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Influence of Atomic Size on Mechanism: Displacement of Chelating Ligands Coordinating through Sulfur from Their Chromium and Molybdenum Carbonyl Complexes

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Variable-pressure kinetics studies (to 150 MPa) at various temperatures for chelate ring displacement from *cis*-$(S_2)M(CO)_4$ complexes (S_2 = dithiaalkane, dithiaalkene (2,5-dithiahexane, 3,6-dithiaoctane, and *cis*-2,2,7,7-tetramethyl-3,6-dithiaoct-4-ene); M = Cr, Mo) by L (=Lewis base ($P(OR)_3$, R = Me, Et, *i*-Pr, Ph)) in chlorobenzene (CB) and 1,2-dichloroethane (DCE) have been carried out. All reactions obey the rate law $-d[(S_2)M(CO)_4]/dt = k[(S_2)M(CO)_4][L]$. However, calculated volumes of activation (ΔV^*) and thermal activation parameters (ΔH^*, ΔS^*) indicate that ligand displacement in the Cr complexes takes place via initial, reversible Cr-S bond fission, while for Mo and S_2 = 2,5-dithiahexane and 3,6-dithiaoctane an associative pathway involving significant initial L-Mo bond making is operative. For S_2 = *cis*-2,2,7,7-tetramethyl-3,6-dithiaoct-4-ene and M = Mo, activation parameters (the thermal data were taken over a 70 °C temperature range) are equivocal as to whether the mechanism is best described as an interchange process or in terms of competing dissociative and associative pathways. It is concluded that the mechanistic differences observed in the Cr and Mo systems result from the differing atomic sizes of these metals. The results are also discussed in terms of the properties of the chelating rings.

Introduction

Rate laws for the displacement by Lewis bases (=phosphines, phosphites, L) of chelate rings (S_2) coordinating through sulfur from group VIB metal carbonyl complexes

$$cis\text{-}(S_2)M(CO)_4 + 2L \rightarrow cis\text{-},\ trans\text{-}(L)_2M(CO)_4 + S_2 \qquad (1)$$

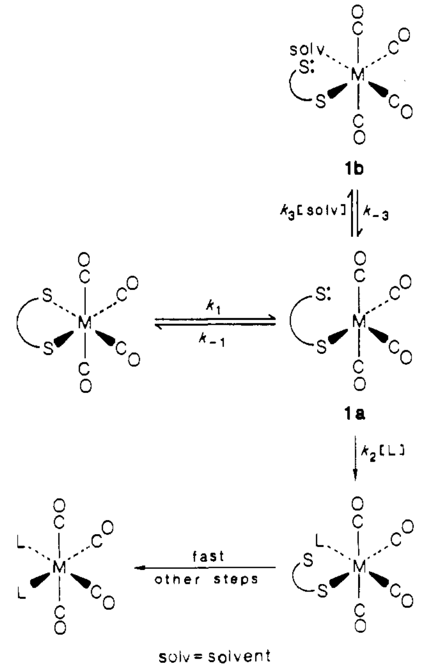
generally fall into two distinct classes. Reactions of S_2 containing flexible backbones and bulky groups such as *tert*-butyl bonded to S obey a rate law

$$-d[(S_2)M(CO)_4]/dt = k_a[(S_2)M(CO)_4][L]/(1 + k_b[L]) \qquad (2)$$

which has been interpreted in terms of a mechanism (eq 3) that involves reversible dissociation of one end of the chelating ligand followed by competitive attack by L at the "ring-opened" intermediate.[5,6] Studies of intermediates (**1b**) generated via pulsed laser flash photolysis have indicated that they are specifically solvated, as is shown in (3),[7] and that competition between chelate ring closure and attack by L, usually competitive processes, probably takes place at a nonsolvated, five-coordinate intermediate (**1a**).[8] For this mechanism, the rate constant k_a in (2) is k_1k_2/k_{-1}, while $k_b = k_2/k_{-1}$. On the other hand, chelating ligands that contain rigid backbones (four-membered rings or five-membered rings containing an olefinic backbone) or those with flexible backbones and small substituents bonded to sulfur (methyl or ethyl groups) obey rate law 4, which may be interpreted in terms either

$$-d[(S_2)M(CO)_4]/dt = k_c[(S_2)M(CO)_4][L] \qquad (4)$$

of a limiting form of (2) in which $k_b[L] \ll 1$ or of a mechanism in which nucleophilic attack by L promotes ring-opening (eq 5).[9-12]



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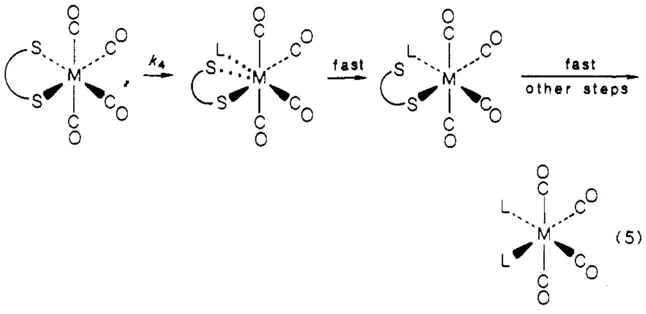

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Entropies of activation have been employed in order to attempt to distinguish between the limiting form of mechanism 3 and mechanism 5 in cases where rate law 4 is observed. Thus, for example, while reactions of $(DTH)M(CO)_4$ (DTH = 2,5-dithiahexane; M = Cr, Mo) with L proceed according to (1) and obey

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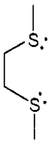
rate law 4, entropies of activation are slightly positive for M = Cr, but are highly negative for M = Mo. These observations were interpreted as indicative of a dissociative mechanism (eq 3) operative in the Cr systems, but an associative mechanism (eq 5) for M = Mo.[10] In several other such systems entropies of activation are close to zero, and the implications with regard to the mechanism responsible for these values were equivocal although they were generally interpreted in terms of a dissociative mechanism.[9,11,12]

There is much evidence that volumes of activation may be a better indicator of mechanism than entropies of activation are in ligand-exchange reactions involving octahedral complexes, particularly where the latter are not too different from zero.[13] Recently, in a preliminary study, volumes of activation for chelate ring displacement by L from $(S_2)Cr(CO)_4$ complexes (S_2 = 3,6-dithiaoctane (dto) and *cis*-2,2,7,7-tetramethyl-3,6-dithiaoct-4-ene (BTE)[7a]) were found to support the dissociative mechanism (eq 3).[14] All these observations prompted a much more extensive investigation of volumes of activation and entropies of activation (where not reported previously) for a number of systems obeying rate law 4, in order to cast additional interpretive light on the mechanism of chelate ring displacement, particularly as a function of the identity of the metal atom. Reported here are studies of ligand exchange for several *cis*-$(S_2)M(CO)_4$ complexes, in which M = Cr, Mo and (S_2) = DTH (**2a**), dto (**2b**), and BTE (**2c**).



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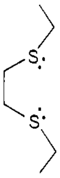

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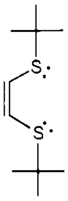

2c

Experimental Section

General Information. Infrared spectra were recorded by employing a Perkin-Elmer Model 621 spectrophotometer. Chemical analyses were carried out by Midwest Microlabs, Inc., Indianapolis, IN.

Materials. The ligand dto was obtained from Chemical Procurement Laboratories, while the synthesis of BTE was that reported in the literature.[11,15] The solvents chlorobenzene (CB) and 1,2-dichloroethane (DCE) were fractionally distilled from P_4O_{10}. The ligands, $P(OMe)_3$, $P(OEt)_3$, $P(O\text{-}i\text{-}Pr)_3$, and $P(OPh)_3$ were purified by fractional distillation from Na under a N_2 bleed at low pressure. Both of the pale yellow Mo complexes $(dto)Mo(CO)_4$ and $(BTE)Mo(CO)_4$ were synthesized and purified as described for a related complex;[5] the carbonyl stretching spectrum for $(dto)Mo(CO)_4$ is as previously reported.[16] Anal. Calcd for $C_{10}H_{14}O_4S_2Mo$ ($(dto)Mo(CO)_4$): C, 33.51; H, 3.94. Found, C, 33.77; H, 4.23. Calcd for $C_{14}H_{20}O_4S_2Mo$ ($(BTE)Mo(CO)_4$): C, 40.48; H, 4.89; Found, C, 40.03; H, 4.89. Carbonyl stretching spectrum ($CHCl_3$ solution): 2028 (ms), 1923 (vs), 1904 (s), 1870 (s) cm^{-1}. The other complexes, $(DTH)M(CO)_4$ (M = Cr, Mo),[10] $(BTE)Cr(CO)_4$,[11] and $(dto)Cr(CO)_4$)[12] were either some of those synthesized in earlier studies or were synthesized via those methods. The reaction products, *cis-* and *trans*-$(L)_2M(CO)_4$ (M = Cr, Mo), reported previously in a related study,[10] were identified via their carbonyl stretching spectra.

Kinetics runs at ambient pressure and various temperatures were carried out at the University of North Texas by employing a Beckman DU-2 direct-reading spectrophotometer and employed standard procedures that have been described previously.[10] Temperature was controlled to ±0.05 °C by employing a Haake Model ED constant-temperature circulator. Observation wavelengths ranged from 390 to 425 nm; at the lower wavelengths, ca. 25 mg of complex was used in 50 mL of solvent; at 425 nm, approximately 80 mg/50 mL was employed. At the wavelengths monitored, absorbances due to the reaction products were negligible, and absorbances of solvent–ligand blanks (A_{bl}) could be substituted for A_∞ values (absorbances at infinite time). At higher temperatures, removal of the reaction solution from the constant-temperature bath quenched the reaction. At lower temperatures, the time required to effect the determination of the absorbance was negligible compared to the time interval between points. For all reactions, pseudo-first-order conditions obtained through use of at least a 20-fold excess of L and plots of $\ln (A_t - A_{bl})$ vs time (A_t is the absorbance at time t), linear to >80% of the completion of the reaction, afforded values of the pseudo-first-order rate constants, k_{obsd}.

The variable-pressure studies, carried out at the University of Witten/Herdecke, employed a Zeiss PMQII spectrophotometer operating in the double-beam mode and equipped with a previously described,[17] thermostated (±0.1 °C) high-pressure cell. Since the cell was continuously exposed to the analyzing light, separate runs at ambient pressure in which the reaction solutions were exposed to the analyzing light only while absorbances were being measured were also carried out. No significant differences in rate were observed. Reaction solutions were prepared in a manner similar to those employed for the ambient-pressure reactions, and the same wavelengths were monitored. Pressures were varied from 0.1 to 150 MPa (ca. 1–1500 atm), and volumes of activation were calculated by employing the relationship

$$(\partial \ln k/\partial P)_T = -\Delta V^\ddagger/RT \qquad (6)$$

Thus, plots of $\ln k_{obsd}$ vs pressure were linear, and volumes of activation were determined from their slopes.

Rate and activation data were analyzed by employing a linear least-squares computer program. The limits of error given in parentheses are the uncertainty of the last cited digit in the experimental value to one standard deviation. Values for all pseudo-first-order rate constants, k_{obsd}, are presented in Appendix 1 (supplementary material).

Results and Discussion

Kinetics data obtained for $(dto)Mo(CO)_4$ and $(BTE)Mo(CO)_4$ at ambient pressure at various temperatures and for $(DTH)M(CO)_4$, $(dto)M(CO)_4$, and $(BTE)M(CO)_4$ (M = Cr, Mo) at various pressures and at various temperatures, all in chlorobenzene or 1,2-dichloroethane, obeyed rate law 4, suggestive, as discussed in the introduction, of two possible mechanisms. The observed second-order rate constants for these reactions are given in Table I. Table II lists the Eyring activation parameters together with volumes of activation for reactions of all six complexes with various L in CB or DCE.

The ranges of values observed for the entropies of activation may be grouped as a function of the metal atom for all complexes. For Cr, they are positive or very slightly negative, suggestive, as discussed in the Introduction, of mechanism 3, for which k_a (rate law 2) is k_1k_2/k_{-1} and $\Delta S_a^\ddagger$ therefore would be $\Delta S_1^\ddagger + \Delta S_2^\ddagger - \Delta S_{-1}^\ddagger$. Thus, the observed entropy of activation might be expected to be slightly positive, with $\Delta S_1^\ddagger$ quite positive, $\Delta S_2^\ddagger$ quite negative, and $\Delta S_{-1}^\ddagger$, which involves unimolecular chelate ring closure and a decrease in the number of rotational degrees of freedom in the molecular backbone[18] in S_2 (a smaller decrease for BTE than for DTH and dto), somewhat negative. On the basis of these expectations, $\Delta S_a^\ddagger$ is expected to be most negative for BTE, as is observed.

For Mo, observed values of $\Delta S^\ddagger$ are all quite negative, indicative of associative or interchange pathways in which $k_c = k_4$ (rate law 4; mechanism 5).

The volumes of activation for these systems are more unequivocal in the assignment of mechanism than are the corresponding entropies of activation. For M = Cr, they all fall in the range +9.3 to +14.7 $cm^3 \, mol^{-1}$, indicative of a larger transition state than ground state, consistent with the ring-opening mechanism (3), where $k_a = k_1k_2/k_{-1}$, and $\Delta V_a^\ddagger = \Delta V_1^\ddagger + \Delta V_2^\ddagger - \Delta V_{-1}^\ddagger$ (rate law 2). In this expression, $\Delta V_{-1}^\ddagger$ and $\Delta V_2^\ddagger$ represent bond formation, most probably at an unsolvated five-coordinate intermediate (vide supra).

There is strong evidence that very little bond formation takes place in attaining the transition state for ligand addition in coordinatively unsaturated species derived from octahedral metal

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Table I. Second-Order Rate Constants for Reactions of $(S_2)M(CO)_4$ Complexes (M = Cr, Mo) with Phosphites (L) in DCE and CB at Various Temperatures and Pressures

S_2	M	solvent	L	P, MPa	T, °C	10^3k, M^{-1} s^{-1}
DTH	Cr	DCE	$P(OMe)_3$	5	60.0	4.02 (13)
				25		3.62 (6)
				50		3.39 (9)
				75		3.14 (4)
				100		2.72 (11)
	Mo			5	40.0	2.42 (6)
				25		2.80 (8)
				50		3.00 (8)
				75		3.41 (16)
				100		3.74 (19)
	Cr	CB		5	50.0	1.49 (4)
				25		1.38 (4)
				50		1.31 (5)
				75		1.18 (4)
				100		1.085 (16)
		DCE	$P(O\text{-}i\text{-}Pr)_3$	5	60.0	2.10 (6)
				25		1.89 (1)[a]
				50		1.73 (1)[a]
				75		1.58 (3)[a]
				100		1.444 (5)[a]
				125		1.321 (5)[a]
DTH	Mo	DCE	$P(O\text{-}i\text{-}Pr)_3$	5	50.0	3.85 (8)
				25		4.08 (10)
				50		4.47 (5)
				75		4.77 (4)
				100		5.02 (11)
				125		5.19 (7)
	Cr		$P(OPh)_3$	5	55.5	0.899 (16)
				25		0.837 (13)
				50		0.792 (18)
				75		0.703 (17)
				100		0.646 (4)
	Mo			5	40.0	1.52 (3)
				25		1.64 (1)
				50		1.80 (1)
				75		1.96 (6)
				100		2.14 (3)
dto			$P(O\text{-}i\text{-}Pr)_3$	5	34.0	0.373 (5)
					40.0	0.672 (4)
					46.0	1.125 (8)
				50		1.311 (3)
				100		1.597 (8)
				150		1.882 (4)
				5	50.0	1.707 (8)
dto	Mo	DCE	$P(O\text{-}i\text{-}Pr)_3$	0.1	36.0	0.683 (7)
					46.0	1.85 (5)
					56.2	4.10 (7)
BTE					11.9	0.01088 (11)
					21.9	0.0462 (6)
					27.8	0.077 (2)
					35.1	0.232 (6)
					36.0	0.206 (4)
					44.5	0.617 (17)
					46.0	0.627 (15)
					49.9	1.18 (4)
					56.0	1.95 (14)
				5		2.173 (16)
				50		2.054 (9)
				100		1.88 (2)
				150		1.78 (3)
				0.1	60.8	3.56 (12)
					70.0	11.3 (6)
					80.0	26.7 (12)[b]

[a] Average deviation. [b] One standard deviation of data for one value of k_{obsd}.

Table II. Activation Parameters and Volumes of Activation for Ligand-Displacement Reactions of $(S_2)M(CO)_4$ Complexes

S_2	M	solvent	L	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta V^{\ddagger}$, cm^3/mol
DTH	Cr	DCE	$P(OMe)_3$	24.7 (3)[a]	4.9 (8)	10.1 (8)
		CB		23.1 (12)[a]	0 (4)[a]	8.8 (4)
		DCE	$P(OPh)_3$	24.6 (1)[b]	2 (3)[b]	9.3 (5)
			$P(O\text{-}i\text{-}Pr)_3$	23.8 (5)[b]	0 (2)[b]	10.4 (4)
	Mo		$P(OMe)_3$	17.1 (2)[a]	−13.6 (8)[a]	−11.3 (5)
		CB		17.3 (15)[a]	−14 (5)[a]	
		DCE	$P(O\text{-}i\text{-}Pr)_3$	18.8 (3)[a]	−12.8 (9)[a]	−10.2 (8)
				15.9 (3)[b]	−20.5 (9)[b]	
			$P(OPh)_3$	16.3 (5)[b]	−19.9 (15)[b]	−9.3 (4)
dto	Cr	DCE	$P(OEt)_3$	29.6 (14)[c]	18.1 (44)[c]	14.7 (7)[d]
	Mo	CB	$P(O\text{-}i\text{-}Pr)_3$	17.3 (6)	−16.5 (18)	−9.4 (2)
				17.9 (4)[e]	−15.7 (12)[e]	
BTE	Cr	DCE	$P(OEt)_3$	22.1 (14)[f]	−2.0 (45)	14.0 (6)[d]
	Mo		$P(O\text{-}i\text{-}Pr)_3$	20.8 (2)	−7.5 (5)	3.9 (3)

[a] Schneider, K.; van Eldik, R. Unpublished results. [b] Reference 10. [c] Reference 12. [d] Reference 14. [e] Determined at 5 MPa (this work). [f] Reference 11.

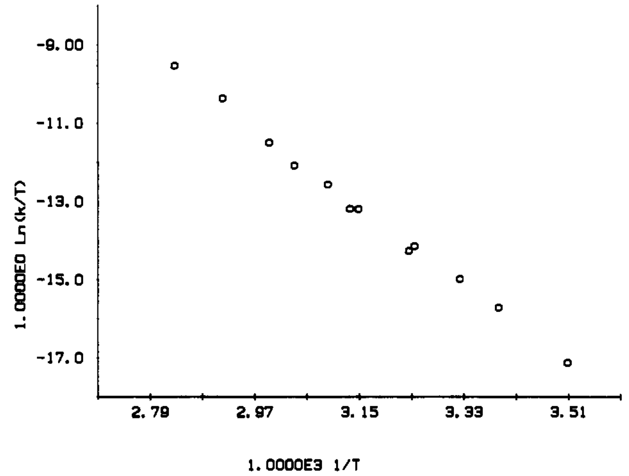

Figure 1. Eyring plot (12–80 °C) for the reaction of $(BTE)Mo(CO)_4$ with triisopropyl phosphite in DCE.

carbonyls. It has been well documented, for example, both in the gas phase and in solution, that the rates of combination of such species as $[Cr(CO)_5]$ with nucleophiles approach that expected for a gas kinetic reaction cross section[19] or for the rate under diffusion control.[20] The lack of discriminating ability observed for species such as $[LW(CO)_4]$ (L = phosphines, phosphites) for a wide variety of nucleophiles that differ dramatically in the strengths of the bonds they form to W, e.g., piperidine and chlorobenzene,[8] also supports a transition state in which there is little metal–L interaction. Thus, according to Hammond's postulate[21] there should be very little molecular rearrangement in attaining the transition state during bond formation, and as a consequence, $\Delta V_{-1}^{\ddagger}$ and $\Delta V_2^{\ddagger}$ should be quite small. Moreover, since these terms are of opposite sign in the expression for $\Delta V_a^{\ddagger}$, their influences on $\Delta V_a^{\ddagger}$ should be minimal, and $\Delta V_1^{\ddagger}$ should be by far the predominant contributor to $\Delta V_a^{\ddagger}$.

For M = Mo, the observed values of $\Delta V^{\ddagger}$ are all quite negative, indicative of an associative process, save for $(BTE)Mo(CO)_4$, where it is slightly positive. These results are consistent with those observed for the entropies of activation, for which that for $(BTE)Mo(CO)_4$ is less negative than are those for the other complexes. This observation raised the possibility that both the dissociative (eq 3) and associative (eq 5) mechanisms or, alternatively, that an interchange pathway involving a later transition state for the associative pathway might be operative. For competing mechanisms, a curved plot of ln (k/T) vs. $1/T$, concave upward,[22-24] is to be expected. Kinetics studies of the reaction

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of $(BTE)Mo(CO)_4$ with $P(O\text{-}i\text{-}Pr)_3$ in CB thus were carried out over the temperature range 12–80 °C. The Eyring plot for these data, shown in Figure 1, perhaps shows slight curvature in the expected direction,[25] but the "later transition state" interchange pathway is by no means ruled out. The accessibility of a later transition state in $(BTE)Mo(CO)_4$ is not unreasonable given that the bulky *tert*-butyl groups bonded to S are expected to accelerate Mo–S bond breaking as can be seen in the relative rates of chelate ring displacement in analogous DTH (methyls bonded to S) and DTO (=2,2,7,7-tetramethyl-3,6-dithiaoctane; *tert*-butyl groups bonded to S) complexes of Cr and Mo.[5,10]

On the basis of both entropy and activation and volume of activation data, it may nonetheless be concluded that displacement by phosphites of S_2 ligands forming chelating rings from their $(S_2)M(CO)_4$ complexes takes place by significantly different mechanistic pathways for Cr vs Mo. The differences may result from the larger covalent radius for Mo (by ca. 0.15 Å) than for Cr in such complexes.[26] The smaller radius of Cr should be expected to promote steric acceleration of Cr–S bond breaking under the influence of the sulfur-containing moiety cis to the bond being broken. In this regard, it is known that rates of W–pip bond fission (pip = piperidine) in *cis*-$(pip)(L)W(CO)_4$ complexes increase with the increasing Tolman cone angle[27] of L.[8] Based on the cone angle concept one can readily determine how that angle[28] will change with an increasing M–L distance. For triisopropyl phosphite, with a cone angle of 130°, this value will decrease approximately 3° from Cr to Mo based upon the P–M bond lengths of 2.364 and 2.506 Å observed in $M(CO)_5P(CH_2CH_2CN)_3$ (cone angle = 132°; M = Cr, Mo)[26] respectively. It is also to be anticipated that for the larger Mo atom an interchange pathway will be facilitated relative to Cr.

Although both entropy of activation and volume of activation data support a mechanism for chelate ring displacement which involves significant Mo–L bond making in the transition state, there are not large effects on rate noted as a function of the identity of L. This may be because the Mo–L bond strenths of the L ligands that have been investigated do not differ by a great deal. Thus, for example, the rates of Cr–L bond dissociation in $LCr(CO)_5$ and *trans*-$(L)_2Cr(CO)_4$ complexes increase only 30–40-fold from L = $P(OMe)_3$ to L = $P(OPh)_3$.[29] The results do suggest, however, an "early transition state" for interchange in the Mo complexes.

There are a number of parallels to the kinetics behavior observed here which have been reported in the literature for other transition-metal systems. It is generally observed that volumes of activation for solvent-exchange processes increase across the first transition series as ionic radii decrease and the exchange mechanism changes from an associative to a dissociative interchange mechanism.[30] It also recently has been noted that a change from a dissociative to an associative mechanism takes place for complex formation reactions of Zn^{2+} and Cd^{2+}, that is, from a smaller to a larger metal center.[31]

In light of the results reported here, also, the ligand exchange in *cis*-$(py)_2Mo(CO)_4$, $(py)Mo(CO)_5$, and $(4\text{-}Mepy)Mo(CO)_5$ (py = pyridine) is best described as a dissociatively activated interchange since values of $\Delta V^{\ddagger}$ range from 0 to +4 cm^3 mol^{-1}.[32] On the other hand, the accessibility of associative ligand exchange at Mo is supported by recent data for the 1:1 NCS^- anation reaction of $Mo(H_2O)_6{}^{3+}$, for which $\Delta V^{\ddagger}$ was determined to be −11.4 (5) cm^3 mol^{-1}.[33]

As the discussion above indicates, ligand-replacement reactions of the Cr and Mo complexes, respectively, of DTH and dto are mechanistically similar. An examination of the corresponding values of $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ for these reactions (Table II) shows that the correlation between $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ is one in which a zero value of $\Delta S^{\ddagger}$ corresponds to a positive volume of activation. Thus these data indicate that "an equivalent extent of disorder in the transition state relative to the ground state" does not necessarily correspond to "no differences in volume between the ground state and the transition state". Thus, a more conclusive mechanistic interpretation of these reactions can be obtained through parallel thermal and pressure studies than through either method alone.

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Supplementary Material Available: Appendix 1, listing values of the pseudo-first-order rate constants, k_{obsd}, for reactions of $(DTH)M(CO)_4$, $(dto)M(CO)_4$, and $(BTE)M(CO)_4$ (M = Cr, Mo) with various phosphites (L) (=$P(OMe)_3$, $P(OEt)_3$, $P(O\text{-}i\text{-}Pr)_3$, $P(OPh)_3$) in CB and DCE at various temperatures and pressures (10 pages). Ordering information is given on any current masthead page.

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(22) For competitive dissociative and associative reactions ($\Delta G^{\ddagger}$'s similar), the rate constant for the reaction with the larger $\Delta H^{\ddagger}$, that is, the one with the more positive $\Delta S^{\ddagger}$, the dissociative pathway, should increase more rapidly with temperature.

(23) While plots of ln k vs pressure also should curve for two competitive pathways, this curvature will probably be negligible over the pressure range accessible here, which results in changes of k_{obsd} of less than a factor of 2. Thus the temperature dependence of k is more suitable to diagnose the presence of two competitive pathways.

(24) See, e.g.: Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 121–123.

(25) Separate plots of data taken at the extremes of the plot exhibited in Figure 1, from 11.9 to 36.0 °C and from 56.0 to 80.0 °C afford $\Delta H^{\ddagger}$ = 21.8 (12) kcal/mol and $\Delta S^{\ddagger}$ = −5.7 (33) cal/(deg mol) for the former and $\Delta H^{\ddagger}$ = 24.8 (11) kcal/mol and $\Delta S^{\ddagger}$ = 5.1 (32) cal/(deg mol) for the latter. These values suggest that over the entire temperature range the plot may be slightly concave upward, as would be expected for competitive dissociative and associative reaction pathways.

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