Figure 2. Plot of log $(k_{NiA}^{-H_2O}/\text{no. of } H_2O \text{ in NiA}) - \log (k_{Ni}^{-H_2O}/6)$ vs. effective $E(A)$.

nopolyacetate $= E(NH_3) + (E(OAc^-))n_O + (\Delta E_{NO} + \Delta E_{ON})n_O; = 1.84 + 0.02n_O$; $E(A)$ for ethylenediaminepolyacetate $= 2E(NH_3) + 2\Delta E_{NN} + (E(OAc^-))n_O + (\Delta E_{NO} + \Delta E_{ON})n_O = 2.58 + 0.02n_O$. Thus calculated effective $E(A)$ values are listed in Table I.

The plot of log $(k_{NiA}^{-H_2O}/\text{no. of } H_2O \text{ in NiA}) - \log (k_{Ni}^{-H_2O}/6)$ vs. effecitve $E(A)$ is given in Figure 2 together with the data for monodentate ligands. Figure 2 indicates that, taking into account the difference in experimental conditions to determine the value of k_{NiA}, the bound-ligand effect of NiA on the water-exchange rate is reasonably well described by eq 1.

The bound-ligand effect of the 1:2 complex NiA_2 on the water-exchange rate can also be estimated by the difference between log $(k_{NiA_2}^{-H_2O}/2)$ and log $(k_{Ni}^{-H_2O}/6)$. The values of $R(A_2)$ thus calculated are 0.90, 1.48, and 1.24 for oxalate, glycinate, and ethylenediamine complexes, respectively. The values of $R(A_2)$ for the latter two complexes are close to the corresponding values of $2R(A)$. The two water molecules in these two bis complexes are thought to be in a cis configuration. Previously the two water molecules on $Ni(en)_2^{2+}$ have been assigned a cis configuration in aqueous solution.[23] The value of $R(A_2)$ for bis(oxalato)nickelate is definitely lower than $2R(A)$. This may suggest a possibility of the trans isomer being involved in the reaction of this complex.

(23) Melvin, W. S.; Rablen, D. P.; Gordon, G. *Inorg. Chem.* **1972**, *11*, 488–93.

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Texas A&M University, College Station, Texas 77843

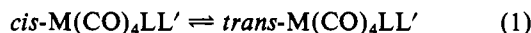# Stereochemical Nonrigidity in Six-Coordinate Group 6B Metal Carbonyl Derivatives via a Nondissociative Pathway

DONALD J. DARENSBOURG* and ROBERT L. GRAY

The *cis*-$M(CO)_4(^{13}CO)PR_3 \rightleftharpoons$ *trans*-$M(CO)_4(^{13}CO)PR_3$ (M = Cr, R = Et; M = W, R = OMe, Me, Et, *i*-Pr) isomerization reactions have been studied kinetically in cyclohexane-d_{12} by ^{13}C NMR spectroscopy. These isomerization reactions were shown to proceed via an *intramolecular* process, based on the lack of ^{13}CO incorporation into the $M(CO)_5PR_3$ derivatives or formation of $M(CO)_5(^{13}CO)$ under reaction conditions of ligand rearrangement. The cis $\rightleftharpoons$ trans CO scrambling process in the tungsten pentacarbonyl derivatives displays a dependence on the steric nature of the phosphorus ligand, with the rate decreasing $PMe_3 > PEt_3 > P$-*i*-Pr_3. The origin of this steric effect is seen in the activation parameters (ΔH = 9.2 kcal mol^{-1} and ΔS = −54.9 eu), which are indicative of gross reorganization in the transition state with little metal–ligand bond weakening. On the other hand, activation parameters for carbon monoxide ligand isomerization in $Cr(CO)_4(^{13}CO)PEt_3$ (ΔH = 26.6 kcal mol^{-1} and ΔS = 1.80 eu) are consistent with considerable metal–ligand bond breaking in the transition state with little reorganization taking place.

Introduction

There is increasing awareness that neutral, six-coordinate molecules of the general formula $M(CO)_4LL'$ can undergo ligand rearrangements in their *intact* state (e.g., eq 1). Investigations where definitive intramolecular isomerization

$$cis\text{-}M(CO)_4LL' \rightleftharpoons trans\text{-}M(CO)_4LL' \qquad (1)$$

mechanisms have been established in complexes containing monoligating groups include (a) $M(CO)_4(ER_3)_2$ (M = Re, Ru, Os; E = Si, Ge, Sn, Pb; R = organic group, Cl),[1,2] Cr-$(CO)_4[C(OMe)Me]PR_3$ (R = Et, Cy),[3] $Mo(CO)_4[PR_3]_2$ (R = Me, Et, *n*-Bu),[4-6] and $PhMn(CO)_4P(OPh)_3$.[7] Presumably, the pathway for these nondissociative, intramolecular rearrangement processes proceeds through either a trigonal-prismatic[8-13] or bicapped-tetrahedron[14] intermediate or transition state.

In the instances cited above there is a thermodynamic preference for either the cis or trans isomeric form depending

(1) Vancea, L.; Pomeroy, R. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1976**, *98*, 1407.
(2) Pomeroy, R. K.; Vancea, L.; Calhoun, H. P.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1508 and references therein.
(3) Fischer, H.; Fischer, E. O.; Werner, H. *J. Organomet. Chem.* **1974**, *73*, 331.

(4) Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680.
(5) Darensbourg, D. J. *Inorg. Chem.* **1979**, *18*, 14.
(6) Cotton, F. A.; Darensbourg, D. J.; Klein, S.; Kolthammer, B. W. S. *Inorg. Chem.* **1982**, *21*, 2661.
(7) Stewart, R. P., Jr. *Inorg. Chem.* **1979**, *18*, 2083.
(8) Bailar, J. C., Jr. *J. Inorg. Nucl. Chem.* **1958**, *8*, 165.
(9) Ray, P.; Dutt, N. K. *J. Indian Chem. Soc.* **1943**, *20*, 81.
(10) Springer, C. S., Jr.; Sievers, R. E. *Inorg. Chem.* **1967**, *6*, 852.
(11) Majunke, W.; Leibfritz, D.; Mack, T.; Tom Dieck, H. *Chem. Ber.* **1975**, *108*, 3025.
(12) Serpone, N.; Bickley, D. G. *Prog. Inorg. Chem.* **1972**, *17*, 391.
(13) Vanquickenborne, L. G.; Pierloot, K. *Inorg. Chem.* **1981**, *20*, 3673.
(14) Hoffmann, R.; Howell, J. M.; Rossi, A. R. *J. Am. Chem. Soc.* **1976**, *98*, 2484.

on both the electronic and steric properties of L and L'. For example, in $Mo(CO)_4[PR_3]_2$ (R = Me, Et, *n*-Bu) derivatives the equilibrium constant describing the cis $\rightleftharpoons$ trans isomerization reaction is less than 1 for the smaller PMe_3 ligand and greater than 1 for the larger PEt_3 and P-*n*-Bu_3 ligands.[6] Hence, electronic factors favor the cis derivative (minimizes mutually trans CO ligands), whereas steric factors favor the *trans* derivative. Consistent with this is the fact that a larger amount of distortion from octahedral shape, as defined by the P–Mo–P angle, is displayed in the solid-state structures of *cis*-$Mo(CO)_4[PR_3]_2$ (R = Et, *n*-Bu) derivatives as compared with that of the *cis*-$Mo(CO)_4[PMe_3]_2$ species.[6]

Dombek and Angelici[15] have examined a system in both the solution and the gas phase where there is no thermodynamic driving force for isomerization, i.e. *trans*-$W(CO)_4(^{13}CO)CS$ $\rightleftharpoons$ *cis*-$W(CO)_4(^{13}CO)CS$. Activation parameters for this ligand rearrangement process were found to be remarkably similar to those for CO ligand dissociation, prompting these researchers to suggest considerable lengthening of a W–CO bond in the activated complex during ligand isomerization. A pathway involving rearrangement of a pentacoordinate intermediate and recombination with CO within a "solvent cage" was ruled out on the basis of the similarity in rate parameters in solution and in the gas phase.

More recently we have shown that phosphine and phosphite derivatives of Cr and W pentacarbonyls undergo intramolecular CO rearrangements.[16,17] This is a nontrivial extension of Dombek and Angelici's results in that it illustrates that intramolecular isomerization in $M(CO)_5L$ derivatives is not limited to those cases where L is very similar to CO (i.e., CS) but is a more general process that readily occurs in instances where L is electronically and sterically quite different from CO. The rate of CO scrambling was found to be metal dependent with the order for the group 6B metals as follows: Cr > W > Mo. This order is contrary to what might be anticipated for a trigonal-twist mechanism (eq 2) on the basis of atomic size of the metal center alone.

$$\qquad (2)$$
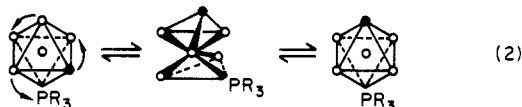
To better understand the nature of these reactions, we have evaluated the activation parameters for CO mobility in $M(CO)_4(^{13}CO)PEt_3$ derivatives of Cr and W and have examined the steric and electronic effects of the phosphorus ligand on the rate of CO rearrangements in a variety of $W(CO)_5L$ species.

Experimental Section

Materials. Cyclohexane-d_{12} (99.5%) was obtained from Chemalog Chemical Dynamics Corp. (South Plainfield, NJ). Phosphine and phosphite ligands were purchased from Strem Chemicals. ^{13}CO gas enriched to >90% was acquired from Prochem, BOC Ltd., London.

Preparation of PPN[LW(CO)₄Cl] (L = PMe₃, PEt₃, P-*i*-Pr₃, P(OMe)₃; PPN = Bis(triphenylphosphine)nitrogen(1+)). These complexes were prepared by following published literature procedures.[18] A mixture of 1.16 g of $W(CO)_6$ and 1.93 g of [PPN]Cl was stirred in 40 mL of DME at 85 °C for 3 h. The reaction mixture was filtered warm, and a slight excess of the ligand, L, was added to the solution. The solution was heated to 50 °C, and the conversion of $[W(CO)_5Cl^-]$ to the product, $[LW(CO)_4Cl^-]$, was monitored by infrared spectroscopy. Upon reaction completion, the solution was cooled to 0 °C and the product was precipitated with hexane. The yellow precipitate was washed several times with hexane and dried in vacuo.

(15) Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4110.
(16) Darensbourg, D. J.; Baldwin, B. J. *J. Am. Chem. Soc.* **1979**, *101*, 6447.
(17) Darensbourg, D. J.; Kudaroski, R.; Schenk, W. *Inorg. Chem.* **1982**, *21*, 2488.
(18) Schenk, W. *J. Organomet. Chem.* **1979**, *179*, 253.
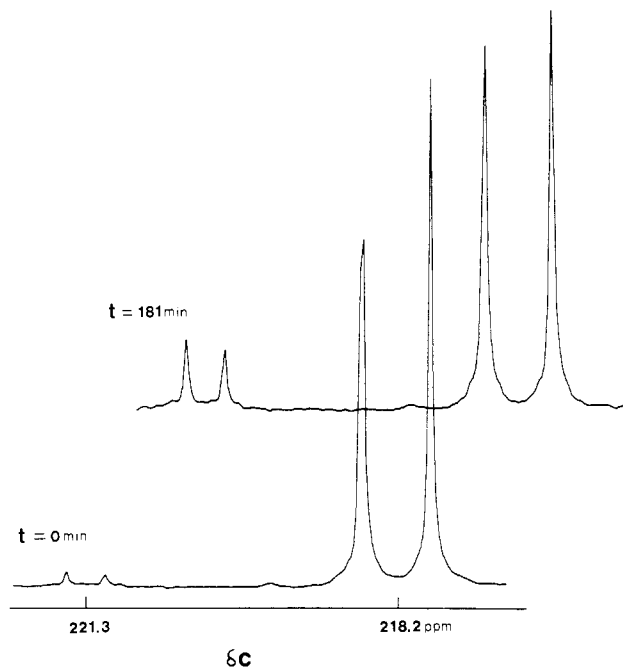(19) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

Figure 1. Carbon-13 NMR spectra of the carbonyl ligands in Cr-$(CO)_4(^{13}CO)PEt_3$ before and after the CO isomerization reaction at 65 °C in cyclohexane.

Preparation of *cis*-W(CO)₄(¹³CO)L (L = PMe₃, PEt₃, P-*i*-Pr₃, P(OMe)₃). Approximately 40 mL of MeOH was slowly added to a Schlenk flask containing 1.5 g of $PPN[LW(CO)_4Cl]$ under 1 atm of ^{13}CO. After the mixture was stirred overnight at room temperature, the solvent was removed under reduced pressure. The product was extracted into hexane and filtered through Celite. Upon removal of hexane under vacuum, a viscous pale yellow liquid remained. The product was left in vacuo overnight.

Preparation of *cis*-Cr(CO)₄(¹³CO)PEt₃. $Et_4N[PEt_3Cr(CO)_4Cl]$ (1.5 g) was cooled to –78 °C under 1 atm of ^{13}CO. Slowly, 40 mL of MeOH was added and the solution was allowed to warm to room temperature. After 8 h, the substitution was complete and the solvent was pumped off. The product was extracted from the residue with hexane. This solution was filtered and the hexane stripped off. The resulting yellow liquid was left under vacuum for 4 h.

Reaction of W(CO)₅L (L = PEt₃, P-*i*-Pr)₃ with ¹³CO. Approximately 1.5 g of $W(CO)_5L$ in 5 mL of cyclohexane was heated to 75 °C under 1 atm of ^{13}CO. After it was heated (25 h for PEt_3 and 7 days for P-*i*-Pr_3), the sample was cooled and examined for ^{13}CO incorporation by infrared spectroscopy.

Reaction of Cr(CO)₅PEt₃ with ¹³CO. This reaction was run with use of the same procedure as described for the tungsten analogue. The reaction temperature was 65 °C with a heating period of 1.5 h.

Kinetic Measurements. The cis $\rightleftharpoons$ trans isomerization reactions of $M(CO)_4(^{13}CO)L$ (M = Cr, W; L = PMe₃, PEt₃, P-*i*-Pr₃, P(OMe)₃) were carried out in sealed 10-mm NMR tubes in cyclohexane-d_{12} solvent. The isomerization was monitored by heating the samples in a constant-temperature bath and periodically recording the ^{13}C NMR spectra (on a Varian FT80 spectrometer) after quenching at –78 °C in dry ice–acetone. Quantitative data were obtained through the appearance of the signal due to the trans isomer. These data were corrected for instrument fluctuations by using a ratio of the trans isomer to the solvent: trans/cyclohexane-d_{12}. Rate constants were calculated by use of a linear least-squares computer program for the first-order rate plots of ln $(R_e - R_t)$ vs. time, where R_t is the trans/cyclohexane-d_{12} ratio at time t and R_e is the ratio at equilibrium.

Infrared Spectral Measurements. The infrared spectra were recorded in 1.0-mm matched NaCl sealed cells on a Perkin-Elmer 283B spectrophotometer equipped with an infrared data station and employing the PECDS software package provided by Perkin-Elmer. The spectra were calibrated against a water-vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1}.

Results and Discussion

The synthesis of preferentially cis ^{13}CO-labeled complexes of Cr and W pentacarbonyl phosphine and phosphite deriva-

Table I. Carbon-13 Chemical Shifts for the Carbonyl Ligands in $M(CO)_5L$ Derivatives[a]

M	L	$\sigma(C)$[b] cis	$\sigma(C)$[b] trans	J, Hz $W-C_c$	J, Hz $P-C_c$	J, Hz $P-C_t$
Cr	PEt_3	218.2	221.3		13.7	7.8
W	PMe_3	197.3	199.1	123.8	7.3	19.9
	PEt_3	197.6	198.6	124.4	7.2	19.6
	$P-i-Pr_3$	198.5	197.7	125.2	7.0	20.0
	$P(OMe)_3$	195.7	197.0	124.6	10.6	37.6

[a] Spectra were determined in cyclohexane-d_{12} at 20 MHz.
[b] Chemical shifts are expressed in ppm relative to $(CH_3)_4Si$, with positive $\sigma(C)$ values being at lower field than $(CH_3)_4Si$.

δC, 221.3 ppm

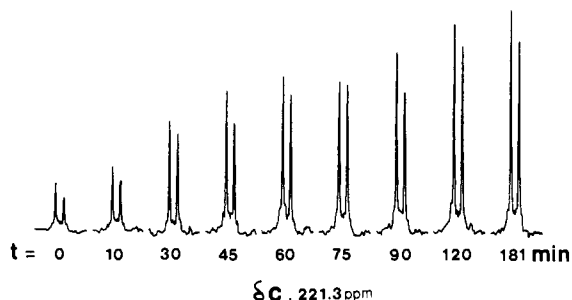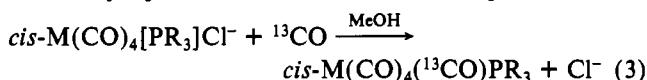**Figure 2.** Time-dependent carbon-13 NMR spectra of the trans-carbonyl ligand in $Cr(CO)_4(^{13}CO)PEt_3$ at 65 °C in cyclohexane.

tives was accomplished in the straightforward manner described by eq 3. This methanol-assisted displacement of a

$$cis-M(CO)_4[PR_3]Cl^- + {}^{13}CO \xrightarrow{MeOH}$$
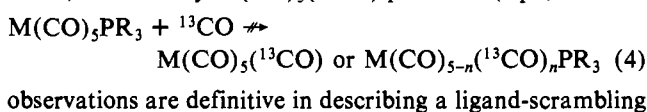$$cis-M(CO)_4(^{13}CO)PR_3 + Cl^- \quad (3)$$

coordinated halide procedure can be carried out at ambient temperature or below, hence affording no loss of stereoselectivity during the synthesis. The stereochemistry of the product was readily ascertained by ^{13}C NMR spectroscopy where only the cis carbonyl ligands displayed signal enhancement over that of the natural-abundance spectrum (Figure 1). Table I contains the carbon resonances for the $M(CO)_5L$ derivatives utilized in these studies.

Rate constants for $cis-M(CO)_4(^{13}CO)PR_3 \rightleftharpoons trans-M-(CO)_4(^{13}CO)PR_3$ equilibration starting from pure $cis-M-(CO)_4(^{13}CO)PR_3$ were measured by monitoring the appearance of the carbon resonance of the trans carbonyl ligand. These data were corrected for instrument fluctuations by normalizing the trans CO carbon's peak height to a solvent peak of cyclohexane-d_{12}. A representative series of uncorrected data is depicted in Figure 2, showing an increase in the resonance signal for the trans CO ligand in $Cr(CO)_4(^{13}CO)PEt_3$ as a function of time, with a concomitant decrease in the resonance signal for the cis CO groups being observed. Equilibration is attained when the ratio of cis/trans carbonyl carbon signals is the same as that in the natural-abundance ^{13}C NMR spectrum (generally ~4-5).

Table II lists rate constants for intramolecular CO rearrangement in tungsten pentacarbonyl derivatives at 75 °C, whereas Table III contains rate data for this process in $M-(CO)_5PEt_3$ (M = Cr, W) as a function of temperature along with the derived activation parameters.

Control experiments were performed where the $M(CO)_5PR_3$ derivatives were subjected to the reaction conditions for isomerization under an atmosphere of ^{13}C-labeled carbon monoxide. No *intermolecular* carbon monoxide exchange was noted, nor was any $M(CO)_5(^{13}CO)$ produced (eq 4). These

$$M(CO)_5PR_3 + {}^{13}CO \nrightarrow$$
$$M(CO)_5(^{13}CO) \text{ or } M(CO)_{5-n}(^{13}CO)_nPR_3 \quad (4)$$

observations are definitive in describing a ligand-scrambling

Table II. Rate Constants for Intramolecular CO Rearrangement in $W(CO)_5L$ Derivatives[a]

L	cone angle,[b] deg	10^5k,[c] s^{-1}
$P(OMe)_3$	107	7.73 ± 0.70
PMe_3	118	9.03 ± 0.92
PEt_3	132	3.82 ± 0.14
$P-i-Pr_3$	160	0.38 ± 0.12

[a] For the reaction $cis-W(CO)_4(^{13}CO)L \rightleftharpoons trans-W(CO)_4(^{13}CO)L$ in cyclohexane at 75 °C. [b] Taken from ref 19. [c] Error limits for rate constants represent 90% confidence limits.

Table III. Temperature Dependence of Rate Constants for Intramolecular CO Rearrangement in $M(CO)_5PEt_3$ Derivatives[a]

M	temp, °C	10^5k, s^{-1}	M	temp, °C	10^5k, s^{-1}
Cr[b]	45	2.23 ± 0.51	W[c]	65	2.29 ± 0.52
	55	9.36 ± 0.99		75	3.82 ± 0.14
	65	28.7 ± 4.2		85	5.17 ± 1.52

[a] Reactions measured in cyclohexane solution. Error limits for rate constants represent 90% confidence limits. [b] $\Delta H^{\ddagger} = 26.6 \pm 4.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = 1.80 \pm 13.1$ eu. [c] $\Delta H^{\ddagger} = 9.2 \pm 3.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -54.9 \pm 11.4$ eu.

process involving no CO or PR_3 dissociation, or a fragmentation process where the departing ligand does not escape the "solvent cage" on the time scale of ligand rearrangement in the five-coordinate intermediate and ligand recombination. This latter process seems unlikely since efforts were made to minimize solvent participation in these reaction processes by employing the relatively inert cyclohexane solvent.[20]

The effect on the rate of intramolecular carbonyl ligand isomerization in $W(CO)_5L$ derivatives of varying the electronic nature of the phosphorus ligand while maintaining approximately constant size parameters was assessed by utilizing the $P(OMe)_3$ and PMe_3 complexes. Here the phosphorus ligands are electronically quite different (good π acceptor vs. good σ donor);[21,22] however, their cone angles differ by only 10°.[19] As noted in Table II, the rates of CO scrambling in these two derivatives are not significantly different. In contrast, the rate of isomerization was significantly retarded upon increasing the spatial requirements for the unique ligand. For the series of phosphorus ligands possessing quite similar electronic character (all good σ donors)[23,24] but widely differing cone angles (118 → 160°), the rate of intramolecular carbon monoxide ligand rearrangement varies $PMe_3 > PEt_3 > P-i-Pr_3$.

The origin of this steric effect is evident when one examines the activation parameters for this process, where $W(CO)_5PEt_3$ is taken as an unexceptional case (Table III). The free energy of activation (27.7 kcal mol^{-1})[25] is dominated by a large negative entropy of activation term with only a small enthalpy of activation component. This is indicative of gross reorganization in the transition state with little metal–ligand bond weakening, a process consistent with a twist mechanism as depicted in eq 2.

The consequence of changing the metal center from tungsten to chromium, while maintaining a constant ligand environment about the metal, is an enhanced rate of isomerization. As mentioned in the Introduction, this was qualitatively demon-

(20) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220.
(21) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315.
(22) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951.
(23) Slight differences in the donor properties of the trialkylphosphines are recognized, where an increase in donor character accompanies an increase in alkyl chain length; i.e. $PMe_3 < PEt_3 < P-i-Pr_3$. See, for example, ref 22 and 24 and references therein.
(24) Bursten, B. E.; Darensbourg, D. J.; Kellogg, G. E.; Lichtenberger, D. L. *Inorg. Chem.*, in press.
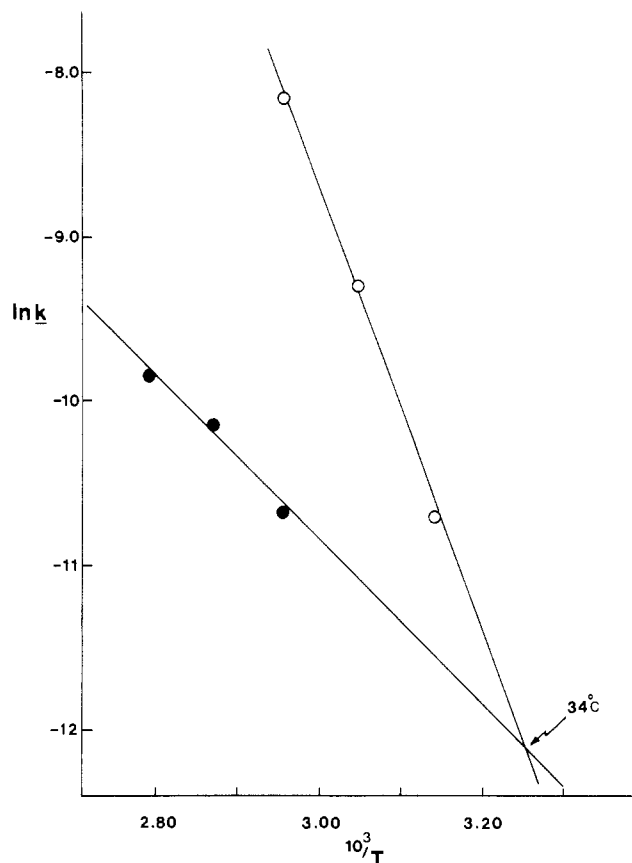(25) The free energy of activation was computed at 65 °C.

Figure 3. Arrhenius plots for the *cis*-M(CO)$_4$(^{13}CO)PEt$_3$ $\rightleftharpoons$ *trans*-M(CO)$_4$(^{13}CO)PEt$_3$ isomerization reaction in cyclohexane-d^{12}: (●) M = W; (○) M = Cr.

strated in our previous publication on this subject for trimethyl phosphite derivatives.[16] Quantitative rate data as a function of temperature for the intramolecular ligand isomerization of *cis*-Cr(CO)$_4$(^{13}CO)PEt$_3$ and *cis*-W(CO)$_4$(^{13}CO)PEt$_3$ are listed in Table III and are represented graphically in Figure 3. These data predict an isokinetic temperature of 34 °C. Hence at temperatures lower than 34 °C W(CO)$_5$PEt$_3$ would undergo CO ligand rearrangement at a rate faster than that of the corresponding chromium derivative.

In sharp contrast to its tungsten analogue the free energy of activation for intramolecular CO scrambling in Cr-(CO)$_5$PEt$_3$ (26.1 kcal mol^{-1})[25] is composed of a large enthalpy of activation with only a small entropy contribution. Hence in this instance there is considerable metal–ligand bond breaking in the transition state with little reorganization taking place. Consistent with this interpretation the intramolecular cis-^{13}CO $\rightleftharpoons$ trans-^{13}CO isomerization in Cr(CO)$_5$PPh$_3$, where steric effects are greater but the Cr–P bond is weaker, occurs more readily ($\sim$2.5 times faster at 40 °C) than in the Cr-

(CO)$_5$PEt$_3$ derivative.[17] Perhaps this isomerization process can be thought of as being akin to ligand scrambling in five-coordinate intermediates, where Cr(CO)$_5$PR$_3$ species containing a greatly elongated metal–ligand bond resemble a pseudopentacoordinate transient.

Summary

Two distinctly different *intimate* pathways for intramolecular carbon monoxide ligand rearrangements in M-(CO)$_5$PR$_3$ derivatives have been observed. These mechanisms were differentiated by means of their activation parameters as well as their response to alterations in the electronic and steric character of the phosphorus ligand. One route involves primarily a reorganization in the transition state with little metal–ligand bond breaking, probably a trigonal-twist process. The other pathway involves a great deal of metal–ligand bond dissociation, possibly via a pseudopentacoordinate transient. This latter process would be expected to prevail when metal–ligand bond dissociation is favored, by either a ground-state weakening of metal–ligand bonds or ligand site preference in the pseudopentacoordinate intermediate.[26]

This is illustrated in the two tungsten examples, W(CO)$_5$CS vs. W(CO)$_5$PR$_3$, where CS[27,28] is a much greater CO-labilizing ligand than is PR$_3$.[29,30] Although the free energies of activation for CO scrambling in these two derivatives are quite similar, the $\Delta H^{\ddagger}$ contributions differ widely, with the $\Delta H^{\ddagger}$ term being much larger in the W(CO)$_5$CS instance. Further depiction of this is seen in *cis*-Mo(CO)$_4$[PR$_3$]$_2$ $\rightleftharpoons$ *trans*-Mo-(CO)$_4$[PR$_3$]$_2$ isomerization reactions. For the R groups Me, Et, and *n*-Bu an intramolecular process is operative,[6] whereas for R = Ph large steric interactions between the two cis-PPh$_3$ units[31] lead to a Mo–P bond dissociative pathway.[32] However, these two processes occur with quite similar activation enthalpies (24.5 vs. 23.6 kcal mol^{-1}). Analogous arguments could be presented for the chromium species proceeding by a mechanism involving a greater degree of M–L bond breaking, for in these instances the metal–ligand bonds are generally weaker than those in corresponding tungsten derivatives.

(26) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366.
(27) Dombek, B. D.; Angelici, R. J. *Inorg. Chem.* **1976**, *15*, 1089.
(28) Pickering, R. A.; Angelici, R. J. *Inorg. Chem.* **1978**, *17*, 2035.
(29) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160.
(30) Darensbourg. D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113.
(31) Cotton, F. A.; Darensbourg, D. J.; Klein, S.; Kolthammer, B. W. S. *Inorg. Chem.* **1982**, *21*, 294.
(32) Darensbourg, D. J.; Graves, A. H. *Inorg. Chem.* **1979**, *18*, 1257.