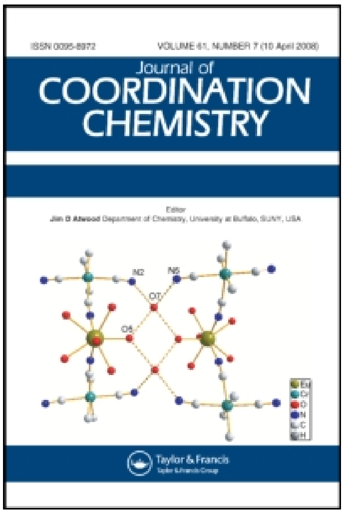

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SOLID-STATE STRUCTURE AND REACTIVITY IN SOLUTION. 3. Mechanism of the Reaction of (3,6-Dithiaoctane)Tetracarbonylchromium(0) with Phosphites

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To cite this Article Dobson, G. R. , Al-saigh, Z. Y. and Binzet, N. S.(1981) 'SOLID-STATE STRUCTURE AND REACTIVITY IN SOLUTION. 3. Mechanism of the Reaction of (3,6-Dithiaoctane)Tetracarbonylchromium(0) with Phosphites', Journal of Coordination Chemistry, 11: 3, 159 — 162

To link to this Article: DOI: 10.1080/00958978108079063

URL: http://dx.doi.org/10.1080/00958978108079063

J. Coord. Chem., 1981, Vol. 11, pp. 159–162
0095-8972/81/1103-0159 $06.50/0

SOLID-STATE STRUCTURE AND REACTIVITY IN SOLUTION.
3.[1] Mechanism of the Reaction of (3,6-Dithiaoctane)Tetracarbonylchromium(0) with Phosphites

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(*Received February 20, 1981*)

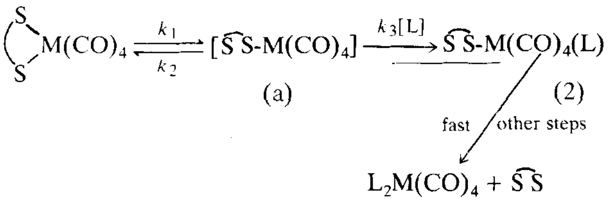
Rate data for the reaction of (3,6-dithiaoctane)tetracarbonylchromium(0) with triethyl phosphite and tri(isopropyl) phosphite in 1,2-dichloroethane support a ring-opening mechanism. The data support rapid ring-reclosure relative to attack by the phosphite at the "ring-opened" five-coordinate intermediate; these relative rates are correlated to a lack of distortion in the (dto)Cr(CO)$_4$ substrate, and are contrasted to kinetics results for substrates in which significant distortion is observed.

INTRODUCTION

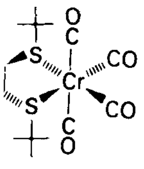
A number of studies of the mechanism of ligand-displacement in (chelate ligand)M(CO)$_4$ complexes (M = Cr, Mo, W; chelate ligand bonds through two S donor atoms) in their reactions with phosphines and phosphites (L),[3-9]

$$(che)M(CO)_4 + 2L \longrightarrow L_2M(CO)_4 + \overset{\frown}{S\ S} \quad (1)$$

have revealed the mechanism (2) to be predominant:



In most instances,[4,5,7-9] it has been found that $k_2 \sim k_3$, an unusual result in that entropy considerations would dictate that unimolecular ring-reclosure (governed by 2-k_2) would be energetically-favored over bimolecular reaction of L with intermediate (2–a), governed by 2-k_3.[10,11] This observation, among others, has prompted X-ray crystallographic studies of (che)M(CO)$_4$ substrates. Thus far, three structures have been determined through collaboration with the laboratory of Professor Ivan Bernal, for (3–5).[1,12] These studies have revealed significant distortions from idealized octahedral geometry in these complexes, the result, at least in part, of steric interaction between the bulky *t*-butyl substituents on S with the M(CO)$_4$ moiety.



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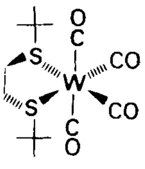

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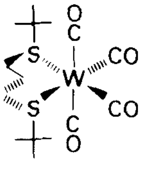
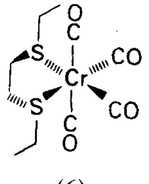


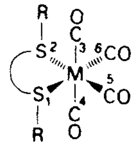
(5)

Baker and Larson have reported the crystal and molecular structure for (dto)Cr(CO)$_4$ (dto = 3,6-dithiaoctane), (6).[13] In contrast to results for (3–5), this molecule exhibits little distortion from octahedral geometry. Table I exhibits bond angles for (3–6) which illustrate this observation. It is also to be noted that it is most improbable that those distortions are the result of packing effects, given that they are independent of both space group and crystal system (Table I). For (dto)Cr(CO)$_4$, in contrast to (3–5), the S–Cr–S angle



(6)

TABLE I
Structural parameters for (che)$M(CO)_4$ complexes



Complex	(3)[1]	(4)[12]	(5)[12]	(6)[13]
Angles, deg				
(a) S_1–M–S_2	79.1	80.8	80.6	85.05
(b) S_1–M–C_5	91.2	92.6	90.7	93.0
S_2–M–C_6	99.4	98.0	99.3	92.7
(c) C_3–M–C_4	173.1	173.3	169.8	174.7
space group	$P2_1/c$	C2/c	$P2_12_12_1$	$P2_1/c$
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic

more closely approaches the expected 90°, and distortion of this angle in the equatorial plane of this molecule is taken up more or less equally by the two adjacent S–Cr–C angles. If a relationship between solid-state structure and reaction in solution exists, it might be expected that a much smaller potential energy barrier to induce distortion upon ring-reclosure would be required for (dto)$Cr(CO)_4$ than for (3–5); this would lead to the prediction that $k_2 \gg k_3$ for reaction of (dto)$Cr(CO)_4$ with L according to (1), in contrast to kinetics results for (3–5), in which $k_3 \sim k_5$.[4,5,7–9] This hypothesis has been tested through a study of the reaction of (dto)$Cr(CO)_4$ with tri(isopropyl) phosphite and triethyl phosphite in 1,2-dichloroethane. Herein are reported the results of that study.

EXPERIMENTAL

Synthetic

The substrate, (dto)$Cr(CO)_4$, was prepared through reaction of 3,6-dithiaoctane (obtained from Chemical Procurement Laboratories), 2.0 g, 0.13 mmole, with $Cr(CO)_6$, 3.0 g, 0.14 mmole, in 100 ml refluxing toluene under nitrogen over six hr. After reaction, the solution was filtered, the volume was reduced to one-third under vacuum, and 150 ml of *n*-hexane was added to the remaining solution. Upon cooling overnight at 0°, 2.5 g of yellow crystals of (dto)$Cr(CO)_4$ were obtained *via* suction filtration. They were washed with small quantities of *n*-hexane, and were dried *in vacuo*. The complex was identified through comparison of its carbonyl stretching spectrum to that of an authentic sample.[14]

Reagents

Purification of 1,2-dichloroethane was carried out by fractional distillation over P_2O_5 under nitrogen. Triethyl phosphite and tri(isopropyl) phosphite were fractionally distilled over sodium under reduced pressure (nitrogen bleed).

Kinetic Runs

Kinetic runs were carried out under pseudo first-order reaction conditions (at least a twenty-fold excess of L)

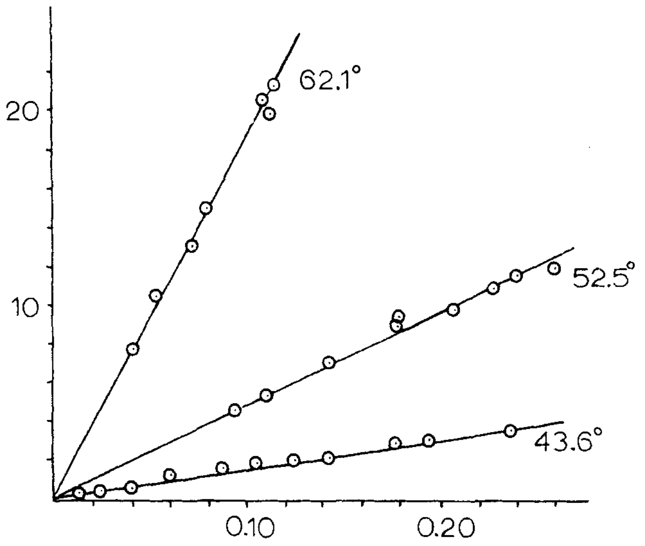


FIGURE 1 Plots of k_{obsd} *vs.* [L] for reaction of (dto)$Cr(CO)_4$ with $P(OEt)_3$ in 1,2-dichloroethane at various temperatures. *Ordinate:* $10^4 k_{obsd}$, sec^{-1}; *Abscissa:* [L], M.

employing a Beckman DU-2 direct reading spectrophotometer monitoring 420 nm. Plots of $\ln(A_t - A_{bl})$ *vs.* time were linear to at least 80 per cent of reaction completion (A_t and A_{bl} are absorbances at a given time, and of a blank; the reaction products do not absorb significantly at 420 nm). Values of the pseudo first-order rate constants, k_{obsd}, are presented in Table II. Figure 1 presents plots of k_{obsd} *vs.* [L] for the reaction of the substrate with tri(isopropyl) phosphite at three temperatures. Table III presents values for the slopes and intercepts of the k_{obsd} plots, and activation parameters derived for both L from data taken for three temperatures. Data were analyzed employing a National Advance Systems AS5000 computer; limits of error given in parenthesis represent one standard deviation in the last significant figure shown for the rate constant or activation parameter.

RESULTS AND DISCUSSION

Rate data (Tables II, III) and plots of k_{obsd} *vs.* [L] (for L = $P(OEt)_3$, Figure 1) support a second-order rate law,

$$-d[(dto)Cr(CO)_4]/dt = k[(dto)Cr(CO)_4][L] \quad (7)$$

This rate law is consistent with mechanism (2), for which the steady-state rate law (2-a is the steady-state

TABLE II
Rate data for reaction of $(dto)Cr(CO)_4$ with L in 1,2-dichloroethane at various temperatures

L, (T, °C) [L], M	10^4k_{obsd}, sec^{-1}
$P(OEt)_3$, 43.6°	
0.0138	0.34(2)
0.0240	0.44(2)
0.0401	0.53(1)
0.0603	1.27(4)
0.0891	1.54(5)
0.106	1.79(2)
0.126	2.02(2)
0.143	2.09(2)
0.178	2.79(3)
0.196	3.03(3)
0.218	3.45(4)
$P(OEt)_3$, 52.5°	
0.094	4.51(4)
0.1101	5.3(1)
0.144	7.1(1)
0.178	7.94(8)
0.180	8.38(7)
0.209	9.8(2)
0.229	10.8(2)
0.242	11.4(2)
0.251	11.9(2)
$P(OEt)_3$, 62.1°	
0.0401	7.7(1)
0.0522	10.4(1)
0.0706	13.0(4)
0.0775	14.9(2)
0.111	19.8(2)
0.108	20.5(6)
0.114	21.4(3)
$P(OPr^i)_3$, 42.75°	
0.213	0.243(6)
0.364	0.429(5)
0.540	0.88(1)
$P(OPr^i)_3$, 42.5°	
0.625	0.727(8)
0.917	1.04(3)
1.008	1.122(4)
1.200	1.36(1)
1.270	1.45(2)
1.403	1.58(2)
1.539	1.68(3)
$P(OPr^i)_3$, 51.0°	
0.192	0.74(1)
0.244	0.85(2)
0.433	1.51(2)
0.544	1.8
0.773	2.66(2)
0.878	2.97(3)
0.920	3.01(5)
1.016	3.47(1)
1.480	4.78(4)
$P(OPr^i)_3$, 61.8°	
0.167	2.6(1)
0.323	4.37(4)
0.440	6.2(2)
0.515	6.65(5)
0.646	8.2(2)
0.749	9.5(1)
0.989	12.2(1)
1.264	12.9(2)
1.280	14.8(1)

TABLE III
Rate constants and activation parameters for reaction of $(dto)Cr(CO)_4$ with phosphites (L) in 1.2-dichloroethane

$L = P(OEt)_3$			$L = P(OPr^i)_3$		
T, °C	$10^4k_{(int)}$[a] (sec^{-1})	$10^4k_{(sl)}$[b] ($M^{-1}\ sec^{-1}$)	T, °C	$10^4_{(int)}$[a] (sec^{-1})	$10^4_{(sl)}$[b] ($M^{-1}\ sec^{-1}$)
43.6	0.23(8)	14.3(7)	42.8	0.023(1)	1.1(1)
52.5	0.1(2)	46.0(1)	51.0	0.01(3)	3.17(4)
62.1	0.8(6)	178.0(7)	61.8	1.0(2)	11.1(3)

$\Delta H_1^\ddagger + \Delta H_3^\ddagger - \Delta H_2^\ddagger = 27.3(6)$ kcal/mole　　$\Delta H_1^\ddagger + \Delta H_3^\ddagger - \Delta H_2^\ddagger = 24.9(2)$ kcal/mole

$\Delta S_1^\ddagger + \Delta S_3^\ddagger = \Delta S_2^\ddagger = 26.9(15)$ cal/deg-mole　　$\Delta S_1^\ddagger + \Delta S_3^\ddagger - \Delta S_2^\ddagger = 17.6(10)$ cal/deg-mole

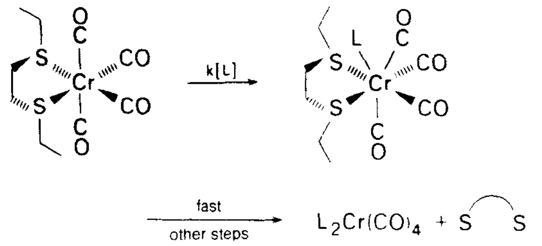
[a] values of intercepts of plots of k_{obsd} *vs.* [L].
[b] values of the slopes of plots of k_{obsd} *vs.* [L]; $k_{(sl)} = k_1k_3/k_2$ – see Eq. (2).

intermediate) is.

$$-d[(dto)Cr(CO)_4]/dt = k_1k_3[(dto)Cr(CO)_4][L]/(k_2 + k_3[L]); \quad (8)$$

rate law (8) is a limiting form of (7) when $k_2 \gg k_3$.

This mechanism is to be preferred to one involving nucleophilic attack of L at the substrate, on the basis of the positive entropies of activation observed for the reactions. These entropies of activation, based upon the rate constant k_1k_3/k_2 (=k) are $\Delta S_1^\ddagger + \Delta S_3^\ddagger - \Delta S_2^\ddagger$, expected to be positive. For an associative mechanism (9), a negative entropy of activation is anticipated. These mechanisms have been distinguished on the basis of the signs of the entropies of activation for other systems.[3]



Thus $(dto)Cr(CO)_4$ reacts with L *via* ring-opening in a "normal" manner, in which the rate of ring-reclosure is significantly greater than the rate of attack by L on intermediate (2-a). These results lend further credence to the hypothesis that $k_2 \sim k_3$ only for substrates in which there is significant distortion from octahedral geometry; other systems are being examined both structurally and kinetically to test this hypothesis further.

ACKNOWLEDGEMENT

The support of this research by the Robert A. Welch Foundation under grant B-434 is gratefully acknowledged.

REFERENCES

1. Part 2: G. M. Reisner, I. Bernal and G. R. Dobson, *Inorg. Chim. Acta*, **50**, 227 (1981).
2. Robert A. Welch Foundation Post-doctoral Fellow.
3. G. C. Faber and G. R. Dobson, *Inorg. Chem.*, **7**, 584 (1968).
4. G. R. Dobson, *Inorg. Chem.*, **8**, 90 (1969).
5. G. R. Dobson and G. C. Faber, *Inorg. Chim. Acta*, **4**, 87 (1970).
6. L. D. Schultz and G. R. Dobson, *J. Coord. Chem.*, **5**, 163 (1976).
7. L. D. Schultz and G. R. Dobson, *J. Organometal. Chem.*, **124**, 19 (1977).
8. G. R. Dobson and L. D. Schultz, *J. Organometal. Chem.*, **131**, 285 (1977).
9. G. R. Dobson, L. D. Schultz, B. E. Jones and M. Schwartz, *J. Inorg. Nucl. Chem.*, **41**, 119 (1979).
10. G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 2344 (1952).
11. L. E. Orgel, *An Introduction to Transition Metal Chemistry: Ligand-Field Theory*, Wiley, New York, (1960), pp. 14–15.
12. G. M. Reisner, I. Bernal and G. R. Dobson, *J. Organometal. Chem.*, **157**, 23 (1978).
13. E. N. Baker and N. G. Larson, *J. Chem. Soc. (Dalton)*, 1769 (1976).
14. E. W. Ainscough, E. J. Birch and A. M. Brodie, *Inorg. Chim. Acta*, **20**, 187 (1976).