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Kinetics and Mechanism of Ligand Exchange in Photogenerated (η^2-monoalkylarene)Cr(CO)$_5$ Complexes with Alkenes: Evidence for Involvement of Aliphatic Chains in the Arene and Alkene in the Exchange Process

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The kinetics and mechanism of the reaction of photogenerated (η^2-C_6H_5R)Cr(CO)$_5$ complexes (R = CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9, *c*-C_6H_{11}, (C_6H_5)(CH_2)$_{11}$$CH_3$), in which C_6H_5R is a ligand weakly bonded to Cr (L_w), with strongly coordinating "trapping" nucleophiles containing an olefinic functionality (L_s = 1-hexene, 1-decene, and 1-tetradecene) have been studied by employing pulsed laser flash photolysis with visible and infrared detection. The substituted arene molecules likely bond to the metal "edge-on" *via* a partially delocalized center of unsaturation in the ring. Kinetics data taken "neat" to very high [L_s] and in dilute solution in the "inert" solvents (S) agree closely, indicating that influences of S (C_6H_5R, fluorobenzene, *n*-heptane) are relatively unimportant. The kinetics data are wholly consistent with a single mechanism involving dissociation of C_6H_5R from (η^2-C_6H_5R)Cr(CO)$_5$, followed by competitive reaction of the [Cr(CO)$_5$] intermediate thus produced with C_6H_5R or L_s. Changes in rate constants, k_1, for Cr−L_w bond fission are largely influenced by the electronic properties of R in PhR. Relative rates of attack by L_s at [Cr(CO)$_5$] increase in the order 1-hexene < 1-decene < 1-tetradecene. The "competition ratios" of the rate constants for interaction of L_s and L_w with the photogenerated intermediate vary with the sum of the number of carbons in the chains for L_w and L_s, strongly suggesting that the interchange takes place, at least in part, through the chains. Carbonyl stretching spectra are quite similar for these (L_w)Cr(CO)$_5$ complexes and indicate that they are of C_{4v} local symmetry (octahedra substituted at an apex) and perhaps suggest similar bonding of PhR to Cr for all complexes, but they provide no information about the influence of R on bonding.

Introduction

It has long been known that arenes enter into η^6 bonding with metal carbonyl fragments to afford stable metal carbonyl substitution products, such as (η^6-benzene)Cr(CO)$_3$.[1] Less studied have been complexes in which the arene coordinates to the metal *via* a two electron bond, first investigated by Sheline *et al.*[2] For the group 6 metal carbonyls, bonding of arenes to metal atoms in this fashion is much weaker than is η^6-bonding and likely takes place *via* a ring-edge.[3,4] A brief kinetics survey of a series of photogenerated pentacarbonylchromium complexes of weakly bonding (L_w) substituted arenes (PhR) with more strongly bonding "trapping" nucleophiles (L_s; in this case, 1-hexene) has been reported, eq 1.[4] More detailed kinetics studies of arene displacement in two such complexes, (η^2-benzene)Cr(CO)$_5$[5] and (η^2-fluorobenzene)Cr(CO)$_5$,[6] demonstrated that displacement of the arene by L_s takes place

$$(\eta^2\text{-PhR})\mathrm{Cr(CO)}_5 + \mathrm{L_s} \rightarrow (\eta^2\text{-L}_s)\mathrm{Cr(CO)}_5 + \mathrm{PhR} \quad (1)$$

exclusively *via* a mechanism involving unimolecular arene dissociation followed by competitive reaction of the arene and olefin, Scheme 1.

The steady-state rate law (d[Cr(CO)$_5$]/d$t \approx 0$) for this mechanism under pseudo first-order reaction conditions ([Cr(CO)$_6$] $\ll$ [arene (= PhR)]) is

$$k_{\mathrm{obsd}} = k_1k_2[\mathrm{L_s}]/(k_{-1}[\mathrm{PhR}] + k_2[\mathrm{L_s}]) \quad (2)$$

Under the conditions employed in the brief survey ([PhR] $\gg$ [L_s]),[4] this rate law adopts the limiting form, eq 3, and thus the reported rate complexes are complex.

$$k_{\mathrm{obsd}} = k_1k_2[\mathrm{PhR}]/k_{-1}[\mathrm{L_s}] \quad (3)$$

In order to understand more fully the influences of ring substituents on the nature, strengths, and reactivities of η^2-arene−Cr bonds, studies have now been conducted under nonlimiting rate conditions. The rearrangement of eq 2 affords eq 4. The rate constants, k_1,

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

for unimolecular Ar−Cr bond-breaking and k_2/k_{-1}, the "competition ratios" of rate constants for attack by PhR

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Scheme 1

$$(\eta^2\text{-arene})Cr(CO)_5 \underset{k_{-1}[PhR]}{\overset{k_1}{\rightleftharpoons}} [Cr(CO)_5] \xrightarrow{k_2[L_s]} (\eta^2\text{-}L_s)Cr(CO)_5$$

and L_s at $[Cr(CO)_5]$, can be extracted from plots of $1/k_{obsd}$ *vs* [PhR]/[L_s]. This partitioning of the “limiting” rate constants, k_1k_2/k_{-1}, permits the evaluation of influences of arene ring substituents on both the PhR−Cr bond strengths and the reactivities of $[Cr(CO)_5]$ with both PhR and L_s. Data at several temperatures can afford activation parameters corresponding to these rate constants, and infrared spectra for the photogenerated $(PhR)Cr(CO)_5$ species are of potential use in the interpretation of the data. Reported here are kinetics studies of reactions which proceed according to eqs 1 and 2 for $(\eta^2\text{-PhR})Cr(CO)_5$ complexes (R = CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9, *c*-C_6H_{11}, *n*-$C_{12}H_{25}$) with the trapping nucleophiles L_s (1-hexene, 1-decene, and 1-tetradecene).

Experimental Section

Materials. $Cr(CO)_6$ (Pressure Chemical Co.) was vacuum-sublimed before use. Other reagents were fractionally distilled under N_2 from various drying agents (solvent, source, and drying agent given in parentheses): fluorobenzene (Aldrich, P_2O_5); 1-tetradecane (Aldrich, $MgSO_4$); 1-hexene and 1-decene (Johnson Matthey, anhydrous $MgSO_4$); *n*-heptane and cumene (Sigma−Aldrich, Na); ethylbenzene, cyclohexylbenzene, *tert*-butylbenzene, phenyldodecane (Lancaster Synthesis, Na); toluene (EM Scientific, Na).

Identification of Reaction Intermediates and Products. The identities of $(\eta^2\text{-PhR})Cr(CO)_5$ complexes and the $(\eta^2\text{-}L_s)Cr(CO)_5$ reaction products were determined by employing a pulsed laser flash photolysis system based on a Tachisto model 850 photolyzing excimer laser (N_2 gas fill; 337 nm, 10 mJ, 10 ns fwhi), and a Tektronix 2440 digital oscilloscope, coupled to UV/visible and infrared analyzing trains. The latter employs a Spectra-Physics CW line-tuneable IR diode laser analyzing source. The system has been described in greater detail elsewhere.[7,8]

Spectral changes were monitored in the IR region (1980−1910 cm^{-1}) by employing a 1 mm CaF_2 IR cell with $[Cr(CO)_6] = 3 \times 10^{-3}$ M. Carbonyl stretching spectra were obtained point-by-point (1−2 cm^{-1} intervals) after pulsed laser flash photolysis of $Cr(CO)_6$/0.5 M PhR/0.25 M 1-hexene/*n*-heptane solutions, which minimized possible band-broadening as a consequence of high [1-hexene]. Attempts to observe the very weak, high energy A_1 bands expected at *ca.* 2080 cm^{-1} for $(\eta^2\text{-PhR})Cr(CO)_5$ and $(\eta^2\text{-}L_s)Cr(CO)_5$[9] were not successful. Plots of absorbance *vs* time taken in the absence of 1-hexene exhibited “step functions” over several milliseconds, indicating that the photogenerated $(\eta^2\text{-PhR})Cr(CO)_5$ complexes are stable on this time scale. Infrared spectra for the reaction products $(\eta^2\text{-1-hexene})Cr(CO)_5$ and $(\eta^2\text{-1-decene})Cr(CO)_5$ have been reported,[10] while that for $(\eta^2\text{-1-tetradecene})Cr(CO)_5$ is given in Table 1 (*vide infra*).

Laser Flash Photolysis Kinetics Studies. Solutions *ca.* 3.5×10^{-3} M in $Cr(CO)_6$ also containing large excesses of solvent and trap were employed to insure pseudo first-order reaction conditions. The solvents and traps 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 jacketted quartz 1 cm cell. Values for k_{obsd} were obtained, monitoring 490 nm, 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). Kinetics studies were carried out by employing visible, rather than infrared detection because of the superior signal-to-noise ratio and the greater analyzing signal stability of the visible signal. Neat solutions (containing only $Cr(CO)_6$, PhR, and trapping nucleophile (L_s)) were also found to afford better signals than did solutions in which $[Cr(CO)_6] \ll$ [PhR], $[L_s] \ll$ [S] (fluorobenzene, *n*-heptane). For PhR = toluene, kinetics data were also taken in dilute solution (S = *n*-heptane) to confirm, as has been observed previously,[10] that results obtained in “neat” and “dilute” solutions (eq 4) are comparable (Figure 1). Where PhR was phenyl-*n*-dodecane, the viscosities of the neat solutions precluded their use, and *n*-heptane was used as S.

Table 1. Carbonyl Stretching Frequencies and Activation Parameters

R	$A_1(2)$ (cm^{-1})	E (cm^{-1})	$\Delta H_1^\ddagger$ (kcal/mol)	$\Delta S_1^\ddagger$ (cal/k mol)
	$(\eta^2\text{-RPh})Cr(CO)_5$			
H	1927 (m)	1954 (s)	9.4(1)[a]	−2.4(3)
CH_3	1927 (m)	1952 (s)	12(2)	4(8)
C_2H_5	1930 (m)	1954 (s)	12.4(14)	6(4)
$CH(CH_3)_2$	1925 (m)	1955 (s)	10.0(10)	−2(3)
$C(CH_3)_3$	1927 (m)	1955 (s)	11.3(13)	3(4)
c-C_6H_{11}	1930 (m)	1954 (s)	10.3(12)	−2(4)
n-$C_{12}H_{25}$	1923 (m)	1952 (s)	11.6(12)	3(4)
	$(\eta^2\text{-tetradecene})Cr(CO)_5$			
		1961		

[a] Reference 5; the error limits given reflect the deviation of the rate constants from a plot of $\ln(k_1)$ *vs* $1/T$ rather than the experimental uncertainties for values of k_1.

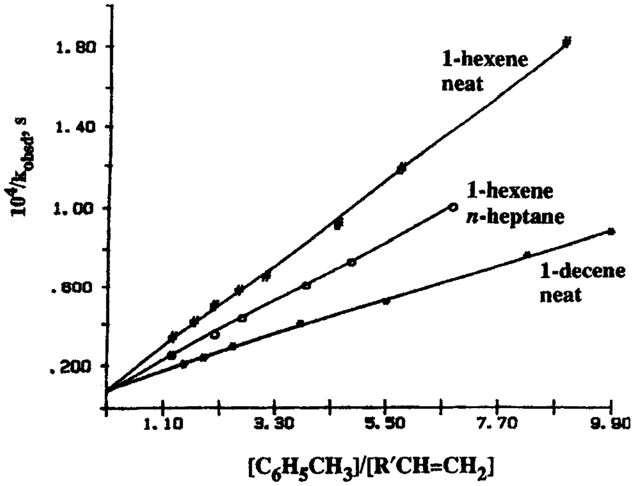

Figure 1. Plots of $1/k_{obsd}$ *vs* $[PhCH_3]/[R'CH{=}CH_2]$ for reactions taking place after pulsed laser flash photolysis of $Cr(CO)_6/PhCH_3$/1-hexene, $Cr(CO)_6/PhCH_3$/1-decene, and $Cr(CO)_6/PhCH_3$/1-hexene/*n*-heptane solutions at 25.0 °C.

The kinetics data were analyzed employing ASYST-based computer programs developed in-house. All plots exhibited correlation coefficients >0.99. Values of k_{obsd} are given in the Supporting Information; error limits, given in parentheses as the uncertainties of the last digit of the cited value, are one standard deviation.

Results

Identification of Reaction Intermediate and Products. The carbonyl stretching frequencies for the $(\eta^2\text{-PhR})Cr(CO)_5$ reactants, together with those for the trapping products, $(\eta^2\text{-}L_s)Cr(CO)_5$, are shown in Table 1. Time-resolved spectra were taken after pulsed laser flash photolysis of a $Cr(CO)_6/C_6H_5CH_3$ (0.5 M)/1-hexene (0.25 M)/*n*-heptane solution (Figure 2).[7] They clearly

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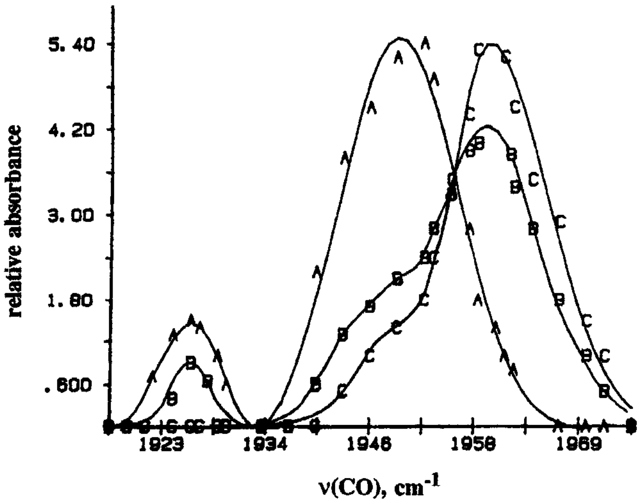


Figure 2. Time-resolved IR spectra for the reaction of photogenerated (η^2-PhCH$_3$)Cr(CO)$_5$ with 1-hexene in n-heptane solution. Times after the flash: (a) 10 μs; (b) 40 μs; (c) 150 μs.

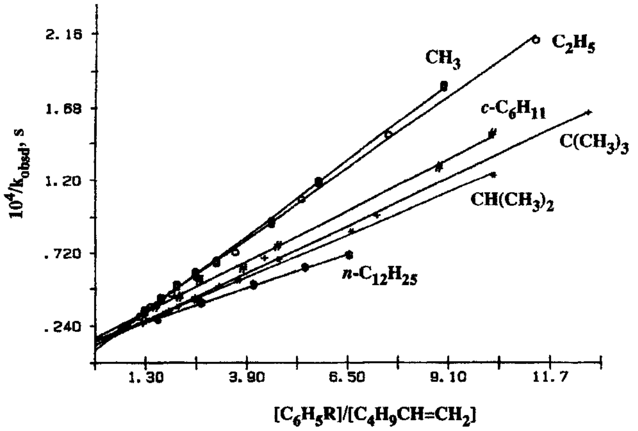


Figure 3. Plots of $1/k_{obsd}$ *vs* [PhR]/[1-hexene] for reactions taking place after pulsed laser flash photolysis of Cr(CO)$_6$/PhR/1-hexene and Cr(CO)$_6$/Ph(n-C$_{12}$H$_{25}$)/1-hexene/n-heptane solutions at 25.0 °C.

indicate that photogenerated (η^2-PhCH$_3$)Cr(CO)$_5$ is converted to the known (η^2-1-hexene)Cr(CO)$_5$ product (eq 1). The close similarity of the kinetics observed for reactions taking place after pulsed laser flash photolysis of Cr(CO)$_6$/PhR solutions containing 1-decene and 1-tetradecene as the trapping nucleophiles confirmed that analogous reactions were taking place.

Kinetics Studies. The reactions adhere to the rate law expected for the mechanism shown in scheme 1; plots of $1/k_{obsd}$ *vs* [PhR]/[L$_s$] for all systems were linear (Figure 3). For PhCH$_3$/L$_s$ solutions in which L$_s$ was varied, these plots (L$_s$ = 1-hexene, 1-decene) exhibited a common intercept (Figure 1), as is expected (eq 3) since the intercept, $1/k_1$, should be independent of the identity of L$_s$. For neat solutions, concentrations of both PhR and L$_s$ were varied widely (PhR = 8.5−4.2 M; L$_s$, 0.7−4.4 M). Table 2 presents the rate constants, k_1k_2/k_{-1}, k_1, and k_2/k_{-1}, for the reactions. Activation parameters are presented in Table 1.

Discussion

Kinetics and Mechanism. Linear "double reciprocal plots", Figures 1 and 3, and the good agreement among intercepts of these plots for three different L$_s$ (Figure 1, Table 2) clearly show that the reaction of photogenerated (η^2-PhR)Cr(CO)$_5$ complexes with olefinic traps, L$_s$, obey the "reversible dissociation−competition for intermediate" mechanism shown in Scheme 1. As observed previously,[10] solvent effects in these systems are not large (Figure 1), and thus neat data were taken where possible.

Table 2. Rate Constants

Ph*R*	L$_s$	*T* (°C)	$10^{-4}k_1k_2/k_{-1}$ (M^{-1} s^{-1})	$10^{-4}k_1$ (s^{-1})	k_2/k_{-1}
		Neat			
CH$_3$	1-hexene	10.0	1.56(4)	3.8(9)	0.42(10)
		15.0	2.49(4)	6.2(7)	0.40(6)
		25.0	5.28(8)	11.0(11)	0.48(6)
		30.0	7.95(8)	17.2(12)	0.46(4)
neat	1-decene	15.0	5.91(12)	5.5(4)	1.07(17)
		25.0	12.22(16)	11.8(6)	1.03(11)
		35.0	24.8(5)	23.0(15)	1.08(9)
C$_2$H$_5$	1-hexene	15.0	2.68(3)	4.6(3)	0.59(5)
		25.0	5.54(7)	9.4(7)	0.59(5)
		35.0	12.1(3)	20.0(16)	0.61(5)
CH(CH$_3$)$_2$		10.0	2.90(6)	3.1(2)	0.92(8)
		15.0	4.03(14)	4.7(6)	0.85(15)
		25.0	9.1(2)	7.8(5)	1.16(10)
CH(CH$_3$)$_2$	1-hexene	30.0	12.4(4)	11.3(9)	1.10(13)
C(CH$_3$)$_3$		15.0	3.95(11)	5.4(7)	0.73(11)
		25.0	8.20(19)	9.3(8)	0.88(12)
		35.0	15.7(4)	20.8(3)	0.76(11)
c-C$_6$H$_{11}$		10.0	2.55(5)	2.43(14)	1.05(8)
		15.0	3.44(14)	3.7(5)	0.92(10)
		25.0	7.80(17)	5.9(3)	1.32(10)
		30.0	10.2(4)	9.5(11)	1.08(18)
		Diluted with *n*-Heptane			
CH$_3$	1-hexene	25.0	7.23(11)	13.1(11)	0.53(6)
n-C$_{12}$H$_{25}$		15.0	5.7(2)	3.3(2)	1.75(19)
		25.0	11.5(3)	6.9(3)	1.67(11)
		35.0	21.7(7)	13.2(10)	1.64(19)
	1-decene	25.0	15.6(5)	7.06(16)	2.52(10)
	1-tetradecene	25.0	27.6(14)	8.2(5)	3.3(4)

The data indicate that the dominant influence on rate as a function of the identity of PhR derives from variations in the competition ratios (k_2/k_{-1}), rather than in k_1, the rate constants for PhR dissociation. Values of k_1 decrease in the order R = H^5 ≫ CH$_3$ > C$_2$H$_5$ ≈ *i*-C$_3$H$_7$ ≈ *t*-C$_4$H$_9$ > *c*-C$_6$H$_{11}$ ≈ *n*-C$_{12}$H$_{25}$, indicative of decreasing reactivity as the electron-releasing influences of R increase. However, the inductive influences of R are rapidly attenuated along the series. For the alkyl substituents, these inductive influences are small, with a roughly 2-fold change along the series. The nearly 3-fold decrease in rate from R = H to CH$_3$ may be attributable to the disruption of electronic delocalization in the ring engendered by R, which affords double bond character *ortho* and *para* to the substituent.

Surprisingly, the influences on overall rate engendered by R on k_2/k_{-1} are substantially larger, increasing some 5-fold along the series from R = H to C$_{12}$H$_{25}$ for L$_s$ = 1-hexene and also increasing as a function of the identity of L$_s$ in the order 1-hexene < 1-decene < 1-tetradecene. The overall increase is some 10-fold. This increase would appear to be largely entropic in nature because, for all the data reported here, there is little or no evidence that values of k_2/k_{-1} are temperature-dependent. Very roughly, values of k_2/k_{-1} increase with the increased bulk (molar volumes) of L$_w$ and L$_s$. On the basis of diffusion coefficients,[11] one would expect values of both k_{-1} and k_2 to decrease with the increasing

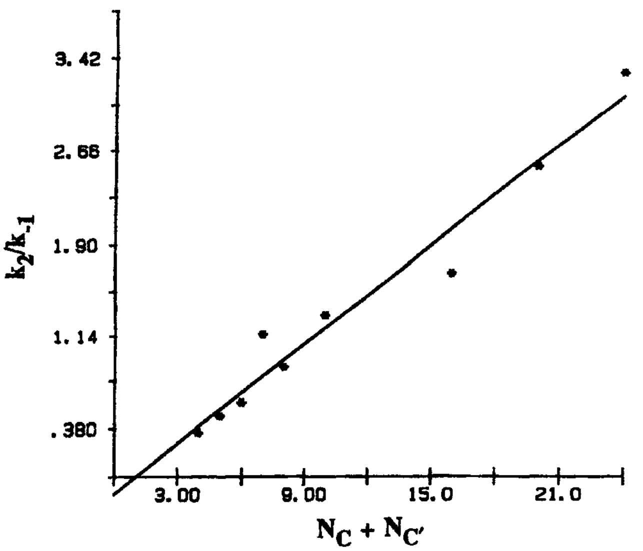


Figure 4. Plot of the "competition ratios", k_2/k_{-1}, *vs* the number of carbons N_C, $N_{C'}$ in R, R′ for PhR (L_w in (η^2-PhR)Cr(CO)$_5$, the photogenerated intermediate) and in (η^2-CH$_2$=CHR′)Cr(CO)$_5$, the reaction product.

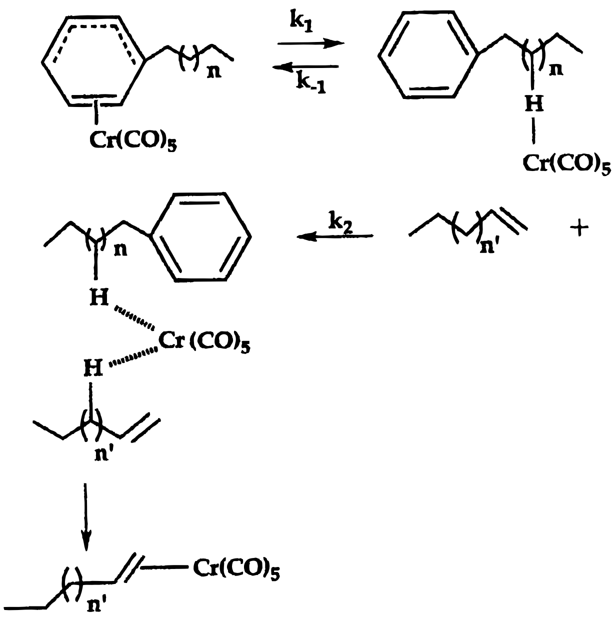
bulk of R, consistent with the data for L_w, but the *opposite* of what one would anticipate for PhR. There are no apparent correlations between rate constants and the carbonyl stretching frequencies determined for the (η^2-PhR)Cr(CO)$_4$ complexes (Table 1), which change rather little along the series.

The carbonyl stretching spectra are consistent with C_{4v} local symmetry of the carbonyls about Cr, as would be expected for replacement of one CO from the octahedron, affording a square pyramidal geometry for the Cr(CO)$_5$ moiety.

Several correlations of the competition rations, k_2/k_{-1}, with various properties of PhR and L_s were evaluated, the best of which is a linear relationship between the number of carbons, N_C and $N_{C'}$, in the chains for PhR and R′(CH=CH$_2$), respectively, and the competition ratios. For nine data sets (Figure 4) the correlation coefficient is 0.986.

This empirical relationship strongly suggests that both R and R′ play a vital role in the exchange process. The chain-walk mechanism first proposed by Simon and Xie, which hypothesizes that the Cr moves along the chain through a sucession of −C−H···Cr···H−C− transition states,[12] must be considered in this regard. This mechanism was first applied to results from studies of rates of reaction of [Cr(CO)$_5$] with long-chained alcohols. It was later considered as a possible *intra*molecular process to account for near-zero entropies of activation and significantly lower enthalpies of activation *vs* L_w−Cr bond strengths,[7] for L_w, L_s exchange in a number of (L_w)Cr(CO)$_5$ complexes. Zerić and Hall have calculated that a nondissociative transition state exists between C(H)−W interactions involving each of the two carbons in ethane.[13]

Scheme 2



Activation parameters derived from k_1 for these reactions are given in Table 1, *vide supra*. The error limits for values for $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$ were derived through propagation of the rather large experimental uncertainties associated with the intercepts of the reciprocal plots. They are the same within experimental error. The entropies of activation, near zero, are certainly consistent with a chain-to-chain exchange process.

In simplest terms, one can view the exchange process, at least at low concentrations of trap, as a pre-equilibrium, k_1/k_{-1}[PhR], between the edge-on and agostically-bonded (PhR)Cr(CO)$_5$ species, followed by the chain-interchange process governed by k_2[L_s] (Scheme 2). If the chain-interchange process were governed by a probability of exchange based solely on the number of H's on each chain (N_H, $N_{H'}$), the variation in overall rates would be based on an entropy effect; log(N_H)($N_{H'}$) would vary linearly with k_2/k_{-1}. This fit (concave downward) is not as good ($R = 0.96$) as is the fit of the plot of ($N_C + N_{C'}$) *vs* k_2/k_{-1} (Figure 4). However, when one considers all the factors which should be involved in such a complex process, which include, but are not limited to, chain folding, differences in exchange rates involving primary, secondary, and tertiary hydrogens,[13] and influences in k_1/k_{-1} as functions of chain length and chain branching, it would be premature to speculate further. Studies are in progress to assess the generality of the influence of chain length on k_2/k_{-1} and to attempt to evaluate some of the factors which might influence the relationship.

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Supporting Information Available: Tables of values of k_{obsd} for the kinetics studies (7 pages). Ordering information is given on any current masthead page.

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