Ground-State versus Transition-State Effects in Arene Displacement Reactions of the Complexes (η^6-arene)Cr(CO)$_3$: Linear Dependence of Transition-State Energies and Resonance Energies of the Arene Ligands

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The rates of displacement of arene and thiophene ligands by P(n-Bu)$_3$ in decalin and PPh$_3$ in toluene have been studied. The reactions are first order in complex and incoming ligand. Rates of reaction increase in the order benzene < styrene < triphenylene < pyrene < phenanthrene < dimethylthiophene < naphthalene < thiophene < anthracene and span roughly 8 orders of magnitude. The thermodynamic stability of these species has also been investigated by solution calorimetry and equilibrium studies. The order of decreasing thermodynamic stability is benzene > dimethylthiophene > triphenylene > phenanthrene > thiophene > naphthalene > anthracene > pyrene and spans about 7 kcal/mol. The combination of kinetic and thermodynamic data is used to construct reaction profiles for these reactions. On the basis of the assumption that the transition state occurs on the way to formation of (η^4-arene)Cr(CO)$_3$(L) a linear correlation exists between the enthalpy of formation of the transition-state complex and changes in resonance energy of the fused arene ligands attributable to localization of the π bonds of the proposed η^4 intermediate. The rate of binding of C$_6$H$_6$ to (THF)$_3$Cr(CO)$_3$ is 10% slower than for C$_6$D$_6$, implicating the importance of (η^1-C$_6$H$_6$)Cr(CO)$_3$(THF)$_2$ as an intermediate on the pathway to formation of (η^6-C$_6$H$_6$)Cr(CO)$_3$.

Fused arene ligands represent a special type of chelate system in organometallic chemistry. The six electrons donated are all part of the same highly stable π system. Dissociation of one of the bonds is intimately related to the remaining bonds in terms of both bonding to the metal and delocalization within the ring systems. In spite of considerable work dealing with simple arenes,[1] there are relatively few kinetic and thermodynamic studies of fused polynuclear aromatic hydrocarbon ligands in the literature.[2]

The arene exchange reaction has been widely studied, since it represents an important step in converting stoichiometric arene reactions to catalytic ones. Ring slippage as a possible mechanism of associative arene displacement was first reported in 1966.[2b] The pioneering work of Strohmeier,[3] Muetterties,[4] and most recently Traylor[5] has shown the complexity of this reaction. It cannot be said to be fully understood, even for the widely studied (η^6-arene)Cr(CO)$_3$ complexes. Detailed work by Traylor and co-workers showed the apparent importance of dinuclear complexes; however, the exact nature of these complexes remained a matter of speculation.[5] A starting point in understanding the more complex reaction mechanism of replacement of one η^6-arene ligand with another η^6-arene ligand may be replacement by simple donor ligands. The rate of displacement of naphthalene from (η^6-napht)Cr(CO)$_3$ (napht = naphthalene) by CH$_3$CN and P(OMe)$_3$ has been reported,[6,7] but a systematic study of fused arene displacement by the same or comparable ligands as a function of the arene ligands has not been done. That is unfortunate, since the stabilities of the widely proposed (η^4-arene)Cr(CO)$_3$–L intermediates should depend on the nature of the fused arene and this could provide information regarding the mechanism of displacement.

In spite of the frequent citation[8] of η^4-arene complexes as intermediates, and the structural studies of a few coordinatively saturated derivatives, there are no stable examples for the group VI metals. Several Ru(0) complexes containing η^4-arenes have been prepared, including Ru(η^6-C$_6$Me$_6$)(η^4-OMN) (OMN = octamethylnaphthalene),[9] and recently the X-ray structure of (η^4-

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naphtht)Mn(CO)$_3^-$ has been reported.[10] Spectroscopic studies of solvolysis of (η^6-napht)Cr(CO)$_3$ have been cited as evidence for (η^4-napht)Cr(CO)$_3$(THF):[11]

$$(\eta^6\text{-napht})\mathrm{Cr(CO)_3} + \mathrm{THF} \rightleftharpoons (\eta^4\text{-napht})\mathrm{Cr(CO)_3(THF)} \quad (1)$$

However, the theoretical work cited above[2] concluded that (η^4-C_6H_6)Cr(CO)$_3$(C_2H_4) (C_6H_6 = benzene) collapses to (η^6-C_6H_6)Cr(CO)$_3$ with no activation barrier and hence should not be stable.

In spite of no definitive evidence for their existence, (η^4-arene)Cr(CO)$_3$(L) complexes are the most logical intermediates for the first step in arene displacement (L = two-electron donor), direct arene exchange (L = η^2- or η^1-arene), or autocatalyzed exchange (L = (η^6-arene)Cr(CO)$_3$). Arene ligands (particularly fused ring systems) have the potential for stabilization of the transition state by acceptance of a pair of electrons on the ligand itself, thus reducing the overall activation energy normally suffered by breaking the metal–ligand bond. This effect was first clearly demonstrated for the nitrosyl ligand.[12] The vanadium complex shown in eq 2 undergoes substitution reactions which follow a two-term rate law. Dissociative pathways are accelerated by

$$\mathrm{V(CO)_5(NO)} + \mathrm{L} \rightarrow \mathrm{V(CO)_4(NO)(L)} + \mathrm{CO} \quad (2)$$

the high trans effect of the NO ligand, but associative reactions occur concurrently with relatively low enthalpies of activation (13–16 kcal/mol), presumably through the ability of a nitrosyl ligand to accept a pair of electrons and stabilize the transition state while changing from linear (sp) to bent (sp^2) hybridization.[13] Since fast ligand exchange is important in catalytic applications of organometallic complexes,[14] these effects have been widely studied.

A striking example of acceleration of ligand substitution reactions is in the "ring slippage" reactions of cyclopentadienyl (C_5H_5)[15] and indenyl (C_9H_7)[16] complexes. Several years ago it was shown that substitutions of (η^5-C_9H_7)Rh(CO)$_2$ were 8–9 orders of magnitude faster[17] than corresponding reactions of (η^5-C_5H_5)Rh(CO)$_2$. These reactions are presumed to follow the mechanism shown in eq 3. The transition state for this

$$(\eta^5\text{-}C_9H_7)\mathrm{Rh(CO)_2} + \mathrm{L} \rightleftharpoons (\eta^3\text{-}C_9H_7)\mathrm{Rh(CO)_2(L)} \rightarrow (\eta^5\text{-}C_9H_7)\mathrm{Rh(CO)(L)} + \mathrm{CO} \quad (3)$$

reaction occurs on the pathway to formation of (η^3-C_9H_7)Rh(CO)$_2$(L). The observed rate acceleration for indenyl versus cyclopentadienyl could be attributed to ground-state destabilization, transition-state stabilization, or a combination of both. Due to the similarity of the carbonyl stretch frequencies of the cyclopentadienyl and indenyl complexes, the ligand donor abilities were deemed similar and the accelerated rate of reaction of the indenyl complex was attributed to transition-state stabilization.[17]

Thermochemical studies done recently on analogous group VI complexes indicate that ground-state bond energy differences can also play an important role. Thus, the enthalpies of reactions such as that shown in eq 4 indicated that the W–(η^5-indenyl) bond is some 14

$$(\eta^5\text{-}C_9H_7)\mathrm{W(CO)_3H} + C_5H_6 \rightarrow (\eta^5\text{-}C_5H_5)\mathrm{W(CO)_3H} + \text{indene} \quad (4)$$

kcal/mol weaker than the W–(η^5-cyclopentadienyl) bond.[18] These results imply that the fused indenyl ring system is a weaker ligand donor to begin with, in spite of similarities in ν-CO for these complexes.

Complexes of fused arenes such as naphthalene and anthracene have been known for some time to be more labile than corresponding benzene complexes.[1] Thermochemical data have been reported which indicate that the Cr–naphthalene bond is about 6 kcal/mol weaker than the Cr–benzene bond,[19] but conclusions regarding other fused arene system stabilities rely on qualitative observations. A recent paper[2a] has focused on kinetic and theoretical studies of arene exchange reactions of naphthalene and pyrene complexes of chromium tricarbonyl.

$$(\eta^6\text{-napht})\mathrm{Cr(CO)_3} + \text{arene} \rightarrow (\eta^6\text{-arene})\mathrm{Cr(CO)_3} + \text{napht} \quad (5)$$

The exchange reaction was found to follow kinetics that were first order in complex and a linear combination of zero order and first order in incoming arene ligand. Theoretical calculation of the most favorable path for the arene-independent pathway showed direct conversion from η^6 or η^1 coordination for naphthalene and pyrene, respectively. No evidence for η^4 coordination in terms of a discrete intermediate was found in the calculations.

It is clear that arenes and polynuclear aromatic systems represent a special type of chelate system. Although there is a growing body of evidence[20] for organic reactions indicating that changes in resonance energies of arenes in reaction transition states play key roles in determining reactivities, no such observations have been reported for organometallic complexes where arenes are either reacting or ancillary ligands. In spite

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[20] (a) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 3rd ed.; Plenum Press: New York, 1990; Chapter 9. (b) Although speculations were made that higher reactivities of naphthalene complexes compared with those of benzene complexes are due to the ability of naphthalene to more easily form an η^4 intermediate without substantial loss of resonance delocalization energy, other experimental results show that naphthalene is a weaker η^6 ligand than is benzene.[19] Tucker, J. R.; Riley, D. P. *J. Organomet. Chem.* **1985**, *279*, 49–62. Kundig, E. P.; Desobry, V.; Grivet, C.; Rudolph, B.; Spichiger, S. *Organometallics* **1987**, *6*, 1173.

of the fact that the Cr—benzene bond in (η^6-C_6H_6)Cr(CO)$_3$ is estimated to be only on the order of 50 kcal/mol[21]—a very low value for a ligand that occupies three coordination sites at the metal—it is a highly stable compound. This paper reports for the first time systematic kinetic and thermodynamic studies of ligand substitutions of fused arene, cyclic olefin, and thiophene complexes of chromium tricarbonyl—all kinetically more reactive than the benzene complex. The combination of techniques used in this study gives some insight into the role the fused ring system plays in ground-state versus transition-state effects in these complexes.

Experimental Section

Reagents. All starting reagents (chromium carbonyl, arene and thiophene ligands, etc.) were obtained from Aldrich; ^{13}CO was obtained from Matheson. Dibutyl ether, toluene, and decalin were dehydrated with Na and distilled over Na under N_2 before use. Tetrahydrofuran was distilled from sodium–benzophenone ketyl under argon. The compounds were synthesized and purified by literature methods[22] and stored under N_2. Manipulations were carried out using standard Schlenk-tube and inert-atmosphere techniques.

Kinetic Studies. Reactions were followed with a Nicolet 5 PC-FTIR spectrophotometer using a 0.2-mm NaCl solution cell. Reactions were performed under pseudo-first-order conditions using at least a 10/1 ratio of ligand to metal. Constant temperatures ±0.1 °C were maintained by an external circulating bath (Neslab RTE-8) and silicone oil bath with temperature controller (Cole-Palmer 2186-00).

In a typical experiment, a solution of phosphine or phosphite in decalin or toluene was mixed with a solution of the arene complex in a deoxygenated flask under N_2. After the flask was vigorously shaken, a 0.2-mL sample was removed from the flask by syringe and transferred into an IR cell which had been sealed with rubber septa and flushed with N_2 prior to use. Rate constants were obtained by monitoring the decay in absorption of the peak of the highest frequency carbonyl band of the arene complex as a function of time.

Calorimetric Measurements. Calorimetric measurements on enthalpies of solution and reaction were measured with a Setaram Calvet calorimeter using techniques strictly analogous to those described in detail elsewhere.[23]

Equilibrium and Solvolysis Measurements. Infrared measurements were made on a Perkin-Elmer 1850 FTIR spectrophotometer using a high-pressure cell with Ge windows obtained from Harrick Scientific, which has been described previously.[24] Fitted to the jacketed FTIR cell was a thermostated stainless steel high-pressure bomb with a calibrated precision thermistor probe obtained from Omega Scientific that was in direct contact with the solution. In a typical reaction, a solution was prepared in the glovebox in freshly distilled THF that was 98.9 mM in naphthalene (purified by recrystallization from CH_2Cl_2/heptane) and a 22.5 mM solution of (η^6-napht)Cr(CO)$_3$ was prepared and loaded into the infrared cell in the glovebox. The reaction vessel was taken out of the glovebox and pressurized with 100 psi of argon to maintain an inert atmosphere. Equilibrium measurements were made at a fixed temperature over a period of hours until there was no further change in the spectrum. Solvent spectra used in computer subtraction were run under identical conditions of temperature and pressure. Equilibrium data shown are the averages of three different runs at each temperature.

Reaction of (η^6-napht)Cr(CO)$_3$ with ^{13}CO. A saturated solution of (η^6-napht)Cr(CO)$_3$ in heptane was loaded into the high-pressure cell in the glovebox. After the cell was taken out of the glovebox, it was filled with ^{13}CO at 100 psi. Continuous monitoring of the spectrum showed a smooth decrease in the bands at 1977, 1916, and 1903 cm^{-1} due to (η^6-napht)Cr(CO)$_3$ and an increase in bands at 2007, 1961, 1953, and 1943 cm^{-1} which we attribute to various isomers of Cr(CO)$_3$(^{13}CO)$_3$.[25] No peaks at wavenumber lower than 1916 and 1903 cm^{-1} (split E peaks of the (η^6-napht)Cr(CO)$_3$) were observed. When the reaction went to completion—several days—and the pressure cell was opened, the solution was colorless, in keeping with complete conversion of the orange naphthalene complex to the colorless hexacarbonyl. Similar results were observed with (η^5-Me$_2$thp)Cr(CO)$_3$ (thp = thiophene), which also showed no evidence for incorporation of ^{13}CO and produced a final spectrum identical with that obtained from (η^6-napht)Cr(CO)$_3$.

Qualitative Observation on Rate and Equilibria for Binding of Arenes. Approximately 0.1 g of (η^6-anth)Cr(CO)$_3$ (anth = anthracene) was dissolved in about 50 mL of freshly distilled THF in a Schlenk tube, and this solution was transferred via syringe to a thermostated reaction vessel maintained at 30 °C. After about 20 min an aliquot was withdrawn and FTIR analysis verified near complete conversion to (THF)$_3$Cr(CO)$_3$. At that time, 1 mL of the arene to be added was injected or 1 g of the solid arene was added and the reaction followed by FTIR until conversion to (η^6-arene)Cr(CO)$_3$ was complete. Reaction times varied considerably as a function of the arene ligand. Addition of cycloheptatriene resulted in an immediate color change, and an infrared spectrum run after 5 min showed only a trace of residual (THF)$_3$Cr(CO)$_3$. Addition of anthracene resulted in establishment of a new equilibrium ratio between (η^6-anth)Cr(CO)$_3$ and (THF)$_3$Cr(CO)$_3$, which reached equilibrium in roughly 10 min. Addition of naphthalene resulted in near-quantitative conversion to (η^6-napht)Cr(CO)$_3$ with establishment of the equilibrium in roughly 20 min. Addition of thiophene resulted in behavior similar to that of naphthalene. Reaction with triphenylene occurred in roughly 2 h. Benzene required nearly 6 h to go to completion, as did pyrene (pyn), which established an equilibrium between (η^6-pyn)Cr(CO)$_3$ and (THF)$_3$Cr(CO)$_3$.

Results

Kinetics of Arene and Thiophene Displacement. Rates of ligand displacement by phosphines were studied for the arene complexes as shown in eq 6. The

$$(\eta^6\text{-arene})\mathrm{Cr(CO)_3} + 3\mathrm{PR_3} \rightarrow \textit{fac- or mer-}\mathrm{Cr(CO)_3(PR_3)_3} + \text{arene} \quad (6)$$

product formed depends on the phosphine ligand and reaction conditions. For the majority of this work P(n-Bu)$_3$ was used and the product at low temperatures was the *fac* isomer. At the higher temperatures needed to study the least reactive arenes such as benzene and styrene, the *mer* isomer was obtained. Isomerization of the *fac* to the *mer* isomer[26] probably is a secondary process occurring at higher temperatures, and its rate is fast relative to the presumed rate-determining ring

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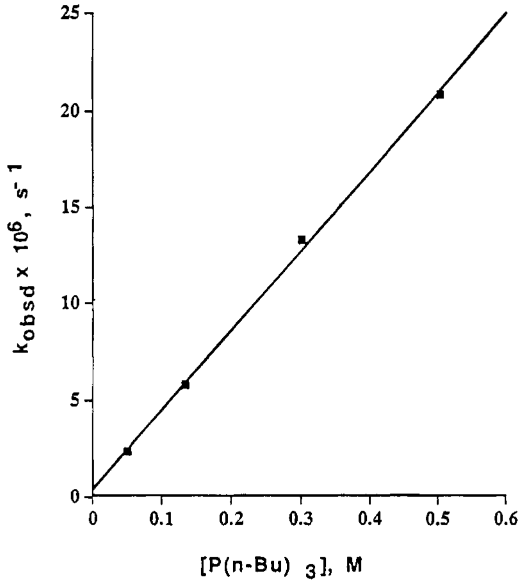

Figure 1. Plot of k_{obsd} vs ligand concentration for reaction of (η^6-C_6H_6)Cr(CO)$_3$ with P(n-Bu)$_3$ at 135 °C in decalin.

slippage. During the course of the reactions, no signs of carbonyl loss to yield phosphine-substituted complexes such as that shown in eq 7 were detected:

$$(\eta^6\text{-arene})Cr(CO)_3 + PR_3 \nrightarrow (\eta^6\text{-arene})Cr(CO)_2(PR_3) + CO \quad (7)$$

The mechanisms of these reactions were assumed to follow eq 8:

$$(\eta^6\text{-arene})Cr(CO)_3 + L \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} (\eta^4\text{-arene})Cr(CO)_3(L) + L \xrightarrow{k_b} \text{products} \quad (8)$$

This would follow the rate law

$$dP/dt = k_a k_b[(\eta^6\text{-arene})Cr(CO)_3][L]^2/[k_{-a} + k_b[L]] \quad (9)$$

According to eq 9 the kinetics should be first order in complex and between first and second order in ligand. As shown in Figures 1 and 2, plots of k_{obsd} versus [L] were linear for conditions that are pseudo first order in complex for substitution reactions of both P(n-Bu)$_3$ and PPh$_3$. This implies $k_{-a} \ll k_b[L]$ and $k_{obsd} = k_a$. Primary rate data are available as supplementary material, and a summary of rate constants and activation parameters is listed in Table 1. Additional evidence that k_{-a} is of minor importance for strong ligands is failure to incorporate ^{13}CO, discussed in a later section.

Displacement of anthracene by P(n-Bu)$_3$ was sufficiently rapid that reaction with PPh$_3$ was studied in its place. Due to solubility problems, this reaction was studied in toluene rather than in decalin. To ensure that arene versus alkane solvent did not significantly affect the rate of reaction, the reaction of the naphthalene complex was investigated and found to be slightly faster in decalin than in toluene. The enthalpies of activation determined in the two solvents differ by 0.8 ± 0.9 kcal/mol. Activation parameters for displacement of the anthracene ligand by P(n-Bu)$_3$ in decalin are estimated from the data for replacement by PPh$_3$ in toluene.

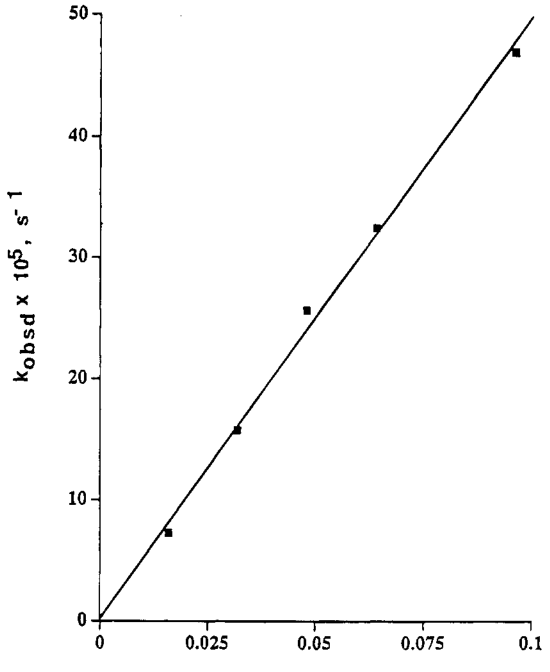

Figure 2. Plot of k_{obsd} vs ligand concentration for reaction of (η^6-napht)Cr(CO)$_3$ with PPh$_3$ at 15 °C in decalin.

Reaction of (η^6-napht)Cr(CO)$_3$ and (η^5-Me$_2$thp)-Cr(CO)$_3$ with ^{13}CO. The lack of reversibility in the first substitution was further investigated by reaction with the weaker nucleophile ^{13}CO, as shown in eq 10.

$$(\eta^6\text{-arene})Cr(CO)_3 + {}^{13}CO \rightarrow (\eta^4\text{-arene})Cr(CO)_3({}^{13}CO) \xrightarrow{+2{}^{13}CO} Cr(CO)_3({}^{13}CO)_3 + \text{arene} \quad (10)$$

Reaction 10 was investigated for both naphthalene and dimethylthiophene. At room temperature and 100 psi of ^{13}CO there was no sign of incorporation of ^{13}CO into the arene complexes in the dark, only smooth conversion to Cr(CO)$_3$(^{13}CO)$_3$. No indication of reversibility and formation of (η^6-arene)Cr(CO)$_2$(^{13}CO) was observed.

Variable-Temperature Study of the Solvolysis of (η^6-napht)Cr(CO)$_3$. In tetrahydrofuran solution, the equilibrium shown in eq 11 is established in about 1 h at room temperature. Solutions of (THF)$_3$Cr(CO)$_3$ formed via this reaction are very air sensitive. Oxidation of 1 mol of complex releases 3 mol of carbon monoxide, which reacts to yield the tetracarbonyl complex:

$$(\eta^6\text{-napht})Cr(CO)_3 + 3THF \rightleftharpoons (THF)_3Cr(CO)_3 + \text{napht} \quad (11)$$

$$4(THF)_3Cr(CO)_3 + \text{ox} \rightarrow Cr(\text{ox})(THF)_n + 3(THF)_2Cr(CO)_4 \quad (12)$$

The net result is that 1 mol of oxidant can destroy 4 mol of the complex, since (THF)$_2$Cr(CO)$_4$ does not bind arenes. Even with careful handling, solutions that have a high concentration of (THF)$_3$Cr(CO)$_3$ do not appear

Table 1. Second-Order Rate Constants and Activation Parameters for the Reaction (η^6-arene)$Cr(CO)_3$ + $3PR_3$ → $Cr(PR_3)_3(CO)_3$ + arene in Decalin

arene	T, °C	10^4k_2,[a] $M^{-1}\,s^{-1}$	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$, cal/(mol K)
	L = P (n-Bu)$_3$			
benzene	112	0.0800	23.4 ± 0.8	−21.4 ± 3.2
	135	0.410		
	150	1.29		
	165	3.81		
triphenylene (in toluene)	80	3.52	14.2 ± 0.7	−34.4 ± 1.9
	90	6.55		
	100	10.9		
phenanthrene	30	3.08	15.6 ± 0.2	−23.2 ± 0.6
	45	11.2		
	70	71.4		
pyrene	34	5.84	13.5 ± 0.6	−29.5 ± 2.1
	50	19.8		
	70	66.5		
naphthalene	5	50.0	9.9 ± 0.4	−33.5 ± 1.0
	15	92.6		
	24	167		
thiophene	2.2	45.2	11.1 ± 0.7	−28.7 ± 2.2
	15.0	113		
	23.8	215		
2,5-dimethylthiophene	25.2	7.89	13.8 ± 0.2	−26.6 ± 0.6
	36.6	19.5		
	46.2	39.0		
styrene	102	0.173	20.9 ± 0.2	−25.0 ± 0.4
	122	0.758		
	142	2.77		
	L = PPh_3			
anthracene (in toluene)	5	22.9	11.2 ± 0.9	−30.2 ± 3.3
	15	49.6		
	25	104		
	35	179		
naphthalene (in toluene)	39.5	1.47	15.2 ± 0.2	−27.5 ± 0.4
	50.0	3.32		
	66.2	10.9		
naphthalene	39.5	5.83	14.4 ± 0.7	−27.6 ± 2.0
	49.8	12.1		
	60.0	25.6		

[a] Rate constants and all primary kinetic data are accurate to typically ±10%. Complete experimental data are available as supplementary material.

to be stable for long periods of time and slow buildup of $(THF)_xCr(CO)_{6-x}$ ($x = 0-2$) could not be avoided by us. The solutions are more stable in the presence of excess free naphthalene, and this allowed accurate determination of the equilibrium constant. The solutions showed only small decomposition over a 1-day period while stored under pressure of argon in a stainless steel autoclave fitted with an FTIR cell with germanium windows. A plot of ln K_{eq} versus $1/T$ is shown for this reaction in Figure 3. Thermodynamic data derived from this plot are $\Delta H = -6.8 \pm 0.2$ kcal/mol and $\Delta S = -47.8 \pm 0.7$ cal/(mol deg).

Attempted Spectroscopic Detection of (η^4-napht)-$Cr(CO)_3(THF)$ and (1,3-CHD)$Cr(CO)_3(THF)$. Literature data on solvolysis of the naphthalene complex in THF have included a peak at 1940 cm^{-1}, which has been assigned as an intermediate in the solvolysis reaction.[11] In a number of equilibrium and spectroscopic experiments this band was never observed by us. No evidence for equilibrium concentrations of (η^4-napht)$Cr(CO)_3(THF)$ was seen.

In an attempt to detect a model for the η^4-arene complexes, binding of 1,3-cyclohexadiene (1,3-CHD) was investigated:

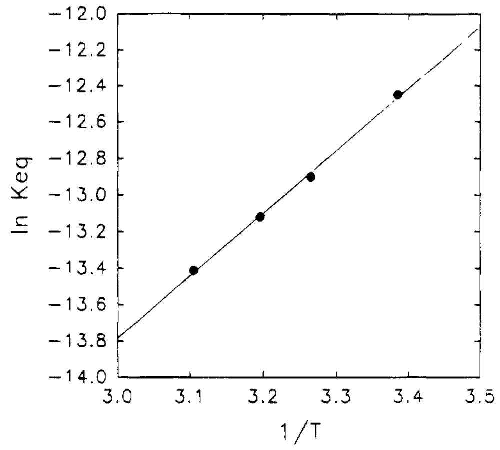

Figure 3. Plot of ln K_{eq} vs $1/T$ for the reaction (η^6-napht)$Cr(CO)_3$ + 3THF → $(THF)_3Cr(CO)_3$ + napht.

$$(\eta^6\text{-anth})Cr(CO)_3 + 3THF \rightleftharpoons (THF)_3Cr(CO)_3 + \text{anth} \quad (13)$$

$$(THF)_3Cr(CO)_3 + 1,3\text{-CHD} \not\rightleftharpoons (1,3\text{-CHD})Cr(CO)_3(THF) \quad (14)$$

A solution of $(THF)_3Cr(CO)_3$ was prepared by solvolysis of the anthracene complex (eq 13). Addition of 1,3-cyclohexadiene in 10-fold excess showed no signs of formation of any complexes except those present in the equilibrium shown in eq 13.

Enthalpies of Binding of Polycyclic Arenes and Thiophenes. Calorimetric data are based on two types of reactions. The first is reaction of the solid arene complex with pyridine (eq 15). The second is direct

$$\underset{\text{solid}}{(\eta^6\text{-arene})Cr(CO)_3} + \underset{\text{soln}}{3py} \xrightarrow{\text{THF, 50 °C}} \underset{\text{soln}}{Cr(CO)_3(py)_3} + \underset{\text{soln}}{\text{arene}} \quad (15)$$

displacement of one arene by another, in most cases by benzene (eq 16). Reaction with pyridine is fast but has

$$\underset{\text{solid}}{(\eta^6\text{-arene})Cr(CO)_3} + \underset{\text{soln}}{\text{arene}'} \xrightarrow{\text{THF, 50 °C}} \underset{\text{soln}}{(\eta^6\text{-arene}')Cr(CO)_3} + \underset{\text{soln}}{\text{arene}} \quad (16)$$

the disadvantage that it is highly exothermic and thus small differences in stability could be lost in experimental error. Direct measurement of displacement by benzene measures directly the enthalpy of exchange but has the disadvantage of being slow. As discussed later, in spite of its thermodynamic stability, benzene is kinetically one of the slowest arene ligands to bind. In 10% benzene/90% THF solution at 30 °C, calorimetric runs take approximately 6 h to go to completion. This is due to the slow rate of binding of benzene to $(THF)_3Cr(CO)_3$. Base line drift of the calorimeter can limit the accuracy of slow reactions that are only marginally exothermic. For that reason, other arenes were also used for direct calorimetric measurement. Experimental data on enthalpies of reaction are re-

Table 2. Enthalpies (kcal/mol) of Solution and Reaction of (η^6-arene)Cr(CO)$_3$ Complexes

arene	ΔH_{soln}(tol)	ΔH_{soln}(THF)	ΔH_{rxn}(py)	ΔH_{rxn}(arene)
benzene	4.7 ± 0.1	3.4 ± 0.1		
2,5-dimethylthiophene	5.2 ± 0.2	2.8 ± 0.1	−17.9 ± 0.5	1.4 ± 0.5 (benzene)
thiophene	3.2 ± 0.1	2.3 (est)[a]	−21.4 ± 0.2	−1.9 ± 0.2 (benzene)
naphthalene	5.3 ± 0.1	3.4 ± 0.2	−20.9 ± 0.2	−1.5 ± 0.3 (benzene) 0.5 ± 0.2 (2,5-Me$_2$thp) 0.9 ± 0.5 (triphenylene) 2.2 ± 0.4 (phenanthrene)
anthracene	5.0 ± 0.2	3.3 (est)[a]	−22.1 ± 0.5	−2.5 ± 0.1 (benzene)
pyrene				1.0 ± 0.6 (anthracene)[b]

[a] Value for enthalpy of solution in THF for this complex was estimated on the basis of the ratio of enthalpies of solution of analogous complexes in toluene versus THF, or on analysis of the initial endothermic response of the calorimeter. [b] Enthalpy of displacement of pyrene by anthracene estimated on the basis of equilibrium measurements as described in the text.

Table 3. Calculated Enthalpies[a] of the Reaction (η^6-C$_6$H$_6$)Cr(CO)$_3$ + nL → L$_n$Cr(CO)$_3$ + C$_6$H$_6$

L	av ΔH^b	individual measurements[c]
P(n-Bu)$_3$	−41	
pyridine	−19.4	
THF	−1.8	
benzene	0.0	
2,5-dimethylthiophene	1.6	1.4 (benzene), 1.3 (py), 2.0 (napht)
triphenylene	2.4	2.4 (napht)
phenanthrene	3.7	3.7 (napht)
thiophene	4.2	4.2 (benzene), 4.3 (py)
naphthalene	4.9	4.9 (benzene), 4.9 (py)
anthracene	5.9	5.8 (benzene), 6.0 (py)
pyrene	6.9	6.9 (anth)[d]

[a] Values in kcal/mol. Errors are on the order of ±1 kcal/mol, as discussed in the text. [b] Average enthalpy of exchange based on either direct measurement or average of several methods. [c] Enthalpies of exchange in THF solution calculated from data in Table 2, corrected for enthalpies of solution and standardized relative to benzene (=0.0). [d] Based on equilibrium between anthracene and pyrene complexes as discussed in the text.

ported in Table 2, and average enthalpies of exchange in THF solution are listed in Table 3.

Since some of the complexes are solvolyzed by THF, enthalpies of solution were measured initially in toluene (tol; eq 17).

$$\underset{\text{solid}}{(\eta^6\text{-arene})\text{Cr(CO)}_3} \xrightarrow{\text{tol, 50 °C}} \underset{\text{soln}}{(\eta^6\text{-arene})\text{Cr(CO)}_3} \tag{17}$$

Enthalpies of reaction were typically measured in THF, and so it was necessary to investigate enthalpies of solution, where possible, in this solvent as well. For example, the enthalpy of solution of the naphthalene complex in THF was measured in the presence of a large excess of free naphthalene, which inhibits the solvolytic reaction shown by eq 18.

$$\underset{\text{solid}}{(\eta^6\text{-napht})\text{Cr(CO)}_3} \xrightarrow{\text{THF, napht}} \underset{\text{soln}}{(\eta^6\text{-napht})\text{Cr(CO)}_3} \tag{18}$$

The enthalpy of solution of the Me$_2$thp complex was also measured in the presence of a 10% Me$_2$thp/90% THF solution. The enthalpy of solution of the anthracene complex was estimated on the basis of the ratio of ΔH_{soln}(THF)/ΔH_{soln}(tol) for related complexes. The enthalpy of solution of the thiophene complex was estimated on the basis of analysis of the thermograms in which only partial solvolysis occurred. As seen in Table 2, the enthalpies of solution are generally less endothermic in THF versus those in toluene, in keeping with the increased solubility in THF. For arene exchange reactions the differences in enthalpy of solution largely cancel between the product and reactant complex in going from one solvent to another and enthalpies of arene exchange in THF, toluene, CH$_2$Cl$_2$, and alkane solvents are probably the same within experimental error on the order of 1 kcal/mol for the exchange reaction.

Enthalpies of exchange of ligands relative to (η^6-C$_6$H$_6$)Cr(CO)$_3$ are shown in Table 3. The average value adopted for stability is based on the several measurements taken for each complex. There was generally good agreement between the various methods used. The enthalpy of formation of the pyrene complex was evaluated on the basis of analysis of the equilibrium reaction (eq 19). FTIR comparison of the equilibrium shown in

$$(\eta^6\text{-anth})\text{Cr(CO)}_3 + \text{pyn} \overset{\text{THF}}{\rightleftharpoons} (\eta^6\text{-pyn})\text{Cr(CO)}_3 + \text{anth} \tag{19}$$

eq 19 showed that it favored formation of the anthracene complex by a factor of 5−10-fold at room temperature. This corresponds to approximately 1 kcal/mol preference in the free energy of binding. For the structurally similar ligands in eq 19 it seems reasonable to assign this difference to enthalpic rather than entropic factors.

Qualitative Observations of Rates of Arene Binding, Dissociation, and Equilibrium.

$$(\text{THF})_3\text{Cr(CO)}_3 + \text{arene} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\eta^6\text{-arene})\text{Cr(CO)}_3 + 3\text{THF}$$

The slow nature of some of the calorimetric and equilibrium measurements prompted additional qualitative investigation of rates and equilibria of solvolysis by THF.

i. Equilibrium Position. Quantitative data were generated only for solvolysis of the naphthalene complex. The degree of solvolysis by THF at equilibrium was observed qualitatively to follow the order pyrene > anthracene > naphthalene > thiophene > phenanthrene. No evidence was found for solvolysis by THF of the triphenylene and benzene complexes. This was in agreement with the order of thermodynamic stability in Table 3 and with other literature observations.[1] One exception to the degree of solvolysis following the enthalpy of binding was dimethylthiophene. Solutions of this complex in THF showed comparable solvolysis to the thiophene complex in spite of the more favorable enthalpy of binding.

ii. Rates of Solvolysis. The rates of solvolysis by THF were observed qualitatively to be in the order anthracene > naphthalene > phenanthrene > thiophene > dimethylthiophene > pyrene. Benzene, triphenylene, cycloheptatriene, and cyclooctatetraene were not observed to undergo solvolysis, and so the rate of displacement by THF could not be evaluated.

iii. Rates of Arene Binding. Solvolysis of the naphthalene and anthracene complexes yields solutions with a high concentration of $(\text{THF})_3\text{Cr(CO)}_3$. Addition of excess arene ligand to these solutions allows evaluation of the rate of binding of the arene ligand, as shown in eq 20. Qualitative observations on rates of binding

$$(\text{THF})_3\text{Cr(CO)}_3 + \text{arene} \rightarrow (\eta^6\text{-arene})\text{Cr(CO)}_3 + 3\text{THF} \quad (20)$$

indicated the following order: cycloheptatriene > anthracene > naphthalene > thiophene ≫ pyrene, benzene. Relative rates of binding of C_6H_6 and C_6D_6 were investigated according to eq 20. The rate of binding of C_6D_6 was found to be 10% faster than that of C_6H_6.

Discussion

Arene displacement can be considered to occur stepwise as shown in eq 21. The reaction profile would be

$$(\eta^6\text{-arene})\text{Cr(CO)}_3 \underset{k_{-a},\,-\text{L}}{\overset{k_a,\,+\text{L}}{\rightleftharpoons}} (\eta^4\text{-arene})\text{Cr(CO)}_3(\text{L}) \underset{k_{-b},\,-\text{L}}{\overset{k_b,\,+\text{L}}{\rightleftharpoons}}$$
$$(\eta^2\text{-arene})\text{Cr(CO)}_3(\text{L})_2 \underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}}$$
$$(\eta^1\text{-arene})\text{Cr(CO)}_3(\text{L})_2 \underset{k_{-d}}{\overset{k_d,\,+\text{L}}{\rightleftharpoons}}$$
$$\text{Cr(CO)}_3\text{L}_3 + \text{arene} \quad (21)$$

expected to change as a function of incoming ligand as well as the nature of the bound arene. An η^1-arene complex is shown as the site of initial binding, or final departure of the arene ligand is included, based on the kinetic isotope effect studies described above, which indicated 10% faster binding of C_6D_6. However, that does not rule out a branched path involving direct formation of an η^2-arene.[27] Evidence will be presented later which supports that the highest energy point in displacement by strong ligands occurs on the way to formation of $(\eta^4\text{-arene})\text{Cr(CO)}_3(\text{L})$. It should be kept in mind, however, that no direct evidence for any of the possible intermediates in eq 21 is available and that the transition state could conceivably occur at different points for different conditions of arene, L, temperature, and solvent.

Thermochemistry of Arene, Thiophene, and Diene Binding. Relative enthalpies of binding of fused arenes span a range of about 7 kcal/mol in the order benzene > triphenylene > phenanthrene > naphthalene > anthracene > pyrene, as shown in Table 3. With few exceptions, this is the order of stability that has been observed in synthetic chemistry since the original preparation of these complexes.[1] Recent work by Own[28] and co-workers reports high regioselectivity of coordination of the Cr(CO)_3 group of 21 fused ring complexes. Site selectivity was found to follow π bond order as calculated by LCAO-MO methods. As shown in Figure 4, there is a direct correlation between heat of binding of an arene and its total π electron density.

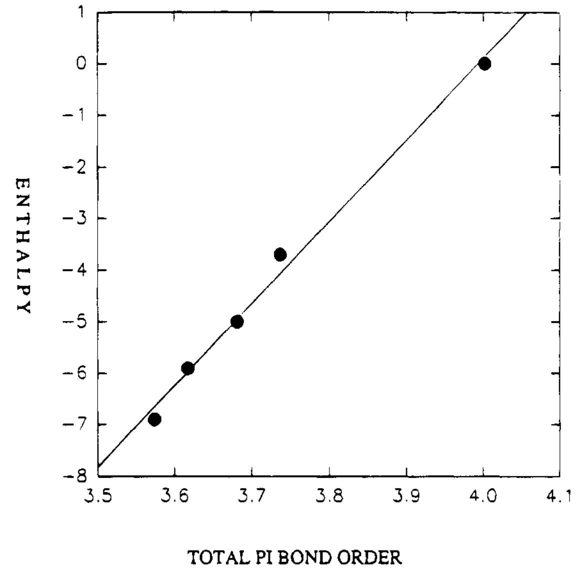

Figure 4. Plot of the enthalpy of arene exchange in $(\eta^6\text{-arene})\text{Cr(CO)}_3 + C_6H_6 \rightarrow (\eta^6\text{-}C_6H_6)\text{Cr(CO)}_3 + \text{arene}$ vs total π bond order of coordinated arene ring.[28]

$(\eta^5\text{-thp})\text{Cr(CO)}_3$ is only one of a few mononuclear η^5-thiophene complexes.[29] As shown in Table 3, the Cr—thiophene bond strength is comparable to that of naphthalene. Dimethylthiophene is some 2.4 kcal/mol more stable than is thiophene and only 1.6 kcal/mol weaker than benzene as a ligand. The greater stability of the methyl-substituted thiophene complex is similar to that observed for methyl-substituted arenes; for example, 1,3,5-trimethylbenzene binds with an enthalpy of reaction 4.3 kcal/mol greater than that of benzene.[30]

In spite of empty acceptor orbitals on the arene ligand, coordination to Cr(CO)_3 results in net removal of electron density from the bound arene comparable to that of a nitro group.[31] The greater stability, with regard to enthalpy of binding, of Me_2thp versus thiophene implies that similar bonding and net removal of electron density are occurring in the thiophene system as well. No increased bond strength in $\eta^5\text{-C}_5\text{Me}_5$ versus $\eta^5\text{-C}_5\text{H}_5$ bonding has been observed.[32] Earlier reports by Tolman and co-workers[33] showed that methyl substitution resulted in decreased equilibrium constants of binding of olefins. The enthalpy of binding of a parent ligand versus its methylated analog may provide a useful gauge of whether electron donation or back-bonding is more important in the complex. The more favorable binding of $\eta^5\text{-Me}_2\text{thp}$ versus thiophene may indicate that, like arenes, electron donation from ligand to metal is dominant in this system.

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[27] Oxidative addition of ethylene versus formation of π-bonded ethylene has been investigated: Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732. Two different pathways may exist for π bond coordination and agostic (or oxidative addition) bond formation.

[28] Own, Z. Y.; Wang, S. M.; Chung, J. F.; Miller, D. W.; Fu, P. P. *Inorg. Chem.* **1993**, *32*, 152–159.

[29] Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387.

[30] Data for Cr is listed in ref 19. For data on Mo, See: Nolan, S. P.; de la Vega, R. L.; Hoff, C. D. *Organometallics* **1986**, *5*, 2529.

[31] Semmelhack, M. F. *Pure Appl. Chem.* **1981**, *37*, 3957.

[32] Nolan, S. P.; Hoff, C. D.; Landrum, J. L. *J. Organomet. Chem.* **1985**, *282*, 357.

[33] Tolman, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 2780.

In spite of the more favorable enthalpy of binding, the equilibrium constants for displacement by THF are similar for both thiophene and dimethylthiophene. This implies that the reaction (eq 22) has a free energy change near zero. The lack of free energy change is

$$(\eta^5\text{-Me}_2\text{thp})\text{Cr(CO)}_3 + \text{thp} = (\eta^5\text{-thp})\text{Cr(CO)}_3 + \text{Me}_2\text{thp} \quad (22)$$

presumably due to a larger entropy of binding of dimethylthiophene due to steric hindrance—hindered rotation either of the methyl groups or of the ring as a whole could result in small entropic factors favoring binding of thiophene rather than its dimethyl analog. Hindered rotation of complexes of alkyl-substituted benzenes has been widely investigated by NMR,[34] and it appears that this carries over to thiophene complexes as well.

The enthalpy of binding of cyclooctatetraene (COT) was also investigated and found to be 4.3 kcal/mol weaker than that of cycloheptatriene (CHPT). This is in keeping with earlier work on related molybdenum complexes, where COT was found to be 6.6 kcal/mol weaker than CHPT.[35] Presumably this derives from greater configurational strain imposed on COT versus CHPT complexation (eq 23). In spite of the relatively

$$(\eta^6\text{-COT})\text{Cr(CO)}_3 + \text{CHPT} \rightarrow (\eta^6\text{-CHPT})\text{Cr(CO)}_3 + \text{COT} \quad (23)$$

high stability of the CHPT complex, its reaction with trimethyl phosphite, or nitriles, occurs rapidly[36] (eq 24).

$$(\eta^6\text{-CHPT})\text{M(CO)}_3 + 3\text{P(OMe)}_3 \rightarrow fac\text{-(P(OMe)}_3)_3\text{M(CO)}_3 + \text{CHPT} \quad (24)$$

M	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/(mol deg))
Cr	16.5 ± 0.7	−25 ± 2
Mo	9.8 ± 0.5	−30 ± 2
W	11.3 ± 0.8	−29 ± 2.5

The literature data show that the rate and activation parameters for displacement of (η^6-CHPT)Cr(CO)$_3$ are about in the middle of those shown in Table 1 for the arene and thiophene ligands studied here in spite of the fact that the complex is between 6.5 and 13 kcal/mol more stable. The general trend of the M—L bond strength is W > Mo > Cr. In spite of that, the highest enthalpy of activation occurs for Cr, presumably since there is more associative character to the displacements at Mo and W. The larger metals probably allow more establishment of the M—PR$_3$ bond at the transition state. The entropies of activation are similar for all three metals and are also similar to the data for arene displacement reported here.

The entropy of displacement of η^6-naphthalene by THF as shown in eq 11 is relatively close to that recently reported for displacement of cyclopentadienyl by acetonitrile (eq 25).[18] The value of $\Delta S = -51.3 \pm 2.0$ cal/(mol

$$(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3\text{H} + 3\text{MeCN} \rightleftharpoons \text{Mo(CO)}_3(\text{MeCN})_3 + \text{C}_5\text{H}_6 \quad (25)$$

deg) is similar and is in keeping with estimates made using the Sackur—Tetrode equation and entropy cycles.[37] It seems reasonable to consider that, for reactions of this type, an entropy change on the order of −50 cal/(mol deg) can be expected and that the net entropy of reaction for displacement as proposed in the mechanism shown in eq 21 will occur in the first two steps which, to a first order of approximation, would be expected to have entropy changes on the order of −25 cal/(mol deg). That is approximately the value observed in the entropy of activation values in Table 1, in agreement with formation of an associative structure of the type (η^X—arene)-Cr(CO)$_3$(L).

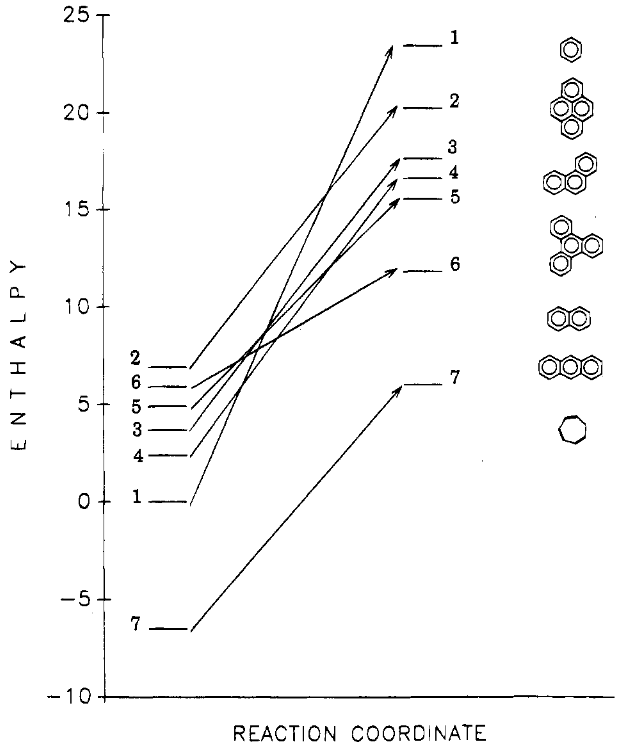

Figure 5. Reaction diagram (enthalpy of reaction in kcal/mol) showing relative energies for the complexes (η^6-arene)-Cr(CO)$_3$ and proposed transition-state complexes (η^4-arene)-Cr(CO)$_3$• •P(n-Bu)$_3$.

Kinetic Studies and Total Energy Diagram. The rate constants for arene displacement span a range of 10^8 from benzene to anthracene. Several arguments support a rate-determining first step: (i) the rate law is first order in complex and ligand, (ii) activation parameters show a high negative entropy of activation, and (iii) we fail to detect side products incorporating ^{13}CO or PR$_3$ into the starting material which might be expected if the transition state were further along the reaction pathway.

The combination of kinetic and calorimetric data can be used to construct the potential energy diagram shown in Figure 5. The stable complex (η^6-C$_6$H$_6$)Cr(CO)$_3$ is taken as the zero point. Enthalpies of ligand exchange are shown on the left side of the diagram, and enthalpies

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[34] Configurational studies of (η^6-arene)Cr(CO)$_3$ by NMR techniques have been applied extensively.[1] For an early variable-temperature study see: Rogues, B. P.; Segard, S.; Combriosson, S.; Wehrli, F. *J. Organomet. Chem.* **1974**, *73*, 327.

[35] Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 201.

[36] Gower, M.; Kane-Maguire, L. A. P. *Inorg. Chim. Acta* **1979**, *37*, 79.

[37] Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

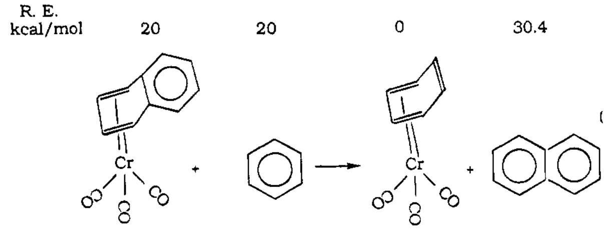
Table 4. Relative Energies and Loss of Resonance Energies of Transition States for Reactions of (arene)Cr(CO)$_3$

ligand	RE^a (kcal/mol)	ΔRE^b (kcal/mol)	$\Delta H_T{}^c$ (kcal/mol)
benzene	19.99	19.99	23.4
triphenylene	56.90	12.90	16.9
phenanthrene	44.00	13.57	19.3
pyrene	47.89	17.71	20.3
naphthalene	30.43	10.44	14.9
anthracene	37.72	7.29	11.8^d

^{a} Resonance energies calculated with experimental atomization energies.[40] ^{b} Loss of resonance energies due to η^4-arene formation. ^{c} $\Delta H_T = \Delta H^{\ddagger} + \Delta H_G$. ^{d} Assuming that the difference in $\Delta H^{\ddagger}$ values for reactions of anthracene and of naphthalene complexes with P(n-Bu)$_3$ in decalin is about the same as that for the reactions with PPh$_3$ in toluene, one can estimate $\Delta H^{\ddagger}$ for the reaction of the anthracene complex with P(n-Bu)$_3$ in decalin to be 9.9 − 4.0 = 5.9 (kcal/mol). The relative transition-state energy was calculated using this estimated $\Delta H^{\ddagger}$.

of activation are added to each of these to show the positions of the transition states for each of the complexes. No conclusions can be made from this diagram regarding the structures of the transition-state complexes. The diagram in Figure 5 does fix their enthalpies of formation within the sum of the experimental errors of the kinetic and thermodynamic studies. The combined error is on the order of 1−2 kcal/mol. The cycloheptatriene complex is shown using literature data[36] for its reaction with P(OMe)$_3$ and adjusted[38] to its reaction with P(n-Bu)$_3$ as estimated from the reaction of (η^6-napht)Cr(CO)$_3$ with P(OMe)$_3$[39] and with P(n-Bu)$_3$ (Table 1).

As mentioned above, the structures of the transition-state complexes are not known, but the ordering of energies is consistent with the simple model proposed here. It is assumed that a loosely associated η^4-complex is the transition state and that the dominant factor retarding this formation is due to energetic changes primarily involving the ligand during "ring slippage". This is illustrated by consideration of the enthalpy of exchange reaction shown for the hypothetical η^4 complexes in eq 26. In this reaction, it is considered that localization of the bond of the arene in the η^4 mode results in loss of the resonance energy of that ring only. Literature data for the resonance energies, taken from Dewar,[40] are shown in Table 4. An estimate made in the net change in delocalization energy for eq 26 considers the coordinated η^4-naphthalene complex to have the resonance energy of its one benzene ring, or 20 kcal/mol. The net change in resonance energy is +10 kcal/mol, which is actually close to the 9 ± 2 kcal/mol difference in energies of the transition states 1 and 5 shown in Figure 5.



(26)

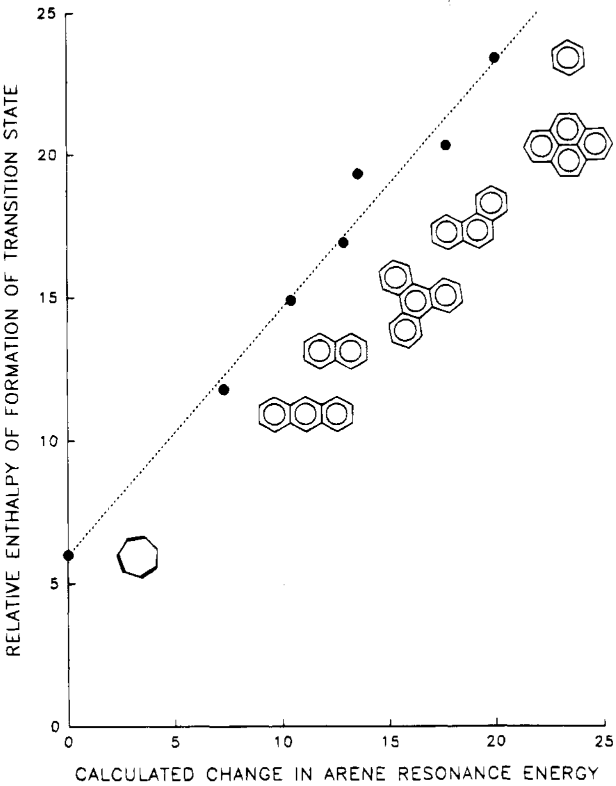
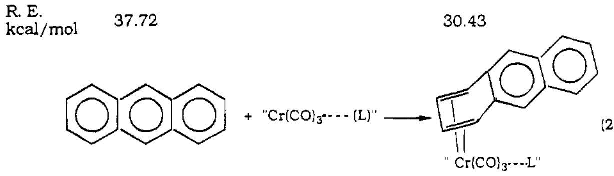


Figure 6. Plot of the enthalpy of formation of the η^4 transition state (kcal/mol) vs loss of resonance energy of the arene system. See text for details.

For the other arene ligands, the expected loss in resonance energy on forming an η^4 complex is estimated by taking the difference in total resonance energy of the free arene and the resonance energy of the uncoordinated fragment in the complex. For example, the change in resonance energy within the arene framework in formation of an η^4-anthracene complex would be the resonance energy (kcal/mol) of anthracene (37.72) minus the resonance energy of naphthalene (30.43), for a net loss of 7.29 as shown in Table 5 and illustrated in eq 27. A plot of the loss of resonance energy estimated in this way versus transition-state energies is shown in Figure 6. The good correlation indicates that this effect, or one comparable to it, is in operation. The position of cycloheptatriene, which has no resonance energy to lose, is also shown in this figure. In fused arene ring systems, the ability of the uncomplexed fragment to accept the electron pair released at the transition state appears to be a deciding factor. Like all conclusions regarding possible intermediates, this should be considered as a tentative assignment. In view of the established structures of at least some η^4-arene complexes of other metals,[8−10] and the logical necessity of cleaving the benzene one bond at a time, it seems to be a reasonable conclusion.



(27)

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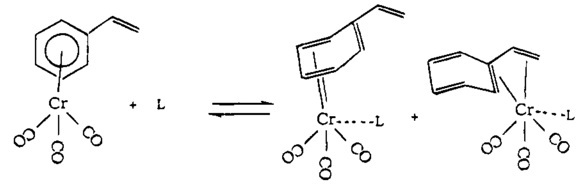
(38) The difference in activation energies for reactions of (η^6-napht)Cr(CO)$_3$ with P(n-Bu)$_3$ (9.9 ± 0.4 kcal/mol; this work) and with P(OMe)$_3$ (14.5 kcal/mol[39]) is about 4 kcal/mol. Assuming that the difference in $\Delta H^{\ddagger}$ values for the reactions of (η^6-CHPT)Cr(CO)$_3$ is about the same as that for (η^6-napth)Cr(CO)$_3$, one could estimate $\Delta H^{\ddagger}$ for reaction of (η^6-CHPT)Cr(CO)$_3$ with P(n-Bu)$_3$ to be 16.5 − 4 = 12.5 kcal/mol, and $\Delta H_T = \Delta H^{\ddagger} + \Delta H_G$ = 23.6 − 6.5 = 6 kcal/mol.

(39) Howell, J. A. S.; Dixon, D. T.; Kola, J. C.; Ashford, N. F. *J. Organomet. Chem.* **1985**, *294*, C1.

(40) Dewar, M. J.; Liano, C. D. *J. Am. Chem. Soc.* **1969**, *91*, 789.

It should also be mentioned that attack of fused arene ligands could conceivably lead to different transition states depending upon which bond of the fused arene ligand were attacked. The weakest interior bond is also the one subject to the most steric constraint if the attacking nucleophile is constrained to attack the bond directly. This could result in differences in entropies of reaction, but such fine points are beyond the accuracy of the experimental data. Theoretical treatment of this problem, beyond the scope of this paper, could shed additional light on this problem. The reader is referred to the excellent recent review covering arene exchange for related systems.[15b]

Several additional observations were made during this work that warrant comment. Thiophene and dimethylthiophene show increased reactivity relative to benzene which exceeds their thermodynamic instability. Presumably this involves acceptance of the lone pair of electrons onto the S atom and stabilization of the η^4-thiophene intermediate. The difference in enthalpy of activation between dimethylthiophene and thiophene is parallel to the ground-state difference in energies and implies that electronic factors are probably most important for these two complexes. The kinetics of reaction of the styrene complex were investigated to see if there would be rapid reactivity either through resonance effects or through formation of the external η^4-bound complex shown in eq 28. The reactivity of the styrene complex resembled more that of benzene than that of the fused arene ring systems, indicating that any effects of this type were small.



(28)

The slow nature of binding of benzene to (THF)$_3$Cr(CO)$_3$ was surprising, since it is thermodynamically the most stable and the least sterically encumbered. Presumably this is due to microscopic reversibility of the pathway and high barriers at either the η^2 or η^4 stage. To test for the possible participation of an η^1 complex, we observed that binding of C_6H_6 was about 10% *slower* than that of C_6D_6. It would be expected, on analysis of changes in zero point energy,[41] that C_6H_6 would form a more stable "agostic" complex than C_6D_6. Reports of different kinetics of binding to M(CO)$_5$(η^1-C_6H_6) and M(CO)$_5$(η^1-C_6D_6) have been reported.[42] These were obtained using rapid kinetic techniques, but even for the slow net binding observed here there is a clear isotope effect. Since an η^1 complex must convert to η^2, the higher stability of the presumed Cr(CO)$_3$(THF)$_2$(η^1-C_6H_6) complex serves to slow down the subsequent transformations.

Failure To Observe η^4 Complexes of Naphthalene or CHD and Failure To Observe ^{13}CO Incorporation. In spite of the proposal here that the (η^4-arene)Cr(CO)$_3$$\cdots$(L) structure is key to the transition state, there is no observation of formation of a stable structure here. Literature reports assigning bands to (η^4-napht)Cr(CO)$_3$(THF) were not observed. In fact, we did not observe formation of a complex with 1,2-cyclohexadiene of the type (η^4-1,3-cyclohexadiene)Cr(CO)$_3$(THF) obtainable in THF from (THF)$_3$Cr(CO)$_3$, which would be expected to be more stable. This could be due to the fact that entropic factors, which play a key role in stabilizing these chelates, would be expected to be less favorable for dienes than for trienes and arenes.[43] The failure to observe stable η^4 complexes implies that under these conditions they did not have appreciable lifetimes, but it does not rule out their role as transition states.[44]

Conclusion

In simple chelate systems, cleavage of individual bonds can be expected to exert primarily steric forces on the remaining bonds. For arene ligands, conversion of η^6 to η^4 changes the electronic nature not only of the metal–ligand bond but also of the nonbonded ring which may accept the electron pair. This work began with a simple question regarding whether ground-state or transition-state energies were more important in arene displacement. The simple answer is that both are but that the transition-state energies are more important and there is a reasonable chance that this is due to the ability of the fused arene to stabilize η^4 intermediates by acceptance of an electron pair.

1. Enthalpies of binding of fused arenes span about 7 kcal/mol. There is a good correlation between the total electron density of the π bond and the enthalpy of binding. Arene ligands, on a per-bond basis, are among the weakest donors to the Cr(CO)$_3$ group, but entropic factors favor their binding, especially at higher temperature.
2. Displacement by phosphines is first order in both nucleophile and complex. The enthalpy of activation spans some 16 kcal/mol and shows a dramatic increase in reactivity for the fused arene systems. Entropies of activation in the range −23 to −35 cal/(mol deg) are supportive of an associative displacement.
3. Conclusion 2 is supportive of (η^4-arene)Cr(CO)$_3$$\cdots$(PR$_3$) as the transition state. There is a reasonable correlation with resonance energy stabilization of the remaining arene fragment which supports the idea that the released π electron density is channeled back into the fused arene fragment, which remains a "sink" and can accept it, thus lowering the energy of the transition state.

One of the surprising results of this work was also the relatively slow rate of binding of benzene to (THF)$_3$Cr(CO)$_3$ and the faster rate of binding of C_6D_6 versus that of C_6H_6. The fused arene ring systems, which might be expected to bind more slowly since they are less thermodynamically stable and also more sterically hindered, bind much more rapidly. It is clear that these reactions depend on a number of factors. Three

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[41] Kinetic isotope effects in the complexes (P(C_6H_{11})$_3$)$_2$W(CO)$_3$ and (P(C_6D_{11})$_3$)$_2$W(CO)$_3$ have been reported: Gonzalez, A. A.; Zhang, K.; Hoff, C. D. *Inorg. Chem.* **1989**, *28*, 4285.

[42] Zhang, S.; Dobson, G. R.; Zang, V.; Bajaj, H. C.; van Eldik, R. *Inorg. Chem.* **1990**, *29*, 3477.

[43] On the basis of its analogy to eq 11, the entropy of the reaction 1,3-cyclohexadiene + (THF)$_3$Cr(CO)$_3$ → (η^4-1,3-CHD)Cr(CO)$_3$(THF) would be expected to be roughly 25 cal/(mol deg).

[44] Casey, C. P.; O'Connor, J. M. *Organometallics* **1985**, *4*, 384.

cases stand out: (i) irreversible cleavage by strong ligands, (ii) reversible cleavage by weak ligands, and (iii) arene exchange. The driving forces, both enthalpic and entropic, vary for these reactions, which may be expected also to influence the total reaction profile. Arguments given in this work provide additional support to the idea that ring slippage to the (η^4-arene)Cr(CO)$_3$···(L) transition state is a key factor in the reactivity and that this is favored for arenes whose π system is best suited to receive the electron pair from the metal. Benzene and fused arenes are deceptively simple chelating ligands.

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Supplementary Material Available: Table 1s, listing actual values of k_{obsd} for all reactions investigated (3 pages). Ordering information is given on any current masthead page.

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