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Mechanism of Linkage Isomerization in (η^1-5-Chloropentene)pentacarbonylchromium(0)

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(η^1-5-Chloropentene)pentacarbonylchromium(0), (η^1-ol−Cl)$Cr(CO)_5$, **1**, and (η^2-5-chloropentene)pentacarbonylchromium(0), (η^2−Cl−ol)$Cr(CO)_5$, **2**, respectively, in which 5-chlorobenzene is bonded to Cr *via* a lone pair on chlorine or through the olefinic linkage, respectively, are produced *via* pulsed laser flash photolysis of $Cr(CO)_6$/Cl−ol solutions. Compound **1** then isomerizes to **2** on the submillisecond time scale. This process has been monitored both by IR and visible spectrophotometry by employing fluorobenzene (FB) as an inert diluent. Parallel studies of flash photolysis of $Cr(CO)_6$ in solutions containing 1-chlorobutane and 1-hexene, both neat and diluted with FB, where the Cl and ol functional groups are not linked, also were carried out. The data support a dissociative isomerization mechanism involving rate-determining Cr−Cl bond breaking. Activation parameters for this process have been obtained. The accessibility of a proposed low-energy pathway involving "agostic" C−H−Cr interactions in the transition state is evaluated.

Introduction

Specific bonding interactions in solution between coordinatively-unsaturated metal carbonyl fragments and weakly bonding ligands, L_w, have been well-documented. For example, for photogenerated [$Cr(CO)_5$], these include "agostic" three-center Cr−H−C− interactions (alkanes, arenes),[1] "ring-edge" bonding,[2] and "conventional" (albeit weak) coordination to Cr of functional groups such as Cl and Br (halogenated alkanes and arenes).[3] All of these possible modes of bonding are accessible upon initial L_w−$Cr(CO)_5$ interaction, since [$Cr(CO)_5$] is expected to be a poor discriminator among them.[4,5] Since the resulting bonds are weak and energetically similar, isomerization among them can take place before the thermodynamically most stable species is formed.

There have been reported several examples of the accessibility of multiple bonding sites in L_w molecules. Zhang and Dobson have observed that C_6H_5X (X = Cl, F) bonds to [$Cr(CO)_5$] *via* a lone pair on chlorine for X = Cl, but "edge-on" through an isolated double bond of the ring for X = F.[6,7] Zhang, Brown, and Dobson studied the kinetics of the linkage isomerization of (L_w)$Cr(CO)_5$ complexes (L_w = $HSiClMe_2$, $HSiClPh_2$) in which L_w interacts with Cr *via* either an agostic Si−H−Cr bond or a coordinate covalent Si−Cl−Cr bond.[8] Xie and Simon studied rates of reaction of [$Cr(CO)_5$] with long-chained alcohols and interpreted the kinetics results as indicating initial bonding of the alcohol to Cr *via* an agostic C−H−Cr interaction at any chain position, followed by an intramolecular walk of Cr along the chain to afford the thermodynamically-stable O-bonded product (Scheme 1).[9]

The "chain walk" would not be detected explicitly during its microscopic reverse, involving *dissociation* of the O-bonded alcohol, because the transition state is dominated by Cr−O bond breaking. However, residual C−H−Cr bonding in the transition state leading to bond breaking has been proposed to account for near-zero entropies of activation observed for the displacement of L_w from (L_w)$Cr(CO)_5$ transients.[10,11]

Thus, there are important reasons to study a possible chain walk in an ambidentate ligand in which a hydrocarbon chain bridging two functional groups offers the possibility to afford a low-energy pathway to linkage isomerization.

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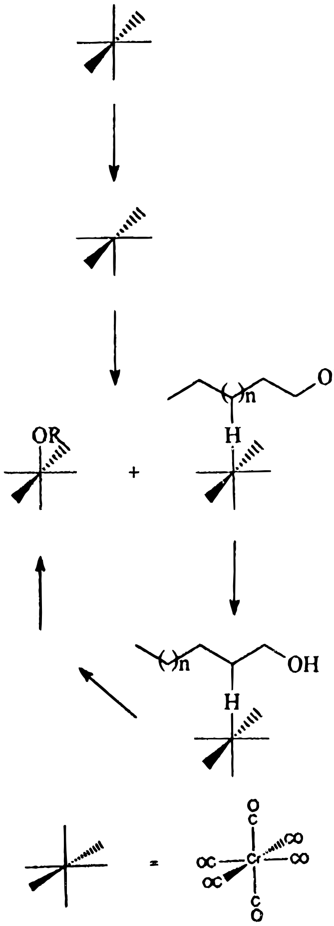
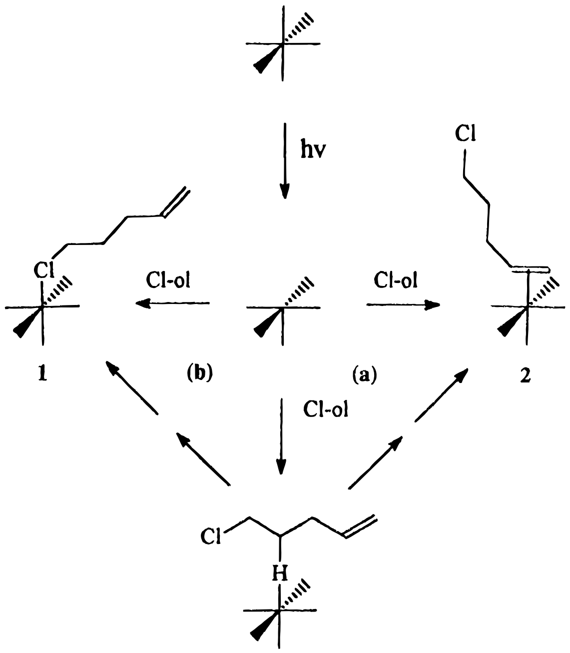
Scheme 1. Chain-Walk Mechanism



Scheme 2. Initial Steps after Photolysis of $Cr(CO)_6$ and 5-Chloropentene



5-Chloropentene (Cl−ol) is an ambidentate system of two relatively deep potential wells connected by the hydrocarbon chain ($L_w(CH_2)_nL_s$; L_s = strongly bonding ligand, which contains the more strongly bonded functional group and affords the thermodynamically-favored reaction product), where L_w and L_s are −Cl and $-CH{=}CH_2$, respectively. It possesses the requisite qualifications for such a kinetics study.

Scheme 2 shows what might be anticipated immediately after the flash if the chain walk is accessible. The two linkage isomers would be produced on the subnanosecond time-scale,[4] followed by the slower conversion of the less-stable to the more-stable isomer:

$$(\eta^1\text{-}L_s(CH_2)_nL_w)Cr(CO)_5 \rightarrow (\eta^2\text{-}L_w(CH_2)_nL_s)Cr(CO)_5 \quad (1)$$

$$(L_w(CH_2)_nL_s = Cl(CH_2)_3CH{=}CH_2,\ Cl{-}ol)$$

The energetics of this process could then be compared to that observed for systems in which the Cl and ol functional groups, L_w and L_s, are produced simultaneously but in which the chain is absent. Selected for this purpose were the ambidentate ligand 5-chloropentene (Cl−ol, $ClCH_2CH_2CH_2CH{=}CH_2$, $L_w{-}L_s$, and the related monodentate ligands 1-chlorobutane (BuCl), $ClCH_2CH_2CH_2CH_3$, L_w and 1-hexene (hex), $CH_3CH_2CH_2CH_2CH{=}CH_2$, L_s.

Experimental Section

Materials. $Cr(CO)_6$ (Pressure Chemical Co.) was vacuum-sublimed before use. The following liquids were fractionally distilled under nitrogen from the drying agents given in parentheses, which also contain the source: 1-chlorobutane (EM Science, P_2O_5); fluorobenzene (Aldrich, P_2O_5); 5-chloropentene (Wiley Organic, P_2O_5); 1-hexene (Johnson Matthey, anhydrous $MgSO_4$); *n*-heptane (hep, Sigma−Aldrich, Na).

Identification of the Reaction Intermediates and Products. The identities of the photogenerated (η^1-ol−Cl)$Cr(CO)_5$ and (BuCl)$Cr(CO)_5$ intermediates were confirmed by employing flash photolysis (FP) with IR-detection, FP-IR (*vide infra*), with $[Cr(CO)_6] = 3 \times 10^{-3}$ M. Details are given in the Results section. A schematic diagram for the FP-IR equipment is shown in Figure 1 of the Supporting Information. The pulsed laser beam and the CW IR beam converged on the infrared cell in a nearly colinear (*ca.* 15° angle) fashion.

Spectral changes taking place upon pulsed laser flash photolysis (Tachisto Model 850 excimer laser, N_2 gas fill; 337 nm, 10 mJ, 10 ns fwhm) were monitored over 1980−1910 cm^{-1}. Carbonyl stretching spectra were obtained by point-by-point analysis of the data. Studies of carbonyl stretching band broadening, which can take place in the presence of high concentrations of the "trapping" nucleophile, were carried out for stable complexes.[12] They indicate that for trap concentrations of up to 0.5 M, bands are not broadened nor significantly altered in position from those to be observed in pure hep. Trap concentrations of <0.5 M were thus, employed; thus the carbonyl stretching spectra for the photogenerated species closely approximate those which would be observed if the transients could have been isolated and then dissolved in pure hep. Attempts to observe the very weak, high-energy $A_1(1)$ band, expected *ca.* 2070 cm^{-1},[13] were not successful.

Laser Flash Photolysis Kinetics Studies. Attempts were made to ascertain the ratio, [**2**]:[**1**], of products formed immediately after photogeneration of $[Cr(CO)_5]$ (via paths a and b, respectively, Scheme 2) by employing both IR and UV-vis spectrophotometry; these attempts have thus far been unsuccessful.[14] Because of the superior signal-to-noise ratios in the visible spectral region, kinetics studies were monitored at 490 nm. Solutions *ca.* 3.5×10^{-3} M in $Cr(CO)_6$ also

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(12) The carbonyl stretching spectra for "stable" complexes, *e.g.*, (piperidine)$Cr(CO)_5$, were obtained in *n*-heptane/BuCl solutions of varying concentrations (Nicolet 20-SXB FT-IR spectrometer), and it was found that no significant band broadening takes place in solutions <0.5 M BuCl in *n*-heptane.

(13) See, *e.g.*, Orgel, L. *Inorg. Chem.* **1962**, *1*, 25.

(14) Since evidence has been presented that vibrational de-excitation of $[Cr(CO)_5]$ after photolysis takes place on the time scale of solvation, these ratios (the primary competition ratios) need not be the same as the secondary ratios, k_2/k_1, where $[Cr(CO)_5]$ exists primarily in its vibrational ground state (ref 4h,i). Employing both IR and visible detection, we determined the primary competition ratios, but have thus far been unable to obtain consistent agreement between the two methods for a variety of L_w and L_s. Work on this problem continues.

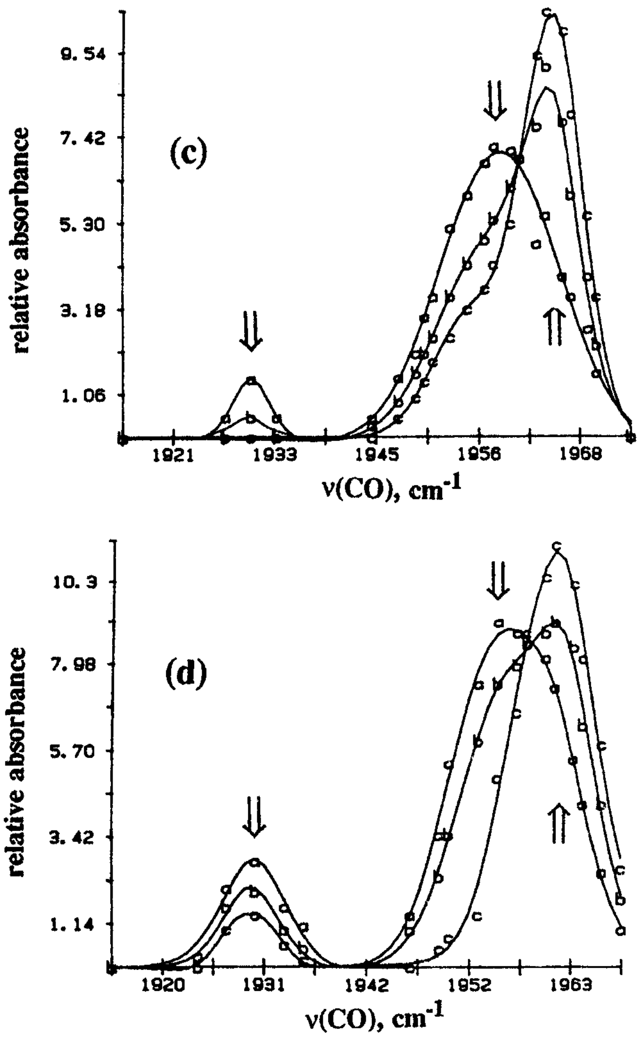


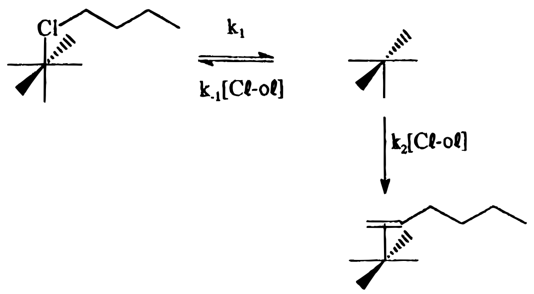
Figure 1. Time-resolved spectra (1920−1970 cm^{-1}): (c) after flash photolysis of a Cr(CO)$_6$/1-chlorobutane/1-hexene/*n*-heptane solution (times after flash (ms), (line a), 0.25, (line b) 1.0, (line c) 1.75; (d) after flash photolysis of a Cr(CO)$_6$/5-chloropentene/*n*-heptane solution (times after flash (ms), (line a) 0.25, (line b), 0.75, (line c), 1.5. Figure 1a,b are in Supporting Information.

containing large excesses of L$_w$ and L$_s$ (to ensure pseudo-first-order reaction conditions) were employed. L$_w$ and L$_s$ were weighed so that their concentrations were known with accuracy. Temperatures were maintained within ±0.05 °C by employing a VWR 1140 external circulator and a jacketed quartz 1 cm cell. Values for k_{obsd} were obtained from averages of 3−10 traces of plots of ln($A_t - A_\infty$ *vs* time (A_t and A_∞ are measured absorbances at time t and at infinite time, respectively). The kinetics data were analyzed employing ASYST-based computer programs developed in-house. All plots exhibited correlation coefficients of >0.99. Values of k_{obsd} are given in Table 1 of the Supporting Information. Error limits, given in parentheses as the uncertainties of the last digit of the cited value, are 1 standard deviation.

Results

Identification of Reaction Intermediates and Products. Reaction intermediates and products were identified by time-resolved infrared spectrophotometry. Four different systems were studied: (a) Cr(CO)$_6$/BuCl (0.5 M)/hep; (b) Cr(CO)$_6$/hex (0.5 M)/hep; (c) Cr(CO)$_6$/[BuCl] = [hex] (0.25 M each)/hep; and (d) Cr(CO)$_6$/Cl−ol (0.5 M)/hep. For a and b, plots of absorbance *vs* time at a given wavelength are "step functions", indicative of the kinetic stabilities of photogenerated (BuCl)-Cr(CO)$_5$ and (hex)Cr(CO)$_5$ on the submillisecond time scale in the absence of trapping nucleophiles. The resulting carbonyl stretching spectra are shown in Figure 2 of the Supporting Information. Observed carbonyl stretching frequencies are as follows: (η^1-BuCl)Cr(CO)$_5$ = 1930 (A$_1$(2), m), 1956 (E, vs) cm^{-1} and (η^2-hex)Cr(CO)$_5$ = 1964 (A$_1$ + E, vs) cm^{-1}.

Scheme 3. Competition for Intermediate Mechanism



These spectra were compared to those taken at various times after the flash for solutions c and d (Figure 1) and clearly show that immediately after the flash, intermediates bonded through both Cl and ol are produced and that those bonded through Cl are then converted to those bonded through the olefinic linkage. The rates of these processes for data at a particular wavelength were compared to those observed for the kinetics studies and were found to be the same, within experimental error.

Kinetics Studies. The linkage isomerization of photogenerated (η^1−Cl−ol)Cr(CO)$_5$ (eq 1) involves conversion of a species containing an η^1−Cl−Cr bond to one containing an η^2-ol−Cr bond. The displacement of BuCl from photogenerated (BuCl)-Cr(CO)$_5$ by hex (eq 2)

$$(\mathrm{BuCl})\mathrm{Cr(CO)}_5 + \mathrm{hex} \rightarrow (\mathrm{hex})\mathrm{Cr(CO)}_5 + \mathrm{BuCl} \qquad (2)$$

$$(\mathrm{BuCl} = \mathrm{L_w};\ \mathrm{hex} = \mathrm{L_s})$$

also involves such a conversion, in which, unlike the isomerization of Cl−ol, the two functional groups are not conjoined. Both neat solutions, containing only BuCl and hex, and solutions in which BuCl and hex were diluted with the inert solvent, fluorobenze (FB),[15,16] were studied.

Studies of related systems[6,15,17] suggested that the predominant ligand-exchange reaction pathway might involve initial Cr−L$_w$ bond breaking followed by competition for the [Cr(CO)$_5$] intermediate thus produced by L$_w$ and L$_s$ (Scheme 3). For this mechanism, presuming a steady-state concentration of [Cr-(CO)$_5$], the rate law

$$-\mathrm{d}[(\mathrm{L_w})\mathrm{Cr(CO)}_5]/\mathrm{d}t = k_1k_2[(\mathrm{L_w})\mathrm{Cr(CO)}_5][[\mathrm{L_s}]/(k_{-1}[\mathrm{L_w}] + k_2[\mathrm{L_s}]) \qquad (3)$$

is applicable. In terms of the pseudo-first-order rate constants k_{obsd} ([L$_w$], [L$_s$] ≫ [Cr(CO)$_6$]), eq 3 can be rearranged to

$$1/k_{obsd} = 1/k_1 + k_{-1}[\mathrm{L_w}]/k_1k_2[\mathrm{L_s}]) \qquad (4)$$

and plots of 1/k_{obsd} *vs* [L$_w$]/[L$_s$] are expected to be linear with finite intercepts. For both neat and dilute data (L$_w$ = BuCl; L$_s$

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(15) Zhang, S.; Dobson, G. R. *Organometallics* **1992**, *11*, 2447.

(16) For these reactions in an inert solvent, the rate behavior for displacement of FB from photogenerated (FB)Cr(CO)$_5$ has been studied in great detail.[15] That study indicates that FB bonds edge-on to the Cr-(CO)$_5$ moiety, that it is displaced by L$_s$ exclusively *via* a dissociative mechanism, and that the rate constant for this dissociation is *ca.* 1.5 × 10^6 s^{-1}, some 400 times larger than is the rate constant for dissociation of BuCl from (BuCl)Cr(CO)$_5$. Thus, (FB)Cr(CO)$_5$ is a steady-state intermediate in rapid equilibrium with [Cr(CO)$_5$] on the time scale of the reaction of (BuCl)Cr(CO)$_5$ with L$_s$.

(17) Zhang, S.; Dobson, G. R. *Inorg. Chim. Acta* **1991**, *181*, 103.

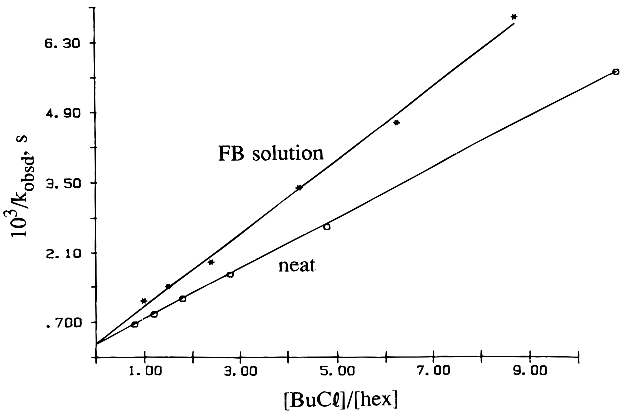


Figure 2. Plots of $1/k_{obsd}$ *vs* [BuCl]/[hex], (a) neat and (b) diluted with fluorobenzene, for reactions taking place after flash photolysis of $Cr(CO)_6$/1-chlorobutane/1-hexene solutions at 25 °C.

Table 1. Rate Constants after Flash Photolysis of $Cr(CO)_6$/1-Chlorobutane/1-Hexene Solutions, Neat and Diluted with Fluorobenzene, at Various Temperatures

T, °C	$10^{-3}\,k_1k_2/k_{-1}$, s^{-1}	$10^{-3}\,k_1$, s^{-1}	k_2/k_{-1}
	Neat[a]		
25.0	1.964(10)	3.9(2)	0.50(3)
35.0	4.44(4)	6.9(6)	0.65(6)
45.0	8.73(4)	16.7(7)	0.52(3)
	Diluted with Fluorobenzene[b]		
25.0	1.39(2)	3.2(7)	0.44(9)
35.0	3.06(4)	6.4(9)	0.48(7)
45.0	6.46(4)	13.8(10)	0.47(4)

[a] Neat data: $\Delta H_1^‡ = 12.6(12)$ kcal/mol; $\Delta S_1^‡ = 1(3)$ cal/(K mol). [b] Dilute data: $\Delta H_1^‡ = 13.2(5)$ kcal/mol; $\Delta S_1^‡ = 2(2)$ cal/(K mol).

= hex), these plots (Figure 2) are linear with positive intercepts, consistent with eq 4. Their similarity, with slopes differing by only 40% and intercepts within experimental uncertainty, indicates only a slight influence of the predominant solvent (whether FB or noncoordinating BuCl/hex) on the rate. Rate constants (= k_1k_2/k_{-1}, k_1 and k_2/k_{-1}), together with the corresponding activation parameters, are presented in Table 1.

Rate data for the $Cr(CO)_6$/Cl−ol solutions, where [Cl−ol] ($L_w(CH_2)_3L_s$, eq 1) was varied by means of dilution with FB, together with analogous data for $Cr(CO)_6$/[BuCl] = [hex] ([L_w] = [L_s])/FB solutions also were obtained. Plots of k_{obsd} *vs* [Cl−ol] and k_{obsd} *vs* [BuCl] = [hex] taken at 25 °C are presented in Figure 3. These plots are qualitatively similar, strongly suggesting that connectivity does not significantly influence rate or mechanism.

Where [L_w] = [L_s], rearrangement of eq 3 in terms of the pseudo-first-order rate constant, k_{obsd} ([L_w], [L_s] $\gg$ [$Cr(CO)_6$]), affords

$$k_{obsd} = k_1k_2/(k_{-1} + k_2) = k_{int} \tag{5}$$

Thus, plots of k_{obsd} *vs* [L_w] = [L_s] or k_{obsd} *vs* [$L_w(CH_2)_nL_s$] should be linear, with intercepts $k_1k_2/(k_{-1} + k_2)$ and slope = 0. The observed plots, comparing data for [BuCl] = [hex] and Cl−ol (Figure 3), obey the equation

$$k_{obsd} = k_{int} + k_{sl}[\text{hex}]. \tag{6}$$

and have the expected large intercepts (k_{int}) but small positive slopes (k_{sl}), which could be attributable to bulk solvent effects or a competing [L_s]-dependent pathway (*vide infra*). The rate constants k_{int} and k_{sl} together with the activation parameters derived from k_{int} are presented in Table 2.

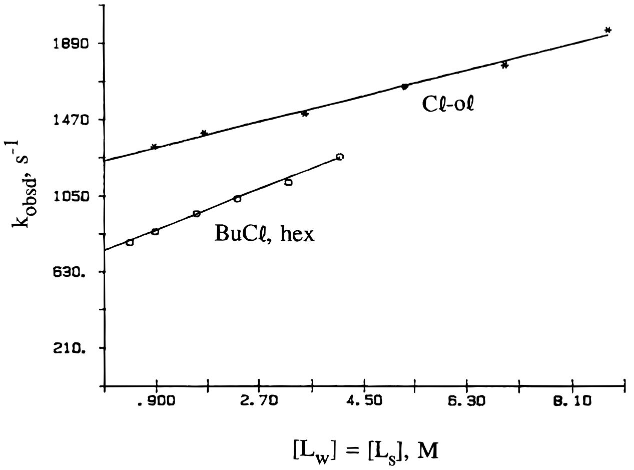


Figure 3. Plots of k_{obsd} *vs* [L_w] = [L_s] for reactions taking place after flash photolysis of $Cr(CO)_6$/5-chloropentene/fluorobenzene and $Cr(CO)_6$/1-chlorobutane/1-hexene/fluorobenzene solutions at 25 °C.

Table 2. Rate Constants for Reactions After Flash Photolysis of $Cr(CO)_6$/5-Chloropentene and $Cr(CO)_6$/[1-Chlorobutane] = [1-Hexene] Solutions Diluted with Fluorobenzene

T, °C	L_w/L_s	$10^{-3}\,k_{int}$, s^{-1}	$10^{-3}\,k_{sl}$, $M^{-1}\,s^{-1}$
25.0	Cl−ol[a]	1.243(15)	0.079(3)
35.0		2.846(10)	0.125(19)
45.0		5.69(20)	0.39(4)
25.0	BuCl/hex[b]	0.743(11)	0.125(4)
35.0		1.74(4)	0.36(4)
44.8		4.04(6)	0.52(2)

[a] From intercept for 5-chloropentene data ($k_1k_2/k_{-1} + k_2$): $\Delta H^‡ = 13.7(3)$ kcal/mol; $\Delta S^‡ = 2.0(11)$ cal/(K mol). [b] From intercept of [1-chlorobutane] = [1-hexene]/fluorobenzene data ($k_1k_2/(k_{-1} + k_2)$): $\Delta H^‡ = 13.9(7)$ kcal/mol; $\Delta S^‡ = 1(2)$ cal/(K mol).

Presuming the reversible dissociation mechanism to be operative, eqs 5 and 6 may be combined and rearranged to afford

$$k_{obsd} = 1/(1/k_1 + k_{-1}/k_1k_2) + k_{sl}[\text{hex}]. \tag{7}$$

Thus, the intercepts of the plots given in Figure 3 (eqs 5−7) can also be obtained from the variable concentration double reciprocal plots (Figure 2, eq 4) as

$$k_{obsd} = 1/(\text{intercept} + \text{slope}) + k_{sl}[\text{hex}] \tag{8}$$

The agreement between $k_1k_2/(k_{-1} + k_2)$, [BuCl] = [hex] experimental data and the values of $k_1k_2/(k_{-1} + k_2)$ determined from the slopes and intercepts of plots of $1/k_{obsd}$ *vs* [BuCl]/[hex] (Tables 1 and 2; eqs 7 and 8) is excellent, the average deviation of corresponding values being <10%. All of these data are summarized in Table 2 of the Supporting Information. Thus, it is clearly demonstrated that the equal concentration data are a subset of the variable concentration data and that the kinetics behavior is well-explained by the dissociative mechanism (Scheme 3).

It is reasonable to attribute the slight slopes quantified by k_{sl} to changes in rate engendered by the changing nature of the bulk solvent from one in which FB predominates to one in which the Cl and ol functional groups predominate. If the slope is instead the result of a bimolecular interchange process, such a competing pathway is small indeed (*ca.* 5% of the observed rate at [hex] = 1 M).

Discussion

General Observations. Several general observations may be summarized from this study of linkage isomerization of (η^1-

Table 3. Comparisons of Activation Enthalpies for Solvent−M Bond Dissociation with Bond Enthalpies Detmined from Photoacoustic Calorimetric Data for (Solvent)M(CO)$_5$ Complexes

solvent	$\Delta H^{\ddagger}$, kcal/mol	H^{a}, kcal/mol	H^{b}, kcal/mol
	M = Cr		
benzene	9.4(4)^{c}	15.0(22)	
RCl	13.2(5)^{d,e}	15.6(35)^{f}	
chlorobenzene	14.0(4)^{g}	19.4(78)	
tetrachloromethane	12.5(7)^{h}	19.5(21)	
	M = W		
n-heptane	8.4(5)	13.4(28)	
cyclohexane	8.2(4)		11.6(30)

[a] Reference 10. [b] (i) Ishikawa, Y.; Brown, C. E.; Hackett, P. A.; Raynor, D. M. *Chem. Phys. Lett.* **1988**, *150*, 306. (ii) Brown, C. E.; Ishikawa, Y.; Hackett, P. A.; Rayner, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 2530. These data were obtained from equilibrium studies in the gas phase. Note that while the data of Dobson and Hackett and that of Hackett and Burkey agree within experimental uncertainty, the data of Dobson and Burkey do not. [c] Reference 6. [d] This work. [e] 1-Chlorobutane. [f] 1,2-Dichloroethane. [g] Reference 15. [h] Reference 17.

ol−Cl)Cr(CO)$_5$ and parallel studies of solvent displacement of (η^1-BuCl)Cr(CO)$_5$ by hex to afford (η^2-hex)Cr(CO)$_5$:

(a) Mechanistically the reactions are very similar, whether there is connectivity between the functional groups or not; they also are little influenced by the nature of the bulk solvent, even when it is BuCl/hex, strongly indicating that the slopes of the plots of k_{obsd} *vs* [BuCl] = [hex] and k_{obsd} *vs* [Cl−ol] (Figure 3) result from bulk solvent effects rather than a competing associative ligand-displacement mechanism.

(b) Within experimental uncertainty, activation parameters are the same, whether there is connectivity or not or whether dilute or neat solutions are employed (Tables 1 and 2), consistent with a close mechanistic similarity in all of the studied systems.

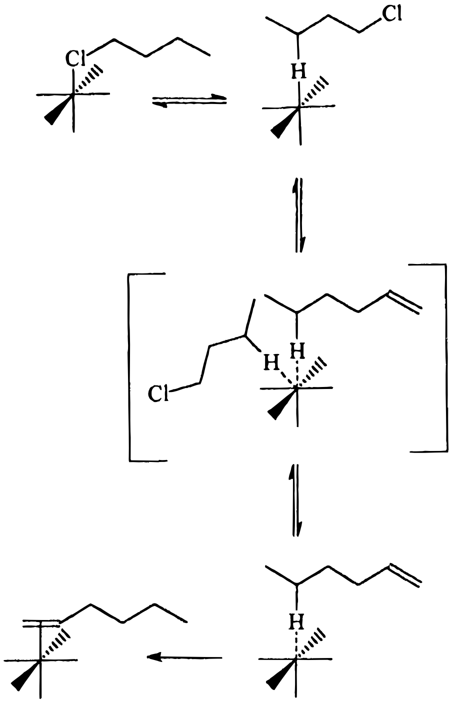
(c) The competition ratios, k_2/k_{-1}, for all systems are temperature independent, indicating little difference in the enthalpies of activation for attack at [Cr(CO)$_5$] and suggesting little bond making in the transition state for the Cl and ol functional groups,[18] considering the much greater stabilities of the Cr−ol *vs* the Cr−Cl bonds.

The data thus are very well described in terms of a single dissociative mechanism involving competition for a [Cr(CO)$_5$] intermediate by the functional groups, −Cl and −CH=CH$_2$ (Scheme 3). Nonetheless, entropies of activation for ligand exchange are about zero, despite the apparent strongly dissociative nature of the exchange process. Similar results were obtained in several related studies.[6,15,17]

The Chain-Walk Mechanism. Near-zero entropies of activation observed for the dissociative process are accompanied by enthalpies of activation some 3−7 kcal/mol lower than are the analogous bond-dissociation energies obtained from time-resolved photoacoustic calorimetric (TRPAC) data (Table 3).[10] These observations might suggest a mechanism which is dissociative in nature, but in which agostic −C−H−Cr bonding is retained in the transition state. The chain walk proposed by Simon and Xie[9] (Introduction) offers such a possibility.

A chain walk in the Cr(CO)$_6$/Cl−ol system may be envisioned as follows (Scheme 2): the intial reaction steps after flash photolysis (nanosecond time scale) afford, predominantly, species agostically bonded through the chain, since, on a statistical basis, there are many more C−H than −Cl or −CH=CH$_2$ binding sites. The chain-walk then will afford the thermodynamically more stable Cr−Cl and Cr−ol species, **1** and **2**. Zarić and Hall have carried out *ab initio* calculations for bonding in (ethane)W(CO)$_5$, which indicate that the intramolecular chain-walk is energetically favored over C−H−W agostic bond dissociation.[19]

Scheme 4. Intermolecular Chain-Walk Mechanism



An *inter*molecular chain walk (Scheme 4) could convert (η^1-BuCl)Cr(CO)$_5$ to (η^2-hex)Cr(CO)$_5$ or facilitate linkage isomerization in (η^1-ol−Cl)Cr(CO)$_5$ while retaining hydrogen bonding in the transition state. However, the rate constant ($k_{\text{CC}'}$) for the along-the-chain exchange might be expected to have a symmetrical transition state, for which it is difficult to envision the observed competition ratios, $k_2/k_{-1} \approx 0.5(1)$. This might suggest that the *hetero* chain walk steps, Cr−H−C to Cr−Cl (k_{CCl}) and Cr−ol (k_{Col}), have higher energy barriers than does the intermolecular chain walk.

However, one need not invoke the intermolecular chain walk to rationalize the data. The low entropies of activation possibly could be an artifact of weak L$_{\text{w}}$−Cr bonding, and the differences between enthalpies of activation and TRPAC bond enthalpies could be systematic. The very fast rates of solvation observed for [Cr(CO)$_5$] species,[4] together with the temperature independence observed for the competition ratios in this study, support similar low enthalpies of activation for reaction of L$_{\text{w}}$ and L$_{\text{s}}$ with [M(CO)$_5$] (M = Cr, Mo, W) and little change in structure along the reaction coordinate from the transition state to the intermediate.[18] If this is the case, enthalpies of activation for M−L$_{\text{s}}$ and M−L$_{\text{w}}$ should closely approximate M−solvent bond energies (the minimal $\Delta H^{\ddagger}$, low $\Delta S^{\ddagger}$ assumption).[17] However, it also is possible that *enthalpies* of Cr−L$_{\text{w}}$ bond dissociation could be significantly higher (as observed, Table 3), while *free energies* are lower, if the increase in enthalpy upon bond dissociation is overmatched by an increase in entropy. Thus, while the intermediate and its adjoining transition states may differ little in free energy, they might differ significantly in structure (high $\Delta H^{\ddagger}$, high $\Delta S^{\ddagger}$” assumption).[10] At ambient temperature, a decrease of entropy by 10−20 cal/(K mol) could compensate for the observed differences in the enthalpies of activation given in Table 3. This could account for the anomalously low entropies of activation which are observed.

The possibility that the $\Delta H^{\ddagger}$, ΔH discrepencies (Table 3) originate in the high $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ rationale can be addressed by

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(18) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(19) Zarić, S; Hall, M. B. *J. Am. Chem. Soc.*, submitted for publication.

comparing entropies of activation for bond dissociation in complexes in which the substituent is weakly or strongly bonded to the metal (M−L$_w$ and M−L$_s$); in the latter, presumably, the slopes along the reaction coordinate of the potential well in which the intermediate exists would be steeper, leading a smaller change in $S^\ddagger$ for a given change in H along the reaction coordinate from the intermediate to its adjacent transition states: $\Delta S^\ddagger$ thus would be expected to be more positive where ligand−metal bonds are stronger.

To examine this possibility, 13 (amine)M(CO)$_5$ complexes (M = Cr, Mo) exhibiting enthalpies of activation in the range of 22−28 kcal/mol for M−amine bond dissociation[20,21] can be compared to 8 (L$_w$)M(CO)$_5$ species, (L$_w$ = benzene, halogenated organics),[6,15,17] for which $\Delta H^\ddagger$ values are in the range of 9−14 kcal/mol. The kinetics results for these reactions indicate that they are mechanistically similar.[6,15,17,20,21] The corresponding entropies of activation are quite similar, in the ranges −2 to +10 cal/K mol (average = 4) and −4 to +19 cal/K mol (average = 7), respectively. This difference corresponds to about 1 kcal/mol at ambient temperature and does not support the high $\Delta H^\ddagger$, $\Delta S^\ddagger$ proposal.[10] This marginal difference could well result from a weaker steric interaction in the ground state for L$_w$−M bonding than for L$_s$−M bonding.

The other possible explanation for the $\Delta H^\ddagger$, ΔH discrepencies is systematic error. While Burkey and co-workers have gone to great lengths to analyze factors which might influence their TRPAC data,[10] their derived M−solvent bond-dissociation energies depend critically on values for enthalpies of activation for M−CO bond dissociation. They are represented by the differences between the M−CO activation energies and energy changes (TRPAC) accompanying the conversion of photogenerated (solvent)Cr(CO)$_5$ to a complex containing a trapping nucleophile, *e.g.*, (piperidine)M(CO)$_5$. To avoid possible M−H−C− transition state stabilization influences for M−CO bond dissociation in solution, they adopted the gas-phase enthalpies of activation for M−CO bond dissociation reported by Golden *et al.*[22] Table 4 exhibits relevant data, both in solution and in the gas phase, for M−CO bond fission. Nine sets of data, three each for Cr(CO)$_6$, Mo(CO)$_6$, and W(CO)$_6$, the work of Angelici,[23] Calderazzo,[24] Werner,[25] Cetini,[26] and their co-workers, all agree closely, whether the work was done in solution or in the gas phase. This agreement suggests that stabilization of the transition state leading to M−CO bond breaking in solution (*vs* in the gas phase) *via* M−H−C agostic bonding is not significant. Moreover, there are substantial nonsystematic differences between the Golden[22] values employed by Burkey and those of the other research groups. However, theoretical studies have also have evaluated M−CO bond strengths, and taking into consideration the experimental values cited above, estimated M−CO bond dissociation energies are quite close to the Golden values. For Cr, the theoretically-determined value is about 8 kcal/mol greater than the value adopted through consideration of the experimental evidence.[27]

Table 4. Activation Enthalpies for M−CO Bond Breaking in M(CO)$_6$ Complexes (M = Cr, Mo, W)

L	M	$\Delta H^\ddagger$, solution, kcal/mol	$\Delta H^\ddagger$, gas phase, kcal/mol	ref
CO	Cr	38.1	38.7	24, 25
		40.2(6)	36.8(30)	23, 22
CO	Mo	30.2	30.2	24, 25
		31.7(14)	40.5(30)	23, 22
	W	39.0	39.8	24, 25
		39.9(16)	46.0(30)	23, 22

It thus would appear difficult to know which enthalpies of activation for M−CO bond breaking to select to obtain *absolute* solvent−M bond dissociation energies from TRPAC data. However, this is not to say that *differences* in bond dissociation energies determined from TRPAC data do not accurately represent differences in bond dissociation energies for related complexes.

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Supporting Information Available: Tables of pseudo first-order rate constants (Table 1) and $k_1k_2/k_{-1} + k_2$) values (Table 2), schematic diagram for pulsed laser flash photolysis system (Figure 1), and carbonyl stretching spectra (7 pages). Ordering information is given on any current masthead page.

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