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Kinetic and Equilibrium Studies of Bi- and Tridentate Chelate Ring-Opening Reactions of Metal Carbonyl Complexes

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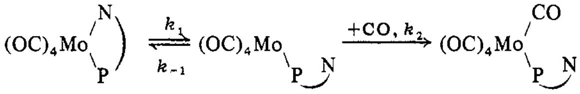
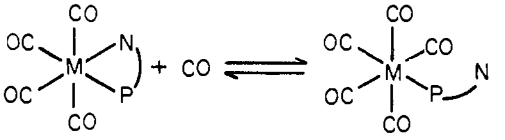
Complexes of the type $\mathrm{Mo(CO)_4(P\text{-}N)}$, where P-N is a pyridylphosphine bidentate ligand such as $\mathrm{(C_6H_5)_2PNHC_5H_4N}$, $\mathrm{(C_6H_5)_2PCH_2C_5H_4N}$, $\mathrm{(C_6H_5)_2PCH_2CH_2C_5H_4N}$, or $\mathrm{(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N}$, react with CO to give the pyridyl-displaced $\mathrm{Mo(CO)_5(P\text{-}N)}$ product. Kinetic studies support the following mechanism.



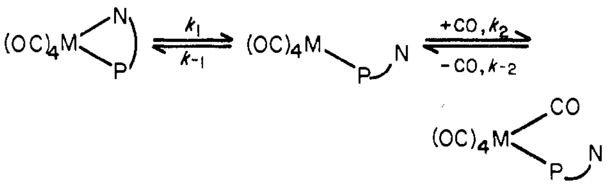
The rate law shows a first-order dependence on both $\mathrm{Mo(CO)_4(P\text{-}N)}$ and CO concentrations. In the presence of high concentrations of trifluoroacetic acid, the pyridyl group is rapidly protonated in the five-coordinate intermediate, and the rate of ring opening becomes much faster and independent of CO concentration. The overall rates of ring opening (k_1k_2/k_{-1}) and also the k_1 values increase with increasing size of the chelate ring: $\mathrm{(C_6H_5)_2PNHC_5H_4N} \sim \mathrm{(C_6H_5)_2PCH_2C_5H_4N} < \mathrm{(C_6H_5)_2PCH_2CH_2C_5H_4N} < \mathrm{(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N}$. Equilibrium studies of these reactions show that the formation of $\mathrm{Mo(CO)_5(P\text{-}N)}$ is much more complete for the seven-membered chelate than for the six-membered analog. Thermodynamic parameters, ΔH and ΔS, for the reaction of $\mathrm{Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]}$ with CO are -8.9 kcal/mol and -12.3 eu, respectively. The complex, *fac*-$\mathrm{Mo(CO)_3(PNP)}$, where PNP is $\mathrm{[(C_6H_5)_2PCH_2CH_2]_2NC_2H_5}$, reacts with CO to give *cis*-$\mathrm{Mo(CO)_4(PNP)}$ in which the N atom is no longer coordinated. The rate of this reaction is also first order in complex and in CO suggesting a mechanism analogous to that for the $\mathrm{Mo(CO)_4(P\text{-}N)}$ complexes. Equilibrium studies yielded ΔH and ΔS values of -10.5 kcal/mol and -17.1 eu, respectively, for this reaction.

In the previous paper,[2] we presented kinetic results for phosphorus-nitrogen donor chelate ring-opening reactions of the type



(1)

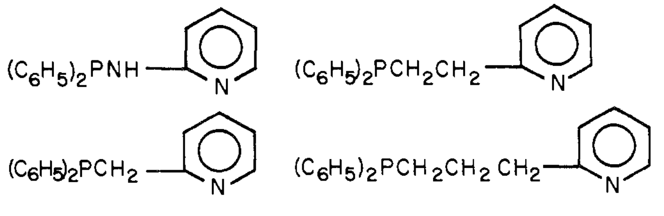
where M was Cr, Mo, or W and the P-N ligands were $\mathrm{(C_6H_5)_2PCH_2CH_2NH_2}$, $\mathrm{(C_6H_5)_2PCH_2CH_2N(CH_3)_2}$, $\mathrm{(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2}$, and $\mathrm{(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2}$. Those results strongly supported a mechanism for ring opening which involved reversible dissociation of the N-donor group followed by CO attack on the five-coordinate intermediate.



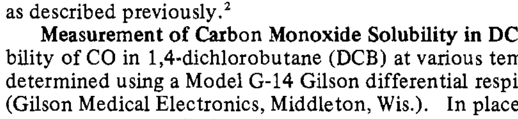
(2)

Because all of these equilibria lay far toward the $\mathrm{Mo(CO)_5\text{-}(P\text{-}N)}$ products, it was not possible to measure their equilibrium constants.

In the present study, we have used a series of pyridine donor P-N ligands in reaction 1. These ligands have allowed the evaluation not only of kinetic parameters but in some cases thermodynamic values as well.



Kinetic and thermodynamic results are also reported for the novel reaction of a tridentate ligand complex, $\mathrm{Mo(CO)_3(PNP)}$, where P-N-P is $\mathrm{(C_6H_5)_2PCH_2CH_2N(C_2H_5)CH_2CH_2P(C_6H_5)_2}$.



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All of the reactions are discussed in terms of their mechanisms and of the structural features of the complexes that affect their kinetic and thermodynamic behaviors.

Experimental Section

Materials. The $\mathrm{Mo(CO)_4(P\text{-}N)}$[3] and $\mathrm{Mo(CO)_3(PNP)}$[4] complexes were prepared as described elsewhere. All other materials were used as described previously.[2]

Measurement of Carbon Monoxide Solubility in DCB. The solubility of CO in 1,4-dichlorobutane (DCB) at various temperatures was determined using a Model G-14 Gilson differential respirometer (Gilson Medical Electronics, Middleton, Wis.). In place of the conventional Warburg flask was used the indicator flask shown in Figure 1. In a typical determination, solvent (~2 ml) was added to a tared indicator flask and degassed by placing it under vacuum (<0.1 mm) for 15 min. While under vacuum, the side-arm bulb of the flask was *completely* filled with solvent by tilting the flask. After closing the bulb stopcock, excess solvent in the main body of the flask was poured out; the flask was then rinsed with acetone and dried. It was reweighted to determine the amount of solvent in the side-arm bulb. After adding a small amount of solvent (~1 ml) to the main body of the flask to balance the solvent vapor pressure within the reference flask on the respirometer, the flask (frequently three were run simultaneously) was attached to the respirometer, and the entire system (manifold, manometers, and indicator flasks) were purged with CO for 30 min. The system was closed to the atmosphere and thermally equilibrated at the desired temperature for 1 hr. Then the system was momentarily vented to the atmosphere to adjust the CO pressure to atmospheric pressure. The preweighed solvent in the bulb was

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

[2] W. J. Knebel and R. J. Angelici, *Inorg. Chem.*, 13, 627 (1974).

[3] W. J. Knebel and R. J. Angelici, *Inorg. Chim. Acta.*, in press.

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

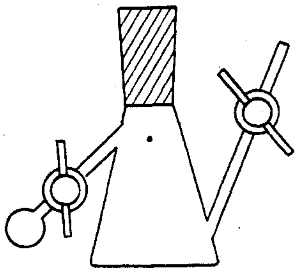

Figure 1. Indicator flask used for CO solubility measurements.

then admitted to the main body of the flask. The volume of CO taken up by the solvent was determined by adjusting a digital micrometer on the volumometer so that the original pressure was reestablished. From this volume of CO taken up, the solvent volume and the temperature, Bunsen coefficients (α), and molarities of CO in solution were calculated. Henry's law was assumed valid for adjustments to 1 atm of pressure. Average values of three to six determinations are summarized in Table I. Solubilities at temperatures greater than 60° were obtained by extrapolation from a plot of log α *vs.* $1/T$. To ensure the accuracy of our results, CO solubilities were measured in other solvents for which data were available in the literature. Our α values together with literature values (in parentheses)[5] for various solvents at 25.0° follow: 1,2-dichloroethane, 0.134 (0.135); chloroform, 0.178 (0.179); toluene, 0.163 (0.167).

Kinetic Measurements. The apparatus and infrared monitoring procedures described in the previous paper[2] were used to follow the rates of all of the reactions (eq 1 and 3) of the $Mo(CO)_4(P\text{-}N)$ and $Mo(CO)_3(PNP)$ complexes with CO in the absence of acid; the reactions of $Mo(CO)_4[(C_6H_5)_2PCH_2C_5H_4N]$ and $Mo(CO)_4[(C_6H_5)_2PNHC_5H_4N]$ in the presence of acid were also followed by this method. For reactions of the $Mo(CO)_4(P\text{-}N)$ complexes, the infrared spectrum[3] of the $Mo(CO)_4(P\text{-}N)$ complexes with $\nu(C{\equiv}O)$ at 2018 (m), 1911 (s), 1898 (s), and 1850 (s) cm^{-1} disappeared as that of the product $Mo(CO)_5(P\text{-}N)$ at 2075 (m), 1982 (w), 1956 (s), and 1942 (s) cm^{-1} increased. These latter frequencies are essentially identical with those of $Mo(CO)_5P(C_6H_5)_3$ in DCB.[2] Rates of reaction were determined by following the decrease in intensity of the 2018-cm^{-1} absorption with time. Plots of ln $(A_t - A_\infty)$ *vs.* time were linear to at least 70% conversion and gave slopes which were the pseudo-first-order rate constants, k_{obsd}, for the reactions. Values of A_∞ were generally nearly zero except for reactions (noted in the tables) in which the equilibria did not lie far toward the product. In these cases, the slopes were equal to the sum of the forward and reverse pseudo-first-order rate constants ($k[CO] + k_r$). From the measured equilibrium constant K (which is related to the forward and reverse rates by the expression $K = k/k_r$) and the k_{obsd} values, k (which is the same as $k_{obsd}/[CO]$ for the other reactions) could be calculated. Average deviations for k_{obsd} values were generally less than 6%.

For the complexes containing six- and seven-membered chelate rings, the initial ring-opening reaction was followed by the much slower CO substitution of the phosphorus donor to form $Mo(CO)_6$. For the very slow reactions (in the absence of acid) of the complexes containing five-membered rings, both the ring-opening and phosphorus-replacement reactions occurred at about the same rates; hence, little of the $Mo(CO)_5(P\text{-}N)$ complexes was observed during the course of these reactions.

The reaction of $Mo(CO)_3(PNP)$ with CO according to eq 3 was followed by the disappearance of the reactant $\nu(C{\equiv}O)$ bands at 1930 (s), 1831 (s) and 1804 (s) cm^{-1} in DCB and the concomitant growth of the $Mo(CO)_4(PNP)$ bands at 2017 (m), 1912 (s), 1901 (s), and 1873 (m) cm^{-1}. The presence of four terminal $\nu(C{\equiv}O)$ absorptions in the product and the similarity of their positions to those of $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$[6] indicate the cis product to be that shown in eq 3. Rates of reaction 3 were followed by the decrease in intensity of the 1804-cm^{-1} band. The data were plotted in the manner described for the $Mo(CO)_4(P\text{-}N)$ complexes.

The reactions of $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]$ and $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N]$ with CO in the presence of acid proceeded with half-lives in a range of 10 to 60 sec. Since the starting compounds were bright yellow and the products were almost colorless, these reactions were followed by noting the decrease of a reactant absorption at 396 ± 2 nm (ϵ_{max} 2450 ± 50 M^{-1} cm^{-1}) on a Cary Model 14 ultraviolet-visible spectrophotometer. The identity of the products as $Mo(CO)_5(P\text{-}NH^+)$ was established not only by their uv spectra but also by their infrared spectra which were nearly identical with those of the product obtained in the absence of acid. These runs were conducted as follows; a 2.0-ml aliquot of a freshly prepared solution of the starting complex (1.0×10^{-3} M) in DCB was transferred to a 1.0-cm quartz cell and saturated with CO ($\sim 5 \times 10^{-3}$ M) by bubbling the gas through it for 3 min. The cell was capped with a rubber septum and thermostated in the cell compartment of the spectrophotometer. After 15 min, a 0.5-ml thermostated solution of the acid in DCB was syringed into the cell. The cell was shaken quickly (~5 sec) and returned to the spectrophotometer. Plots of ln $(A_t - A_\infty)$ *vs.* t were linear and gave slopes which were k_{obsd}. All reactions with acid proceeded to completion.

Table I. Solubility of CO in 1,4-Dichlorobutane (DCB) at Various Temperatures

Temp, °C	α^a	$10^3[CO]$,^{b} mol/l.
0.1	0.124	5.54
20.6	0.127	5.67
30.2	0.128	5.72
40.1	0.132	5.89
50.1	0.136	6.07
59.7	0.138	6.16
69.6	0.142^c	6.34^c
80.0	0.144^c	6.43^c
90.0	0.147^c	6.57^c
100.0	0.150^c	6.69^c

^{a} Defined as milliliters of CO at 1 atm and 0° dissolved by 1 ml of solvent when the partial pressure of CO is 1 atm. Values are accurate to ±0.002. ^{b} Under 1 atm of pressure. ^{c} Extrapolated value.

The reaction of $Mo(CO)_3(PNP)$ with CO in the presence of acid was studied by standard stopped-flow techniques using a Durrum-Gibson Model D-110 stopped-flow spectrophotometer. Carbon monoxide was bubbled through a DCB solution of the complex to give a CO concentration of approximately 5×10^{-3} M. The rates of reaction were followed by noting the disappearance of a $Mo(CO)_3(PNP)$ absorption at 405 nm (ϵ 1020 ± 50 M^{-1} cm^{-1}); at this wavelength the ϵ value for the product $Mo(CO)_4(PNPH^+)$ was 300 ± 50 M^{-1} cm^{-1}. Slopes of ln $(A_t - A_\infty)$ *vs.* time gave k_{obsd} for these reactions. The product, $Mo(CO)_4(PNPH^+)$, had an infrared spectrum that was nearly identical with that of $Mo(CO)_4(PNP)$ produced in the absence of acid.

Equilibrium Measurements. Equilibrium constants for the reactions of $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]$ with CO (eq 1) were determined at the end of kinetic runs after which the infrared absorbances of products and reactants were constant for several hours. The absorptions of $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]$ at 2018 cm^{-1} (ϵ 2450 ± 50 M^{-1} cm^{-1}) and of $Mo(CO)_5[(C_6H_5)_2PCH_2CH_2C_5H_4N]$ at 2075 cm^{-1} (ϵ 1700 ± 50 M^{-1} cm^{-1}, obtained for $Mo(CO)_5[(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N]$ and used for this complex) were used to calculate the concentrations of these species present at equilibrium. The equilibrium constant, $K = [Mo(CO)_5(P\text{-}N)]/[Mo(CO)_4(P\text{-}N)]\cdot[CO]$, was then calculated from these values and the known CO concentration.

For the reaction of $Mo(CO)_3(PNP)$ with CO (eq 3), equilibrium constants were calculated from the intensity of the reactant absorption at 1804 cm^{-1} (ϵ 2790 ± 50 M^{-1} cm^{-1}) when this absorption remained unchanged for several hours at the end of the kinetic runs. Knowing the initial and equilibrium reactant concentrations, the equilibrium $Mo(CO)_4(PNP)$ concentration was calculated. These values were used to calculate the equilibrium constant, $K = [Mo(CO)_4(PNP)]/[Mo(CO)_3(PNP)][CO]$.

Results

Kinetic Studies. Reactions of the $Mo(CO)_4(P\text{-}N)$ complexes with CO according to eq 1 follow the rate law

$$\text{rate} = k[Mo(CO)_4(P\text{-}N)][CO] \qquad (4)$$

where $k = k_{obsd}/[CO]$. The slightly increasing value of $k_{obsd}/[CO]$ for $Mo(CO)_4[(C_6H_5)_2PNHC_5H_4N]$, for example, with decreasing [CO] is almost certainly due to decomposition of the complex (Table II). Thus, in the absence of CO (*i.e.*, N_2 atmosphere), the rate constant for complex decomposition

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(5) W. T. Linke, "Solubilities of Inorganic and Metal Organic Compounds," 4th ed, Vol. 1, Van Nostrand, Princeton, N. J., 1958; "International Critical Tables," Vol. 3, McGraw-Hill, New York, N. Y., 1928.

(6) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961).

Table II. Rate Data for the Reactions of $Mo(CO)_4$(P–N) with CO in DCB According to Eq 1

Temp, °C	10^3[CO], mol/l.	10^3k_{obsd}/[CO], M^{-1} sec^{-1}	Temp, °C	10^3 [CO], mol/l.	10^3k_{obsd}/[CO], M^{-1} sec^{-1}
	$Mo(CO)_4[(C_6H_5)_2PNHC_5H_4N]^a$			$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]^b$	
69.6	6.33	0.890	69.6	6.30	12.7
90.0	6.57	5.04	80.0	6.67	29.2
100.0	6.58	14.2	90.0	6.68	$72.0^{f,h}$
100.0	6.62	14.4^c	100.0	6.69	$159^{f,i}$
100.0	3.83	17.5	100.0	6.68	$176^{f,g,j}$
100.0	0.00	*d*	100.0	3.17	$129^{f,k}$
	$Mo(CO)_4[(C_6H_5)_2PCH_2C_5H_4N]^a$			$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N]^b$	
69.6	6.37	0.412	60.0	6.14	43.0
90.0	6.55	2.39	69.6	6.32	117
100.0	6.64	4.70	79.5	6.40	319
100.0	6.72	4.89^e			
100.0	3.35	5.88			
100.0	1.78	7.75			

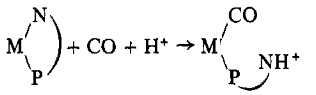
[a] Initial complex concentrations ranged from 2.53×10^{-3} to 3.61×10^{-3} *M*. [b] Initial complex concentrations ranged from 3.15×10^{-3} to 4.69×10^{-3} *M*. [c] With 0.109 *M* free pyridine added. [d] $k_{obsd} = 5.50 \times 10^{-5}$ sec^{-1}. [e] With 0.123 *M* free pyridine added. [f] Reaction does not go to completion. Constant calculated from k_{obsd} and *K* data as described in text. [g] With 0.082 *M* free pyridine added. [h] $k_{obsd} = 6.24 \times 10^{-4}$ sec^{-1}. [i] $k_{obsd} = 1.50 \times 10^{-3}$ sec^{-1}. [j] $k_{obsd} = 1.66 \times 10^{-3}$ sec^{-1}. [k] $k_{obsd} = 7.64 \times 10^{-4}$ sec^{-1}.

(5.50×10^{-5} sec^{-1}) is not much smaller than that (6.70×10^{-5} sec^{-1}) for reaction with the lower concentration (3.83×10^{-3} *M*) of CO. That decomposition contributes to the overall rates at low CO concentrations is also evidenced by a yellow-orange color formation in these reaction solutions. Thus, the most reliable rate data for reaction 1 were obtained at the higher CO concentrations; the related reactions of the phosphorus-alkylamine chelate complexes exhibited similar behavior.[2]

Since it was noted[2] that slow decomposition of the solvent (DCB) produced a species (presumably HCl) which catalyzed these reactions, some reactions were run in the presence of pyridine to neutralize the potential catalyst. As noted (Table II), added pyridine had no effect on the rates when freshly purified solvent was used.

The reaction of $Mo(CO)_3$(PNP) with CO according to eq 3 also followed (Table III) the rate law given in eq 4. Activation parameters associated with the rate constants, *k*, for all of these complexes are given in Table IV.

When acid was added to the reaction solutions, the rates of reaction were dramatically enhanced and the protonated product was obtained.


(5)

As seen from the data for $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N]$ in Table V, the rate of reaction increased with increasing acid concentrations until a plateau was reached beyond which there was no further increase. In general, the rates were measured at high acid concentrations where the reaction was independent of acid. Under these conditions, the rate of reaction 5 followed the expression

$$\text{rate} = k_{obsd}[Mo(CO)_4(P\text{-}N)] \qquad (6)$$

The independence of these high acid reactions on CO concentration is demonstrated by rate data (Table V) for $Mo(CO)_4[(C_6H_5)_2PCH_2C_5H_4N]$.

The rate of the reaction of $Mo(CO)_3$(PNP) with CO in the presence of acid showed an unusually strong dependence on the acid concentration and did not exhibit a distinct leveling off at high acid concentrations (Table V). This acid-catalyzed reaction may follow a mechanism different from that of the $Mo(CO)_4$(P-N) derivatives, perhaps one involving protonation at the metal or at a carbonyl oxygen atom.

Table III. Rate Data for the Reaction of $Mo(CO)_3(PNP)^a$ with CO in DCB According to Eq 3

Temp, °C	10^3[CO], mol/l.	10^3k_{obsd}/[CO], M^{-1} sec^{-1}
69.6	6.39	72.4
80.0	6.66	$150^{b,c}$
90.0	6.85	$298^{b,d}$
90.0	3.41	$282^{b,e}$
100.0	6.90	$679^{b,f}$

[a] Initial complex concentrations ranged from 1.81×10^{-3} to 2.66×10^{-3} *M*. [b] Reaction does not go to completion. Constant calculated from k_{obsd} and *K* data as described in text. [c] $k_{obsd} = 1.31 \times 10^{-3}$ sec^{-1}. [d] $k_{obsd} = 2.89 \times 10^{-3}$ sec^{-1}. [e] $k_{obsd} = 1.44 \times 10^{-3}$ sec^{-1}. [f] $k_{obsd} = 7.73 \times 10^{-3}$ sec^{-1}.

Table IV. Activation Parameters[a] for the Reactions of $Mo(CO)_4$(P–N) and $Mo(CO)_3$(PNP) with CO in DCB at 69.6° According to Eq 1 and 3

Compd	ΔH^*, kcal/mol	ΔS^*, eu
$Mo(CO)_4[(C_6H_5)_2PNHC_5H_4N]$	22.8 ± 2.4	−8.3 ± 7.0
$Mo(CO)_4[(C_6H_5)_2PCH_2C_5H_4N]$	20.0 ± 1.9	−15.9 ± 5.4
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]$	21.4 ± 0.8	−7.0 ± 2.1
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N]$	22.7 ± 0.8	3.1 ± 2.3
$Mo(CO)_3$(PNP)	17.2 ± 0.3	−15.8 ± 0.8

[a] Error limits are average deviations.

Equilibrium Studies. In the $Mo(CO)_4$(P-N) series of complexes, it was possible to determine accurate equilibrium constants and thermodynamic parameters only for $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]$; these values are summarized in Table VI. The chelate ring-opening reaction (eq 1) of this complex is reversible as indicated by the occurrence of ring reclosure when the CO atmosphere over a solution at equilibrium is replaced by N_2. A small amount of decomposition occurred during the reclosure reaction.

Equilibrium constants could not be obtained for the reaction of $Mo(CO)_4[(C_6H_5)_2PCH_2C_5H_4N]$ with CO because of the slowness of the reaction and the concomitant replacement of the phosphorus donor from the $Mo(CO)_5[(C_6H_5)_2PCH_2C_5H_4N]$ product. The reaction of $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N]$ with 6.57×10^{-3} *M* CO at 90.0° in DCB proceeded to give an approximate equilibrium $[Mo(CO)_5(P\text{-}N)]/[Mo(CO)_4(P\text{-}N)]$ ratio of 33; this corresponds to an equilibrium constant of ~5×10^3 M^{-1}. Under the same conditions, this ratio is only 3.5 for $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]$ and $K = 5.12 \times 10^2$ M^{-1}.

Table V. Rate Data for the Reactions of $Mo(CO)_4(P\text{-}N)$ and $Mo(CO)_3(PNP)$ with CO^a in DCB with Added Acid According to Eq 5

Temp, °C	10^3[Acid],^{b} mol/l.	10^5k_{obsd}, sec^{-1}
	$Mo(CO)_4[(C_6H_5)_2PNHC_5H_4N]^c$	
40.0	83	5.50^d
50.0	66	9.79^e
69.6	65	35.8^f
69.6	160	35.3^g
	$Mo(CO)_4[(C_6H_5)_2PCH_2C_5H_4N]^c$	
40.0	60	7.54^h
50.0	52	14.2^i
69.6	68	31.0^j
69.6	62	30.8^k
69.6	156^l	31.4^m
	$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]^n$	
14.7	4.6	780
14.7	23	1600
14.7	34	2700
14.7	46	4300
14.7	69	4100
14.7	110	4200
25.0	110	10,000
34.4	110	22,000
69.6		$260,000^o$
	$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N]^n$	
3.0	110	8000
14.7	4.6	2700
14.7	23	7500
14.7	34	11,000
14.7	46	16,000
14.7	69	19,000
14.7	110	21,000
14.7	460	21,000
69.6		$830,000^o$
	$Mo(CO)_3[PNP]^p$	
25.8	26.9	2.29×10^5
25.8	67.5	7.45×10^5
25.8	135	15.4×10^5
25.8	202	48.8×10^5
25.8	269	131×10^5
25.8	404	140×10^5
25.8	538	144×10^5
25.8	675	154×10^5
25.8	1350	279×10^5

[a] $[CO] \cong 5 \times 10^{-3}$ *M*, except where noted otherwise. [b] Trifluoroacetic acid, except where indicated otherwise. [c] Initial complex concentrations ranged from 2.59×10^{-3} to 3.59×10^{-3} *M*. [d] $[CO] = 5.92 \times 10^{-3}$ *M*. [e] $[CO] = 6.11 \times 10^{-3}$ *M*. [f] $[CO] = 6.28 \times 10^{-3}$ *M*. [g] $[CO] = 6.36 \times 10^{-3}$ *M*. [h] $[CO] = 5.86 \times 10^{-3}$ *M*. [i] $[CO] = 6.02 \times 10^{-3}$ *M*. [j] $[CO] = 6.22 \times 10^{-3}$ *M*. [k] $[CO] = 2.03 \times 10^{-3}$ *M*. [l] Trichloroacetic acid. [m] $[CO] = 3.16 \times 10^{-3}$ *M*. [n] Initial complex concentrations were 8×10^{-4} *M*. [o] Value obtained by extrapolation from data at other temperatures. [p] Initial complex concentrations ranged from 3.78×10^{-4} to 3.91×10^{-4} *M*.

Table VI. Equilibrium Data for the Reactions of $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]$ and $Mo(CO)_3(PNP)$ with CO in DCB According to Eq 1 and 3

Temp, °C	$10^3\times$ [react],^{a} mol/l.	$10^3\times$ [prod],^{b} mol/l.	$10^3\times$ [CO], mol/l.	*K*, M^{-1}
		$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]^c$		
80.0	0.825	3.79	6.43	7.15×10^2
90.0	0.990	3.31	6.68	5.01×10^2
90.0	1.49	2.64	3.46	5.12×10^2
100.0	1.32	3.18	6.69	3.61×10^2
		$Mo(CO)_3(PNP)^d$		
69.6	0.289	1.52	6.39	8.26×10^2
80.0	0.446	1.41	6.66	4.74×10^2
90.0	0.718	1.72	6.85	3.50×10^2
100.0	1.05	1.61	6.90	2.23×10^2

[a] Concentration of reactant complex at equilibrium. [b] Concentration of product complex at equilibrium. [c] $\Delta H = -8.95 \pm 0.2$ kcal/mol; $\Delta S = -12.3 \pm 0.6$ eu; at 69.6°. [d] $\Delta H = -10.5 \pm 1.3$ kcal/mol; $\Delta S = -17.1 \pm 3.5$ eu; at 69.6°.

Equilibrium constants and thermodynamic parameters for the reaction of $Mo(CO)_3(PNP)$ with CO according to eq 3 are also given in Table VI. This reaction too can be cycled back and forth by changing the $CO\text{-}N_2$ atmosphere. There is virtually no decomposition in the back reaction here as opposed to that which was observed for $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]$. Since at equilibrium $K = k/k_r$, the rate constant for the reverse reaction k_r may be calculated from the measured values of *K* and *k*. At 90.0°, the calculated k_r value is 0.85×10^{-3} sec^{-1}. This compares favorably with the experimentally measured value of 1.1×10^{-3} sec^{-1} for this reaction.

Discussion

Kinetics and Mechanism. Like the chelate ring-opening reactions[2] of $Mo(CO)_4[(C_6H_5)_2P(CH_2)_nNR_2]$, where $n = 2$ or 3 and R = H, CH_3, or C_2H_5, the rates of reactions 1 and 3 reported here are first order in complex and first order in CO (eq 4). However, in the presence of high concentrations of strong acids such as trifluoro- and trichloroacetic acids, the reactions (eq 5) are much faster and are no longer dependent upon the CO concentration (eq 6).

The most reasonable interpretation of these results is in terms of the mechanism (eq 2) in which dissociation of the pyridine donor yields an intermediate which competitively either undergoes ring reclosure to re-form the reactant or reacts with CO to give the product. In the presence of acid, the dangling pyridine is rapidly protonated, thereby preventing ring reclosure. Under acid conditions, the measured k_{obsd} is equal to k_1 in terms of mechanism 2. In the absence of acid, the rate law for this mechanism, assuming a steady-state concentration of the intermediate and that k_{-2} is negligibly small, is

$$\text{rate} = \frac{k_1k_2[Mo(CO)_4(P\text{-}N)][CO]}{k_{-1} + k_2[CO]} \qquad (7)$$

Under conditions where k_{-1} is much larger than $k_2[CO]$, the expression reduces to rate = $(k_1k_2/k_{-1})[Mo(CO)_4(P\text{-}N)][CO]$. In terms of the experimental rate law (eq 4), $k_1k_2/k_{-1} = k_{obsd}/[CO]$. From experimental values of k_1 (Table V) and $k_{obsd}/[CO]$ (Table II), the ratio k_{-1}/k_2 may be calculated. Values of k_{-1}/k_2 for the complexes in this study are given in Table VII.

Although there appear to be complications in the presence of acid as noted in the Results, it is assumed that $Mo(CO)_3(PNP)$ reacts with CO (eq 3) by mechanism 2 in the absence of acid. Some support for this is obtained from the reaction[7] of $Mo(CO)_3(PNP)$ with ^{13}CO for which it has been shown that the ^{13}CO in the $Mo(CO)_3(^{13}CO)(PNP)$ product goes stereospecifically into a position cis to both P's. A similar cis ^{13}CO uptake was found in the reaction of $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$ with ^{13}CO to give $Mo(CO)_4(^{13}CO)[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$. These results could be explained by assuming the intermediate has a square pyra-

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Table VII. Rate Constants and Activation Parameters[a] for the Reactions of $Mo(CO)_4(P–N)$ and $Mo(CO)_3(PNP)$ with CO According to Mechanism 2 in DCB at 69.6°

Compd	10^5k_1, sec^{-1}	k_{-1}/k_2, M	$10^3k_{obsd}/[CO]$, M^{-1} sec^{-1}	ΔH_1*, kcal/mol	ΔS_1*, eu	ΔH_{-1}* – ΔH_2*, kcal/mol	ΔS_{-1}* – ΔS_2*, eu
$Mo(CO)_4[(C_6H_5)_2PNHC_5H_4N]$	35.5	0.40 ± 0.04	0.890	12.5 ± 1.1	−38.5 ± 3.0	−10.3	−30.2
$Mo(CO)_4[(C_6H_5)_2PCH_2C_5H_4N]$	31.1	0.75 ± 0.07	0.412	10.0 ± 1.2	−45.6 ± 3.4	−10.0	−29.7
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]$	260,000[b]	210 ± 32	12.7	14.3 ± 0.3	−15.0 ± 1.2	−7.1	−8.0
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N]$	830,000[b]	71 ± 30	117	12.3 ± 1.3	−13.7 ± 3.7	−10.4	−16.8

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

midal geometry or that the intermediate has another geometry but the incoming ^{13}CO adds stereospecifically cis to the P atoms.

Factors Affecting the Rates of Chelate Ring Opening. The overall rates ($k_{obsd}/[CO]$) of chelate ring opening (eq 1) for the series of pyridyl-phosphine complexes at 69.6° are summarized in Table VII. The rates of the two five-membered chelates are very similar indicating that the CH_2 or NH group linking the P and pyridyl ring has but a small effect on the rate of reaction. The activation parameters (Table IV) associated with these reactions are also very similar.

Increasing the size of the chelate ring beyond five members greatly increases the overall rate of ring opening as follows: $(C_6H_5)_2PCH_2C_5H_4N \ll (C_6H_5)_2PCH_2CH_2C_5H_4N < (C_6H_5)_2PCH_2CH_2CH_2C_5H_4N$. This increase is entirely due to ΔS* becoming more positive (Table IV), whereas changes in ΔH* oppose this trend.

To understand these overall trends, it is useful to examine the rate constants k_1 and k_{-1}/k_2 which comprise the $k_{obsd}/[CO]$ values. The two five-membered ring chelate complexes of $(C_6H_5)_2PNHC_5H_4N$ and $(C_6H_5)_2PCH_2C_5H_4N$ not only have very similar overall rates but also nearly identical rate constants (k_1 and k_{-1}/k_2) and activation parameters (Table VII) associated with these constants. For this reason only $(C_6H_5)_2PCH_2C_5H_4N$ will be discussed in further comparisons.

Considering initially the rate of N-donor dissociation (k_1), Table VII indicates a trend in increasing k_1 with increasing size of the chelate ring: $(C_6H_5)_2PCH_2C_5H_4N \ll (C_6H_5)_2PCH_2CH_2C_5H_4N < (C_6H_5)_2PCH_2CH_2CH_2C_5H_4N$. More limited but similar trends were observed previously with the alkylamine-phosphine chelates, $(C_6H_5)_2PCH_2CH_2N(CH_3)_2 < (C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2$,[2] and those of the dithio ethers, $(CH_3)_3CSCH_2CH_2SC(CH_3)_3 < (CH_3)_3CSCH_2CH_2CH_2SC(CH_3)_3$.[8] In all cases the ΔS_1* values are substantially lower for the five-membered chelates as compared to their six-membered analogs. It is reasonable that opening of the larger chelate ring would be associated with a more positive entropy. On the other hand, it is not clear why the ΔS_1* values are negative, *e.g.*, −45 eu for $Mo(CO)_4[(C_6H_5)_2PCH_2C_5H_4N]$ and −12.5 eu for $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$, unless there is significant solvent involvement in the activated complex. The value of ΔS_1* for $W(CO)_4[(CH_3)_3CSCH_2CH_2SC(CH_3)_3]$ studied in xylene solvent is somewhat higher at 1.6 eu.

While rates and activation parameters for monodentate alkylamine and pyridine dissociation are similar in complexes of the types *cis*-$Mo(CO)_4[P(C_6H_5)_3](L)$[9] and $Mo(CO)_5L$,[10] these quantities are quite different when the alkylamine or pyridine group is incorporated into a chelate ring. Thus, the rate constants k_1 are markedly smaller for $(C_6H_5)_2PCH_2C_5H_4N$ (3.1×10^{-4} sec^{-1} at 69.6°) than for the five-membered $(C_6H_5)_2PCH_2CH_2NR_2$ (6×10^{-3} to 8×10^{-2} sec^{-1}) complexes. On the other hand, in the six-membered series, the pyridyl donor (2.6 sec^{-1}) dissociates more rapidly than the amine of $(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2$ (0.4 sec^{-1}). These comparisons indicate that there is an unusual stability to ring opening (k_1) for the five-membered $(C_6H_5)_2PCH_2C_5H_4N$ chelate. This could be associated with the planarity of the pyridine group which provides for an excellent chelation geometry in five-membered chelate rings. This inertness to ring opening is not due to a high ΔH_1* value since this value (Table VII) is actually lower than observed for pyridine dissociation from *cis*-$Mo(CO)_4[P(C_6H_5)_3](py)$[9] and $Mo(CO)_5(py)$.[10] It is the inexplicably (see above) low ΔS_1* value that is responsible.

The other term, k_{-1}/k_2, contributing to the overall rate of ring opening was found[2] to be relatively constant, ranging from 1.1 to 5.1, for the $Mo(CO)_4[(C_6H_5)_2P(CH_2)_nNR_2]$ complexes. In the pyridyl-phosphines, however, this ratio varies from 0.75 for the five-membered chelate to 210 for the six-membered ring and back down to 71 for the seven-membered ring. Assuming k_2 to be essentially the same for all 3 ligands, this means the rate of ring reclosure (k_{-1}) is unusually favorable for the six-membered ring. Dobson and Faber[8] found the opposite trend for the dithio ether chelate complexes $W(CO)_4(S–S)$ where k_{-1}/k_2 was found to be larger for the five-membered chelate. Since five-membered chelates in general appear to be more stable than larger rings, our high value of k_{-1}/k_2 for the six-membered complex is surprising and unexplained. It nevertheless demonstrates that both k_1 and the k_{-1}/k_2 ratio contribute to the overall rate of ring opening for the pyridyl-phosphine chelates.

Equilibrium Studies. Accurate equilibrium constants (Table VI) could be measured only for reaction 1 with P-N = $(C_6H_5)_2PCH_2CH_2C_5H_4N$ and for reaction 3 with $Mo(CO)_3(PNP)$. Qualitatively, it was established, however, that the equilibrium constant for the reaction of the seven-membered chelate complex $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N]$ was much larger than that for the six-membered $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]$ analog. This is consistent with the decreasing stability of chelate rings as they increase in size from the most stable five-membered derivatives.

Thermodynamic parameters (Table VI) have been determined for both reactions. Both are exothermic suggesting that the Mo–CO bond is ~10 kcal/mol stronger than the Mo–N bond. It is perhaps surprising that the equilibrium for ring opening in $Mo(CO)_3(PNP)$ is so favorable, particularly since it involves the elimination of two stable five-membered rings to form one relatively unstable eight-member chelate ring. Part of the reason may be that the tridentate ligand is severely strained in $Mo(CO)_3(PNP)$. An X-ray crystallographic study[11] of $Cr(CO)_3(PNP)$ shows that the ethylene bridges are not long enough to allow the N atom to occupy

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a regular octahedral coordination site. This strain puts the N donor in an irregular position with an unusually long Cr-N bond. With the larger Mo atom in $Mo(CO)_3(PNP)$, the distortion is likely to be even greater.

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Registry No. $Mo(CO)_4[(C_6H_5)_2PNHC_5H_4N]$, 49626-24-6; $Mo(CO)_4[(C_6H_5)_2PCH_2C_5H_4N]$, 49626-25-7; $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]$, 49626-26-8; $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N]$, 49626-27-9; $Mo(CO)_3[PNP]$, 49626-28-0; $Mo(CO)_4[PNP]$, 49626-29-1; CO, 630-08-0.

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Organometallic Chemistry of the Transition Metals. XXVIII. Some Novel Olefinic Manganese Carbonyl Derivatives[1,2]

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Reactions of $[HMn(CO)_4]_3$ with excesses of various olefins and acetylenes under mild conditions (boiling hexane or neohexane) give novel organomanganese carbonyl derivatives, in addition to much $Mn_2(CO)_{10}$. Thus, reaction of $[HMn(CO)_4]_3$ with 1,3-cyclohexadiene gives the cyclohexadienyl derivative $C_6H_7Mn(CO)_3$. Reaction of $[HMn(CO)_4]_3$ with cycloheptatriene gives the cycloheptadienyl derivative $C_7H_9Mn(CO)_3$. A similar reaction of $[HMn(CO)_4]_3$ with 1,3-cycloheptadiene gives a mixture of the same cycloheptadienyl derivative $C_7H_9Mn(CO)_3$ and the cycloheptenyl derivative $C_7H_{11}Mn(CO)_4$. Reaction of $[HMn(CO)_4]_3$ with cyclooctatetraene gives a mixture of yellow crystalline $C_8H_9Mn(CO)_3$ and fluxional orange crystalline $C_8H_8Mn_2(CO)_6$. Reaction of $[HMn(CO)_4]_3$ with 1,3,5-cyclooctatriene gives a mixture of yellow crystalline 1,2,3,4,5-h^5-$C_8H_{11}Mn(CO)_3$, yellow crystalline 1,2,3,5,6-h^5-$C_8H_{11}Mn(CO)_3$, and air-sensitive yellow liquid $C_8H_{11}Mn(CO)_4$. Reaction of $[HMn(CO)_4]_3$ with dimethylaminofulvene gives the orange liquid substituted cyclopentadienylmanganese tricarbonyl derivative $(CH_3)_2NCH_2C_5H_4Mn(CO)_3$. Reaction of $[HMn(CO)_4]_3$ with azulene gives the yellow crystalline bimetallic derivative $[C_{10}H_8Mn(CO)_3]_2$. Reaction of $[HMn(CO)_4]_3$ with norbornadiene gives red crystalline $C_7H_8Mn_2(CO)_7$. Reaction of $[HMn(CO)_4]_3$ with 3-hexyne results in cyclotrimerization to give the 1,2,3,4,5,6-hexaethylcyclohexadienyl derivative $(C_2H_5)_6C_6HMn(CO)_3$. However, reaction of $[HMn(CO)_4]_3$ with diphenylacetylene results in linear dimerization to give *cis,cis*-1,2,3,4-tetraphenylbutadiene.

Introduction

A major impetus to the development of transition-metal organometallic chemistry has been the preparation of compounds with unusual metal-carbon bonding by reactions of various metal carbonyls with olefins and acetylenes.[4] Notable reactions of this type include the preparations of various (diene)$Fe(CO)_3$ derivatives from 1,3-dienes and $Fe(CO)_5$[5] and the preparations of various (arene)$Cr(CO)_3$ derivatives from arenes and $Cr(CO)_6$.[6] The number of unusual organometallic structures that have been prepared by reactions of various olefins and acetylenes with simple metal carbonyls such as $M(CO)_6$ (M = Cr, Mo, and W), $M_2(CO)_{10}$ (M = Mn and Re), $Fe(CO)_5$, $Co_2(CO)_8$, and $Ni(CO)_4$ is now very large.

A significant limitation in the preparation of transition-metal organometallic compounds by reactions of olefins and acetylenes with the simple metal carbonyls $M(CO)_6$ (M = Cr, Mo, and W), $M_2(CO)_{10}$ (M = Mn and Re), and $Fe(CO)_5$ is the need for elevated temperatures (generally 100 to 150°) before displacement of carbonyl groups by olefinic ligands can take place. In the cases of some of the more temperature-sensitive olefinic metal carbonyl derivatives, the elevated temperatures required for these reactions may exceed the decomposition temperatures of the desired products. In order to circumvent this difficulty, more complex but more reactive metal carbonyl derivatives can be used in the place of the simple metal carbonyl derivatives for the reactions with olefins or acetylenes. For example, the polymetallic iron carbonyls $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ react with olefins and acetylenes under much milder conditions than $Fe(CO)_5$.[4] In general, the reactivities of these more reactive metal carbonyl derivatives depend upon the rupture of some bond weaker than the metal-carbonyl bond, such as the iron-iron bonds in $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ and the metal-ligand bonds involving ligands that are both poor σ donors and poor π acceptors in the complexes $(CH_3CN)_3M(CO)_3$ (M = Cr,[7] Mo,[7] and W)[8] and (diglyme)$Mo(CO)_3$.[9]

When this research was initiated, a similar principle had not been used for the synthesis of olefinic manganese carbonyl derivatives. The known range of olefinic manganese carbonyl derivatives was therefore limited to compounds either which could survive the relatively high temperatures (above 100°) required for reactions of $Mn_2(CO)_{10}$ with ole-

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[1] For part XXVII of this series, see R. B. King and P. N. Kapoor, *J. Organometal. Chem.*, 33, 383 (1971).

[2] Portions of this work were presented at the Sixth International Conference on Organometallic Chemistry, Amherst, Mass., August 1973.

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