{obsd} = k$[CO]. Activation parameters associated with k are also given in Table I. Because solvent decomposition (see the Experimental Section) apparently gave an acidic product which greatly accelerated the rates of reaction, excess triethylamine was added in some cases (Table I) to neutralize any acid present; it had no effect indicating that there was no acid catalysis when the solvent was freshly purified.

Under conditions (69.6° and 1 atm CO) where $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2]$ reacted with a half-life of 50 min in the solvent DCB, there was no measurable reaction of the solid complex (*i.e.*, no solvent) after 92 hr. Attempts to measure the rate of the reverse of reaction 1 under an N_2 atmosphere in DCB yielded predominantly decomposition with little $M(CO)_4(P\text{-}N)$ being formed. For $Mo(CO)_5[(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2]$ at 69.6° this decomposition occurred about ten times more slowly than the forward reaction of eq 1. It was clear that reaction 1 was not reversible; the equilibrium lies far toward the $M(CO)_5(P\text{-}N)$ product.

Extended observation of the reaction of the initial product, $Mo(CO)_5[(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2]$, with CO (eq 1) in DCB at 69.6° showed that this product reacted further with 5×10^{-3} M CO to give an equilibrium mixture of the monodentate complex (~1 part) and $Mo(CO)_6$ (~3 parts) at a rate $k_{obsd} = 5.2 \times 10^{-6}$ sec^{-1}. This was much slower than the initial ring-opening reaction.

The infrared spectrum of $Mo(CO)_5[(C_6H_5)_2PCH_2CH_2NH_2]$ was the same as that of the other products. There was no evidence for amine attack at a cis CO carbon atom to form a carbamoyl complex; such complexes have been formed by reactions of a variety of metal carbonyl complexes with amines.[16]

Added Acid. In the presence of added acid the rate of ring opening was much faster (Table II). In these cases, the amine-protonated species was the product.


(3)

Under the conditions given in Table II, the rate of reaction was independent of the CO and acid (usually trifluoroacetic acid) concentrations.

$$\text{rate} = k_{obsd}[M(CO)_4(P\text{-}N)] \qquad (4)$$

Strong acids, trifluoroacetic and trichloroacetic acids, gave essentially the same rates. On the other hand, benzoic acid in concentrations equal to that of the complex had no significant effect on the rate of the reactions, and octanoic acid in concentrations five times greater than that of the complex gave a rate only twice that observed in the absence of acid.

Monodentate Complexes. The rates of piperidine replacement by CO in $Mo(CO)_5(NHC_5H_{10})$ and *cis*-$Mo(CO)_4[P(C_6H_5)_3](NHC_5H_{10})$

$$Mo(CO)_4(L)(NHC_5H_{10}) + CO \rightarrow Mo(CO)_5(L) + NHC_5H_{10} \qquad (5)$$

where L = CO or $P(C_6H_5)_3$ are summarized in Table III. The k_{obsd} constants are independent of both the CO and added NHC_5H_{10} concentrations in the concentration ranges studied. The rate law is

$$\text{rate} = k_1[Mo(CO)_4(L)(NHC_5H_{10})] \qquad (6)$$

where $k_1 = k_{obsd}$. The rate of the $Mo(CO)_5(NHC_5H_{10})$ reaction is not affected by added trifluoroacetic acid. The lack of a NHC_5H_{10} dependence in the reaction of *cis*-$Mo(CO)_4[P(C_6H_5)_3](NHC_5H_{10})$ is in contrast to the inverse dependence found by Hyde and Darensbourg.[17] Their reaction conditions were very similar to ours; the different solvent (*n*-hexane) may be responsible for the different kinetic behavior.

Discussion

Mechanism of Reaction 1. The first-order dependence on the CO concentration (eq 2) of reaction 1 suggests two possible mechanisms: (1) attack of CO directly on the starting complex, or (2) reversible dissociation of the N donor of

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[16] R. J. Angelici, *Accounts Chem. Res.*, 5, 335 (1972).

[17] C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.*, 12, 1286 (1973).

Table II. Rate Data for the Reactions of $M(CO)_4(P\text{-}N)^a$ with CO in DCB with Added Acid According to Eq 3

Temp, °C	10^3[CO], mol/l.	10^3[Acid],[b] mol/l.	10^5k_{obsd}, sec^{-1}
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2NH_2]$			
69.6	6.30	40	613
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$			
40.0	5.86	40	49
50.0	6.04	46	139
69.6	6.32	7.3	835
69.6	6.44	20	761
69.6	6.33	180	730
69.6	3.11	18	776
69.6	1.56	47[c]	692
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2]$			
22.0	5.68	38	26.3
30.0	5.70	40	78.1
40.0	5.86	38	294
69.6			7,940[d]
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$			
22.0	5.69	15	247
22.0	5.70	90[c]	248
22.0	1.91	18	239
30.0	5.67	57	565
40.0	5.86	51	2,120
69.6			41,000[d]
$Cr(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$			
69.6	6.31	37	310
69.6	2.55	31	298
$W(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$			
69.6	6.33	39	9.40
69.6	2.74	42	10.6

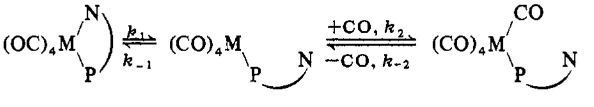
[a] Initial complex concentrations ranged from 3.16×10^{-3} to 5.00×10^{-3} *M*. [b] Trifluoroacetic acid, except where indicated otherwise. [c] Trichloroacetic acid. [d] Value obtained by extrapolation from rate data at other temperatures.

Table III. Rate Data for the Reactions of $Mo(CO)_5(NHC_5H_{10})$ and *cis*-$Mo(CO)_4[P(C_6H_5)_3](NHC_5H_{10})$ with CO in DCB

$Mo(CO)_5(NHC_5H_{10})^a$			*cis*-$Mo(CO)_4[P(C_6H_5)_3](NHC_5H_{10})^e$		
Temp, °C	$10^3 \times$ [CO], mol/l.	$10^5 \times$ k_{obsd}, sec^{-1}	Temp, °C	$10^3 \times$ [CO], mol/l.	$10^5 \times$ k_{obsd}, sec^{-1}
40.0	5.87	9.80	40.0	5.94	175
40.0	5.87	9.85[b]	40.0	2.93	168[f]
40.0	2.89	9.60[c]	59.8	6.16	1360
40.0	1.45	9.52[d]	69.6		3430[g]
69.6	6.28	185			

[a] Initial complex concentrations ranged from 1.03×10^{-3} to 1.25×10^{-3} *M*. [b] With 4.0×10^{-2} *M* trifluoroacetic acid added. [c] With 6.21×10^{-3} *M* NHC_5H_{10} added. [d] With 5.75×10^{-3} *M* NHC_5H_{10} added. [e] Initial complex concentrations ranged from 3.13×10^{-3} to 3.54×10^{-3} *M*. [f] With 3.54×10^{-2} *M* NHC_5H_{10} added. [g] Value obtained by extrapolation from data at other temperatures.

the bidentate ligand followed by attack of the CO on the five-coordinate intermediate. This latter mechanism follows



(7)

Assuming a steady-state concentration of the intermediate and that k_{-2} is negligibly small, the rate expression for this mechanism becomes

$$\text{rate} = \frac{k_1k_2[M(CO)_4(P\text{-}N)][CO]}{k_{-1} + k_2[CO]} \tag{8}$$

Thus under conditions where k_{-1} is much larger than k_2[CO], the rate would be first order in CO concentration.

The lack of a CO dependence (eq 6) in the piperidine substitution reactions of the monodentate ligand complexes $Mo(CO)_5(NHC_5H_{10})$ and *cis*-$Mo(CO)_4[P(C_6H_5)_3](NHC_5H_{10})$ indicates that CO attack is not a common substitution mechanism for these types of complexes.[2] This has also been found for other substitution and decomposition reactions of these complexes.[10,17] For this reason it would be an unlikely pathway for the reactions of the $M(CO)_4(P\text{-}N)$ complexes as well.

On the other hand, the large rate accelerations of reaction 1 by acid argue strongly for the reversible dissociation mechanism (eq 7). In the presence of acid the reaction proceeds to give the N-protonated $M(CO)_5(P\text{-}NH^+)$ as in eq 3, and the rate of this reaction is independent of CO and acid concentrations. It appears that the acid acts in eq 7 by rapidly protonating the uncoordinated nitrogen group in the five-coordinate intermediate thereby eliminating the possibility of reclosure of the chelate. Thus, under these conditions, the experimental k_{obsd} values are the same as k_1 in eq 7. Average values of k_1 are given in Table IV. It should be noted (Table III) that there was no observable acid catalysis of the reaction of $Mo(CO)_5(NHC_5H_{10})$.

In terms of mechanism 7, the experimental k_{obsd}/[CO] values (Table I) measured in the absence of acid are equal to k_1k_2/k_{-1}. Together with the k_1 values obtained under acid conditions, these values allow the calculation of the ratio k_{-1}/k_2 for ring reclosure to CO attack on the five-coordinate intermediate. These ratios at 69.6° are summarized in Table IV. For the conditions employed (69.6° and 5×10^{-3} *M* CO), the rate of ring reclosure is approximately 10^3 times faster than CO attack.

From values of k_1 and k_{-1}/k_2 at different temperatures, activation parameters for these steps have been calculated; these values are reported in Table IV. There are rather large errors associated with the k_{-1}/k_2 activation parameters for $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$ because of the large errors in the activation parameters for k_{obsd}/[CO], Table I. There is no obvious reason for this discrepancy, which is not found in the other systems.

Reaction 1 has also been carried out with $Mo(CO)_4$·$[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$ and ^{13}CO in order to establish the position of the incoming CO in the product.[18] Both ^{13}C nmr and infrared results indicate that the ^{13}CO stereospecifically goes into a position cis to the phosphorus donor. This suggests that the five-coordinate intermediate has either the square pyramidal structure, resulting from dissociation of the N-donor group, or a trigonal bipyramidal structure, onto which ^{13}CO attack occurs cis to the phosphorus atom. In substitution reactions of $Mo(CO)_5(NHC_5H_{10})$, there is evidence[19] that the $Mo(CO)_5$ intermediate has a trigonal bipyramidal or highly distorted square pyramidal structure.

Factors Affecting k_1. For the monodentate complexes, the rate (k_1) of piperidine dissociation (Table IV) from *cis*-$Mo(CO)_4[P(C_6H_5)_3](NHC_5H_{10})$ is about 20 times faster than that for $Mo(CO)_5(NHC_5H_{10})$. This marked acceleration, noted previously by Hyde and Darensbourg,[17] is caused primarily by a more positive entropy of activation. The greater rate for the phosphine complex may be due to either the stronger electron donation of $P(C_6H_5)_3$ as compared to CO which weakens the Mo-N bond or the larger size of P-

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Table IV. Rate Constants and Activation Parameters[a] for the Reactions of $Mo(CO)_4(L)(NHC_5H_{10})$ and $M(CO)_4(P\text{–}N)$ According to Mechanism 7 in DCB at 69.6°

Compd	10^5k_1, sec^{-1}	k_{-1}/k_2, M	$10^3k_{obsd}/[CO]$, M^{-1} sec^{-1}	$\Delta H_1{}^*$, kcal/mol	$\Delta S_1{}^*$, eu	$\Delta H_{-1}{}^* - \Delta H_2{}^*$, kcal/mol	$\Delta S_{-1}{}^* - \Delta S_2{}^*$, eu
$Mo(CO)_5(NHC_5H_{10})$	185			20.4 ± 0.2	−11.8 ± 0.7		
$Mo(CO)_4[P(C_6H_5)_3](NHC_5H_{10})$	3,430[b]			20.7 ± 0.4	−5.1 ± 1.2		
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2NH_2]$	613	5.11 ± 0.62	1.20				
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$	776	1.23 ± 0.15	6.32	19.2 ± 0.7	−12.5 ± 2.1	6.5	19.2
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2]$	7,940[b]	2.21 ± 0.55	36.9	23.9 ± 0.3	5.9 ± 0.9	1.7	6.5
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$	41,000[b]	1.07 ± 0.25	382	21.2 ± 0.4	1.5 ± 1.4	−0.3	−0.9
$Cr(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$	304	1.86 ± 0.24	1.63				
$W(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$	10.0	0.308 ± 0.01	0.305				

[a] Error limits for activation parameters are average deviations. [b] Extrapolated value, see Table II or III.

$(C_6H_5)_3$ which sterically favors piperidine dissociation to give the less crowded five-coordinate intermediate.

Although an exact comparison is not possible, $Mo(CO)_4[P(C_6H_5)_3](NHC_5H_{10})$ compares sterically and electronically most closely with the chelated complex $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2]$. Their rates (Table IV) of N-donor dissociation (k_1) are also very similar. Complexes with less bulky N-donor groups, as in the $(C_6H_5)_2PCH_2CH_2NH_2$ and $(C_6H_5)_2PCH_2CH_2N(CH_3)_2$ complexes, react more slowly as expected.[20] Thus, the five-membered chelate ring seems not to alter greatly the rates of N-donor dissociation as compared to those for similar monodentate complexes.

On the other hand, the rate of N-donor dissociation in the six-membered chelate complex $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$ is substantially faster than the monodentate and five-membered chelate systems. The strain inherent in a six-membered chelate ring, as suggested by models, is probably the reason for this increased rate. A similar conclusion was reached by Dobson and Faber[4] when comparing rates of S-donor dissociation in the reactions with phosphites of the five-membered chelate complex $W(CO)_4[(CH_3)_3CSCH_2CH_2SC(CH_3)_3]$ and the six-membered chelate analog $W(CO)_4[(CH_3)_3CSCH_2CH_2CH_2SC(CH_3)_3]$. In that study, the initial $W(CO)_5(S\text{–}S)$ complex was not detected; it apparently rapidly reacted further with the phosphite ligand (L) to give the observed $W(CO)_4L_2$ product. For both studies, changes in both $\Delta H_1{}^*$ and $\Delta S_1{}^*$ contribute to the large differences in k_1 observed for chelates of different ring size.

For the series of complexes $M(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$ the rate of N-donor dissociation (k_1) decreases in the order: Mo > Cr ≫ W. This is a trend that is commonly observed[2] for dissociative reactions of carbonyl complexes of these metals.

Factors Affecting k_{-1}/k_2. The magnitude of the k_{-1}/k_2 ratios (Table IV) indicates that under the conditions of the studies, the five-coordinate intermediate is much more likely to undergo ring reclosure (k_{-1}) than to react with CO (k_2). A concentration of approximately 1.0 M CO would allow these reactions to proceed at roughly the same rate.

The most remarkable feature of the k_{-1}/k_2 values is their similarity even for a wide range of bidentate ligand structures. Assuming that k_2 is the same for the $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2NR_2]$ intermediates, the rate of ring closure (k_{-1}) then becomes about the same regardless of the R group on the nitrogen donor. Moreover, it means that k_{-1} is essentially the same for the five-membered chelate complex and its six-membered analog. Thus, the five-coordinate intermediate is very nondiscriminating with respect to its reactions with the N-donor group of different chelating ligands, an observation also made for related monodentate complexes.[17] Among the small variations observed in k_{-1}/k_2 there are no obvious trends; to be sure, these ratios will change, according to the magnitude of $(\Delta H_{-1}{}^* - \Delta H_2{}^*)$, depending on the temperatures selected for comparison.

The k_{-1}/k_2 values for the series of complexes $M(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$ decrease in the order, Cr > Mo > W, although the differences are again not large. A similar k_{-1}/k_2 trend for Mo and W in the reactions of the $M(CO)_4[(CH_3)_2NCH_2CH_2CH_2N(CH_3)_2]$ complexes with phosphites has also been observed.[4]

Factors Affecting the Overall Rates of Reaction 1. Rates for the overall reaction 1 at 69.6° are given by the values (Table IV) of $k_{obsd}/[CO]$. For the series $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2NR_2]$ these rates increase with the bulkiness of the NR_2 donor group: $NH_2 < N(CH_3)_2 < N(C_2H_5)_2$. For the $Mo(CO)_4[(C_6H_5)_2P\text{-}N(CH_3)_2]$ complexes, the rate is about 60 times faster for the six-membered chelate complex than for the five-membered derivative. Both of these trends are determined by the rate of N-donor dissociation (k_1), since the other term contributing to $k_{obsd}/[CO]$ is k_{-1}/k_2, which as already noted is very similar for all of these complexes. Thus, it appears that the rate of N-donor dissociation (k_1) is the predominant factor affecting the rate of chelate ring opening in these complexes.

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Registry No. $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2NH_2]$, 49626-17-7; $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$, 49626-18-8; $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2]$, 14971-44-9; $Mo(CO)_4[(C_6H_5)_2P(H_2CH_2CH_2N(CH_3)_2]$, 49626-20-2; $Cr(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$, 49626-21-3; $W(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$, 49626-22-4; $Mo(CO)_5(NHC_5H_{10})$, 19456-57-6; *cis*-$Mo(CO)_4[P(C_6H_5)_3](NHC_5H_{10})$, 38780-82-4; CO, 630-08-0; $\{Mo(CO)_5[(C_6H_5)_2PCH_2CH_2N(CH_3)(C_2H_5)_2]\}I$, 49626-30-4; $\{Mo(CO)_5[(C_6H_5)_2PCH_2CH_2N(H)(C_2H_5)_2]\}BF_4$, 49626-31-5.

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