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Solid-State Structure and Reactivity in Solution. 4.[1] Structure and Reactivity via Chelate Ring Displacement for (*cis*-1,2-Bis(*tert*-butylthio)ethylene)tetracarbonylchromium(0)

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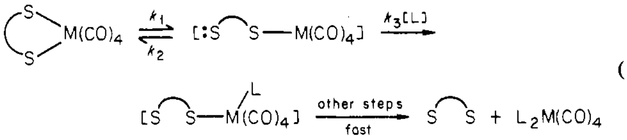
(*cis*-1,2-Bis(*tert*-butylthio)ethylene)tetracarbonylchromium(0) ((BTE)Cr(CO)$_4$) has been synthesized, its structure has been determined by X-ray crystallographic methods, and the kinetics and mechanism of the displacement of BTE by P(OR)$_3$ (=L; R = C_2H_5, $CH(CH_3)_2$) in 1,2-dichloroethane (DCE) to afford $L_2Cr(CO)_4$ complexes have been investigated. Crystals of (BTE)Cr(CO)$_4$ are monoclinic, with a = 14.098 (6) Å, b = 8.960 (4) Å, c = 15.221 (8) Å, β = 112.73 (4)°, space group $P2_1/n$, and d(calcd, Z = 4) = 1.38 g cm^{-3}. The structure was solved by the Patterson method and refined by full-matrix least-squares methods to R = 0.024 using 2726 reflections measured on a four-circle diffractometer with Mo Kα radiation. The coordination about the central Cr atom is a distorted octahedron with a S1–Cr–S2 angle of 83.94 (3)°. The deviation of the Cr atom from the basal plane formed by S1, S2, C3, and C4 is 0.122 Å. Kinetics data indicate that (BTE)Cr(CO)$_4$ reacts with L via a mechanism involving reversible dissociation of one end of the BTE ligand followed by competition for the five-coordinate intermediate thus formed between ring reclosure and attack by L and other, rapid, steps. The rate of ring reclosure is much greater than the rate of attack by L. The structure of (BTE)Cr(CO)$_4$ and the kinetics data are compared to those for other closely related systems.

Introduction

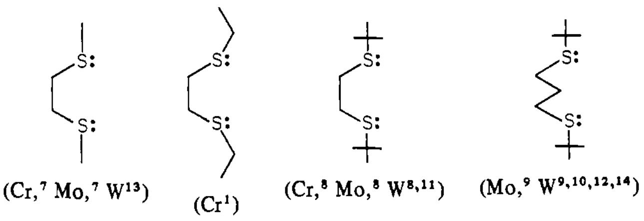
The kinetics and mechanism of chelate ring displacement by Lewis bases (usually phosphines and phosphites) of bidentate chelating ligands bonding through sulfur have been found to proceed predominantly via a mechanism involving reversible dissociation of one end of the chelating ligand (che) and competition for the five-coordinate intermediate thus formed between chelate ring reclosure and attack by L (eq 1).[7-14]

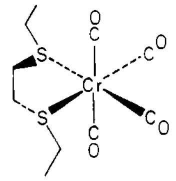


(1)

Among the chelating ligands that have been investigated kinetically are those in Chart I; thus, information with regard to reactivity has been obtained by comparing systems differing in the identity of the metal atom, the substituent bonded to sulfur, and the chelate ring size. In several instances, including **1** and **2**, X-ray crystallographic determination of complex structure has been correlated to reactivity via chelate ring displacement.[15,16] For **2**, substrate distortions induced by the bulky substituents bonded to S have been found to exert significant influence on the structures and thus, presumably, on reactivity. Thus **3**, (*cis*-1,2-bis(*tert*-butylthio)ethylene)tetracarbonylchromium(0) ((BTE)Cr(CO)$_4$), has been synthesized to investigate such influences. Herein are reported the synthesis, an X-ray structural determination, and the kinetics of chelate ring displacement for (BTE)Cr(CO)$_4$, through which these questions will be addressed.

Chart I





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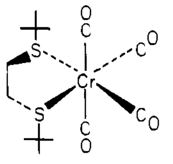

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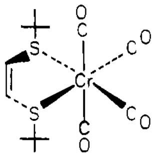

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Experimental Section

General Information. The chemical analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, TN. Infrared spectra were obtained on a Perkin-Elmer Model 621 grating spectrophotometer.

Materials. The ligand *cis*-1,2-bis(*tert*-butylthio)ethylene was synthesized by employing the method of Flynn, Badiger, and Truce.[17] Triethyl phosphite and triisopropyl phosphite (Aldrich) were purified by fractional distillation at low pressure (nitrogen bleed) over sodium. 1,2-Dichloroethane (Matheson) was purified by fractional distillation under nitrogen over P_2O_5. (BTE)Cr(CO)$_4$ was synthesized as follows: A 2.74-g quantity of BTE (14.1 mmol) and 3.00 g of Cr(CO)$_6$ (Pressure Chemical Co.; 13.6 mmol) in 300 mL of toluene were heated at reflux under nitrogen for 12 h. The toluene was removed under vacuum, and the product was recrystallized from toluene–hexane to afford yellow crystals of (BTE)Cr(CO)$_4$, which were obtained through filtration under vacuum. Anal. Calcd for $C_{14}H_{20}CrO_4S_2$: C, 45.64; H, 5.47. Found: C, 45.86; H, 5.47. Carbonyl stretching spectrum (cyclohexane solution): 2021 (w), 1923 (m), 1917 (w, sh), 1905 (w), 1899 (s), 1887 (s) cm^{-1}.

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(1) Part 3: Dobson, G. R.; Al-Saigh, Z. Y.; Binzet, N. S. *J. Coord. Chem.* **1981**, *11*, 159.
(2) Robert A. Welch Foundation undergraduate scholar, North Texas State University.
(3) Robert A. Welch Foundation postdoctoral fellow, North Texas State University and University of Houston.
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(5) University of Houston.
(6) Deceased.
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Table I. Crystallographically Important Data Collection and Processing Information

empirical formula	$CrS_2C_{14}O_4H_{20}$
mol wt	368.3
cell constants	$a = 14.098$ (6) A $b = 8.960$ (4) A $c = 15.221$ (8) A $\beta = 112.73$ (4)°
unit cell vol	1773.5 A^3
space group	$P2_1/n$
d(calcd)	1.38 g cm^{-3}
abs coeff	8.7 cm^{-1}
radiation used for data collection	Mo Kα ($\lambda = 0.71069$ A)
scanning range for 2θ	$2° \leq 2\theta \leq 40°$
standards for intensity control	(600)
scan width	$\Delta\theta = (0.50 + 3.5 \tan\theta)°$
max scan time	180 s
scan technique	ω-2θ
total no. of reflcns collected	3448
no. of contributing reflcns in the last cycle of least squares	2726
no. of variables	270
wtg scheme	unit wts
abs cor	not applied
final $R(F)$	0.024
final $R_w(F)$	0.025

X-ray Structural Determination. The crystals were yellow polyhedra with well-developed faces. Intensity measurements were carried out by employing an Enraf-Nonius CAD-4 computer-controlled diffractometer. A summary of the crystallographically important parameters for data collection and processing is given in Table I. Accurate cell constant determination and data collection were similar to those described elsewhere[18] and thus are not repeated here.

Data decoding was accomplished with use of a locally written program. Lorentz and polarization factors were applied in converting the intensities to structure factor amplitudes, $|F_o|$. No corrections for absorption were made due to the low value of the absorption coefficient ($\mu = 8.7$ cm^{-1}). Standard deviations in the structure factor amplitudes, $\sigma(|F_o|)$, were estimated as $\sigma(|F_o|) = \sigma(I)/2Lp|F_o|$. All data processing and calculations were carried out by employing the SHELX-76[19] system of programs. A three-dimensional Patterson map was computed, and the position of the chromium atom was determined. Successive difference Fourier syntheses revealed all the remaining 20 non-hydrogen atoms, which were isotropically refined to convergence at $R = 0.08$. At this stage, hydrogen atoms were added at theoretically calculated positions (C–H = 0.95 Å). Anisotropic refinement of the non-hydrogen atoms and isotropic refinement of the hydrogens yielded the final agreement factor of 0.024. Corrections for the real terms of the anomalous dispersion for Cr and S were applied. The values used for these corrections were those given in ref 20. The estimated standard deviations were computed from the inverse matrix of the final, full-matrix, least-squares cycle. No unusually high correlations were noted between any variables in the final cycle. Final atomic coordinates and thermal parameters are presented in Table II (supplementary material). Interatomic distances and angles are given in Table III. The equations of the least-squares planes through selected groups of atoms are presented in Table IV (supplementary material). The stereo drawings (Figures 1–3) were obtained with use of Johnson's ORTEP 2.[21]

Table III. Molecular Geometry with Estimated Standard Deviations in Parentheses

(a) Bond Lengths (A)

Cr–S1	2.410 (1)	C1–H1	0.89 (3)
Cr–S2	2.404 (1)	C2–H2	0.90 (3)
Cr–C3	1.846 (2)	C8–H81	1.01 (3)
Cr–C4	1.835 (2)	C8–H82	1.00 (3)
Cr–C5	1.907 (2)	C8–H83	0.88 (3)
Cr–C6	1.898 (2)	C9–H91	0.92 (3)
S1–C1	1.753 (3)	C9–H92	0.93 (3)
S1–C11	1.866 (2)	C9–H93	0.94 (3)
S2–C2	1.758 (3)	C10–H101	0.93 (3)
S2–C7	1.876 (2)	C10–H102	0.92 (3)
C3–O1	1.149 (3)	C10–H103	0.94 (2)
C4–O2	1.156 (3)	C12–H121	0.97 (2)
C5–O3	1.134 (3)	C12–H122	0.90 (3)
C6–O4	1.142 (2)	C12–H123	0.98 (3)
C1–C2	1.318 (4)	C13–H131	0.95 (3)
C7–C8	1.522 (3)	C13–H132	0.89 (3)
C7–C9	1.514 (4)	C13–H133	1.00 (3)
C7–C10	1.517 (3)	C14–H141	1.03 (3)
C11–C12	1.526 (4)	C14–H142	1.01 (3)
C11–C13	1.524 (4)	C14–H143	0.87 (3)
C11–C14	1.522 (4)		

(b) Angles (Deg)

S1–Cr–S2	83.94 (3)	C2–S2–C7	102.6 (1)
C3–Cr–C4	89.5 (1)	S1–C1–C2	122.7 (2)
S1–Cr–C3	92.6 (1)	C1–C2–S2	122.8 (2)
S2–Cr–C3	173.6 (1)	S1–C11–C12	107.0 (2)
S1–Cr–C4	171.7 (1)	S1–C11–C13	110.7 (2)
S2–Cr–C4	93.2 (1)	S1–C11–C14	104.4 (2)
S1–Cr–C5	85.3 (1)	C12–C11–C13	112.4 (3)
S2–Cr–C5	86.1 (1)	C12–C11–C14	110.5 (3)
S1–Cr–C6	99.3 (1)	C13–C11–C14	111.4 (3)
S2–Cr–C6	98.9 (1)	S2–C7–C8	107.1 (2)
C3–Cr–C5	88.2 (1)	S2–C7–C9	105.2 (2)
C3–Cr–C6	87.0 (1)	S2–C7–C10	111.2 (2)
C4–Cr–C5	86.8 (1)	C8–C7–C9	110.8 (3)
C4–Cr–C6	88.8 (1)	C8–C7–C10	111.5 (2)
C5–Cr–C6	173.5 (1)	C9–C7–C10	110.7 (2)
Cr–S1–C1	105.3 (1)	Cr–C3–O1	178.9 (2)
Cr–S1–C11	120.6 (1)	Cr–C4–O2	177.8 (2)
C1–S1–C11	102.9 (1)	Cr–C5–O3	175.9 (2)
Cr–S2–C2	105.2 (1)	Cr–C6–O4	174.0 (2)
Cr–S2–C7	120.0 (1)		

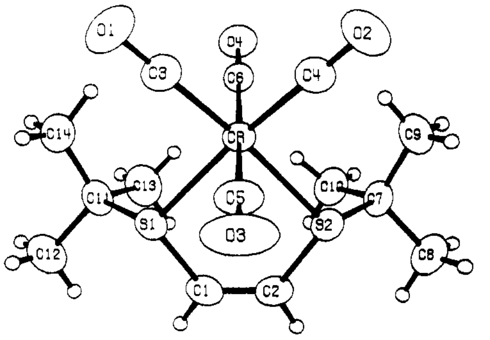

Figure 1. General view of the $(BTE)Cr(CO)_4$ molecule, showing the numbering scheme employed in the crystallographic study. The thermal ellipsoids are 50% probability envelopes for the heavy atoms and are of convenient size for the hydrogen atoms.

Determination of Reaction Rates. Rates of reaction of $(BTE)Cr(CO)_4$ with triethyl phosphite and triisopropyl phosphite (L) in 1,2-dichloroethane solvent, which afforded $L_2Cr(CO)_4$ products, were determined by employing a Beckman Model DU-2 direct-reading spectrophotometer monitoring 425 nm. A 20-mg quantity of substrate in 50 mL of reaction solution was employed. Methods of preparation of reaction solutions, and of sampling, have been described previously.[7] Since at the wavelength monitored the reaction products did not exhibit significant absorption, the value of a solvent–ligand blank was employed as a t_∞ value. Plots of ln $(A_t - A_\infty)$ vs. time (A_t and A_∞ are the absorbances at time t and at infinite time, respectively) were linear to at least two half-lives. At least 20-fold excesses of L for each kinetics run ensured that the pseudo-first-order reaction conditions obtained. Rate data (Table V, supplementary material) were analyzed by employing a linear least-squares program (North Texas State University HP-2000 computer; limits of error are given in parentheses as the uncertainty of the last digit of an experimental value at the 95% confidence limit).

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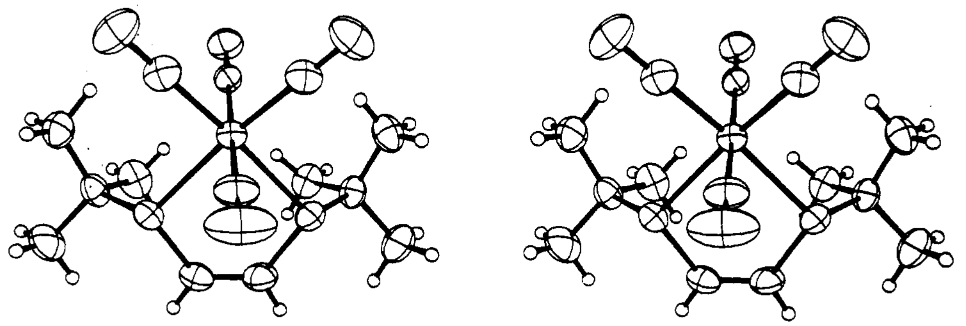

Figure 2. Stereopair view of (BTE)Cr(CO)$_4$.

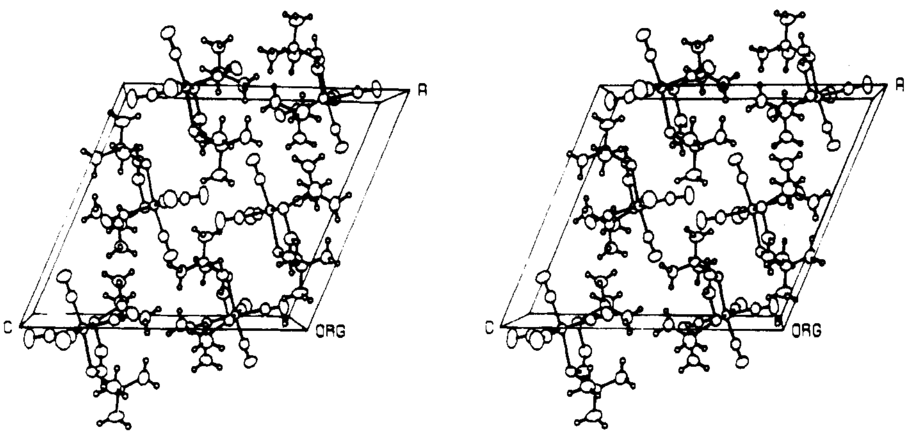

Figure 3. Packing diagram of (BTE)Cr(CO)$_4$.

Table VII. Comparison of Molecular Parameters between Compounds **1**, **2**, and **3**

compd	substituents at the S atoms	position with respect to chelate ring	dev of the Cr atom from eq plane, A	S-Cr-S[a]	S-Cr-C(eq)	C(eq)-Cr-C(eq)	C(ax)-Cr-C(ax)
1	ethyl	anti	0.016	85.05 (3)	93.0 (1) 92.7 (1)	89.3 (1)	174.7 (1)
2	*tert*-butyl	anti	0.033	80.60 (4)	90.7 (2) 99.3 (1)	89.9 (2)	169.8 (2)
3	*tert*-butyl	syn	0.122	83.94 (3)	92.6 (1) 93.2 (1)	89.5 (1)	173.5 (1)

[a] Angles in degrees.

Results and Discussion

Solid-State Structure of (BTE)Cr(CO)$_4$. The compound exists in the crystal form as discrete molecules in which the BTE moiety functions as a bidentate ligand, with the two sulfurs as donor atoms.

The coordination about the central chromium atom is a distorted octahedron, the equatorial plane being formed by the two sulfurs and the two carbonyls trans to them. The deviation of the chromium atom from the equatorial plane is 0.122 Å. A large deviation from the ideal octahedral geometry is observed for the S1–Cr–S2 angle, for which a contraction from 90 to 83.94 (3)° occurs. The deviations of the principal axes from linearity are shown by the angles S2–Cr–C3 (173.6 (1)°), S1–Cr–C4 (171.7 (1)°), and C5–Cr–C6 (173.5 (1)°). The two Cr–S bonds have lengths of 2.410 (1) and 2.404 (1) Å and are consistent with a significant π component to the bond.[15] Two different chromium–carbon bond distances are observed: Cr–C3 = 1.846 (2), Cr–C4 = 1.835 (2) Å; Cr–C5 = 1.907 (2), Cr–C6 = 1.898 (2) Å. The shorter distances are those trans to the sulfur atoms, whereas the longer ones are mutually trans. A similar behavior for chromium–carbon bond lengths has been observed for a variety of complexes having carbonyls trans to sulfur,[15,17] nitrogen,[22] and arsenic[23] atoms.

The relative distances are attributable to greater Cr–CO π bonding trans to sulfur than trans to CO, as a consequence of weaker Cr–S than Cr–C π bonding. As expected, the C–O distances for the mutually trans carbonyls (1.134 (3) and 1.142 (2) Å) are shorter than are those trans to S (1.149 (3) and 1.156 (3) Å). The carbonyls are coordinated in the usual angular fashion, the Cr–C–O angles being smaller (175.9 (2) and 174.0 (2)°) for the mutually trans carbonyls than for the carbonyls trans to sulfur (178.9 (2) and 177.8 (2)°). It has been suggested[15] that this bending may be due to repulsions from the lone pairs of the sulfur atoms.

The five-membered chelate ring is planar, the angle between the equatorial plane of the octahedron and the chelate ring being 4°. The two *tert*-butyl substituents are syn with respect to the chelate ring plane, with the distances of C7 and C11 from this plane being 1.483 and 1.446 Å, respectively. Bond lengths within the chelate ring are normal. The bond angles about the sulfur atoms vary considerably (from 102.6 (1) to 120.6 (1)°). This wide range may arise mainly from a slight bending of the *tert*-butyl substituents away from the C6–O4 carbonyl group in order to reduce steric hindrance between the carbonyl and the methyl groups (closest intramolecular approaches are given in Table VI (supplementary material)). This bending results in increasing angles Cr–S1–C11 and

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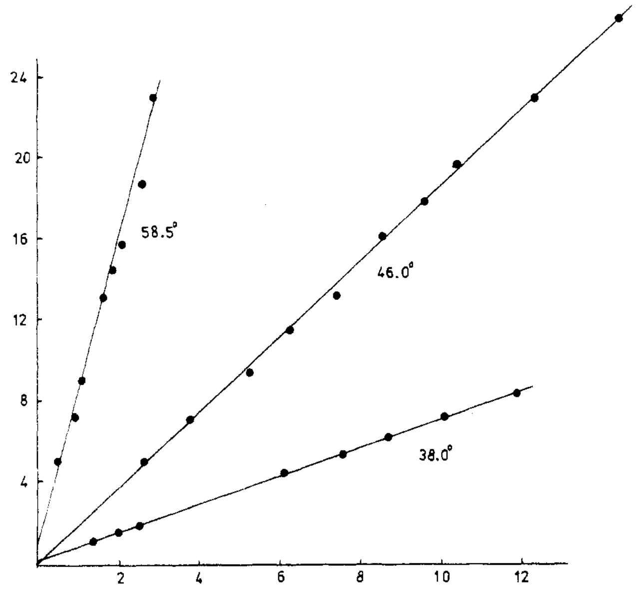


Figure 4. Plots of k_{obsd} (s^{-1}) vs. [$P(OC_2H_5)_3$] (M) for reaction of (BTE)$Cr(CO)_4$ with $P(OC_2H_5)_3$ in 1,2-dichloroethane at various temperatures: ordinate, 10^4k_{obsd}, s^{-1}; abscissa, [$P(OC_2H_5)_3$], M.

Cr–S2–C7 to 120.6 (1) and 120.0 (1)°, respectively, and decreasing angles C1–S1–C11 and C2–S2–C7 to 102.9 (1) and 102.6 (1)°, respectively. Additional close contacts that were found, for C1---H133 and C2---H101, may produce the slight distortions observed for the angles around C7 and C11 (increasing S1–C11–C13 and S2–C7–C10 to 110.7 (2) and 111.2 (3)°, respectively).

For comparison of the geometry of the present compound **3** with those found for **1** and **2**, Table VII was prepared. The most important differences among the three complexes are the bulkiness of the substituents bonded to sulfur and their relative positions with respect to the five-membered ring. Thus, compound **1** has two ethyl substituents, which are in an anti configuration; the substituents in **2** are *tert*-butyl groups also in an anti configuration, whereas for **3**, the *tert*-butyl groups are syn. The bulkiness and relative positions of these substituents seem to cause slight but important changes in the geometries of these complexes, especially in the deviations from ideal octahedral geometry about the central chromium atom. Compound **2**, with two bulky *tert*-butyl substituents in anti positions, shows high deviations from ideal octahedral geometry. Thus, the S–Cr–S angle contracts from the ideal 90° to 80.60 (4)°, and this decrease is compensated in the equatorial plane by an increase in only one of the S–Cr–C(eq) angles (99.3 (1)°), while the other angle remains largely undisturbed (90.7 (2)°). It has been suggested that these high and unsymmetrical deviations are due to steric hindrance between *one* of the *tert*-butyl groups and the carbonyls.[17] Compound **3**, which also has two *tert*-butyl substituents, but in the syn configuration, shows different distortions from ideal octahedral geometry. Thus, the deviation of the chromium atom from the equatorial plane is much greater for complex **3** than for complexes **1** and **2**. The angles about the chromium atom observed for compound **3** are closer to the ideal values and resemble those found for complex **1**. However, we note that the different deviations of the Cr atoms from the equatorial plane necessarily influence the angles about the metal. It would be tempting to speculate that the greater S–Cr–S angle found for **3** (83.94 (3)°) compared to that observed in **2** (80.60 (4)°) is at least partly due to the steric hindrance between the two syn *tert*-butyl groups (H103---H131 = 2.60 Å).

Chemistry in Solution. Data in Table V, illustrated as plots of k_{obsd} vs. [L] in Figure 4 (L = $P(OC_2H_5)_3$) and Figure 5 (L = $P(OCH(CH_3)_2)_3$), indicate that the reactions of (BTE)$Cr(CO)_4$ with these ligands in 1,2-dichloroethane proceed via a second-order rate law

$$-d[(BTE)Cr(CO)_4]/dt = k[(BTE)Cr(CO)_4][L] \quad (2)$$

over the entire range of concentrations of L. From data at three temperatures for both ligands, activation parameters have been determined, which are presented together with the calculated second-order rate constants in Table VIII. Table IX presents comparisons of activation parameters for ligand-exchange reactions with these two L groups for the substrates **1** and **2** and those obtained in the present study. It is to be noted that the entropies of activation obtained in this study

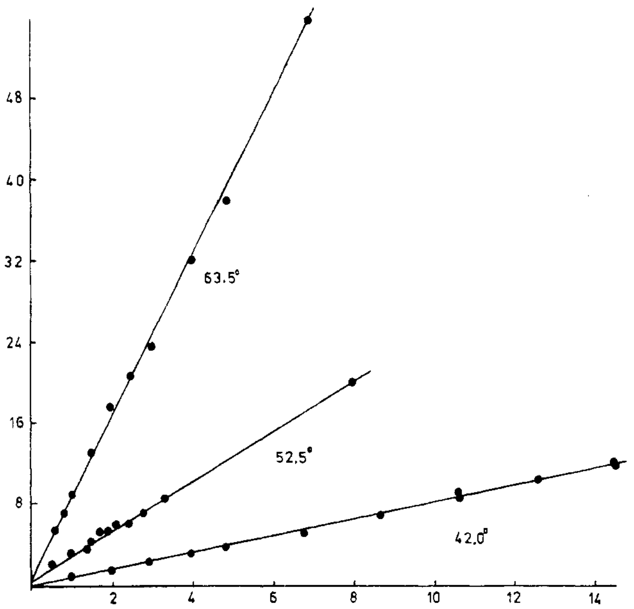


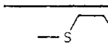
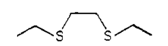
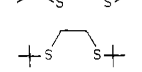
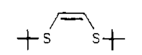
Figure 5. Plots of k_{obsd} (s^{-1}) vs. [$P(OCH(CH_3)_2)_3$] (M) for reaction of (BTE)$Cr(CO)_4$ with $P(OCH(CH_3)_2)_3$ in 1,2-dichloroethane at various temperatures: ordinate, 10^4k_{obsd}, s^{-1}; abscissa, [$P(OCH(CH_3)_2)_3$], M.

Table VIII. Rate Constants and Activation Parameters for Reaction of (BTE)$Cr(CO)_4$ with Triethyl and Triisopropyl Phosphite in 1,2-Dichloroethane

L	T, °C	10^4k_1, s^{-1}	10^4k_2, M^{-1} s^{-1}
$P(OEt)_3$[a]	38.0	0.08 (1)	7.07 (2)
	46.0	0.05 (8)	18.4 (2)
	58.5	1.4 (4)	68.0 (3)
$P(i\text{-}PrO)_3$[b]	42.0	−0.2 (1)	8.3 (1)
	52.5	0.52 (8)	24.4 (3)
	63.5	1.5 (3)	77 (1)

[a] $\Delta H_2^\ddagger$ = 22.1 (14) kcal/mol; $\Delta S_2^\ddagger$ = −2.0 (45) eu. [b] $\Delta H_2^\ddagger$ = 21.2 (14) kcal/mol; $\Delta S_2^\ddagger$ = −5.5 (42) eu.

Table IX. Activation Parameters for Displacement of Chelating Ligands Bonding through S by L from (che)$Cr(CO)_4$ Complexes in 1,2-Dichloroethane

che	L	$\Delta G^\ddagger$, kcal/mol	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
	$P(OEt)_3$	22.5[a]	28.1 (18)	16.9 (56)
	$P(i\text{-}PrO)_3$	24.2[a]	25.0 (6)	2.3 (19)
	$P(OEt)_3$	20.9[b]	23.6 (16)	8.2 (50)
	$P(i\text{-}PrO)_3$	23.2[c]	23.5 (22)	1.0 (67)
	$P(OEt)_3$	23.1[c]	27.6 (24)	14.2 (77)
	$P(OEt)_3$	22.7[d]	22.1 (14)	−2.0 (45)
	$P(i\text{-}PrO)$	22.9[b]	21.2 (14)	−5.5 (42)

[a] At 55.5 °C. [b] At 52.5 °C. [c] At 42.1 °C. [d] At 46.0 °C.

are slightly negative, in contrast to those observed for the other systems.

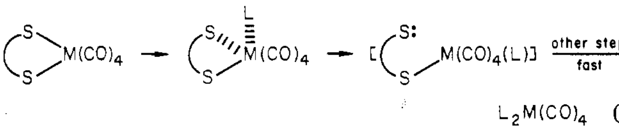
In interpreting these data, it is instructive to consider results for ligand exchange in such systems in general[24] and of chelate ring displacement in particular. In many systems, ligand exchange in octahedral metal carbonyl complexes has been found to proceed via two competitive and closely related pathways, D and I$_d$, dissociative and dissociative interchange (eq 3).[25] The latter pathway, in which there is some bond

$$CO + L_xL'M(CO)_{5-x} \leftarrow LM(CO)_{6-x} \rightarrow L_{x-1}L'M(CO)_{6-x} + L \tag{3}$$

making in the transition state, is, in general, observed to have a lower enthalpy of activation and a more negative entropy of activation than the dissociative path. However, since the two pathways often are truly competitive, the free energies of activation for each path are quite similar.

For displacement of a chelating ligand coordinating through sulfur, for which many systems have been studied,[1,7–14] two related pathways are also observed. The first involves unimolecular ring opening (eq 1), and the second, concerted ring opening under the influence of the incoming nucleoplile, L (eq 4). Results for (2,5-dithiahexane)M(CO)$_4$ systems[7,13] and for (2,2,8,8-tetramethyl-3,7-dithianonane)M(CO)$_4$[9,10,12] have been interpreted in terms of these two pathways. For the D process, which results in the formation of a five-coordinated intermediate, there is, therefore, subsequent competition between ring reclosure and attack at the intermediate by L (eq 1). In this simplest case, the rate law, based upon an assumed steady-state concentration of the intermediate, is

$$-d[(che)M(CO)_4]/dt = k_1k_3[(che)M(CO)_4][L]/(k_2 + k_3[L]) \tag{5}$$



(4)

Depending upon the relative magnitudes of k_2 and k_3 (the ratio of these is called the "competition ratio"), either "second-order" (eq 6; $k_2 >> k_3$) or complex rate behavior (eq 5; $k_2 \approx k_3$) is

$$-d[(che)M(CO)_4]/dt = k_1k_3/k_2[(che)M(CO)_4][L] \tag{6}$$

observed. In the latter case, for reactions under pseudo-first-order reaction conditions as are normally employed, the pseudo-first-order rate constant, $k_{obsd} = k_1k_3[L]/(k_2 + k_3\,[L])$, and linear "reciprocal plots" (eq 7) are obtained. The normally

$$1/k_{obsd} = 1/k_1 + k_2/k_1k_3[L] \tag{7}$$

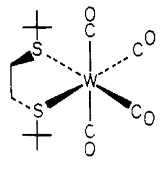
expected result is that $k_2 >> k_3$, and that second-order kinetics are to be observed, since, entropically, unimolecular ring reclosure is to be favored over bimolecular interaction of L with the intermediate.[26] In several instances, however, this has been found not to be the case, and this perhaps unexpected result has been correlated to distortion in the substrate. If it is assumed that this distortion results from the steric requirements imposed by the chelating ligand and that, therefore, this distortion does not persist in the five-coordinate ring-opened species, ring reclosure, which induces such distortion, is expected to render that process less favorable energetically. This could render the path involving attack by L more competitive.

Table X. Structural and Rate Data for (che)M(CO)$_4$ Complexes Coordinating through Sulfur

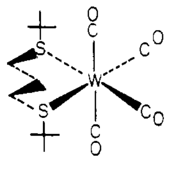
	1	2	3	4	5
angles, deg					
S1-M-S2	85.05	80.6	83.94	80.8	79.1
S1-M-C3	93.0	90.7	92.6	92.6	91.2
S2-M-C4	92.7	99.3	93.2	98.0	99.4
C5-M-C6	174.7	169.8	173.5	173.3	173.1
dev[d]	0.016	0.041	0.122	0.116	0.033
k_2/k_3	very large	~10[b]	very large	~1.6[a]	~0.2[c]

[a] At 89.2 °C.[11] [b] At 31.9 °C.[8] [c] At 66.5 °C.[12] [d] Deviation of metal from equatorial plane.

Table X presents selected structural parameters for a variety of (che)M(CO)$_4$ substrates, including **4** and **5**, together with the qualitative ratios of k_2/k_3, which support this conclusion. For (BTE)Cr(CO)$_4$ it is noted that substrate distortion, as indicated by those parameters, is not great. It has also been pointed out[1] that packing forces cannot explain trends in such distortions—which therefore are very probable to persist in solution. This leads to the prediction, assuming the accessibility of the ring-opening mechanism, that $k_2 >> k_3$. For $k_2 >> k_3$, rate data obey eq 7, consistent with this prediction.



4



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A comparison of the activation parameters for the four (che)Cr(CO)$_4$ systems for which kinetics data have been obtained (Table IX) indicates that the free energies of activation, roughly, are independent of the identity of the (che)Cr(CO)$_4$ substrate and the identity of L. In several systems, $\Delta S^{\ddagger}$ is positive, supporting more bond breaking than bond making in the transition state and favoring the D mechanism for ring opening rather than the I$_d$ path. For the (BTE)Cr(CO)$_4$ system, however, values of $\Delta S^{\ddagger}$ are slightly negative. This is not unreasonable when one considers the rigidity of the BTE ligand, which will persist to a significant degree, given the rigid-ring backbone, upon ring opening. Thus, unimolecular ring opening, entropically, is expected to be less favored in (BTE)Cr(CO)$_4$ relative to other (che)Cr(CO)$_4$ species. Since for the D path, $\Delta S^{\ddagger} = \Delta S_1^{\ddagger} + \Delta S_3^{\ddagger} - \Delta S_2^{\ddagger}$, both the $\Delta S_1^{\ddagger}$ and $\Delta S_2^{\ddagger}$ paths (ring opening and ring reclosure) are expected to afford a less favorable entropy effect for (BTE)Cr(CO)$_4$ reacting via this pathway.

This is what is observed. It would seem unlikely that the more negative entropies of activation observed for (BTE)Cr(CO)$_4$ could arise from a competing I$_d$ path.

It is further to be noted that, for each related system studied, the entropies of activation for the P(OC$_2$H$_5$)$_3$ reactions are more positive than those for the analogous reactions with P(OCH(CH$_3$)$_2$)$_3$. If this observation is indeed significant, it implies a substantial steric interaction between the five-coordinate intermediate and the incoming nucleophile in the step governed by k_3. While such an interaction is not unreasonable given the crowded steric environment that should exist in this step, it is in contrast to data for other systems, perhaps not as sterically demanding, in which the five-coordinate intermediate in its reactions with various L groups[27] is not discriminating. A recent study, however, in which the sterically demanding intermediate (1,2-bis(diphenylphosphino)ethane)Mo(CO)$_3$ is allowed to react with the bulky ligands

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(24) Dobson, G. R. *Acc. Chem. Res.* **1976**, *8*, 300.
(25) Langford, C. H.; Gray, H. B. "Ligand Substitution Processes", 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1974; Chapter 1.
(26) Schwarzenbach, G. *Helv. Chim. Acta* **1952**, *35*, 2344.
(27) For a summary, see, e.g.: Dobson, G. R. *Inorg. Chem.* **1980**, *19*, 1413.

$P(C_6H_5)_{3-n}(o\text{-}C_6H_4CH_3)_n$ (n = 1–3) shows significant steric influence on the rates of combination of the intermediate with those L groups, an observation that might be attributed to the kinds of steric interactions envisioned here.[28] Here again, the results could be interpreted in terms of a competing I_d path (eq 4).

It is also of interest to note that six carbonyl stretching bands are observed in the infrared spectrum of (BTE)$Cr(CO)_4$ in cyclohexane solvent. A similar situation was noted previously for the carbonyl stretching spectrum of (2,2,7,7-tetramethyl-3,6-dithiaoctane)$Cr(CO)_4$.[8] Given that in these complexes two orientations of the *tert*-butyl groups with respect to the equatorial molecular plane (syn and anti) have been observed, it is reasonable to presume that the additional bands in the carbonyl stretching spectra are the result of the presence of both conformers in solution for such species. The slightly differing carbonyl stretching frequencies observed for the two stereomers, if this indeed is the explanation, thus would be interpreted as arising through differing interactions of the *tert*-butyl groups in these species with the $Cr(CO)_4$ moiety; that such interactions in fact exist in the solid state is well demonstrated in the solid-state structures of the respective complexes (vide supra).

If this is in fact the explanation for the observed supernumerary carbonyl stretching bands, there is a recent precedent for differing compound conformers to exist in the solid state and in solution.[29] In the present instance, it is interesting to note that only a single stereomer is observed in the solid state for each complex—attributable to the energetics of crystallization, which favor a particular conformer, or to kinetics of crystallization, which again favor one conformer over the other.

Given the evident effects of deviations from ideal octahedral geometry around the metal produced by various substituents bonded to sulfur, it will be of interest to prepare and determine the structures of other complexes containing such substituents, of varying degrees of bulkiness such as methyl, isopropyl, or cyclohexyl, for example, both in the solid state and in solution.

In this context, studies of the conformational behavior of such complexes (by temperature-dependent ^1H NMR spectrometry) should also be of interest. There has been considerable recent interest in conformational barriers involving some related five-membered ring systems. Thus, Hawkins et al.,[30] who studied conformational behavior of the five-membered chelate rings in (*N,N,N',N'*-tetramethylethylenediamine)M$(CO)_4$ complexes (M = Cr, Mo, W), found interconversion barriers of about 9.3 kcal/mol between the two minimum-energy conformations. Somewhat higher barriers (13–14 kcal/mol) were reported by Donaldson et al.[31] for complexes of 1,2-bis(isopropylseleno)ethane in their Cr, Mo, and W carbonyl complexes. These results are not inconsistent with the postulation of two conformational forms present in solution in (BTE)$Cr(CO)_4$ and (2,2,7,7-tetramethyl-3,6-dithiaoctane)$Cr(CO)_4$.

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Registry No. (BTE)$Cr(CO)_4$, 82978-88-9; $Cr(CO)_6$, 13007-92-6; $P(OC_2H_5)_3$, 122-52-1; $P(OCH(CH_3)_2)_3$, 116-17-6.

Supplementary Material Available: Atomic coordinates and thermal parameters for (BTE)$Cr(CO)_4$ (Table II), least-squares planes through selected groups of atoms and their deviations from the planes (Table IV), rates of reaction of (BTE)$Cr(CO)_4$ with triethyl and triisopropyl phosphite in 1,2-dichloroethane at various temperatures (Table V), and shortest (up to 2.90 Å) intra- and intermolecular approaches (Table VI) (5 pages). Ordering information is given on any current masthead page.

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(28) Dobson, G. R.; Al-Saigh, Z. Y., paper in preparation.

(29) Kessler, H.; Zimmermann, G.; Forster, H.; Engl, J.; Oepon, G.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1053.

(30) Hawkins, C. J.; Peachey, R. M.; Szoredi, C. *Aust. J. Chem.* **1978**, *31*, 973.

(31) Donaldson, R.; Hunter, G.; Massey, R. *J. Chem. Soc., Dalton Trans.* **1974**, 288.