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Octahedral Metal Carbonyls. 62.[1] The Mechanism of Piperidine (pip) Displacement by Phosphines and Phosphites (L′) from *cis*-(pip)(L)W(CO)$_4$ Complexes in Chlorobenzene

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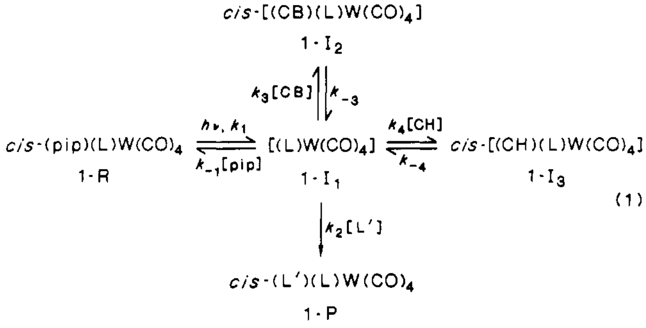
Abstract: Parallel thermal and pulsed laser flash photolysis studies of *cis*-(pip)(L)W(CO)$_4$ complexes (pip = piperidine; L = phosphines and phosphites) in their reactions with L′ in chlorobenzene (CB) solvent and in CB/CH mixtures (CH = cyclohexane) indicate these reactions to proceed via reversible fission of the W–pip bond to produce square-pyramidal [(L)W(CO)$_4$] intermediates in which L occupies a position in the equatorial plane. These species undergo very rapid competitive reaction with pip, with L′, and with CB to afford, ultimately, the thermally stable *cis*-(L′)(L)W(CO)$_4$ products, which may undergo subsequent isomerization. The "competition ratios" for reactions of chlorobenzene, pip, and L′ with [(L)W(CO)$_5$] have been measured photochemically and/or thermally, and these ratios have assisted in the identification of *cis*-[(CB)(L)W(CO)$_4$], in which CB functions as a coordinating ligand, as the predominant species formed after photolysis. Rate constants and activation parameters for most steps in the ligand–substitution process are reported and are discussed in terms of the steric and electronic properties of both coordinated L, incoming L′, and solvent.

It recently has been reported that parallel flash photolysis and thermal investigations of ligand exchange in octahedral metal carbonyl complexes can offer information in heretofore unattainable detail about the ligand–substitution process.[4,5] It has been found in particular that the intermediate produced via thermal and photochemical metal–ligand bond fission is often one and the same species, an observation which facilitates the determination of the identity of the photogenerated intermediate.[5] Further, the thermal and photochemical studies are complementary and afford each rate constant in thermal processes which proceed through reversible formation of the solvated intermediate and its subsequent reaction with an incoming nucleophile.[4,5] The conclusions drawn through such studies have been confirmed through flash photolysis investigations which have employed infrared detection to aid in the identification of the photogenerated intermediates.[6]

Such studies have, in particular, identified a number of *cis*-[(S)(L)M(CO)$_4$] transients (M = Cr, Mo, W; L = phosphine, phosphite) in which even nonpolar solvents (S) such as *n*-heptane occupy discrete "coordination sites" in the octahedron.[6] These species may be thought of as extremely reactive "solvent-substituted" octahedral complexes rather than as square-pyramidal species possessing a vacant coordination site. They serve as models for the intermediates present in predominant abundance which are implicated in important transition-metal-promoted processes in solution, including olefin hydrogenation and isomerization.[7] Consequently, factors which influence their reactivities and their selectivities toward incoming nucleophiles are of prime interest.

Reported here are studies of a series of *cis*-[(pip)(L)W(CO)$_4$] complexes (pip = piperidine) in their thermal and photochemical reactions with phosphines and phosphites (= L, L′) according to mechanism 1. Of particular interest have been the elucidation of the mechanistic pathways involved and the study of the reactivities of the transients generated thermally and photochemically during the reaction's course with respect to the steric and electronic properties of coordinated L, incoming L′, and the solvent.



(1)

pip = piperidine; L = PR$_3$, P(OR)$_3$; CB = chlorobenzene; CH = cyclohexane

Experimental Section

General Methods. Infrared spectra for reactants and products were obtained employing a Perkin-Elmer Model 621 grating or 1710 FT-IR spectrometer. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

Materials and Syntheses. Chlorobenzene (CB, Fisher) and 1,2-dichloroethane (DCE, Fisher) were fractionally distilled over P_4O_{10} under nitrogen. Reagent grade cyclohexane (CH, Fisher) was fractionally distilled over sodium under nitrogen. The ligands trimethyl phosphite, triethyl phosphite, tri(isopropyl) phosphite, triphenyl phosphite, and tri(*n*-butyl)phosphine (Aldrich) were fractionally distilled (nitrogen bleed/0.2 Torr) over sodium. Triphenylphosphine (Fluka) was recrystallized from absolute ethanol and dried under vacuum. Dimethylphenylphosphine (Aldrich) was used without further purification. The "constrained phosphite" (CP), 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, was prepared through the published procedure,[8] was twice sublimed under reduced pressure into a wide-mouthed condenser, and was then recrystallized under nitrogen from hot *n*-hexane. Piperidine (Aldrich) was fractionally distilled from anhydrous KOH.

The complexes *cis*-(pip)(L)W(CO)$_4$ (L = CP, P(OEt)$_3$, P(O-*i*-Pr)$_3$, PPh$_3$, PPhMe$_2$) were prepared from W(CO)$_6$ via *cis*-(pip)$_2$W(CO)$_4$ employing the general methods of Darensbourg and Kump[9] as described in

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[1] Part 61: Dobson, G. R.; Awad, H. H.; Basson, S. S. *Inorg. Chim. Acta* **1986**, *118*, L5.

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[7] See e.g.: (a) Darensbourg, D. J.; Nelson, H. H., III; Murphy, M. A. *J. Am. Chem. Soc.* **1977**, *99*, 896. (b) Heaton, B. T.; McCaffrey, D. J. A. *J. Chem. Soc., Dalton Trans.* **1979**, 1078 and references cited therein.

[8] (a) Wadsworth, W. S., Jr.; Emmons, W. D. *J. Am. Chem. Soc.* **1962**, *84*, 610. (b) Heitsch, C. W.; Verkade, J. G. *Inorg. Chem.* **1962**, *1*, 392.

[9] Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680.

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Table I. Analytical Data

complex (L, L′)	anal. calcd C	anal. calcd H	anal. found C	anal. found H	$a_{\nu(CO)}$, cm^{-1} (cyclohexane solv)
cis-(pip)(L)W(CO)$_4$					
P(O-*i*-Pr)$_3$	ref 6				2018 m, 1913 s, 1889 vs, 1867 s
P(OEt)$_3$	ref 6				2019 m, 1914 s, 1891 vs, 1870 vs
PPh$_3$	ref 6				2013 m, 1904 s, 1888 vs, 1865 s
P(OCH$_2$)$_3$CCH$_3$	31.78	3.81	31.95	3.84	2024 m, 1916 s, 1897 vs, 1875 s^b
PPhMe$_2$	39.32	4.27	39.05	4.35	2010 m, 1903 s, 1881 vs, 1865 s
(P(O-*i*-Pr)$_3$P)(L′)W(CO)$_4$					
P(O-*i*-Pr)$_3$	37.09	5.94	37.32	6.17	2029 (m), 1926 s, 1902 vs^c 2036 vvw, 1961 vw, 1904 vs^d
P(OEt)$_3$	34.05	5.41	34.22	5.66	2031 m, 1929 s, 1908 vs^c 1903 vs^d
P(OMe)$_3$	30.59	4.81	31.28	4.84	2032 m, 1933 vs, 1910 vs, 1892 sh^c 1962 vw, 1905 vs^d
P(OPh)$_3$	45.72	4.46	45.16	4.63	2037 m, 1945 s, 1920 vs, 1892 sh^c 2045 vvw, 1969 vw, 1927 vs^d
PPh$_3$	48.60	4.73	48.67	4.71	2024 m, 1930 s, 1905 vs, 1894 s^c 1900 vs^d
P(*n*-Bu)$_3$	42.50	6.85	42.91	7.40	2018 m, 1920 s, 1899 vs, 1885 sh^c 1945 vw, 1890 vs^d
PPhMe$_2$	39.27	5.02	39.50	5.18	2022 m, 1924 s, 1900 vs, 1893 sh,^{c} 1898 vs^d
P(OCH$_2$)$_3$CCH$_3$	33.15	4.64	33.07	4.49	2040 m, 1933 s, 1922 vs, 1910 sh,^{c} 1946 vw, 1922 vs^d

[a] Relative intensities: s = strong, m = medium, w = weak, v = very, sh = shoulder. [b] Toluene solution. [c] Cis isomer. [d] Trans isomer.

detail by Dobson, Poliakoff, Turner et al.[6] The complexes for L = CP and PMe$_2$Ph have not previously been reported. Their chemical analyses and the carbonyl stretching spectra for all the complexes are presented in Table I.

Products of thermal and photochemical reaction of *cis*-(pip)(L)W(CO)$_4$ with L′ and *cis*- and *trans*-(L)(L′)W(CO)$_4$ (L = CP, P(OEt)$_3$, P(O-*i*-Pr)$_3$, PPh$_3$, PMe$_2$Ph; L′ = P(O-*i*-Pr)$_3$, and L = P(O-*i*-Pr)$_3$; L′ = P(OMe)$_3$, P(OPh)$_3$, P(*n*-Bu)$_3$) were synthesized to ascertain whether or not L was displaced together with pip or if L, L′ labilized one another in the (L′)(L)W(CO)$_4$ reaction products. The syntheses of all the products were analogous to that for the reaction of *cis*-(pip)(CP)W(CO)$_4$ with L′ given here except as noted below. *cis*-(pip)(CP)W(CO)$_4$ (1.9 mmol, 1.0 g) and P(O-*i*-Pr)$_3$ (2.3 mmol, 0.48 g) were stirred in 30 mL of chlorobenzene at 100 °C for 24 h. The reaction solution was nearly colorless after this time. The solution was filtered hot, the volume was reduced to 10 mL, *n*-hexane was added until crystallization was observed, and the solution was cooled to 0 °C. The nearly colorless crystals were collected by suction filtration and were recrystallized from toluene–hexane. For P(OEt)$_3$ and P(O-*i*-Pr)$_3$, the solvent was completely removed, and the residue was shaken at 0 °C with the minimum amount of methanol required to cause crystallization. The products were recrystallized from CH$_2$Cl$_2$/CH$_3$OH at −25 °C. Carbonyl stretching spectra and chemical analyses for these complexes are also presented in Table I.

Thermal Kinetics Studies. Reactions of *cis*-(pip)(L)W(CO)$_4$ in the presence of large excesses of pip and L′, which proceeded according to eq 2, were followed by one of two methods. For reactions above 50 °C,

$$cis\text{-(pip)(L)W(CO)}_4 + \text{L}' \rightarrow cis\text{-}, trans\text{-(L}')\text{(L)W(CO)}_4 + \text{L} \quad (2)$$

rates were monitored by previously described techniques[10] which involve removing aliquots of the reaction solution from a constant-temperature bath (Haake Model ED) which maintained the temperature to 0.05 °C and recording the absorbance of the reaction solution at 435 nm (Beckman DU-2 direct-reading spectrophotometer, monitoring the disappearance of the substrate). At this wavelength the reaction products did not absorb, and the absorbance of a ligand-solvent blank could be substituted for the absorbance at infinite time. Substrate concentrations employed were ca. 5 × 10^{-4} M, and pseudo-first-order conditions were attained through use of at least 20-fold excesses of *both* pip and L′. Plots of ln(A_t − A_{bl}) vs. time (A_t and A_{bl} are absorbances at time t and of a ligand-solvent blank, respectively) were linear to 2 or more half-lives. For reactions taking place below 50 °C, which therefore were quite slow, solutions were placed in screw-capped 10-mm Pyrex cells (Spectrocell), were degassed by bubbling with prepurified nitrogen, and were placed in the constant-temperature bath for later absorbance readings. Plots of ln(A_t − A_{bl}) vs. time were linear to 3 half-lives. Values of k_{obsd} obtained through use of both methods are given in Appendix I (Supplementary Material).

Pulsed Laser Flash Photolysis Studies. Kinetics studies were carried out at the Center for Fast Kinetics Research, University of Texas at Austin (CFKR), employing a Quantel Q-switched Nd:YAG laser (third harmonic (355 nm), 11 ns FWHI, 100 mJ maximum energy) as the photolysis source and a Xe lamp (Oriel; 430 nm) as the monitoring source. Substrate concentrations approximated 5 × 10^{-4} M. Data, taken as the computer average of 5–10 shots employing the same sample, were reproducible in studies carried out at different times with separately purified materials. Rates of reaction of the photogenerated [(CB)(L)W(CO)$_4$] transients were determined in the presence of excess pip (determination of k''_{pip}) and, separately, of L′ (determination of various $k''_{L'}$'s; vide infra). For the latter studies a second slower decay, attributable to *trans*-[(CB)(L)W(CO)$_4$], was also observed. Since it was not possible to monitor this decay to its t_∞ value and thus to analyze both decays employing this value, the values of t_∞ for the faster decay were taken as those values which afforded the best fit of the fast decay data; a typical plot of A_t vs. time, for disappearance of the photolysis products of *cis*-(pip)(PPh$_3$)W(CO)$_4$ in excess P(O-*i*-Pr)$_3$ in CB, is exhibited in

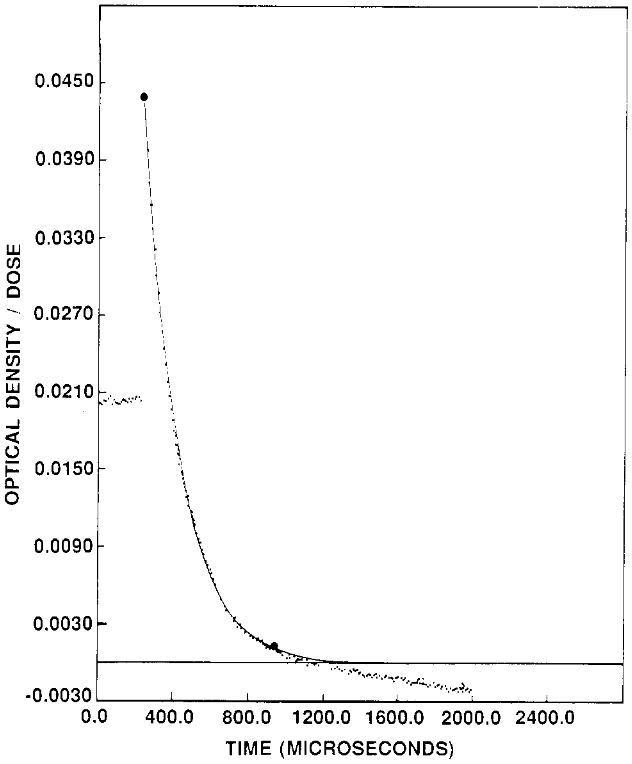

Figure 1. Plot of absorbance vs. time after pulsed laser flash photolysis of *cis*-(pip)(PPh$_3$)W(CO)$_4$ in P(O-*i*-Pr)$_3$/chlorobenzene solution at 31.1 °C.

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

Figure 1. As a result of the presence of two decays, values of k_2 are subject to greater uncertainty than are values of k_{-1}, which are obtained from plots for which no slow decay was observed. However, values of k_2 are believed accurate to within <10%. Other experimental details have been described elsewhere.[11] Values of k_{obsd} and of the second-order rate constants k''_{pip} and $k''_{L'}$ for reaction of the photogenerated transient with pip and L′ respectively are given in Appendix II (Supplementary Material).

Results and Discussion

Mechanism. There are three separate elements to the mechanistic studies: (a) thermal kinetics studies of reactions of *cis*-(pip)(L)W(CO)$_4$ with both pip and L′ in CB; (b) flash photolysis studies employing the *cis*-(pip)(L)W(CO)$_4$ substrates in the presence, separately, of pip and L′ in CB solution; and (c) flash photolysis studies employing these same substrates in the presence of both pip and CB in CH solution. These elements taken together provide a detailed picture of the overall ligand-exchange reactions of L′ with *cis*-(pip)(L)W(CO)$_4$ in CB; each element will be considered separately.

Thermal Kinetics Studies. The isolation of the products of the reactions of *cis*-(pip)(L)W(CO)$_4$ (L = PPh$_3$, PPhMe$_2$, CP, and P(OEt)$_3$) with L′ (= P(O-*i*-Pr)$_3$) and for L = P(O-*i*-Pr)$_3$ with L′ = P(OMe)$_3$, P(OPh)$_3$, P(*n*-Bu)$_3$, P(OEt)$_3$, and PPh$_3$ in CB under conditions approximating those employed in the thermal kinetics studies and their chemical analyses revealed the products to be *cis*- and *trans*-(L′)(L)W(CO)$_4$. Thus pip and pip alone is displaced by L′ during the ligand-exchange process. The reactions thus obey the stoichiometry shown in eq 2.

The isomerization of *cis*-(L′)(L)W(CO)$_4$ formed initially via thermal dissociation of pip from *cis*-(pip)(L)W(CO)$_4$ occurs in all liklihood via a nondissociative scrambling process. This conclusion is strongly supported by the observation that thermal reactions of *cis*-(pip)(L)W(CO)$_4$ complexes with L′ afford only (L′)(L)W(CO)$_4$ complexes (i.e., that no W–L or W–L′ bond breaking is observed to temperatures of 100 °C) and is consistent with results previously reported for L, L′ = PPh$_3$, and related complexes;[1,12] scrambling is likely to involve a "trigonal twist". Further, as is shown below, no stereochemical rearrangement in the solvated intermediates produced via W–pip bond breaking takes place on the time scale of the interaction of L′ with these species.

Thermal kinetics studies of the reactions of *cis*-(pip)(L)W(CO)$_4$ with both pip and L′ under pseudo-first-order reaction conditions employing either conventional sampling techniques or sealed cells, monitoring the disappearance of the *cis*-(pip)(L)W(CO)$_4$ (1-R), obeyed the rate law

$$-d[1\text{-R}]/dt = k[1\text{-R}][L']/([\text{pip}] + k'[L']) = k_{obsd}[1\text{-R}] \quad (3)$$

Values of k_{obsd} are given in Appendix I (Supplementary Material).

Expressed in terms of k_{obsd}, the pseudo-first-order rate constants, this expression can be rearranged to

$$1/k_{obsd} = [\text{pip}]/k[L'] + k'/k \quad (4)$$

This rate behavior is consistent with mechanism 1, involving initial dissociation of pip and rapid competitive reaction of the resulting five-coordinate intermediate [(L)W(CO)$_4$] (1-I$_1$) with CB, pip, and L′; the latter pathway affords the kinetically inert *cis*-(L′)(L)W(CO)$_4$ (1-P) product. Here it is assumed (an assumption to be addressed experimentally below) that the mechanism of displacement of CB from *cis*-[(CB)(L)W(CO)$_4$] (1-I$_2$) by L′ is analogous to that for displacement of pip from 1-R, i.e., it is a dissociative rather than an associative or interchange process. For this mechanism, assuming steady-state concentrations of 1-I$_1$ and 1-I$_2$, $k = k_1k_2/k_{-1}$ and $k' = k_2/k_{-1'}$ the "competition ratio" of rate constants for attack at intermediate 1-I$_1$ by L′ and pip. The reciprocals of the intercepts of the reciprocal plots (eq 4), k/k', equal to k_1, the rate constants for unimolecular dissociation of pip from 1-R, are expected to be independent of the identity of L′, as is shown to be the case in Figure 2, which illustrates plots of $1/k_{obsd}$ vs. [pip]/[L′] for the reaction of *cis*-(pip)(L)W(CO)$_4$ (L = P(O-*i*-Pr)$_3$) for three different L′. Table II presents values of k/k' (= k_1) and of k' (= k_2/k_{-1}) for five different L's in chlorobenzene at several temperatures. The kinetics results and the interpretation of the rate data are analogous to those proposed by Hyde and Darensbourg,[13] who investigated rates of reaction of various L′ with *cis*-(amine)(PPh$_3$)Mo(CO)$_4$ complexes (amine = pip, py (= pyridine)).

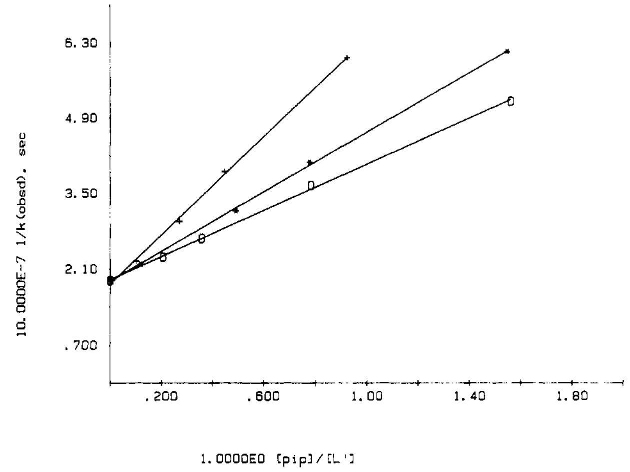

Figure 2. Plots of $1/k_{obsd}$ vs. [pip]/[L′] for reactions of *cis*-(pip)(P(O-*i*-Pr)$_3$)W(CO)$_4$ with L′ in chlorobenzene at 31.1 °C: 0, L′ = P(OMe)$_3$; *, L′ = P(OEt)$_3$; +, L′ = P(OPh)$_3$.

Table II. Rate Constants for the Thermal Reactions

L, L′	T, °C	10^6k_1 s^{-1}	k_2/k_{-1}
P(O-*i*-Pr)$_3$, P(OMe)$_3$	31.1	0.527 (8)	0.89 (3)
P(O-*i*-Pr)$_3$, P(OEt)$_3$		0.534 (9)	0.68 (5)
P(O-*i*-Pr)$_3$, P(O-*i*-Pr)$_3$		0.542 (5)	0.44 (1)
	60.0	35. (3)	
	70.0	129. (4)	
P(O-*i*-Pr)$_3$, P(OPh)$_3$	31.1	0.552 (11)	0.40 (2)
P(O-*i*-Pr)$_3$, P(*n*-Bu)$_3$		0.544 (8)	0.78 (2)
P(O-*i*-Pr)$_3$, PPh$_3$		0.58 (1)	0.49 (4)
P(OEt)$_3$, P(O-*i*-Pr)$_3$	70.0	10.7 (7)	0.77 (9)
	80.0	45.7 (9)	0.67 (3)
	90.0	166. (5)	0.64 (5)
PPh$_3$	33.3	1.12 (3)	0.53 (2)
P(OCH$_3$)$_2$CCH$_3$	55.0	0.72 (2)	0.75 (4)
	80.0	17.0 (4)	0.75 (3)
	88.0	44.7 (2)	0.81 (2)
PMe$_2$Ph	70.3	75.7 (18)	0.62 (4)
	80.0	295. (16)	0.52 (4)
	88.0	768. (45)	0.50 (5)

Flash Photolysis Studies in CB. Pulsed laser flash photolysis of solutions of 1-R (L = PPh$_3$) in the presence of excess pip in CB over the range of observation wavelengths 380–550 cm^{-1} afforded the time-resolved spectra shown in Figure 3. These spectra indicate 430 nm to be a suitable observation wavelength. The isosbestic point exhibited at 410 nm indicates that the photogenerated species decays to a single product. Photolysis monitoring 430 nm of solutions of 1-R in the presence of large excesses of pip *or* of L′ in chlorobenzene afforded traces of which Figures 4 and 1, respectively, are typical. Figure 4 exhibits a plot of absorbance vs. time for photolysis of 1-R (L = PPh$_3$) in the presence of excess pip, which exhibits a logarithmic decay to a new base line. A plot of absorbance vs. time for the same substrate in the presence of PPh$_3$ (Figure 1) exhibits two decays, the first of which is logarithmic, and the second of which is too slow to permit the determination of an accurate base line. As mentioned in the Experimental Section and as will be further discussed below, the second decay is attributable to formation of *trans*-[(CB)-

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[13] Hyde, C. K.; Darensbourg, D. J. *Inorg. Chem.* **1973**, *12*, 1286.

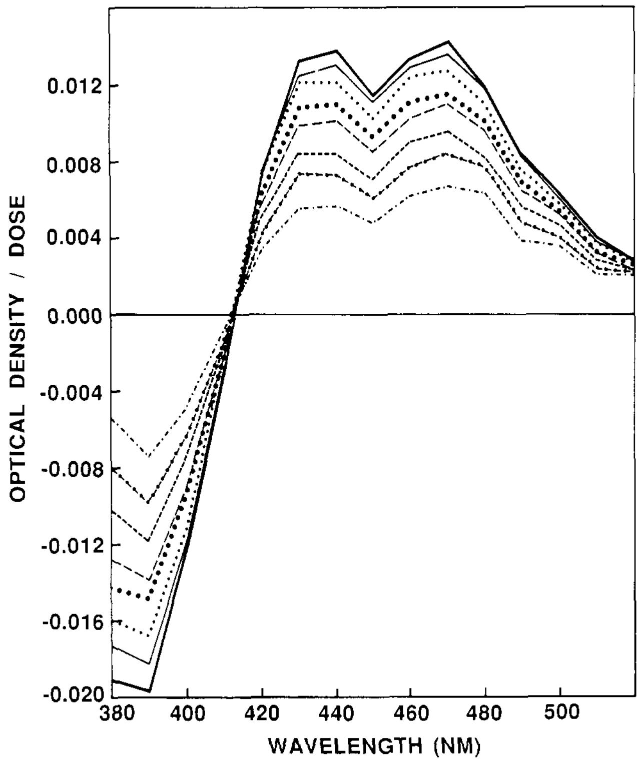

Figure 3. Time-resolved spectra after pulsed laser flash photolysis of *cis*-(pip)(PPh$_3$)W(CO)$_4$ in pip/chlorobenzene solution at 31.1 °C. Times after flash, starting with curve exhibiting highest optical density at 430 nm and in order of decreasing OD: 5, 20, 35, 65, 85, 135, 185, 272.5 μs, respectively.

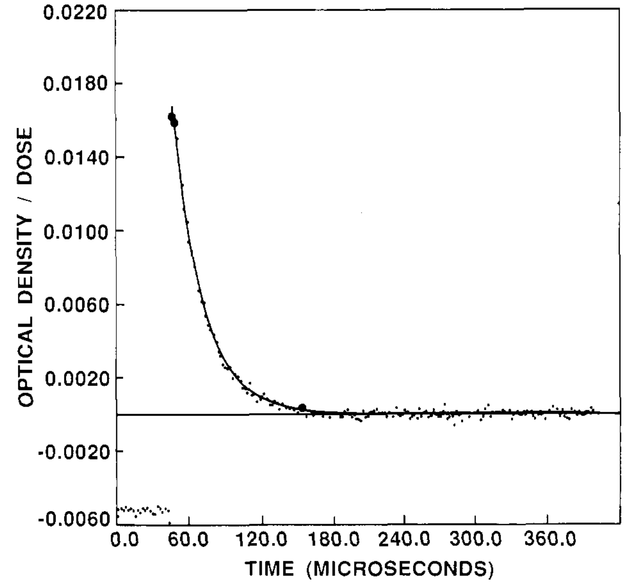

Figure 4. Plot of absorbance vs. time after pulsed laser flash photolysis of *cis*-(pip)(PPh$_3$)W(CO)$_4$ in pip/chlorobenzene solution at 31.1 °C.

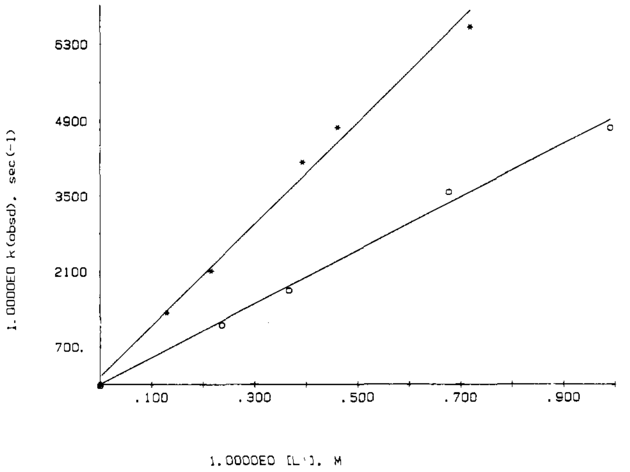

Figure 5. Plots of k_{obsd} vs. [pip] and vs. [P(O-*i*-Pr)$_3$] after pulsed laser flash photolysis of *cis*-(pip)(P(O-*i*-Pr)$_3$)W(CO)$_4$ in the presence of these ligands (L′) at 31.1 °C in chlorobenzene: *, pip; 0, P(O-*i*<<hpPr)$_3$.

Table III. Rate Constants for the Thermal Reactions Taking Place after Flash Photolysis

L, L′	T, °C	$10^{-4}k''_{pip}$, M^{-1} s^{-1}	$10^{-4}k''_{L'}$, M^{-1} s^{-1}
P(O-*i*-Pr)$_3$, P(OMe)$_3$	31.1	1.00 (5)	0.95 (4)
P(O-*i*-Pr)$_3$, P(OEt)$_3$		1.00 (5)	0.62 (2)
P(O-*i*-Pr)$_3$, P(O-*i*-Pr)$_3$	21.1	0.49 (2)	0.28 (3)
	31.1	1.00 (5)	0.479 (8)
	38.5	1.49 (4)	0.81 (2)
P(O-*i*-Pr)$_3$, P(OPh)$_3$	31.1	1.00 (5)	0.34 (2)
P(O-*i*-Pr)$_3$, PPh$_3$		1.00 (5)	0.57 (2)
P(O-*i*-Pr)$_3$, P(*n*-Bu)$_3$		1.00 (5)	0.81 (1)
P(OEt)$_3$, P(O-*i*-Pr)$_3$	21.1	0.238 (12)	0.123 (6)
	31.1	0.423 (6)	0.23 (1)
	38.5	0.67 (2)	0.355 (9)
PPh$_3$	31.1	4.0 (3)	1.9 (1)
P(OCH$_2$)$_3$CCH$_3$	21.1	0.076 (5)	0.049 (3)
	31.3	0.184 (7)	0.11 (1)
	38.5	0.264 (3)	0.176 (4)
PMe$_2$Ph	21.1	0.310 (9)	0.23 (1)
	31.1	0.51 (2)	0.425 (9)
	38.5	0.891 (9)	0.670 (2)

(PPh$_3$)W(CO)$_4$]. The faster decay proceeds to a base line for which absorbance is lower than is that of 1-R, which strongly suggests that pip is replaced by L′, since it is known that metal–carbonyl complexes containing ligands coordinating through phosphorus absorb less strongly in the "yellow" region than do those containing amines.[14] If this is indeed the case, these plots both indicate that two photoproducts are produced, since reformation of R in the presence of pip should result in decay to the original base line. Thus, for photolysis of 1-R in the presence of pip, it may be concluded that the second photoproduct, by analogy to the results for the reaction of 1-R with L illustrated in Figure 1, decays too slowly to be measured.

The decays of the more reactive photoproduct obey the rate law 5

$$k_{obsd} = k''_{pip}[pip] \qquad \text{or} \qquad k_{obsd} = k''_{L'}[L'] \qquad (5)$$

Plots of k_{obsd} vs. [pip] and vs. [P(O-*i*-Pr)$_3$] in CB at 31.1 °C are exhibited in Figure 5; values of k_{obsd} and of the corresponding values of k'' (= k_{obsd}/[pip] or k_{obsd}/[L′]) are presented in Appendix II while values of the rate constants k'' obtained via least-squares analyses of plots of k_{obsd} vs. [pip] and of k_{obsd} vs. [L′] are presented in Table III.

Pulsed laser flash photolysis of *cis*-(NP)Mo(CO)$_4$ (NP = 1-(diethylamino)-2-(diphenylphosphino)ethane), which contains a *chelating* ligand coordinating through N and P but which otherwise is very similar to the *cis*-(pip)(L)W(CO)$_4$ complexes discussed here, has also been found to afford two transients upon photolysis.[11] The faster of the two decay processes has unequivocally been attributed to reaction of the "ring-opened" *cis*-[(S)(η^1-NP)Mo(CO)$_4$] intermediate (S = CB, toluene, 1,2-dichloroethane; N not coordinated) based upon the two-term rate law observed for its disappearance—by both unimolecular chelate ring reclosure and by competitive bimolecular interaction with L′—together with other evidence.[11] It thus is reasonable to presume that for flash photolysis of the *cis*-(pip)(L)W(CO)$_4$ complexes the fast decay is attributable to an analogous intermediate, *cis*-[(CB)(L)W(CO)$_4$]. If this is indeed the case, the

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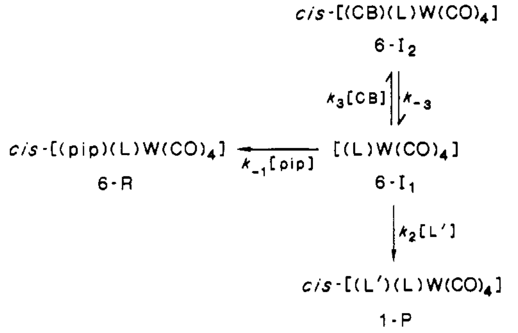
Table IV. Competition Ratios for Reactions of *cis*-(S)(L)W(CO)$_4$[a] Produced Thermally and Photochemically[b]

L′	k_2/k_{-1} (thermal)	$k''_{L'}/k''_{pip}$ (photochemical)
$P(OMe)_3$	0.89 (3)	0.94 (8)
$P(OEt)_3$	0.68 (5)	0.62 (5)
$P(O\text{-}i\text{-}Pr)_3$	0.44 (3)	0.48 (3)
$P(OPh)_3$	0.40 (2)	0.34 (4)
PPh_3	0.49 (4)	0.48 (6)
$P(n\text{-}Bu)_3$	0.78 (2)	0.81 (6)

[a] S = chlorobenzene; L = $P(O\text{-}i\text{-}Pr)_3$. [b] Various L′ at 31.1 °C.

fast decays in the presence of pip and L′ result from reactions of these intermediates (6-I_2, mechanism 6); cf. mechanism 1.



(6)

pip = piperidine; L,L′ = PR$_3$, P(OR)$_3$; CB = chlorobenzene

If mechanism 6 is applicable, assuming a steady-state concentration of 6-I_1, eq 7 and 8 can be derived through consideration of eq 5

$$k''_{pip} = k_{-1}k_{-3}/(k_3[CB] + k_{-1}[pip]) \quad (7)$$

$$k''_{L'} = k_2k_{-3}/(k_3[CB] + k_2[L']) \quad (8)$$

In the limiting cases where $k_3[CB] \gg k_{-1}[pip]$, $k_2[L']$

$$k''_{pip} = k_{-1}K_{eq}/[CB] \quad (9)$$

and

$$k''_{L'} = k_2K_{eq}/[CB] \quad (10)$$

where K_{eq} is the equilibrium constant, k_{-3}/k_3, for dissociation of CB from *cis*-[(CB)(L)W(CO)$_4$] (6-I_2) (eq 11).

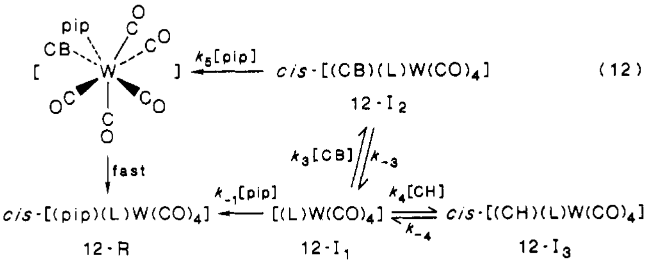
$$cis\text{-}[(CB)(L)W(CO)_4] \underset{k_3}{\overset{k_{-3}}{\rightleftharpoons}} [(L)W(CO)_4] + CB \quad (11)$$

The assumption that the fast decay is attributable to the disappearance of *cis*-[(CB)(L)W(CO)$_4$] (6-I_2) can further be tested through comparison of the "competition ratios", k_2/k_{-1}, for the thermal reactions as discussed above with the ratios $k''_{L'}/k''_{pip}$ from the photochemical data. In the event the *cis*-[(CB)(L)W(CO)$_4$] is produced both thermally and photochemically, these ratios k_2/k_{-1} (thermal) and $k''_{L'}/k''_{pip}$ (photochemical) should be the same for data taken at the same temperature. These comparisons, for six L′, P(OMe)$_3$, P(OEt)$_3$, P(O-*i*-Pr)$_3$, P(OPh)$_3$, PPh$_3$, and P(*n*-Bu)$_3$ for the *cis*-(pip)(P(O-*i*-Pr)$_3$)W(CO)$_4$ thermal and photochemical precursor at 31.1 °C are given in Table IV. They each are the same, within experimental error, providing strong evidence that the identity of the transient exhibiting the fast decay is *cis*-[(CB)(P(O-*i*-Pr)$_3$)W(CO)$_4$] and that the applicable mechanistic interpretations as discussed above and as presented in eq 1 and 6 are correct.

Flash photolysis with *infrared detection* of some of these same substrates in *n*-heptane solvent, conducted while this work was in progress,[6] has unequivocally confirmed the identities of the species exhibiting the faster decay as *cis*-[(*n*-heptane)(L)W(CO)$_4$] and has demonstrated that they exhibit geometries based upon the octahedron with the solvent specifically occupying the "vacant coordination site". The slower decays observed here and in that study[6] are attributable to *trans*-[(S)(L)W(CO)$_4$], as was also proposed for the (NP)M(CO)$_4$ systems (vide supra).[11] As was observed in those investigations, the separate decays attributable here to the cis and trans intermediates indicate that their interconversion is not fast on the time scale of their bimolecular interaction with L′. The reactivities of the trans intermediates, which are not produced during the thermal ligand-substitution process reported here, will be the subject of a separate study.[15]

Flash Photolysis Studies in CB/CH Mixtures. The infrared evidence cited above[6] demonstrates that solvent molecules occupy specific sites in the octahedral coordination sphere and thus permits consideration of solvated intermediates as analogues of the coordination complexes from which they are derived. This raises the intriguing possibility that the mechanism of desolvation may be further probed through studies of the competition for a potential five-coordinate intermediate such as 1-I_1 by a solvent (S) and ligand in a second solvent (S′) in which *cis*-[(S′)(L)W(CO)$_4$] would be a steady-state intermediate. Such a situation should obtain for the solvents CB and cyclohexane (CH), for which preliminary data demonstrate that the rate constant for displacement of the latter by pip from *cis*-[(S)(P(O-*i*-Pr)$_3$)W(CO)$_4$] is 3.7 × 10^3-fold greater than for displacement of the former at 31.1 °C.[16]

Consider the two possible limiting solvent displacement mechanisms illustrated in eq 12 (cf. mechanism 1) for the reaction



(12)

pip = piperidine; CB = chlorobenzene; CH = cyclohexane

of *cis*-[(CB)(L)W(CO)$_4$] (12-I_2) created via pulsed laser flash photolysis with pip in CB/CH (= cyclohexane) mixtures. The first involves reversible CB dissociation governed by k_{-3} and k_3 and competition for the resulting five-coordinate intermediate, [(L)W(CO)$_4$] by CB and pip. Assuming steady-state concentrations of *cis*-[(CH)(L)W(CO)$_4$] (12-I_3) and [(L)W(CO)$_4$] (12-I_1), in the limiting case in which $k_3[CB] \gg k_{-1}[pip]$, second-order rate behavior will be expected, as is observed (see Figure 5), and the second-order rate constant, k''_{pip}, will be that given in eq 9. The associative or interchange pathway governed by k_5 (eq 12) will also obey a second-order rate law, in which $k''_{pip} = k_5$.

In CB/CH solvent mixtures, however, [CB] can be varied and "nonlimiting" conditions created in which the expression

$$k_{obsd} = k_{-1}k_{-3}[pip]/(k_3[CB] + k_{-1}[pip]) \quad (13)$$

which can be obtained from eq 5 and 7, will be obeyed.

Reactions of *cis*-[(CB)(P(O-*i*-Pr)$_3$)W(CO)$_4$] with pip have been studied in CB/CH mixtures so that the [pip]/[CB] ratios could be varied widely.[17] Appendix III provides values of k_{obsd} at various [pip] to [CB] ratios at three temperatures. Figure 6 exhibits plots of k_{obsd} vs. [pip]/[CB] for data at three temperatures. The

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(15) Dobson, G. R.; Cortês, J. E.; Awad, H. H., manuscript in preparation.

(16) Dobson, G. R.; Wermer, P. W.; Awad, H. H.; Cortês, J. E., unpublished results.

(17) This method is applicable because competition ratios for reaction of CH, CB, and pip with [(L)W(CO)$_4$] (L = P(O-*i*-Pr)$_3$) do not differ greatly from unity. Initially, *cis*-[(CH)(L)W(CO)$_4$] is the predominant reaction species formed upon photolysis, with smaller quantities of the *cis*-[(CB)(L)W(CO)$_4$] intermediate and of the *cis*-(pip)(L)W(CO)$_4$ reaction product also being produced directly from [(L)W(CO)$_4$]. The [(CH)(L)W(CO)$_4$] transient then reacts to form the corresponding CB and pip complexes via the unsolvated [(L)W(CO)$_4$] intermediate. Preliminary studies of these reactions, to be communicated in another context, afford rate constants of ca. 1 × 10^7 and 2 × 10^7 M^{-1} s^{-1}, respectively, at 31.1 °C. Thus on the 100-μs time scale the reaction solution contains as the predominant reaction species *cis*-[(CB)(L)W(CO)$_4$] and the final reaction product, *cis*-(pip)(L)W(CO)$_4$. The conversion of the former to the latter thus can be monitored as a function of [pip]/[CB] in CH.

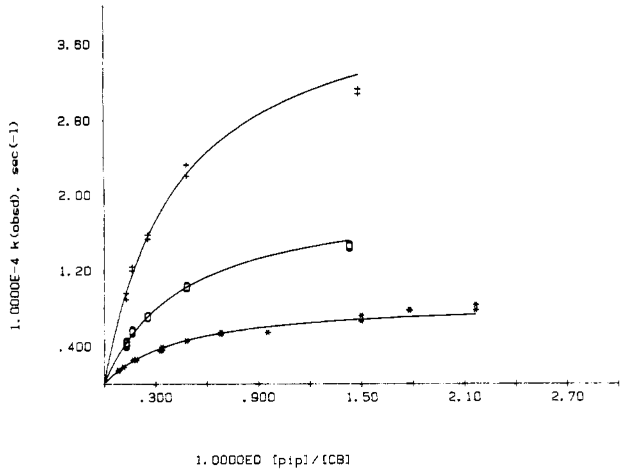

Figure 6. Plots of k_{obsd} vs. [pip]/[CB] after flash photolysis of *cis*-(pip)(P(O-*i*-Pr)$_3$)W(CO)$_4$ in piperidine/chlorobenzene/cyclohexane solutions at various temperatures: *, 11.1; 0, 20.2; +, 31.1 °C.

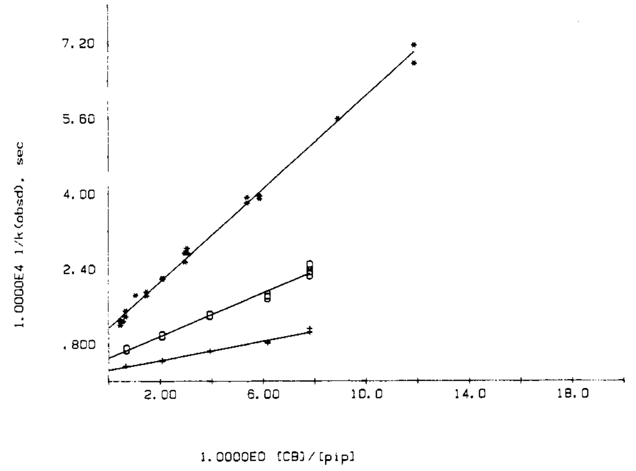

Figure 7. Plots of $1/k_{obsd}$ vs. [CB]/[pip] after flash photolysis of *cis*-(pip)(P(O-*i*-Pr)$_3$)W(CO)$_4$ in piperidine/chlorobenzene/cyclohexane solutions at various temperatures: *, 11.1; 0, 20.2; +, 31.1 °C.

nonlinearity of these plots rules out an interchange or associative mechanism for solvent displacement for this reaction.

Rearrangement of (13) affords

$$1/k_{obsd} = 1/k_{-3} + k_3[\mathrm{CB}]/k_{-1}k_{-3}[\mathrm{pip}] \qquad (14)$$

thus plots of $1/k_{obsd}$ vs. [CB]/[pip] are expected to be linear, with intercepts $1/k_{-3}$ and slopes $k_3/k_{-1}k_{-3}$. These plots, for data at three temperatures, are shown in Figure 7 and are consistent with the dissociative solvent-displacement mechanism (eq 12).

These data permit a comparison of the value of k''_{pip} (= $k_{-1}K_{eq}/[\mathrm{CB}]$) (eq 9) obtained in pure CB with the reciprocal of the slope of the reciprocal plots of $1/k_{obsd}$ vs. [CB]/[pip] for the reaction of *cis*-[(CB)(P(O-*i*-Pr)$_3$)W(CO)$_4$] with pip in CB/CH, which is $k_{-1}K_{eq'}$ or $k''_{pip}[\mathrm{CB}]$. The close agreement of the values of $k_{-1}K_{eq}$ for the former and the latter (9.8 (5) × 10^4 s^{-1} vs. 9.7 (5) × 10^4 s^{-1}) demonstrates the internal consistency of the mechanistic interpretation. Values of k_{-3}, the rate constants for CB dissociation, together with those for $k_{-1}K_{eq}$ and for the "competition ratios", $k_3/k_{-1'}$ for reaction [(L)W(CO)$_4$] with CB and pip, respectively, are presented in Table V.

The thermal and flash photolysis kinetics data thus are entirely consistent with mechanism 1.

Rates and Energetics of Ligand Exchange. The rate data obtained through these studies provide detailed information about influences of coordinated ligands, L, of incoming nucleophiles, L′, and of the nature of the solvent on these ligand-exchange processes.

Table V. Rate Constants and Activation Parameters for Reversible Chlorobenzene (CB) Loss from *cis*-[(CB)(P(O-*i*-Pr)$_3$)W(CO)$_4$] in the Presence of Piperidine in Cyclohexane Solvent[a]

T, °C	$10^{-3}k_{-3}$, s^{-1}	$10^{-4}k_{-3}k_{-1}/k_3$, s^{-1}	k_3/k_{-1}
11.1	8.8 (3)	2.02 (3)	0.44 (2)
20.2	19.2 (13)	4.50 (13)	0.43 (4)
31.1	42.6 (53)	9.71 (55)	0.44 (8)

[a] $\Delta H_3^{\ddagger}$ = 13.0 (4) kcal/mol; $\Delta S_3^{\ddagger}$ = +5.6 (11) eu; $\Delta H_{-3}^{\ddagger} + \Delta H_{-1}^{\ddagger} - \Delta H_3^{\ddagger}$ = 12.8 (9) kcal/mol; $\Delta S_{-3}^{\ddagger} + \Delta S_{-1}^{\ddagger} - \Delta S_3^{\ddagger}$ = +6.7 (32) eu.

Table VI. Comparison of Rate Constants for Reactions of *cis*-(S)(L)W(CO)$_4$ Complexes with Triisopropyl Phosphite at 31.1 °C

L	10^7k_1, s^{-1}	$10^{-3}k_{-1}$, M^{-1} s^{-1}	$10^{-3}k_{-3}$, M^{-1} s^{-1}
P(OCH$_2$)$_3$CCH$_3$	0.210 (8)	1.84 (7)[a]	1.1 (1)[a]
P(OEt)$_3$	0.193 (17)	4.23 (6)	2.3 (1)
PMe$_2$Ph	1.78 (28)	5.1 (2)	4.25 (9)
P(O-*i*-Pr)$_3$	5.42 (5)	10.0 (5)	4.79 (8)
PPh$_3$	11.2 (3)[b]	40. (3)	19. (1)

[a] At 31.3 °C. [b] At 33.3 °C. [c] S = chlorobenzene.

Influences on Reactivity of Coordinated L and Incoming L′. The rate constants k_1, k_{-1}, and k_2 for reactions involving displacement of pip from *cis*-(pip)(L)W(CO)$_4$ complexes by P(O-*i*-Pr)$_3$ for five different coordinated L in CB solvent, given in Table VI, vary some 20–50-fold, and all are predominantly influenced by the steric properties of L, increasing with increasing Tolman cone angles of L[18] in the order P(OCH$_2$)$_3$CCH$_3$ < P(OEt)$_3$ < PMe$_2$Ph, P(O-*i*-Pr)$_3$ < PPh$_3$. In contrast, these rate constants for reactions of *cis*-[(CB)(P(O-*i*-Pr)$_3$)W(CO)$_4$] with six different L′ (Tables III and IV) vary less than threefold and are sensitive to both the steric and electronic influences of L′. Thus, for example, for three L′ of differing Tolman electronic ν parameters[18] but similar cone angles, P(OPh)$_3$, P(O-*i*-Pr)$_3$; and P-*n*-Bu$_3$, values of k_2 increase with increasing ligand basicities in the order shown in the ratio 1:1.4:2.4 (Table IV). There also is, however, a definite tendency toward larger values of k_2 for smaller incoming nucleophiles. Thus k_2 values decrease in order of increasing cone angles along the series P(OMe)$_3$, P(OEt)$_3$, and P(O-*i*-Pr)$_3$. The competition ratios observed here are comparable in magnitude to those which have been reported in several other studies of ligand-substitution reactions of octahedral metal carbonyl derivatives.[19]

The Solvation–Desolvation Process. The form of the rate law for reaction of *cis*-[(CB)(P(O-*i*-Pr)$_3$)W(CO)$_4$] in CB/CH together with the observed entropy of activation derived from values of k_{-3}, 5.6 (11) cal/deg-mol, strongly indicates that the mechanism of desolvation is dissociative and thus that the unsolvated [(P(O-*i*-Pr)$_3$)W(CO)$_4$] is the species which reacts with pip. There also is strong evidence which indicates that this latter process is extremely rapid. Simon and Peters have determined that solvation of [Cr(CO)$_5$] is complete within 25 ps,[20] and, more recently, Simon and Xie[21] have found the "rise-time" for solvation of [Cr(CO)$_5$] by methanol to be 2.5 ps and that for solvation of [Cr(CO)$_5$] by CH to be within the resolution of the instrument, 0.8 ps. Langford and co-workers have reported a pseudo-first-order rate constant of 5 × 10^{10} s^{-1} for solvation of [W(CO)$_5$] by perfluoromethylcyclohexane (MCH$_f$).[22] Seder, Church, and Weitz, in studies of [Cr(CO)$_5$] in the gas phase, have found that the rate of recombination of this species with CO is approximately one order or magnitude less than that expected for its gas-kinetics reaction cross section.[23] Activation energies for the solvation process thus are very small, and, therefore, based upon Hammond's postulate,[24] the transition state leading to formation of the solvated species

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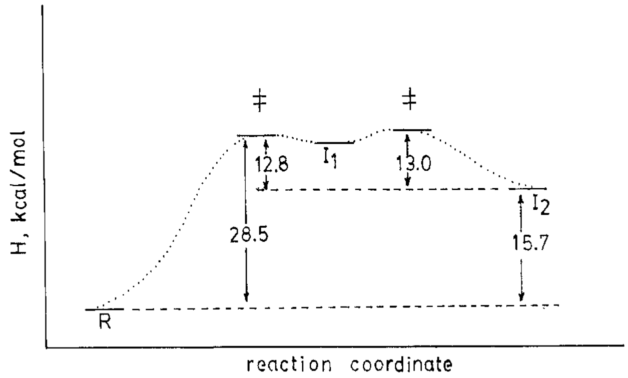

Figure 8. Plot of enthalpy vs. reaction coordinate for conversion of *cis*-(pip)(P(O-*i*-Pr)$_3$)W(CO)$_4$ (R) via *cis*-[(P(O-*i*-Pr)$_3$)W(CO)$_4$] (I$_1$) to *cis*-[(CB)(P(O-*i*-Pr)$_3$)W(CO)$_4$] (I$_2$).

should closely resemble the coordinatively unsaturated intermediate. These data suggest that analogous results should obtain in the present study that activation energies for reaction of CB (and of pip and L′) with the nonsolvated [(L)W(CO)$_4$] intermediates should be quite small and, consequently, that the transition states leading to solvation of these intermediates should very closely resemble [(L)W(CO)$_4$]. These conclusions are supported in the present study by the difference in the enthalpies of activation for interaction of pip and CB with [(P(O-*i*-Pr)$_3$)W(CO)$_4$], −0.2 (12) kcal/mol (Table VI), which may be contrasted to the large difference in the enthalpies of activation for the reverse processes—W–pip and W–CB bond *dissociation*, 15.7 (10) kcal/mol. These relationships are illustrated in Figure 8.

It appears likely that "naked" five-coordinate intermediates such as are postulated here are square-pyramidal, little changed in geometry upon desolvation. Bonneau and Kelly have reported that the weakly bound MCH$_f$ is replaced by the more strongly bound cyclohexane from [(MCH$_f$)Cr(CO)$_5$] at a rate which approaches the diffusion-controlled limit.[25] Thus [(MCH$_f$)Cr(CO)$_5$] as well as [Cr(CO)$_5$] (vide supra) resembles the transition state! These observations suggest that there should be minimal geometrical rearrangement in the –Cr(CO)$_5$ moiety along the reaction coordinate. Further, Seder, Church, and Weitz have found that the carbonyl stretching spectrum for [Cr(CO)$_5$] generated photolytically in the gas phase is characteristic of C_{4v} symmetry and compatible with those observed for [Cr(CO)$_5$] in condensed phases,[23,26] i.e., for the solvated species. It therefore is reasonable also to presume that little change in geometry of the metal carbonyl moiety accompanies transformation of "naked" [(L)W(CO)$_4$] intermediates into their solvated counterparts; thus these nonsolvated species are probably square-pyramidal, with the vacant coordination site cis to L.

The results reported here, together those of the other workers as cited above,[20-25] are at variance with the results of Lees and Adamson[27] for reaction of 4-acetylpyridine (4-acpy) and methylcyclohexane (MCH) with a species produced upon flash photolysis of W(CO)$_6$. Those reactions also have been interpreted in terms of solvent-dissociation and competition between 4-acpy and MCH for [W(CO)$_5$]. In this investigation the inferred difference in energy between [W(CO)$_5$] and [(MCH)W(CO)$_5$] is ca. 1 kcal/mol, inconsistent with the results of Bonneau and Kelly,[25] while the competition ratio, $k_{4\text{-acpy}}/k_{\text{MCH}'}$ was inferred to be very large, 270.

The rate constants k''_{pip} and $k''_{\text{L}'}$ (eq 9 and 10) for replacement of a solvent molecule by pip or L′ are overwhelmingly influenced by the values of $k_{-3'}$ the rate constants for solvent dissociation, that is, by the strength of the solvent–W interaction. This is because, as is discussed above, the values of the other rate constants which contribute to k''_{pip} and $k''_{\text{L}'}$, those for combination of pip, L′, or the solvent with [(L)W(CO)$_4$], k_{-1}, k_2, and k_3, are expected to be very large and similar, approaching those for the limits of diffusion control. The dominance of the W–CB bond-dissociation energies in the determination of values of k''_{pip}[CB] and $k''_{\text{L}'}$[CB] (= $K_{-1}K_{\text{eq}}$ and k_2K_{eq}, respectively) is also apparent from the similarities observed for the activation parameters derived from these rate constants for reaction of *cis*-[(CB)(L)W(CO)$_4$] intermediates with pip and P(O-*i*-Pr)$_3$, presented in Table VII. It has been found in this regard, based upon preliminary results,[16] that the relative rates of solvent displacement from *cis*-[(solvent)(L)W(CO)$_4$] by L′ (L, L′ = P(O-*i*-Pr)$_3$) at 31.1 °C vary widely, increasing in the order bromobenzene (1) < 1,2-dichloroethane (1.5) < CB (12) < fluorobenzene (100) < toluene (2000) < CH (45 000) < *n*-heptane (125 000).

Table VII. Activation Parameters for Displacement of Piperidine from *cis*-(pip)(L)W(CO) Complexes by Triisopropyl Phosphite in Chlorobenzene

	L =			
	P(O-*i*-Pr)$_3$	P(OEt)$_3$	P(OCH$_2$)$_3$CCH$_3$	PMe$_2$Ph
$\Delta H_1^{\ddagger a}$	28.5 (1)	33.3 (4)	28.7 (2)	31.6 (9)
$\Delta S_1^{\ddagger b}$	8.9 (2)	16.4 (12)	2.3 (6)	15.2 (13)
$\Delta H_{-1}^{\ddagger a}$	11.1 (6)	10.2 (4)	12.6 (15)	10.3 (12)
$\Delta S_{-1}^{\ddagger b}$	+1.1 (20)	−3.8 (11)	+2.4 (46)	−1.9 (41)
$\Delta H_2^{\ddagger a}$	10.4 (7)	10.50 (2)	12.8 (4)	10.6 (1)
$\Delta S_2^{\ddagger b}$	−2.7 (31)	−4.0 (1)	+2.2 (15)	−2.5 (5)

[a] kcal/mol. [b] eu.

The parallels observed in pip and CB loss as a function of the steric properties of L (Table V; vide supra) strongly suggest that the same primary factor which influences the rates of dissociation of pip, that is, the steric nature of L, also dominates the solvent-exchange process—desolvation is accelerated by bulky L adjacent to the solvent.

The enthalpy of activation for dissociation of CB from *cis*-[(CB)(P(O-*i*-Pr)$_3$)W(CO)$_4$], 13.3(11) kcal/mol, is indicative of a relatively strong W–CB interaction, no doubt involving coordination of Cl to W. Several examples of complexes containing alkyl and aryl halides coordinated to a transition metal through Br or I have been characterized,[28,29] the structure of one of which has been elucidated through X-ray crystallography. Evidence for the existence of a complex in solution containing Ir–Cl–R bonds has also been presented.[29]

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Supplementary Material Available: (1) Appendices I and II consist of pseudo-first-order constants for reactions of *cis*-(pip)(L)L(CO)$_4$ complexes (pip = piperidine; L, L′ = phosphines, phosphites) in chlorobenzene at various temperatures. Appendix III consists of thermal rate constants after flash photolysis for reactions of *cis*-(pip)(P(O-*i*-Pr)$_3$)W(CO)$_4$ with pip in chlorobenzene/cyclohexane mixtures at various temperatures (13 pages). Ordering information is given on any current masthead page.

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