

Mechanism and Energetics of Silane and THF Displacement from the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$ and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{THF})$ Complexes

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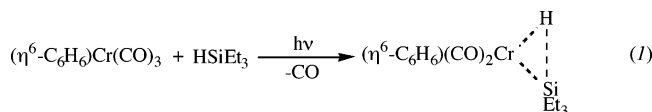
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The displacement of Et_3SiH and THF from the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$ and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{THF})$ complexes has been studied. Both solvents are displaced from the metal center by a dissociative mechanism. Kinetic and thermodynamic measurements suggest that the Cr–HSiEt₃ bond is ~ 3 kcal/mol more stable than the Cr–THF interaction.

Introduction

The study of the metal–silane bond is motivated by the importance of hydrosilation reactions.¹ The bonding between a metal center and a silane molecule can be described as lying between two extremes: an “arrested” oxidative addition complex where the primary interaction is between the $\text{R}_3\text{Si–H}$ bond and the metal center (an η^2 bond) or complete oxidative addition resulting in the formation of two localized M–H and M–Si σ bonds.

The $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$ complex has been generated by the photolysis of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in the presence of silane in low-temperature matrixes and in the solution phase.^{2–4} Previous studies have suggested



that $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$, like the analogous $\text{CpMn}(\text{CO})_2(\text{HSiEt}_3)$ complex, can be described as a σ complex with a three-center two-electron bond between the metal, Si, and H atoms.^{3,5} While the displacement of silane from the metal center in complexes such as $\text{Cr}(\text{CO})_5(\text{HSiEt}_3)$ and $\text{CpMn}(\text{CO})_2(\text{HSiR}_3)$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) has been investigated, we are not aware of any analogous studies with the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$ complex.^{6–8}

Investigating the reactivity of the Cr–HSiEt₃ bond is also of interest because weakly solvated metal complexes have been implicated as intermediates in a variety of organometallic reactions.⁹ Unlike the $\text{M}(\text{CO})_5(\text{solv})$ [$\text{M} = \text{Cr}, \text{Mo}, \text{W}$] and $\text{CpMn}(\text{CO})_2(\text{solv})$ complexes,^{10–12}

relatively little is known about the mechanism and energetics of solvent substitution from the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{solv})$ complexes. The displacement of hydrocarbon solvents such as heptane and cyclohexane from the $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2(\text{solv})$ complexes by CO has been investigated using laser flash photolysis,¹³ and the activation parameters indicated that the substitution reaction proceeded through an interchange mechanism. In contrast, a dissociative pathway was shown to contribute to the displacement of H_2 and N_2 from the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{H}_2)$ and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{N}_2)$ complexes observed in supercritical Xe.⁴ Thus, it would appear that the actual substitution pathway may depend on the strength of the Cr–solvent bond. In the case of weakly coordinating solvents such as hydrocarbons, an interchange mechanism is operative, but with relatively more stable complexes such as $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{H}_2)$ a purely associative or interchange mechanism can be ruled out.

We report in this paper a energetic and mechanistic study of the displacement of triethylsilane and tetrahydrofuran (THF) from the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$ and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{THF})$ complexes. The strength of both Cr–solv bonds is estimated and provides an interesting comparison with the previously determined $\text{Cp}(\text{CO})_2\text{Mn}$ –solv bond strengths.

Experimental Section

Kinetic studies were done under an Ar atmosphere, although runs where air was not rigorously excluded yielded similar results. The UV–vis studies were performed using a HP8453 diode array spectrometer, while IR studies employed a variable-temperature cell (Graesby-Specac) and a Nicolet Magna FTIR operating at 2 cm^{-1} resolution.

(a) Kinetic Experiments. All runs were carried out under pseudo-first-order conditions. For the UV–vis experiments a

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typical run was performed as follows. A 0.9 mM solution of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in HSiEt_3 was added to a jacketed quartz cuvette (0.5 cm path length) using a gastight syringe. After thermal equilibration at the appropriate temperature (± 0.1 °C), the solution was photolyzed by a 150 W Xe arc lamp for 30 s, resulting in the generation of the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2\text{-}(\text{HSiEt}_3)$ complex. The run was initiated by addition of triethylphosphine to the photolyzed solution.

The infrared experiments were conducted in a similar fashion. A solution of 1 mM $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in tetrahydrofuran containing an appropriate amount of HSiEt_3 was added to a 0.2 mm CaF_2 cell. The cell was then cooled to the required temperature (± 1 °C), photolyzed for 15 s, and data collection initiated. All experiments were conducted under conditions where the regeneration of the parent tricarbonyl was always $< 10\%$ and in the majority of cases, $< 5\%$. The observed rate constants (k_{obs}) were obtained from fitting the absorbance versus time plots to a single-exponential function. The run to run reproducibility was found to be within 10%. Activation parameters were obtained from Eyring plots and are reported with 1σ uncertainties.

(b) Equilibrium Constant Determinations. To convert the equilibrium absorbances of the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{solv})$ complexes to concentrations, extinction coefficients of the solvated complexes were determined by photolyzing a known concentration of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in neat solvent for 10 s at 268 K. Since only peaks attributable to the appropriate solvate complex were observed, it was assumed that the amount of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{solv})$ generated was equal to the amount of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ photolyzed (typically $> 80\%$).¹⁴ Equilibrium constants were determined by converting the integrated equilibrium intensities of the CO stretching absorbances of the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$ and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{THF})$ complexes into concentrations. The equilibrium constants represent average values of four individual measurements, two at similar and two at different concentrations of the silane reactant.

All reagents were of $> 99\%$ purity except for triethylphosphine (97%). Anhydrous tetrahydrofuran (Acros), triethylsilane (Aldrich), triethylphosphine (Alfa), and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ (Strem) were used as received.

Results and Discussion

$(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3) + \text{PET}_3$. Photolysis of a 1 mM solution of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in triethylsilane at 268 K results in the formation of the previously observed $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$ complex with CO stretching frequencies of 1924 and 1870 cm^{-1} .²⁻⁴ As shown in Figure 1, in the presence of PET_3 , the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2\text{-}(\text{HSiEt}_3)$ complex is converted to $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{PET}_3)$ absorbing at 332 nm. While the product complex has not previously been observed, the analogous $(\eta^6\text{-C}_6\text{H}_6)\text{-Cr}(\text{CO})_2(\text{PPh}_3)$ complex has been isolated and found to be air stable.¹⁵ The displacement of the silane molecule from the Cr center by PET_3 follows first-order kinetics with the rate of decay of the Cr–silane complex equal to the rate of growth of the product. The observed rate constant (k_{obs}) is found to vary linearly with $[\text{PET}_3]$. While under some conditions, dissociative displacement of silane is expected to yield a linear dependence of k_{obs} on $[\text{PET}_3]$, an interchange or associative pathway can also lead to such a variation. However, it was observed that decreasing the concentration of Et_3SiH upon addition of heptane as the “inert” solvent resulted in an

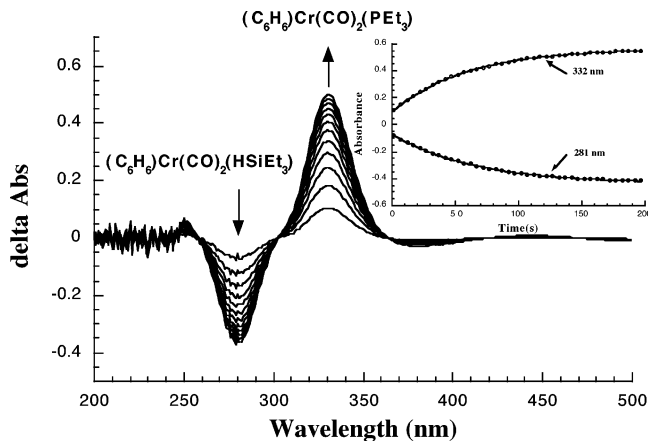
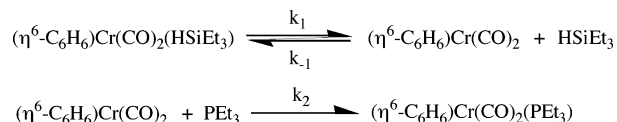


Figure 1. Difference UV–vis spectra obtained at 9 s intervals showing the reaction between $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2\text{-}(\text{HSiEt}_3)$ and PET_3 at 293 K with $[\text{PET}_3] = 0.61$ M. The growth and decay of the complexes is shown in the inset. Solid lines represent a first-order fit to the absorption vs time data.

increase of the observed rate constant. For example, at 288 K with $[\text{HSiEt}_3] = 6.0$ M and $[\text{PET}_3] = 0.32$ M, $k_{\text{obs}} = 9.6 \times 10^{-3} \text{ s}^{-1}$, and under the same concentration of PET_3 but with half as much silane, $k_{\text{obs}} = 1.7 \times 10^{-2} \text{ s}^{-1}$. The inverse dependence of the rate constant on the silane concentration suggests that the overall mechanism must include a step that involves reversible dissociation of the silane solvent molecule from the Cr center.

On the basis of the data, and as discussed later, the substitution reaction most likely follows the dissociative mechanism shown in Scheme 1,

Scheme 1



Applying the steady-state assumption to the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$ fragment, the dependence of k_{obs} on $[\text{HSiEt}_3]$ and $[\text{PET}_3]$ is

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{PET}_3]}{k_{-1} [\text{HSiEt}_3] + k_2 [\text{PET}_3]} \quad (1)$$

Because a plot of k_{obs} versus $[\text{PET}_3]/[\text{HSiEt}_3]$ is linear (Figure 2), we conclude that under the present experimental conditions of $[\text{HSiEt}_3] \gg [\text{PET}_3]$, $k_{-1} [\text{HSiEt}_3] > k_2 [\text{PET}_3]$ and eq 1 reduces to

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{PET}_3]}{k_{-1} [\text{HSiEt}_3]} \quad (2)$$

According to eq 2, the slope of a plot of k_{obs} versus $[\text{PET}_3]/[\text{HSiEt}_3]$ is equal to $k_1 k_2 / k_{-1}$. An Eyring plot obtained from these rate constants, shown in Table 1, yields activation enthalpies and entropies that include contributions from each step in the overall mechanism. Thus, $\Delta H_{\text{tot}}^{\ddagger} = \Delta H_1^{\ddagger} + (\Delta H_2^{\ddagger} - \Delta H_{-1}^{\ddagger})$ and $\Delta S_{\text{tot}}^{\ddagger} = \Delta S_1^{\ddagger} + (\Delta S_2^{\ddagger} - \Delta S_{-1}^{\ddagger})$.

From the temperature independence of the reaction rate constants, gas phase studies have shown that the

(14) This appears to be a reasonable assumption since previous studies have shown that photochemical synthesis of monosubstituted $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2\text{L}$ complexes from $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ proceeds in high yield. See ref 15.

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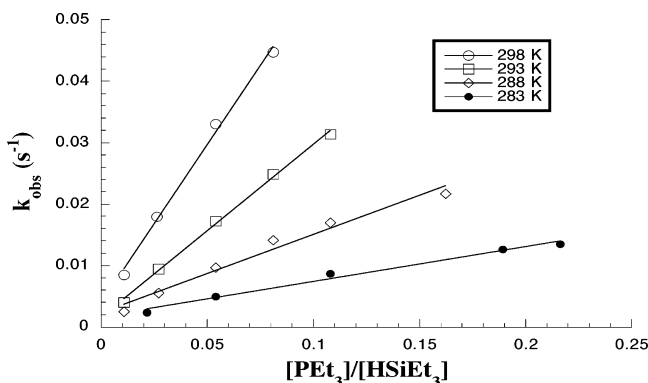


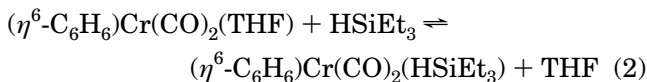
Figure 2. Plot of k_{obs} vs $[\text{PET}_3]/[\text{HSiEt}_3]$ at different temperatures.

Table 1. Values for k_1k_2/k_{-1} Obtained from a Fit to the k_{obs} vs $[\text{PET}_3]/[\text{HSiEt}_3]$ Data

T (K)	$k_1k_2/k_{-1} \times 10^2$ (s^{-1})
283	5.6 ± 0.4
288	12.7 ± 1.0
293	28.1 ± 0.8
298	51.5 ± 2.6

$(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$ fragment reacts without an activation barrier, and so it is likely that $\Delta H^\ddagger_2, \Delta H^\ddagger_{-1} \approx 0$.¹⁶ Under these conditions, $\Delta H^\ddagger_{\text{tot}} \approx \Delta H^\ddagger_1$, and it becomes possible to estimate the strength of the Cr–silane interaction. From the Eyring plots, $\Delta H^\ddagger_{\text{tot}} = 24.3 \pm 1.2$ kcal/mol and $\Delta S^\ddagger_{\text{tot}} = +21.8 \pm 4.1$ eu. Assuming that the activation entropies for the reaction of the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$ fragment with HSiEt_3 and PET_3 are not significantly different, the large positive value for $\Delta S^\ddagger_{\text{tot}}$ ($\approx \Delta S^\ddagger_1$) suggests that the Cr–silane bond is largely dissociated in the transition state. As a further check on the mechanism of the reaction and on the reliability of the activation enthalpy in providing an estimate of the Cr– HSiEt_3 bond strength, we decided to investigate the displacement of the THF molecule from the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{THF})$ complex by Et_3SiH .

The strengths of the $\text{Cp}(\text{CO})_2\text{Mn-HSiEt}_3$ and $\text{Cp}(\text{CO})_2\text{Mn-THF}$ interactions have been estimated at 28 and 24 kcal/mol, respectively.^{7,17,18} These results suggested to us that if the difference in the Cr–solv bond strengths of the analogous $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$ and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{THF})$ complexes was similar, then it would be possible to observe an equilibrium between the two complexes and measure ΔH for the reaction



Thus, if both THF and Et_3SiH undergo dissociative displacement from the respective $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{solv})$ complexes by *different* incoming ligands, and if the activation parameters provide a reasonable estimate for the strength of the Cr–solv interactions, then these kinetic parameters should yield an independent estimate for ΔH . Any similarity between the ΔH values determined by both kinetic and thermodynamic mea-

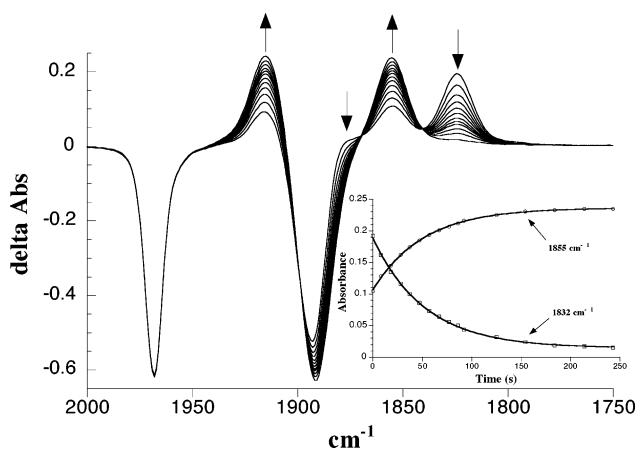


Figure 3. Difference IR spectra showing the reaction of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{THF})$ with HSiEt_3 ($[\text{HSiEt}_3] = 2.50$ M and $[\text{THF}] = 7.37$ M) at 253 K. Spectra are at 10 s intervals except for the last three, which are obtained at 20, 30, and 60 s intervals, respectively. The inset shows the growth and decay of the respective complexes. The solid line represents a first-order fit to the absorbance vs time data.

surements would then strengthen the case for a dissociative mechanism of silane displacement and also provide a reliable estimate for the strength of the Cr– HSiEt_3 and Cr–THF interactions.

$(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{THF}) + \text{HSiEt}_3$. Photolysis of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in THF solvent results in the formation of the previously observed $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{THF})$ complex with CO stretching absorbances at 1883 and 1821 cm^{-1} .¹⁹ This complex is unstable at room temperature, and its reaction with Et_3SiH was studied using IR spectroscopy at below ambient temperatures.

(a) Equilibrium Studies. As shown in Figure 3, photolysis of a solution of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in THF solvent with added Et_3SiH results in the conversion of the initially formed $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{THF})$ complex to the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$ product molecule. Interestingly, under conditions of higher temperature and low silane concentration, equilibrium is reached between the reactant and product complexes (see Figure 4).

The temperature range over which the equilibrium was studied was rather narrow (± 10 K). At higher temperatures the reactant Cr–THF complex was not stable, and at the lower temperatures the low silane concentrations required to observe an equilibrium resulted in significant back-reaction with CO to form the parent tricarbonyl. The K_{eq} values obtained from the equilibrium concentrations of the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{THF})$ and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$ complexes are presented in Table 2. The temperature dependence of the equilibrium constant yields an enthalpy change of $\Delta H = -2.8 \pm 1.0$ kcal/mol and a ΔS (at 273 K) ≈ 0 cal/mol K for reaction 2. Thus, neglecting enthalpic contributions from solvation effects, the results suggest that the Cr– HSiEt_3 bond is ~ 3 kcal/mol stronger than the Cr–THF interaction.

(b) Kinetic Studies. As shown in Figure 3, the decay and growth of the respective complexes exhibit first-order behavior and yield similar observed rate constants. A plot of k_{obs} versus $[\text{Et}_3\text{SiH}]$ is linear and as

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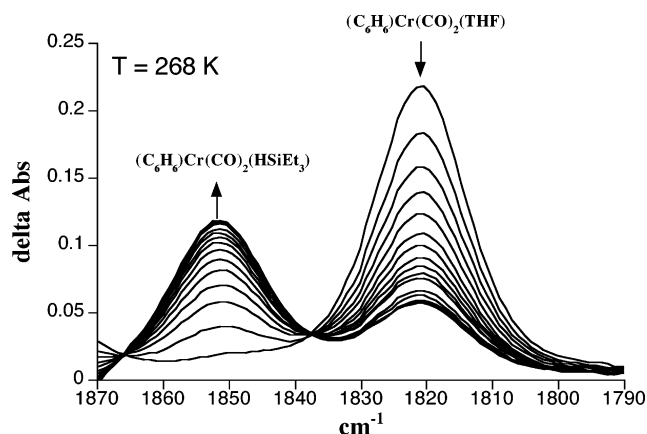
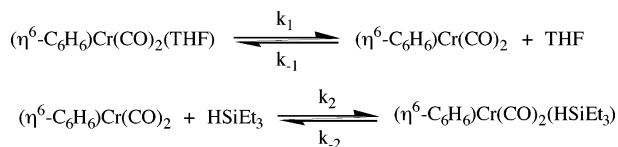


Figure 4. IR spectra showing the establishment of an equilibrium between the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{THF})$ and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$ complexes. ($[\text{THF}] = 12 \text{ M}$, $[\text{Et}_3\text{SiH}] = 0.13 \text{ M}$). First 11 spectra are at 30 s intervals and the remaining at 90 s intervals.

Table 2. Values of k_1k_2/k_{-1} (Scheme 2) and K_{eq} for Reaction 2

T (K)	$k_1k_2/k_{-1} \times 10^2$ (s^{-1})	K_{eq}
273		206 ± 16
268		221 ± 13
263	24.8 ± 0.6	250 ± 16
258	10.5 ± 0.2	
253	4.5 ± 0.2	
248	2.0 ± 0.1	

Scheme 2



noted earlier does not distinguish between an associative, interchange, or dissociative mechanism of THF displacement. However, k_{obs} is inversely related to the THF concentration since it doubles when the concentration of THF is reduced by a factor of 2 while holding $[\text{Et}_3\text{SiH}]$ constant. Thus, similar to the displacement of Et_3SiH by PEt_3 , the experimental data suggest this reaction also proceeds by the dissociative pathway shown in Scheme 2. Since equilibrium is achieved under some experimental conditions, the last step in the reaction (k_{-2}) is shown to be reversible.

Applying the steady-state approximation to the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$ complex and assuming that $k_{-1}[\text{THF}] \gg k_2[\text{HSiEt}_3]$,²⁰ the dependence of k_{obs} on $[\text{HSiEt}_3]$ is

$$k_{\text{obs}} = \frac{k_1k_2[\text{HSiEt}_3]}{k_{-1}[\text{THF}]} + k_{-2} \quad (3)$$

According to eq 3, a plot of k_{obs} versus $[\text{HSiEt}_3]/[\text{THF}]$ should be linear with a nonzero intercept equal to k_{-2} (Figure 5).

(20) Although some experiments were conducted under conditions of $[\text{THF}] \approx [\text{Et}_3\text{SiH}]$, it is still reasonable to suggest that $k_{-1}[\text{THF}] \gg k_2[\text{Et}_3\text{SiH}]$ since previous studies have suggested that coordinatively unsaturated metal carbonyls can show some difference in reactivity toward different ligands (i.e., $k_{-1} > k_2$). For example, the $\text{Cr}(\text{CO})_5$ fragment can react almost 3 times faster with benzene than with 1-hexene.²⁴ Since THF is expected to be a better nucleophile than Et_3SiH , it is reasonable to expect that k_{-1}/k_2 may be greater than 1.

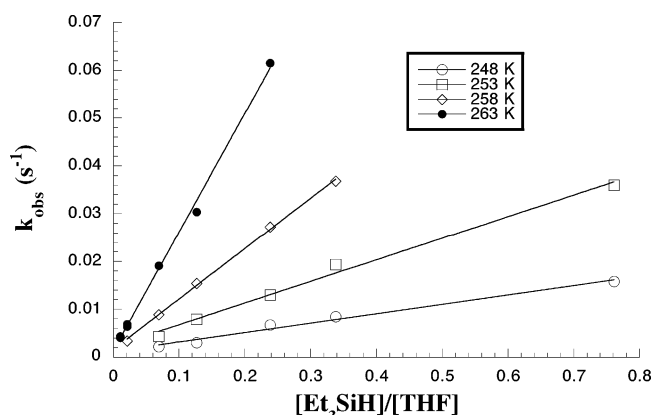


Figure 5. Plot of k_{obs} vs $[\text{HSiEt}_3]/[\text{THF}]$ at different temperatures.

While the intercepts of the k_{obs} versus $[\text{HSiEt}_3]/[\text{THF}]$ plots are nonzero, they do not show a consistent trend with temperature. It would appear therefore that the experimental error associated with extrapolating to $[\text{HSiEt}_3] = 0$ is large enough to prevent an accurate determination of k_{-2} , which is expected to be quite small at these temperatures.²¹ It was not possible to investigate the reaction at low $[\text{Et}_3\text{SiH}]$ to obtain a more reliable estimate of k_{-2} from the intercept since regeneration of the parent tricarbonyl exceeded 10% under these conditions. Using assumptions noted earlier, ΔH^\ddagger_1 for the reaction is found to be $21.4 \pm 0.8 \text{ kcal/mol}$, providing an estimate for the Cr–THF bond enthalpy, and $\Delta S^\ddagger_1 = +20.3 \pm 2.8 \text{ eu}$. Again the large positive entropy change is consistent with a dissociative mechanism, suggesting a large degree of disruption in the Cr–THF bond in the transition state.

Interestingly, the difference in the activation enthalpies (3 kcal/mol) for the displacement of Et_3SiH and THF from the appropriate $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{soln})$ complexes is similar to the enthalpy change obtained for reaction 2 from the equilibrium studies. Admittedly, this agreement is somewhat fortuitous given the narrow temperature ranges over which the activation parameters and K_{eq} were determined. Nonetheless, the similarity between the kinetic and thermodynamic measurements despite the fact that *different* incoming ligands were used for the displacement of the THF and Et_3SiH solvents from the Cr center suggests that both substitution reactions proceed via a common transition state. The most plausible common transition state is the coordinatively unsaturated $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$ fragment, lending further evidence for the dissociative displacement of the THF and Et_3SiH molecules from the respective $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{soln})$ complexes.²² While we cannot completely rule out the presence of concurrent

(21) A measurable equilibrium was observed only at temperatures $\geq 263 \text{ K}$. However, because the reaction rate was too fast to measure at temperatures above 263 K, we only have a complete k_{obs} vs $[\text{HSiEt}_3]/[\text{THF}]$ data set at this temperature and below. Thus, a somewhat reliable value of k_{-2} can only be obtained at 263 K. At this temperature, the intercept of the k_{obs} vs $[\text{HSiEt}_3]/[\text{THF}]$ plot is $1.3 \pm 0.6 \times 10^{-3} \text{ s}^{-1}$, in agreement with a calculated value of $1.8 \times 10^{-3} \text{ s}^{-1}$ for k_{-2} using the activation parameters from the reaction of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$ with PEt_3 , which, as explained in the text, are likely to be those associated with the disruption of the Cr– HSiEt_3 bond (i.e., k_{-2}).

(22) Strictly speaking the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$ complex is an intermediate. However, since this fragment reacts without an activation barrier (see ref 16), there is expected to be little energetic difference between the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$ intermediate and the transition state for these dissociative substitution reactions.

associative or interchange pathways in the solvent displacement as in the case of some $\text{Cr}(\text{CO})_5(\text{solv})$ complexes,^{23,24} the data suggest that such alternate pathways, if present, contribute minimally to the overall mechanism. Also, a change in the hapticity of the arene ring from $\eta^6 \rightarrow \eta^4$ to accommodate the incoming ligand in an associative or interchange step may be energetically unfavorable because of the disruption of the aromaticity of the benzene ring. Finally, a dissociative mechanism for silane displacement is consistent with the relatively large steric bulk of the Et_3SiH ligand. The presence of three alkyl groups would make the metal center inaccessible to attack by an incoming ligand without prior dissociation of the silane.

The agreement between the kinetic and thermodynamic values also suggests that the activation enthalpies are a reliable estimate for the strength of the $\text{Cr}-\text{THF}$ and $\text{Cr}-\text{HSiEt}_3$ interactions. Photoacoustic calorimetry (PAC) has been used to provide an estimate of 28 kcal/mol for the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2-(\text{HSiEt}_3)$ bond enthalpy, a few kcal/mol higher than the value reported in this paper.³ However, the PAC estimate must be treated with caution since early measurements did not take into account changes in reaction volumes and the values reported are likely too high.²⁵ Importantly, the PAC bond strength determination required a reliable estimate of the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2-\text{CO}$ bond dissociation enthalpy, which was not experimentally available, and a value obtained by extended Huckel calculations was used. More recent ab initio studies suggest that the first CO bond dissociation enthalpy in $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ is in the range 40–48 kcal/mol, which when combined with the PAC measurement leads to a $\text{Cr}-\text{HSiEt}_3$ bond enthalpy in the range 23–31 kcal/mol.^{26,27} The 24.3 ± 1.2 kcal/mol kinetic estimate for the $\text{Cr}-\text{HSiEt}_3$ bond enthalpy reported in the present paper falls within this range.

$(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{solv})$ vs $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{solv})$. Both kinetic and PAC measurements have been used to provide estimates of 24 and 28 kcal/mol for the $\text{CpMn}(\text{CO})_2-\text{THF}$ and $\text{CpMn}(\text{CO})_2-(\text{HSiEt}_3)$ bond enthalpies, respectively. Thus, relative to Cr, the Mn complex forms slightly more stable bonds with both solvents. It is interesting to note that the difference in the $\text{Cr}-\text{THF}$ and $\text{Cr}-\text{HSiEt}_3$ bond strengths (3 kcal/mol) is approximately the same as that between the analogous Mn systems (4 kcal/mol), which suggests that the relative bonding abilities of THF and silane are independent of the identity of the metal with which they interact. Matrix isolation studies have shown that the CO stretching frequencies of the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$ complex are lower than those of the $\text{CpMn}(\text{CO})_2$ fragment,

suggesting that the former complex is more electron rich.^{28,29} Since THF is primarily a sigma donor ligand, the degree of $\text{THF} \rightarrow \text{M} \sigma$ donation will be reduced in the more electron-rich Cr fragment relative to the Mn complex, resulting in a slightly weaker bond. However, increased electron density on the Cr center is expected to enhance the degree of $\text{M} \rightarrow \sigma^*$ back-bonding, with the silane ligand strengthening the $\text{Cr}-\text{HSiEt}_3$ interaction. But, as noted above, the difference in the strength of the $\text{M}-\text{THF}$ and $\text{M}-\text{HSiEt}_3$ interactions appears to be independent of the electron density on M. It may therefore be concluded that in these complexes the back-bonding interaction is weak and is not the primary factor in determining the strength of the metal–silane bond. This observation is consistent with the fact that both the $\text{Mn}-\text{HSiEt}_3$ and $\text{Cr}-\text{HSiEt}_3$ complexes have been characterized as η^2 complexes, indicating that the extent of oxidative addition and thus metal–ligand back-bonding is limited.³ The $(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_2\text{Cr}-\text{HSiEt}_3$ interaction may be considered as a more stable version of the metal–alkane σ bond.

Conclusions

The displacement of Et_3SiH from $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2-(\text{HSiEt}_3)$ by PET_3 and THF from $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{THF})$ by Et_3SiH has been investigated using UV–vis and IR spectroscopy. The kinetic data suggest a dissociative mechanism for both substitution reactions, yielding estimates of 24.3 ± 1.2 and 21.4 ± 0.8 kcal/mol for the strength of the $\text{Cr}-\text{HSiEt}_3$ and $\text{Cr}-\text{THF}$ bonds, respectively. Under some conditions an equilibrium is established between the $\text{Cr}-\text{THF}$ and $\text{Cr}-\text{HSiEt}_3$ complexes, and from the temperature dependence of the equilibrium constants, the $\text{Cr}-\text{HSiEt}_3$ complex is found to be 2.8 ± 1.0 kcal/mol more stable than the $\text{Cr}-\text{THF}$ solvate. The agreement between the thermodynamic and kinetic estimates of the relative stabilities of the two complexes strengthens the case for dissociative substitution and suggests that the activation enthalpies can provide a reliable estimate of the metal–solvent bond strength in these systems. Comparison of the relative stabilities of the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$ and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{THF})$ complexes with the analogous $\text{CpMn}(\text{CO})_2(\text{HSiEt}_3)$ and $\text{CpMn}(\text{CO})_2(\text{THF})$ solvates suggests that the primary bonding interaction between the metal center and silane may be described as a three-center two-electron bond between the metal, Si, and H atoms.

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