A Trans Effect on the Rate of Ligand Dissociation from Octahedral Organometallic Complexes. Dissociation of L′ from $Cr(CO)_4LL'$ (L, L′ = PBu_3, PPh_3, $P(OPh)_3$, $P(OMe)_3$, $AsPh_3$)

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Rates of ligand displacement have been measured from the complexes *trans*-$Cr(CO)_4LL'$ (L, L′ = PBu_3, $P(OMe)_3$, $P(OPh)_3$, PPh_3, $AsPh_3$). The kinetic parameters indicate rate-determining dissociation of L′. For any given trans ligand the leaving-group order is the same, $PBu_3 < P(OMe)_3 < P(OPh)_3 < PPh_3 < AsPh_3$. The relative ground-state energies are shown to vary by 13 kcal/mol. For constant leaving groups the trans ligand is shown to have a remarkable effect on the rate. The trans effect order ($PPh_3 > PBu_3 > P(OPh)_3 \approx P(OMe)_3 > CO$) is the same for different leaving groups. This trans effect can span 4 orders of magnitude. The similarity of this trans effect order to the cis labilization order and to rate accelerations in metal carbonyl dimers and clusters is noted. The data strongly suggest that the trans effect arises by a stabilization of the 16-electron intermediate/transition state by strongly donating ligands.

The study of the effect of ligand environment at a metal center on the reactivity at the center has occupied a central place in inorganic chemistry.[1] The strength of the ligand field affects the reactivity of coordination complexes and the trans ligand has been shown to dramatically affect the rate of substitution in square-planar complexes.[1] In organometallic complexes ligand effects are quite significant; often subtle ligand changes affect reactivity of homogeneous catalysts. As an example, tris(triphenylphosphine)rhodium(I) chloride is an active catalyst for hydrogenation of alkenes, the triphenylarsine analogue is much less active and the triphenylphosphite analogue is inactive for the hydrogenation of alkenes.[2,3]

The large number of studies of CO dissociation from octahedral metal carbonyl complexes have been interpreted in terms of CO dissociation occurring cis to weaker π-bonding ligands and further that CO dissociated more rapidly than for stronger π-bonding ligands.[4-7] Thus CO dissociated cis to both Br and PPh_3 in $Mn(CO)_4PPh_3Br$ and at a more rapid rate than from $Mn(CO)_5Br$ and CO dissociated cis to PPh_3 from $Cr(CO)_5PPh_3$ at a more rapid rate than from $Cr(CO)_6$.[5,6] An extensive cis-labilization order was derived: $CO < P(OPh)_3 < PPh_3 < I^- < Br^- < Cl^-$. This cis labilization of CO dissociation was ascribed to a stabilization of the transition state by the presence of the poorer π-bonding ligand in the equatorial position of the square pyramid.[6,7]

A similar labilization of CO has been observed in further substitutions on $Mn_2(CO)_9L$ and $Ir_4(CO)_{11}L$.[8,9] The order of CO dissociation labilities is very similar to that seen for cis labilization: $CO < P(OPh)_3 < AsPh_3 < PPh_3 < PBu_3$. In the case of both $Mn_2(CO)_9L$ and $Ir_4(CO)_{11}L$ the second substitution occurs at a different metal.[8,9] An investigation of ligand dissociation from *cis*-$Mo(CO)_4LL'$ showed selective dissociation of the small ligand.[10] Thus $P(OMe)_3$ dissociated from *cis*-$Mo(CO)_4(P(OMe)_3)P\text{-}c\text{-}Hx_3$. This was interpreted as a steric acceleration of the $P(OMe)_3$ by the larger $P\text{-}c\text{-}Hx_3$.[10]

Table I. Infrared Carbonyl Stretching Frequencies for *trans*-$Cr(CO)_4LL'$ in Hexane

L	L′	ν(CO), cm^{-1}
PPh_3	PPh_3	1892 s[a]
$P(OPh)_3$	PPh_3	2023 w, 1958 w, 1914 vs
$P(OPh)_3$	$AsPh_3$	2020 w, 1958 w, 1914 vs
$P(OMe)_3$	PPh_3	2017 w, 1952 w, 1903 vs
$P(OMe)_3$	$AsPh_3$ [b]	2019 m, 1933 m, 1907 s, 1897 s
$P(OMe)_3$	$AsPh_3$	1903 s
$P(OMe)_3$	$P(OPh)_3$	2038 w, 1970 w, 1925 vs
PBu_3	PPh_3	2004 vw, 1931 vw, 1882 vs
PBu_3	$AsPh_3$	2003 vw, 1930 vw, 1882 vs
PBu_3	$P(OPh)_3$	2018 vw, 1943 vw, 1903 vs
PBu_3	$P(OMe)_3$	2012 w, 1940 w, 1892 s

[a] The solvent is chloroform. [b] Cis isomer.

We have investigated the reactions of *trans*-$Cr(CO)_4LL'$ (L, L′ = PBu_3, $P(OMe)_3$, $P(OPh)_3$, PPh_3, $AsPh_3$) to determine the effect of a trans orientation of ligands. The reaction we chose to investigate

$$trans\text{-}Cr(CO)_4LL' + CO \rightarrow Cr(CO)_5L + L'$$

minimizes the possibility of interference from non-first-order reactions and leads to a unique product in every case except one.

Experimental Section

All reactions were carried out under an argon atmosphere by using Schlenk techniques and an inert-atmosphere glovebox. Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer using 1.0-mm NaCl solution cells.

Materials. Tetrahydrofuran was refluxed over sodium/benzophenone until dry and then distilled under nitrogen prior to use. Methylene chloride and 1,2-dichloroethane were stirred over KOH then distilled from P_2O_5. Ethanol was degassed by using freeze–pump–thaw cycles and stored over molecular sieves. Decane was purified before use by stirring with H_2SO_4, washing with water, passing down an alumina column, and storing over sodium. Diglyme was purchased from Aldrich Chemical Co. and used as obtained. $Et_4NCl{\cdot}H_2O$ was obtained from Aldrich Chemical Co. and $Cr(CO)_6$, PBu_3, $P(OMe)_3$, $P(OPh)_3$, PPh_3, and $AsPh_3$ were purchased from Strem Chemicals, Inc.

Preparation of $Cr(CO)_4(PPh_3)_2$. This complex was prepared according to the procedure of Chatt et al.[11] The infrared spectrum

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in chloroform is described in Table I: yellow crystals; mp 253–254 °C. Anal. Calcd: Cr, 7.55; P, 9.00; C, 69.77; H, 4.39. Found: Cr, 7.22; P, 8.99; C, 69.55; H, 4.27.

Preparation of $Et_4N[Cr(CO)_5Cl]$. This complex was prepared by a modified version of the procedure described by Abel et al.[12] A mixture of 4.0 g of $Cr(CO)_6$ (1.8×10^{-2} mol) and 3.4 g of $Et_4NCl{\cdot}H_2O$ (1.8×10^{-2} mol) in diglyme/THF (20 mL/20 mL) was refluxed under argon for 4 h, giving an orange solution. The presence of THF is necessary to eliminate the problem of sublimation of unreacted $Cr(CO)_6$ and also minimizes decomposition of the product. After the mixture was allowed to cool to room temperature, removal of THF via vacuum followed by addition of 100 mL of pentane caused precipitation of the product $Et_4N[Cr(CO)_5Cl]$. This yellow solid was washed with pentane and then dried in vacuo overnight.

Preparation of $Et_4N[LCr(CO)_4Cl]$ (L = PBu_3, $P(OMe)_3$, $P(OPh)_3$). These previously unreported complexes were prepared by applying an adaptation of the procedure used by Schenk.[13,14] To a THF solution (20 mL) of 1.0 g of $Et_4N[Cr(CO)_5Cl]$ (2.8×10^{-3} mol) was added an excess of the ligand L, and this solution allowed to react at room temperature under argon for a specified time. The amounts of L used and reaction times are as follows: 2 mL of PBu_3 (8.0×10^{-3} mol), 10 min; 1 mL of $P(OMe)_3$ (8.5×10^{-3} mol), 30 min; 2 mL of $P(OPh)_3$ (7.6×10^{-3} mol), 90 min. For L = PBu_3 and $P(OMe)_3$, the reactions were accompanied by noticeable effervescence upon addition of the ligand to the solution. The reactions were stopped by the addition of 100 mL of pentane which caused the formation of a yellow precipitate. This solid, $Et_4N[LCr(CO)_4Cl]$, was washed several times with 20-mL portions of pentane to remove all traces of excess ligand and then dried in vacuo.

Preparation of $Cr(CO)_4LL'$ (L = PBu_3, $P(OMe)_3$, $P(OPh)_3$; L′ = PPh_3, $P(OPh)_3$, $AsPh_3$). Approximately 10 mL of deoxygenated ethanol was added to a Schlenk flask containing 1.0 g of $Et_4N[LCr(CO)_4Cl]$ ($\sim 1.9 \times 10^{-3}$ mol). To this mixture was added a 10 mL of CH_2Cl_2 solution containing 0.5 g of PPh_3 (1.9×10^{-3} mol), 0.5 mL of $P(OPh)_3$ (1.9×10^{-3} mol), or 0.6 g of $AsPh_3$ (1.9×10^{-3} mol). After being stirred for 1 h under argon at room temperature, the originally orange solution turned green-yellow. Solvent removal gave a green-yellow solid which was extracted with hexane. This hexane solution containing the $Cr(CO)_4LL'$ was filtered, and the solvent was pumped off giving a yellow or white solid which was recrystallized from CH_2Cl_2/EtOH in yields from 35 to 65%. The yellow or white crystals were washed with pentane and then dried in vacuo. The infrared spectra are described in Table I.

$Cr(CO)_4(P(OMe)_3)(PPh_3)$: yellow crystals; mp 132–133 °C. Anal. Calcd: Cr, 9.45; P, 11.26; C, 54.56; H, 4.40. Found: Cr, 9.49; P, 11.28; C, 54.54; H, 4.43.

$Cr(CO)_4(P(OMe)_3)(AsPh_3)$: yellow crystals; mp 119–120 °C. Anal. Calcd: Cr, 8.75; P, 5.21; As, 12.61; C, 50.52; H, 4.07. Found: Cr, 8.76; P, 5.59; As, 12.22; C, 50.38; H, 4.32.

$Cr(CO)_4(PBu_3)(PPh_3)$:[15] yellow crystals; mp 141–142 °C (decomposes without melting). Anal. Calcd: Cr, 8.27; P, 9.85; C, 64.96; H, 6.73. Found: Cr, 8.02; P, 9.91; C, 65.08; H, 6.91.

$Cr(CO)_4(PBu_3)(AsPh_3)$: yellow crystals; mp 129–130 °C. Anal. Calcd: Cr, 7.73; P, 4.61; As, 11.14; C, 60.72; H, 6.29. Found: Cr, 7.90; P, 4.91; As, 11.64; C, 60.65; H, 6.42.

$Cr(CO)_4(P(OPh)_3)(PPh_3)$: yellow crystals; mp 149–150 °C. Anal. Calcd: Cr, 7.06; P, 8.41; C, 65.22; H, 4.11. Found: Cr, 7.00; P, 8.31; C, 65.13; H, 4.20.

$Cr(CO)_4(P(OPh)_3)(AsPh_3)$: yellow crystals; mp 138–139 °C. Anal. Calcd: Cr, 6.66; P, 3.97; As, 9.60; C, 61.55; H, 3.87. Found: Cr, 6.43; P, 4.27; As, 9.60; C, 61.82; H, 4.09.

$Cr(CO)_4(P(OMe)_3)(P(OPh)_3)$: white crystals; mp 65–66 °C. Anal. Calcd: Cr, 8.69; P, 10.35; C, 50.18;, H, 4.04. Found: Cr, 8.64; P, 10.56; C, 50.40; H, 6.33.

$Cr(CO)_4(PBu_3)(P(OPh)_3)$:[15] white crystals; mp 47–48 °C. Anal. Calcd: Cr, 7.66; P, 9.42; C, 60.17; H, 6.24. Found: Cr, 7.48; P, 9.37; C, 60.40; H, 4.35.

Kinetics Measurements. The previously reported experimental procedure was followed except that the infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer.[16,17] Decane was the solvent for all of the reactions with the exception of $Cr(CO)_4(PPh_3)_2$ where 1,2-dichloroethane was used because of the low solubility of $Cr(CO)_4(PPh_3)_2$ in hydrocarbon solvents. All quantitative data were obtained from disappearance of the most intense infrared stretching frequency (E mode) of $Cr(CO)_4LL'$. Beer's law plots were constructed (hexane solution) for $Cr(CO)_4(PPh_3)_2$ (chloroform solution), $Cr(CO)_4(P(OMe)_3)(PPh_3)$, $Cr(CO)_4(P(OMe)_3)(AsPh_3)$, $Cr(CO)_4(PBu_3)(PPh_3)$, $Cr(CO)_4(PBu_3)(AsPh_3)$, $Cr(CO)_4(P(OPh)_3)(PPh_3)$, $Cr(CO)_4(P(OPh)_3)(AsPh_3)$, $Cr(CO)_4(P(OMe)_3)(P(OPh)_3)$, and $Cr(CO)_4(PBu_3)(P(OPh)_3)$ with extinction coefficients of 7.32×10^2, 1.30×10^3, 7.53×10^2, 1.96×10^3, 1.68×10^3, 9.74×10^2, 9.19×10^2, 1.10×10^3, and 1.49×10^3 M^{-1}, respectively.

Results

With one exception each of the products of the synthesis, $Cr(CO)_4LL'$, could be assigned to a trans orientation. This is shown by the similarity of the infrared spectra, each with one strong absorption, to those of the complexes where the crystal structures are known.[19] The frequency of the asymmetric stretch (E mode) for the mixed-ligand complexes in every case lies between the homobiligated complexes. The infrared spectrum of $Cr(CO)_4(P(OMe)_3)(AsPh_3)$, with four absorptions of comparable intensity, cannot be assigned to a trans geometry but is explained by a cis complex. The complex readily establishes a cis ↔ trans equilibrium in solution at 35 °C under a CO or argon atmosphere.

$$cis\text{-}Cr(CO)_4(P(OMe)_3)(AsPh_3) \leftrightarrow trans\text{-}Cr(CO)_4(P(OMe)_3)(AsPh_3)$$

The cis complex is somewhat more stable as shown by the equilibrium constant, $K_{eq} = 0.2$. Quantitative data on ligand dissociation from $Cr(CO)_4(P(OMe)_3)(AsPh_3)$ could not be obtained because of the presence of this equilibrium.

The products of the reactions were determined by comparison of the infrared spectra with those known for $Cr(CO)_5L$.[16] The specific reactions investigated are shown in Scheme I. There were no traces of other products or any decomposition.

Scheme I

$$trans\text{-}Cr(CO)_4(PBu_3)(P(OPh)_3) + CO \rightarrow Cr(CO)_5PBu_3 + P(OPh)_3$$

$$trans\text{-}Cr(CO)_4(P(OMe)_3)(P(OPh)_3) + CO \rightarrow Cr(CO)_5P(OMe)_3 + P(OPh)_3$$

$$trans\text{-}Cr(CO)_4(PPh_3)(P(OPh)_3) + CO \rightarrow Cr(CO)_5P(OPh)_3 + Cr(CO)_5PPh_3 + PPh_3 + P(OPh)_3$$

$$trans\text{-}Cr(CO)_4(PBu_3)(PPh_3) + CO \rightarrow Cr(CO)_5PBu_3 + PPh_3$$

$$trans\text{-}Cr(CO)_4(P(OMe)_3)(PPh_3) + CO \rightarrow Cr(CO)_5P(OMe)_3 + PPh_3$$

$$trans\text{-}Cr(CO)_4(PBu_3)(AsPh_3) + CO \rightarrow Cr(CO)_5PBu_3 + AsPh_3$$

$$trans\text{-}Cr(CO)_4(P(OPh)_3)(AsPh_3) + CO \rightarrow Cr(CO)_5P(OPh)_3 + AsPh_3$$

$$trans\text{-}Cr(CO)_4(PBu_3)(P(OMe)_3) + CO \rightarrow Cr(CO)_5PBu_3 + P(OMe)_3$$

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Table II. First-Order Rate Constants for Dissociation of L′ from *trans*-$Cr(CO)_4LL'$

L	L′	temp, °C	k,[b] s^{-1}
PPh_3	PPh_3	50	$(1.96 \pm 0.02) \times 10^{-4}$
		55	$(4.29 \pm 0.02) \times 10^{-4}$
		60	$(8.73 \pm 0.08) \times 10^{-4}$
$P(OPh)_3$	PPh_3[a]	80	$(3.61 \pm 0.13) \times 10^{-5}$
		90	$(1.63 \pm 0.01) \times 10^{-4}$
		100	$(6.23 \pm 0.06) \times 10^{-4}$
$P(OPh)_3$	$AsPh_3$	60	$(1.24 \pm 0.36) \times 10^{-4}$
		65	$(2.45 \pm 0.12) \times 10^{-4}$
		70	$(4.70 \pm 0.17) \times 10^{-4}$
$P(OMe)_3$	PPh_3	100	$(2.10 \pm 0.11) \times 10^{-4}$
		105	$(3.88 \pm 0.14) \times 10^{-4}$
		110	$(7.58 \pm 0.13) \times 10^{-4}$
$P(OMe)_3$	$P(OPh)_3$	110	$(1.44 \pm 0.07) \times 10^{-5}$
		120	$(5.41 \pm 0.08) \times 10^{-5}$
		130	$(1.81 \pm 0.02) \times 10^{-4}$
PBu_3	PPh_3	70	$(1.72 \pm 0.02) \times 10^{-4}$
		75	$(3.43 \pm 0.05) \times 10^{-4}$
		80	$(6.79 \pm 0.11) \times 10^{-4}$
PBu_3	$AsPh_3$	35	$(1.79 \pm 0.02) \times 10^{-4}$
		40	$(3.67 \pm 0.03) \times 10^{-4}$
		45	$(7.19 \pm 0.11) \times 10^{-4}$
PBu_3	$P(OPh)_3$	115	$(2.73 \pm 0.11) \times 10^{-4}$
		120	$(4.83 \pm 0.16) \times 10^{-4}$
		125	$(8.50 \pm 0.34) \times 10^{-4}$
PBu_3	$P(OMe)_3$	110	$(1.18 \pm 0.03) \times 10^{-5}$
		120	$(4.29 \pm 0.07) \times 10^{-5}$
		130	$(1.60 \pm 0.03) \times 10^{-4}$

[a] Both $P(OPh)_3$ and PPh_3 dissociate at equal rates.
[b] All values are the average of at least three experiments. The errors represent 95% confidence limits.

Table III. Activation Enthalpies and Entropies for Dissociation of L′ from *trans*-$Cr(CO)_4LL'$

L	L′	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
PPh_3	PPh_3	31.3 ± 1.2	21.2 ± 3.6
$P(OPh)_3$	PPh_3[a]	36.6 ± 1.3	24.4 ± 3.6
$P(OPh)_3$	$AsPh_3$	29.7 ± 0.3	12.5 ± 0.8
$P(OMe)_3$	PPh_3	35.7 ± 1.6	19.8 ± 4.1
$P(OMe)_3$	$P(OPh)_3$	38.1 ± 0.1	18.2 ± 2.1
PBu_3	PPh_3	32.4 ± 0.5	18.2 ± 1.3
PBu_3	$AsPh_3$	26.5 ± 0.5	10.2 ± 1.6
PBu_3	$P(OPh)_3$	34.6 ± 0.4	12.4 ± 1.0
PBu_3	$P(OMe)_3$	39.2 ± 1.6	20.6 ± 4.2

[a] Both $P(OPh)_3$ and PPh_3 dissociate at equal rates.

The first-order rate constants for the reactions above are listed in Table II. These rate constants were obtained as the slopes of plots of $-\ln A$ vs. time. As shown by the small error limits (95% confidence limits) these reactions led to excellent kinetic data. The activation parameters, as calculated from Eyring plots, are shown in Table III.

We have noted two interesting features which hold true for all of the *trans*-$Cr(CO)_4LL'$ complexes in this study. The first is that the value of the most intense CO stretching frequency (E mode) for *trans*-$Cr(CO)_4LL'$ is the numerical average of the values for *trans*-$Cr(CO)_4L_2$ and *trans*-$Cr(CO)_4L'_2$. For example, *trans*-$Cr(CO)_4(PBu_3)(PPh_3)$ exhibits one intense infrared peak at 1882 cm^{-1} which is the average of the CO stretching frequencies for *trans*-$Cr(CO)_4(PBu_3)_2$ (1872 cm^{-1}) and *trans*-$Cr(CO)_4(PPh_3)_2$ (1892 cm^{-1}), as shown in Table IV. The second feature we have noted is that a plot of $\ln k$ vs. the CO stretching (E mode) of *trans*-$Cr(CO)_4L_2$, *trans*-$Cr(CO)_4L'_2$, and *trans*-$Cr(CO)_4LL'$ is linear, where k is the first-order rate constant for ligand dissociation from *trans*-$Cr(CO)_4L_2$, *trans*-$Cr(CO)_4L'_2$, and *trans*-$Cr(CO)_4LL'$ at 130 °C. Thus, with the knowledge of the rate constants for ligand dissociation from *trans*-$Cr(CO)_4L_2$ and *trans*-$Cr(CO)_4L'_2$ at a particular temperature and knowledge of the corresponding CO stretching frequencies, it is possible to predict the rate of ligand dissociation from *trans*-$Cr(CO)_4LL'$. This is demonstrated in Figure 1. These correlations suggest that the electron density on the metal has a significant influence on the observed reactivity.

Table IV. Infrared Frequency for the Asymmetric Stretching Mode in $Cr(CO)_4LL'$

L	L′	$\nu(CO)$,[a] cm^{-1}
$P(OPh)_3$	PPh_3	1914
$P(OMe)_3$	PPh_3	1903
$P(OMe)_3$	$P(OPh)_3$	1925
PBu_3	PPh_3	1882
PBu_3	$P(OPh)_3$	1903
PBu_3	$P(OMe)_3$	1892

L = L′	ν	L = L′	ν
PPh_3	1892	$P(OPh)_3$	1934
PBu_3	1872	$P(OMe)_3$	1914

[a] Only the most intense peak.

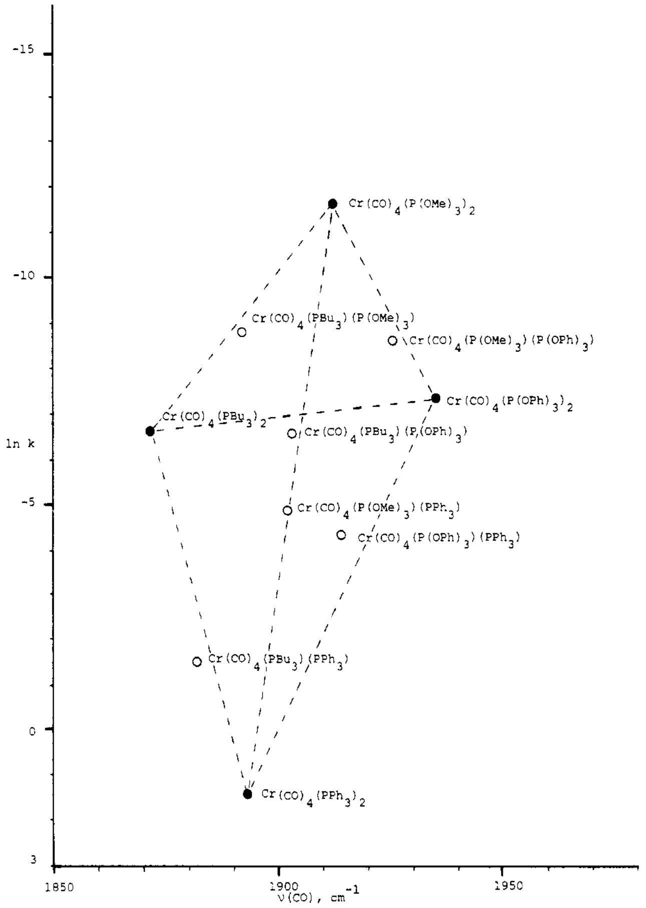

Figure 1. Plot of $\ln k$ vs. $\nu(CO)$ (cm^{-1}). The open circles represent *trans*-$Cr(CO)_4LL'$, and the closed circles represent *trans*-$Cr(CO)_4L_2$ and *trans*-$Cr(CO)_4L'_2$. Each dashed line connects *trans*-$Cr(CO)_4L_2$ to *trans*-$Cr(CO)_4L'_2$.

Discussion

Synthesis. Two methods have been used successfully for the preparation of $Cr(CO)_4LL'$ complexes. The primary procedure involved the displacement of Cl^- by L′ from $Cr(CO)_4LCl^-$.[13,14]

$$cis\text{-}Cr(CO)_4LCl^- + L' \rightarrow trans\text{-}Cr(CO)_4LL' + Cl^-$$

It is interesting that the *cis*-chloro derivative leads, with one exception, to the trans product. We believe that this is because of the steric interactions between L and L′ which lead to the instability of the cis species. The second me-

Table V. Leaving-Group Effects for the Reaction[a] $Cr(CO)_4LL' + CO \rightarrow Cr(CO)_5L + L'$

	L′		
L	$P(OPh)_3$	PPh_3	$AsPh_3$
PPh_3	2.7×10^{-2}	3.9	
PBu_3	1.46×10^{-3}	2.3×10^{-1}	6.3
$P(OPh)_3$	4.0×10^{-4}	2.7×10^{-2}	3.6×10^{-1}
$P(OMe)_3$	1.8×10^{-4}	8.1×10^{-3}	
CO	1.6×10^{-5}	1.0×10^{-4}	1.0×10^{-2}

[a] The numbers are first-order rate constants quoted as s^{-1}; at 130 °C.

thod of synthesis involved displacement of a ligand which readily dissociates ($AsPh_3$ from *trans*-$Cr(CO)_4(PBu_3)(AsPh_3)$).

$$trans\text{-}Cr(CO)_4(PBu_3)(AsPh_3) + P(OMe)_3 \rightarrow trans\text{-}Cr(CO)_4(PBu_3)(P(OMe)_3) + AsPh_3$$

This procedure was only used for preparation of *trans*-$Cr(CO)_4(PBu_3)(P(OMe)_3)$, although it should have more general applicability. The complex, *cis*-$Cr(CO)_4(P(OMe)_3)(AsPh_3)$, was the only species which had cis stereochemistry. The reason why this complex adopts cis geometry is unclear. The $P(OMe)_3$ ligand is smaller than the other ligands, but $AsPh_3$ is relatively large and the bis $P(OMe)_3$ complex forms a trans complex.

Kinetics. The reaction under consideration is the substitution of L′ by CO in *trans*-$Cr(CO)_4LL'$, eq 1. In

$$trans\text{-}Cr(CO)_4LL' + CO \rightarrow Cr(CO)_5L + L' \quad (1)$$

$$L = PBu_3, P(OMe)_3, P(OPh)_3, PPh_3, AsPh_3; \quad L' = P(OPh)_3, PPh_3, AsPh_3$$

all reactions except L, L′ = PPh_3, $P(OPh)_3$ only one product was formed. Excellent first-order plots were obtained which, coupled with the activation parameters, indicate the dissociative nature of the reaction.[20] The entropies of activation are especially significant, since they are all positive and >10 eu. This is for a net reaction where a gas molecule is coordinated and the entropy change for the reaction is undoubtedly negative, indicating clearly that the rate-determining step is not coordination of CO but L′ dissociation. This is consistent with the results obtained for $Cr(CO)_4L_2$ and $Cr(CO)_5L$.[16,17]

Ligand Bond Strengths. In this series of complexes, *trans*-$Cr(CO)_4LL'$, dissociation of only three ligands has been observed, L′ = $P(OPh)_3$, PPh_3, and $AsPh_3$, with the exception of $P(OMe)_3$ from *trans*-$Cr(CO)_4(PBu_3)(P(OMe)_3)$. For any given L the rate is always $AsPh_3 > PPh_3 > P(OPh)_3$ as shown by the data in Table V. This leaving-group effect is remarkably similar through a range of different L groups in the trans position and must represent the bond energies of the ligands to the chromium center. Since $P(OMe)_3$ and PBu_3 do not dissociate, we assume that they are the most strongly bound ligands. This order shows, as discussed for $Cr(CO)_5L$,[16] that the ligands which are most tightly bound are the ligands which are strong binding ligands, regardless of whether the ligand is primarily a σ-donor ligand or primarily a π-acceptor ligand. For a dissociative reaction it is generally assumed that the transition state corresponds to almost total loss of the ligand.[16] Thus the transition state for reaction 1 would have very little dependence on L′. For dissociation of L′ from $Cr(CO)_4LL'$ the transition state for a given L ($Cr(CO)_4L$) should have the same energy for loss of $P(OPh)_3$, PPh_3, and $AsPh_3$, and the activation parameters should reflect the relative ground-state bond energies of Cr–L′. This is shown graphically in Figure 2. The enthalpies of activation as shown in Table VI show that for a given L the ordering of bond strengths is Cr–$P(OMe)_3$ > Cr–$P(OPh)_3$ > Cr–PPh_3 > Cr–$AsPh_3$ with the bond strengths spanning 13 kcal/mol. The fact that the ordering and the differences in magnitude are the same for several different groups in the trans position supports the concept of complete Cr–L′ bond breaking in the transition state. The

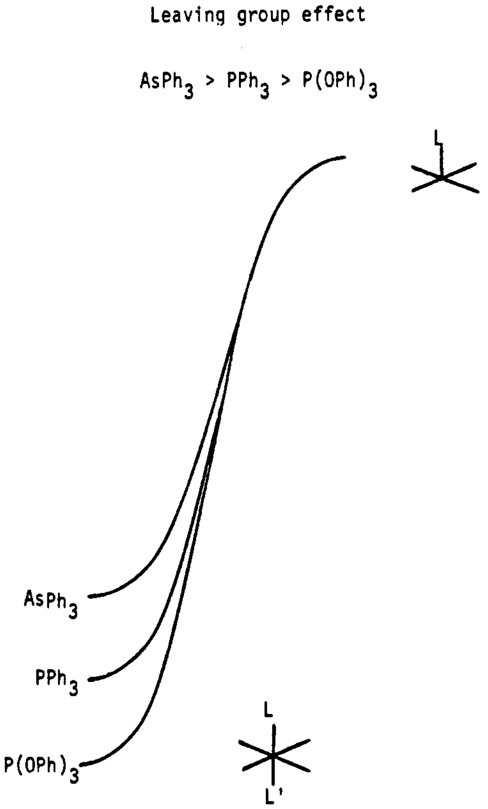

Figure 2. Scheme showing the differences in the gound-state bond energies of Cr–L′.

Table VI. Activation Enthalpies (kcal/mol) for Dissociation of L′ from $Cr(CO)_4LL'$

	L′			
L	$P(OMe)_3$	$P(OPh_3)_3$	PPh_3	$AsPh_3$
PPh_3		36	31	
PBu_3	39	35	32	26
$P(OPh)_3$		38	36	30
$P(OMe)_3$	43	38	36	

Table VII. Relative Rates for L′ Dissociation From *trans*-$Cr(CO)_4LL'$ at 130 °C[a]

	L′		
L	$P(OPh)_3$	PPh_3	$AsPh_3$
PPh_3	860	20000[b]	
PBu_3	94	2400	540
$P(OPh)_3$	13[b]	130	31
$P(OMe)_3$	12	81	
CO	1	1	1

[a] Since the activation enthalpies are different for each ligand the choice of temperature can affect the ratio of rate constants. [b] Corrected for the homobisligated complex since these are two possible sites of dissociation.

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(20) There was no dependence on the pressure of CO in these substitutions. A 50% increase in the CO pressure (from 1–1.5 atm) led to no change in the rate of ligand replacement. As an example reaction of $Cr(CO)_4PBu_3(PPh_3)$ with CO (1 atm) at 70 °C proceeded with a rate constant of 1.72×10^{-4} s^{-1}. Changing to 1.5 atm of CO led to a rate of $(1.6 + 0.1) \times 10^{-4}$ s^{-1}, within experimental error.

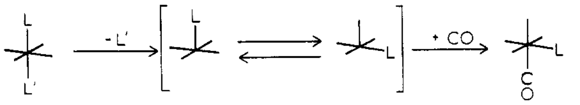

Figure 3. Scheme showing the rearrangement of the five-coordinate intermediate [$Cr(CO)_4L$] formed by the dissociation of L′ from *trans*-$Cr(CO)_4LL'$.

order and magnitude of this evaluation of ligand bond strengths to chromium carbonyl complexes are very similar to the order and magnitude observed for *trans*-$Pt(CH_3)(PMe_2Ph)_2L^+$.[18] The similarity in bond strengths for two rather different metal centers indicates that the order may be general.

Trans Effect. For a given dissociating ligand the effect of the trans ligand on the rate is remarkable. Table VII shows the effect of the trans ligand on the rate of dissociation of PPh_3, $P(OPh)_3$, and $AsPh_3$ for a series of complexes. For dissociation of each of the ligands, the order of labilization by the trans ligand is the same: $PPh_3 > PBu_3 > P(OPh)_3 \approx P(OMe)_3 > CO$. This order can be termed a trans effect order for dissociation from octahedral, 18-electron, organometallic complexes. The rates can span a range of 10^4 as is shown for PPh_3 dissociation.

A kinetic activation of this type can arise by either ground-state destabilization or transition-state stabilization. To assess possible ground-state effects we have studied the crystal structures of the complexes (*trans*-$Cr(CO)_4L(PPh_3)$ (L = $P(OPh)_3$, $P(OMe)_3$, and PBu_3)).[19] The Cr–PPh_3 bond distances (PBu_3, 2.345 (3) Å; $P(OPh)_3$, 2.393 (1) Å; $P(OMe)_3$, 2.362 (6) Å; CO, 2.422 (1) Å) show no correlation with the rates of dissociation of the PPh_3.[19] Thus the trans effect by the ligand L arises predominantly by transition-state stabilization, and the trans effect order must be inversely related to the increase of the energies of the $Cr(CO)_4L$ transition state/intermediate. The intermingling of ground-state and transition-state effects is shown by the dissociation of both PPh_3 and $P(OPh)_3$ from $Cr(CO)_4(PPh_3)(P(OPh)_3)$. As discussed above, $P(OPh)_3$ is bound more tightly than PPh_3 to chromium carbonyl centers and would be lower in ground-state energy. The transition state for $P(OPh)_3$ loss would involve $Cr(CO)_4PPh_3$ which would be lower in energy than the transition state generated by PPh_3 loss, $Cr(CO)_4P(OPh)_3$. Since the rates are almost the same for loss of PPh_3 and $P(OPh)_3$ from $Cr(CO)_4(PPh_3)(P(OPh)_3)$, the transition state represented by $Cr(CO)_4PPh_3$, must be lower in energy than the transition state represented by $Cr(CO)_4P(OPh)_3$ by an amount that is almost equal to the ground-state energy difference between a Cr–$P(OPh)_3$ and Cr–PPh_3 bond. This value would be 2–4 kcal/mol.

The trans effect order is very similar to the order seen for cis labilization which was also explained as transition-state stabilization.[6,7] The important difference is the location of the stabilizing ligand in the transition state. In cis labilization the ligand stabilizing the transition state occupies a basal site in the square pyramid.[6,7] For the trans effect which we have observed the ligand should occupy an axial site in the square-pyramidal transition state. The scheme is shown in Figure 3. Calculations have shown that the basal location of a ligand would be more stable than axial and the rearrangement is shown in Figure 3. Thus the highest energy point (the transition state) involves the presence of L in the apical position of the square-pyramidal species, and there must exist a stabilization by the presence of the ligand in the apical position.

The source of the stabilization of the transition state by the presence of non-carbonyl ligands may be either steric, electronic, or a combination of steric and electronic factors.

Table VIII. Carbonyl Stretching Frequencies (E mode) and Rates of L′ Dissociation from *trans*-$Cr(CO)_4LL'$ at 130 °C

L	L′	ν(CO), cm^{-1}	k, s^{-1}
CO	$P(OPh)_3$	1956	1.57×10^{-5}
$P(OMe)_3$	$P(OPh)_3$	1925	1.81×10^{-4}
PBu_3	$P(OPh)_3$	1903	1.46×10^{-3}
CO	PPh_3	1940	9.97×10^{-5}
$P(OMe)_3$	PPh_3	1903	8.08×10^{-3}
PBu_3	PPh_3	1882	2.35×10^{-1}
CO	$AsPh_3$	1943	1.16×10^{-2}
$P(OPh)_3$	$AsPh_3$	1914	3.60×10^{-1}
PBu_3	$AsPh_3$	1882	6.27

Steric factors have received considerable attention recently in reactions of metal carbonyls.[10,21–23] Steric acceleration as normally thought of would be a ground-state destabilization which can be ruled out in our system. The crystal structure determinations show no evidence in either bond distances or angles for such steric interactions.[19] Steric relaxation in the transition state is a possibility but would be expected to show trends in the entropies of activation. The entropies of activation as shown in Table III do not show any trends with steric size of the ligand. Indeed the entropies of activation for PPh_3 loss from *trans*-$Cr(CO)_4L(PPh_3)$ are within experimental error of each other for L = PBu_3, PPh_3, $P(OPh)_3$, and $P(OMe)_3$. We thus rule out a primary role for steric interactions in the trans effect which we have observed.[24]

Electronic effects could be either σ or π in character. Neither σ nor π nor the ratio of σ-to-π bonding correlates well with the observed rates. It is important to realize, however, that kinetic effects (rate differences) are combinations of ground-state and transition-state effects. While the predominant factor on rates of dissociation appears to be a transition-state stabilization by the ligand, the ligand environment can certainly affect the ligand bonding strength. The primary division between the ligands for the trans effect is between phosphines and phosphites, with the phosphines reacting more rapidly and presumably providing more stabilization of the intermediate. This suggests that the primary factor involved in stabilization of the 16-electron intermediate is the σ-donor strength. A ligand could stabilize the unsaturated intermediate by releasing electron density to the metal. Angelici offered convincing evidence that the ability of substituted *o*-phenanthrolines to donate electron density to the metal stabilized the transition state, $M(CO)_3$(*o*-phen),[25] but the apparent exceptions to this simple explanation have prevented more general interpretations. In examining the trans labilization order in more detail one must also consider ground-state effects. Crystal structure data suggests that a stronger σ-donor ligand trans to PPh_3 strengthens the Cr–PPh_3 bond.[19] This same feature is

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(21) Darensbourg, D. J.; Baldwin, B. J. *J. Am. Chem. Soc.* **1979**, *101*, 6447.

(22) Darensbourg, D. J.; Baldwin, B. J.; Froelich, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 4688.

(23) Darensbourg, D. J.; Graves, A. H. *Inorg. Chem.* **1979**, *18*, 1257.

(24) An alternate possibility which cannot be ruled out based on the kinetics observed is that the trans complexes $Cr(CO)_4LL'$ rearrange to the cis complexes and the dissociation and reactivity arises from the steric interactions in the cis complex. There is no evidence for formation of the cis complexes, and there is considerable indirect evidence suggesting that they are sufficiently unstable with respect to the trans complexes that even if an equilibrium could be formed, the concentrations of the cis complex would be exceedingly small. In isomerizations of $Mo(CO)_4L_2$ complexes Darensbourg has observed both dissociative and nondissociative routes.[20–22]

(25) Angelici, R. J.; Jacobson, S. E.; Ingemanson, C. M. *Inorg. Chem.* **1968**, *78* 2466.

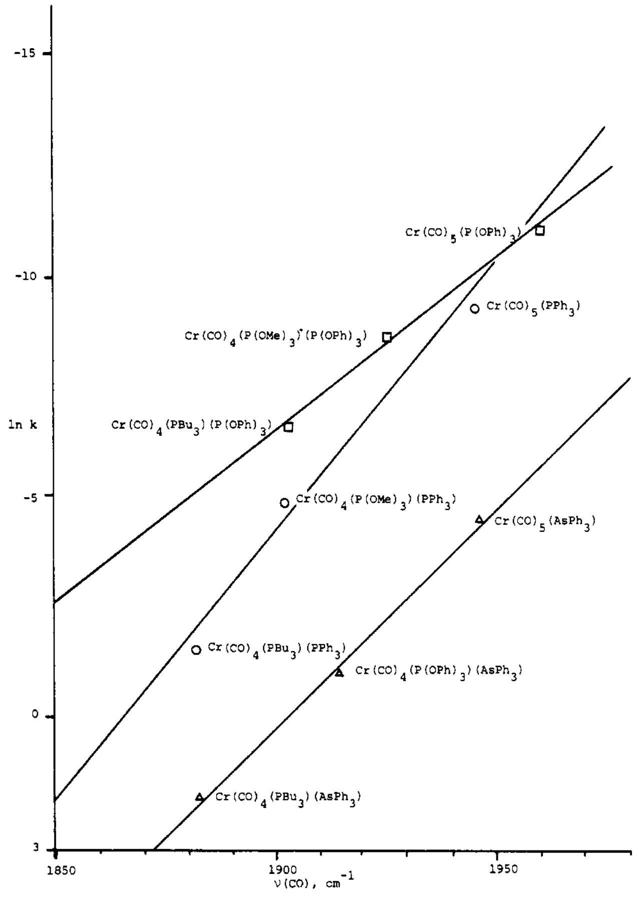

Figure 4. Plot of ln *k* vs. ν(CO) (cm^{-1}). The squares represent $Cr(CO)_4(P(OPh)_3)L$, the circles represent $Cr(CO)_4(PPh_3)L$, and the triangles represent $Cr(CO)_4(AsPh_3)L$.[26]

exhibited in Cr–$P(OPh)_3$ complexes.[19] Thus in dissociation of PPh_3 from $Cr(CO)_4(PBu_3)PPh_3$, PBu_3 provides more stabilization in the transition state/intermediate ($Cr(CO)_4L$) than PPh_3 and it also provides more stabilization of the ground state. The net effect is similar rates of dissociation of PPh_3 whether PBu_3 or PPh_3 is the trans ligand. A similar situation is seen for the phosphites. $P(OMe)_3$ is a considerably stronger σ donor than $P(OPh)_3$ and would be expected to stabilize the transition state for PPh_3 loss from $Cr(CO)_4LPPh_3$. However, the $P(OMe)_3$ complex has a shorter Cr–PPh_3 bond than the $P(OPh)_3$ complex.

The importance of electron density is further shown by a very interesting correlation of the rate of infrared stretching frequency as shown in Table VIII and Figure 4. For a given dissociating ligand from the mixed complexes, $Cr(CO)_4LL'$, the correlation is extremely good.[26] The lower infrared frequencies correlate with a more rapid rate of L′ dissociation. Infrared stretching frequencies are considered to be a measure of the electron density at the metal, lower infrared frequencies indicating more electron density on the metal. The correlation with rate also suggests that the stabilization of the transition state may arise by relief of the electron deficiency in the 16-electron intermediate by donating ligands. This stabilization would occur regardless of the orientation of the ligand in the transition state. The labilization in cis labilization could arise by a similar stabilization and the cis orientation would be because the *trans*-CO is more strongly bound (i.e., a ground-state property). This explanation could also apply to the acceleration of dissociation on $Mn_2(CO)_9L$, $Ir_4(CO)_{11}L$, and *cis*-$Mo(CO)_4LL'$.[8-10]

The qualitative and quantitative similarities between the activation toward dissociative loss of a ligand in the cis position (cis labilization),[4-7] the activation of CO dissociation in $Mn_2(CO)_9L$[8] and $Ir_4(CO)_{11}L$,[9] and the activation of L′ loss in $Cr(CO)_4LL'$ suggests a common origin of these kinetic effects. The body of data strongly suggests that this labilization is a transition-state phenomenon, stabilization of the transition state by the activating ligand. This stabilization occurs whether the activating ligand is cis or trans to the ligand dissociating.

In our study of dissociation of L′ from *trans*-$Cr(CO)_4LL'$ we have shown that the strength of the Cr–L′ bonds are Cr–$P(OMe)_3$ > Cr–$P(OPh)_3$ > Cr–PPh_3 > Cr–$AsPh_3$ and that the ligand L markedly affects the rate of dissociation of L′. This set of complexes, $Cr(CO)_4LL'$, offers the capability to change the bonding characteristics systematically and should prove to be very valuable in physical studies of organometallic complexes.

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Registry No. *trans*-$Cr(CO)_4(PPh_3)_2$, 38800-75-8; *trans*-$Cr(CO)_4(P(OPh)_3)(PPh_3)$, 82613-90-9; *trans*-$Cr(CO)_4(P(OPh)_3)(AsPh_3)$, 82613-91-0; *trans*-$Cr(CO)_4(P(OMe)_3)(PPh_3)$, 82613-92-1; *cis*-$Cr(CO)_4(P(OMe)_3)(AsPh_3)$, 82613-93-2; *trans*-$Cr(CO)_4(P(OMe)_3)(AsPh_3)$, 82659-77-6; *trans*-$Cr(CO)_4(P(OMe)_3)(P(OPh)_3)$, 82613-94-3; *trans*-$Cr(CO)_4(PBu_3)(PPh_3)$, 17652-69-6; *trans*-$Cr(CO)_4(PBu_3)(AsPh_3)$, 82613-95-4; *trans*-$Cr(CO)_4(PBu_3)(P(OPh)_3)$, 17652-71-0; *trans*-$Cr(CO)_4(PBu_3)(P(OMe)_3)$, 82613-96-5; CO, 630-08-0; PPh_3, 603-35-0; $AsPh_3$, 603-32-7; $P(OPh)_3$, 101-02-0; $P(OMe)_3$, 121-45-9.

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(26) The complex $Cr(CO)_4(PPh_3)P(OPh)_3$ is not included in these correlations. This complex did not give a unique product, and only the rate of loss of $Cr(CO)_4(PPh_3)P(OPh)_3$ is known precisely. This rate is the sum of rates of loss of PPh_3 and $P(OPh)_3$.