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Octahedral Metal Carbonyls. 76.[1] Ligand-Exchange Studies of *cis*-(pip)(L)$Cr(CO)_4$ Complexes (pip = Piperidine; L = Lewis Base)

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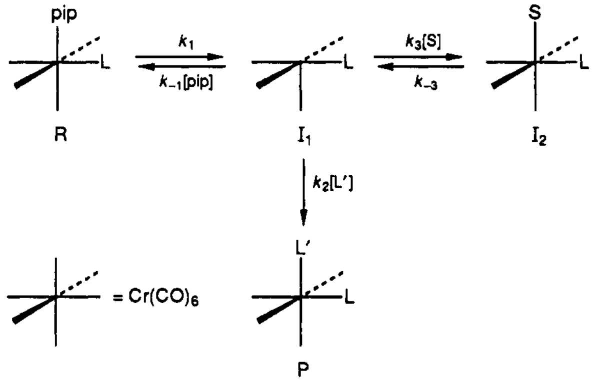
A series of *cis*-(pip)(L)$Cr(CO)_4$ complexes (pip = piperidine; L = $P(OMe)_3$, $P(OEt)_3$, $P(O\text{-}i\text{-}Pr)_3$, $P(OPh)_3$, $P(OCH_2)_3CCH_3$, PPh_3, $P(CH_2)_3N_3C_3H_6$), potential precursors for the creation of $[(L)Cr(CO)_4]$ intermediates via flash photolysis, have been synthesized. The complexes react thermally in chlorobenzene (=CB) with L′ (=$P(OMe)_3$, $P(OEt)_3$, $P(O\text{-}i\text{-}Pr)_3$, $P(OPh)_3$, $P(OCH_2)_3CCH_3$, PPh_3, $P(n\text{-}Bu)_3$) to afford *cis*- and *trans*-(L)(L′)$Cr(CO)_4$ products according to a mechanism that kinetics data indicate to involve reversible dissociation of pip from *cis*-(pip)(L)$Cr(CO)_4$ and competition between pip and L′ for the *cis*-$[(L)Cr(CO)_4]$ intermediates thus produced. Intramolecular isomerization follows, affording largely *trans*-(L′)(L)$Cr(CO)_4$, where both L and L′ are phosphines or are phosphites, but also substantial quantities of the cis isomer for "mixed" complexes containing one phosphine and one phosphite ligand. This observation is attributed to intramolecular hydrogen bonding (P–O··H–C–P) in the mixed complexes. Where the L ligands are phosphites, rates of dissociation of pip from *cis*-(pip)(L)$Cr(CO)_4$ complexes increase with increasing steric bulk of L; the $[(L)Cr(CO)_5]$ intermediates produced upon Cr–pip bond breaking show little discriminating ability among incoming L′. The rate of pip dissociation from *cis*-(pip)($P(CH_2)_3N_3C_3H_6$)$Cr(CO)_4$ at 31.1 °C is 137 (2) times faster than that for *cis*-(pip)($P(OCH_2)_3CCH_3$)$Cr(CO)_4$, in which L is sterically similar. This rate enhancement arises from a lack of intramolecular (N–H··O–P) hydrogen bonding between pip and L in the latter complex, which is present in the former. Activation energies suggest the strength of the hydrogen bond to be ca. 5 kcal/mol. These data suggest that the enthalpy of activation for Cr–pip bond dissociation closely approximates and represents an upper limit for the Cr–pip bond dissociation energy in this complex.

Introduction

The availability of pulsed lasers has afforded a much deeper understanding of the mechanisms of ligand-substitution reactions of the group VI-B metal carbonyls, $M(CO)_6$ (M = Cr, Mo, W), in that attention has been focused on reactivities of the intermediates produced after M–CO bond fission. This has been particularly true for $Cr(CO)_6$, for which a variety of studies have probed rates of solvation (picosecond time scale) of the $[Cr(CO)_5]$ intermediate produced after flash photolysis,[3] as well as rates, mechanism, and energies of desolvation reactions of (solv)$Cr(CO)_5$ species, which take place more slowly.[4] While there is much yet to be understood about these processes, it is clear that a next step will be to conduct analogous studies of substituted chromium carbonyls so that steric and electronic influences of these substituents on solvation/desolvation rates and mechanisms can be evaluated. Thus, the need exists to create molecules that, upon thermolysis or photolysis, will afford $[(L)Cr(CO)_4]$ intermediates.

Scheme I



It has been shown that disubstituted complexes containing both amine and phosphine or phosphite substituents undergo thermal loss of the amine to afford square-pyramidal $[LM(CO)_4]$ intermediates (M = Mo,[5] W[6]) in which the vacant coordination site is cis to L; the mechanism favored for their reaction with L′ (=phosphine, phosphite) is that shown in Scheme I.

In contrast, upon photolysis of *cis*-(pip)(L)$W(CO)_4$ complexes (pip = piperidine),[6,7] and the related *cis*-(NP)$M(CO)_4$ complexes (M = Cr, Mo, W; NP = chelating

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Table I. Carbonyl Stretching Frequencies for (L′)(L)Cr(CO)$_4$ Complexes in Cyclohexane Solution

		carbonyl stretching frequency, cm^{-1}			
L′	L	A′[a]	A′	A″	A″ + E$_{\text{trans}}$[b]
pip	CO	2066 (m)[c]	1932 (s)		1915 (m)
pip[d,e]	P(OMe)$_3$	2017 (s)	1921 (s)	1896 (vs)	1869 (s)
	P(OEt)$_3$	2015 (m)	1918 (s)	1893 (vs)	1866 (s)
	P(O-*i*-Pr)$_3$	2013 (m)	1915 (m)	1891 (vs)	1862 (s)
	PPh$_3$	2088 (m)	1906 (s)	1889 (vs)	1862 (s)
	P(OPh)$_3$	2024 (m)	1930 (s)	1913 (vs)	1880 (s)
	CP[f]	2030 (m)		1908 (vs)	1866 (s)
	TPA[f]	2006 (m)	1893 (s)	1885 (vs)	1845 (s)
PPh$_3$	P(O-*i*-Pr)$_3$	2015 (m)	1929 (m)		1900 (vs)
P(*n*-Bu)$_3$		2010 (m)	1917 (m)	1897 (s)	1888 (vs)
P(O-*i*-Pr)$_3$		2036 (vw)			1902 (vs)
P(OPh)$_3$		2036 (vw)			1921 (vs)
P(OMe)$_3$		2025 (vw)			1908 (vs)
P(OEt)$_3$		2023 (vs)			1906 (vs)
CP		2034 (vw)			1921 (vs)
TPA[d]		2011 (m)	1917 (s)	1897 (vs)	1882 (sh)

[a] Symmetries of normal modes in overall C_s symmetry of molecule. [b] Symmetry of normal mode in overall C_{4v} symmetry of trans product. [c] Symmetries of normal modes, C_{4v} symmetry molecule: A$_1$, A$_1$′, E, respectively. [d] Cis isomer only was observed. [e] This work and ref 11. [f] Chlorobenzene solution.

Table II. Elemental Analyses for (L′)(L)Cr(CO)$_4$ Complexes

		calcd		found	
L′	L	% C	% H	% C	% H
pip	P(OMe)$_3$	38.61	5.40	38.44	5.50
	P(OEt)$_3$	43.38	6.31	43.37	6.51
	P(O-*i*-Pr)$_3$	47.26	7.05	47.25	6.99
	P(OPh)$_3$	57.96	4.68	58.18	4.65
	CP	42.33	5.08	42.42	5.21
	TPA	44.34	5.71	43.69	5.79
P(OPh)$_3$	P(O-*i*-Pr)$_3$	54.54	5.32	54.80	5.61
P(OMe)$_3$		38.71	6.09	38.65	6.15
P(OEt)$_3$		42.38	6.74	42.55	6.68
CP		41.55	5.81	41.72	5.73
TPA		43.10	6.28	43.34	6.41

ligand containing both amine and phosphine functional groups),[8] while exclusive M–N bond fission also is observed, coordinatively unsaturated transients in which the vacant coordination sites are *both* cis and trans to the phosphorus-containing substituent are produced. Thus, it should be possible to study solvation and desolvation reactions of both *cis*- and *trans*-[(L)Cr(CO)$_4$] transients upon flash photolysis of *cis*-(pip)(L)Cr(CO)$_4$ complexes.

While a variety of *cis*-(pip)(L)M(CO)$_4$ complexes (M = Mo, W) have been synthesized,[5,6,9,10] preparation of their Cr analogues has proven to be more difficult. Schwenzer, Darensbourg, and Darensbourg reported the instability of *cis*-(pip)(PPh$_3$)Cr(CO)$_4$,[9] and the only reported *cis*-(pip)(L)Cr(CO)$_4$ was that for L = P(OMe)$_3$, which is stabilized through intramolecular O–H bonding between the phosphite and pip.[11]

This work describes the synthesis of several *cis*-(pip)-(L)Cr(CO)$_4$ complexes (L = phosphite, phosphine), the thermal and photochemical synthesis of a number of (L′)(L)Cr(CO)$_4$ reaction products (L = P(O-*i*-Pr)$_3$) from them (eq 1), and the thermal kinetics studies of this lig-

$$\textit{cis}\text{-(pip)(L)Cr(CO)}_4 + \text{L}' \rightarrow \textit{cis,trans}\text{-(L}')\text{(L)Cr(CO)}_4 + \text{pip} \quad (1)$$

and-exchange reaction. These investigations demonstrate conclusively that ligand exchange takes place exclusively through Cr–pip bond breaking and thus that *cis*-(pip)-(L)Cr(CO)$_4$ complexes are suitable precursors to the synthesis of five-coordinate [(L)Cr(CO)$_4$] intermediates.

Experimental Section

General Methods. Infrared spectra for reactants and products were obtained by employing a Nicolet 20SXB FT-IR spectrometer. Elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, IN.

Materials and Syntheses. Cr(CO)$_6$ (Pressure Chemical Co.) was used as obtained. Chlorobenzene (CB; Fisher) was fractionally distilled over P$_4$O$_{10}$ under nitrogen. Tetrahydrofuran (THF; Baker Analyzed Reagent) was fractionally distilled under nitrogen from lithium aluminum hydride. The ligands trimethyl phosphite, triethyl phosphite, triisopropyl phosphite, triphenyl phosphite, and tri-*n*-butylphosphine (Aldrich) were fractionally distilled (nitrogen bleed/0.2 Torr) over sodium. Triphenylphosphine (Fluka) was recrystallized from absolute ethanol and dried under vacuum. The "constrained phosphite" 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (CP) was prepared through the published procedure,[12] was twice sublimed under reduced pressure into a wide-mouthed condenser, and was then recrystallized under nitrogen from hot *n*-hexane. The "constrained phosphine" 3,5,8-triaza-1-phosphaadamantane (TPA) was synthesized and purified by the literature method.[13] Piperidine (Aldrich) was fractionally distilled from anhydrous KOH.

The complexes *cis*-(pip)(L)Cr(CO)$_4$ (L = P(OMe)$_3$, P(OEt)$_3$, P(O-*i*-Pr)$_3$, P(OPh)$_3$, CP, TPA) were prepared from Cr(CO)$_6$ via (L)Cr(CO)$_5$ by employing the following procedure, patterned after that of Schwenzer, Darensbourg, and Darensbourg[9] in their unsuccessful attempts to synthesize *cis*-(pip)(PPh$_3$)Cr(CO)$_4$. Chromium hexacarbonyl (2.0 g, 9 mmol) in 150 mL of dry THF was irradiated under nitrogen for 3 h at room temperature by employing a 450-W Hanovia medium-pressure mercury lamp in a quartz immersion reactor. The resulting yellow solution of (THF)Cr(CO)$_5$ was stirred with 9 mmol of L for 30 min, during which time the solution turned colorless. The solution was filtered over Celite to remove decomposition products, the THF was removed under vacuum, and unreacted Cr(CO)$_6$ was removed through vacuum sublimation (<1 Torr, 45 °C). The LCr(CO)$_5$ product was dissolved in 150 mL of dry THF, and the solution was irradiated under nitrogen as before for 30 min, after which the THF was removed under vacuum. The remaining oily residue was then taken up in 3 mL of cold (ca. 0 °C) CHCl$_3$, and 10 mL

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of cold methanol was added to this solution. The products, which precipitated upon overnight storage of the solution in a freezer, were collected by suction filtration under nitrogen. The yellow crystalline complexes were washed with cold hexanes and dried under vacuum. Yields were <40%. For L = PPh$_3$, a satisfactory analysis of the complex could not be obtained, but its carbonyl stretching spectrum (infrared) was recorded. Carbonyl stretching data are presented in Table I; elemental analyses for the complexes are given in Table II.

Products of thermal and photochemical reactions of *cis*-(pip)(P(O-*i*-Pr)$_3$)Cr(CO)$_4$ with L′, *cis*- and *trans*-(L′)(P(O-*i*-Pr)$_3$)Cr(CO)$_4$ (L′ = P(OMe)$_3$, P(OEt)$_3$, P(OPh)$_3$, CP, PTA; eq 1), none of which had previously been synthesized, together with *trans*-(P(O-*i*-Pr)$_3$)$_2$Cr(CO)$_4$,[14] were prepared to ascertain whether or not P(O-*i*-Pr)$_3$ was displaced together with pip or if P(O-*i*-Pr)$_3$ and L′ labilized one another in the (L′)(L)Cr(CO)$_4$ reaction products. These results, together with kinetics data (vide infra), provided no evidence that *cis*-(pip)(L)Cr(CO)$_4$ reacts with L′ via any initial step other than Cr–pip bond breaking. Thermal and photochemical synthesis of (L′)(L)Cr(CO)$_4$ products were carried out as follows:

Thermal Syntheses. *cis*-(pip)(P(O-*i*-Pr)$_3$)Cr(CO)$_4$ (0.5 g, 1.1 mmol) and 10 mmol of L′ (P(OMe)$_3$, P(OEt)$_3$, P(O-*i*-Pr)$_3$, P(OPh)$_3$, CP, TPA) were allowed to react in chlorobenzene (25 mL) at 40 °C for 12 h (overnight). Solutions were colorless at the end of this time. The solvent was removed under vacuum, and the reaction products precipitated upon addition of 20 mL of cold (0 °C) *n*-hexane to the residue. The products were collected by suction filtration and were recrystallized from chloroform/methanol solutions (1:4).

Photochemical Syntheses. Solutions of *cis*-(pip)(L)Cr(CO)$_4$ (0.2 g, 0.4 mmol; L = P(O-*i*-Pr)$_3$) in 150 mL of THF were irradiated for 15 min at room temperature. The resulting yellow solutions of *cis*-(THF)(L)Cr(CO)$_4$ were stirred with 2-fold excesses of L′ for 30 min, during which time the solutions turned almost colorless. The solutions were filtered over Celite, and the solvent was removed under reduced pressure. After addition of 15 mL of cold (0 °C) hexanes, the products were collected by suction filtration and recrystallized from chloroform/methanol (1:4). Infrared spectra of the products are presented in Table I, while elemental analyses are given in Table II.

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

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

For faster reactions, rates were monitored by removing aliquots of the reaction solution from a constant-temperature bath[14] (Haake Model ED) that maintained the temperature to ±0.05 °C and recording the absorbance of the reaction solution at 430 nm (Beckman DU-2 or Perkin Elmer 124 UV–visible spectrophotometer), monitoring the disappearance of the subtrate. At this wavelength the reaction products did not absorb, and the absorbance of a ligand–solvent blank could be taken as 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 slower reactions, 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 supplementary material Tables I and II. Limits of error, given in parentheses as the uncertainties of the last digit(s) of the experimental values, are one standard deviation.

Results and Discussion

Complexes. While most *cis*-(pip)(L)M(CO)$_4$ complexes (M = Mo, W, and the one Cr complex, where L = P(OMe)$_3$) hitherto reported were synthesized through thermal reactions of *cis*-(pip)$_2$M(CO)$_4$ with various L ligands under relatively mild conditions,[6,10,11] this method for the synthesis of *cis*-(pip)(L)Cr(CO)$_4$ complexes was found not to be satisfactory, since in most cases the reactions proceed with the displacement of the second pip molecule to afford (L)$_2$Cr(CO)$_4$ products. To minimize this second thermal step, *cis*-(pip)(L)Cr(CO)$_4$ complexes were synthesized photochemically, stepwise, via (L)Cr(CO)$_5$. It now is evident from the kinetics studies to be reported below that this synthetic approach is required for all but the least sterically demanding phosphites, those in which intramolecular hydrogen bonding between pip and the phosphite oxygen can decrease sufficiently the labilities of the *cis*-(pip)(L)Cr(CO)$_4$ complexes toward further reaction with L. In view of the much greater lability of such complexes in which L is a phosphine, it is doubtful that such complexes containing bulky phosphines can be prepared through either method.

Carbonyl stretching spectra and, in several cases, chemical analyses of the products of the reactions of *cis*-(pip)(L)Cr(CO)$_4$ (L = P(O-*i*-Pr)$_3$ and L′ = P(OMe)$_3$, P(OEt)$_3$, P(O-*i*-Pr)$_3$, P(OPh)$_3$, CP, PPh$_3$, P(*n*-Bu)$_3$, and TPA in CB) under conditions approximating those employed in the thermal kinetics studies showed them to be the mixed (L′)(L)Cr(CO)$_4$ products. Thus, pip and pip alone is displaced by L′ during these ligand-exchange processes. The reactions thus obey the stoichiometry shown in eq 2.

An examination of the carbonyl stretching spectra for these products indicated that where L′ is a phosphite (and, thus, where both L and L′ are phosphites), the *trans*-(L′)(L)Cr(CO)$_4$ products are obtained in overwhelmingly predominant concentration. However, where L′ is PPh$_3$ and P(*n*-Bu)$_3$, the reactions afford a mixture of cis and trans isomers and for L′ = TPA only the cis isomer is observed. These observations cannot be related to the steric bulk of L′; cone angles[15] for the phosphines employed are 145, 132, and 102°, respectively, while those for the phosphites are 101 (CP), 107 (P(OMe)$_3$), 109 (P(OEt)$_3$), 130 (P(O-*i*-Pr)$_3$), and 128° (P(OPh)$_3$). The greater stabilities of the *cis*-(L′)(L)Cr(CO)$_4$ isomers, where L′ is a phosphine, are most reasonably attributable to intramolecular hydrogen bonding, expected to be extremely weak, between the phosphine and triisopropyl phosphite (L), respectively. This bonding would be analogous to the intramolecular hydrogen bonding observed in *cis*-(pip)(L)M(CO)$_4$ complexes;[11,16] in *cis*-(L′)(L)Cr(CO)$_4$ species it would involve interaction between a carbon-bound hydrogen on the phosphine and the phosphite oxygen (P–C–H··O–P).

The isomerization of *cis*-(L)(L′)Cr(CO)$_4$ formed initially via thermal dissociation of pip from *cis*-(pip)(L)Cr(CO)$_4$ occurs, in all likelihood, via a nondissociative scrambling process. This conclusion is strongly supported by the observation that the thermal reactions of *cis*-(pip)(L)Cr(CO)$_4$ with L′ afford only (L′)(L)Cr(CO)$_4$ products; i.e., no Cr–L or Cr–L′ bond breaking is observed to take place. This is consistent with results previously reported for analogous complexes of Mo and W;[17] isomerization is likely to involve a "Bailar twist".[18,19] Further, no stereochemical rearrangement in the solvated intermediates produced via Cr–pip bond breaking takes place on the time scale of the

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Table III. Rate Constants and Activation Parameters for Ligand-Exchange Reactions of *cis*-(pip)(L)Cr(CO)$_4$ Complexes with Triisopropyl Phosphite in Chlorobenzene

L′ (θ, deg)[a]	T, °C	10^5K_1, s^{-1}	k_2/k_{-1}	$\Delta H_1^\ddagger$, kcal/mol	$\Delta S_1^\ddagger$, cal/(deg mol)
CP (101)	31.1	0.378 (2)	0.90 (5)	29.8 (2)	16.2 (8)
	39.9	1.511 (9)			
	51.3	8.70 (3)			
TPA (102)	22.6	15.5 (4)		25.0 (2)	9.3 (5)
	31.1	51.7 (3)	0.99 (3)		
	37.2	121 (6)			
P(OMe)$_3$ (107)	31.1	1.68 (3)	0.76 (2)	29.2 (2)	17.0 (9)
	37.2	4.6 (2)			
	49.1	26.8 (3)			
P(OEt)$_3$ (109)	31.1	2.18 (2)	0.57 (1)	30.0 (2)	19.9 (7)
	40.6	10.35 (5)			
	51.3	50.9 (2)			
P(O-*i*-Pr)$_3$ (130)	31.1	5.65 (3)	0.538 (6)	29.4 (4)	20 (1)
	40.0	24.3 (2)			
	51.3	125 (9)			
P(OPh)$_3$ (128)	31.1	6.05 (1)	0.89 (1)	29.4 (2)	20.0 (6)
	37.2	16.5 (3)			
	49.1	98 (2)			

[a] Cone angle.[15]

interaction of L′ with these species.[20]

Thermal Kinetics Studies. Reactions of *cis*-(pip)(L)Cr(CO)$_4$ with both pip and L′ under pseudo-first-order reaction conditions in CB solution employing either conventional sampling techniques or sealed cells, monitoring the disappearance of *cis*-(pip)(L)Cr(CO)$_4$ (1-R), obeyed the rate laws (3) and (4). This rate behavior is consistent with

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

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

a mechanism (Scheme I) involving initial dissociation of pip and rapid competitive reaction of the resulting five-coordinate intermediate [(L)Cr(CO)$_4$] (1-I$_1$) with CB, pip, and L′; the latter pathway affords the kinetically inert *cis*-(L′)(L)Cr(CO)$_4$ product (1-P), which undergoes subsequent isomerization. Here it is assumed, as is true for the analogous W complexes,[6] that the mechanism for displacement of CB from *cis*-[(CB)(L)Cr(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 $k' = k_2/k_{-1}$ (eq 4), 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', are k_1, the rate constants for unimolecular dissociation of pip from 1-R. These are expected to be independent of the identity of L′, as is shown to be the case in Figure 1, which illustrates plots of $1/k_{\text{obsd}}$ vs [pip]/[L′] for the reaction of *cis*-(pip)(L)Cr(CO)$_4$ (L = P(O-*i*-Pr)$_3$) for three different L′.

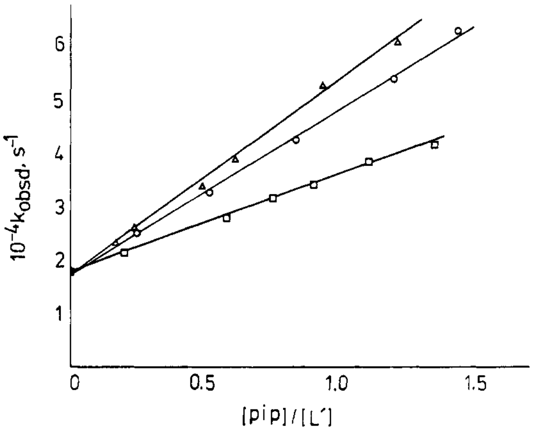

Figure 1. Plots of $1/k_{\text{obsd}}$ vs [pip]/[L′] for the reaction of *cis*-(pip)(P(O-*i*-Pr)$_3$)Cr(CO)$_4$ with L′ = PPh$_3$ (△), P(OPh)$_3$ (○), and P(*n*-Bu)$_3$ (□) in chlorobenzene at 31.1 °C.

Reactions of *cis*-(pip)(L)Cr(CO)$_4$ with P(O-*i*-Pr)$_3$. Table III presents values of k/k' ($=k_1$) and of k' ($=k_2/k_{-1}$) for six different L (L′ = P(O-*i*-Pr)$_3$) in CB at several temperatures. Values of k_1 given in Table III show that where L is a phosphite there is a moderate increase in the rates of pip dissociation with the increasing steric bulk of L; from data taken at 31.1 °C, relative rates increase with the Tolman cone angle of L (in parentheses) in the order CP, 1 (101°) < P(OMe)$_3$, 4.4 (107°) < P(OEt)$_3$, 5.8 (109°) < P(O-*i*-Pr)$_3$, 14.9 (130°) < P(OPh)$_3$, 16.0 (128°). However, the relative rate of pip displacement from *cis*-(pip)(TPA)Cr(CO)$_4$ (TPA has a cone angle of 102°)[21] is 137, far out of line with the other values. This increased rate can be attributed to a lack of intramolecular hydrogen bonding in this complex as compared to *cis*-(pip)(CP)Cr(CO)$_4$, where such bonding is observed;[9] this hydrogen bonding, in this instance between a pip hydrogen and CP oxygen (N–H··O–P), greatly inhibits the ability of pip to dissociate.

The extent of this inhibition is further indicated by the activation enthalpies for pip dissociation from the six *cis*-(pip)(L)Cr(CO)$_4$ complexes (Table III). Where the L ligands are phosphites, enthalpies of activation are all within the range 29.2 (2)–30.0 (2) kcal/mol, while that for *cis*-(pip)(TPA)Cr(CO)$_4$, where this type of hydrogen bonding is not possible, is 25.0 (2) kcal/mol. It is not unreasonable to take the difference between these values, ca. 4–5 kcal/mol, as an approximation of the strengths of the –N–H··O–P– hydrogen bonds in the phosphite complexes.[22] This is within the normal range of strengths of weak hydrogen bonds.[23]

Entropies of activation for dissociation of pip from the five phosphite complexes vs *cis*-(pip)(TPA)Cr(CO)$_4$ (Table III) also are consistent with the existence of intramolecular –N–H··O–P– hydrogen bonding in the former but not in the latter. For the five phosphite-containing complexes,

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(22) This enthalpic difference is not noted for ligand-substitution reactions for the analogous W complexes.[6]

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Table IV. Rate Constants for Ligand-Exchange Reactions of *cis*-(pip)(P(O-*i*-Pr)$_3$)Cr(CO)$_4$ with Phosphines and Phosphites (=L′) at 31.1 °C in Chlorobenzene Solution

L′	10^5k_1, s^{-1}	k_2/k_{-1}	L′	10^5k_1, s^{-1}	k_2/k_{-1}
CP	5.5 (2)	0.85 (1)	P(OPh)$_3$	5.81 (1)	0.57 (1)
P(OMe)$_3$	5.82 (5)	0.87 (3)	P(*n*-Bu)$_3$	5.69 (5)	0.94 (3)
P(OEt)$_3$	5.74 (3)	0.79 (3)	PPh$_3$	5.78 (6)	0.48 (2)
P(O-*i*-Pr)$_3$	5.61 (1)	0.538 (6)			

values of ΔS^* range from 16.1 (8) to 20 (1) cal/(deg mol), while, for *cis*-(pip)(TPA)Cr(CO)$_4$, it is 9.3 (5) cal/(deg mol). The more positive values observed for the five phosphite-containing complexes may be attributed to the requirement of breaking the hydrogen bond as well as the Cr–pip bond to attain the transition state.

The competition ratios of the rate constants for reactions of [(L)Cr(CO)$_4$] with P(O-*i*-Pr)$_3$ and those for recombination of the intermediate with pip, k_2/k_{-1}, are very close to 1 and vary only some 1.8-fold (0.538 (6)–0.99 (3)) in comparison with the 137-fold variation in k_1 as a function of coordinated L. In particular, in contrast to the great difference observed between the rate of Cr–pip bond dissociation in *cis*-(pip)(CP)Cr(CO)$_4$ and its TPA analogue, values for the competition ratios, k_2/k_{-1}, for these two complexes are very similar, 0.90 (5) and 0.99 (3). These observations support little pip–Cr or (*i*-PrO)$_3$P–Cr bonding, or pip–P(O-*i*-Pr)$_3$ hydrogen bonding, in the transition states leading to formation of *cis*-(pip)(L)Cr(CO)$_4$ or *cis*-(L′)(L)Cr(CO)$_4$. These observations, together with Hammond's postulate,[24] suggest that the transition state is very similar in nature to an (idealized) square-pyramidal [(L)Cr(CO)$_4$] intermediate in which the vacant coordination state is axial and L is equatorial. They also are inconsistent with a suggestion that significant hydrogen bonding in the transition state might persist where L is a phosphite,[16] since labilization of pip by phosphine oxides in (pip)M(CO)$_5$ complexes also has been observed to be promoted by *inter*molecular –P=O··H–N– hydrogen bonding.[25]

These results are also quite consistent with the very rapid combination of [Cr(CO)$_5$] with various solvents, which also suggests a low barrier to activation along the reaction coordinate leading to formation of (solvent)Cr(CO)$_5$ molecules.[3] Trends in these k_2/k_{-1} values support both steric and electronic factors to exert the small influences that are observed of the nature of L (and pip) on rates of recombination with [(L)Cr(CO)$_4$]. If, as the results suggest, little bond making takes place in attaining the transition state, activation enthalpies (ΔH_1^*) for dissociation of pip from various *cis*-(pip)(L)Cr(CO)$_5$ complexes should closely approximate and represent the upper limit for the pip–Cr bond strength in *cis*-(pip)(TPA)Cr(CO)$_4$, in which there is no L–pip hydrogen bonding. This value, 25.0 (2) kcal/mol, compares favorably with the activation enthalpy for dissociation of pip from (pip)Cr(CO)$_5$ in hexane solvent, 25.7 (6) kcal/mol.[26]

Reactions of *cis*-(pip)(P(O-*i*-Pr)$_3$)Cr(CO)$_4$ with Various L′. Competition ratios, k_2/k_{-1}, of the rate constants for combination of [(P(O-*i*-Pr)$_3$)Cr(CO)$_4$] with seven phosphines and phosphites (L′), CP, P(OMe)$_3$, P(OEt)$_3$, P(O-*i*-Pr)$_3$, P(OPh)$_3$, P(*n*-Bu)$_3$, and PPh$_3$, vs the rate constants for combination of this intermediate with pip were obtained from data at 31.1 °C (Table IV). Again, only small influences (about a 2-fold variation in k_2/k_{-1} over the series of L′, including pip) were observed, consistent with little discriminating ability of the square-pyramidal [(P(O-*i*-Pr)$_3$)Cr(CO)$_4$] intermediate among various L′ and pip. Variations in k_2/k_{-1} again would appear to be attributable both to steric and electronic properties of L′; the same conclusions with regard to the absence of significant bonding in the transition states can be drawn from these data as were inferred from competition ratios for reactions of various *cis*-(pip)(L)Cr(CO)$_4$ complexes with P(O-*i*-Pr)$_3$. In the comparison of these data with those obtained for the analogous *cis*-(pip)(PPh$_3$)Mo(CO)$_4$[5] and *cis*-(pip)(L)W(CO)$_4$[6] complexes, the smaller atomic size of Cr vs Mo and W (the M–C bond lengths in the hexacarbonyls are 1.916 (3),[27] 2.06 (2),[28] and 2.06 (4)[29] Å, respectively)[25] would appear to exert little influence on the selectivity of the five-coordinate intermediate among the nucleophiles employed.[30]

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Supplementary Material Available: Tables of pseudo-first-order rate constants for reactions of *cis*-(pip)(L)Cr(CO)$_4$ complexes with pip and P(O-*i*-Pr)$_3$ in CB at various temperatures and pseudo-first-order rate constants for reactions of *cis*-(pip)(P(O-*i*-Pr)$_3$)Cr(CO)$_4$ with pip and L′ in CB at 31.1 °C (5 pages). Ordering information is given on any current masthead page.

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[30] However, there is a wider range of selectivity exhibited by [Cr(CO)$_5$] when nucleophiles such as 1-hexene and acetonitrile are included.[4e] This selectivity may result in part from the displacement of the solvent from (solvent)Cr(CO)$_5$, rather than from attack of nucleophiles at [Cr(CO)$_5$].[4f,g]