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Flash Photolysis Studies of Organotransition-Metal Complexes. Kinetics and Mechanism of Substitution Reactions of $[Co(CO)(L)(THF)NO]$ (THF = Tetrahydrofuran; L = CO, PPh_3, $P(OPh)_3$)

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Flash photolysis of $Co(CO)_2(L)NO$ complexes (L = CO, PPh_3, $P(OPh)_3$) in tetrahydrofuran (THF) solution results in Co–CO bond fission and formation of $[Co(CO)(L)(THF)NO]$ in predominant concentration. The kinetics of replacement of THF by L′ (=PPh_3, trialkyl and triaryl phosphites, $AsPh_3$, 1-hexene) in these species has been investigated. For L = PPh_3 and $P(OPh)_3$, the mechanism involves addition of L′ to the three-coordinate $[Co(CO)(L)NO]$ intermediate produced after reversible THF dissociation. For L = CO, a second pathway, involving bimolecular displacement of THF by L′, also is observed. Studies in mixed solvents (THF/cyclohexane) have been employed to probe mechanistic details. For the dissociative pathway, the observed discriminating ability of $[Co(CO)_2NO]$ and entropies of activation suggest a significant barrier to reaction of this coordinatively unsaturated species, perhaps the result of geometrical changes in the coordination sphere upon dissociation of THF or association of L.

In contrast to the general observation that ligand-substitution reactions of metal carbonyls take place largely via dissociative pathways,[1] $Co(CO)_3NO$ reacts with various Lewis bases primarily by means of an associative mechanism.[2,3] This anomalous behavior has been attributed to the ability of the nitrosyl ligand to accept an electron pair while NO in the formal Co–NO bonding scheme is changed from NO^+ to NO^-. The associative process thus involves a change in Co–NO bonding from linear to bent. As a result of this transfer of electrons from Co to NO, nucleophilic attack at the metal center is facilitated.[2,4,5] For very weak nucleophiles such as Ph_3As and CO, it has been found that a dissociative mechanism, affording the $[Co(CO)_2NO]$ intermediate, also is accessible.[2,3]

The subsequent dissociation of a second CO from $Co(CO)_2(L)NO$ also has been observed to take place under more rigorous reaction conditions to afford $Co(CO)(L)_2NO$ complexes. Here, too, both associative and dissociative reaction pathways are observed.[6] The relative contributions of these pathways to the overall ligand-substitution process are strongly dependent upon the nature of coordinated L; in particular, it was observed that bulky coordinated ligands promoted CO dissociation.[6]

More recently, attention has been turned to substitution products of $Co(CO)_3NO$ containing weakly coordinating ligands, including some that are implicated as intermediates in important homogeneous catalysis processes. Thus, Crichton and Rest have observed $Co(CO)_2(N_2)NO$ after photolysis in N_2 matrices at 20 K,[7] and Turner and co-workers have likewise employed photolysis to produce $[Co(CO)_2NO]$ in liquid-xenon solution at 169 K and to obtain the IR spectra of $Co(CO)_2(L)NO$ complexes in which a number of relatively weak nucleophiles, such as 1-butene,[8] H_2,[9] and 1,3-butadiene,[10] are coordinated to cobalt. These last studies aroused our interest in the kinetics and mechanism of the displacement of such weakly coordinating nucleophiles from $Co(CO)_2(L)NO$, particularly in view of the importance of such processes to catalysis. Apparently, the kinetics and mechanism of no reactions of species in which a ligand other than CO is displaced upon ligand substitution in cobalt carbonyl nitrosyl complexes have been investigated.

Table I. Carbonyl and Nitrosyl Stretching Frequencies (Cyclohexane Solution) for Cobalt Carbonyl Nitrosyl Complexes

complex	L, L′	ν(CO), cm^{-1}	ν(NO), cm^{-1}
$Co(CO)_3NO$		2100.4, 2034.1	1806.9
$Co(CO)_2(L)NO$	$P(OPh)_3$	2053.3, 2001.0	1783
	$P(O\text{-}i\text{-}Pr)_3$	2045.3, 1990.4	1762
	PPh_3	2035.5, 1981.0	1763
$Co(CO)(L)_2NO$	$P(O\text{-}i\text{-}Pr)_3$	1982.1	1727
$Co(CO)(L)(L')NO$	$P(O\text{-}i\text{-}Pr)_3$, $P(OPh)_3$	1987	1738
	$P(O\text{-}i\text{-}Pr)_3$, PPh_3	1960.8	1724

Thorsteinson and Basolo, in a brief study of solvent effects on reactivity via ligand substitution in $Co(CO)_3NO$,[2] observed little influence upon reactivity regardless of the identity of the solvent. One solvent employed by those workers was tetrahydrofuran (THF), which as a consequence of the relatively weak bonding of oxygen to coordinatively unsaturated metal carbonyls, quintessential "soft acids",[11] is expected to enter into relatively weak interactions with their metal atoms. Reported here, therefore, are the results of a kinetics study of the displacement of THF from $[Co(CO)_2(THF)NO]$ and $[Co(CO)(THF)(L)NO]$ (L = PPh_3, $P(OPh)_3$), produced in situ after flash photolysis of $Co(CO)_3(NO)$ or $Co(CO)_2(L)NO$ in THF solution.

Experimental Section

General Procedures. Infrared spectra were recorded by employing a Nicolet 20 SXB FT-IR spectrometer.

Materials. The solvents, cyclohexane and THF (Baker Analyzed Reagent), were fractionally distilled over Na under nitrogen. The ligands $P(O\text{-}i\text{-}Pr)_3$ and $P(O\text{-}n\text{-}Bu)_3$ (Aldrich) were fractionally distilled from Na under vacuum (nitrogen bleed) at 56 °C/2.5 Torr and 95 °C/0.7 Torr, respectively, while $P(OPh)_3$ (Aldrich) was similarly distilled from anhydrous $MgSO_4$ (bp 170 °C/0.3 Torr). PPh_3 (Lancaster Synthesis) and $AsPh_3$ (Aldrich) were recrystallized from methanol and dried in vacuo. 1-Hexene (Aldrich) was fractionally distilled from anhydrous $MgSO_4$ under nitrogen. $Co(CO)_3NO$ was synthesized from $Co_2(CO)_8$ (Pressure Chemical Co.) and purified by employing the literature method.[12] The known monosubstituted complexes $Co(CO)_2(PPh_3)NO$ and $Co(CO)_2(P(OPh)_3)NO$ were prepared from $Co(CO)_3NO$ by employing the published procedure.[2] All three complexes were identified through their carbonyl stretching spectra (Table I).

Identification of Reaction Products. It has been observed that photolysis of $Co(CO)_3NO$ in solution and in matrices results exclusively in CO dissociation and in the presence of Lewis bases (L) produces the CO-displacement products $Co(CO)_2(L)NO$.[4,7-10] These observations

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(1) For a review of ligand-substitution reactions at low-valent four-, five-, and six-coordinate transition-metal centers, see: Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557.

(2) Thorsteinson, E. M.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 3929.

(3) Cardaci, G.; Foffani, A.; Distefano, G.; Innorta, G. *Inorg. Chim. Acta* **1967**, *1*, 340.

(4) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

(5) Evans, W.; Zink, J. I. *J. Am. Chem. Soc.* **1981**, *103*, 2635.

(6) Cardaci, G.; Murgia, S. M.; Reichenbach, G. *Inorg. Chim. Acta* **1970**, *4*, 118.

(7) Crichton, O.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1977**, 536.

(8) Gadd, G. E.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1986**, *25*, 3604.

(9) Gadd, G. E.; Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 2547.

(10) Gadd, G. E.; Poliakoff, M.; Turner, J. J. *Organometallics* **1987**, *6*, 391.

(11) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

(12) Job, R.; Rovang, J. *Synth. React. Inorg. Met.-Org. Chem.* **1976**, *6*, 367.

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were confirmed under the present experimental conditions as follows: A 2×10^{-3} M solution of $Co(CO)_3NO$ and 0.1 M PPh_3 in THF was flashed 10 times by employing the flash photolysis system described below. The THF solvent and excess $CO(CO)_3NO$ were then evaporated under a stream of N_2, and the residue was dissolved in cyclohexane. The carbonyl stretching spectrum after photolysis was identical with that of the authentic sample of $Co(CO)_2(PPh_3)NO$.[2] The products of the photolysis reactions of $Co(CO)_2(L)NO$ with L′ in THF, Co(CO)(L)(L′)NO (L = PPh_3, $P(OPh)_3$; L′ = $P(O\text{-}i\text{-}Pr)_3$), were identified similarly through workup of solutions obtained after 15 flashes. That these indeed were the Co(CO)(L)(L′)NO "cross-products", resulting exclusively from Co–CO bond fission, was confirmed through comparison of their carbonyl and nitrosyl stretching spectra to those obtained after direct reaction of $Co(CO)_3NO$ with L′, which afforded $Co(CO)(L')_2NO$. Carbonyl stretching frequencies for these complexes are also given in Table I.

Flash Photolysis Studies. The flash photolysis apparatus employed a Xenon Corp. Model 720 flash photolysis system, which incorporated two high-pressure Xe lamps and a 12.7-cm jacketed cell. Pyrex inserts between the flash lamps and the cell filtered out UV light of wavelengths <300 nm. Two shutters (Uniblitz Electronics) placed between the analyzing light source and the reaction cell were controlled by a Kinetics Instruments sequence generator, which also contained an I_0 backoff module, which compensated for the detector voltage produced by the analyzing light. The slower shutter, designed primarily for use with the 150-W Xe analyzing light source available for faster reactions but not employed in these studies, protected the faster shutter, which was not triggered until 180 μs before the flash to minimize photolysis of the reaction sample by the analyzing light. The spectrophotometric system incorporated a 40-W tungsten lamp powered by a Harrison 6274A dc power supply. The light emerging from the photolysis cell was focused onto a Bausch and Lomb 33-86-20 monochromator and was detected by employing a Hamamatsu R928 photomultiplier tube operated by a Bertan PMT-2.0A-PN power supply. The spectrophotometer's output was digitized by employing a Nicolet 2090 IIa digital oscilloscope whose output was analyzed by employing weighted linear-least-squares programs written for the Leading Edge microcomputer to which it is interfaced. The temperature within the jacketed cell was regulated by employing a Forma-Temp Jr. Model 2095 J circulating bath and monitored within the cell with a Keithley 872 digital thermometer (FeCuNi thermocouple) immediately before and after the flash. The temperatures obtained through these measurements were the same to within 0.1 °C. Solutions 2×10^{-3} M in $Co(CO)_3NO$ or $Co(CO)_2(L)NO$ containing at least 10-fold excesses of triphenylphosphine, various phosphites, triphenylarsine, and 1-hexene were employed to ensure that pseudo-first-order reaction conditions were attained. The wavelength monitored was 550 nm. Values of the pseudo-first-order rate constants, k_{obsd}, are presented in the Appendix (supplementary material). Limits of error are given in parentheses as the uncertainty of the last digit(s) of the cited value to one standard deviation.

Results

Reactions of $Co(CO)_2(L)NO$ after Flash Photolysis in Pure THF. Flash photolysis of $Co(CO)_2(L)NO$ (L = CO, PPh_3, $P(OPh)_3$) in the presence of L′ (= PPh_3, $P(O\text{-}i\text{-}Pr)_3$) in THF obeys the stoichiometry

$$Co(CO)_2(L)NO + L' \rightarrow Co(CO)(L)(L')NO + CO \quad (1)$$

which indicates that upon photolysis a Co–CO bond is broken. Thus, the species produced immediately after photolysis are [Co(CO)(L)NO] (**1**). These intermediates are expected to react rapidly with the solvent, THF, or with L′ to produce [Co(CO)(L)(THF)NO] (**2**) and Co(CO)(L)(L′)NO. On the basis of results obtained for other metal carbonyl systems (vide infra), the 16-electron intermediates **1** produced upon flash photolysis were expected to be poorly discriminating among incoming nucleophiles; thus, the "solvate", **2**, should be produced in predominant abundance. Therefore, it is this species whose decay is monitored after the flash as it reacts with various L′.

A typical plot of A_t vs time, fitted as an exponential decay, for flash photolysis of $Co(CO)_3NO$ in the presence of $P(O\text{-}i\text{-}Pr)_3$ (0.1076 M) at 25.0 °C in THF is shown in Figure 1; the inset shows this decay plotted as log $(A_t - A_\infty)$ vs time (A_t and A_∞ are the absorbances at time t and infinite time, respectively) and fitted as a first-order process. Series of rates determined as a function of [L′] show that reactions of the three species **2** (L = CO, PPh_3, $P(OPh)_3$) with L′ obey the rate law

$$-d[\mathbf{2}]/dt = k[\mathbf{2}][L'] \qquad k_{obsd}/[L'] = k \quad (2)$$

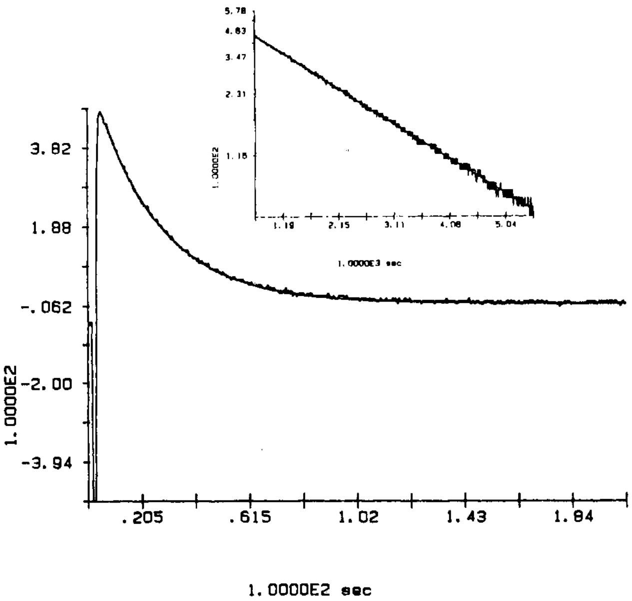

Figure 1. Plot of A_t vs time for reaction of $[Co(CO)_2(THF)NO]$ produced after flash photolysis with 0.1076 M $P(O\text{-}i\text{-}Pr)_3$ in THF at 25.0 °C. The inset shows a plot of ln $(A_t - A_\infty)$ vs time for the same reaction.

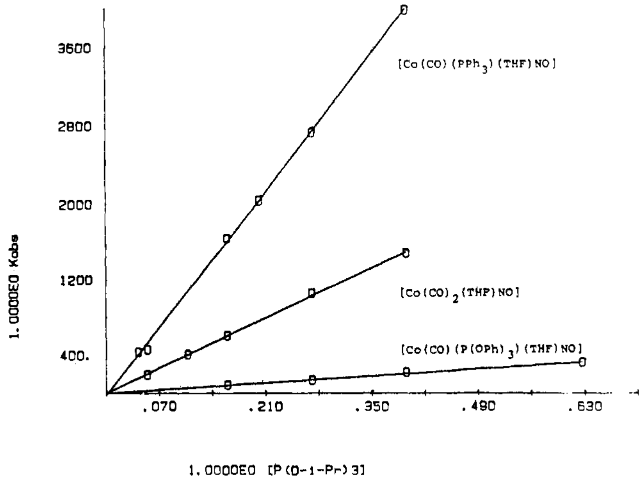

Figure 2. Plots of k_{obsd} vs $[P(O\text{-}i\text{-}Pr)_3]$ for reactions of [Co(CO)(L)(THF)NO] produced after flash photolysis of $Co(CO)_2(L)NO$ in THF solution at 25.0 °C.

Plots of k_{obsd} vs $[P(O\text{-}i\text{-}Pr)_3]$ for the three photogenerated intermediates **2** for data taken at 25.0 °C are illustrated in Figure 2.

The rate law given in eq 2 could be ascribed to a number of possible mechanisms, two of the most probable of which are illustrated in eq 3. Path 3a envisions reversible dissociation of

$$\begin{tikzcd}
\underset{\mathbf{2}}{[Co(CO)(L)(THF)NO]} \arrow[r, shift left, "k_1"] \arrow[d, "\text{path b}\ k_3{[L']}"'] & \underset{\mathbf{1}}{[Co(CO)(L)NO]} \arrow[l, shift left, "k_{-1}{[THF]}"] \arrow[d, "\text{path a}\ k_2{[L']}"'] \\
{[Co(CO)(L)(THF)(L')NO]} \arrow[r, "\text{fast}"] & Co(CO)(L)(L')NO + THF
\end{tikzcd} \quad (3)$$

THF from photogenerated **2** and competitive attack by L′ at **1** produced through that dissociation. The rate law for this mechanism, presuming a steady-state concentration of [Co(CO)(L)NO], is

$$-d[\mathbf{2}]/dt = k_1k_2[\mathbf{2}][L']/(k_{-1}[THF] + k_2[L']) \quad (4)$$

In pure THF it is reasonable to assume that $k_{-1}[THF] \gg k_2[L']$, for which rate law 4 would become

$$-d[\mathbf{2}]/dt = k_1k_2[\mathbf{2}][L']/k_{-1}[THF] \quad (5)$$

for which, with [THF] constant, $k_1k_2/k_{-1}[THF]$ would be constant

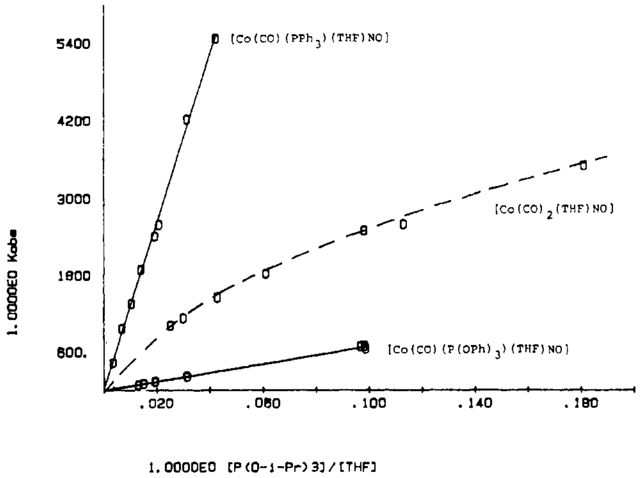

Figure 3. Plots of k_{obsd} vs $[P(O\text{-}i\text{-}Pr)_3]/[THF]$ for reactions of $P(O\text{-}i\text{-}Pr)_3$ with $[Co(CO)(L)(THF)NO]$ produced after flash photolysis of $Co(CO)_2(L)NO$ in THF/cyclohexane solutions at 25.0 °C.

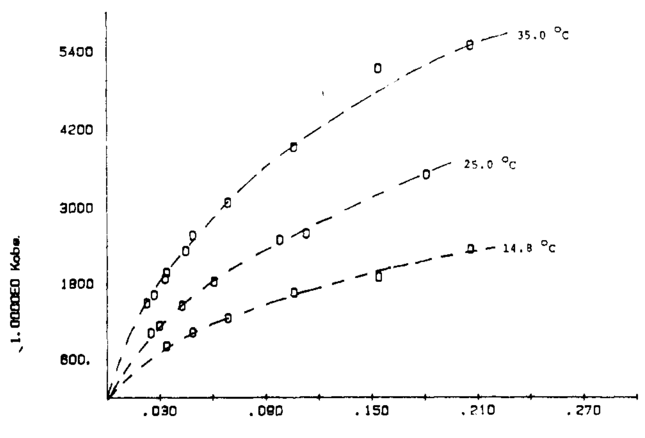

Figure 4. Plots of k_{obsd} vs $[P(O\text{-}i\text{-}Pr)_3]/[THF]$ for reaction of $P(O\text{-}i\text{-}Pr)_3$ with $[Co(CO)_2(THF)NO]$ produced after flash photolysis of $Co(CO)_3NO$ in THF/cyclohexane solutions at three temperatures.

(=k), in agreement with eq 2. The alternative mechanism (3b) envisions nucleophilic attack by L′ at **2** with displacement of THF, for which the rate law would be

$$-d[\mathbf{2}]/dt = k_3[\mathbf{2}][L'] \tag{6}$$

Thus, either or both of these mechanisms are consistent with the observed rate law (eq 2).

Reactions after Flash Photolysis of $Co(CO)_2(L)NO$ in THF/Cyclohexane Mixtures. In order to probe further the mechanistic possibilities, studies of rates of reaction after flash photolysis were also carried out in THF/CH solvent mixtures (CH = cyclohexane) containing varying concentrations of L′. These experiments were designed to probe competition of THF and L′ for **1** were it to be produced from **2** via mechanism 3a. In view of the much weaker bonding anticipated between Co and CH than between Co and THF,[13] [Co(CO)(L)(CH)NO] is expected to be a steady-state intermediate on the time scale of the reactions of **2** with L′.[14]

Reactions after flash photolysis were studied in solution containing ratios of [THF]/[L′] > 5 so that THF would remain the predominant reaction species, i.e., so that a significant portion of the photolysis product would form the [Co(CO)(L)(THF)NO] complex rather than be converted to Co(CO)(L)(L′)NO without its intermediacy. Plots of k_{obsd} vs [L′]/[THF] for reactions after flash photolysis of $Co(CO)_2(L)NO$ for L = PPh_3 and $P(OPh)_3$ were found to be linear, with zero intercepts (Figure 3). For reactions after flash photolysis of $Co(CO)_3NO$ at three temperatures, however, these plots were curved (Figure 4), suggestive of a mechanism consisting of one or more reversible steps such as path 3a. For this pathway, eq 4 can be expressed in terms of the pseudo-first-order rate constants, k_{obsd}, as

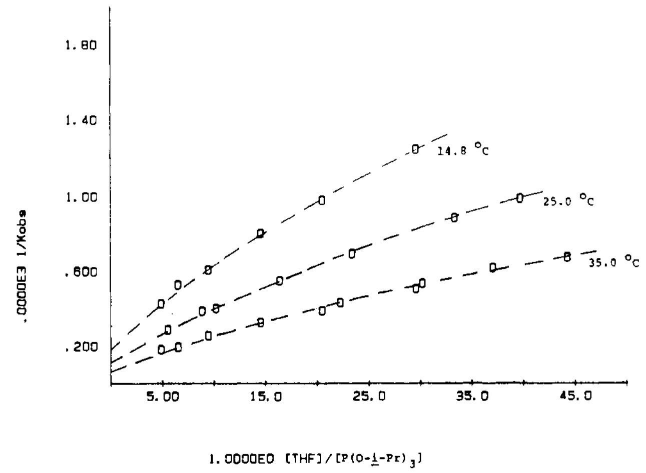

Figure 5. Plots of $1/k_{obsd}$ vs $[THF]/[P(O\text{-}i\text{-}Pr)_3]$ at three temperatures for reaction of $P(O\text{-}i\text{-}Pr)_3$ with $[Co(CO)_2(THF)NO]$ produced after flash photolysis of $Co(CO)_3NO$ in THF/cyclohexane solutions.

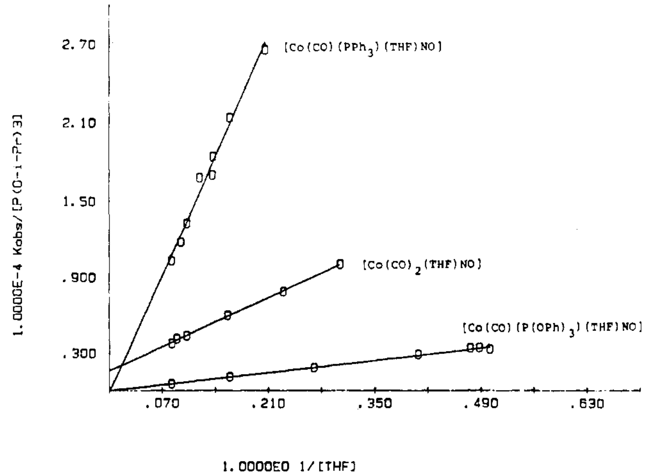

Figure 6. Plots of $k_{obsd}/[P(O\text{-}i\text{-}Pr)_3]$ vs 1/[THF] for reactions of $[Co(CO)(L)(THF)NO]$ with $P(O\text{-}i\text{-}Pr)_3$ in THF/cyclohexane solution.

$$1/k_{obsd} = 1/k_1 + k_{-1}[THF]/k_1k_2[L'] \tag{7}$$

However, plots of $1/k_{obsd}$ vs [THF]/[L′] were found *not* to be linear, as expected for this mechanism (Figure 5). The rough form of these plots was, however, consistent with a mechanism involving *both* pathways 3a and 3b. This mechanism, similar to that shown in eq 3 but modified to take into account the existence of [Co(CO)(L)(CH)NO] as a steady-state intermediate, is illustrated in eq 8. It should be noted that this mechanism, involving as it does both associative and dissociative reaction pathways, is that observed for thermal reactions of $Co(CO)_3NO$

$$\begin{tikzcd}
 & {[Co(CO)(L)(CH)NO]} \arrow[d, shift left, "k_{-4}"] \\
{[Co(CO)(L)(THF)NO]} \arrow[r, shift left, "k_1"] \arrow[d, "k_3[L']"'] & {[Co(CO)(L)NO]} \arrow[l, shift left, "k_{-1}[THF]"] \arrow[u, shift left, "k_4[CH]"] \arrow[d, "k_2[L']"] \\
{[Co(CO)(L)(THF)(L')NO]} \arrow[r, "fast"] & Co(CO)(L)(L')NO + THF
\end{tikzcd} \tag{8}$$

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[13] Presuming there to be rough parallels in reactivity for most coordinatively unsaturated metal carbonyl intermediates, it is to be noted that $[(alkane)W(CO)_5]$ complexes react with L′ via alkane displacement on the microsecond time scale, while their $[(THF)W(CO)_5]$ counterpart is stable on a time scale longer than milliseconds: Dobson, G. R.; Zhang, S. Unpublished results.

[14] See, e.g.: Asali, K. J.; Basson, S. S.; Tucker, J. S.; Hester, B. C.; Awad, H. H.; Dobson, G. R. *J. Am. Chem. Soc.* **1987**, *109*, 5386.

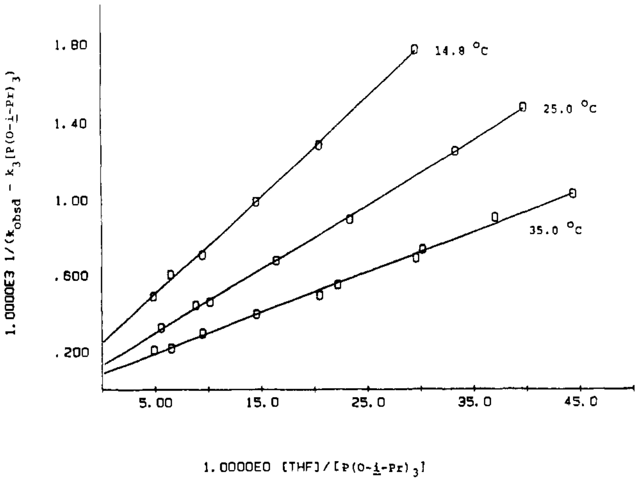

Figure 7. Plots of $1/(k_{obsd} - k_3[P(O\text{-}i\text{-}Pr)_3])$ vs $[THF]/[P(O\text{-}i\text{-}Pr)_3]$ for reactions of $[Co(CO)_2(THF)NO]$ with $P(O\text{-}i\text{-}Pr)_3$ in THF/cyclohexane solutions at three temperatures.

and $Co(CO)_2(L)NO$ with L′.[2,3,6] Assuming also a steady-state concentration of $[Co(CO)(L)(CH)NO]$, the rate law for this mechanism is

$$-d[\mathbf{2}]/dt = (k_1k_2/(k_{-1}[THF] + k_2[L']) + k_3)[\mathbf{2}][L'] \qquad (9)$$

In order to determine whether or not the nonlinear plots of $1/k_{obsd}$ vs [THF]/[L′] shown in Figure 5 are consistent with this mechanism, an attempt was made to simplify the experimentally observed rate behavior by choosing [THF]/[L′] ratios >100 so that $k_{-1}[THF] \gg k_2[L']$. Under these conditions, eq 9 becomes

$$-d[\mathbf{2}]/dt = (k_1k_2/k_{-1}[THF] + k_3)[\mathbf{2}][L'] \qquad (10)$$

or, in terms of k_{obsd}

$$k_{obsd}/[L'] = k_1k_2/k_{-1}[THF] + k_3 \qquad (11)$$

Figure 6 illustrates plots of $k_{obsd}/[L']$ vs 1/[THF] for these data for reactions of photogenerated **2** for L = CO, PPh_3, and $P(OPh)_3$ and L′ = $P(O\text{-}i\text{-}Pr)_3$. It is noted that these plots exhibit an intercept for $[Co(CO)_2(THF)NO]$ (but, obviously (Figure 3), are linear with zero intercepts for the $[Co(CO)(PPh_3)(THF)NO]$ and $[Co(CO)(P(OPh)_3)(THF)NO]$ complexes). These observations suggest that reactions of the latter two complexes proceed exclusively via the dissociative pathway, while that for $[Co(CO)_2(THF)NO]$ takes place via competitive pathways, one dissociative and the other associative.

If mechanism 8 indeed is responsible for the kinetics behavior observed in Figure 6 for reactions after flash photolysis of $Co(CO)_3NO$ in THF/CH solutions containing $P(O\text{-}i\text{-}Pr)_3$, the steady-state rate law derived from it, given in eq 9, can be rearranged to

$$1/(k_{obsd} - k_3[L']) = k_{-1}[THF]/k_1k_2[L'] + 1/k_1 \qquad (12)$$

Thus, plots of $1/(k_{obsd} - k_3[L'])$ vs [THF]/[L′] will be linear, with intercepts $1/k_1$ and slopes k_{-1}/k_1k_2. These plots, which employ values of k_{obsd} obtained from the data illustrated in Figure 5 and values of "k_3", the intercepts of plots such as are shown in Figure 6, are illustrated in Figure 7. The linearity of these plots provides strong evidence that mechanism 8 is indeed operative for reactions of $[Co(CO)_2(THF)NO]$ with L′. Further, values of k_1k_2/k_{-1} obtained for both reactions obeying eq 11 and eq 12 are in good agreement (see Table II, below), indicating that the mechanism outlined in eq 8 is obeyed over the entire range of concentrations of THF and L′ that were employed (1.3 M to "neat" THF and 0.025–0.63 M $P(O\text{-}i\text{-}Pr)_3$).

The linear plots with zero intercept for reactions with L′ observed after flash photolysis of $Co(CO)_2(L)NO$ (L = PPh_3, $P(OPh)_3$) in neat THF and in THF/CH mixtures (Figure 3) can be understood in terms of the mechanism illustrated in eq 8 if $k_{-1}[THF] \gg k_2[L]$ and $k_3[L'] = 0$. Presumably, in these more highly substituted complexes, inhibition of the associative pathway results from steric crowding in a five-coordinate transition state containing two bulky phosphorus-containing ligands. Similarly, the smaller "competition ratios" of attack at [Co(CO)(L)NO] than at $[Co(CO)_2NO]$, which may be inferred from the absence of curvature of plots of k_{obsd} vs [L′]/[THF] in the former but its presence for similar [THF]/[L′] ratios in the latter (Figure 3), is reasonably attributed to the faster rate of attack at [Co(CO)(L)NO] expected for THF vs the more sterically demanding $P(O\text{-}i\text{-}Pr)_3$.

Table II. Rate Constants and Activation Parameters for Reactions with L′ (=Lewis Base) after Flash Photolysis of $Co(CO)_2(L)NO$ (L = CO, PPh_3, $P(OPh)_3$) in THF and THF/Cyclohexane Solutions at Various Temperatures

L	L′	T, °C	$10^{-3}k_1$, s^{-1}	$10^{-4}k_1k_2/k_{-1}$, s^{-1}	$10^{-3}k_3$, $M^{-1}\ s^{-1}$
CO^a	$P(O\text{-}i\text{-}Pr)_3$	14.8	4.1 (2)	1.79 (4)[d] 1.95 (3)[e]	1.12 (8)
		25.0	7.8 (5)	2.77 (4)[d] 2.96 (3)[e] 2.7 (3)[f]	1.59 (7)
		35.0	12 (2)	4.13 (14)[d] 4.67 (11)[e]	2.5 (3)
CO^b	PPh_3	14.8		2.10 (3)	2.95 (6)
		25.0		3.39 (7)	4.06 (14)
		35.0		4.81 (6)	5.64 (10)
CO^c	$P(OPh)_3$	14.8		0.745 (6)	0.31 (1)
		25.0		1.26 (3)	0.46 (5)
		35.0		1.97 (4)	0.70 (8)
	$P(OBu)_3$	25.0		3.41 (7)	2.36 (15)
	$AsPh_3$			2.39 (7)	2.41 (15)
	1-hexene			0.082 (1)	0.007 (2)
PPh_3	$P(O\text{-}i\text{-}Pr)_3$			13.2 (6)[d] 12.4 (1)[f]	
$P(OPh)_3$				0.70 (2)[d] 0.63 (4)[f]	

[a] $\Delta H_1^* = 8.8$ (6) kcal/mol, $\Delta S_1^* = -11$ (2) cal/(deg mol), $\Delta H_1^* + \Delta H_2^* - \Delta H_{-1}^* = 6.71$ (1) kcal/mol, $\Delta S_1^* + \Delta S_2^* - \Delta S_{-1}^* = -15.62$ (4) cal/(deg mol), $\Delta H_3^* = 6.3$ (4) kcal/mol, $\Delta S_3^* = -22.7$ (14) cal/(deg mol);[d] $\Delta H_1^* + \Delta H_2^* - \Delta H_{-1}^* = 7.0$ (3) kcal/mol, $\Delta S_1^* + \Delta S_2^* - \Delta S_{-1}^* = -14.4$ (9) cal/(deg mol).[e] [b] $\Delta H_1^* + \Delta H_2^* - \Delta H_{-1}^* = 6.7$ (3) kcal/mol, $\Delta S_1^* + \Delta S_2^* - \Delta S_{-1}^* = -15.5$ (11) cal/(deg mol), $\Delta H_3^* = 5.06$ (13) kcal/mol, $\Delta S_3^* = -25.0$ (4) cal/(deg mol). [c] $\Delta H_1^* + \Delta H_2^* - \Delta H_{-1}^* = 7.88$ (12) kcal/mol, $\Delta S_1^* + \Delta S_2^* - \Delta S_{-1}^* = -13.2$ (4) cal/(deg mol), $\Delta H_3^* = 6.54$ (9) kcal/mol, $\Delta S_3^* = -24.3$ (3) cal/(deg mol). [d] Data obtained from plots of $k_{obsd}/[L']$ vs 1/[THF]. [e] Data obtained from plots of $1/(k_{obsd} - k_3[L'])$ vs [THF]/[L′]. [f] Data obtained from plots of k_{obsd} vs [L′].

Discussion

Table II contains values of the rate constants k_1, k_1k_2/k_{-1}, and k_3 for reactions of the three **2** complexes; for $[Co(CO)_2(THF)NO]$, data were obtained for six L′: PPh_3, $AsPh_3$, $P(OBu)_3$, $P(O\text{-}i\text{-}Pr)_3$, $P(OPh)_3$, and 1-hexene. Plots of $k_{obsd}/[L']$ vs 1/[THF] obeying eq 11, which afforded those data, are illustrated in Figure 8.

For values of k_3 obtained for associative reactions of photogenerated $[Co(CO)_2(THF)NO]$, the rate constants vary for L′ in the order PPh_3 (4.06 (14) × 10^3) > $AsPh_3$ (2.41 (15) × 10^3) ≃ $P(OBu)_3$ (2.36 (15) × 10^3) > $P(O\text{-}i\text{-}Pr)_3$ (1.59 (7) × 10^3) ≫ $P(OPh)_3$ (4.6 (5) × 10^2) ≫ 1-hexene (7 (2) $M^{-1}\ s^{-1}$), respectively. These values vary by some 580-fold and are consistent with an associative mechanism in which there is very considerable bond making in the transition state leading to displacement of THF by L′. A substantial sensitivity of the value of the rate constant for bimolecular attack by L′ at $Co(CO)_3NO$ was also noted by Thorsteinson and Basolo.[2] Activation parameters obtained from k_3 for L′ = PPh_3, $P(O\text{-}i\text{-}Pr)_3$, and $P(OPh)_3$ (Table II) all have entropies of activation in the range −22.7 to −25.0 cal/(deg mol), indicative of an associative process. The enthalpies of activation are in the range 5–7 kcal/mol, with the higher values observed for the slower reactions.

The influences of the steric and electronic properties of incoming L′ coordinating through P on the relative rates of k_3 can be probed through a consideration of the Tolman steric and electronic pa-

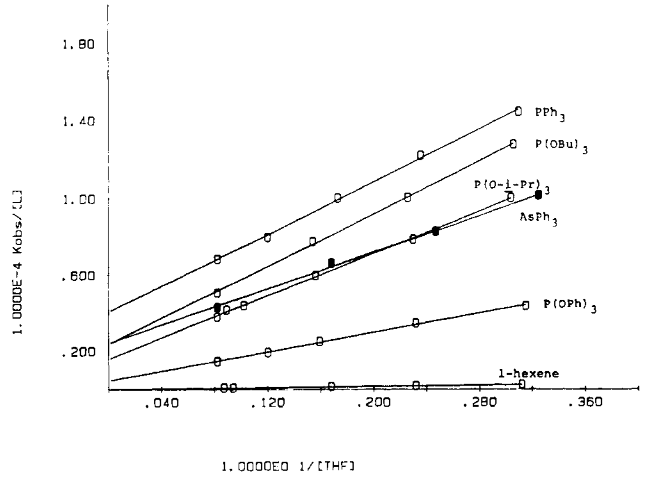

Figure 8. Plots of $k_{obsd}/[L]$ vs $1/[THF]$ for reactions of $[Co(CO)_2(THF)NO]$ with six ligands (L′) in THF/cyclohexane solutions at 25.0 °C.

rameters, θ and ν, respectively.[15] For this purpose the equation developed by Poë and co-workers[16]

$$\log k = a\theta + b\nu + c \qquad (13)$$

is useful. A multiple linear regression to fit k_3, θ, and ν (eq 13) afforded eq 14, for which the correlation coefficient, R, is 0.997.

$$\log k_3 = -0.005498\theta - 0.0632\nu + 135 \qquad (14)$$

This value suggests that the observed rate behavior is well expressed in terms of the Tolman parameters. Separate plots of log k_3 vs ν and vs θ (not illustrated) afford correlation coefficients of 0.899 and 0.206, respectively. The much better fit obtained for ν indicates a dominant electronic influence on k_3. The negative value for the a parameter (eq 14) indicates decreasing rates of nucleophilic attack at **2** with increasing ligand size, while the negative value of the b parameter indicates a decrease in the rate of bimolecular attack at **2** as the electron-withdrawing ability of the nucleophile increases; both trends are expected.

The composite rate constants k_1k_2/k_{-1} afford the relative values of k_2, the rates of bimolecular interaction of L′ at the coordinatively unsaturated $[Co(CO)_2NO]$ intermediate, since k_1/k_{-1} (or K_{eq}) is the ratio of rate constants for dissociation of THF from $[Co(CO)_2(THF)NO]$ and for its association, respectively, and is independent of the identity of L′. Values of k_1k_2/k_{-1} can be obtained from the slopes of eq 4 or 11 or from the reciprocals of the slopes of eq 12. The relative values of k_2 can also be expressed as "competition ratios" of rate constants for attack at $[Co(CO)_2NO]$ by L′ and THF, respectively, k_2/k_{-1}. These ratios can be obtained from k_1k_2/k_{-1} (vide supra) and k_1 (eq 12). The use of competition ratios permits THF to be included in the series of relative rates of attack at $[Co(CO)_2NO]$ by L′. Values of k_2/k_{-1} vary in the order $P(OBu)_3$ (4.7 (5)) ≃ PPh_3 (4.6 (5)) > $P(O\text{-}i\text{-}Pr)_3$ (3.8 (3)) > $AsPh_3$ (3.3 (4)) > $P(OPh)_3$ (1.7 (2)) > THF (1) ≫ 1-hexene (0.11 (1)). This variation, some 43-fold, is much less than that observed for interactions of these L′ with $[Co(CO)_2(THF)NO]$ (eq 10), whose values vary some 580-fold over this same series of ligands.

The variation of competition ratios as a function of L′ is, however, significantly greater than is that observed for attack by various L′ at coordinatively unsaturated intermediates derived from group VIB metal carbonyls and derivatives. Thus, for example, the rates of interaction of $P(O\text{-}i\text{-}Pr)_3$ and 1-hexene with $[PPh_3W(CO)_4]$ (square pyramidal; vacant coordination site cis to PPh_3) are the same, within experimental error,[17] but vary some 35-fold for reaction with $[Co(CO)_2NO]$. These results suggest that the degree of bond making in attaining the transition state for reaction of these species with various L varies as $[PPh_3W(CO)_4]$ ≪ $[Co(CO)_2NO]$ ≪ $[Co(CO)_2(THF)NO]$.

Evaluation of the steric and electronic influences as expressed by Tolman parameters[15] and employing Poë's equation (eq 13) affords

$$\log (k_1k_2/k_{-1}) = -0.006230\theta - 0.0329\nu + 73.5 \qquad (15)$$

for which R = 0.987. Separate plots of log (k_1k_2/k_{-1}) vs ν and vs θ (not illustrated) afforded R values of 0.779 and 0.025, respectively, again suggestive of a dominant electronic influence on k_2. The fit of the former plot, however, is less good than is that for the analogous plot of log k_3 vs ν (R = 0.899; vide supra). This may indicate a less pronounced electronic influence for the dissociative pathway, governed by k_1k_2/k_{-1}, than for the associative pathway, governed by k_3. The ratios a/b[18] (eq 14 and 15) obtained for the associative and dissociative pathways, 0.087 and 0.189, respectively, also are in agreement with this conclusion. As was noted for variations in k_3 and as might be expected, the negative value for the parameter a derived from k_1k_2/k_{-1} indicates decreased rates of nucleophilic attack at $[Co(CO)_2NO]$ with increased ligand size, while the negative value of b indicates a decrease in the rate of bimolecular attack at $[Co(CO)_2NO]$ as the electron-withdrawing ability of the nucleophile increases.

Rates of THF loss from $[Co(CO)(L)(THF)NO]$ intermediates vary as PPh_3 > CO > $P(OPh)_3$, an order that seemingly reflects both the steric and electronic properties of L.

Table II also presents activation parameters derived from k_1k_2/k_{-1} for L′ = PPh_3, $P(O\text{-}i\text{-}Pr)_3$, and $P(OPh)_3$, together with those derived from k_1 for L′ = $P(O\text{-}i\text{-}Pr)_3$. Those based on k_1k_2/k_{-1} were determined from data obeying the rate laws given both in eq 10 and 12. Activation parameters corresponding to the competition ratios, k_2/k_{-1}, indicate that enthalpy barriers increase and entropies of activation become more positive with the decreasing size of L, in the order PPh_3, $P(O\text{-}i\text{-}Pr)_3$, $P(OPh)_3$, and THF.

Of particular interest are the negative entropies of activation derived from both k_1k_2/k_{-1} and k_1, −11 to −15 cal/(deg mol). Those derived from k_1k_2/k_{-1}, $\Delta S_1^{\ddagger} + \Delta S_2^{\ddagger} - \Delta S_{-1}^{\ddagger}$, contain two terms expected to be positive, $\Delta S_1^{\ddagger}$ and $-\Delta S_{-1}^{\ddagger}$, and one expected to be negative, $\Delta S_2^{\ddagger}$, while that derived from k_1, $\Delta S_1^{\ddagger}$, represents a dissociative process. These values are, however, less negative by 10–15 cal/(deg mol) than are those observed for displacement by L′ of THF from $[Co(CO)_2(THF)NO]$ (Table II). The observed negative entropies of activation for predominantly dissociative processes are possibly related to changes in geometry that accompany loss of THF from $[Co(CO)_2(THF)NO]$ or addition of THF or L to $[Co(CO)_2NO]$. Such geometrical changes are not unexpected, for studies of $[Ni(CO)_3]$ indicate it to possess D_{3h} symmetry, or to be nearly a trigonal plane.[19,20] If the same also is true for isoelectronic $[Co(CO)_2NO]$, significant changes in geometry take place both upon dissociation of THF from $[Co(CO)_2(THF)NO]$ and upon associative addition of THF to $[Co(CO)_2NO]$. Such geometrical changes might account for both the observed negative entropies of activation and the selectivity observed for reactions of $[Co(CO)_2NO]$. However, for ligand-

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exchange studies of $Ni(CO)_4$, in which it may be presumed the observed first-order rate constant involves Ni–CO bond fission to afford $[Ni(CO)_3]$, the observed entropy of activation is positive,[21] although those reactions are some 6 orders of magnitude slower than are those reported here.

In contrast, the insensitivity of the rates of reaction of coordinatively unsaturated group VIB metal carbonyls and derivatives to the steric and electronic nature of L, together with evidence which indicates that those reactions take place at rates which approach that of diffusion control,[22] have been interpreted as indicating that the coordinatively unsaturated intermediate is geometrically little changed from its coordinatively saturated counterpart. Indeed, the gas-phase IR spectrum of $[Cr(CO)_5]$ is consistent with this conclusion.[23] It will be of interest to determine volumes of activation corresponding to the rate constants determined in the present study through flash photolysis investigations at various pressures[24] to ascertain if there is a correspondence in the entropy of activation and volume of activation data in these systems and if the latter may be correlated with changes in molecular geometry accompanying coordination of L′ to $[Co(CO)_2NO]$ and dissociation of THF from $[Co(CO)_2(THF)NO]$.

Conclusion

The kinetics results reported here for displacement of the weak nucleophile THF from $Co(CO)_2(THF)NO$ by a variety of Lewis bases indicate that the dissociative pathway is significantly more important than for analogous reactions of $Co(CO)_3NO$. It is reasonable to presume that the displacement of other weak nucleophiles such as N_2,[7] 1-butene,[8] H_2,[9] and 1,3-butadiene from their cobalt dicarbonyl nitrosyl complexes, of great current interest, will be mechanistically similar.

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Registry No. **2** (L = PPh_3), 118141-73-4; **2** (L = CO), 118141-74-5; **2** (L = $P(OPh)_3$), 118141-75-6; THF, 109-99-9; $Co(CO)_3NO$, 14096-82-3; $Co(CO)_2(PPh_3)NO$, 13681-96-4; $Co(CO)_2(P(OPh)_3)NO$, 14406-76-9; $Co(CO)_2(P(O\text{-}i\text{-}Pr)_3)NO$, 21494-34-8; $Co(CO)(P(O\text{-}i\text{-}Pr)_3)_2NO$, 22597-80-4; $Co(CO)(P(O\text{-}i\text{-}Pr)_3)(P(OPh)_3)NO$, 118169-83-8; $Co(CO)(P(O\text{-}i\text{-}Pr)_3)(PPh_3)NO$, 118141-76-7; $P(O\text{-}i\text{-}Pr)_3$, 116-17-6; $P(OPh)_3$, 101-02-0; $P(OBu)_3$, 102-85-2; $AsPh_3$, 603-32-7; PPh_3, 603-35-0; 1-hexene, 592-41-6.

Supplementary Material Available: A listing of rate constants for reactions taking place after flash photolysis of cobalt carbonyl complexes in THF and THF/cyclohexane solutions at various temperatures (Appendix) (6 pages). Ordering information is given on any current masthead page.

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Activation Volumes for Aquation of Chromium(III) Pentaammine Complexes with Neutral Leaving Groups: Comparison with and Mechanistic Differentiation from Cobalt(III) Analogues

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The pressure dependence of the spontaneous aquation of a series of $Cr(NH_3)_5L^{3+}$ complexes with L = formamide, dimethylformamide, urea, *N,N′*-dimethylurea, dimethyl sulfoxide, trimethyl phosphate, and *N,N*-dimethylacetamide has been determined. The temperature dependence of aquation of the series has also been determined. The activation volume (ΔV^*) lies in the limited range −3.2 to −8.7 $cm^3\ mol^{-1}$ and is not related clearly to leaving group size. An approximate correlation between ΔV^* and activation entropy (ΔS^*) exists. The average ΔV^* of ∼−6 $cm^3\ mol^{-1}$ is an estimate of the solvent-independent intrinsic component of ΔV^* for reaction of a chromium(III) complex and is interpreted as being indicative of an associative interchange (I_a) mechanism, contrasting with an average ΔV^* of ∼+2 $cm^3\ mol^{-1}$ in the analogous cobalt(III) series where a dissociative interchange (I_d) mechanism apparently applies. Apparent molar volumes of the series of complexes were determined. The "volume profile" approach applied earlier to the cobalt(III) series yields in the case of the chromium(III) series a different result that supports a mechanistic differentiation between chromium(III) and cobalt(III).

Introduction

Extensive studies of the aquation reactions of pentaammine complexes of cobalt(III) and chromium(III) have appeared over recent decades.[4–7] The generally held view from these studies is that reactions in each system are mechanistically distinct, with a dissociative type reaction favored for cobalt(III) and an associative type reaction favored for chromium(III). A limiting mechanism in either case is not likely, the reactions being distinguished by differing degrees of bond making and bond breaking in the transition state involving the entering and leaving groups. Determinations of activation volumes (ΔV^*) for a range of complexes, mainly with ionic leaving groups, have been reported over the past 2 decades and have largely been interpreted in terms of these disparate mechanisms.[8–15]

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