crease in the rate over that of the parent complex. Along with the increase in rate, a change in selectivity for the isomerization reaction was observed. The gold adduct is more selective for the production of *trans*-2-hexene while the parent is more selective for *cis*-2-hexene. It is not known why the gold changes the activity and selectivity, but work is in progress to gain a better understanding of this isomerization reaction. Analysis of the other five complexes discussed in this paper did not show evidence for catalytic activity in the isomerization of 1-hexene under similar conditions over a 24-h period.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-851923) and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We gratefully acknowledge the Johnson Matthey Co. for a generous loan of gold and iridium salts. B.D.A. also thanks General Electric Co. and the University of Minnesota Graduate School for fellowships.

Supplementary Material Available: Figures S1 and S2, displaying the ORTEP drawings of **1** and **3**, a complete table of crystal data and data collection parameters, Tables S1–S8, listing general temperature factor expressions, final positional and thermal parameters for all atoms including those of the solvate molecules, calculated hydrogen atom positions and thermal parameters, distances and angles, and least-squares planes (39 pages); Tables S9 and S10, listing observed and calculated structure factor amplitudes (79 pages). Ordering information is given on any current masthead page.

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Octahedral Metal Carbonyls. 63.[1] Chelate Ring Displacement of DTHp from *cis*-(DTHp)W(CO)$_4$ by Lewis Bases (DTHp = 2,2,6,6-Tetramethyl-3,5-dithiaheptane, Lewis Base = L (Phosphine, Phosphite))

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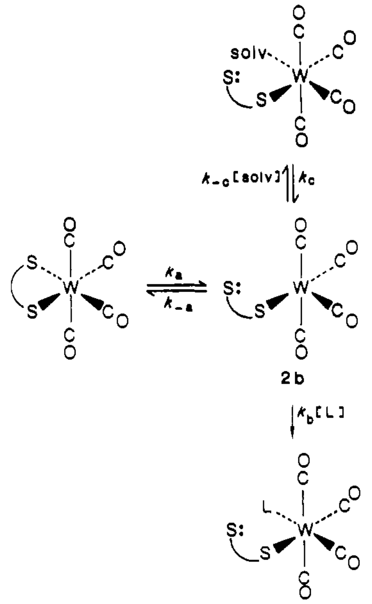
Reactions of *cis*-(DTHp)W(CO)$_4$, in which DTHp forms a four-membered chelate ring, with L (DTHp = 2,2,6,6-tetramethyl-3,5-dithiaheptane; L = P(OMe)$_3$, P(O-*i*-Pr)$_3$, P(OPh)$_3$, P(OCH$_2$)$_3$CCH$_3$, P(*n*-Bu)$_3$) in chlorobenzene (CB) proceed via displacement of DTHp according to *cis*-(DTHp)W(CO)$_4$ + 2L → *cis*- and *trans*-(L)$_2$W(CO)$_4$ + DTHp. Kinetics data in CB indicate the reaction to be biphasic, with *cis*-(L)(η^1-DTHp)W(CO)$_4$ present as a predominant species during the reaction's course; this intermediate has been characterized for L = P(OCH$_2$)$_3$CCH$_3$. In contrast to results observed for related systems containing five- and six-membered chelating rings, evidence here suggests that significant L–W bond making takes place in the transition states leading to chelate ring opening and closing. This conclusion is supported by activation parameters both for chelate ring opening and for chelate ring closure after pulsed laser flash photolysis in 1,2-dichloroethane (DCE) and bromobenzene (BB) solvents (solv), which generates *cis*-[(solv)(η^1-DTHp)W(CO)$_4$]; evidence suggests that this intermediate is not produced thermally. The *cis*-(L)(η^1-DTHp)W(CO)$_4$ products produced via the first phase of the biphasic thermal process undergo unimolecular W–S bond fission. Rate constants for this process vary significantly and are largely influenced by the steric properties of coordinated L, increasing in the order of larger Tolman cone angles. This W–S bond dissociation is followed by solvation to afford *cis*-[(CB)(L)W(CO)$_4$] intermediates, previously characterized, which then react via rapid reversible desolvation and attack at the five-coordinate, square-pyramidal [(L)W(CO)$_4$] intermediates by L, to afford *cis*-(L)$_2$W(CO)$_4$. Subsequent nondissociative isomerization of this species forms the equilibrium mixture of *cis*- and *trans*-(L)$_2$W(CO)$_4$ products ultimately obtained. These several steps involved in the overall chelate displacement process are discussed in detail.

Thermal displacement by phosphines and phosphites (L) of chelating ligands S$_2$ (S$_2$ = DTO = 2,2,7,7-tetramethyl-3,6-dithiaoctane, (CH$_3$)$_3$CSCH$_2$CH$_2$SC(CH$_3$)$_3$) and DTN (DTN = 2,2,8,8-tetramethyl-3,7-dithianonane, (CH$_3$)$_3$SCH$_2$CH$_2$CH$_2$SC(CH$_3$)$_3$), which form five- and six-membered chelating rings, respectively

$$cis\text{-}(S_2)W(CO)_4 + 2L \rightarrow trans\text{- and } cis\text{-}(L)_2W(CO)_4 + S_2 \tag{1}$$

has been studied extensively.[2,3] Rate data for the initial ring-opening process were interpreted in terms of a predominant dissociative mechanism, (2).[4] The results were of particular interest because, contrary to the expectation that chelate ring closure should be much faster than bimolecular interaction of L with **2b**; i.e., $k_{-a} \gg k_b$,[5] these two pathways were found to be competitive at readily accessible concentrations of L (ca. 0.1–1 M). Thus, nonlimiting rate behavior was observed, and it was possible to evaluate "competition ratios", k_b/k_{-a}, for reaction of **2b** via attack by L and by chelate ring closure. Since rates of chelate ring reclosure are independent of the identity of L, the selectivity of **2b** among various L species thus could be evaluated.[2,3]



(2)

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[1] Part 62: Asali, K. J.; Basson, S. S.; Tucker, J. S.; Hester, B. C.; Cortês, J. E.; Awad, H. H.; Dobson, G. R. *J. Am. Chem. Soc.* **1987**, *109*, 5386.

[2] (a) Dobson, G. R. *Inorg. Chem.* **1969**, *8*, 90. (b) Schultz, L. D.; Dobson, G. R. *J. Organomet. Chem.* **1976**, *124*, 19.

[3] (a) Dobson, G. R.; Faber, G. C. *Inorg. Chim. Acta* **1970**, *4*, 87. (b) Dobson, G. R.; Schultz, L. D. *J. Organomet. Chem.* **1977**, *131*, 285.

[4] It has recently been demonstrated[1] that replacement of CB solvent by piperidine from the closely related complex *cis*-[(CB)(P(O-*i*-Pr)$_3$)W(CO)$_4$] is dissociative; it therefore will be assumed, initially (however, see the discussion below), that replacement of solvent by L in *cis*-[(CB)(η^1-DTHp)W(CO)$_4$] intermediates also is dissociative, as is shown in eq 2.

[5] Schwarzenbach, G. *Helv. Chim. Acta* **1952**, *35*, 2344.

More recently, the rate constants $k_{-a}k_c/k_{-c}$ and k_bk_c/k_{-c} were obtained directly by employing pulsed laser flash photolysis.[6,7] The present work extends these investigations to the wholly analogous complex containing the four-membered chelate ring, *cis*-(DTHp)W(CO)$_4$ (DTHp = 2,2,6,6-tetramethyl-3,5-dithiaheptane, $(CH_3)_3CSCH_2SC(CH_3)_3$).

Experimental Section

General Considerations. Infrared spectra were obtained with a Nicolet 20 SXB Fourier transform spectrometer for isolated complexes but with a Perkin-Elmer Model 621 grating spectrophotometer for spectra obtained in situ. The latter spectra were calibrated against a band of polystyrene at 1601.4 cm^{-1}. NMR spectra employed in the characterization of the ligands were obtained employing a JEOL FX-90Q spectrometer; those used to study isomerization in *cis*-(P(*n*-Bu)$_3$)$_2$W(CO)$_4$ were taken on a Varian VXR-300 spectrometer. Elemental analyses were carried out by Midwest Microlab, Indianapolis, IN.

Preparation and Purification of Materials. Chlorobenzene (CB; Fisher) and 1,2-dichloroethane (DCE; Fisher) were stirred and refluxed under nitrogen over P_4O_{10} for 24 h before they were fractionally distilled. Bromobenzene (BB; Matheson Coleman and Bell) was stirred for 3 h over anhydrous $MgSO_4$ and then refluxed for 4 h over P_2O_5. It then was fractionally distilled under nitrogen. The ligands (L) P(OMe)$_3$, P(O-*i*-Pr)$_3$, P(OPh)$_3$, and P(*n*-Bu)$_3$ (Aldrich) were purified as described previously.[2b,8] The "constrained phosphite", $P(OCH_2)_3CCH_3$ (CP), was synthesized by employing the method of Wadsworth and Verkade and their co-workers[9] and was purified as described elsewhere.[1] DTHp was synthesized by a method similar to that employed by Dobson and Faber for the synthesis of DTN.[3a] In a 1-L three-necked flask equipped with a magnetic stirrer, reflux condenser, dropping funnel, and nitrogen inlet, 1 mol of sodium (23 g) was allowed to react with 500 mL of absolute ethanol. After the Na had dissolved, 90 g (1.00 mol) of *tert*-butyl mercaptan was added dropwise under ice cooling. After the reaction mixture was stirred at room temperature for 2 h, the solution again was cooled and 87 g (0.50 mol) of dibromomethane (Aldrich) was added dropwise. The solution was then filtered under an aspirator vacuum to remove precipitated NaBr, and the ethanol was removed under vacuum. The resulting oil was then vacuum-distilled (52–53 °C (1 Torr)) to afford 55.8 g (58.1%) of colorless product. The proton NMR spectrum ($CDCl_3$) exhibited a singlet at δ 3.62 (2 H, $-CH_2-$) and a singlet at δ 1.28 (18 H, $-C(CH_3)_3$). The ^{13}C NMR spectrum ($CDCl_3$) exhibited a singlet at δ 43.39 (quaternary C), a quartet at δ 30.81 (methyl carbons), and a triplet at δ 27.83 (methylene carbon). The *cis*-(DTHp)W(CO)$_4$ complex was synthesized as follows: 3.0 g (10.4 mmol) of DTHp and 3.0 g (8.5 mmol) of W(CO)$_6$ were dissolved in 350 mL of hexanes and were irradiated under nitrogen bubbling with a 450-W Hanovia medium-pressure Hg lamp in a water-cooled quartz reaction vessel. The reaction's progress was monitored by withdrawing samples from the reactor and observing the growth of a band at 2017 cm^{-1} attributable to *cis*-(DTHp)W(CO)$_4$ and the disappearance of a band at 1985 cm^{-1} attributable to the hexacarbonyl. After 3 h the precipitated product was collected by suction filtration under nitrogen, was washed with several portions of hot hexanes (ca. 100 mL total volume), and was recrystallized from toluene/hexanes to afford 0.7 g (22%) of bright yellow product. Anal. Calcd for $C_{13}H_{20}O_4S_2W$: C, 31.98; H, 4.13. Found: C, 32.01; H, 4.30. The carbonyl stretching spectrum (CB solution) exhibited bands at 2017 (w), 1898 (s, sh), 1890 (vs), and 1862 (m) cm^{-1}. Scans of the infrared spectra of solutions containing *cis*-(DTHp)W(CO)$_4$ and the various L species revealed rapid formation of bands attributable to *cis*-(L)(η^1-DTHp)W(CO)$_4$, which then more slowly decayed. The carbonyl stretching spectra for these complexes for various L species, as determined in situ in CB, are as follows (cm^{-1}): P(OMe)$_3$, 2025 (m), 1917 (sh), 1900 (vs), 1872 (s); P(OPh)$_3$, 2030 (m), 1927 (sh), 1910 (vs), 1886 (s); P(*n*-Bu)$_3$, 2008 (m), 1901 (sh), 1880 (vs), 1869 (vs); P(O-*i*-Pr)$_3$, 2025 (m), 1919 (sh), 1902 (vs). The *cis*-(CP)(η^1-DTHp)W(CO)$_4$ intermediate was characterized as follows: in a 100-mL volumetric flask fitted with a Teflon stopcock and rubber septum was placed 0.30 g (0.61 mmol) of *cis*-(DTHp)W(CO)$_4$ and 0.15 g (1.0 mmol) of CP in 50 mL of DCE. The flask was placed in a constant-temprature bath at 30 °C, and the progress of the reaction was followed by withdrawing samples of the solution at various time intervals and monitoring the disappearance of a band at 2017 cm^{-1} due to the reactant and the appearance of a band at 2029 cm^{-1} for the product. When the maximum concentration of product was present (ca. 20 min), the reaction solution was quenched in an ice/water bath. The solvent was removed under vacuum, and the resulting pale yellow solid was then recrystallized from toluene/hexanes. Anal. Calcd for $C_{18}H_{29}O_7PS_2W$: C, 33.97; H, 4.60. Found: C, 33.90; H, 4.35. Carbonyl stretching spectrum (CB solution): 2029 (m), 1925 (s), 1907 (vs), 1887 (s) cm^{-1}.

The complex *cis*-(pip)(P(O-*i*-Pr)$_3$)W(CO)$_4$ (pip = piperidine), employed in a flash photolysis study of the solvated *cis*-[(CB)(P(O-*i*-Pr)$_3$W(CO)$_4$] intermediate also produced through dissociation of DTHp from *cis*-(P(O-*i*-Pr)$_3$)(η^1-DTHp)W(CO)$_4$, was prepared and purified via the published procedure.[10,11]

Complete displacement of DTHp from *cis*-(DTHp)W(CO)$_4$ affords, initially (vide infra), *cis*-(L)$_2$W(CO)$_4$ products and then, for L = P(OMe)$_3$, P(O-*i*-Pr)$_3$, and P(*n*-Bu)$_3$, equilibrium mixtures also containing the *trans*-(L)$_2$W(CO)$_4$ analogues. Carbonyl stretching spectra for these complexes, obtained in situ after the completion of the reactions, are in agreement with those previously reported.[1,12,13]

Thermal Kinetics Runs. Initially, the reactions of *cis*-(L)(η^1-DTHp)W(CO)$_4$ with L were monitored by employing a Beckman DU-2 direct-reading spectrophotometer through use of conventional sampling techniques that have been described in detail elsewhere.[3a,14] These methods were inadequate for the study of the fast initial reactions of *cis*-(DTHp)W(CO)$_4$ with L, and thus the procedures outlined below were adopted and employed in all subsequent kinetics studies. Values of k_{obsd} obtained for the reactions of *cis*-(L)(η^1-DTHp)W(CO)$_4$ with L by either method were in good agreement.

The UV-visible spectrophotometric system employed a 40-W tungsten lamp operating from a Hewlett-Packard dc power supply (Harrison 6274A), a Bausch and Lomb 33-86-20 monochromator and Hamamatsu R 136 side-on photomultiplier tube, an Aminco linear-log photometer, and an Aminco dual power supply. The spectrophotometer's output was digitized by employing a Nicolet 2090 IIA digital oscilloscope. Approximately 1.5 mL of ligand/solvent solution was allowed to equilibrate in a jacketed cell whose temperature was regulated by employing a Haake ED external circulator. The solution was flushed with nitrogen, and approximately 2 mg of substrate was quickly introduced. The ligand was present in large excess, and thus pseudo-first-order conditions obtained. Dissolution and mixing were complete within 5 s, and the oscilloscope was immediately triggered. The analyzing light was permitted to impinge on the sample only when readings were being taken. The temperature of the reaction solution was monitored by employing a Keithley 872 digital thermometer (FeCuNi thermocouple). The wavelength monitored was 415 nm. The *cis*-(L)$_2$W(CO)$_4$ reaction products do not absorb significantly at this wavelength, and thus the absorbances of solvent/ligand blanks (A_{bl}) were employed as t_∞ values. Rate constants for the stepwise displacement of the two sulfurs of DTHp from *cis*-(DTHp)W(CO)$_4$ to afford *cis*-(L)$_2$W(CO)$_4$ were determined from the two linear portions of the plots of ln ($A_t - A_{bl}$) vs time (A_t is the absorbance of the solution at time t).

Where L = P(*n*-Bu)$_3$, the isomerization of the *cis*-(L)$_2$W(CO)$_4$ product initially produced to its trans analogue afforded an increase in absorbance subsequent to the two aforementioned linear segments. The rate constants for the isomerization process were obtained from these plots of ln ($A_\infty - A_t$) vs time (A_∞ is the absorbance of the reaction solution for which an equilibrium between *cis*- and *trans*-(P(*n*-Bu)$_3$)$_2$W(CO)$_4$ products had been attained). Only values of A_t taken after complete displacement of DTHp to afford *cis*-(P(*n*-Bu)$_3$)$_2$W(CO)$_4$ were employed. All data were analyzed by employing a linear least-squares computer program; limits of error, given in parentheses as the uncertainty of the last digit(s) of the cited value, are 1 standard deviation. Values of k_{obsd} are given in Supplementary Tables I and II.

Pulsed Laser Flash Photolysis Studies. Pulsed laser flash photolysis studies of *cis*-(DTHp)W(CO)$_4$ in CB, DCE, and BB in the absence and presence of L at various temperatures and of *cis*-(pip)(P(O-*i*-Pr)$_3$)W(CO)$_4$ with P(O-*i*-Pr)$_3$ in CB at 35.2 °C were carried out as described previously.[6] Values of k_{obsd} are presented in Supplementary Tables III and IV.

Determination of Values of K_{eq} for the Isomerization of *cis*-(P(*n*-Bu)$_3$)$_2$W(CO)$_4$. The separation of the ^{31}P resonances attributable to the

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(14) Dobson, G. R.; Faber, G. C. *Inorg. Chem.* **1968**, *7*, 584.

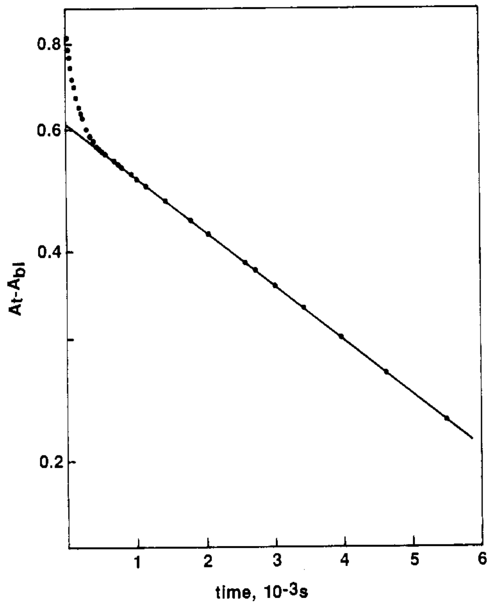

Figure 1. Plot of ln $(A_t - A_{bl})$ vs time for reaction of *cis*-(DTHp)W(CO)$_4$ with P(O-*i*-Pr)$_3$ (0.3084 M) at 31.1 °C monitored at 415 nm in chlorobenzene.

cis- and *trans*-(P(*n*-Bu)$_3$)$_2$W(CO)$_4$ products in the NMR spectrum makes ^{31}P NMR spectrometry a method for determination of K_{eq} superior to infrared spectrophotometry, for which severe overlap of carbonyl stretching absorbances attributable to the two isomeric products is observed. Accordingly, values of K_{eq} were determined from the integrated intensities of the resonances attributable to the cis and trans isomers by employing a Varian VXR 300 NMR spectrometer. Samples of *cis*-(DTHp)W(CO)$_4$ in ca. 0.04 M P(*n*-Bu)$_3$/CB solutions were placed in NMR tubes and allowed to remain in a constant-temperature bath (Haake ED) for 10–24 h, depending upon the temperature. The tubes then were removed from the bath and were quickly transported in the 50-mL beakers containing water from the bath to the probe of the spectrometer, which had been brought to the bath temperature. Data were accumulated over 0.5 h (pulse interval 5 s) with use of an 85% H$_3$PO$_4$ external standard. the spectra (43.6 °C) exhibited peaks at δ −1.9 ($^1J_{PW}$ = 266 Hz, trans) and δ −9.6 ($^1J_{PW}$ = 218 Hz, cis), in reasonable agreement with some of those previously reported.[12,15,16]

Results and Discussion

Stoichiometry. Scans of the carbonyl stretching spectra for reactions of *cis*-(DTHp)W(CO)$_4$ with various L ligands in chlorobenzene under pseudo-first-order conditions ([*cis*-(DTHp)W(CO)$_4$]$_0$ $\ll$ [L]) at 31.1 °C revealed that within several hundred seconds after mixing this complex was converted into *cis*-(η^1-DTHp)(L)W(CO)$_4$ species, characterized for L = CP, which then much more slowly were transformed into the known[1,12,13] *cis*-(L)$_2$W(CO)$_4$ products and thence, for L = P(OMe)$_3$, P(O-*i*-Pr)$_3$, and P(*n*-Bu)$_3$, to equilibrium mixtures of those complexes and their trans analogues. The stoichiometry for the overall process is thus as is shown in (3). All of the

$$cis\text{-(DTHp)W(CO)}_4 \xrightarrow{k_{obsd}} cis\text{-(L)}(\eta^1\text{-DTHp})\text{W(CO)}_4 \xrightarrow{k'_{obsd}} cis\text{-(L)}_2\text{W(CO)}_4 \overset{K_{eq}}{\rightleftharpoons} trans\text{-(L)}_2\text{W(CO)}_4 \quad (3)$$

chemical species illustrated in (3) attain significant concentration during the reactions' course. The three processes governed by

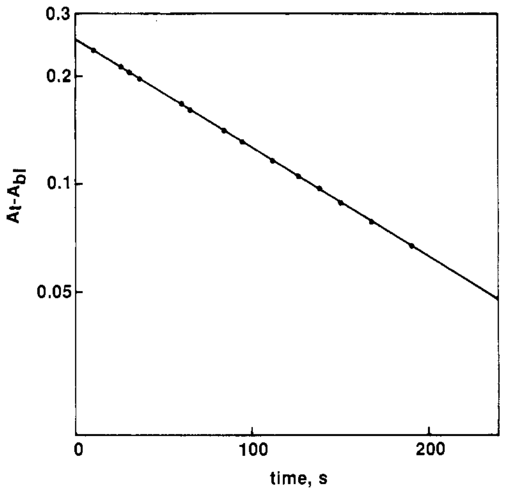

Figure 2. Plot of ln $(A_t - A_{bl})$ vs time, from which has been subtracted the absorbance (at the appropriate times) of the second linear segment, extrapolated to time zero, of the plot in Figure 1. The reaction is that of *cis*-(DTHp)W(CO)$_4$ with P(O-*i*-Pr)$_3$ (0.3084 M) at 31.1 °C monitored at 415 nm in chlorobenzene.

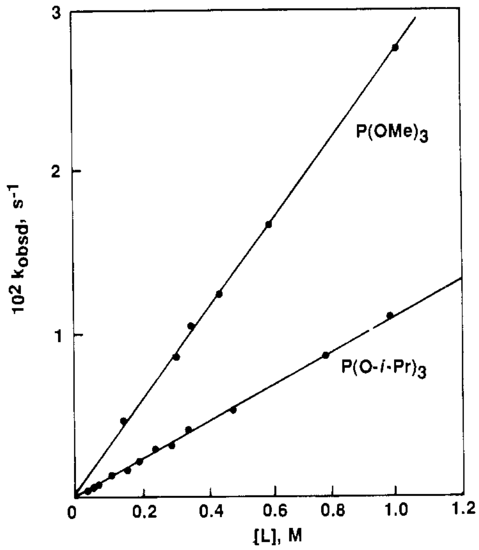

Figure 3. Plots of k_{obsd} vs [L] for L = P(OMe)$_3$ and P(O-*i*-Pr)$_3$ at 21.1 °C in chlorobenzene for values obtained for the rate constants attributable to the first linear segment of plots of ln $(A_t - A_{bl})$ vs time (e.g., Figure 2) for the reactions of *cis*-(DTHp)W(CO)$_4$ with L.

k_{obsd}, k'_{obsd}, and K_{eq} will each be considered in turn.

Chelate Ring Opening in *cis*-(DTHp)W(CO)$_4$ in the Presence of L. Kinetics studies of the rapid conversion of *cis*-(DTHp)W(CO)$_4$ to the *cis*-(L)(η^1-DTHp)W(CO)$_4$ intermediates (governed by the rate constant, k_{obsd} (eq 3)) required the implementation of techniques through use of which it was possible to commence monitoring the reaction within 5 s of mixing. With use of these methods the rates of the disappearance of both *cis*-(DTHp)W(CO)$_4$ and *cis*-(L)(η^1-DTHp)W(CO)$_4$ were investigated as a function of the concentration of L over the temperature range 22.1–44.5 °C. The plots of ln $(A_t - A_{bl})$ vs time, such as are illustrated in Figure 1, are typical of a "biphasic" reaction and consist of two linear segments.[17] The values of k'_{obsd} (eq 3) can be determined from the slopes of the second (slower) segment; a discussion of them will be deferred until the next section. The overall rate constants, k_{obsd} (eq 3), for the first reaction step may be evaluated by extrapolation of ln $(A_t - A_{bl})$ for the second linear segment to zero time and subtraction of its value at any time from the corresponding value of ln $(A_t - A_{bl})$ for the initial segment.

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(15) McFarlane, H. C. E.; McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1976**, 1616.

(16) The values of the chemical shifts and coupling constants obtained here are in reasonable agreement with those in ref 15 (δ −10.4, −2.6 (trans, cis)) and $^1J_{PW}$ = 270, 221 Hz (trans, cis)) but differ from those reported by Howell and co-workers[12] (δ −6.03, 2.24 (trans, cis) and $^1J_{PW}$ = 270.4, 226.2 Hz (trans, cis)) and by: Grim, S. O.; Wheatland, D. A. *Inorg. Chem.* **1969**, *8*, 1716 (δ 10.4, 2.5 (trans, cis) and $^1J_{PW}$ = 265, 225 Hz (trans, cis)). While the coupling constants for all reports are in agreement, the chemical shifts reported by Howell et al. appear to be "offset" by ca. 4 ppm, while those of Grim and Wheatland are reversed in sign from our values and those of McFarlane and co-workers.

(17) See: Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 65–71.

Table I. Rate Constants for the Reaction of *cis*-(DTHp)W(CO)$_4$ with L (=P(OMe)$_3$, P(O-*i*-Pr)$_3$) in Chlorobenzene at Various Temperatures To Afford *cis*-(L)(η^1-DTHp)W(CO)$_4$ Products

L	T, °C	10^2k_1, M^{-1} s^{-1}
P(OMe)$_3$	21.1	2.73 (5)
P(O-*i*-Pr)$_3$[a]	21.1	1.09 (1)
	31.1	2.61 (5)
	35.2	3.67 (11)
	44.5	7.8 (3)

[a] Activation parameters: $\Delta H^* = 15.00$ (4) kcal/mol; $\Delta S^* = -16.1$ (1) cal/(deg mol).

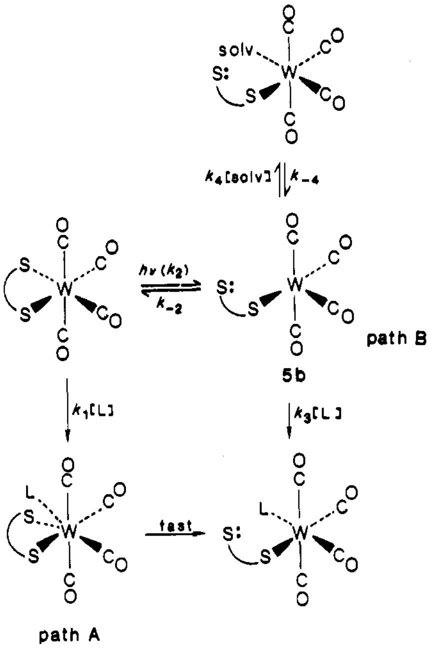
Such a plot, derived from that in Figure 1, is illustrated in Figure 2. Plots of values of k_{obsd} obtained for the initial rapid decay vs [L] for L = P(O-*i*-Pr)$_3$ and P(OMe)$_3$ at 21.1 °C in CB are shown in Figure 3; these plots, and those for rate data at other temperatures, obey the rate law

$$-d[cis\text{-(DTHp)W(CO)}_4]/dt = k_1[cis\text{-(DTHp)W(CO)}_4][\text{L}]$$

$$k_{obsd} = k_1[\text{L}] \qquad (4)$$

The values of the pseudo-first-order rate constants, k_{obsd}, as a function of [L] and of temperature are given in Supplementary Table I.

The second-order rate constants, k_1 (eq 4; vide infra), are presented in Table I.



(5)

S S = DTHp; solv = chlorobenzene

This rate law is consistent either with an associative mechanism involving displacement of one end of the chelating DTHp ligand by L (mechanism 5, path A) or with a dissociative pathway in which unimolecular fission of a W–S bond produces a "ring-opened" intermediate that can undergo competitive chelate ring reclosure or attack by L (mechanism 5, path B). As is noted above, this is the mechanism that has been proposed to be predominant in ligand-substitution reactions of the analogous five- and six-membered-ring complexes *cis*-(DTO)W(CO)$_4$[2] and *cis*-(DTN)W(CO)$_4$ (cf. eq 2).[3] For this mechanism, assuming a steady-state concentration of **5b**, in terms of the pseudo-first-order rate constant, k_{obsd}, the pseudo-first-order rate law is

$$k_{obsd} = k_2k_3[\text{L}]/(k_{-2} + k_3[\text{L}]) \qquad (6)$$

Where the rate of chelate ring closure in the intermediate, governed by k_{-2}, is much greater than the rate of its attack by L, governed by k_3, eq 6 also affords a rate law of the form of eq 4

$$k_{obsd} = k_2k_3[\text{L}]/k_{-2} \qquad (7)$$

although for displacement of the five- and six-membered chelate ligands DTO and DTN from their *cis*-(S$_2$)W(CO)$_4$ complexes its nonlimiting form was observed.[2,3]

For reaction of *cis*-(DTHp)W(CO)$_4$ with L (=P(O-*i*-Pr)$_3$) in CB to produce *cis*-(L)(η^1-DTHp)W(CO)$_4$, the entropy of activation (Table I), determined from data at four temperatures, is −16.1 (1) cal/(deg mol), which is suggestive of extensive bond making in the transition state, favoring the associative mechanism ((5), path A). The ratio of rate constants for attack at *cis*-(DTHp)W(CO)$_4$ by P(OMe)$_3$ vs that by P(O-*i*-Pr)$_3$ is ca. 3, greater than might be expected for attack at a coordinatively unsaturated site created after W–S bond breaking.[1,6]

Further insight into the mechanism of the ring-opening reaction step was obtained through pulsed laser flash photolysis studies of *cis*-(DTHp)W(CO)$_4$, which were carried out in a manner analogous to those reported for the reactions of *cis*-(DTO)W(CO)$_4$ and *cis*-(DTN)W(CO)$_4$ with L.[6,7] In these last two systems a unimolecular decay observed after the flash was shown to be attributable to chelate ring reclosure in *cis*-[(solv)(η^1-S$_2$)W(CO)$_4$], which is a predominant species produced during the flash.[18] Flash photolysis of *cis*-(DTHp)W(CO)$_4$ in CB at 31.1 °C in the absence of L produces an analogous decay whose rate approaches the instrumental response time, with a rate constant of 9.1 (9) × 10^6 s^{-1}. This decay similarly is attributable to chelate ring closure in *cis*-[(CB)(η^1-DTHp)W(CO)$_4$]. Its rate is ca. 20–50 times faster than is ring closure in the five- and six-membered-ring analogues under similar experimental conditions.[6,7]

It has been shown that the rates of reaction of photogenerated *cis*-[(solv)(L)W(CO)$_4$] intermediates are largely influenced by the strength of interaction between the solvent and metal.[1] It was concluded that in these species halogenated solvents are themselves coordinating ligands, although the halogen–W interaction is much weaker than is that of W with ligands such as amines and phosphines.[1] Accordingly, in order to bring the rates of chelate ring closure after flash photolysis of *cis*-(DTHp)W(CO)$_4$ within the "time window" of the flash photolysis system, this reaction was also investigated in 1,2-dichloroethane (DCE) and bromobenzene (BB) solutions; both of these solvents have been shown to form stronger coordinate-covalent bonds with tungsten than does CB.[1]

The first-order rate constants determined for chelate ring closure after flash photolysis of *cis*-(DTHp)W(CO)$_4$ in DCE and BB in the absence of L (=P(O-*i*-Pr)$_3$) at various temperatures are presented in Supplementary Table III. In the absence and presence of L (>1 M), similar rates were observed, indicating that trapping of the *cis*-[(solv)(η^1-DTHp)W(CO)$_4$] by L is not competitive with chelate ring closure. On the basis of the observed rates of reaction of *cis*-[(DCE)(η^1-DTO)W(CO)$_4$] with L, which are competitive with chelate ring closure,[6] this is to be expected, since rates of attack by L at "ring-opened" complexes containing DTHp and DTO should be similar; these ligands differ by only one methylene group in the ring backbone.

Activation parameters for chelate ring closure in *cis*-[(solv)(η^1-DTHp)W(CO)$_4$] intermediates in both BB and DCE were determined from data taken over a temperature range of 10–45 °C. Enthalpies of activation for desolvation (DCE, 5.6 (5) kcal/mol; BB, 6.4 (3) kcal/mol) are significantly smaller than is that (13.0 (4) kcal/mol) for loss of CB from *cis*-[(CB)(P(O-*i*-Pr)$_3$)W(CO)$_4$], a process that has been found to be dissociative in nature.[1] Moreover, that study showed that CB dissociates more rapidly from that complex than does either BB or DCE, suggestive of W–BB and W–DCE bonding being stronger than that of W–CB.[1] The enthalpies of activation reported here are also smaller than the *n*-hept–Cr bond strength (ca. 10 kcal/mol; *n*-hept

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[18] It has been shown, in general, that flash photolysis of *cis*-(L)(L′)M(CO)$_4$ complexes (L, L′ = a Lewis base coordinating through N, P, or S) affords both the cis and trans five-coordinate species; the trans isomer reacts much more slowly than does the cis. Moreover, the trans isomer, when it contains a η^1 bidentate ligand, cannot react via chelate ring closure. See ref 1, 6, 7, and (a) Poliakoff, M. *Inorg. Chem.* **1976**, *15*, 2892. (b) Dobson, G. R.; Bernal, I.; Reisner, G. M.; Dobson, C. B.; Mansour, S. E. *J. Am. Chem. Soc.* **1985**, *107*, 525.

= *n*-heptane) estimated in [(*n*-hept)Cr(CO)$_5$] from time-resolved photoacoustic calorimetry data,[19] although there is much evidence which indicates that Cl–W bonds are stronger than are those between hydrocarbons and W.[1]

The observed entropies of activation are quite negative, −12.7 (7) and −11.2 (8) cal/(deg mol), respectively, for DCE and BB. Highly negative entropies of activation (−19 to −21 cal/(deg mol))[14] and negative volumes of activation (−9 to −11 cm^3/mol)[20] also have been observed for displacement of DTH (=2,5-dithiahexane) from *cis*-(DTH)Mo(CO)$_4$ by various alkyl and aryl phosphites.

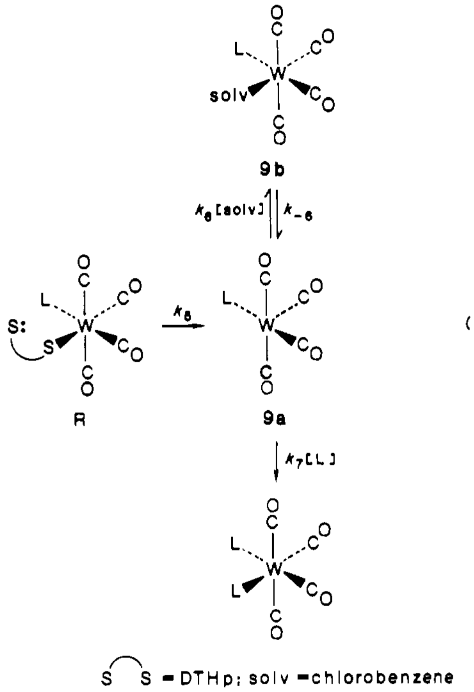
These activation parameters and the entropies of activation observed for the thermal ring-opening process as discussed above suggest a concerted mechanism for chelate ring opening and closure in *cis*-(DTHp)W(CO)$_4$ (cf. mechanism 5A) rather than one largely involving W–S bond dissociation such as is observed for chelate ring displacement in *cis*-(DTO)W(CO)$_4$, for example.[2,6] The thermal reactions of *cis*-(DTHp)W(CO)$_4$ would thus produce *cis*-(L)(η^1-DTHp)W(CO)$_4$ without the creation of an intervening *cis*-[(η^1-DTHp)W(CO)$_4$] intermediate as do the photochemical pathways and the thermal reactions of complexes containing five- and six-membered chelate rings.[2,3]

Mechanism of the Formation of *cis*-(L)$_2$W(CO)$_4$ from *cis*-(L)(η^1-DTHp)W(CO)$_4$. The slow subsequent conversion of the thermally produced *cis*-(L)(η^1-DTHp)W(CO)$_4$ to *cis*-(L)$_2$W(CO)$_4$ afforded the pseudo-first-order rate constants k'_{obsd} (eq 3), given in Supplementary Table II, which were found to obey the pseudo-first-order rate law

$$k'_{\text{obsd}} = k_5 \qquad (8)$$

Values of k_5 are presented in Table II.

This reaction step is best attributed to a mechanism involving rate-determining dissociation of the coordinated end of the bidentate ligand, governed by k_5 in eq 9, followed by other rapid steps (vide infra).



(9)

S S = DTHp; solv = chlorobenzene

The rate constants (s^{-1}) for displacement of DTHp from *cis*-(L)(η^1-DTHp)W(CO)$_4$ in CB at 44.5 °C vary as a function of coordinated L in the order CP (4.48 (8) × 10^{-5}) ≪ P(OMe)$_3$ (1.53 (4) × 10^{-4}) ≪ P(OPh)$_3$ (1.18 (9) × 10^{-3}) < P(O-*i*-Pr)$_3$ (1.43 (3) × 10^{-3}) < P(*n*-Bu)$_3$ (2.89 (12) × 10^{-3}). The steric and electronic influences of coordinated L on these rates can be analyzed through use of an equation developed by Poë and coworkers[21]

Table II. Rate Constants and Activation Parameters for the Reaction of *cis*-(L)(η^1-DTHp)W(CO)$_4$ Complexes with L in Chlorobenzene at Various Temperatures To Afford *cis*-(L)$_2$W(CO)$_4$ Products

L	*T*, °C	10^3k_5, s^{-1}	ΔH^*, kcal/mol	ΔS^*, cal/(deg mol)
P(OCH$_2$)$_3$CCH$_3$	44.5	0.0448 (8)	25.1 (6)	1.4 (11)
	57.5	0.205 (7)		
	68.1	0.728 (1)		
P(OMe)$_3$	44.5	0.153 (4)	25.8 (1)	6.1 (2)
	57.0	0.736 (17)		
	68.1	2.75 (22)		
P(OPh)$_3$	44.5	1.18 (9)		
P(O-*i*-Pr)$_3$	21.1	0.0380 (10)	28.2 (6)	18.1 (2)
	31.1	0.170 (6)		
	33.9	0.293 (13)		
	35.2	0.327 (1)		
	44.5	1.43 (3)		
P(*n*-Bu)$_3$	44.5	2.89 (12)		

$$\log k_5 = a\theta + b\nu + c \qquad (10)$$

where θ and ν are the Tolman steric and electronic parameters, respectively,[22] and *a*, *b*, and *c* are coefficients that provide the best fit of the data. When a multiple linear regression is employed to fit k_5, θ, and ν, the equation becomes

$$\log k_5 = 0.0472\theta - 0.0102\nu + 12.2 \qquad (11)$$

with a correlation coefficient of 0.991. The ratios $|a|/(|a| + |b|)$ and $|b|/(|a| + |b|)$, which reflect the relative contributions of steric and electronic influences to the values of the rate constants, k_5, are 0.808 and 0.192, respectively. Thus, steric influences of coordinated L on rates of dissociation of DTHp predominate, with a positive correlation observed between the rate constants, k_5, and the Tolman cone angles, θ. It thus may be concluded that steric acceleration of DTHp loss is promoted by bulkier L. A similar trend also has been noted in thermal reactions of *cis*-(pip)(L)W(CO)$_4$ in which pip is replaced by L′.[1]

The *b* coefficient, −0.0102, indicates that rates of DTHp–W bond breaking decrease with increasing values of the Tolman electronic parameter, ν. Increasing values of ν indicate increasing withdrawal by L of electron density from the metal atom with a consequent increase in the metal's Lewis acidity and the strength of the S–W coordinate bond; thus, the electronic influences of coordinated L on the W–S bond strength are largely σ-bonding effects.

The observed entropies of activation for DTHp loss, given in Table II, become more positive with increased steric demands of coordinated L, indicating that the steric influences of L on rates of DTHp dissociation are largely entropic in nature.

The fast steps that take place subsequent to rate-determining S–W bond fission in *cis*-(L)(η^1-DTHp)W(CO)$_4$ have been probed in another context, through thermal and flash photolysis studies of *cis*-(pip)(L)W(CO)$_4$.[1] That investigation demonstrated that the same intermediate, *cis*-[(solv)(L)W(CO)$_4$], is generated both thermally and photochemically, and that for CB as the solvent, as is the case here, its replacement by incoming L takes place via a mechanism involving initial reversible solvent dissociation followed by rapid attack by L at the nonsolvated intermediate, likely of square-pyramidal geometry with L in the equatorial plane ("*cis*-[(L)W(CO)$_4$]"; cf. eq 2).[1] After dissociation of DTHp, the reaction of L with *cis*-[(L)(η^1-DTHp)W(CO)$_4$] follows an identical sequence of thermal reaction steps (eq 9), since both reactions initially afford five-coordinate *cis*-[(L)W(CO)$_4$] intermediates (**9a**). Assuming a steady-state concentration of **9a**, the rate law for this pathway is

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(19) Yang, C. K.; Peters, K. S.; Vaida, V. *Chem. Phys. Lett.* **1986**, *125*, 566.

(20) Awad, H. H.; Dobson, C. B.; Dobson, G. R.; Leipoldt, J. G.; Schneider, K.; van Eldik, R.; Wood, H. E., submitted for publication in *Inorg. Chem.*

(21) Dahlinger, K.; Falcone, F.; Poë, A. *Inorg. Chem.* **1986**, *25*, 2654.

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$$-d[\mathbf{9b}]/dt = k_{-6}k_7[\mathbf{9b}][L]/(k_6[CB] + k_7[L]) \qquad (12)$$

Since [CB] ≫ [L] and, as will be discussed below, $k_6 \simeq k_7$, under pseudo-first-order reaction conditions ([L] ≫ [**9b**])

$$-d[\mathbf{9b}]/dt = k_{-6}k_7[\mathbf{9b}][L]/k_6[CB] = k''_{obsd}[\mathbf{9b}] \qquad (13)$$

and a plot of k''_{obsd} vs [L] will be linear, with a zero intercept, as is observed, with slope $k_{-6}k_7/k_6[CB]$.

For reaction of *cis*-[(CB)(P(O-*i*-Pr)$_3$)W(CO)$_4$] with P(O-*i*-Pr)$_3$ at 35.2 °C, a value for $k_{-6}k_7/k_6$ of 7.1 (3) × 10^4 s^{-1} is obtained. The temperature was chosen to afford direct comparisons of the several rate constants that have been obtained for the overall reaction (vide infra). Values of k''_{obsd} are given in Supplementary Table IV.

The approximate value for the rate constant for W–CB bond dissociation, k_{-6}, 6.5 (14) × 10^4 s^{-1} at 35.2 °C, can be derived from the experimentally determined value of the "competition ratio", k_7/k_6, 1.14 (20) at 31.1 °C, obtained from values of k_6/k_8, 0.43 (5), and k_7/k_8, 0.48 (3) (eq 14).[1] The temperature difference between the values for $k_{-6}k_7/k_6$ and k_7/k_6 can be neglected since it also has been found that the "competition ratios" k_6/k_8 and k_7/k_8 are constant, within experimental error, over 20 °C temperature ranges near ambient temperature.[1] The near-identity of the rates of CB and P(O-*i*-Pr)$_3$ attack at *cis*-[P(O-*i*-Pr)$_3$W(CO)$_4$] and the insensitivity of these "competition ratios" to changes in temperature are quite expected, since it is strongly indicated that interactions of nucleophiles with coordinatively unsaturated metal carbonyl transients take place at rates which approach that of the diffusion-controlled limit,[1,23] that is, with similar rates and with enthalpies of activation that approach zero. Activation parameters for CB dissociation from *cis*-[(CB)(P(O-*i*-Pr)$_3$W(CO)$_4$] are 13.0 (4) kcal/mol for ΔH^* and 5.6 (11) cal/(deg mol) for ΔS^*.[1,24]

$$\begin{tikzcd}
cis\text{-}[(CB)(P(O\text{-}i\text{-}Pr)_3)W(CO)_4] \arrow[d, shift left, "k_{-6}"] & \\
cis\text{-}[(P(O\text{-}i\text{-}Pr)_3)W(CO)_4] \arrow[u, shift left, "k_6[CB]"] \arrow[r, shift left, "k_8[pip]"] \arrow[d, "k_7[P(O\text{-}i\text{-}Pr)_3]"] & cis\text{-}(pip)(P(O\text{-}i\text{-}Pr)_3)W(CO)_4 \arrow[l, shift left, "h\nu"] \quad (14) \\
cis\text{-}(P(O\text{-}i\text{-}Pr)_3)_2W(CO)_4 &
\end{tikzcd}$$

Isomerization of *cis*-(P(*n*-Bu)$_3$)$_2$W(CO)$_4$. The cis–trans isomerization has been investigated previously in group VIB metal carbonyl complexes containing a variety of phosphines and phosphites.[12,13,25] A dissociative isomerization pathway was ruled out since no reaction products that would result from the trapping of a potential five-coordinate species formed after W–CO or W–P bond fission were observed. A nondissociative isomerization (eq 15), probably involving a trigonal twist, was thus proposed. It

$$\underset{\mathbf{15a}}{cis\text{-}(L)_2W(CO)_4} \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} \underset{\mathbf{15b}}{trans\text{-}(L)_2W(CO)_4} \qquad (15)$$

was also found by Dixon, Kola and Howell, in studies of cis–trans isomerization of (L)$_2$W(CO)$_4$ complexes formed after displacement of norbornadiene (NBD) from (NBD)W(CO)$_4$,[12] that those containing less bulky ligands such as trimethyl phosphite and triphenyl phosphite isomerize more slowly than does that containing the bulkier P(*n*-Bu)$_3$. This observation also argues against a dissociative scrambling mechanism involving rate-determining W–L or W–CO bond breaking since, as shown here and elsewhere,[1] bulky ligands promote W–L bond fission.

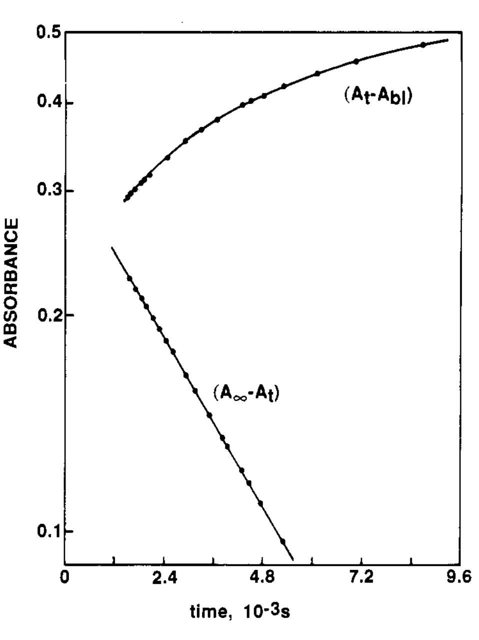

Figure 4. Plots of (top) ln ($A_t - A_{bl}$) vs time for the third segment of this plot, obtained by monitoring at 415 nm, for reaction of *cis*-(DTHp)W(CO)$_4$ with P(*n*-Bu)$_3$ (0.1084 M) at 44.5 °C and (bottom) these data plotted as ln ($A_\infty - A_t$) vs time.

Table III. Rate Constants and Activation Parameters, Values of K_{eq}, and Thermodynamic Parameters for the Isomerization of *cis*-(P(*n*-Bu)$_3$)$_2$W(CO)$_4$ in Chlorobenzene

T, °C	10^5k_9,[a] s^{-1}	10^5k_{-9},[b] s^{-1}	K_{eq}
35.2	3.56[d]	1.21[d]	2.94[c,d]
44.5	16.9	5.89	2.88
54.6	74.7	26.4	2.82

[a] $\Delta H_9^* = 30.9$ (5) kcal/mol; $\Delta S_9^* = 22.4$ (14) cal/(deg mol). [b] $\Delta H_{-9}^* = 31.3$ (5) kcal/mol; $\Delta S_{-9}^* = 21.6$ (16) cal/(deg mol). [c] $\Delta H = -0.4$ (9) kcal/mol; $\Delta S = 0.8$ (30) cal/(deg mol). [d] Error limits for determination of the integrated intensities of the ^{31}P NMR absorptions are estimated to be ca. ±3%.

Isomerization of *cis*-(P(*n*-Bu)$_3$)$_2$W(CO)$_4$ consistent with mechanism 15 was found by Howell and co-workers[12] to take place on a time scale similar to that observed for displacement of DTHp from *cis*-(DTHp)W(CO)$_4$ by P(*n*-Bu)$_3$. An *increase* in absorbance at 415 nm attributable to this isomerization process is observed to take place after displacement of DTHp by P(*n*-Bu)$_3$ from *cis*-(DTHp)W(CO)$_4$ (eq 3). Infrared spectra of the reaction solutions taken after DTHp displacement confirmed the presence of the *trans* isomer for L = P(O-*i*-Pr)$_3$ and P(OMe)$_3$ (but not for P(OCH$_2$)$_3$CCH$_3$ or P(OPh)$_3$), but no increase in absorbance monitoring 415 nm was observed. In terms of eq 15, a plot of ln ($A_\infty - A_t$) vs time is expected to be linear, with slope $k_9 + k_{-9}$. A typical plot of ln ($A_t - A_{bl}$) vs time for the absorbance increase is shown in Figure 4, which also exhibits the corresponding plot of ln ($A_\infty - A_t$) vs time; the rate constants $k_9 + k_{-9}$ given in Supplementary Table V were obtained from this latter plot. Since, at equilibrium

$$k_9[\mathbf{15a}] = k_{-9}[\mathbf{15b}] \qquad (16)$$

$$K_{eq} = [\mathbf{15b}]/[\mathbf{15a}] = k_9/k_{-9} \qquad (17)$$

rate constants k_9 and k_{-9} may be determined from values of $k_9 + k_{-9}$ and K_{eq}. The values of K_{eq} were determined at three temperatures, with use of ^{31}P NMR spectrometry, from the relative integrated intensities of the resonances at δ −1.9 and −9.6, which have been assigned to the trans and cis isomers, respectively. Table III exhibits these values, together with those for K_{eq} and the corresponding activation and thermodynamic parameters. The values of K_{eq} differ significantly from that reported by Howell

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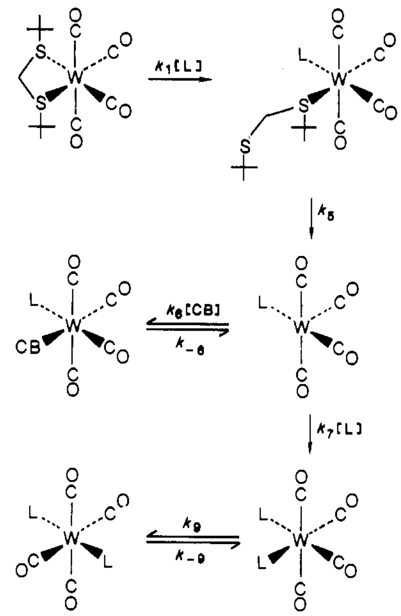
(23) (a) Welch, J. A.; Peters, K. S.; Vaida, V. *J. Phys. Chem.* **1982**, *86*, 1941. (b) Simon, J. D.; Peters, K. S. *Chem. Phys. Lett.* **1983**, *98*, 53. (c) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1986**, *90*, 6715. (d) Langford, C. H.; Moralejo, C.; Sharma, D. K. *Inorg. Chim. Acta* **1987**, *126*, L11. (e) Simon, D. D.; Xie, X. *J. Phys. Chem.* **1987**, *91*, 5538.

(24) This value is labeled "ΔH_3^*" and "ΔS_3^*" rather than "ΔH_{-3}^*" and "ΔS_{-3}^*", the correct designation, in Table V of ref 1.

(25) (a) Darensbourg, D. J. *Inorg. Chem.* **1979**, *18*, 14. (b) Darensbourg, D. J.; Baldwin, B. J. *J. Am. Chem. Soc.* **1979**, *101*, 6447. (c) Darensbourg, D. J.; Kudaroski, R.; Schenk, W. *Inorg. Chem.* **1982**, *21*, 2488. (d) Cotton, F. A.; Darensbourg, D. J.; Klein, S.; Kolthammer, B. W. S. *Inorg. Chem.* **1982**, *21*, 2661. (e) Darensbourg, D. J.; Gray, R. L. *Inorg. Chem.* **1984**, *23*, 2993. (f) Dobson, G. R.; Awad, H. H.; Basson, S. S. *Inorg. Chim. Acta* **1986**, *118*, L5.

and co-workers (K_{eq} = 8.93) under very similar conditions (46 °C; toluene solution), but values of $k_9 + k_{-9}$ for the two studies are in reasonable agreement (2.28 (3) $\times 10^{-4}$ s^{-1} at 44.5 °C (this study) vs 3.5 (4) $\times 10^{-4}$ s^{-1} (Howell et al.[12])). No reason for the lack of agreement for K_{eq} is apparent. The highly positive entropies of activation for both isomerization processes ($\Delta S_9^{\ddagger}$ = 22.4 (14) cal/(deg mol) and $\Delta S_{-9}^{\ddagger}$ = 21.6 (16) cal/(deg mol)) are consistent with significantly greater organization in the ground states than the transition state, but there is no evidence to support dissociation of P(n-Bu)$_3$ during the isomerization process.

Summary. The overall mechanism favored by the evidence presented here for displacement of DTHp by L from (DTHp)W(CO)$_4$, together with values of the rate constants for individual reaction steps as determined at 35.2 °C in CB, are given in eq 18.



(18)

CB = chlorobenzene; L = P(O-i-Pr)$_3$

k_1 = 2.61 (5) $\times 10^{-2}$ M^{-1} s^{-1}

k_5 = 3.27 (1) $\times 10^{-4}$ s^{-1}

k_5 = 3.27 (1) $\times 10^{-4}$ s^{-1}

k_9 = 3.56 $\times 10^{-5}$ s^{-1} (35.5 °C)

k_{-9} = 1.21 $\times 10^{-5}$ s^{-1} (35.5 °C)

k_7/k_6 = 1.14 (20)

Acknowledgment. The support of this research by the National Science Foundation (Grant No. CHE 84-15153) is gratefully acknowledged. The flash photolysis experiments and analyses of the data produced were carried out at the Center for Fast Kinetics Research (CFKR), University of Texas at Austin. The CFKR is supported jointly by the Biotechnology Branch of the Division of Research Resources of the NIH (Grant No. RR00886) and by the University of Texas at Austin. The help and expertise of the staff at CFKR are greatly appreciated. We also appreciate the experimental assistance of T. Corby Young, David Dumond, and Hani H. Awad.

Supplementary Material Available: Values of k_{obsd} for the thermal reaction of *cis*-(DTHp)W(CO)$_4$ with L to afford *cis*-(L)(η^1-DTHp)W(CO)$_4$ and for the further reaction of this intermediate with L to afford *cis*-(L)$_2$W(CO)$_4$ (Supplementary Tables I and II, respectively), rate constants at various temperatures for unimolecular ring closure in *cis*-[(solv)(η^1-DTHp)W(CO)$_4$] complexes after flash photolysis (solv = 1,2-dichloroethane, bromobenzene) (Supplementary Table III), pseudo-first-order rate constants for thermal reactions of P(O-i-Pr)$_3$ with *cis*-[(CB)(P(O-i-Pr)$_3$)W(CO)$_4$] produced after flash photolysis of *cis*-(pip)(P(O-i-Pr)$_3$)W(CO)$_4$ at 35.2 °C (Supplementary Table IV), and pseudo-first-order rate constants and values of K_{eq} for the cis–trans isomerization of *cis*-(P(n-Bu)$_3$)$_2$W(CO)$_4$ (Supplementary Table V) (7 pages). Ordering information is given on any current masthead page.

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Octahedral Metal Carbonyls. 64.[1] Ligand Exchange in *fac*-(py)(diphos)Mo(CO)$_3$ in Toluene (T) Solution (Py = Pyridine; Diphos = 1,2-Bis(diphenylphosphino)ethane): The *fac*-[(T)(diphos)Mo(CO)$_3$] Intermediate

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fac-(py)(diphos)Mo(CO)$_3$ (**1**; py = pyridine; diphos = 1,2-bis(diphenylphosphino)ethane) reacts thermally with phosphines, phosphites, and triphenylstibine (=L) in toluene to afford *fac*-(L)(diphos)Mo(CO)$_3$ products (**2**). The observed rate law suggests that the mechanism involves dissociation of py from **1** and competitive reaction of the resulting steady-state intermediate, *fac*-[(diphos)Mo(CO)$_3$] (**3**), with py (reversibly) and with L (irreversibly). Pulsed laser flash photolysis of (diphos)Mo(CO)$_4$ also affords **3**, identified through comparisons of its reactivities with L to those observed for **3** produced thermally. Evidence suggests, however, that a *predominant reaction species* formed after pulsed laser flash photolysis of (diphos)Mo(CO)$_4$ is *fac*-[(T)(diphos)Mo(CO)$_3$] (**4b**) (T = toluene), in which toluene occupies a site in the octahedral coordination sphere of Mo and probably interacts with Mo via an "agostic" hydrogen; reversible dissociation of toluene from **4b** affords **3**. Rate data after flash photolysis also support the formation of [(η^1-diphos)Mo(CO)$_4$] and *cis*-[(T)(η^1-diphos)Mo(CO)$_4$] (**5**). The latter undergoes irreversible chelate ring closure with concerted expulsion of toluene to afford (diphos)Mo(CO)$_4$. Rate constants and activation parameters for various reaction steps are presented and are discussed in terms of the steric and electronic properties of L.

Introduction

Recent studies have demonstrated that intermediates produced upon flash photolysis of group VIB metal carbonyl derivatives can be identified through their kinetics behavior even where spectroscopic methods are inadequate for the task.[4-6] Thus, for example, where photolysis induces chelate ring opening in (η^2-chelate)M(CO)$_4$ complexes (M = Cr, Mo, W) to afford solvated *cis*-[(η^1-bidentate)M(CO)$_4$] species, the latter can be identified on the basis of the two-term rate law expected and observed for

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(1) Part 63: Dobson, G. R.; Cortes, J. E. *Inorg. Chem.*, preceding paper in this issue.

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