Inorg. Chem. **1984**, *23*, 4315–4321

applied. Especially for **6** this resulted in a dramatic data improvement. The program is designed so that it will attempt to correct for systematic intensity errors such as those caused by the partial ω scans described above. The *R* index dropped to 0.07, and most of the H atoms could be located in a difference map. In the final stages of the refinement all non-hydrogen atoms were given anisotropic temperature factors. The hydrogen atoms were included as fixed-group atoms with thermal parameters linked to the anchor atoms. Refinement was by the block-cascade technique of the SHELXTL system.

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Registry No. **3**, 87039-36-9; **2**, 93000-14-7; **7**, 92958-57-1; **8**, 92958-59-3; $Pd[(Ph_2P)_2py]_2Cl_2$, 92984-18-4; $Pd_3[\mu\text{-}(Ph_2P)_2py]_3Br_6$, 92958-60-6; $[Pd((Ph_2P)_2py)Br_2]_n$, 92958-62-8; (COD)$PdCl_2$, 12107-56-1; (COD)$PtCl_2$, 12080-32-9.

Supplementary Material Available: Tables of structure factors, atomic thermal parameters, hydrogen atom positions, and bond angles and bond lengths for both *cis,cis*-$Pt_2[\mu\text{-}(Ph_2P)_2py]_2Cl_4{\cdot}6CH_2Cl_2$ and *trans,trans*-$Pt_2[\mu\text{-}(Ph_2P)_2py]_2I_4{\cdot}2CH_2Cl_2$ and a packing diagram for the former compound (46 pages). Ordering information is given on any current masthead page.

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(22) The method obtains an empirical absorption tensor from an expression F_o and F_c: Hope, H.; Moezzi, B. Department of Chemistry, University of California, Davis, CA.

Contribution from Anorganische Chemie III, Eduard-Zintl-Institut
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Ligand Substitution in Molybdenum(0) Carbonyl Complexes $Mo(CO)_5$(amine) and *cis*-$Mo(CO)_4(amine)_2$: Kinetics and High-Pressure Effects

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Visible spectrophotometry at ambient and at high pressure has been applied to study the kinetics of ligand substitution in molybdenum(0) carbonyl complexes *cis*-$Mo(CO)_4(py)_2$ (py = pyridine) and $Mo(CO)_5$(amine) (amine = py, 4-Mepy (4-methylpyridine), 4-CNpy (4-cyanopyridine)) by bidentate nitrogen donor ligands N⌒N (= dab (biacetyl bis(phenylimine)), dab-OCH_3 (biacetyl bis((4-methoxyphenyl)imine)), dab-Cl (biacetyl bis((4-chlorophenyl)imine)), bpy (2,2′-bipyridine), phen (1,10-phenanthroline)) in the solvent toluene to form $Mo(CO)_4$(N⌒N). The rate of product formation follows the one-term rate law rate = k_{obsd}[*cis*-$Mo(CO)_4(py)_2$] and rate = k_{obsd}[$Mo(CO)_5$(amine)], respectively. It has been found for system A (*cis*-$Mo(CO)_4(py)_2$/N⌒N/toluene) and for system B ($Mo(CO)_5$(amine)/N⌒N/toluene) that rate constant k_{obsd} is independent of both the concentration and the nature of the incoming chelate ligand N⌒N. For system A the rate-reducing effect of excess pyridine added to the system can be quantitatively accounted for by mass law retardation, which strongly supports system A to follow a pure D mechanism. The activation parameters found for system A are $\Delta H^* = 24.5$ kcal·mol^{-1}, $\Delta S^* = 13.5$ eu, and $\Delta V^* = 3.6$ cm^3·mol^{-1} (N⌒N = dab). For system B (with amine = 4-Mepy) the rate of substitution at 25 °C is approximately 120 times smaller than for system A and rate constant k_{obsd} depends on the basicity of the leaving amine ligand. The nature of the rate-reducing effect of excess pyridine added to system B (with amine = py) is more complex than in system A. The activation parameters obtained for system B (with amine = 4-Mepy) are $\Delta H^* = 23.3$ kcal·mol^{-1}, $\Delta S^* \approx 0$, and $\Delta V^* \approx 0$. Most of the kinetic data collected for system B support a dissociatively controlled mechanism.

Introduction

The activation volume ΔV^* as obtained from high-pressure studies has become a well-established tool for the investigation of the mechanism of substitution reactions in transition-metal complexes.[1] Despite an increasing interest in the mechanistic pathways for ligand substitution processes in transition-metal carbonyls[2] the information available on the effect of pressure on the reaction of carbonyls is very scarce. Brower and Chen[3] reported in 1973 first-order kinetics and positive ΔV^* values for monodentate nucleophiles entering $Ni(CO)_4$, $Mo(CO)_6$, and $Cr(CO)_6$. For the analogous reaction of $W(CO)_6$, which is described to be of second order, a negative activation volume was obtained. No information appears to be available on the effects of high pressure on the substitution kinetics in octahedral carbonyl complexes of the type $M(CO)_5L$ and $M(CO)_4L_2$.

The present work was undertaken to study the kinetics of two types of substitution reactions that are known to be of considerable preparative importance (eq 1 and 2; N⌒N = bidentate nitrogen donor). This contribution presents rate

$$cis\text{-}M(CO)_4(amine)_2 + N^{\frown}N \rightleftharpoons M(CO)_4(N^{\frown}N) + 2\,amine \quad (1)$$

$$M(CO)_5(amine) + N^{\frown}N \rightleftharpoons M(CO)_4(N^{\frown}N) + amine + CO \quad (2)$$

constants, rate laws, and activation parameters (including ΔV^*) for reactions 1 and 2 as studied for M = Mo(0) and amine = py (pyridine or pyridine substituted in the 4-position) in toluene as solvent. The bidentate nitrogen donor N⌒N represents chelate ligands such as bpy (2,2′-bipyridine), phen (1,10-phenanthroline), and dab (biacetyl bis(phenylimine)).

Experimental Section

Ligands and Complexes. The ligands bpy, phen·H_2O, py, 4-Mepy (γ-picoline), and 4-CNpy (4-cyanopyridine) were analytical grade. The ligand dab and the corresponding substituted ligands dab-Cl (biacetyl bis((4-chlorophenyl)imine)) and dab-OCH_3 (biacetyl bis((4-methoxyphenyl)imine)) were prepared by condensation of 1 mol of biacetyl with 2 mol of aniline (dab), 4-chloroaniline (dab-Cl), or 4-methoxyaniline (dab-OCH_3) in *i*-PrOH and recrystallization from

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Table I

(a) Analytical Data of Ligands and Complexes

	mp, °C	calcd			found		
		% C	% H	% N	% C	% H	% N
dab	139 (139[a])	81.32	6.83	11.85	81.16	6.79	11.88
dab-Cl	172 (175[b])	62.96	4.62	9.18	62.89	4.48	9.19
dab-OCH_3	186–187 (186–187[a])	72.94	6.80	9.45	72.77	6.81	9.47
$Mo(CO)_5py$	105–110 dec	38.12	1.60	4.44	38.43	1.60	4.50
$Mo(CO)_5$(4-Mepy)		40.14	2.14	4.25	39.24	2.10	4.21
$Mo(CO)_5$(4-CNpy)	80–90 dec	38.85	1.18	8.24	38.10	1.12	7.81
cis-$Mo(CO)_4(py)_2$	112–117 dec	45.92	2.75	7.65	45.67	2.74	7.60
$Mo(CO)_4$(dab)	155–160 dec	54.07	3.63	6.31	54.15	3.65	6.29
$Mo(CO)_4$(dab-OCH_3)	165–170 dec	52.39	3.99	5.55	52.64	3.92	5.55
$Mo(CO)_4$(bpy)	170–180 dec	46.30	2.22	7.71	45.87	2.25	7.66
$Mo(CO)_4$(phen)	135–140 dec	49.50	2.08	7.22	48.83	2.75	6.67

(b) Spectroscopic Characterization of the Complexes

	λ, nm (ε, $M^{-1}\cdot cm^{-1}$)[c]	ν_{CO}, cm^{-1} [d]
$Mo(CO)_5py$	335 (2800), 395 (2650)	1905, 1940, 1955, 2080 (1890, 1944, 1987, 2075)[e]
$Mo(CO)_5$(4-Mepy)	405 (3800), 320 (3700)	1925, 1075, 2000, 2070 (1910, 1921, 1942, 2069, 2075)[f]
$Mo(CO)_5$(4-CNpy)	400 (4050)	1940, 1955, 2010, 2080
cis-$Mo(CO)_4(py)_2$	392 (4350)	1830, 1880, 1910, 2010 (1839, 1881, 1907, 2025)[e]
$Mo(CO)_4$(dab)	550 (10950)	1840, 1875, 1910, 2010 (1840, 1880, 1910, 2020)[g]
$Mo(CO)_4$(dab-OCH_3)	555 (11000)	1840, 1870, 1910, 2000 (1850, 1880, 1910, 2000)[g]
$Mo(CO)_4$(bpy)	495 (5800)	1825, 1880, 1925, 2010 (1829, 1878, 1909, 2017)[e]
$Mo(CO)_4$(phen)	495 (5850)	1835, 1875, 1915, 2010 (1833, 1881, 1910, 2014)[h]

[a] See ref 7. [b] Erlenmeyer, H.; Lehr, H.; Bloch, H. *Helv. Chim. Acta* **1945,** *28,* 1413. [c] Solvent toluene. [d] KBr pellets; the numbers in brackets are data taken from the literature. [e] See ref 4; solvent $CHCl_3$. [f] Dennenberg, R. J.; Darensbourg, D. J. *Inorg. Chem.* **1972,** *11,* 72. [g] See ref 7; KBr pellets. [h] See ref 6; solvent $CHCl_3$.

n-PrOH (for elemental analyses and melting points see Table I).

The complexes *cis*-$Mo(CO)_4(py)_2$, $Mo(CO)_5py$, $Mo(CO)_5$(4-Mepy), and $Mo(CO)_5$(4-CNpy) were prepared from $Mo(CO)_6$ by thermolytic procedures as described in the literature.[4] The complexes $Mo(CO)_4(N^\frown N)$ ($N^\frown N$ = bpy,[5] phen,[6] dab,[7] dab-Cl,[8] dab-OCH_3[7]) were obtained by stirring stoichiometric amounts of *cis*-$Mo(CO)_4(py)_2$ and dab-OCH_3[7]) corresponding ligand $N^\frown N$ in very little toluene at 30–35 °C under argon for approximately 4 h. Upon cooling of the solution the complexes began to precipitate in very pure form. If necessary, they were recrystallized from toluene. Their purity was controlled by elemental analysis and by UV/vis and IR spectroscopy (see Table I). The complexes do not exhibit sharp melting points but decompose.[5-8]

Solvent. The solvent toluene (analytical grade; Merck, Darmstadt, West Germany) was dried over 4-Å molecular sieves and purged with Ar before use.

Kinetic Measurements. The kinetic measurements at ambient pressure were done with a UV/vis spectrophotometer (Perkin-Elmer 554) in thermostated quartz cells under argon. The formation of the product $Mo(CO)_4(N^\frown N)$ was followed at approximately 500 nm ($Mo(CO)_4$(bpy), $Mo(CO)_4$(phen)) and at approximately 550 nm ($Mo(CO)_4(N^\frown N)$, with $N^\frown N$ = dab, dab-Cl, dab-OCH_3) under pseudo-first-order conditions ($[N^\frown N] \gg$ [complex]). The completeness of the reactions (>90%) was determined by UV/vis spectroscopy and the purity of the product $Mo(CO)_4(N^\frown N)$ by IR spectroscopy and by elemental analysis. Self-decomposition of the starting complex and of the product complex was studied separately.

The rate constants k_{obsd} were calculated from the slope of the straight lines obtained upon plotting log $(A_\infty - A)$ vs. t by least-squares fitting (A = absorbance). The error of the data obtained for k_{obsd} was of the order of ±0.5–2%, and data are given in Tables II–IV.

High-Pressure Studies. The experiments were carried out at the University of Frankfurt (Institut für Physikalische Chemie, Dr. R. van Eldik) in a special high-pressure cell.[9] The reactions were followed spectrophotometrically (Zeiss PMQ II) under pseudo-first-order conditions ($[N^\frown N] \gg$ [complex]) in the pressure range 20–1500 atm.

The activation volume ΔV^* was calculated from the slope of the straight lines obtained upon plotting log k_{obsd} vs. pressure p by least-squares fitting.

Results and Discussion

The kinetic studies were carried out with two different types of complexes, namely *cis*-$Mo(CO)_4(py)_2$ and $Mo(CO)_5$(amine). To avoid confusion and shorten the discussion, the terms "system A" and "system B" will be used for reactions 3 and 4.

System A

$$cis\text{-}Mo(CO)_4(py)_2 + N^\frown N \rightarrow Mo(CO)_4(N^\frown N) + 2py \quad (3)$$

System B

$$Mo(CO)_5(amine) + N^\frown N \rightarrow Mo(CO)_4(N^\frown N) + amine + CO \quad (4)$$

Kinetic Results at Ambient Pressure for System A. Ligand substitution according to (3) was studied at 17, 25, and 35 °C in toluene as solvent and with an excess of bidentate ligands $N^\frown N$ = dab, dab-OCH_3, dab-Cl, bpy, and phen.

The observed first-order rate constants are summarized in Table II. Looking at the data obtained for $N^\frown N$ = dab at different excess concentrations of dab and at two different concentrations of the carbonyl complex, one recognizes that at a given temperature the size of k_{obsd} is independent of the excess concentration of the entering ligand (the scattering of the data lies within the limits of error of approximately 5–8%). It follows furthermore that at a given temperature the averaged rate constants $\bar{k}_{obsd}$ obtained for $N^\frown N$ = dab, dab-OCH_3, dab-Cl, phen, and bpy are all the same within the limits of error, which means that the rate of reaction 3 is independent of the concentration as well as of the nature of the attacking ligand $N^\frown N$. The experimental rate equation for (3) is therefore given by (5).

$$\text{rate} = d[Mo(CO)_4(N^\frown N)]/dt = k_{obsd}[cis\text{-}Mo(CO)_4(py)_2] \quad (5)$$

Table II presents some additional information that is of interest for the mechanistic interpretation. The addition of

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Table II. Rate Constants for Ligand Substitution in the System *cis*-$Mo(CO)_4(py)_2$/N⌒N/Toluene

	entering ligand N⌒N			
T, °C	type	10^3[N⌒N], M	$10^3 k_{obsd}$, s^{-1} [a]	$10^3 \bar{k}_{obsd}$, s^{-1}
[*cis*-$Mo(CO)_4(py)_2$] = 2.5×10^{-5} M				
17	dab	0.75	0.690 ± 0.004	0.690
		1.00	0.684 ± 0.005	
		2.50	0.702 ± 0.004	
		5.00	0.683 ± 0.008	
25	dab	0.50	2.01 ± 0.03	2.15
		1.50	2.11 ± 0.03	
		1.88	2.26 ± 0.02	
		1.88	2.18 ± 0.02	
		2.50	2.13 ± 0.03	
		5.00	2.21 ± 0.02	
25	dab	1.88	2.13 ± 0.02[b]	2.19
		1.88	2.12 ± 0.02[b]	
		1.88	2.22 ± 0.02[b]	
		1.88	2.27 ± 0.02[b]	
25	dab	0.125	2.11 ± 0.02	2.09
		0.50	2.05 ± 0.02	
		1.00	2.07 ± 0.03	
		2.50	2.09 ± 0.03	
		5.00	2.14 ± 0.02	
25	bpy	0.50	2.30 ± 0.01	2.44
		1.00	2.45 ± 0.01	
		2.50	2.48 ± 0.01	
		5.00	2.52 ± 0.02	
25	phen	1.00	2.37 ± 0.02	2.43
		1.50	2.42 ± 0.02	
		2.00	2.35 ± 0.02	
		5.00	2.48 ± 0.02	
		10.00	2.55 ± 0.02	
35	dab	0.50	8.52 ± 0.18	8.78
		1.00	8.67 ± 0.27	
		2.50	8.72 ± 0.19	
		5.00	9.22 ± 0.21	
[*cis*-$Mo(CO)_4(py)_2$] = 1×10^5 M				
25	dab	0.25	2.15 ± 0.04[c]	2.37
		0.50	2.32 ± 0.04[c]	
		1.00	2.48 ± 0.06[c]	
		1.50	2.43 ± 0.06[c]	
		2.50	2.45 ± 0.05[c]	
25	dab-OCH_3	0.50	2.18 ± 0.01	2.13
		1.00	2.14 ± 0.02	
		2.50	2.05 ± 0.02	
		5.00	2.15 ± 0.04	
25	dab-Cl	0.50	2.55 ± 0.01	2.41
		1.00	2.41 ± 0.04	
		2.50	2.30 ± 0.03	
		5.00	2.38 ± 0.02	

[a] The errors given for k_{obsd} are those obtained upon computer fitting of absorbance/time data to an exponential function. [b] Rate constants obtained in the presence of tetrahydrofuran ([THF] = 6.25×10^{-3}, 3.13×10^{-3}, 6.25×10^{-2}, and 1.56×10^{-1} M). [c] Rate constants obtained in the presence of 1×10^{-2} M 2,6-di-*tert*-butyl-4-methylpyridine.

tetrahydrofuran (up to 1.56×10^{-1} M) to the system *cis*-$Mo(CO)_4(py)_2$/dab/toluene does not change the rate of substitution. The four values obtained for k_{obsd} in the presence of THF average to $\bar{k}_{obsd} = 2.19 \times 10^{-3}$ s^{-1}, which is in good agreement with $\bar{k}_{obsd} = 2.15 \times 10^{-3}$ s^{-1} for the THF-free system. One can conclude from this finding that solvento species are not involved in the rate-controlling step. The addition of 2,6-di-*tert*-butyl-4-methylpyridine, a sterically hindered base able to "catch" residual water in the system, has no substantial effect either ($\bar{k}_{obsd} = 2.37 \times 10^{-3}$ s^{-1} as compared to 2.15×10^{-3} s^{-1}).

Averaging the total of the eight different $\bar{k}_{obsd}$ values as determined for reaction 3 at 25 °C (see Table II), one obtains a mean of 2.28×10^{-3} s^{-1} with a standard deviation of ±6.6% as measure for the error in k_{obsd}.

It is well-known that carbonyl complexes such as *cis*-$Mo(CO)_4(py)_2$ tend to decompose slowly in solution. Following the self-decomposition of the complex *cis*-$Mo(CO)_4(py)_2$ (3×10^{-5} M) in toluene spectrophotometrically at 25 °C, one finds a decay that can be described as a first-order process with $k_{obsd} = (2.9 \pm 0.2) \times 10^{-4}$ s^{-1}. This number would mean that within the time necessary for a 90% conversion of *cis*-$Mo(CO)_4(py)_2$ to $Mo(CO)_4$(N⌒N) according to (3) approximately 25% of the complex *cis*-$Mo(CO)_4(py)_2$ is lost through self-decomposition. This percentage, however, is not realistic since in the presence of 2.5×10^{-3} M pyridine the rate constant for self-decomposition decreases from 2.9×10^{-4} to 3.85×10^{-5} s^{-1}. Assuming that the presence of the entering ligand N⌒N exerts a decomposition-reducing effect similar to that for pyridine, the expected percentage of loss through self-decomposition reduces from 25 to 4%. In line with this the computer fitting of the absorbance/time data to an exponential function leads to numbers for A_0 and A_∞ (A = absorbance) which agree with those calculated from the known absorption coefficients within ±10%. In conclusion, the effect of self-decomposition on the kinetics of reaction 3 does not need to be considered as a serious source of error.

Table III summarizes the data for k_{obsd} obtained in the presence of increasing amounts of pyridine. The rate of substitution in system A is clearly reduced in the presence of additional pyridine and decreases with increasing pyridine concentration. An interesting detail is the finding that for the system *cis*-$Mo(CO)_4(py)_2$/dab the rate-decreasing effect of pyridine is much stronger than that of 4-cyanopyridine.

In Figure 1 the parameter k_{obsd}^{-1} is plotted vs. the ratio [py]/[N⌒N]. For N⌒N = dab, dab-OCH_3, and dab-Cl

Table III. Rate Constants at 25 °C for Ligand Substitution in the Systems *cis*-$Mo(CO)_4(py)_2$/N⌒N/Toluene and $Mo(CO)_5py$/N⌒N/Toluene in the Presence of Additional Pyridine

complex (concn, M)	entering ligand N⌒N (concn, M)	10^3[py], M	$10^4 k_{obsd}$, s^{-1} [a]
cis-$Mo(CO)_4(py)_2$ (3×10^{-5})	dab (1.88×10^{-3})	0.25	21.2 ± 0.1
		1.0	12.9 ± 0.03
		2.5	6.45 ± 0.05
		5.0	4.23 ± 0.01
		10.0	2.28 ± 0.01
		25.0	0.919 ± 0.012
		50.0	0.486 ± 0.003
cis-$Mo(CO)_4(py)_2$ (3×10^{-5})	dab-OCH_3 (1.88×10^{-3})	1.0	15.0 ± 0.04
		2.5	9.78 ± 0.01
		5.0	5.76 ± 0.01
		10.0	3.20 ± 0.02
		25.0	1.32 ± 0.01
		50.0	0.684 ± 0.001
cis-$Mo(CO)_4(py)_2$ (3×10^{-5})	dab-Cl (1.88×10^{-3})	0.25	17.7 ± 0.1
		0.50	14.5 ± 0.1
		1.00	10.7 ± 0.1
		2.50	6.30 ± 0.05
		5.00	3.71 ± 0.02
		62.5	0.584 ± 0.009
		125.0	0.325 ± 0.004
cis-$Mo(CO)_4(py)_2$ (3×10^{-5})	dab (1.88×10^{-3})	0.25[b]	22.4 ± 0.4
		1.00[b]	20.2 ± 0.3
		2.50[b]	17.4 ± 0.7
		3.75[b]	15.6 ± 0.4
		5.00[b]	15.3 ± 0.4
$Mo(CO)_5py$ (3×10^{-5})	dab (1.88×10^{-3})	...	1.63 ± 0.002[c]
		0.025	1.31 ± 0.001[c]
		0.125	0.823 ± 0.007[c]
		0.250	0.605 ± 0.007[c]
		0.500	0.470 ± 0.007[c]

[a] For the errors in k_{obsd} see footnote *a* in Table II. [b] 4-Cyanopyridine instead of pyridine. [c] Rate constants at 40 °C.

Table IV. Rate Constants for Ligand Substitution in the System $Mo(CO)_5(amine)/N\frown N/Toluene$

T, °C	entering ligand $N\frown N$ type	$10^3[N\frown N]$, M	$10^4 k_{obsd}$, s^{-1} [a]	$10^4 \bar{k}_{obsd}$, s^{-1}
	$[Mo(CO)_5(4\text{-}Mepy)] = 2.5 \times 10^{-5}$ M			
25	dab	0.50	0.193 ± 0.005	0.181
		1.00	0.172 ± 0.003	
		2.50	0.190 ± 0.002	
		5.00	0.168 ± 0.002	
40	dab	0.50	1.04 ± 0.03	1.09
		1.00	0.98 ± 0.03	
		1.25	1.02 ± 0.02	
		2.50	1.24 ± 0.01	
		5.00	1.15 ± 0.01	
40	dab	1.88	1.29 ± 0.03[b]	1.20
		1.88	1.01 ± 0.03[b]	
		1.88	1.30 ± 0.04[b]	
40	phen	0.50	1.34 ± 0.02	1.44
		1.00	1.32 ± 0.02	
		2.00	1.36 ± 0.02	
		5.00	1.47 ± 0.02	
		10.00	1.71 ± 0.01	
	$[Mo(CO)_5(4\text{-}Mepy)] = 1 \times 10^{-5}$ M			
40	bpy	0.50	1.43 ± 0.02	1.39
		1.00	1.40 ± 0.02	
		1.25	1.38 ± 0.02	
		2.50	1.39 ± 0.02	
		5.00	1.37 ± 0.02	
	$[Mo(CO)_5py] = 2.5 \times 10^{-5}$ M			
40	dab	0.75	1.95 ± 0.04	1.95
		0.87	2.00 ± 0.04	
		1.00	1.87 ± 0.04	
		2.50	1.92 ± 0.02	
		5.00	2.03 ± 0.02	
	$[Mo(CO)_5(4\text{-}CNpy)] = 2.5 \times 10^{-5}$ M			
40	dab	0.75	9.20 ± 0.13	9.24
		1.00	9.20 ± 0.12	
		1.25	9.03 ± 0.08	
		2.50	9.28 ± 0.11	
		5.00	9.47 ± 0.09	

[a] The errors given for k_{obsd} are those obtained upon computer fitting of the absorbance/time data to an exponential function.
[b] Rate constants obtained in the presence of tetrahydrofuran ($[THF] = 6.25 \times 10^{-3}$, 3.13×10^{-2}, and 1.56×10^{-1} M).

straight lines of different slope but with a joint intercept are obtained. The data collected in the presence of additional 4-cyanopyridine (which are not shown in Figure 1) also result in a straight line when plotted according to $k_{obsd}^{-1} = f([4\text{-}CNpy]/[N\frown N])$.

Kinetic Results at Ambient Pressure for System B. Ligand substitution according to eq 4 was studied with the complex $Mo(CO)_5(4\text{-}Mepy)$ at 25 and 40 °C and with different ligands $N\frown N$. The general findings correspond to those obtained for system A (see Table II) in the sense that (i) the observed rate constant does not depend on the concentration of the entering ligand $N\frown N$, (ii) the averaged rate constants $\bar{k}_{obsd}$ obtained for $N\frown N$ = dab, phen, and bpy at a given temperature appear to agree within the limits of error, and (iii) the addition of increasing amounts of tetrahydrofuran does not change the rate of substitution, which can be described by rate law 6. The

$$\text{rate} = d[Mo(CO)_4(N\frown N)]/dt = k_{obsd}[Mo(CO)_5(amine)] \quad (6)$$

average of all four $\bar{k}_{obsd}$ values obtained for the complex $Mo(CO)_5(4\text{-}Mepy)$ at 40 °C amounts to 1.28×10^{-4} s^{-1} with a standard deviation of $\pm 0.16 \times 10^{-4}$ s^{-1}. Comparing systems A and B, one learns therefore that the complex *cis*-$Mo(CO)_4(py)_2$ forms the product $Mo(CO)_4(N\frown N)$ considerably faster than the complex $Mo(CO_5(4\text{-}Mepy)$. This is also true for the complexes $Mo(CO)_5py$ and $Mo(CO)_5(4\text{-}CNpy)$, although replacement of 4-methylpyridine in $Mo(CO)_5(4\text{-}Mepy)$ by pyridine and 4-cyanopyridine increases $\bar{k}_{obsd}$ from 1.28×10^{-4} s^{-1} to 1.95×10^{-4} and 9.24×10^{-4} s^{-1} at 40 °C (see Table IV).

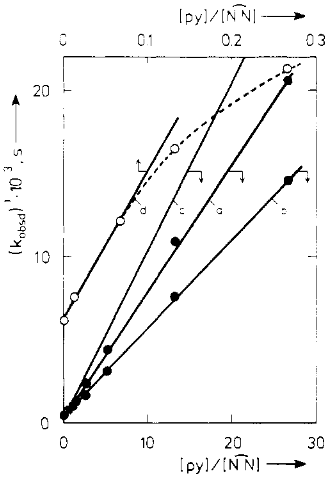

Figure 1. Plot of the reciprocal rate constant k_{obsd} (see Table II) vs. the concentration ratio $[py]/[N\frown N]$ for the system *cis*-$Mo(CO)_4(py)_2/N\frown N/py/toluene$ with $N\frown N$ = dab (curve a), dab-OCH_3 (curve b), and dab–Cl (curve c) and for the system $Mo(CO)_5py/dab/py/toluene$ (curve d). The data points for curve c are omitted for the sake of clarity at $[py]/[dab\text{-}Cl] < 2$ and because $[py]/[dab\text{-}Cl] > 30$ for several data points.

A clearly different behavior is observed when reaction 4 with amine = py and $N\frown N$ = dab is carried out in the presence of additional pyridine (see Table III). As observed for system A, rate constant k_{obsd} decreases with increasing pyridine concentration. The studies are limited however to $[py] \leq 5 \times 10^{-4}$ M because of incomplete conversion of $Mo(CO)_5py$ to $Mo(CO)_4(dab)$ at higher pyridine concentrations and because of side reactions beginning to play a major role. When the data obtained are plotted according to $k_{obsd}^{-1} = f([py]/[N\frown N])$ as in system A, a different type of curve is obtained (see curve d in Figure 1) at higher pyridine concentrations.

The self-decomposition of the complex $Mo(CO)_5(amine)$ was also studied in some detail. It was found that as in the case of the complex *cis*-$Mo(CO)_4(py)_2$ the decomposition rate is decreased by the presence of additional amine. The observed order of instability is $Mo(CO)_5(4\text{-}CNpy) > Mo(CO)_5py > Mo(CO)_5(4\text{-}Mepy)$, and the complex $Mo(CO)_5(4\text{-}Mepy)$ was therefore chosen for the high-pressure studies. While reaction 4 is followed up to approximately 90% conversion, the loss of $Mo(CO)_5(amine)$ through simultaneously occurring self-decomposition is of the order of 10%.

Activation Parameters $\Delta H^‡$ and $\Delta S^‡$. Table V presents the data obtained for $\Delta H^‡$ and $\Delta S^‡$ from the temperature dependence of k_{obsd}. Although the calculations are based on three temperatures only, it is obvious that systems A and B (with amine = 4-Mepy) agree more or less in the size of $\Delta H^‡$ and disagree clearly in the size of $\Delta S^‡$. For system A an activation entropy of +13.5 eu is obtained whereas for system B one finds $\Delta S^‡ = 0$.

Kinetic Results at High Pressure. The results obtained upon measuring reactions 3 and 4 at high pressure are shown in Figure 2. For system A with $N\frown N$ = dab (see curve a) as well as with $N\frown N$ = bpy (see curve b) the rate constant k_{obsd} decreases with increasing pressure. In contrast to this the rate of system B with amine = 4-Mepy and $N\frown N$ = dab is practically independent of pressure.

The experimental activation volume $\Delta V_{exptl}^‡$ as derived from

Table V. Activation Parameters for Ligand Substitution in the Systems *cis*-$Mo(CO)_4(py)_2$/N⌒N/Toluene and $Mo(CO)_5$(4-Mepy)/dab/Toluene

complex	entering ligand N⌒N	temp, °C	pressure, atm	$\Delta H^{\ddagger}$, kcal·mol^{-1}	$\Delta S^{\ddagger}$, eu	$\Delta V^{\ddagger}$,[b] cm^3·mol^{-1}
cis-$Mo(CO)_4(py)_2$	dab	17, 25, 35	1	24.5 ± 0.4	13.5 ± 1.3	
cis-$Mo(CO)_4(py)_2$	dab	17	20, 500, 1000, 1500			3.6 ± 0.8
cis-$Mo(CO)_4(py)_2$	bpy	17	20, 500, 1000, 1500			3.9 ± 0.8
$Mo(CO)_5$(4-Mepy)	dab	25, 40, 50[a]	1	23.3 ± 1.3	0 ± 4.5	
$Mo(CO)_5$(4-Mepy)	dab	50	20, 500, 1000, 1500			0.7 ± 0.8

[a] The k_{obsd} value at 50 °C is the one determined at a pressure of 20 atm (see Figure 2). [b] The error given for $\Delta V^{\ddagger}$ is the averaged error obtained for the slope of curves a and b in Figure 2 by least-squares fitting.

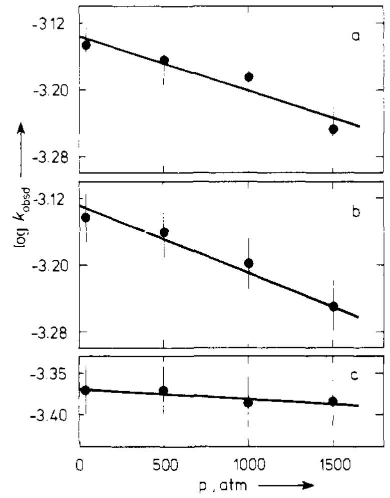

Figure 2. Plot of the logarithm of the rate constant k_{obsd} vs. pressure p for the system *cis*-$Mo(CO)_4(py)_2$/N⌒N/toluene with N⌒N = dab (curve a, 17 °C) and bpy (curve b, 17 °C) and for the system $Mo(CO)_5$(4-Mepy)/dab/toluene (curve c, 50 °C) ([complex] = 1×10^{-4} M, [dab] = [bpy] = 5×10^{-3} M).

the slope of curves a–c in Figure 2 represents the sum of an intrinsic part and a solvation part.[1]

$$\Delta V_{\text{exptl}}^{\ddagger} = \Delta V_{\text{intr}}^{\ddagger} + \Delta V_{\text{solv}}^{\ddagger}$$

The latter contribution reflects solvent effects and is of major significance in those systems where charged species and, hence, strong electrostatic interactions with the solvent are involved. This does not apply to systems A and B, where uncharged species react in the rather nonpolar solvent toluene. It is assumed, therefore, that $\Delta V_{\text{solv}}^{\ddagger} = 0$, so that $\Delta V_{\text{exptl}}^{\ddagger} = \Delta V_{\text{intr}}^{\ddagger} = \Delta V^{\ddagger}$.

The data obtained for $\Delta V^{\ddagger}$ are presented in Table V. For system A with N⌒N = dab and bpy positive activation volumes are found, namely 3.6 and 3.9 cm^3·mol^{-1}, respectively. Considering the error obtained upon least-squares fitting of the rate constants in Figure 2, one is inclined to take these numbers as being equal within the limits of error. A clearly different value of only 0.7 cm^3·mol^{-1} is found however for system B. Here, consideration of the limits of error leads to the result $\Delta V^{\ddagger} \approx 0$.

The compounds $Mo(CO)_4$(dab) and $Mo(CO)_4$(bpy) are known to be solvatochromic.[10] It is not really surprising, therefore, to see that their visible spectra are pressure dependent. As shown in Figure 3, the spectra of the complexes $Mo(CO)_4$(dab) and $Mo(CO)_4$(bpy) (produced in situ via reaction 3 in toluene) are slightly blue shifted and the intensity of absorption is slightly increased at 1500 atm. Blue shift and increase in absorption intensity occur stepwise when the pressure is raised stepwise, and both effects are reversible in the sense that even a repeated change in pressure from 20 to 1500 atm and vice versa lead reproducibly to the spectra shown in Figure 3.[11]

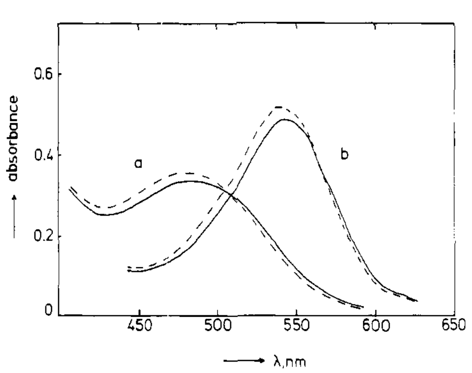

Figure 3. Visible spectra of the complexes $Mo(CO)_4$(bpy) (a) and $Mo(CO)_4$(dab) (b) at a pressure of 20 atm (—) and 1500 atm (- - -) in toluene at 17 °C. The complexes were produced in situ via reaction 3 at [*cis*-$Mo(CO)_4(py)_2$] = 1×10^{-4} M and [bpy] = [dab] = 5×10^{-4} M.

Mechanism of Ligand Substitution for System A. It is well documented[12] that the kinetics of amine substitution in group 6B metal pentacarbonyl amine derivatives with monodentate phosphorus donor ligands follow rate law 7.

$$\text{rate} = (k_1 + k_2[PR_3])[M(CO)_5(\text{amine})] = k_{obsd}[M(CO)_5(\text{amine})] \quad (7)$$

There appears to be general agreement on the first-order term k_1 in (7) to represent a purely dissociative (D) mechanism. Ligand substitution in system A follows the one-term rate law (5), which is independent of the concentration of the entering bidentate ligand N⌒N.

$$\text{rate} = k_{obsd}[cis\text{-}Mo(CO)_4(py)_2] \quad (5)$$

A straightforward mechanistic interpretation of (5) would be the assumption $k_{obsd} \triangleq k_1$; i.e., the dissociation of one molecule of pyridine is rate controlling:

$$cis\text{-}Mo(CO)_4(py)_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Mo(CO)_4py + py \quad (8)$$

$$Mo(CO)_4py + N^\frown N \xrightarrow{k_3} (CO)_4pyMo\text{–}N^\frown N \xrightarrow{\text{fast}} (CO)_4Mo(N^\frown N) + py \quad (9)$$

Application of the steady-state approximation for the concentration of the five-coordinate intermediate $Mo(CO)_4py$ leads to rate expression 10.

$$\text{rate} = d[Mo(CO)_4(N^\frown N)]/dt = \frac{k_1k_3[N^\frown N][cis\text{-}Mo(CO)_4(py)_2]}{k_2[py] + k_3[N^\frown N]} \quad (10)$$

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(10) Renk, I. W.; tom Dieck, H. *Chem. Ber.* **1972**, *105*, 1403, 1419.

(11) Since the spectra shown are based on the complexes as produced via reaction 3 (i.e., in the presence of N⌒N and py), outer-sphere complexation with excess dab or bpy at high pressure might be invoked. High-pressure studies with solutions of $Mo(CO)_4$(dab) and $Mo(CO)_4$(bpy) in the absence of N⌒N and py proved however that the spectral changes observed at high pressure are due to the pure complexes and that outer-sphere complexation can be ruled out (van Eldik, R.; Elias, H.; Macholdt, H.-T., to be submitted for publication).

(12) Darensbourg, D. J.; Ewen, J. A. *Inorg. Chem.* **1981**, *20*, 4168.

The experimentally fulfilled condition $[\mathrm{N}^\frown\mathrm{N}] \gg [\mathrm{py}]$ can lead to the consequence $k_3[\mathrm{N}^\frown\mathrm{N}] \gg k_2[\mathrm{py}]$, which converts (10) to (11).

$$\text{rate} = k_1[cis\text{-}\mathrm{Mo(CO)_4(py)_2}] = k_{\mathrm{obsd}}[cis\text{-}\mathrm{Mo(CO)_4(py)_2}] \tag{11}$$

A crucial experiment to test the validity of sequence (8) and (9) and hence to support (11) is the investigation of the kinetic effect of additional pyridine in the system. On the basis of eq 10 relationship 12 can be derived.

$$k_{\mathrm{obsd}}^{-1} = (1/k_1) + (k_2/k_1k_3)([\mathrm{py}]/[\mathrm{N}^\frown\mathrm{N}]) \tag{12}$$

As shown in Figure 1, plotting of k_{obsd}^{-1} vs. the ratio $[\mathrm{py}]/[\mathrm{N}^\frown\mathrm{N}]$ clearly proves for $\mathrm{N}^\frown\mathrm{N}$ = dab, dab-OCH$_3$, and dab-Cl the kinetic effect of mass law retardation, i.e., the rate-reducing competition of the ligands py and $\mathrm{N}^\frown\mathrm{N}$ for the intermediate Mo(CO)$_4$py according to (8) and (9). The curves a–c shown coincide at $[\mathrm{py}]/[\mathrm{N}^\frown\mathrm{N}] = 0$, thus delivering rate constant k_1 (which should be and which is independent of the nature of $\mathrm{N}^\frown\mathrm{N}$) and hence the ratio k_2/k_3 from the slope of the curves. The data obtained are compiled in Table VI. The average of the k_1 data derived for $\mathrm{N}^\frown\mathrm{N}$ = dab, dab-OCH$_3$, and dab-Cl amounts to $\bar{k}_1 = 2.52 \times 10^{-3}$ s^{-1}, which is only 10% greater than the mean of all k_{obsd} data obtained at 25 °C (2.28 × 10^{-3} s^{-1}). The data for k_2/k_3 describing the relative reactivities of the various ligands $\mathrm{N}^\frown\mathrm{N}$ compared to that of pyridine are all greater than 1, which means that the ligands $\mathrm{N}^\frown\mathrm{N}$ are the better entering ligands. As shown by the data for the parameter k_3(rel) (describing the nucleophilic reactivity of a ligand $\mathrm{N}^\frown\mathrm{N}$ relative to that of $\mathrm{N}^\frown\mathrm{N}$ = dab), the methoxy group increases the nucleophilicity of the ligand dab by approximately 40% whereas the chloro group reduces it by approximately 30%. This result is in line with the electron-releasing and electron-withdrawing effects of these substituents on the donor nitrogen.

When pyridine is replaced by 4-cyanopyridine (a less basic nucleophile), the kinetic effect of mass law retardation is less pronounced (see Table III). With $\mathrm{N}^\frown\mathrm{N}$ = dab the ratio k_2/k_3 decreases from 1.73 to 0.19. The value $k_1 = 2.23 \times 10^{-3}$ s^{-1} obtained with excess 4-cyanopyridine can be taken as a rough measure for the dissociation rate of the complex *cis*-Mo(CO)$_4$py(4-CNpy).

In conclusion, the experiments carried out in the presence of additional leaving ligand pyridine strongly support the interpretation of reaction 3 as being purely dissociative according to eq 8 and 9. The reaction Mo(CO)$_4$py + $\mathrm{N}^\frown\mathrm{N}$ → (CO)$_4$pyMo–$\mathrm{N}^\frown\mathrm{N}$ and also the ring closure reaction (CO)$_4$pyMo–$\mathrm{N}^\frown\mathrm{N}$ → (CO)$_4$Mo($\mathrm{N}^\frown\mathrm{N}$) + py appear to be fast consecutive steps, which is documented by the finding that k_{obsd} is independent of the concentration and of the nature of the attacking ligand $\mathrm{N}^\frown\mathrm{N}$. In agreement with the dissociative nature of the substitution process a positive activation entropy of 13.5 eu is found. The fact that the addition of tetrahydrofuran does not affect the rate of substitution (see Table II) proves in addition that the solvento species Mo(CO)$_4$py(THF), if formed, is of no kinetic significance.

The effect of high pressure on reaction 3 is a reduction in rate (see Figure 2). For $\mathrm{N}^\frown\mathrm{N}$ = dab and for $\mathrm{N}^\frown\mathrm{N}$ = bpy the corresponding activation volumes are $\Delta V^* = 3.6$ and 3.9 cm^3·mol^{-1} (see Table V). Since all kinetic evidence points to a pure D mechanism for reaction 3, one obviously has to learn that the activation volume associated with the breaking of the relatively weak Mo–py bond in *cis*-Mo(CO)$_4$(py)$_2$ is comparatively small. As a matter of fact, there is rather little information available on the size of activation volumes for dissociative processes in which a neutral substrate breaks apart to form neutral species. For the splitting of di-*tert*-butyl peroxide $\Delta V^* = 10$ cm^3·mol^{-1} was found,[13] but a reaction such as (13) has an activation volume of only 3 cm^3·mol^{-1}.[14]

$$\mathrm{ArCON_3} \rightarrow \mathrm{N_2} + \mathrm{ArNCO} \tag{13}$$

Since Brower and Chen[3] reported $\Delta V^* = 10$ cm^3·mol^{-1} for the dissociation of Mo(CO)$_6$ at 103 °C, one could consider the argument that the actual size of the positive activation volume describing the dissociation of a molybdenum carbonyl complex might also have to do with the strength of the metal–ligand bond to be broken and hence with the nature of the neighboring ligands.

Another approach to explain the finding that ΔV^* for dissociatively controlled ligand substitution in carbonyl complexes is unexpectedly[15] small could lie in the argument that possibly the partial molar volume of a 6-coordinate carbonyl complex is much greater than that of a 5-coordinate one such as Mo(CO)$_4$py so that consequently the overall volume change upon dissociation according to ML$_6$ → ML$_5$ + L is small.

Mechanism of Ligand Substitution for System B. The results obtained for system B (with amine = py, 4-CNpy, and 4-Mepy) appear to agree with those obtained for system A, namely (i) the rate of substitution is independent of concentration and nature of the entering bidentate ligand $\mathrm{N}^\frown\mathrm{N}$, (ii) in the presence of additional amine the rate of substitution is reduced, and (iii) the addition of tetrahydrofuran has no kinetic effect. The following scheme would apply for a D mechanism:

$$\mathrm{Mo(CO)_5(amine)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{Mo(CO)_5} + \text{amine} \tag{14}$$

$$\mathrm{Mo(CO)_5} + \mathrm{N}^\frown\mathrm{N} \xrightarrow{k_3} \mathrm{(CO)_5Mo{-}N}^\frown\mathrm{N} \xrightarrow{\text{fast}} \mathrm{(CO)_4Mo(N}^\frown\mathrm{N)} + \mathrm{CO} \tag{15}$$

As shown for system A (see eq 10), this scheme leads to eq 16, as experimentally found for the condition $[\mathrm{N}^\frown\mathrm{N}] \gg$

$$\text{rate} = k_1[\mathrm{Mo(CO)_5(amine)}] = k_{\mathrm{obsd}}[\mathrm{Mo(CO)_5(amine)}] \tag{16}$$

[amine]. Figure 1 demonstrates, however (see curve d), that plotting of the data obtained in the presence of additional pyridine according to eq 12 leads to the expected linear relationship at low concentrations of pyridine only. At higher concentrations the curve begins to level off (a further increase of the pyridine concentration led to conditions under which side reactions became dominant).

On the basis of a D mechanism as described by scheme 14 and 15 the activation parameters $\Delta S^* \approx 0$ and $\Delta V^* \approx 0$ (see Table V) are surprising.

The D mechanism implies that ring closure is a fast consecutive step (see eq 15). Considering the fact that the ligand CO is more strongly bound than the ligand py, one might suggest a scheme in which ring closure is rate controlling:

$$\mathrm{Mo(CO)_5(amine)} \overset{K_1}{\rightleftharpoons} \mathrm{Mo(CO)_5} + \text{amine} \tag{17}$$

$$\mathrm{Mo(CO)_5} + \mathrm{N}^\frown\mathrm{N} \overset{K_2}{\rightleftharpoons} \mathrm{(CO)_5Mo{-}N}^\frown\mathrm{N} \tag{18}$$

$$\mathrm{(CO)_5Mo{-}N}^\frown\mathrm{N} \xrightarrow{k_i} \mathrm{(CO)_4Mo(N}^\frown\mathrm{N)} + \mathrm{CO} \tag{19}$$

If equilibria 17 and 18 could be considered to be relatively fast

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[13] Walling, C.; Metzger, G. *J. Am. Chem. Soc.* **1959**, *81*, 5365.

[14] le Noble, W. J. In "High Pressure Chemistry", Kelm, H., Ed.; D. Reidel: Dordrecht, Holland, 1978; p 399.

[15] For dissociative water exchange in 6-coordinate aquo cations T. W. Swaddle (*Inorg. Chem.* **1983**, *22*, 2663) predicts on the basis of model calculations that the limits for ΔV^* should be of the order of 12–14 cm^3·mol^{-1}.

Table VI. Rate Constants at 25 °C Derived for Ligand Substitution in the System *cis*-$Mo(CO)_4(py)_2/N^\frown N/py/$Toluene on the Basis of the Observed Rate Constants (Table III), Eq 12, and Figure 1

entering ligand $N^\frown N$	10^3k_1, s^{-1}	k_2/k_3[a]	k_3(rel)[b]
dab	2.35	1.73	1.0
dab-OCH_3	3.05	1.25	1.38
dab-Cl	2.17	2.38	0.73
dab	2.23[c]	0.19[c]	

[a] Obtained by multiplication of the slope of the straight lines a–c in Figure 1 with $\bar{k}_1 = 2.28 \times 10^{-3}\ s^{-1}$ (mean of all k_{obsd} data obtained at 25 °C; see Table II) according to slope = $(k_2/k_3)(1/k_1)$ (see eq 12). [b] Obtained by dividing the ratio k_2/k_3(dab) by k_2/k_3; k_3(rel) describes the nucleophilic reactivity of a ligand $N^\frown N$ relative to that for $N^\frown N$ = dab. [c] Data obtained in the presence of 4-CNpy instead of py.

preequilibria and if the "interchange" step (19) were rate-controlling, any formal rate expression to be derived on the basis of eq 17–19 should involve the concentration of the entering ligand $N^\frown N$, which is experimentally not found.

The extreme assumption that due to the excess concentration of $N^\frown N$ all of the complex $Mo(CO)_5$(amine) is completely converted to $(CO)_5Mo–N^\frown N$ in a series of steps that are fast relative to the rate of (19), is of some attractiveness. This assumption would explain the fact that the rate of substitution is independent of the concentration of $N^\frown N$. It could also be a reasonable basis for rationalizing the finding $\Delta V^{\ne} \approx 0$,[16] since in a rate-controlling I_d-like step (19) a CO group in a cis position leaves and is simultaneously replaced by the second nitrogen donor atom of the bidentate ligand $N^\frown N$, bound as a monodentate ligand at that stage. The argument that the complete conversion $Mo(CO)_5(\text{amine}) \rightarrow (CO)_5Mo–N^\frown N$ should be accompanied by spectral changes (which were actually not observed) is not a very convincing argument, since for such a conversion a Mo–N(pyridine) bond is just replaced by a rather similar Mo–N bond formed with ligands such as bpy, phen, and dab. A very strong argument against this interpretation is however the finding that the rate constant $\bar{k}_{obsd}$ as obtained for reaction 4 depends on the amine coordinated in the complex $Mo(CO)_5$(amine) studied (see Table IV). For amine = 4-Mepy, py, and 4-CNpy the data for $\bar{k}_{obsd}$ are 1.09×10^{-4}, 1.95×10^{-4}, and $9.24 \times 10^{-4}\ s^{-1}$, respectively. These rate constants should indeed agree within the limits of error of approximately ±10% if all of the complex $Mo(CO)_5$(amine) were converted to the species $(CO)_4Mo–N^\frown N$ prior to product formation according to eq 19. The fact that these rate constants disagree clearly and that they seem to follow the substituent effects of the methyl and cyano groups on the basicity of the pyridine indicate on the other hand that the breaking of the Mo–N(pyridine) bond obviously is a rate-controlling factor.

The interpretation of reaction 4 to follow an I_d mechanism as described by the sequence (20)–(22) has its problems. The

$$Mo(CO)_5(\text{amine}) + N^\frown N \overset{K_{os}}{\rightleftharpoons} Mo(CO)_5(\text{amine}),\ N^\frown N \tag{20}$$

$$Mo(CO)_5(\text{amine}),\ N^\frown N \xrightarrow{k_i} (CO)_5Mo–N^\frown N + \text{amine} \tag{21}$$

$$(CO)_5Mo–N^\frown N \xrightarrow{\text{fast}} (CO)_4Mo(N^\frown N) + CO \tag{22}$$

corresponding rate equation (23) is reduced to the simple

$$\text{rate} = \frac{k_iK_{os}[N^\frown N]}{1 + K_{os}[N^\frown N]}[Mo(CO)_5(\text{amine})] \tag{23}$$

$$\text{rate} = k_i[Mo(CO)_5(\text{amine})] = k_{obsd}[Mo(CO)_5(\text{amine})] \tag{24}$$

experimentally observed form (24) only for $K_{os}[N^\frown N] \gg 1$. At concentrations $[N^\frown N] = 0.5 \times 10^{-3}–5 \times 10^{-3}$ M the postulate $K_{os}[N^\frown N] \gg 1$ would mean however that the outer-sphere complex formation constant K_{os} is of the order of $2 \times 10^4–2 \times 10^3\ M^{-1}$, thus leading to $[N^\frown N]K_{os} \approx 10$. The assumption of such strong outer-sphere complexation appears to be as extreme as the postulate of complete conversion of $Mo(CO)_5$(amine) to $(CO)_5Mo–N^\frown N$ described above.

The dissociation of two cis ligands according to eq 25 is a mechanistic alternative,[17] which might be considered as well.

$$Mo(CO)_5py \rightleftharpoons Mo(CO)_4 + CO + py \tag{25}$$

As a matter of fact, species such as $Mo(CO)_4$ have been postulated[18] and their formation in the present system might help to explain the unexpected mass law retardation at higher pyridine concentrations.

On the other hand, one would expect, however, that in the presence of CO the species $Mo(CO)_4$ leads to the formation of the inert complex $Mo(CO)_6$,[19] which would prevent complete conversion of $Mo(CO)_5$(amine) to $Mo(CO)_4(N^\frown N)$.

In conclusion, most of the experimental results obtained for system B can be explained by assuming that ligand substitution according to eq 4 follows a D mechanism. The postulate of an I_d mechanism and the assumption of ring closure to be rate controlling is inconsistent with several experimental facts.

Acknowledgment. We thank Prof. Dr. H. Kelm (Universität Frankfurt) and especially his colleague Dr. R. van Eldik for providing access to their high-pressure facilities and for introducing one of us (H.-T.M.) to the technique of high-pressure measurements. Stimulating discussions with Dr. van Eldik on the manuscript are also appreciated. Financial support through the "Deutsche Forschungsgemeinschaft" and the "Verband der Chemischen Industrie e.V." is gratefully acknowledged.

Registry No. *cis*-$Mo(CO)_4(py)_2$, 16742-99-7; $Mo(CO)_5(py)$, 14324-76-6; $Mo(CO)_5$(4-Mepy), 21285-55-2; $Mo(CO)_5$(4-CNpy), 80925-83-3; dab, 5393-49-7; dab-OCH_3, 19215-52-2; dab-Cl, 19215-48-6; bpy, 366-18-7; phen, 66-71-7.

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(16) Palmer, D. A.; Kelm, H. In ref 14, p 442.

(17) This alternative was suggested by one of the reviewers.

(18) Dobson, G. R.; Asali, K. J. *Inorg. Chem.* **1983**, *22*, 1835.

(19) Darensbourg, D. J.; Brown, T. L. *Inorg. Chem.* **1968**, *7*, 1679.