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Octahedral Metal Carbonyls.
58*. Rate Constants for Ring-displacement in Metal Carbonyl Complexes Containing 5- and 6-Membered Chelate Rings Coordinating through Sulfur

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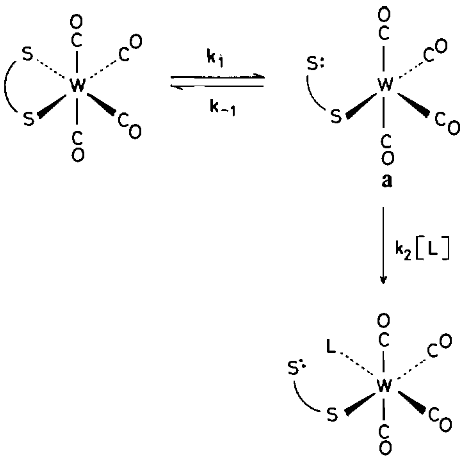
Recently it has been confirmed experimentally that reaction intermediates (1, **a**) produced thermally and through pulsed laser flash photolysis of substituted octahedral metal carbonyls containing chelating ligands, e.g., (1), are one and the same [2], *i.e.*, that the photophysical and solvation processes accompanying the photolysis rapidly afford the electronic and vibrational ground-state of the intermediate [3]. The identities of such intermediates thus can be established definitively through comparisons of their reactivities when they are generated both photochemically and thermally. This is true since although little information about the nature of the intermediates generated photochemically is gained through their observation in the UV-Vis. spectral regions [4], their identities have been confirmed through thermal studies which have employed infrared spectroscopy in the identification of the predominant species formed during the reactions [5]. Thus, for ligand-substitution reactions of (DTO)W(CO)$_4$ (DTO = 2,2,7,7-tetramethyl-3,6-dithiaoctane) with phosphines and phosphites (= L) in chlorobenzene (CB), which proceed via mechanism (1), the 'competition ratios', k_2/k_{-1}, obtained both from thermal kinetics data and through time-resolved laser photolysis[‡], are the same within experimental error. This observation confirms the identity of the photochemically-generated intermediate (1, **a**) [2b]. However, it was not possible to apply this technique to the study of the analogous complex containing the six-membered chelate ring, (DTN)W(CO)$_4$ (DTN = 2,2,8,8-tetramethyl-3,7-dithianonane) since in this system a second thermal reaction pathway was also observed, complicating the interpretation of the rate data [6].



(1)

We wish to report evidence that for the reaction of (DTN)W(CO)$_4$ with L = tri(isopropyl) phosphite in CB, this second reaction pathway is not accessible, *i.e.*, that for this reaction, mechanism (1) is strictly obeyed. Thus, all rate constants for ligand displacement from both (DTO)W(CO)$_4$ and (DTN)W(CO)$_4$ via mechanism (1) can be compared. Such a comparison provides unparalleled insight into the dynamics of chelate ring-displacement as a function of chelate ring-size.

Tri(isopropyl) phosphite was chosen as the ligand, of all those previously investigated, most likely to react exclusively by way of mechanism (1) [6b]. This was confirmed through a comparison of the 'competition ratios', k_2/k_{-1}, obtained both photochemically, and thermally under identical reaction conditions (CB solvent, 35.2°) through methods previously described [2b]. The ratios, 0.87(4) obtained photochemically [2b] and 0.97(9) obtained thermally (this study), are expected to be identical only when mechanism (1) is applicable [6b].

The rate constants k_1, k_{-1} and k_2 for chelate ring-displacement of both DTO and DTN in their tetracarbonyltungsten complexes (= (η^2-S$_2$)W(CO)$_4$) at 35.2° in CB are exhibited in Table I. It can be seen that the predominant factor influencing the much faster rate observed for ligand-displacement in (DTN)W(CO)$_4$ is the acceleration of chelate ring-opening

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[‡] Thermally, under pseudo first-order reaction conditions (large excess of L), the relationship $1/k_{\text{obsd}} = 1/k_1 + k_{-1}/k_1k_2$ can be derived. The intercept/slope of this linear plot affords the competition ratio k_2/k_{-1}. Similarly, for the photochemical process, $-d[1, a]/dt = k_{-1}[1, a] + k_2[1, a][L]$, for which slope/intercept affords the same competition ratio.

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TABLE 1. Rate Constants, Thermodynamic Data and Activation Parameters for Reactions of $(\eta^2\text{-}S_2)W(CO)_4$ with Tri(isopropyl) Phosphite in Chlorobenzene; Rate Constants and Thermodynamic Data Determined at 35.2 °C.

S_2	$10^5\ k_1$ (s^{-1})	$10^{-5}\ k_{-1}$ (s^{-1})	$10^{-5}\ k_2$ $(M^{-1}\ s^{-1})$	k_2/k_{-1} (M^{-1})	$10^{11}\ K_{eq(1,-1)}$ (M)	$\Delta H_1^{\neq}$ (kcal/mol)	$\Delta S_1^{\neq}$ (cal/deg mol)	$\Delta H_2^{\neq} - \Delta H_{-1}^{\neq}$ (kcal/mol)	$\Delta S_2^{\neq} - \Delta S_{-1}^{\neq}$ (cal/deg mol)	$\Delta G_{(1,-1:\,35.2°)}$ (kcal/mol)
DTO	$^a0.156(29)$	–	–	$^a0.28(7)$	0.27(6)	$^a29.0(12)$	$^a1.8(37)$	$^a{-2.3}(24)$	$^a{-4.5}(60)$	16.3(1)
	–	$^b5.67(2)$	$^b1.2(2)$	$^b0.21(5)$		–	–	$^b{-0.7}(38)$	$^b{-5.6}(129)$	
DTN	$^a6.5(5)$	–	–	$^a0.97(9)$	31.0(3)	$^a25.5(3)$	$^a{-5.2}(8)$	$^a{-3.8}(21)$	$^a{-11.1}(65)$	13.4(1)
	–	$^b2.04(3)$	$^b1.78(5)$	$^b0.87(4)$		–	–	$^b{-4.9}(11)$	$^b{-15.5}(36)$	

[a] Data obtained through thermal generation of $[(\eta^1\text{-}S_2)W(CO)_4]$ intermediate, ref. 2b and this study. Limits of error in parentheses, uncertainty of last digit(s), one standard deviation. [b] Data obtained through photochemical generation of $[(\eta^1\text{-}S_2)W(CO)_4]$ intermediate, ref. 2b. Error limits in parentheses, one standard deviation.

for the six-membered, as opposed to the five-membered chelate ring. This acceleration is some forty-fold, as compared to an approximately three-fold deceleration of the rate of chelate ring-closure in (DTN)W-$(CO)_4$ *vs.* (DTO)W$(CO)_4$. This observation provides convincing evidence that the transition state for the ring-opening process more closely resembles the 'ring-opened' intermediate than it does the substrate [7]. The forty-fold differences in k_1 in the two complexes may be understood on the basis of the greater distortions observed in (DTN)W$(CO)_4$ than in (DTO)W-$(CO)_4$, which include a smaller S–W–S angle, a smaller 'bite' (non-bonded S–S distance), a more distorted average W–S–C_{ring} angle, and a longer W–S bond-length [8]. Activation parameters for k_1 and k_2/k_{-1} for reactions of (DTO)W$(CO)_4$ and (DTN)-W$(CO)_4$ with triisopropyl phosphite in CB over 35.2 °C–100.0 °C for the former and 35.2–60.7 °C for the latter are also presented in Table I. Those for the 'competition ratios', while subject to rather large experimental uncertainties*, are the same thermally and photochemically. Moreover, the rate data demonstrate unequivocally that these ratios decrease with increasing temperature; thus the enthalpies of activation for chelate ring-closure are greater than are those for attack by L at (1, **a**). The difference may be attributable to steric strain induced in the $(\eta^2\text{-}S_2)W(CO)_4$ complexes as a result of conformational preferences required in the chelating ring; such effects are not present in the *cis*-(L)$(\eta^1\text{-}S_2)W(CO)_4$ species formed through interaction of (1, **a**) with L. Since the two pathways are competitive, these enthalpy differences are counterbalanced by a more favorable entropy of activation for unimolecular ring-closure than for bimolecular interaction of L with (1, a), as might be expected.

Parallel thermal and photochemical rate studies under continuing investigation in these laboratories, together with recent developments in IR detection of transients in solution by Schaffner [9], Turner [10] and their groups offer great opportunities to probe reactivity of organometallic transients, an area of research of prime significance to the development of a detailed understanding of transition metal homogeneous catalysis.

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*This is particularly true for (DTO)W$(CO)_4$, for which very small values for the intercepts of the reciprocal plots are observed.

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