Contribution from the Department of Chemistry,
North Texas State University, Denton, Texas 76203-5068

Solid-State Structure and Reactivity in Solution. 7.[1] Flash Photolytic Studies of Tetracarbonyltungsten(0) Complexes Containing Five- and Six-Membered Chelating Rings Coordinating through Sulfur
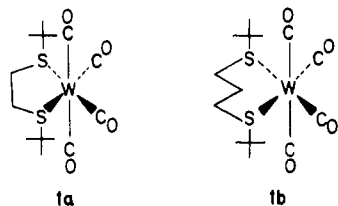
GERARD R. DOBSON,* CHARLES B. DOBSON, and SABER E. MANSOUR

Pulsed-laser ligand-substitution photochemistry for (DTO)W(CO)$_4$ and (DTN)W(CO)$_4$ (DTO = 2,2,7,7-tetramethyl-3,6-dithiaoctane; DTN = 2,2,8,8-tetramethyl-3,7-dithianonane) with Lewis bases (=L: alkylphosphines and alkyl phosphites) proceeds via initial fission of a W–S bond to produce five-coordinate intermediates in which vacant (solvated) coordination sites are both cis and trans to the undisplaced sulfur for DTN but largely cis for DTO. The rates of reaction of these species via chelate ring closure and competitive bimolecular interaction of L for the cis intermediate, together with activation parameters for these processes, and rates of reaction via bimolecular interaction of L with the trans intermediate in the case of DTN have been determined. The rate of chelate ring closure is significantly faster for the DTO complex, in which ring closure produces a five-membered chelate ring, than for the DTN complex, which affords a six-membered ring system. Thermal kinetics studies for reaction of (DTO)W-(CO)$_4$ with L under the identical reaction conditions as were employed in the photochemical studies afford a value of the "competition ratio" (of the rate constants for ring reclosure vs. attack by L at the cis site) that conclusively demonstrates that the intermediates produced thermally and photochemically are one and the same and provides strong evidence as to the validity of the interpretation of the photochemical results. Activation parameters for ring closure for the DTO and DTN complexes reveal a significantly greater enthalpy barrier to closure of the six-membered ring and to ring closure in the DTN complex vs. attack at the cis intermediate by L. For both substrates the entropy of activation for the latter, bimolecular process is more unfavorable than for the competitive unimolecular ring closure. Data are interpreted in light of the previously reported structures for both complexes.

Introduction

Pulsed-laser flash photolysis at 355 nm of (chelate)M(CO)$_4$ complexes (M = Cr, Mo, W), in which one or more of the coordinating atoms in the chelate ring is N or S, has indicated that chelate ring opening is a prominent reaction pathway,[1,2] affording an opportunity to study the reaction dynamics of chelate ring closure for a variety of complexes. One of the factors that influences reactivity by ring opening is the size of the chelate ring. It has also been proposed, where chelate ring closure is competitive with attack at the "ring-opened" species by a Lewis base (L), that distortion in the substrate induced by conformational preferences in the ring and by steric interactions between the ring and the M(CO)$_4$ moiety increases the enthalpy of activation for ring closure so that it counterbalances the less unfavorable entropy change expected for unimolecular ring closure as opposed to bimolecular interaction of the intermediate with L.[3] The complexes (DTO)W(CO)$_4$ (DTO = 2,2,7,7-tetramethyl-3,6-dithiaoctane) and (DTN)W(CO)$_4$ (DTN = 2,2,8,8-tetramethyl-3,7-dithianonane) (1a and 1b, respectively) thus offer an excep-

tional opportunity to address such questions for the following reasons:

(a) They have been found to react photolytically at 355 nm exclusively via chelate ring opening.[2b]

(b) Their thermal ligand-exchange kinetics have been studied extensively and indicate that after initial chelate ring opening, chelate ring closure is competitive with attack at the five-coordinate intermediate by L.[4]

(c) They are identical in all respects save for the size of the chelate ring.

(d) Their crystal and molecular structures, obtained through X-ray diffraction studies, have been reported, and the molecules exhibit significant distortions from octahedral geometry.[5]

Herein are reported pulsed-laser flash photolysis and thermal kinetics studies of these molecules in their reactions with alkylphosphines and alkyl phosphites (L), through which the questions discussed above have been addressed.

Experimental Section

The (DTO)W(CO)$_4$ and (DTN)W(CO)$_4$ complexes were synthesized and purified as previously described.[4a,b] Solvents were purified by fractional distillation over phosphorus pentoxide (chlorobenzene (CB), 1,2-dichloroethane (DCE)) or sodium (toluene). Trimethyl phosphite and triethyl phosphite were distilled over sodium under prepurified nitrogen. Triisopropyl phosphite and tri-n-butylphosphine were distilled over sodium at reduced pressure (0.2 torr).

Thermal kinetics studies were carried out as follows: Solutions containing known concentrations of triisopropyl phosphite (at least a 20-fold excess of L over substrate, to ensure that pseudo-first-order reaction conditions obtained) and amounts of (DTO)W(CO)$_4$ so as to give an initial absorbance at 437 nm of ca. 1.5 absorbance units (about 40 mg in 10 mL total volume of solution determined at the reaction temperature) were placed in 1-cm glass cuvettes, which were cooled to liquid-nitrogen temperature, evacuated, and sealed. The cuvettes then were placed in a constant-temperature bath; the absorbance of the reaction solution was measured periodically by employing a Beckman DU-2 direct-reading UV–visible spectrophotometer. Data were accumulated over several months; after 2 half-lives or more of the reactions, the cells were warmed to 100 °C until reaction was complete. 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 then employed to determine values of k_{obsd}. The initial portions of the data (ca. 15 data points) were analyzed by employing a linear least-squares program (HP 2000 computer, North Texas State University Computing Center). Rate constants are presented in Table I (supplementary material). These kinetics systems have been studied extensively under other reaction conditions; the identities of the reaction products, cis- and trans-L$_2$W(CO)$_4$, have been well documented.[4a,c]

Pulsed-laser flash photolytic studies were carried out at the Center for Fast Kinetics Research (CFKR), University of Texas at Austin, by employing a Quantel Q-switched Nd:YAG laser (355-nm irradiating

(1) Part 6: Dobson, G. R.; Bernal, I.; Reisner, G. M.; Dobson, C. B.; Mansour, S. E. *J. Am. Chem. Soc.* **1985**, *107*, 525–532.
(2) (a) Dobson, G. R.; Mansour, S. E.; Halverson, D. E.; Erikson, E. S. *J. Am. Chem. Soc.* **1983**, *105*, 5505–5506. (b) Dobson, G. R.; Dobson, C. B.; Halverson, D. E.; Mansour, S. E. *J. Organomet. Chem.* **1983**, *253*, C27–C32.
(3) Dobson, G. R.; Al Saigh, Z. Y.; Binzet, N. S., *J. Coord. Chem.* **1981**, *11*, 159–162.
(4) (a) Dobson, G. R. *Inorg. Chem.* **1969**, *8*, 90–95. (b) Dobson, G. R.; Faber, G. C. *Inorg. Chim. Acta* **1970**, *4*, 87–92. (c) Schultz, L. D.; Dobson, G. R. *J. Organomet. Chem.* **1976**, *124*, 19–28. (d) Dobson, G. R.; Schultz, L. D. *J. Organomet. Chem.* **1976**, *131*, 285–296.
(5) Reisner, G. M.; Bernal, I.; Dobson, G. R. *J. Organomet. Chem.* **1978**, *157*, 23–39.
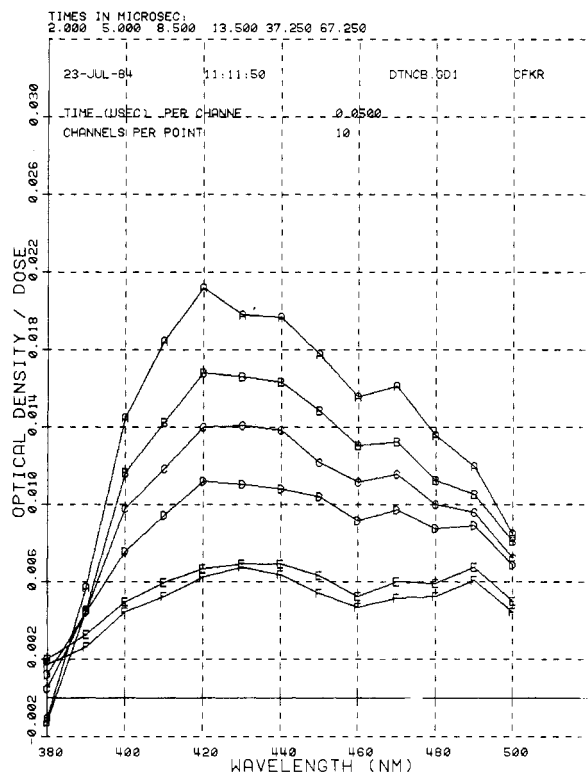
Figure 1. Time-resolved spectra after pulsed-laser flash photolysis for (DTN)W(CO)$_4$ in chlorobenzene at ambient temperature. Times after flash, μs: (a) 2.000; (b) 5.000; (C) 8.500; (d) 13.500; (e) 37.250; (f) 67.250.

Figure 2. Plot of absorbance vs. time for reaction after pulsed-laser flash photolysis of (DTN)W(CO)$_4$ in chlorobenzene at 25.1 °C. The curve is fitted as an exponential decay to a new base line.

wavelength, 11-ns fwhi). Temperature at the jacketed observation cell was maintained through use of an external circulating bath (Lauda K-2/RD) and monitored by employing a digital thermometer (copper–constantan thermocouple). Concentrations of substrate were approximately 5 × 10^{-4} M, and various concentrations of L were employed. The pseudo-first-order rate constants (k_{obsd}) were evaluated by employing an iterative linearized least-squares analysis program (PDP 11/70 computer). Each value of k_{obsd} was determined from an average of five or more successive pulses for a given reaction solution. Rate constants are given in Table I (supplementary material).

Reaction products formed through photolysis were identified to be exclusively the *trans*- and *cis*-L$_2$W(CO)$_4$ species (vide supra) through irradiation of (DTO)W(CO)$_4$ and (DTN)W(CO)$_4$ in chlorobenzene in the presence of excess triisopropyl phosphite with a 450-W Hanovia medium-pressure mercury lamp. No carbonyl loss was detected under the conditions of irradiation, and thus it was concluded that no carbonyl loss would result from irradiation at 355 nm (there is a Hg line at 365 nm).

Results and Discussion

Figure 1 exhibits time-resolved spectra (of absorbance vs. wavelength at various times after the flash) for the decay of an intermediate produced through pulsed-laser flash photolysis at 355 nm of (DTN)W(CO)$_4$ in CB which indicate that the optimal wavelength for observation of the decay of the intermediate is ca. 430 nm. The time-resolved spectra for (DTO)W(CO)$_4$ in CB were qualitatively nearly identical; 430 nm was the observation wavelength employed for monitoring both substrates. Typical plots (for (DTN)W(CO)$_4$) of absorbance vs. time at this wavelength, at zero ligand concentration and at [L] = 1.088 M (triisopropyl phosphite in CB), are exhibited in Figures 2 and 3. For the DTN complex, these plots indicate that two species decay after formation via the flash; only one rate process was observed for DTO.

Analysis of such plots (the rate constants are the pseudo-first-order rate constants k_{obsd}) as a function of varying concentrations of L demonstrate that the fast process obeys the rate law
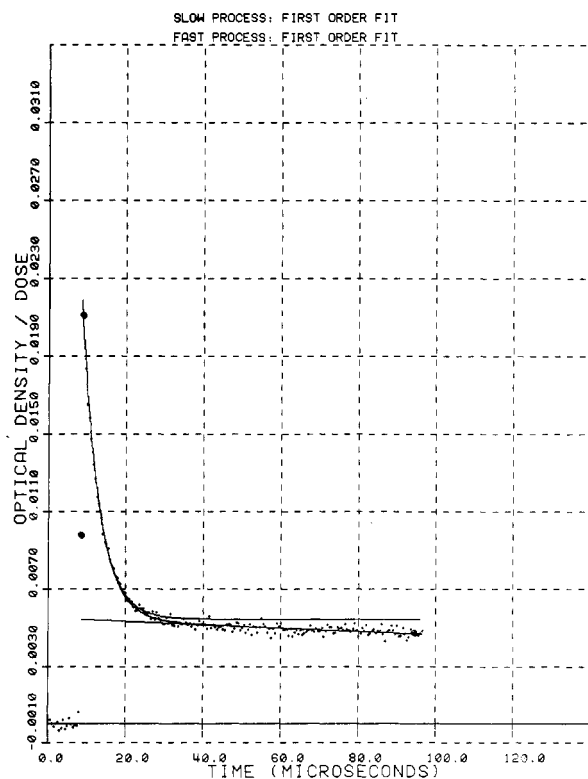
$$-d[\text{Int}]/dt = k_{-1}[\text{Int}] + k_2[\text{Int}][\text{L}] \qquad (1)$$

while the slower obeys the rate law

$$-d[\text{Int}]/dt = k'_2[\text{Int}][\text{L}] \qquad (2)$$
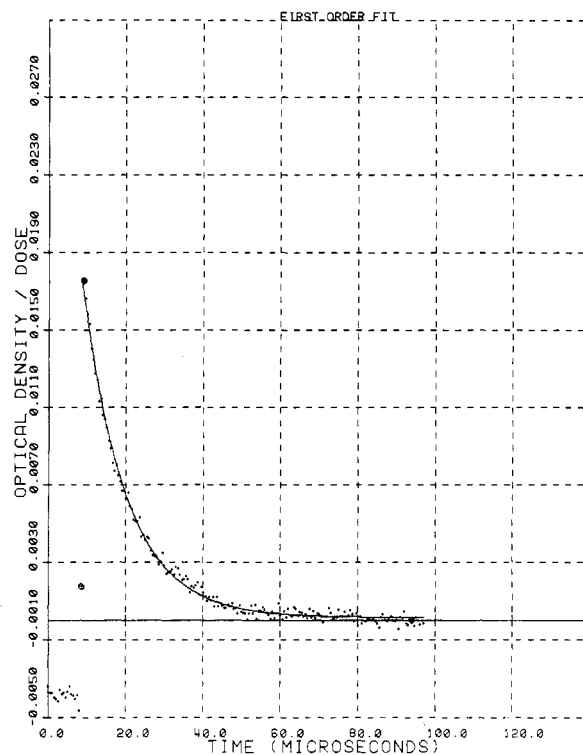
Figure 3. Plot of absorbance vs. time for reaction after pulsed-laser flash photolysis of (DTN)W(CO)$_4$ in the presence of 1.088 M triisopropyl phosphite in chlorobenzene at 25.1 °C. The curve is fitted as two independent exponential decays to the ground-state base line.

Plots of k_{obsd} vs. [L] for the fast processes for (DTO)W(CO)$_4$ and (DTN)W(CO)$_4$ (L = triisopropyl phosphite in CB), supportive of rate law 1, are exhibited in Figures 4 and 5. Figure 6 exhibits a plot, fitted to an exponential decay, of absorbance vs. time for the slow path, observed after photolysis of (DTN)W(CO)$_4$ in DCE in the presence of 1.15 M triisopropyl phosphite; in Figure 7 is
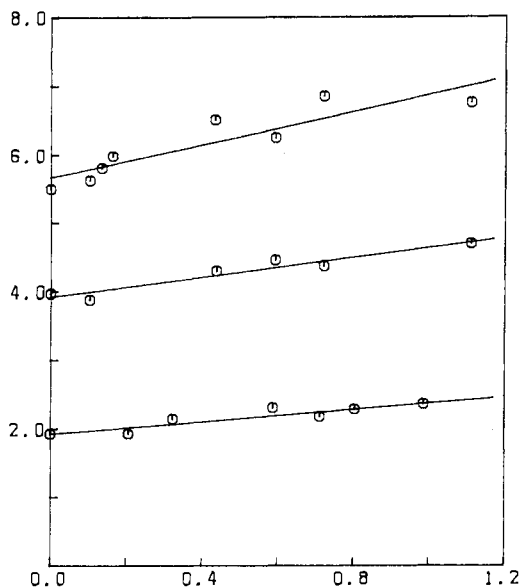
Figure 4. Plots of k_{obsd} vs. [L] after pulsed-laser flash photolysis of $(DTO)W(CO)_4$ in triisopropyl phosphite/chlorobenzene solutions at various temperatures. Labeling of axes: ordinate, $10^{-5} k_{obsd}$, s^{-1}; abscissa, $[P(OPr-i-)_3]$, M.
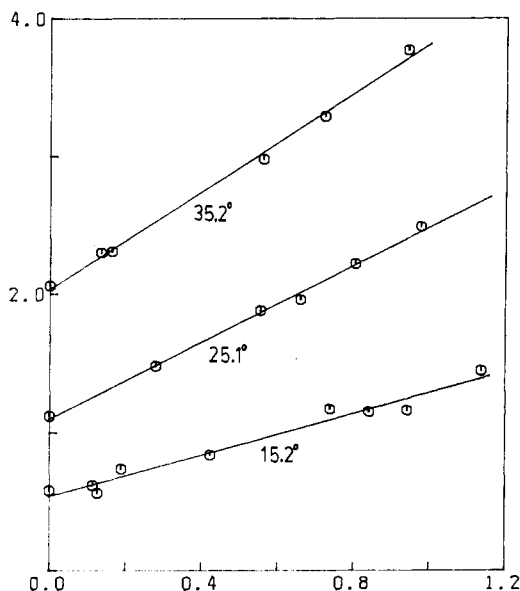

Figure 5. Plots of k_{obsd} vs. [L] for the fast decay after pulsed-laser flash photolysis of $(DTN)W(CO)_4$ in triisopropyl phosphite/chlorobenzene solutions at various temperatures. Labeling of axes: ordinate, $10^{-5}k_{obsd}$, s^{-1}; abscissa, $[P(OPr-i)_3]$, M.

Table II. Rate Constants for Reaction of Five-Coordinate Intermediates

solvent	T, °C	L	$10^{-4}k_{-1}$, s^{-1}	$10^{-4}k_2$,[a] M^{-1} s^{-1}
		$[(\eta^1\text{-DTO})W(CO)_4]$		
DCE	25.2	$P(OPr-i)_3$	7.5 (9)	0.60 (4)
CB	15.0	$P(OPr-i)_3$	19.5 (6)	4.5 (9)
CB	26.4	$P(OPr-i)_3$	39.2 (6)	7.2 (10)
CB	35.2	$P(OPr-i)_3$	56.7 (2)	12.1 (22)
		$[(\eta^1\text{-DTN})W(CO)_4]$		
DCE	25.1	$P(OPr-i)_3$	1.35 (5)	0.97 (8)[a]
DCE	25.5	$P(Bu-n)_3$	1.45 (1)	1.24 (3)
CB	15.2	$P(OPr-i)_3$	5.4 (3)	7.5 (5)
CB	25.1	$P(OMe)_3$	11.3 (2)	17.0 (4)
CB	25.1	$P(OEt)_3$	11.3 (1)	14.2 (3)
CB	25.1	$P(OPr-i)_3$	11.0 (2)	13.9 (4)
CB	35.2	$P(OPr-i)_3$	20.4 (3)	17.8 (5)
toluene	25.1	$P(OPr-i)_3$	38.5 (56)	62.5 (106)

[a] $k_2' = 0.0539$ (31) $\times$ 10^4 M^{-1} s^{-1}.

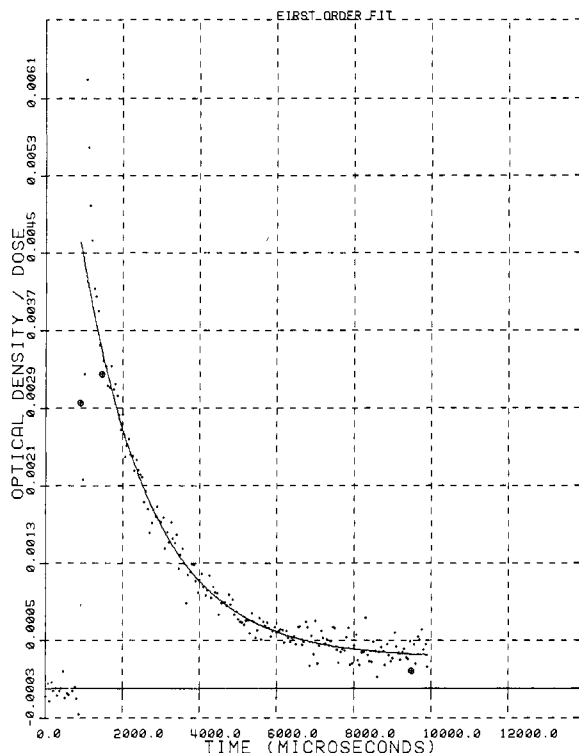**Figure 6.** Plot of absorbance vs. time for the slow decay after pulsed-laser flash photolysis of $(DTN)W(CO)_4$ in the presence of 1.15 M triisopropyl phosphite in chlorobenzene at 26.3 °C. The curve is fitted as an exponential decay to a new base line.

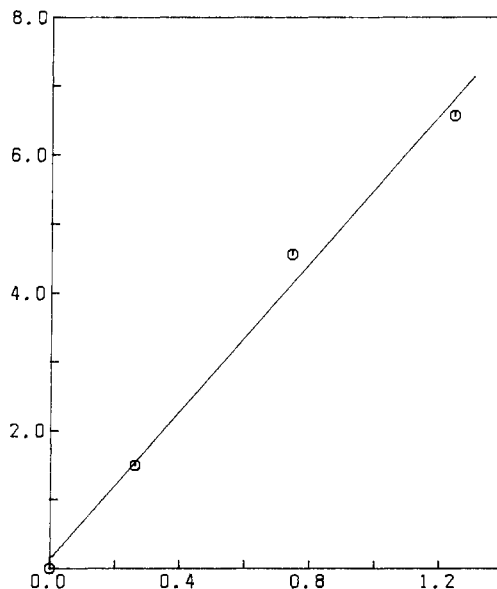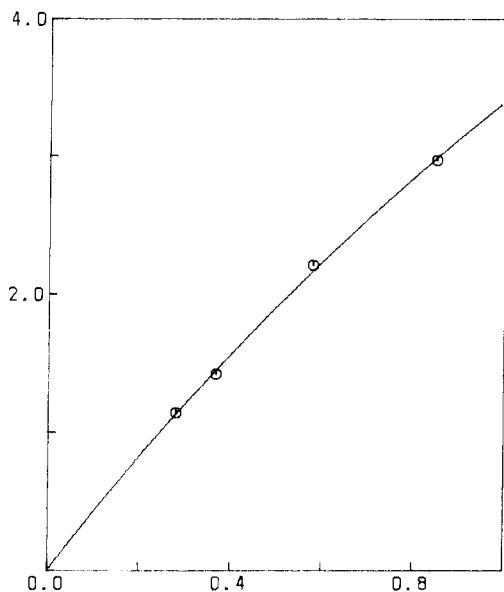**Figure 7.** Plot of k_{obsd} vs. $[P(OPr-i-)_3]$ for the slow decay after pulsed-laser flash photolysis of $(DTN)W(CO)_4$ in triisopropyl phosphite/chlorobenzene solutions at 25.2 °C. Labeling of axes: ordinate, $10^{-3}k_{obsd}$, s^{-1}; abscissa, $[P(OPr-i)_3]$, M.

exhibited a plot of k_{obsd} vs. [L] for this process (L = triisopropyl phosphite in CB at 25.1 °C), consistent with rate law 2. Values of k_{obsd} are given in Table I (supplementary material). The rate constants k_{-1}, k_2, and k'_2 determined from these values are presented in Table II.

This rate behavior has previously been observed for pulsed-laser flash photolysis of $(NP)Mo(CO)_4$ (NP = 1-(diethylamino)-2-(diphenylphosphino)ethane), for which it has been attributed to chelate ring opening (via fission of the Mo–N bond), affording cis- and trans-$[LM(CO)_4]$ intermediates.[1] The cis intermediate decays through competitive chelate ring reclosure and bimolecular combination with L, while the trans intermediate, which cannot react via ring closure, disappears by bimolecular combination with
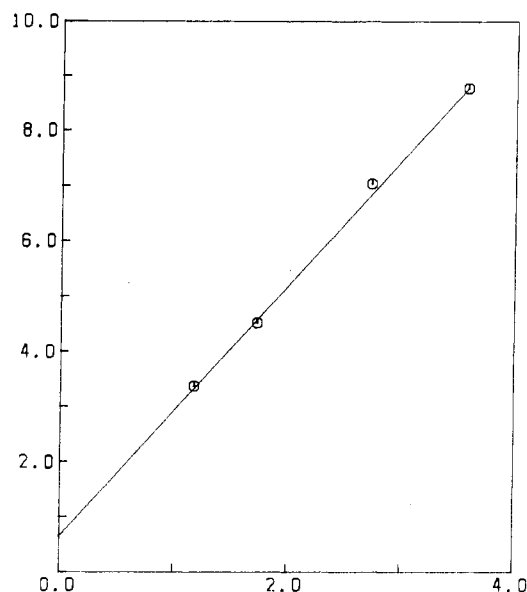
Figure 8. Plot of k_{obsd} vs. [L] for the thermal reaction of $(DTO)W(CO)_4$ and triisopropyl phosphite in chlorobenzene at 35.2 °C. Labeling of axes: ordinate, $10^7 k_{obsd}$, s^{-1}; abscissa, $[P(OPr-i-)_3]$, M.

L. Failure to observe the slow process for DTO indicates that the trans isomer is not produced in significant quantities upon photolysis in that system, particularly in view of the fact that the slow process *is* observed for the DTN system; the ring opened intermediates produced from photolysis of the DTO and DTN complexes are expected to be nearly identical in steric and electronic properties at the trans site, given that they differ only by a single methylene group in the "backbone" of the bidentate ligands. That two first-order processes are observed for DTN also indicates that there is no interconversion of the isomeric five-coordinate intermediates on the time scale of ligand substitution. This observation may be contrasted to results obtained for the $[(PPh_3)W(CO)_4]$ intermediate by Darensbourg, Dobson, and Moradi-Araghi in DCE,[6] in which evidence indicated the intermediate to be stereochemically nonrigid on the time scale of ligand substitution. Thus, as has been observed in other systems,[7] the stereochemical nonrigidity of such species is influenced by the identity of coordinated groups in the five-coordinate intermediates.
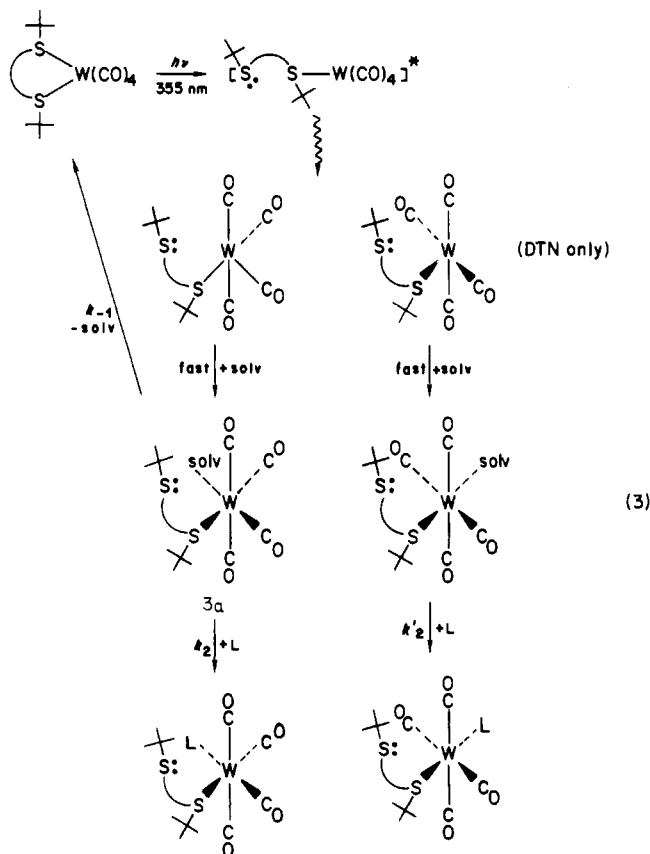
The photochemical mechanism proposed is in congruence with observations of Poliakoff for matrix-isolation photolysis of SCW-$(CO)_5$, which were interpreted in terms of the creation of a vibrationally or electronically excited square-pyramidal intermediate following CO loss; this intermediate decays to the ground state via a trigonal-pyramidal transition state to afford square-pyramidal cis and trans intermediates.[8]

A strong dependence of rates on the identity of the solvent is observed. Thus, ratios of k_{-1} and k_2, respectively, in DCE, CB, and toluene are 1:8:29 and 1:14:65 under identical reaction conditions $((DTN)W(CO)_4$ and triisopropyl phosphite at 25.1 °C). Similar behavior, indicative of significant solvation of the vacant coordination site, which increases with increased solvent polarity, was also observed for $(NP)Mo(CO)_4$.[1] As was noted by Poliakoff for photolysis of $(SC)W(CO)_5$ in various solvent matrices[8] and is suggested by our data,[9] the ratio of intermediates produced upon

(6) Darensbourg, D. J.; Dobson, G. R.; Moradi-Araghi, A. *J. Organomet. Chem.* **1976**, *116*, C17–C20.

(7) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113–150.

(8) Poliakoff, M. *Inorg. Chem.* **1976**, *15*, 2892–2897.

(9) It is observed (see, e.g., Figure 3), that the fast decay, attributable to formation of the cis five-coordinate intermediate, does not proceed to the ground-state base line. The difference between the ground-state base line and the base line observed after the fast decay is related to the amount of the trans intermediate produced via the flash. This difference increases as a function of solvent in the order DCE < CB < toluene, the order of decreasing solvent polarity. For $(DTO)W(CO)_4$, for which the cis intermediate is overwhelmingly favored, fast decay to within an average of less than 10% of the ground-state base line is observed at zero ligand concentration.

Figure 9. Plot of $1/k_{obsd}$ vs. $1/[L]$ for the thermal reaction of (DTO)-$W(CO)_4$ and triisopropyl phosphite in chlorobenzene at 35.2 °C. Labeling of axes: ordinate, $10^{-6}/k_{obsd}$, s; abscissa, $1/[P(OPr-i-)_3]$, M^{-1}.

photolysis (trans:cis) is solvent dependent. The ratio increases with decreased solvent polarity. The overall mechanism is summarized in (3).

(3)

Additional support for mechanism 3 is derived from thermal investigations of $(DTO)W(CO)_4$ in its reaction with triisopropyl phosphite in chlorobenzene under conditions identical with those employed in the photochemical investigations. The thermal kinetics for this system have previously been studied in detail;[4c] rate data from that study indicate that displacement of DTO by L takes place via steady-state rate law 4, consistent with mechanism 5. From (4) are derived (6), the rate law expressed in terms of k_{obsd}, and the "reciprocal relationship" (7). The data[4c] also indicate

$$-d[(DTO)W(CO)_4]/dt = k_1 k_2 [(DTO)W(CO)_4][L]/(k_{-1} + k_2[L]) \quad (4)$$

5a
(steady state intermediate)
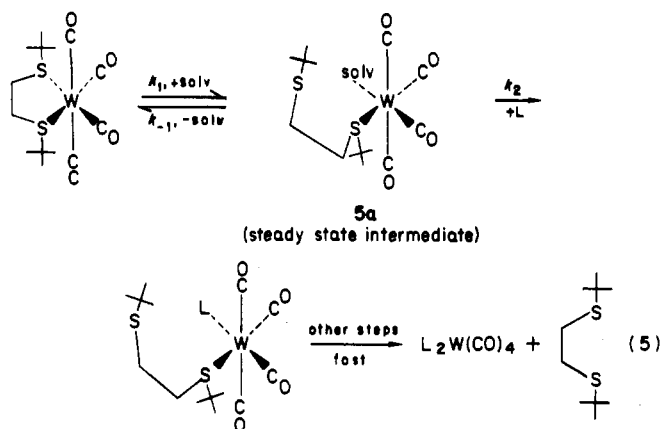
Rate constants in CB at 35.2 °C: $k_1 = 1.6 (3) \times 10^{-6}$ s^{-1};

$k_{-1} = 5.7 (1) \times 10^5$ s^{-1}; $k_2 = 1.2 (2) \times 10^5$ M^{-1} s^{-1}

$$k_{obsd} = k_1 k_2 [L]/(k_{-1} + k_2[L]) \quad (6)$$

$$1/k_{obsd} = 1/k_1 + k_{-1}/k_1 k_2 [L] \quad (7)$$

that ring closure (governed by k_{-1}) and attack at the five-coordinate, ring-opened intermediate by L (governed by k_2) are competitive. For (6), (for $k_{-1} \approx k_2$), curved plots of k_{obsd} vs. [L] and, for (7), linear "reciprocal plots" of $1/k_{obsd}$ vs. $1/[L]$ are expected. These are exhibited in Figures 8 and 9 for L = triisopropyl phosphite in CB at 35.2 °C. From the intercept/slope of the reciprocal plots can be extracted ratios of k_2/k_{-1}, which may be compared to these same ratios obtained from the plots of k_{obsd} vs. [L] for the fast photochemical pathway (1), as slope/intercept (Figure 4). These ratios are 0.28 (7) (thermal) and 0.21 (5) (photochemical), which are the same within experimental error. It would be fortuitous, indeed, were these ratios to be the same unless the intermediates generated thermally (**5a**) and photochemically (**3a**) were the same and unless the mechanistic interpretations presented for the thermal and photochemical data were correct.

The rate of chelate ring *opening* can be evaluated as the reciprocal of the intercept of the "reciprocal plot" for the thermal data. Data obtained in this study thus afford all rate constants for the *thermal* process, which are exhibited in (5).

Values of the rate constants k_2, taken under identical reaction conditions for the ligands triisopropyl, triethyl, and trimethyl phosphite, indicate that rates of bimolecular association of these ligands with the five-coordinate intermediates vary slightly with the steric nature of the L, the ratio being 1:1:1.2, respectively. These small differences may be compared to a larger difference in reactivity via metal–ligand bond dissociation for two of these ligands from the related *fac*-(*o*-phen)(L)Cr(CO)$_3$ complexes, for which the ratio of rate constants for triisopropyl and triethyl phosphite is 1:1.7 in DCE at 35.0 °C.[10] This suggests, on the basis of Hammond's postulate,[11] as been proposed in many other related systems,[12] that the five-coordinate intermediate and the transition state leading to bond formation are closely related.

It is also interesting to note that rates of bimolecular attack by L at the cis DTN intermediate are generally observed to be about twice as fast as at the cis DTO intermediate under similar reaction conditions. This indicates that the DTO ligand is better able to inhibit attack by L, perhaps on the basis of the greater extension of its uncoordinated end ligand toward the vacant coordination site.

The ratio of rate constants for bimolecular interaction of triisopropyl phosphite with the cis and trans five-coordinate inter-

Table III. Activation Parameters for Reaction of Five-Coordinate Intermediates

solvent	ΔH_{-1}^*, kcal/mol	ΔS_{-1}^*, eu	ΔH_2^*, kcal/mol	ΔS_2^*, eu
	[(η^1-DTO)W(CO)$_4$]			
DCE	9.8 (1)	−2.9 (5)		
CB	8.8 (5)	−3.5 (16)	8.1 (33)	−9.1 (113)
	[(η^1-DTN)W(CO)$_4$]			
DCE	11.9 (4)	1.2 (12)		
CB	11.5 (3)	2.6 (15)	6.6 (8)	−12.9 (21)

mediates for (DTN)W(CO)$_4$ in CB is ca. 20, which may be compared to the analogous ratio observed for the [(η^1-NP)Mo-(CO)$_4$] intermediate, some 2 orders of magnitude.[1]

Activation parameters for ring closure and for bimolecular interaction of L at the cis ring-opened five-coordinate intermediates produced from the DTO and DTN complexes are presented in Table III. Some differences in rate reflected in activation parameters, solvation effects, and the influence of the differences between the two bidentate ligands on rates of bimolecular addition of L at the solvated cis coordination site, have been discussed above, since rate constants are a much more sensitive measure of small kinetic differences than are activation parameters. Moreover, there are observed to be rather large error limits associated with the activation parameters derived from k_2 for DTO, because k_{-1} dominates the values of the rate constants for eq 1, and thus uncertainties in the values of k_2 are quite significant.

Entropies of activation for ring closure for both "ring-opened" intermediates (ΔS_{-1}^*) are approximately zero, not unreasonable for a process that involves solvent displacement upon ring closure. They do not vary significantly between the solvents DCE and CB. In both DCE and CB, entropies of activation for ring closure are significantly more positive for (DTN)W(CO)$_4$ than for (DTO)-W(CO)$_4$. A possible explanation for this trend lies in the greater flexibility expected for anchored DTN, which may result in more possible conformations of DTN that have the proper orientation to result in ring reclosure than those of DTO.[13] Entropies of activation for bimolecular interaction of triisopropyl phosphite at the cis-solvated site (ΔS_2^*) are significantly more negative than are corresponding values for unimolecular ring closure, as might be anticipated. In CB, for example, for the DTN intermediate, they are −12.9 (21) and 2.6 (15) cal/(deg mol), respectively.

Enthalpies of activation (ΔH_{-1}^*) for ring closure for the DTN intermediate, leading to formation of a six-membered chelate ring, are significantly greater than are those for ring closure in the DTO intermediate, which affords a five-membered ring. In CB, for example, they are 11.4 (3) vs. 8.8 (5) kcal/mol, respectively. This difference may be related to differences in substrate geometry, which have been detailed previously[5] and which indicate that the chelate ring is more strained in the DTN complex than in the DTO complex. Thus, the "creation of strain" upon ring closure would explain the greater enthalpy of activation observed for the DTN complex, as "release of strain" explains the greater ease of chelate ring opening suggested in these complexes on the basis of thermal kinetics data.[5,14] For the DTN complex in chlorobenzene, although chelate ring closure and attack at the solvated cis coordination site are competitive, the similar values for the free energies of activation results from a more favorable (lower) enthalpy of activation for bimolecular interaction of the intermediate with L, which balances a less favorable (more negative) entropy of activation for that process. It is presumed that less deviation from idealized octahedral geometry is introduced upon bimolecular interaction of unidentate L with the intermediate than through chelate ring closure. Unfortunately, for metal carbonyl complexes at least, structural studies that would test this supposition, through

(10) Dobson, G. R.; Smith, L. A. H. *Inorg. Chem.* **1970**, *9*, 1001–1003.
(11) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–340.
(12) (a) Covey, W.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2820–2825. (b) Dobson, G. R.; Strunk, H. T. *J. Inorg. Nucl. Chem.* **1977**, *39*, 159–163. (c) Atwood, J. D.; Wovkulich, M. J.; Sonnenberger, D. C. *Acc. Chem. Res.* **1983**, *16*, 350–355.

(13) Bernal, I., personal communication, 1984.
(14) Among the small but statistically significant differences noted in (DTN)W(CO)$_4$ relative to (DTO)W(CO)$_4$, all of which are indicative of greater ring distortion in the former,[5] are a smaller S–W–S angle, a smaller "bite" (nonbonded S–S distance), a more distorted average W–S–C$_{ring}$ angle, and a longer average W–S bond length.

comparisons of the structures of cis disubstituted complexes that contain chelate rings to analogous complexes that do not, have yet to be reported. It will be of great interest to make such comparisons.

Registry No. 1a, 21948-42-5; **1b**, 29832-09-5; trimethyl phosphite, 121-45-9; triethyl phosphite, 122-52-1; triisopropyl phosphite, 116-17-6; tri-n-butylphosphine, 998-40-3.

Supplementary Material Available: Pseudo-first-order rate constants for reactions of $(DTO)W(CO)_4$ and $(DTN)W(CO)_4$ with L in DCE and CB at various temperatures (Table I) (5 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Faculty of Science, Kanazawa University, Kanazawa 920, Japan

Thermal Reactions of Metal Complexes under Quasi-isothermal and -isobaric Conditions. 4.[1] Solid-Phase Thermal Reactions of Ruthenium(II)–Pentaammine Complexes Containing Dinitrogen and Related Ligands

AKIRA UEHARA,[*2] MIKITO KITAYAMA, MASATATSU SUZUKI, and RYOKICHI TSUCHIYA

A series of Ru^{II}–pentaammine complexes of the form $[Ru(NH_3)_5(L)]X_n \cdot mH_2O$ were prepared, where L = N_2, CO, NO^+, CH_3CN, CH_3NC, X = Cl^-, Br^-, I^-, n = 2, 3, and m = 0, 1. The thermal reactions of the complexes in the solid phase were investigated under quasi-isothermal and -isobaric conditions (Q conditions) and under open dynamic conditions (D conditions). It was found that the thermal reaction patterns of the complexes are considerably different from one another, depending upon the kinds of ligands (L). In the thermal reaction processes of $[Ru(NH_3)_5(N_2)]X_2$, the evolution of NH_3 precedes that of dinitrogen, indicating that the $Ru^{II}–N_2$ bond is unexpectedly stable in the solid state, whereas the bond has been found to be easily broken in aqueous media. The thermal reaction patterns of the CO, CH_3CN, and CH_3NC complexes are essentially similar to those of the dinitrogen complexes. $[Ru(NH_3)_5(NO)]X_3$ was converted into *trans*-$[Ru(NH_3)_4X(NO)]X_2$ when X was Cl^- or Br^-, but into *cis*-$[Ru(NH_3)_4I(NO)]I_2$ when X was I^-. The cleavage temperatures of $Ru^{II}–L$ bonds contained in the complexes $[Ru(NH_3)_5(L)]Cl_n$ increase in the order CH_3CN (191 °C) < N_2 (255 °C) < CO (286 °C) < CH_3NC (312 °C) < NO^+ (324 °C), which is parallel to the order of the strength of π back-bonding from Ru^{II} to L except for the case of the CH_3NC complex. The high cleavage temperature of the CH_3NC complex may come from the stronger σ bonding due to the –NC group rather than the π back-bonding.

Introduction

Since the (dinitrogen)ruthenium(II) complex $[Ru(NH_3)_5(N_2)]Cl_2$ was first isolated by Allen et al.,[3,4] studies have been devoted mainly to clarifying the possibilities of reducing the nitrogen molecule under mild conditions by the use of metal complexes.[5–8] Such attempts have not yet led to good results because of the strength of the N–N bond. Our interest concerns whether or not the dinitrogen complexes are stable in the solid state. We recently noticed two different papers on this topic: one stated that $[Ru(NH_3)_5(N_2)]X_2$ complexes are so unstable that they easily evolve the dinitrogen molecule in an anhydrous state[4] as well as in solution;[9,10] the other reported that the solid complexes do not expel the dinitrogen molecule even at 201 °C (for chloride), 183 °C (for bromide), and 155 °C (for iodide).[11] To settle the discrepancy, the present study was undertaken to learn the details of the solid-phase thermal reactions of $[Ru(NH_3)_5(N_2)]X_2$ (X = Cl^-, Br^-, I^-) under quasi-isothermal and -isobaric conditions.[1,12]

In $[Ru(NH_3)_5(N_2)]Cl_2$, the $Ru–N_2$ bond involves π backbonding between the Ru $d\pi$ orbital and the $p\pi^*$ orbital of the N_2 ligand.[13] It therefore seemed of interest to extend the present study by considering the effect of other π-accepting ligands (L) on the thermal stability of $[Ru(NH_3)_5(L)]X_n$ complexes. Therefore, a series of Ru^{II}–pentaammine complexes containing a variety of π-accepting ligands other than dinitrogen were prepared and their solid-state thermal behaviors were investigated. In the present study, N_2, CO, NO^+, CH_3CN, and CH_3NC were selected as the π-accepting ligands.

Experimental Section

Preparation of Starting Materials. The starting complexes $[Ru(NH_3)_5Cl]Cl_2$[14] and $[Ru(NH_3)_6]Cl_3$[15] were prepared by a modification of

(1) Part 3: Uehara, A.; Terabe, S.; Tsuchiya, R. *Inorg. Chem.* **1983**, *22*, 2864.
(2) To whom correspondence should be addressed.
(3) Allen, A. D.; Senoff, C. V. *Chem. Commun.* **1965**, 621.
(4) Allen, A. D.; Bottomley, F.; Harris, R. O.; Reinsalu, V. P.; Senoff, C. V. *J. Am. Chem. Soc.* **1967**, *89*, 5595.
(5) Kahn, M. M. T.; Martel, A. E. "Homogeneous Catalysis by Metal Complexes"; Academic Press: New York, 1974; Vol. 1, Chapter 3.
(6) Stiefel, E. S. *Prog. Inorg. Chem.* **1977**, *22*, 1.
(7) (a) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589. (b) Yamamoto, A.; Kitazume, S.; Pu, L. S.; Ikeda, S. *Chem. Commun.* **1967**, 79. (c) Collman, J. P.; Kang, J. W. *J. Am. Chem. Soc.* **1966**, *88*, 3459.
(8) Yamabe, T.; Hori, K.; Fukui, K. *Inorg. Chem.* **1982**, *21*, 2046.
(9) Armour, J. N.; Taube, H. *J. Am. Chem. Soc.* **1970**, *92*, 6170.
(10) Ford, P. C. *Coord. Chem. Rev.* **1970**, *5*, 75.
(11) Kohata, S.; Itoh, N.; Kawaguchi, H.; Ohyoshi, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2264.
(12) Tsuchiya, R.; Uehara, A.; Kobayashi, K. *Bull. Chem. Soc. Jpn.* **1981**, *53*, 921.
(13) Bottomley, F.; Nyburg, S. C. *Chem. Commun.* **1966**, 899; *Acta Crystallogr.* **1968**, *324*, 1289.
(14) Fergusson, J. E.; Love, J. L. *Inorg. Synth.* **1972**, *13*, 211.
(15)