thioether ligand due to its rigid endodentate conformation. Our result highlights the important relationship between the preferred conformation of thioether ligands and their coordination behavior.

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## Chelate Ring Closure in (*o*-Phenanthroline)$M(CO)_5$ Transients (M = Cr, Mo, W) Generated by Pulsed Laser Flash Photolysis

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Chelate ring closure in $(\eta^1\text{-bid})M(CO)_5$ complexes (bid = bidentate, potentially chelating ligand; M = Cr, Mo, W; eq 1)

$$(\eta^1\text{-bid})M(CO)_5 \rightarrow (\eta^2\text{-bid})M(CO)_4 + CO \qquad (1)$$

has been studied both for systems in which $(\eta^1\text{-bid})M(CO)_5$ can be isolated[2] and for systems where such species can be produced in situ and have sufficient lifetimes (>s) that they can be probed via diode array UV-visible[3,4] or rapid-scan FTIR[5] spectrophotometry. More recently, where the presence of rigid bidentate ligands afford yet more reactive $(\text{bid})M(CO)_5$ species in which bid is formally monodentate, they have been produced via pulsed laser flash photolysis and studied on the microsecond to millisecond time scales. Thus, Oishi[6] and Kalyanasundaram[7] have investigated chelate ring closure in $(\text{phen})M(CO)_5$ (phen = *o*-phenanthroline), while Zhang and Dobson have studied this process for conversion of $(\text{NBD})Mo(CO)_5$ to $(\text{NBD})Mo(CO)_4$ (NBD = norbornadiene).[8] In the studies of Oishi[6] and Zhang and Dobson,[8] evidence was presented that supports significant interaction between the noncoordinated functional group of the rigid bidentate ligand and the $M(CO)_5$ moiety prior to extrusion of CO through chelate ring closure.

The present investigation further probes possible interactions of this type in $(\text{phen})M(CO)_5$ produced in situ after pulsed laser flash photolysis through determination of thermal activation parameters and volumes of activation accompanying chelate ring closure (eq 1); these data provide related but complementary information about the ring-closure process. The previously unreported rates of chelate ring closure in $(\text{phen})Cr(CO)_5$ have also been obtained.

## Experimental Section

**Materials.** $Cr(CO)_6$ and $W(CO)_6$ (Pressure Chemical Co.) and $Mo(CO)_6$ (Climax Molybdenum Co.) were vacuum-sublimed before use. Fluorobenzene (Aldrich Chemical Co.) was fractionally distilled from $P_4O_{10}$ under nitrogen. *o*-Phenanthroline (Aldrich) was used as obtained.

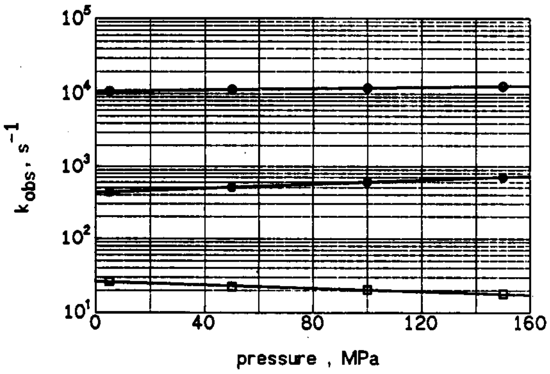

**Figure 1.** Plots of log $k_{obsd}$ vs pressure for ring-closure reactions taking place after pulsed laser flash photolysis of $M(CO)_6$/fluorobenzene/*o*-phenanthroline (=0.05 M) solutions at 25.00 (5) °C. Top to bottom: M = Mo, W, Cr.

**Kinetics Studies.** The pulsed laser flash photolysis studies were carried out by employing a Lumonics TE-430 excimer laser ($Xe/F_2/He$ gas mixture at 351 nm, 25-mJ maximum energy, and 14-ns fwhi per pulse). Other details of the flash photolysis apparatus have been given elsewhere.[9] For studies at ambient pressure, a jacketted quartz cuvette was employed. The equipment for the variable-pressure studies (to 150 MPa), which employed a quartz "pillbox" observation cell,[10] also has been described previously.[11,12] Since it has been shown that benzene, the solvent employed in the previous studies,[6,7] freezes at ambient temperature at pressures >80 MPa,[13] fluorobenzene (FB) was employed as the solvent in this investigation. The kinetics and mechanism of the reaction steps (eq 2) that generate $(L)M(CO)_5$ after flash photolysis of $M(CO)_6/L/FB$ solutions have been studied in detail for several L (=1-hexene, piperidine, pyridine) both at ambient pressure[14] and at variable pressures to 150 MPa.[15] Consequently, these steps, through which $(\text{phen})M(CO)_5$ species are generated in situ on the microsecond time scale, are not further discussed here.

$$M(CO)_6 \xrightarrow{h\nu} [M(CO)_5] \xrightarrow{+FB} (FB)M(CO)_5 \xrightarrow{+L} LM(CO)_5 + FB \qquad (2)$$

Solutions ca. $3 \times 10^{-3}$ M in $M(CO)_6$ containing large excesses (>0.05 M) of phen were employed so that pseudo-first-order reaction conditions obtained. The monitoring wavelengths for formation of $(\text{phen})M(CO)_4$ from $(\text{phen})M(CO)_5$ according to eq 1 were 500-520 nm, as reported previously.[6,7] Values of the pseudo-first-order rate constants, $k_{obsd}$, were determined from data of 1-10 kinetics traces, depending on the observed signal-to-noise ratio. Data were analyzed by employing Asyst-based computer programs developed in-house. The limits of error, given in parentheses as the uncertainties of the last digit(s) of the experimental values, are one standard deviation.

## Results and Discussion

Plots of ln $(A_\infty - A_t)$ vs time ($A_\infty$ and $A_t$ are the absorbances at infinite time and time *t*, respectively) at various temperatures are linear, consistent with pseudo-first-order kinetics behavior. The changes in absorbance are attributable to the formation of $(\text{phen})M(CO)_4$ from $(\text{phen})M(CO)_5$ via chelate ring closure.[6,7] Values of the pseudo-first-order rate constants, $k_{obsd}$, were obtained from the slopes of these plots. Data for four or five concentrations over a 2.5-5-fold concentration range, depending upon M, demonstrated that the rates for chelate ring closure are independent of [phen]. Thus the data obey the rate law

$$-d[(\text{phen})M(CO)_5]/dt = k[(\text{phen})M(CO)_5] \qquad (3)$$

where *k* are first-order rate constants for chelate ring closure. The rate data are in reasonable agreement with those of the previous studies,[6,7] despite use of fluorobenzene rather than benzene as

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**Table I.** Rate Constants and Activation Parameters for Chelate Ring Closure in (*o*-Phenanthroline)M(CO)$_5$ Complexes (M = Cr, Mo, W)

| M | $T$, °C | $P$, MPa | $10^{-2}k$, s$^{-1}$ | $\Delta H^\ddagger$, kcal/mol | $\Delta S^\ddagger$, cal/(deg mol) | $\Delta V^\ddagger$, cm$^3$/mol |
|---|---|---|---|---|---|---|
| Cr | 15.0 | 0.1 | 0.114 (7) | 12.5 (4) | −10.1 (14) | +6.2 (5) |
| | 25.0 | 0.1 | 0.269 (5) | | | |
| | | 5.0 | 0.265 (2) | | | |
| | | 50.0 | 0.225 (2) | | | |
| | | 100.0 | 0.221 (3) | | | |
| | | 150.0 | 0.181 (2) | | | |
| | 34.5 | 0.1 | 0.53 (2) | | | |
| | 43.1 | 0.1 | 0.86 (3) | | | |
| Mo | 5.0 | 0.1 | 25.5 (1) | 11.2 (4) | −2.2 (16) | −2.87 (2) |
| | 10.0 | 0.1 | 43.2 (4) | | | |
| | 15.0 | 0.1 | 58.4 (5) | | | |
| | 25.0 | 0.1 | 115 (7) | | | |
| | | 5.0 | 104 (2) | | | |
| | | 50.0 | 114 (2) | | | |
| | | 100.0 | 121 (1) | | | |
| | | 150.0 | 128 (1) | | | |
| | 30.0 | 0.1 | 155 (6) | | | |
| W | 5.0 | 0.1 | 0.79 (3) | 12.3 (4) | −5.5 (12) | −8.2 (2) |
| | 15.0 | 0.1 | 1.92 (1) | | | |
| | 25.0 | 0.1 | 4.32 (6) | | | |
| | | 5.0 | 4.37 (8) | | | |
| | | 50.0 | 5.10 (6) | | | |
| W | | 100.0 | 6.06 (11) | | | |
| | | 150.0 | 7.04 (25) | | | |
| | 34.5 | 0.1 | 7.24 (16) | | | |
| | 43.1 | 0.1 | 13.62 (4) | | | |

solvent, suggesting solvent effects to be relatively unimportant. Rate constants as a function of pressure were also determined, from plots of ln $k_{obsd}$ vs pressure,[16] the slopes of which are $-\Delta V^\ddagger/RT$; these plots are shown in Figure 1. Rate constants ($k$), thermal activation parameters determined from data taken at four or five temperatures, and volumes of activation determined at 25.0 °C over a pressure range of 5–150 MPa are presented in Table I.

As discussed by Oishi,[6] the differences in the observed rates, which vary in the order Mo ≫ W > Cr, may be contrasted to those observed for dissociation of CO from the metal hexacarbonyls themselves, which vary in the order Mo ≫ Cr ≫ W.[17] This difference in order of reactivity as a function of M will be discussed later. The rate of ring closure in (phen)Cr(CO)$_5$, for which Oishi gave a limit of <10 s$^{-1}$ at 24 (1) °C,[6] was determined to be 26.9 (5) s$^{-1}$ at 25.00 (5) °C.

The observed variations in rate as a function of M are attributable to differences in both the enthalpies and entropies of activation for chelate ring closure, although the former vary little for the three metals, falling within the range of 11.2 (4)–12.5 (4) kcal/mol; the latter are in the range −2.2 (16) to −10.1 (14) cal/(deg mol). The observed entropies of activation are quite consistent with interchange processes for CO extrusion from (phen)M(CO)$_5$ upon chelate ring closure. As was observed in ($\eta^2$-NBD)Mo(CO)$_5$, the rates of chelate ring closure for the rigid phen ring are much faster than are those observed for "nonrigid" chelating ligands such as 2,2′-bipyridyl (bpy; >3 orders of magnitude)[4,7] and ethylenediamine (en; 8–9 orders of magnitude).[18] A comparison of activation parameters for analogous phen and bpy ring closure (M = W) indicates that $\Delta H^\ddagger$ is some 7 kcal/mol less and $\Delta S^\ddagger$ some 10 cal/(deg mol) more negative for ring closure in the former, also strongly supporting an associative ring-closure pathway for phen.

Comparisons of entropies of activation and volumes of activation for the ring-closure process are more revealing. For M = Mo and W, these values are negative, supporting the interchange mechanism, as discussed above. For M = Cr, however, $\Delta S^\ddagger$ is −10.1 (24) cal/(deg mol), which may be contrasted to the volume of activation, +6.2 (5) cm$^3$/mol. The negative entropy of activation suggests significantly greater steric congestion in the transition state relative to the ground state of Cr, while the positive volume of activation indicates a greater molar volume in the transition state relative to the ground state. The latter could arise from steric congestion around the smaller Cr atom as a consequence of more Cr–CO bond lengthening than Cr–N bond shortening as the rigid chelating ring adjusts into the transition state; intramolecular rearrangement in attaining the transition state is significantly different for Cr than for Mo and W. Oishi has suggested that an observed increase in the d–d transition noted for (phen)Cr(CO)$_5$ relative to nonrigid (bpy)Cr(CO)$_5$ may result from octahedral-wedge or pentagonal-bipyramidal distortion in (phen)Cr(CO)$_5$.[6] The influence of ring rigidity on the carbonyl stretching spectrum of ($\eta^2$-norbornene)Mo(CO)$_4$, attributed to weakened $\pi$-bonding of norbornene to Mo as a consequence of steric interaction of the metal and ligand, has also been noted.[8] It should be mentioned that the differences in the Cr vs Mo and W systems also are reflected in the slower rates of chelate ring closure noted for Cr relative to Mo and W (vide supra). The evidence thus would seem to support both significant $\eta^2$-phen–M and M–CO(axial) bonding in the ground states, which thus can best be described in terms of 7-coordinate, 20-electron intermediates, geometrically different for Cr vs Mo and W. If these interpretations are correct, rapid ring closure in (che)M(CO)$_5$ complexes containing rigid chelating ligands arises not so much from a "high local concentration" of the "free" end of the potentially chelating ligand[19] but as the result of intramolecular interactions engendered by the rigid ligand, which significantly raise the ground-state energies of the complexes. Thermal and pressure activation data, sensitive to different aspects of the activation process, are complementary and can offer unique insight into the nature of the activation process.

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