Investigating the Reactivity of the (η^6-C$_6$H$_5$R)Cr(CO)$_2$−(η^2-C$_6$H$_5$R) [R = H, CH$_3$, CF$_3$] Bond: A Laser Flash Photolysis Study with Infrared Detection

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The (η^6-C$_6$H$_5$R)Cr(CO)$_2$−(η^2-C$_6$H$_5$R) complexes (R = H, CH$_3$, CF$_3$) are generated upon photolysis of (η^6-C$_6$H$_5$R)Cr(CO)$_3$ in the appropriate arene. The energetics and mechanism of the displacement of the η^2-coordinated arene from the metal center by piperidine are studied using the technique of laser flash photolysis. The substitution reaction is tentatively assigned as proceeding through an I$_d$ mechanism, and the activation enthalpy of 11.5 ± 0.9 kcal/mol provides a lower limit for the strength of the (η^6-C$_6$H$_6$)Cr(CO)$_2$−(η^2-C$_6$H$_6$) bond. The substitution rate decreases as the metal center becomes more electron poor or the arene electron rich, suggesting that L→M σ donation is the primary bonding interaction between the (η^6-C$_6$H$_5$R)Cr(CO)$_2$ fragment and the arene ligand. This reactivity is different from that of the Cr−(η^2-alkene) bond, where it was found that increasing the electron density on the metal center decreased the rate of substitution of cyclooctene from the (η^6-C$_6$H$_5$R)Cr(CO)$_2$−(η^2-cyclooctene) complex by pyridine.

Introduction

Arene rings η^2-coordinated to transition metal centers are an important class of compounds. Such complexes have been implicated in a variety of catalytic processes and are often invoked as intermediates in the activation of arene C−H bonds, an important reaction in organic synthesis and industrial processes.[1−3] Dihapto coordination of an arene ring to an electron-rich metal center has a profound effect on the reactivity of the ring, "leading to otherwise inaccessible transformations on the coordinated organic ligand by disrupting the π system of the bound aromatic molecule".[4]

If dihapto coordination is understood as an interaction between a fixed double bond on the arene ring and the metal center, it can be described in terms of the traditional Dewar−Chatt−Duncanson bonding model of olefins.[5,6] Thus, two factors contribute to the strength of the overall interaction, σ donation from the π cloud of the aromatic ligand to a metal-centered orbital (L→M σ donation) and back-donation from the filled metal dπ to the empty π^* orbitals of the organic ligand. If the metal is a good π base, increased back-bonding results in a strong metal−(η^2-arene) bond and a disruption in the aromaticity of the arene ligand.[4,7,8] On the other

hand, in the case of electron-deficient metal centers such as Cr(CO)$_5$, the arene ligand is bound to the metal by a primarily σ interaction, resulting in a relatively weak metal−(η^2-arene) bond.[9−12] Given the interest and relevance of dihapto-coordinated arene complexes in a number of organic transformations and catalytic processes, it is important to investigate the energetic and mechanistic profile of the arene displacement reaction. A better understanding of this interaction can be achieved by studying the effect of varying the electronic properties of the metal and the arene ring upon the reactivity of the metal−(η^2-arene) bond.

Examples of organometallic complexes with weak metal−(η^2-arene) bonds are relatively few and include the Cr(CO)$_5$(η^2-benzene),[9−12] CpMn(CO)$_2$(η^2-toluene),[13] and Cp*Re(CO)$_2$(η^2-benzene) complexes.[14,15] Kinetic investigations yielded a range of 10 to 20 kcal/mol for the strength of the metal−(η^2-arene) bond in these systems. Although to our knowledge the (η^6-C$_6$H$_6$)Cr(CO)$_2$(η^2-arene) complex has not been observed before, it has been invoked as a possible intermediate in the arene exchange reactions of (η^6-arene)Cr(CO)$_3$ complexes.[16] By analogy with the weakly bound metal−(η^2-arene) complexes mentioned above, which were formed by photolyzing the parent carbonyl in the presence of arene, we

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thought it possible to generate the $(\eta^6\text{-}C_6H_5R)Cr(CO)_2$-$(\eta^2\text{-arene})$ complexes in a similar manner. The proposed complexes are particularly attractive candidates for probing the metal$-(\eta^2\text{-arene})$ interaction because a wide variety of monosubstituted $(\eta^6\text{-}C_6H_5R)Cr(CO)_3$ precursor complexes can be synthesized, making it possible to systematically alter the steric and electronic environment on the metal center.[17] In the present study the technique of laser flash photolysis with infrared detection is utilized to study the mechanism and energetics of η^2-arene displacement from the $(\eta^6\text{-}C_6H_6)Cr(CO)_2(\eta^2\text{-arene})$ complex (eq 1). To obtain a better understanding of the metal$-(\eta^2\text{-arene})$ bond in this system, the effect of changing the electron density on both the metal center and the arene upon the displacement rate is also investigated.

$$\text{(1)}$$

[R = H, CH$_3$, CF$_3$]
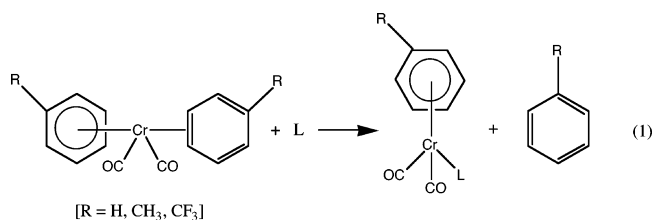
Experimental Section

General Procedures. The experimental apparatus used in this investigation has been described in detail elsewhere.[18] Briefly, a Nd:YAG laser (355 nm, 10 ns pulse width, 1 Hz repetition rate, 50 mJ/pulse) was used to photolyze a $\sim$0.6 mM solution of $(\eta^6\text{-arene})Cr(CO)_3$ in the appropriate arene containing the required concentration of ligand (either piperidine or pyridine). The subsequent changes in the absorption of the transient complexes generated upon photoexcitation were monitored with IR light from a Pb-salt diode laser (1930$-$1850 cm^{-1}). The solution was flowed through a temperature-controlled ($\pm$1 °C) IR cell (CaF$_2$ windows, 0.75 mm path length) to ensure that each laser shot photolyzed a fresh sample. The signal was averaged over 10 laser shots. All runs were conducted under pseudo-first-order conditions. The observed rate constants, k_{obs}, were determined by fitting either the decay of the reactant $(\eta^6\text{-}C_6H_5R)Cr(CO)_2(\eta^2\text{-arene})$ complex or the growth of the product $(\eta^6\text{-}C_6H_5R)Cr(CO)_2L$ complex to a first-order exponential function. Time-resolved spectra were built up point by point by recording absorption traces as a function of the monitoring frequency. The kinetics of the longer time scale reactions were monitored with either traditonal IR or UV/vis spectroscopy utilizing a procedure similar to that described previously.[19]

All arenes were either anhydrous grade (99%) or dried over CaH$_2$ prior to distillation. *cis*-Cyclooctene (95%) was used as received. The metal complexes, $(\eta^6\text{-arene})Cr(CO)_3$, were either commercially available ([arene] = C$_6$H$_6$) or synthesized according to literature methods ([arene] = C$_6$H$_5$CF$_3$, C$_6$H$_5$CH$_3$).[17] The photolysis solutions were prepared under an Ar atmosphere.

Results and Discussion

As shown in Figure 1, photolysis of a $\sim$0.6 mM solution of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ in benzene results in the generation of a species with a CO stretching absorbance at 1856 cm^{-1} (Table 1). This transient has a half-life of
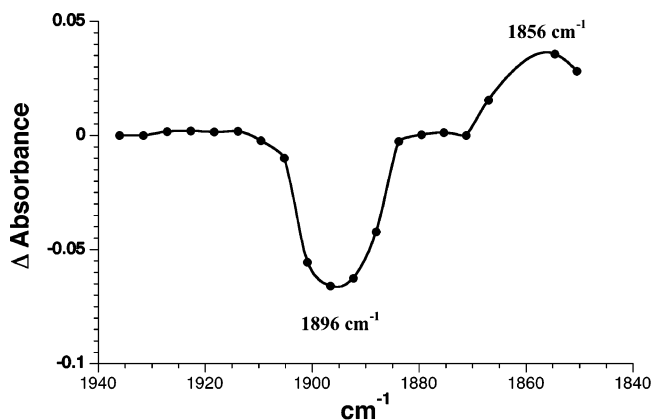

Figure 1. Time-resolved IR spectrum obtained 1 μs after 355 nm photolysis of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ in benzene solvent at 295 K. The absorption at 1856 cm^{-1} is assigned to the CO stretch of the $(\eta^6\text{-}C_6H_6)Cr(CO)_2(\eta^2\text{-benzene})$ complex, while the negative absorption observed at 1896 cm^{-1} is due to depletion of the parent tricarbonyl upon photolysis.

Table 1. CO Stretching Frequencies for the Complexes Investigated in This Study (* = 4 cm^{-1}, all other frequencies are $\pm$1 cm^{-1})

complex	ν_{CO} (cm^{-1})
$(\eta^6\text{-}C_6H_6)Cr(CO)_3$	1972, 1896
$(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$	1966, 1892
$(\eta^6\text{-}C_6H_5CF_3)Cr(CO)_3$	1988, 1919
$(\eta^6\text{-}C_6H_6)Cr(CO)_2(\text{piperidine})$	1874, 1815
$(\eta^6\text{-}C_6H_6)Cr(CO)_2(\text{pyridine})$	1880, 1825
$(\eta^6\text{-}C_6H_6)Cr(CO)_2(\eta^2\text{-}C_6H_6)$	1856*
$(\eta^6\text{-}C_6H_6)Cr(CO)_2(\eta^2\text{-}C_6H_5CH_3)$	see text
$(\eta^6\text{-}C_6H_6)Cr(CO)_2(\eta^2\text{-}C_6H_5CF_3)$	1859*
$(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_2(\eta^2\text{-}C_6H_6)$	1852*
$(\eta^6\text{-}C_6H_5CF_3)Cr(CO)_2(\eta^2\text{-}C_6H_6)$	1877*

$\sim$0.2 ms at 294 K. We assign this species to the $(\eta^6\text{-}C_6H_6)Cr(CO)_2(\text{benzene})$ complex on the basis of the observation that this species is generated immediately upon photolysis (within 70 ns) and the fact that previous studies have shown that UV photoexcitation of transition metal carbonyls in condensed phase results in the formation of the solvated complex within picoseconds of CO loss.[20] Specifically, photolysis of $(\eta^6\text{-arene})Cr(CO)_3$ in alkane solvent leads to the immediate generation of the $(\eta^6\text{-arene})Cr(CO)_2(\text{alkane})$ transient.[21] Furthermore, other metal$-$arene complexes such as Cr(CO)$_5$(benzene), CpMn(CO)$_2$(toluene), and Cp*Re(CO)$_2$(arene) are also formed promptly following loss of a CO ligand upon photolysis of the parent tricarbonyl in the presence of the appropriate arene. By analogy with similar complexes, benzene is most likely bound to the $(\eta^6\text{-}C_6H_6)$-Cr(CO)$_2$ fragment through a fixed double bond on the arene ring, an η^2 interaction. There is precedence for this type of interaction in other short-lived organometallic complexes,[9–15] and several isolable metal$-(\eta^2$-arene) complexes have also been synthesized.[4,7,8,22] This structural assignment is also consistent with the observation that the $(\eta^6\text{-}C_6H_6)Cr(CO)_2(\text{benzene})$ complex is less reactive than the analogous $(\eta^6\text{-arene})Cr(CO)_2$-(alkane) complex, in which the primary interaction is between the metal center and the electron density in

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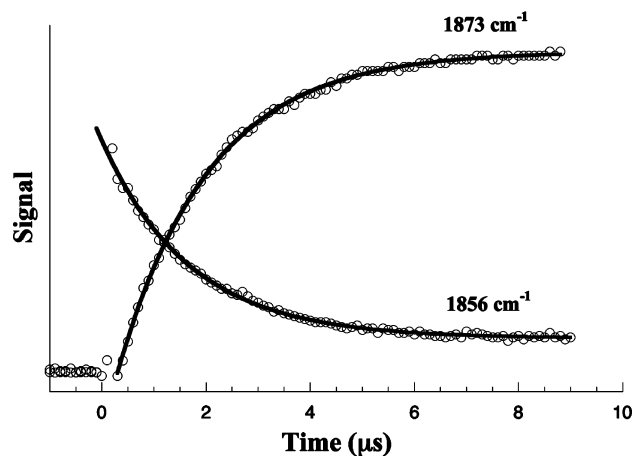
Figure 2. Decay of the (η^6-C$_6$H$_6$)Cr(CO)$_2$(η^2-benzene) complex and concurrent growth of (η^6-C$_6$H$_6$)Cr(CO)$_2$-(piperidine) upon photolysis of a ∼0.6 mM solution of (η^6-C$_6$H$_6$)Cr(CO)$_3$ in benzene in the presence of 0.196 M piperidine at 318 K. The reactant exhibits residual absorbance due to overlap with the product complex. The solid line represents a first-order exponential fit to the data.

the C−H bond.[21,23] The (η^6-C$_6$H$_6$)Cr(CO)$_2$(η^2-benzene) complex should have two CO stretching absorbances, and while only one is observed (at 1856 cm^{-1}), it is reasonable to conclude that the second band expected at ∼1900−1910 cm^{-1} overlaps with the broad parent tricarbonyl absorption at 1896 cm^{-1}.[24]

As shown in Figure 2, in the presence of piperidine, the (η^6-C$_6$H$_6$)Cr(CO)$_2$(η^2-benzene) transient reacts to form the previously characterized (η^6-C$_6$H$_6$)Cr(CO)$_2$-(piperidine) complex absorbing at 1873 cm^{-1}.[25]The identity of this product was further confirmed by photolyzing a benzene solution of (η^6-C$_6$H$_6$)Cr(CO)$_3$ containing piperidine and acquiring a FTIR spectrum that showed the presence of CO stretching absorbances at 1874 and 1815 cm^{-1}. While the higher frequency band is observed in the flash photolysis experiment, the lower frequency absorption is beyond the range of our IR diode laser. The observed rate constant, k_{obs}, obtained by fitting the decay of the (η^6-C$_6$H$_6$)Cr(CO)$_2$(η^2-benzene) complex to a first-order exponential function shows a linear dependence on the piperidine concentration (Figure 3). Unfortunately, a linear dependence of k_{obs} on piperidine concentration does not assist in distinguishing between an associative (A), dissociative (D), or interchange mechanism (I) of benzene substitution from the Cr center.[26] To further clarify the mechanism, the displacement reaction was also studied by using pyri-
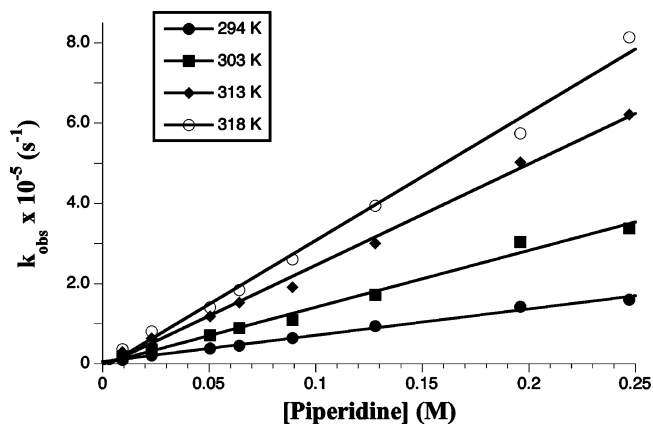
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(24) The (η^6-C$_6$H$_6$)Cr(CO)$_2$(heptane) complex has CO bands at 1927 and 1877 cm^{-1} (see ref 21). Assuming a similar 50 cm^{-1} difference in the symmetric and antisymmetric CO stretching modes of the (η^6-C$_6$H$_6$)Cr(CO)$_2$(η^2-benzene) complex, the "missing" peak should be at ∼1906 cm^{-1}.

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Figure 3. Plot of k_{obs} vs [piperidine] at several temperatures for the reaction of (η^6-C$_6$H$_6$)Cr(CO)$_2$(η^2-benzene) with piperidine

Table 2. Second-Order Rate Constants Obtained from the Slope of the k_{obs} vs [L] Plots for the Reaction of (η^6-C$_6$H$_6$)Cr(CO)$_2$(η^2-benzene) with L = Piperidine and Pyridine

	$k_{second} \times 10^{-5}$ (M^{-1} s^{-1})	
T (K)	piperidine	pyridine
294	6.56 ± 0.24	9.52 ± 0.9
303	14.2 ± 0.6	19.7 ± 1.0
313	25.2 ± 0.7	31.7 ± 1.7
318	31.8 ± 1.2	38.5 ± 0.6
	$\Delta H^{\ddagger} = 11.5 \pm 0.9$ kcal/mol	$\Delta H^{\ddagger} = 10.1 \pm 1.0$ kcal/mol
	$\Delta S^{\ddagger} = +7.6 \pm 2.9$ eu	$\Delta S^{\ddagger} = +3.4 \pm 3.3$ eu

dine as the incoming ligand, and as shown in Table 2, the results show only a slight dependence of the rate constants on the identity of the displacing ligand. Given the substantial difference in the basicity and hence nucleophilicity of piperidine and pyridine, the similar second-order rate constants suggest that the reaction most likely does not proceed through either an A or I$_a$ mechanism. We therefore favor a D or an I$_d$ mechanism of benzene displacement from the metal center. It is difficult to further distinguish between these two mechanistic possibilities. However, since assignment of a D mechanism is formally contingent upon the identification of an intermediate with reduced coordination number, i.e., the "naked" (η^6-C$_6$H$_6$)Cr(CO)$_2$ complex, which is not observed in the present study, we tentatively suggest that the reaction proceeds through an I$_d$ mechanism. Consistent with this assignment, the displacement of other weakly bound solvent molecules from (η^6-arene)Cr(CO)$_2$(solvent) complexes [solvent = H$_2$, N$_2$, Et$_3$Si−H, THF] was also shown to proceed through either a D or I$_d$ pathway.[19,27] However, dissociative substitution of the alkane was ruled out in the case of the (η^6-arene)Cr(CO)$_2$(alkane) complexes.[21] The moderately positive activation entropy, $\Delta S^{\ddagger} = +7.6 \pm 2.9$ eu, obtained from an Eyring analysis (Table 2) of the reaction with piperidine is also consistent with an I$_d$ mechanistic assignment, which implies that the reaction proceeds through a single transition state with significant Cr−(η^2-benzene) bond disruption and the incoming ligand either loosely bound to the metal center or present in the first solvation shell. The activation enthalpy of $\Delta H^{\ddagger} = 11.5 \pm 0.9$ kcal/mol is therefore

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Table 3. Second-Order Rate Constants for the Displacement of the η^2-Coordinated Arene from Complexes 1−4 by Piperidine

	$k_{\text{second}} \times 10^{-5}$ ($M^{-1}\,s^{-1}$)			
T (K)	1	2	3	4
294	3.6 ± 0.3	8.4 ± 0.2	5.8 ± 0.1	37.2 ± 2.3
303	5.4 ± 0.5	18.3 ± 0.6	10.1 ± 0.6	60.2 ± 2.3
313	12.1 ± 0.6	29.9 ± 0.4	24.0 ± 2.0	115 ± 2.4
318	16.9 ± 0.3	35.0 ± 0.4	28.7 ± 0.8	
	$\Delta H^{\ddagger} = 11.6 \pm 1.2$ kcal/mol	$\Delta H^{\ddagger} = 10.4 \pm 1.3$ kcal/mol	$\Delta H^{\ddagger} = 12.3 \pm 1.0$ kcal/mol	$\Delta H^{\ddagger} = 10.2 \pm 0.8$ kcal/mol
	$\Delta S^{\ddagger} = +6.4 \pm 3.9$ eu	$\Delta S^{\ddagger} = +4.3 \pm 4.3$ eu	$\Delta S^{\ddagger} = +9.8 \pm 3.2$ eu	$\Delta S^{\ddagger} = +6.4 \pm 2.6$ eu

expected to provide a lower limit to the strength of the $(\eta^6\text{-arene})Cr(CO)_2-(\eta^2\text{-benzene})$ bond, similar to that of the $CpMn(CO)_2-(\eta^2\text{-toluene})$ interaction, which has been estimated at ~14 kcal/mol.[13]

$(\eta^6\text{-}C_6H_5CF_3)Cr(CO)_2(\eta^2\text{-benzene})$ vs $(\eta^6\text{-}C_6H_5CH_3)$-$Cr(CO)_2(\eta^2\text{-benzene})$. To investigate the effect of varying the metal electron density on the reactivity of the $Cr-(\eta^2\text{-benzene})$ bond, the reaction of $(\eta^6\text{-}C_6H_5CF_3)Cr(CO)_2(\eta^2\text{-benzene})$ (**1**) and $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_2(\eta^2\text{-benzene})$ (**2**) with piperidine was studied. These complexes are expected to have considerably different electron density as indicated by the position of the CO stretching absorbances for the respective parent tricarbonyl complexes (Table 1).[17] Importantly, differences in the reactivity of these two complexes can be readily attributed to electronic and not steric effects. Throughout the following discussion we make the reasonable assumption that all of the displacement reactions proceed through a similar (I_d) mechanism and that therefore any difference in the reactivity of the metal−$(\eta^2\text{-arene})$ bond can be related to the stability of this interaction.

Although **1** and **2** are expected to be the primary photoproducts upon photolysis of the respective parent tricarbonyls in benzene solution, previous reports indicate that η^6 arene exchange can also occur in the presence of an arene different from the one bound to the Cr center.[28] Upon prolonged steady-state photolysis (2 min) of $(\eta^6\text{-}C_6H_5CF_3)Cr(CO)_3$ and $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$ in neat benzene with a 150 W Xe Arc Lamp, the formation of a small amount of the $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ complex is observed in the FTIR spectrum. However, because every shot of the laser photolyzes a fresh sample, and since $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ is not involved in the reaction of **1** or **2** with piperidine, the presence of a potentially small amount of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ is not expected to be an issue in the flash photolysis experiments.

As shown in Figure 4, the benzene solvent is displaced by piperidine more rapidly from **2** than from **1**. The second-order rate constants shown in Table 3 suggest that complex **2** reacts approximately 2−3 times faster than **1**, suggesting that increasing the electron density on the metal center yields a less stable dihapto interaction. This observation indicates that donation of π electron density from a localized double bond on the benzene ligand to the metal (L→M σ bond) is the primary component of the $Cr-(\eta^2\text{-benzene})$ interaction. If M→L π back-bonding were the dominant interaction, it is expected that increasing the electron density on the metal would result in a stronger and hence less reactive $Cr-(\eta^2\text{-benzene})$ bond, which is contrary to the

experimental data. We may therefore conclude that the aromaticity of the arene ligand is not affected significantly upon binding with the metal center.
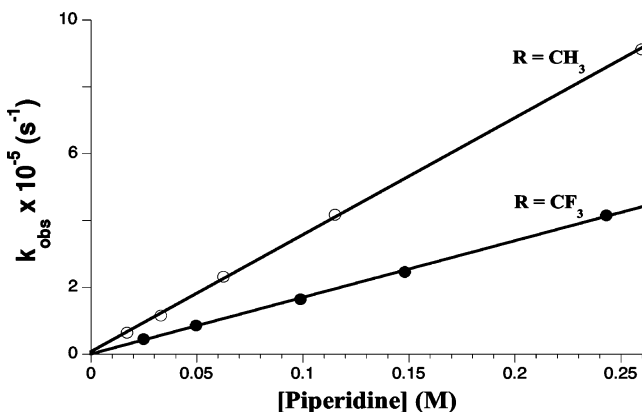

Figure 4. Plot of k_{obs} vs [piperidine] at 318 K for the displacement of the dihapto-coordinated benzene ligand from $(\eta^6\text{-}C_6H_5R)Cr(CO)_2(\eta^2\text{-benzene})$.

The $Cr-(\eta^2\text{-arene})$ bond in these systems is significantly different from that between potent π bases such as $TpRe(CO)(\text{imidazole})$ and benzene, which involves a strong π-back-bonding interaction leading to the dearomatization of the η^2-coordinated arene.[7] Furthermore, the importance of π back-bonding in the Re system was evidenced by the kinetic stabilities of the $Re-(\eta^2\text{-arene})$ complexes. Thus, unlike the findings of the present study, the rate of dissociation of the arene ligand from the Re fragment was found to decrease as the electron density on the metal increased.[29]

$(\eta^6\text{-}C_6H_6)Cr(CO)_2(\eta^2\text{-}C_6H_5CF_3)$ vs $(\eta^6\text{-}C_6H_6)Cr(CO)_2(\eta^2\text{-}C_6H_5CH_3)$. To further investigate the dihapto interaction, we studied the effect of changing the electronic characteristics of the η^2-coordinated arene upon the reactivity of the $Cr-(\eta^2\text{-arene})$ bond. Photolysis of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ in $C_6H_5CH_3$ and $C_6H_5CF_3$ yields the $(\eta^6\text{-}C_6H_6)Cr(CO)_2(\eta^2\text{-}C_6H_5CH_3)$ (**3**) and $(\eta^6\text{-}C_6H_6)Cr(CO)_2(\eta^2\text{-}C_6H_5CF_3)$ (**4**) complexes, respectively. Since toluene solvent absorbs IR light strongly in the region where **3** is expected to be observed (≈ 1856 cm^{-1}), k_{obs} was determined by monitoring the growth of the product $(\eta^6\text{-}C_6H_6)Cr(CO)_2(\text{piperidine})$ complex. The second-order rate constants shown in Table 3 indicate that **4** reacts almost 6 times faster than **3**. This finding is consistent with the earlier conclusion that σ bonding is the primary interaction between the Cr center and the η^2-coordinated arene. Since $C_6H_5CF_3$ is a weaker σ donor than $C_6H_5CH_3$, it is expected that the resulting L→M dative bond will be less stable, and hence more reactive, than that

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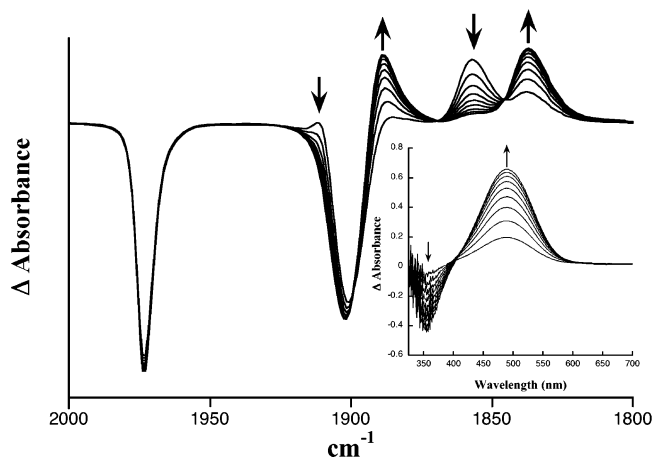
Figure 5. FTIR spectra obtained at 150 s intervals showing the reaction of (η^6-C$_6$H$_5$CH$_3$)Cr(CO)$_2$(η^2-cyclooctene) with 0.58 M pyridine at 293 K in cyclooctene solvent. The peaks marked ↑ are the CO bands of the (η^6-C$_6$H$_5$CH$_3$)-Cr(CO)$_2$(pyridine) complex, while those marked ↓ are associated with the η^2-cyclooctene reactant. The inset shows the same reaction followed by UV−vis spectroscopy at 60 s intervals with [pyridine] = 1.1 M.

between the Cr center and the more electron-rich toluene ligand.

By contrasting the reactivity of **1** and **2** with that of **3** and **4**, it is also evident that changes in the electron density of the dihapto-coordinated arene effect the Cr−(η^2-arene) bond more than variations in the electronic characteristics of the metal center. While the differences in the reactivities are small (less than a factor of 10), they are nonetheless chemically significant since the observed trends yield important information about the metal−(η^2-arene) interaction.

(η^6-C$_6$H$_5$R)Cr(CO)$_2$(η^2-arene) vs (η^6-C$_6$H$_5$R)Cr-(CO)$_2$(η^2-alkene). In contrast to the results reported in the present study, evidence in the literature suggests that the (η^6-C$_6$H$_5$R)Cr(CO)$_2$−(η^2-alkene) bond becomes *more reactive* as the electron density on the Cr center is decreased. Thus, reaction of CS$_2$ with (η^6-C$_6$H$_4$R$_2$)Cr-(CO)$_2$−(η^2-cyclooctene) to form the (η^6-C$_6$H$_4$R$_2$)Cr(CO)$_2$-(CS) complex proceeds faster when R = CO$_2$CH$_3$ than when R = CH$_3$.[30] This difference in reactivity is opposite that observed in the case of the Cr−(η^2-arene) complexes (**1** vs **2**) and can be readily attributed to the aromaticity of the arene ligand, suggesting that a dihapto-coordinated arene binds to the (η^6-C$_6$H$_5$R)Cr(CO)$_2$ fragment in a different manner than does an alkene.

To obtain more quantitative data on the difference in reactivity between the Cr−(η^2-arene) and Cr−(η^2-alkene) bonds, we studied the displacement of the cyclooctene ligand from (η^6-C$_6$H$_5$R)Cr(CO)$_2$(η^2-cyclooctene) (R = CH$_3$, CF$_3$) by pyridine. As shown in Figure 5, photolysis of a solution of (η^6-C$_6$H$_5$R)Cr(CO)$_3$ in cyclooctene in the presence of pyridine results in the generation of the previously observed (η^6-C$_6$H$_5$R)Cr-(CO)$_2$(η^2-cyclooctene) and (η^6-C$_6$H$_5$R)Cr(CO)$_2$(pyridine) complexes.[25,31] The cyclooctene complex then converts to the more stable pyridine complex. The displacement reaction appears to proceed by a dissociative mechanism
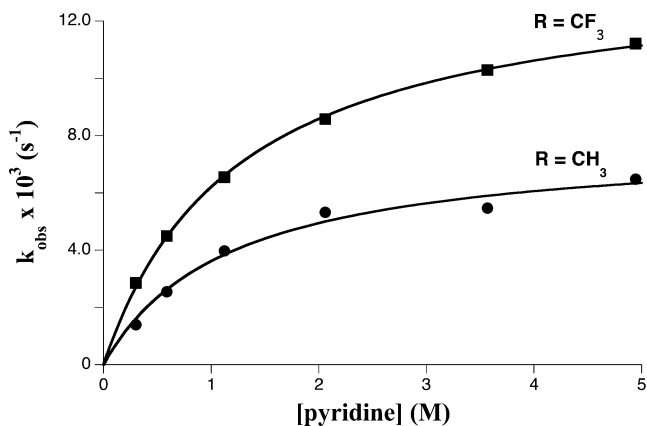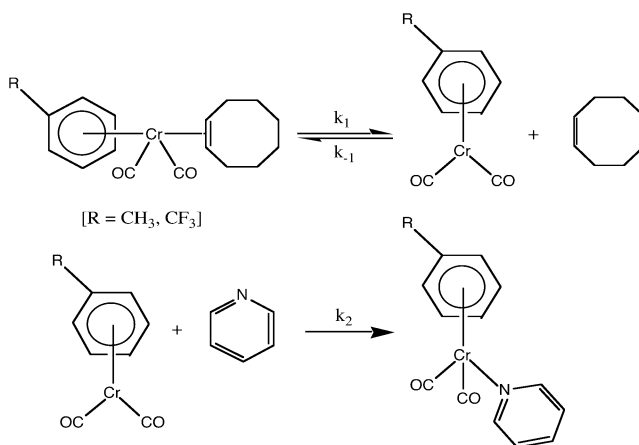
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Figure 6. Plot of k_{obs} vs [pyridine] at 293 K for the displacement of cyclooctene from the (η^6-C$_6$H$_5$R)Cr(CO)$_2$-(η^2-cyclooctene) complex by pyridine.

Scheme 1

since k_{obs} approaches a limiting value at high pyridine concentration (Figure 6). Such rate behavior implies the reversible generation of an intermediate that precedes the formation of the product complex. A reasonable mechanism for this reaction is shown in Scheme 1. Applying the steady-state approximation to the (η^6-C$_6$H$_5$R)Cr(CO)$_2$ fragment yields the following dependence of k_{obs} on [pyridine]:

$$k_{obs} = \frac{k_1 k_2 [\text{pyridine}]}{k_{-1}[\text{cyclooctene}] + k_2[\text{pyridine}]} \quad (1)$$

Since in these reactions cyclooctene is both a solvent and a reactant, eq 1 must be modified to take into account the fact that addition of increasing amounts of pyridine necessarily decreases the concentration of cyclooctene. The concentration of cyclooctene may be expressed as:

$$[\text{cyclooctene}] = [\text{cyclooctene}]_0 - a[\text{pyridine}] \quad (2)$$

Here [cyclooctene]$_0$ = 7.67 M and a is the ratio of the concentrations of pure cyclooctene and pyridine (0.62). Substitution of eq 2 into 1 yields:

$$k_{obs} = \frac{k_1 k''[\text{pyridine}]}{7.67 + (k'' - a)[\text{pyridine}]} \left\{ k'' = \frac{k_2}{k_{-1}} \right\} \quad (3)$$

A fit of the k_{obs} vs [pyridine] data to eq 3 yields k_1 values

of $(7.2 \pm 0.4) \times 10^{-3}$ and $(12.7 \pm 0.2) \times 10^{-3}$ s^{-1} at 293 K for the displacement of cyclooctene from $(\eta^6\text{-}C_6H_5\text{-}CH_3)Cr(CO)_2(\eta^2\text{-cyclooctene})$ and $(\eta^6\text{-}C_6H_5CF_3)Cr(CO)_2\text{-}(\eta^2\text{-cyclooctene})$, respectively. The ratios k_2/k_{-1} are ~ 7 for each complex, suggesting that the $(\eta^6\text{-}C_6H_5R)Cr(CO)_2$ fragment is more selective toward reaction with pyridine than with cyclooctene but that this relative reactivity is unaffected by the presence of the different R groups.

Consistent with the earlier literature reports discussed above, the difference in the k_1 values shows that the reactivity of the $Cr-(\eta^2\text{-cyclooctene})$ bond increases when the electron density on the metal decreases. This reactivity is contrary to that observed for the $Cr-(\eta^2\text{-arene})$ complexes discussed earlier, and it would therefore appear that π back-bonding is a relatively more important factor in the $Cr-(\eta^2\text{-cyclooctene})$ interaction. It is perhaps not surprising that π back-bonding is minimized in the $Cr-(\eta^2\text{-arene})$ complexes because the potential loss of aromaticity would be energetically costly. Obviously, dihapto coordination of alkenes is not subject to such considerations and $M \rightarrow L$ π back-bonding can lead to a more stable structure.

Conclusions

The $(\eta^6\text{-}C_6H_5R)Cr(CO)_2(\eta^2\text{-}C_6H_5R)$ complexes (R = H, CH$_3$, CF$_3$) are formed by photolyzing $(\eta^6\text{-}C_6H_5R)Cr(CO)_3$ in the presence of the appropriate arene. The displace-ment of the η^2-coordinated arene ligand by piperidine is found to proceed through an I_d mechanism. The activation enthalpy yields an estimate of 11.5 ± 0.9 kcal/mol for the strength of the $(\eta^6\text{-}C_6H_6)Cr(CO)_2-(\eta^2\text{-}C_6H_6)$ bond. The factors influencing the reactivity of the $Cr-(\eta^2\text{-arene})$ bond were probed by varying the electron density on both the metal center and the arene. It was found that when the electron density on the metal center was increased or that of the arene decreased, the rate of η^2 arene displacement increased, suggesting that $L \rightarrow M$ σ donation is the primary bonding interaction in these complexes. In contrast to the results of the $Cr-(\eta^2\text{-arene})$ system, it was found that the rate of displacement of η^2-bound cyclooctene from the $(\eta^6\text{-}C_6H_5R)Cr\text{-}(CO)_2(\eta^2\text{-cyclooctene})$ complex increased as the electron density on the metal center decreased, suggesting that π back-bonding is an important factor in the $Cr-(\eta^2\text{-alkene})$ interaction. It would be of interest to theoretically model the η^2 coordination of arenes and alkenes to the $(\eta^6\text{-}C_6H_5R)Cr(CO)_2$ fragment to provide more quantitative insight into the relative importance of σ and π bonding in these complexes.

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