F-Bonded (1-Fluorohexane)pentacarbonyltungsten(0)

Gerard R. Dobson,* Jaap P. Smit, Santino Ladogana, and Waylan B. Walton

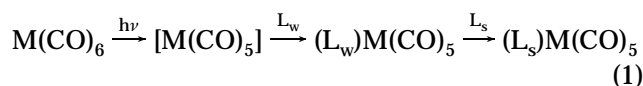*Department of Chemistry, University of North Texas, Denton, Texas 76203*

Fluoroalkanes, potentially ambidentate, can interact with W through coordination of F or agostically through a three-center, two-electron C(H)−M bond. The site of bonding of 1-fluorohexane to [W(CO)$_5$] in (1-C$_6$H$_{13}$F)W(CO)$_5$ generated by pulsed laser flash photolysis of W(CO)$_6$/1-fluorohexane solutions in the absence and presence of 1-hexene as a trapping nucleophile has been evaluated. The data indicate that W−F bonding is favored and suggest that linkage isomerization takes place through an intramolecular pathway.

Introduction

Weak nucleophiles (L$_w$) such as halogenated alkanes and arenes are potentially ambidentate. Thus, in their (L$_w$)Cr(CO)$_5$ complexes, C$_6$H$_5$X molecules (X = F, Cl, Br) exhibit two accessible binding sites, either through a lone pair on X (Cl, Br) or in a di*hapto* fashion edge-on to the ring (F).[1,2] In such cases, it is of interest to determine which binding site is thermodynamically the more stable and to probe possible "linkage isomerization" through which it might be interconverted.

Fluoroalkanes have the potential to bind weakly to W either through a three-center, two-electron C−H−W agostic interaction[3] or through a lone pair on F. Hackett, Rayner, and co-workers obtained gas-phase equilibrium constants for the interaction of photogenerated [W(CO)$_5$] with short-chained fluoroalkanes, CH$_3$F, CH$_3$-CH$_2$F, and others, and *presumed* they bound agostically to W.[4] Very recently, Zarić and Hall carried out *ab initio* calculations from which the L$_w$−W bond energies for (L$_w$)W(CO)$_5$ species (L$_w$ = CH$_4$, C$_2$H$_6$, C$_3$H$_8$, CH$_3$F, and others) have been determined.[5] For alkanes, they found that the lowest energy geometry is di*hapto*, involving interaction of both H and C with W, and that bond strength increases with increasing substitution of H by C in the C−H$_n$ functionality. However, their calculations also indicate that the CH$_3$F−W bond is lower in potential energy than are the agostic bonds; otherwise, their results are largely in agreement with the experimental results of Hackett, Rayner, and co-workers.[4]

It, thus, is important to ascertain *experimentally* whether the preferred binding site to W(CO)$_5$ is through F or C(H). This can be achieved by comparing the kinetics and mechanism of the displacement of L$_w$ from photogenerated (L$_w$)W(CO)$_5$ by a more strongly-bonding "trapping" nucleophile, L$_s$,

$$M(CO)_6 \xrightarrow{h\nu} [M(CO)_5] \xrightarrow{L_w} (L_w)M(CO)_5 \xrightarrow{L_s} (L_s)M(CO)_5 \tag{1}$$

where L$_w$ is the closely-related *n*-heptane (*n*-C$_6$H$_{13}$CH$_3$) previously studied[6] and 1-fluorohexane (1-C$_6$H$_{13}$F) and L$_s$ = 1-hexene (*n*-C$_4$H$_9$CH=CH$_2$). 1-Fluorohexane was chosen for study to minimize the perturbation produced by F in short hydrocarbon chains.[4,5] If bonding in 1-fluorohexane is agostic rather than through F, the kinetics results are expected to be quite similar to those which have been observed for *n*-heptane.[6]

Experimental Section

Hexacarbonyltungsten(0) (Pressure Chemical Company) was vacuum-sublimed before use. 1-Fluorohexane was obtained from three independent sources (Aldrich, Pfaltz and Bauer, and Lancaster Synthesis); one sample was used as received, and the other two were fractionally distilled under nitrogen from anhydrous MgSO$_4$ or from P$_2$O$_5$. The purified samples were analyzed by gas chromatography (GC), and no other volatile components were observed to be present. 1-Hexene (Johnson Matthey) was fractionally distilled under nitrogen from MgSO$_4$. Pulsed laser flash photolysis studies were carried out both at the Center for Fast Kinetics Research (CFKR), University of Texas at Austin (Nd:YAG laser photolyzing source, 351 nm), and locally (N$_2$ excimer laser photolyzing source, 337 nm). Descriptions of the equipment at CFKR[7] and the photolyzing, infrared, and UV−vis analyzing trains we employ have been given.[8,9]

Reagents were weighed rather than measured volumetrically. Solutions of W(CO)$_6$ (3 × 10^{-3} M)/1-C$_6$H$_{13}$F were prepared both in the absence and presence of 1-hexene as a trapping nucleophile. Photolysis was carried out after the solution had been flushed with nitrogen under a nitrogen blanket. The wavelength monitored for kinetics runs was 430 nm. Pseudo first-order rate constants, k_{obsd}, were analyzed by employing Asyst-based computer programs. Values of k_{obsd} are given in a table in the Supporting Information. Uncertainties of the measurements, given in parentheses, are the limits of error of the last digit(s) of the value, to one standard deviation.

Results and Discussion

Figure 1 illustrates time-resolved visible spectra obtained after pulsed laser flash photolysis of W(CO)$_6$/1-C$_6$H$_{13}$F/*n*-C$_4$H$_9$CH=CH$_2$ solutions, in which [*n*-C$_4$H$_9$-CH=CH$_2$] differed significantly. For each, an intermediate (Int; λ_{max} = 430 nm) is produced initially. At low

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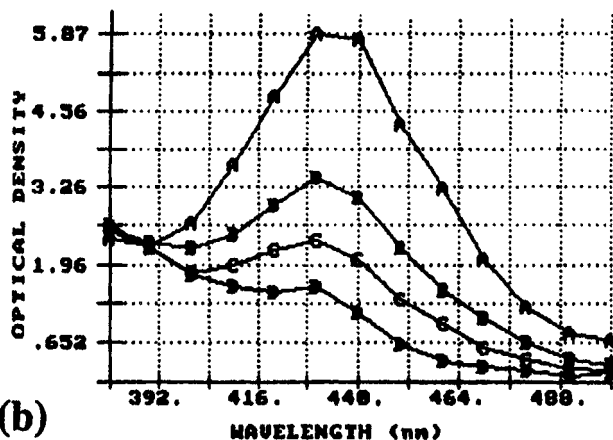(7) Zhang, S.; Dobson, G. R. *Inorg. Chem.* **1989,** *28,* 324−328.
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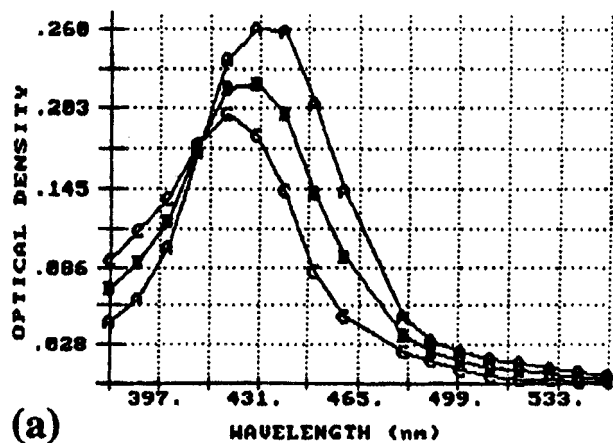
(a)

(b)

Figure 1. (a) Time-resolved spectra for reaction after pulsed laser flash photolysis of $W(CO)_6/1\text{-}C_6H_{13}F/n\text{-}C_4H_9\text{-}CH=CH_2$ (0.0853 M) at 25.0 °C. Times after the flash: curve A, 8.6 μs; curve B, 37.4 μs; curve C, 150.4 μs; (b) Time-resolved spectra of $W(CO)_6/1\text{-}C_6H_{13}F/n\text{-}C_4H_9CH=CH_2$ (1.9698 M). Times after flash: curve A, 5.9 μs; curve B, 11.0 μs; curve C, 17.7 μs; curve D, 74.0 μs.

$[n\text{-}C_4H_9CH=CH_2]$, this transient largely decays to afford a species exhibiting λ_{max} at *ca.* 415 nm. At high $[n\text{-}C_4H_9\text{-}CH=CH_2]$, it decays largely to a species with $\lambda_{max} < 400$ nm. At 25.0 °C, a plot of k_{obsd} *vs* $[n\text{-}C_4H_9CH=CH_2]$ (Figure 2) obeys the equation

$$-d[\text{Int}]/dt = k_a[\text{Int}] + k_b[\text{Int}][n\text{-}C_4H_9CH=CH_2] \quad (2)$$

This rate law is indicative of two competing reaction pathways. It differs qualitatively from that for reaction of photogenerated $(n\text{-}C_6H_{13}CH_3)W(CO)_5$ with $n\text{-}C_4H_9\text{-}CH=CH_2$[6] and for several $(L_w)M(CO)_5$ species (M = Cr, Mo, W; L_w = cyclohexane, benzene, RX (R = $n\text{-}C_4H_9$, C_6H_5; X = F, Cl, Br)),[6,8–12] for which the data support a mechanism in which $(L_w)M(CO)_5$ reversibly dissociates to afford $[M(CO)_5]$, which is trapped by L_s (= 1-hexene), eq 3.

$$(L_w)M(CO)_5 \underset{k_{-1}[L_w]}{\overset{k_1}{\rightleftharpoons}} [M(CO)_5] \xrightarrow{k_2[L_s]} (L_s)M(CO)_5 \quad (3)$$
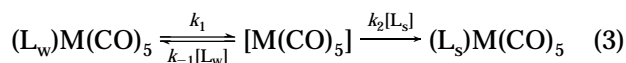
A comparison of Figures 1 and 2 indicates, for plots of k_{obsd} *vs* $[n\text{-}C_4H_9CH=CH_2]$, that the intercept is
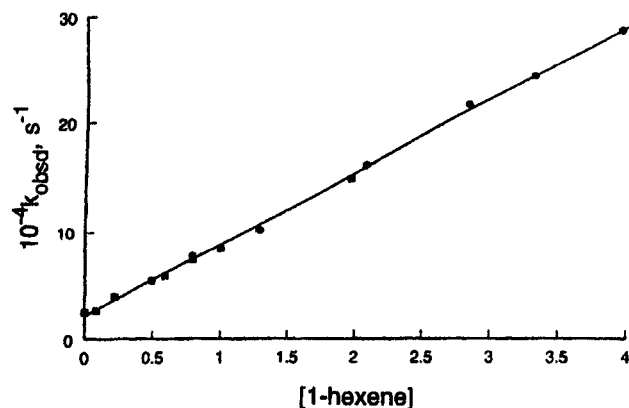
Figure 2. Plot of k_{obsd} *vs* $[n\text{-}C_4H_9CH=CH_2]$ at 25.0 °C after pulsed laser flash photolysis of $W(CO)_6/1\text{-}C_6H_{13}F/n\text{-}C_4H_9\text{-}CH=CH_2$ solutions. ● and ■ represent data obtained from separate studies.

attributable to the unimolecular reaction of Int to afford the species absorbing at 415 nm. The slope corresponds to the rate of disappearance of Int to afford a species which absorbs at <400 nm, *i.e.*, $(\eta^2\text{-}C_4H_9CH=CH_2)W\text{-}(CO)_5$.[11] Activation parameters derived from the intercepts for kinetics runs at seven temperatures (16.2–35.7 °C) are $\Delta H_a^{\ddagger} = 4.5(4)$ kcal/mol and $\Delta S_a^{\ddagger} = -23.3(15)$ cal/K mol. These are qualitatively different from those observed for several related studies, not expected if the ligand-dependent pathway is derived through reaction of the photogenerated $(1\text{-}C_6H_{13}F)W(CO)_5$ with an impurity.[13] Moreover, 1-fluorohexane obtained from three separate sources, purified by two methods, and checked for purity by GC afforded the same values for k_a within ±5%. The intercept is far too large to be attributable to reaction of $[W(CO)_5]$ with either CO, the N_2 blanket, or unphotolyzed $W(CO)_6$.[14]

Attempts to obtain infrared (carbonyl stretching) data for the product of this reaction were hampered by low I_0 values above 1954 cm^{-1}. However, it was found that $(1\text{-}C_6H_{13}F)W(CO)_5$ absorbs at 1952 cm^{-1} and that the growth of an absorption band for the product (1934 cm^{-1}) corresponds to the decay governed by k_a observed at 430 nm (Figure 3; *vide supra*).

We are unable to attribute the species produced by the pathway governed by k_1. Multiple flashes of $W(CO)_6/C_6H_{13}F$ solutions in the absence of a trap afford an insoluble brown product, which could arise from decomposition of the species produced *via* the ligand-independent pathway. A similar two-term rate law is observed after flash photolysis of $W(CO)_6/CCl_4/C_4H_9CH=CH_2$ solutions, which also affords precipitates, active olefinic disproportionation catalysts.[15,16] The activation of carbon–fluorine bonds in transition metal complexes has

(13) A solvent impurity capable of being trapped by photogenerated metal carbonyl fragments contributes an intercept to plots of k_{obsd} *vs* $[L_s]$ for studies such as this since its concentration is proportional to $[L_w]$ over low $[L_s]$ ranges, and $[L_w]$ remains essentially constant under these conditions. However, for carefully purified solvents, this effect should not be large.

(14) One can also rule out the possibility that the intercept is attributable to the formation of either $W_2(CO)_{11}$ produced through combination of photogenerated $[W(CO)_5]$ with $W(CO)_6$ or $(N_2)W(CO)_5$ since no intercept is observed for solvents even more weakly coordinating than 1-fluorohexane under the reaction conditions employed here (flash photolysis experiments were conducted under a nitrogen blanket)(15) Dobson, G. R.; Smit, J. P.; Purcell, W.; Ladogana, T. *J. Organomet. Chem.*, in press.

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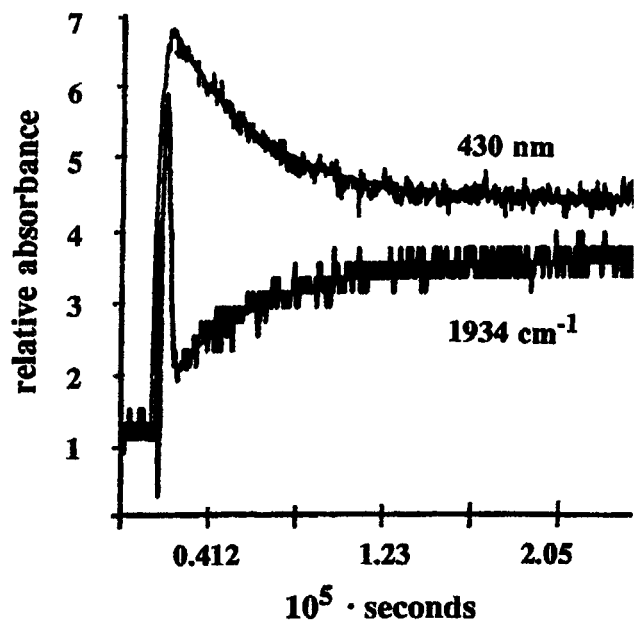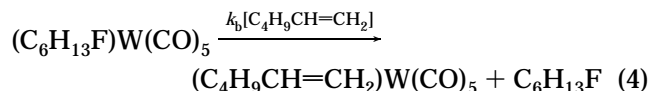
Figure 3. A comparison of plots of relative absorbance *vs* time for reactions taking place after flash photolysis of $W(CO)_6$/1-$C_6H_{13}F$ solutions, monitoring 430 nm and 1934 cm^{-1} at ambient temperature.

Figure 4. Plot of voltage *vs* time after pulsed laser flash photolysis of a $W(CO)_6$/1-$C_6H_{13}F$/$C_4H_9CH=CH_2$ (1.0316 M) solution, monitored at 440 nm at 35.7 °C. The "noise" at the beginning of the trace is electronic; the line represents *ca.* 2 half-lives for the decay of photogenerated (1-$C_6H_{13}F$)W-$(CO)_5$ under the stated reaction conditions. The slow decay represents the disappearance of photogenerated (1-$C_6H_{13}F$)W(CO)$_5$.

been widely observed, and under special circumstances, it has been found that oxidative addition of perfluoro-alkanes can take place in group 6 metal carbonyl complexes (M = Mo, W).[17]

The highly negative entropy of activation associated with k_a is consistent with crowding in the transition state, which might accompany an increase in coordination number, *e.g.*, for an oxidative addition process. It also is known that certain group 4 halides (Ge, Sn) oxidatively add to $W(CO)_6$ to afford $W^{II}(CO)_5(X)(MX_3)$ and CO.[18] However, the carbonyl stretching frequencies observed in these species are significantly elevated from their values in $W(CO)_6$,[19] inconsistent with the observation in this study of a product band at 1934 cm^{-1}.

Two mechanisms for the portion of the rate law governed by k_b (eq 2) should be considered. The linearity of the plots of k_{obsd} *vs* [n-$C_4H_9CH=CH_2$] observed here is consistent with a solvent displacement mechanism, eq 4. The observed activation parameters,

$$(C_6H_{13}F)W(CO)_5 \xrightarrow{k_b[C_4H_9CH=CH_2]}$$
$$(C_4H_9CH=CH_2)W(CO)_5 + C_6H_{13}F \quad (4)$$

$\Delta H_b^{\ddagger} = 8.5(5)$ kcal/mol[5] and $\Delta S_b^{\ddagger} = -7.9(15)$ cal/K mol, are consistent with such a pathway. Moreover, displacement pathways in photogenerated $(L_w)M(CO)_5$ complexes become increasingly prominent along the series Cr, Mo, W.[20] As noted above, the rate law
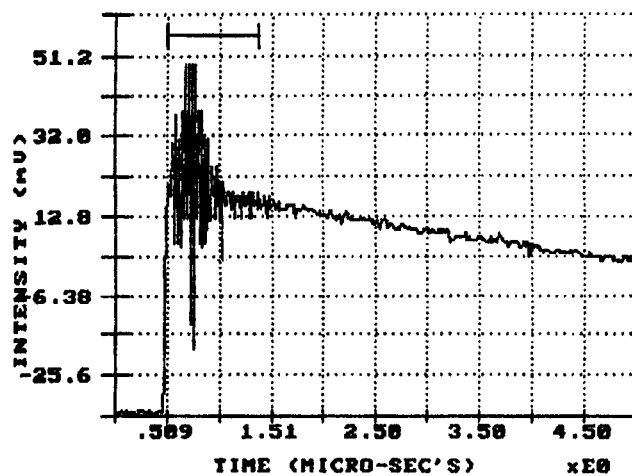
observed here (eq 2) is that observed in analogous reactions of photogenerated $(CCl_4)W(CO)_5$.[15]

The results also are explicable in terms of the mechanism shown in eq 3, where a pre-equilibrium between $(L_w)M(CO)_5$ and $[M(CO)_5]$ exists, *i.e.*, $k_{-1} >> k_2$. Under these conditions, $k_b = k_1k_2[n$-$C_4H_9CH=CH_2]/k_{-1}[L_w]$, consistent with what is observed. However, for the pathway dependent on [n-$C_4H_9CH=CH_2$] most commonly observed in L_w-displacement reactions, including that for $(n$-$C_6H_{13}CH_3)W(CO)_5$, plots of k_{obsd} *vs* [L_s] are usually curved, indicating that a $(C_6H_{13}F)W(CO)_5 \rightleftharpoons [W(CO)_5]$ pre-equilibrium does not exist; for $(n$-$C_7H_{16})W$-$(CO)_5$, k_2/k_{-1} is observed to be *ca.* 1.2.[6]

The second-order rate constant, k_b, for displacement of 1-$C_6H_{13}F$ from (1-$C_6H_{13}F$)W(CO)$_5$ by $C_4H_9CH=CH_2$ is 6.72(6) × 10^4 M^{-1} s^{-1} at 25.0 °C. If the limiting form of the dissociative interchange pathway describes k_b, the n-heptane and 1-fluorohexane data can be compared, since $k_b = k_1k_2/k_{-1}[C_6H_{13}F]$. This value is 5.15(5) × 10^5 M^{-1} s^{-1} [6] or *ca.* 5% of the n-heptane value. Whichever is the mechanism for fluorobenzene displacement, the rate of displacement of 1-fluorohexane from its $(L_w)W$-$(CO)_5$ complex is substantially less than that for $L_w =$ n-heptane. This observation clearly demonstrates that F−Cr bonding is favored over agostic C−H−W bonding.

Since the photogenerated [W(CO)$_5$] species is very reactive (femtosecond time scale),[21] it is difficult to envision the possibility that both −C−H−W and −F−W linkage isomers are not produced immediately after the flash; the alkyl end of 1-$C_6H_{13}F$ is very similar to n-$C_6H_{13}CH_3$. Statistically, interaction of W with the alkyl end of the 1-$C_6H_{13}F$ molecule should be favored over interaction with the F end. A k_1/k_{-1} pre-equilibrium does not exist for $(n$-$C_6H_{13}CH_3)W(CO)_5$ (nor, therefore, for the hydrocarbon end of $C_6H_{13}F$). Thus, displacement of $C_6H_{13}F$ bonded both through −C−H−W and −F−W linkages should afford plots of absorption *vs* time exhibiting *two* exponential decays, a fast decay

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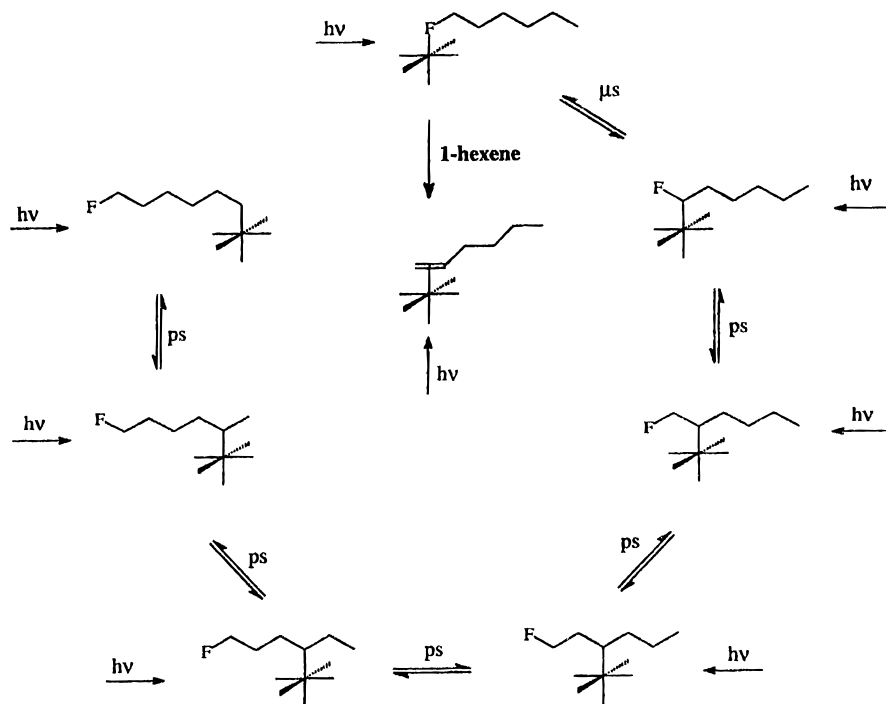
Figure 5. The "chain-walk" mechanism (Xie and Simon, ref 22). It is presumed that all species are produced initially upon photolysis.

for the former and a slow decay for the latter. In systems in which the alkane and a second functional group are present as two *different* molecules, for flash photolysis of $Cr(CO)_5$/*n*-heptane/fluorobenzene solutions in the presence of 1-hexene trap, two decays, the faster for $(n\text{-}C_6H_{13}CH_3)Cr(CO)_5$ and the slower for $(\eta^2\text{-fluoro-robenzene})Cr(CO)_5$, are in fact observed.[10]

However, no fast decay corresponding to displacement of agostically-bonded $C_6H_{13}F$ from $(C_6H_{13}F)W(CO)_5$ is observed for plots of k_{obsd} *vs* $[C_4H_9CH=CH_2]$ on time scales for which it should be observed (Figure 4). The data thus indicate that linkage isomerization (eq 5) does not take place *via* initial $C(H)-W$ bond fission.

$$(FC_5H_{12}CH)W(CO)_5 \rightarrow (C_6H_{13}F)W(CO)_5 \qquad (5)$$
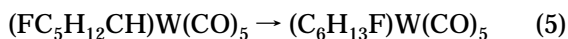
Linkage isomerization may involve an intramolecular "chain walk" along the hydrogens (picosecond time scale; Figure 5), as first proposed by Simon and co-workers.[22] Zarić and Hall have calculated that a nondissociative transition state exists between agostic $C(H)-W$ interactions involving each of the two carbons in ethane in $(\text{ethane})W(CO)_5$.[5] Evidence consistent with the accessibility of an intramolecular chain-walk has been obtained for reactions of $(\eta^2\text{-}C_6H_5R)Cr(CO)_5$ with $R'CH=CH_2$ traps where R,R′ are linear alkyl chains of varying lengths.[23]

The enthalpies of activation for ligand exchange in $(1\text{-}C_6H_{13}F)W(CO)_5$ and $(n\text{-}C_6H_{13}CH_3)W(CO)_5$, 8.5(5) and

8.4(5) kcal/mol, respectively, are the same within experimental error. The entropy of activation is more negative for the $1\text{-}C_6H_{13}F$ complex than for that containing $n\text{-}C_6H_{13}CH_3$, $-7.9(17)$ *vs* $+1.8(17)$ [10] cal/K mol, consistent with more bond breaking in the transition state leading to $n\text{-}C_6H_{13}CH_3$ displacement. This should lower the enthalpy of activation for $1\text{-}C_6H_{13}F$ displacement relative to the $W-F$ bond dissociation energy.

Summary

Kinetics results indicate that 1-fluorohexane binds preferentially to F rather than to C(H) in (1-fluorohexene)$W(CO)_5$ generated by pulsed laser flash photolysis, consistent with the results of the *ab initio* quantum mechanical calculations in closely-related systems. The data suggest an intramolecular $Cr-H-C$ to $Cr-F$ linkage isomerization process in this complex.

Supporting Information Available: A table listing values of k_{obsd} for reactions after pulsed laser flash photolysis of $W(CO)_6$/1-fluorohexane solutions in the absence and presence of 1-hexene trap at various temperatures (1 page). Ordering information is given on any current masthead page.

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