The Arene-Exchange Reaction in Naphthalene- and Pyrene-Cr(CO)₃

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The arene-exchange reaction has been studied for a number of labile (arene)Cr(CO)₃ substrates in hydrocarbon solvents. A two-term rate law was established of the form $-d[S]/dt = k_A[S] + k_B[S][arene']$, where S is the (arene)Cr(CO)₃ substrate and toluene was used as the external, arene', ligand. The lability of S follows the ordering (2,6-dimethylpyridine)- > (pyrene)- > (naphthalene)- > (2,5-dimethyl-thiophene)Cr(CO)₃. Activation parameters for (naphthalene)Cr(CO)₃ were $\Delta H^{\ast}_A = 28$ (1) kcal mol⁻¹, $\Delta S^{\ast}_A = -14$ (2) cal K⁻¹ mol⁻¹, $\Delta H^{\ast}_B = 26$ (1) kcal mol⁻¹, and $\Delta S^{\ast}_B = -23$ (3) cal K⁻¹ mol⁻¹. For (pyrene)Cr(CO)₃ they were determined to be $\Delta H^{\ast}_A = 25$ (1) kcal mol⁻¹, $\Delta S^{\ast}_A = -19$ (3) cal K⁻¹ mol⁻¹, $\Delta H^{\ast}_B = 24$ (1)kcal mol⁻¹, and $\Delta S^{\ast}_B = -22$ (2) cal K⁻¹ mol⁻¹. The substitutional affinity of (pyrene)Cr(CO)₃ for arene' was found to be $C_6H_5CF_3 < C_6H_5Me < m\text{-}C_6H_4Me_2 \approx C_6H_5Bu^t < C_6Me_6 < 1,3,5$-cycloheptatriene. It is suggested that the arene'-independent path in the above rate law proceeds via an (η^y-arene)Cr(CO)₃ intermediate and the other path through an (η^x-arene)Cr(CO)₃(η^{6-x}-arene') intermediate with $y < x$. Molecular orbital calculations at the extended Hückel level were used to construct full potential energy surfaces for ring slippage in benzene, naphthalene, and (pyrene)MnCp. Selected regions were refined for the Cr(CO)₃ derivatives. An $\eta^6 \rightarrow \eta^2$ path was found to be most favorable for the naphthalene system, whereas an $\eta^6 \rightarrow \eta^1$ path required the least energy for pyrene. In (benzene)Cr(CO)₃ both paths were found to be comparable in energy. The calculations correctly predict arene lability to be in the order benzene ≪ naphthalene < pyrene. No evidence for a discrete η^4 intermediate was found for the arene'-independent route.

The sequential complexation, functionalization, and liberation of unsaturated hydrocarbons at a transition-metal center constitute one of the most important reaction sequences in both catalytic and stoichiometric organometallic synthesis. Though some kinetic and mechanistic data exist regarding substitution of π-bound hydrocarbons by σ-bonded ligands such as phosphines and phosphites, relatively little information is available regarding exchange reactions of one π-bound hydrocarbon for another.[1] Such an exchange forms an integral part of many catalytic cycles, and a stoichiometric synthesis may at least be made cyclical if a functionalized hydrocarbon can be exchanged for free hydrocarbon as part of the reaction sequence.

The recent interest in the functionalization of arenes using (arene)Cr(CO)₃ complexes[2] has focused interest on the phenomenon of arene exchange:[3]

$$(\eta^6\text{-arene})M(CO)_3 + arene' \rightarrow$$
$$(\eta^6\text{-arene}')M(CO)_3 + arene \quad (1)$$
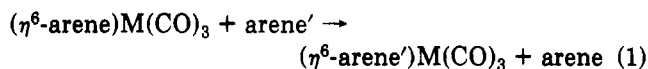
Though this reaction may be catalyzed by donor solvents (ketones, nitriles, alkenes)[4] and oxidatively catalyzed by I₂,[5] the only kinetic studies of *un*catalyzed exchange in hydrocarbon solvents (until recently) were the ¹⁴C-la-

beled-exchange results of Strohmeier et al.[6] On the basis of initial rate measurements, the rate law was represented as

$$-d[S]/dt = k_I[S] + k_{II}[S][L] + k_{III}[S]^2 \quad (2)$$

where S is the initial (arene)Cr(CO)₃ complex and L is the incoming arene. For relatively labile substrates such as (naphthalene)Cr(CO)₃ or (cycloheptatriene)Cr(CO)₃, the third term of (2) is absent, whereas, for less labile monocyclic substrates such as (toluene)Cr(CO)₃, (benzene)Cr(CO)₃, or (chlorobenzene)Cr(CO)₃, the first term is absent.

The mechanisms proposed by Strohmeier, in particular the dissociation to arene and Cr(CO)₃ to account for the first term, have received some criticism.[3,4a,7] The recent work of Traylor et al.[8] has clarified aspects of the exchange process involving monocyclic substrates, in particular the possible self-catalysis of exchange inherent in the $k_{III}[S]^2$ term of Strohmeier. We wish to report here our complete kinetic results[9] on the uncatalyzed arene exchange of polycyclic (naphthalene, pyrene) and heterocyclic (thiophene, pyridine) substrates together with the results of molecular

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(3) Muetterties, E. L.; Bleeke, J. R.; Seivert, A. C. *J. Organomet. Chem.* **1979**, *178*, 197.

(4) (a) Mahaffy, C. A. L.; Pauson, P. L. *J. Chem. Res., Synop.* **1979**, 126. (b) Zimmerman, C. L.; Shaner, S. L.; Roth, S. A.; Willeford, B. R. *J. Chem. Res., Synop.* **1980**, 108.

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Table I. Proton Chemical Shifts and CO Stretching Frequencies for the Compounds in This Study

compd	¹H NMR (CDCl₃)/ppm	ν_{CO} (decalin)/ cm⁻¹
(naphthalene)Cr(CO)₃	5.52 (dd, 2)	1974
	6.12 (dd, 2)	1910
	7.34–7.61 (m, 4)	1898
(pyrene)Cr(CO)₃	5.56 (dd, 1)	1964
	6.00 (d, 2)	1904
	7.45–7.91 (m, 7)	1898
(2,6-dimethylnaphthalene)CrCO₃	2Me 2.41, 2.29	1969
	5.38 (dd, 1)	1905
	6.07 (m, 2)	1891
	7.15–7.47 (m, 3)	
(2,6-dimethylpyridine)Cr(CO)₃	2 Me, 2.38	1984
	5.64 (t, 1)	1924
	5.08 (d, 2)	1914
(2,5-dimethylthiophene)Cr(CO)₃	2 Me, 2.18	1966
	5.23 (s, 2)	1894
		1884
(C₆H₅Me)Cr(CO)₃	Me, 2.15	1977
	5.20 (m, 5)	1902
(C₆H₅CF₃)Cr(CO)₃	5.16–5.58 (m, 5)	1994
		1930
(C₆H₅Buᵗ)Cr(CO)₃	Buᵗ, 1.27	1972
	5.21–5.54 (m, 5)	1898
(1,3-C₆H₄Me₂)Cr(CO)₃	2 Me, 2.17	1970
	5.00 (m, 3)	1898
	5.43 (m, 1)	
(C₆Me₆)Cr(CO)₃	6 Me, 2.26	1952
		1876
(cycloheptatriene)Cr(CO)₃	1.63 (m, 1)	1982
	2.88 (m, 1)	1920
	3.32 (m, 2)	1896
	4.79 (m, 2)	
	5.99 (m, 2)	
(styrene)Cr(CO)₃	6.25 (dd, 1)	1978
	5.24–5.71 (m, 7)	1912

orbital calculations at the extended Hückel level, which allow some discrimination between the variety of mechanistic choices.

Experimental Section

(1) General Considerations. Proton NMR spectra and infrared spectra were recorded on JEOL FX-100 and Perkin-Elmer 257 spectrometers, respectively. UV/visible spectra were recorded on a Varian DMS 100 spectrometer.

(2) Reagents and Materials. Substrate and product (polyene)Cr(CO)₃ complexes were prepared, by using literature methods, from Cr(CO)₃(NH₃)₃[10] (styrene, 2,6-dimethylpyridine) or Cr(CO)₆[11] (the remainder). The pyrene and dimethyl- and octamethylnaphthalene complexes were purified by column chromatography (grade III alumina, 4:1 hexane/diethyl ether followed by pure diethyl ether) to separate the complex from free ligand. Complexes were recrystallized from hexane or CH₂Cl₂/hexane in the case of (pyrene)Cr(CO)₃. A listing of proton chemical shifts and CO stretching frequencies is given in Table I.

Samples of analytical purity were used in the kinetic work. Solvents used in kinetic work (decalin, cyclooctane) were purified by stirring over concentrated H₂SO₄ for 4 h, followed by washing with water, aqueous Na₂CO₃, and again with water. After drying over CaSO₄ (decalin) or MgSO₄ (cyclooctane), the solvent was passed down on an alumina column and distilled under vacuum (15 mmHg) from sodium (decalin) or LiAlH₄ (cyclooctane) and stored under argon.

The arenes and cycloheptatriene used in the kinetic work were purified by literature methods.[12] Purity of solvents and reacting

polyenes was established by gas chromatography.

The copoly(divinylbenzene–styrene) used in exchange experiments was obtained from Polymer Laboratories Ltd. (8% crosslinked, 10-μm bead size) and was purified by washing with water, 1:1 water/ethanol and acetone, followed by Soxhlet extraction with CH₂Cl₂ and drying under vacuum.

Argon used in the kinetic work was passed through molecular sieves and an activated copper catalyst to remove traces of moisture and oxygen.

(3) Kinetic Work. The substrate was dissolved in a solvent/arene solution of appropriate concentration and transferred under argon in the absence of light to a sealed 1-cm glass cell of minimum dead volume equipped with a Teflon stopcock; cells were silylated internally by pretreatment with a 5% w/v ethereal solution of N-(trimethylsilyl)acetamide.

After degassing with argon for a minimum of 15 min, the cell was sealed under a positive pressure of argon and immersed at 120–170 °C in a constant-temperature bath (±0.2 °C). Visible spectra were recorded periodically after removal of the cell from the bath and quenching to room temperature. A cell containing the solvent/arene solution only was used as reference. Reactions were monitored by disappearance of substrate and were followed to at least 3 half-lives; mass balance at completion was established by using visible or infrared spectroscopy by calibration with solutions of known concentrations of authentic samples.

Values of k_{obs} were obtained from least-squares analyses of plots of ln $(A_t - A_\infty)$ versus time, using (in almost all cases) a minimum of 10 absorbance/time data pairs. All plots gave correlation coefficients greater than 0.999. All runs were done in duplicate and generally showed a reproducibility of ±6%.

(4) Polymer Studies. (a) Preparation of Copoly(divinylbenzene–2-vinylnaphthalene).[13] A 100-mL aliquot of water was added to a polymerization vessel equipped with stirrer and thermometer and purged with N₂; 0.125 g of surfactant [copoly(styrene–maleic anhydride)] was added, followed by 5 g of 2-vinylnaphthalene (Aldrich Chemical Co. Ltd.) and 0.25 g of benzoyl peroxide, both dissolved in the minimum amount of toluene. A 0.63-g sample of a 63% solution of divinylbenzene in ethylstyrene was added, and the mixture was stirred for 6 h at 70 °C. The resulting polymer was filtered, washed successively with 50 mL of water, 50 mL of 1:1 water/ethanol, 50 mL of ethanol, and 50 mL of acetone, Soxhlet-extracted with CH₂Cl₂, and dried under vacuum to give 2.0 g of an off-white powder.

(b) Complexation of Copoly(divinylbenzene–2-vinylnaphthalene). A 0.5-g sample of the copolymer was suspended in 50 mL of di-n-butyl ether containing 2 mL of dry tetrahydrofuran and 0.5 g of Cr(CO)₆. The mixture was refluxed for 10 h under argon, and the resulting red powder was filtered, washed with tetrahydrofuran, and dried under vacuum (yield: 0.7 g). Anal. Calcd: C, 79.1; H, 6.0; Cr, 8.6. Infrared (KBr disk): 1966, 1876 cm⁻¹.

(c) Complexation of Copoly(divinylbenzene–styrene). A 0.07-g sample of the copolymer was suspended in 5 mL of decalin containing 0.09 g of (naphthalene)Cr(CO)₃, and the mixture was heated at 130 °C for 48 h under argon. The resulting yellow powder was filtered, washed with tetrahydrofuran, and dried under vacuum (yield: 0.08 g). Anal. Calcd: C, 77.8; H, 6.5; Cr, 7.2. Infrared (KBr disk): 1966, 1882 cm⁻¹.

(d) Exchange Studies. All solutions were degassed with argon for a minimum of 15 min and sealed under 1.4 atm of pressure of argon.

(i) Copoly(divinylbenzene–2-vinylnaphthalene)Cr(CO)₃ (0.1 g) was heated in decalin (5 mL) at 140 °C for 50 h alone, in the presence of copoly(divinylbenzene–styrene) (0.36 g) and in the presence of copoly(divinylbenzene–styrene) (0.36 g) and 2,6-dimethylnaphthalene (0.3 g). The resulting yellow powder was filtered and the filtrate analyzed by infrared spectroscopy for Cr(CO)₆.

(ii) Copoly(divinylbenzene–2-vinylnaphthalene)Cr(CO)₃ (0.1 g) suspended in hexane (8 mL) was reacted with P(OMe)₃ (1.0

(10) (a) McNeese, T. J.; Cohen, M. B.; Foxman, B. M. *Organometallics* **1984**, *3*, 552. (b) Rausch, M. D.; Moser, G. A.; Zaiko, E. J.; Lipman, A. L. *J. Organomet. Chem.* **1970**, *23*, 185.
(11) (a) Desobry, V.; Kündig, E. P. *Helv. Chim. Acta* **1981**, *64*, 1280. (b) Pauson, P. L.; Mahaffy, C. A. L. *Inorg. Synth.* **1979**, *19*, 154.

(12) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, U.K., 1966.
(13) Reports regarding the preparation of such copolymers exist in the patent literature: (a) Uraneck, C. A.; St. John, W. M. *Chem. Abstr.* **1959**, *53*, 17570h. (b) Kuyama, J.; Utsunomiya, Y. *Ibid.* **1968**, *69*, 11111n.

mL) overnight. The resulting yellow powder was filtered, and the colorless solution was analyzed by infrared for *fac*-Cr-(CO)$_3$[P(OMe)$_3$]$_3$. A pure sample of this complex for calibration purposes was prepared by using the literature method.[14]

(iii) Copoly(divinylbenzene–2-vinylnaphthalene)Cr(CO)$_3$ (0.1 g) was heated in toluene (0.5 mL) at 140 °C for 4 h. The resulting yellow powder was filtered and the yellow solution analyzed by infrared spectroscopy for (toluene)Cr(CO)$_3$.

(5) Computational Data. The extended Hückel calculations[15] utilized a modified version of the Wolfsberg–Helmholz formula.[16] The H_{ij} values and orbital exponents were taken from previous work.[17] Idealized geometries for the polyenes were used with C–C = 1.41 Å. The geometry for the Cr(CO)$_3$ group was Cr–C = 1.84 Å, C–O = 1.14 Å, Cr–C–O = 180°, and C–Cr–C = 90°.

Results

The exchange reactions

$$(polyene)M + toluene \rightarrow (toluene)M + polyene$$
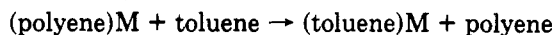
where M = Cr(CO)$_3$ and polyene = naphthalene, pyrene, 2,5-dimethylthiophene, 2,6-dimethylpyridine, were monitored in hydrocarbon solvent (decalin, cyclooctane) by disappearance of the red (pyrene, 530 nm; naphthalene, 470 nm; 2,5-dimethylthiophene, 470 nm) or yellow (2,6-dimethylpyridine, 440 nm) substrates at the wavlengths indicated above. With the exception of the pyridine complex, (toluene)Cr(CO)$_3$ is transparent at the monitoring wavelengths used. At completion, reactions were analyzed by infrared and visible spectroscopy for (toluene)Cr(CO)$_3$ and Cr(CO)$_6$ by using calibration solutions of known concentrations.

Particular mention should be made of the sensitivity of reaction rate to solvent impurities and traces of oxygen. Rate enhancements of up to 10-fold may be observed with unpurified solvents, due, presumably, to catalysis by unsaturated or oxygenated impurities. Although gross decomposition to chromium oxides is evident in the presence of large concentrations of oxygen, the trace amounts of oxygen usually present in commercial argon also effect a catalysis of the exchange reaction without detectable loss of yield; this catalysis also masks the increase in rate with increasing toluene concentration at concentrations less than about 0.1 mol dm^{-3}.[18] Solvents were, therefore, carefully purified, and argon used in kinetic work was passed through molecular sieves and an activated copper catalyst.

Kinetic Results for the (arene)Cr(CO)$_3$ Complexes. Kinetic data are presented in Table II, and plots of k_{obs} against [toluene] are shown in Figure 1. Polyene lability follows the ordering 2,6-dimethylpyridine > pyrene > naphthalene > 2,5-dimethylthiophene. At 150 °C, exchange between toluene and the Cr(CO)$_3$ complexes of styrene, octamethylnaphthalene, and cycloheptatriene was too slow to be kinetically useful. Recent calorimetric results[19] show that (cycloheptatriene)Cr(CO)$_3$ is thermodynamically more stable than (toluene)Cr(CO)$_3$ by approximately 5.0 kcal mol^{-1}, equivalent to an equilibrium constant for the reaction
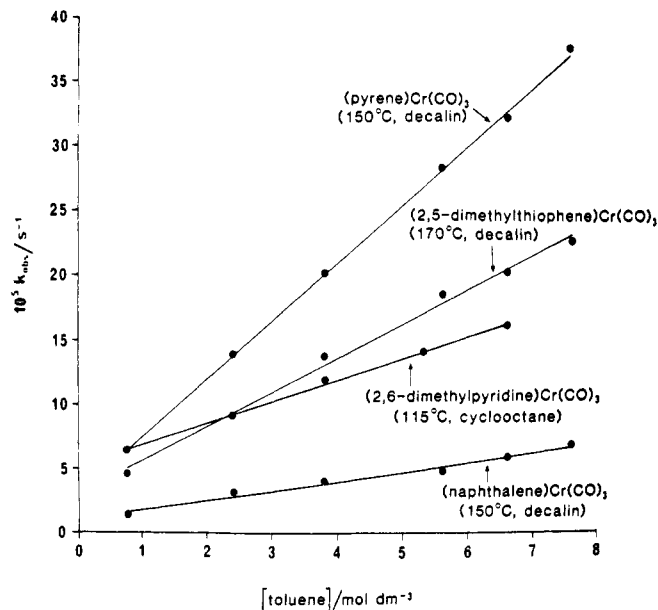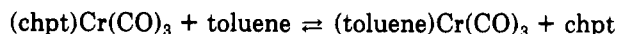
$$(chpt)Cr(CO)_3 + toluene \rightleftharpoons (toluene)Cr(CO)_3 + chpt$$

(14) Pidcock, A.; Taylor, B. W. *J. Chem. Soc. A* **1967**, 877.

(15) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179, 3489; **1962**, *37*, 2872. Hoffmann, R. *Ibid.* **1963**, *39*, 1397.

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(17) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546.

(18) Such a catalysis accounts for the independence of rate on [arene] at low arene concentrations reported earlier.[9]

(19) (a) Hoff, C. D. *J. Organomet. Chem.* **1983**, *246*, C53. (b) Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 201. (c) Nolan, S. P.; Lopez de Vega, R.; Hoff, C. D. *Organometallics* **1986**, *5*, 2529.

Figure 1. Plots of k_{obs} versus [toluene] for the reaction (polyene)Cr(CO)$_3$ + toluene → (toluene)Cr(CO)$_3$ + polyene.

at 150 °C of approximately 2.9 × 10^{-3}. However, at the relative concentrations used in our experiments (10^{-3} mol dm^{-3} (chpt)Cr(CO)$_3$ and 6 mol dm^{-3} toluene), 95% of the bound chromium should be present as (toluene)Cr(CO)$_3$ at thermodynamic equilibrium. The lack of reaction is, therefore, kinetic, rather than thermodynamic, in origin.

All reactions measured exhibit strict first-order behavior with respect to disappearance of substrate. Additionally, the independence of k_{obs} as a function of initial substrate concentration for the (2,6-dimethylpyridine)-, (pyrene)-, and (naphthalene)Cr(CO)$_3$ complexes at both high and low toluene concentrations confirms the experimental rate law as

$$-d[S]/dt = k_A[S] + k_B[S][toluene] \tag{3}$$

Reactions in which the toluene concentration exceeds approximately 0.7 mol dm^{-3} all provide quantitative yields of (toluene)Cr(CO)$_3$. Though the rate law is maintained (for example, in the pyrene and naphthalene cases) down to almost pseudo-first-order limiting conditions ([toluene] = 3 × 10^{-2} mol dm^{-3}, [substrate] = 1 × 10^{-3} mol dm^{-3}), reactions below toluene concentrations of about 0.7 mol dm^{-3} are complicated by concomitant formation of Cr(CO)$_6$ and consequent decreased yields of (toluene)Cr(CO)$_3$. The amount of Cr(CO)$_6$ formed increases from about 5% (based on initial substrate concentration) at [toluene] = 0.7 mol dm^{-3} to about 10% at [toluene] = 0.03 mol dm^{-3} in the case of (naphthalene)Cr(CO)$_3$, and other complexes show similar behavior. Thermal decomposition of both (naphthalene)- and (pyrene)Cr(CO)$_3$ in the absence of toluene provides an approximately 30% yield of Cr(CO)$_6$ and proceeds at rates that are approximately half the value of the extrapolated intercepts of the plots of Figure 1. These intercepts, however, represent a genuine kinetic pathway to product, and not simply a competitive decomposition. At concentrations of toluene greater than 0.7 mol dm^{-3}, where yields of (toluene)Cr(CO)$_3$ are quantitative, the relative values of k_A and k_B show that the reaction is still carried mainly by the k_A term. The constancy of rate values between different samples of purified solvents and the similarity of k_A and k_B values for the exchange of (pyrene)Cr(CO)$_3$ at 150 °C in decalin and cyclooctane indicate that k_A does not reflect a catalysis by undetected solvent impurity. The observed rate law is thus consistent

Scheme I

M = Cr(CO)₃
Ar = arene

Reaction Coordinate

with Strohmeier's exchange study of (naphthalene)Cr(CO)₃ using [^{14}C]naphthalene,[6] though our k_A value for exchange of (naphthalene)Cr(CO)₃ with toluene at 145 °C in cyclo-octane (0.98×10^{-5} s^{-1}) differs by about a factor of 50 from the value reported by Strohmeier in cyclohexane at 140 °C (45.4×10^{-5} s^{-1}). Comparison of k_B values is not meaningful because of the difference in the entering ligand. Activation parameters for the exchange reaction of (naphthalene)Cr(CO)₃ and (pyrene)Cr(CO)₃ with toluene are listed in Table III.

An experimental rate law of this type is not uncommon in organometallic reactions[1a] and, at least for exchange or substitution of monodentate ligands, is generally interpreted as reflecting competing dissociative and I_d pathways. The mechanism that is most consistent with the experimental rate law and with the computational results (vide infra) is shown is Scheme I. One may note the absence (even for self-exchange where arene = arene′) of symmetrical intermediates, except fortuitously when $x = y = 3$. In general terms, microscopic reversibility in this system can best be viewed in terms of two reaction channels that exhibit an energy contour map with an inversion center of symmetry.[20] An energy profile for self-exchange in the associative pathway is shown in Scheme I. A similar profile can be drawn for the dissociative contribution to the mechanism, and both can be extended to cases where arene and arene′ are different.

On the assumption that k_4[arene′] $\gg k_{-3}$ and that $k_{-1} \gg k_2$, application of the steady-state approximation yields the rate law

$$\frac{-d[S]}{dt} = k_3[S] + \frac{k_1 k_2}{k_{-1}}[S][\text{arene}'].\qquad (4)$$

The mechanism thus proceeds by rings of increasing slippage ($y < x$) but with both dissociative and associative pathways contributing to the overall reaction rate. Previously, postulated mechanistic scenarios[1,3] generally contain η^4-arene ($x = y = 4$) in the initial slippage intermediate. Kinetic studies do not provide numerical values for x and y; this question forms the subject of our molecular orbital calculations.

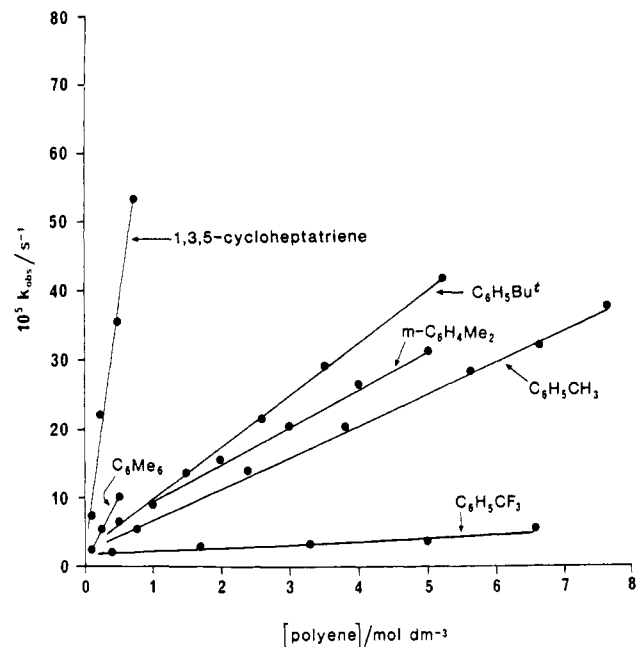The small amounts of Cr(CO)₆ observed at low concentrations of arene′ most probably arise from a competitive,

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Figure 2. Plots of k_{obs} versus [polyene] for the reaction (η^6-pyrene)Cr(CO)₃ + polyene → (η^6-polyene)Cr(CO)₃ + pyrene.

unimolecular decomposition to release CO, which, at the temperatures used, reacts rapidly with substrate to give Cr(CO)₆. We have confirmed that reaction of (naphthalene)Cr(CO)₃ in decalin under 1 atm of CO is rapid ($k_{obs} \approx 3 \times 10^{-3}$ s^{-1} at 120 °C) and produces a quantitative yield of Cr(CO)₆, both in the absence of toluene and in the presence of a 100:1 molar excess of toluene.

Substitutional Affinity of (pyrene)Cr(CO)₃. The effect of a change in the entering arene for exchange with (pyrene)Cr(CO)₃ is consistent with Scheme I (Figure 2). The same rate law is obeyed, with slopes that are arene′-dependent, but with an intercept that is common. When the hexamethylbenzene reaction is omitted, where precision is limited due to the limited solubility of the ligand, no intercept value is further than 4 standard deviations from the average.

The differing slopes may be taken as a measure of the substitutional affinity of the different arenes. Values span a range of about 100 and increase in the order C₆H₅CF₃ < C₆H₅Me < m-C₆H₄Me₂ ≈ C₆H₅Bu^t < C₆Me₆ < 1,3,5-

Table II. Kinetic Data for Arene-Exchange Reactions

solvent/substrate	incoming arene	temp/°C	$10^3[S]/$ mol dm^{-3}	[arene]/ mol dm^{-3}	$10^5k_{obs}/s^{-1}$	$10^5k_A/s^{-1}$	$10^5k_B/$mol^{-1} dm^3 s^{-1}
(pyrene)Cr(CO)$_3$/decalin	C$_6$H$_5$Me	150	1.0	7.6	37.5	2.84 (0.24)	4.50 (0.05)
			10.0	7.6	38.8[b]		
			1.0	6.6	32.0		
			1.0	5.6	28.1		
			1.0	3.8	20.0		
			1.0	2.4	13.9		
			1.0	0.76	6.45		
			0.5	0.76	5.81[b]		
			0.5	2.4	13.7[b]		
			1.0	0.38	3.85[b]		
			1.0	0.19	3.10[b]		
			1.0	0.10	2.85[b]		
(naphthalene)Cr(CO)$_3$/decalin	C$_6$H$_5$Me	150	1.0	7.6	6.88	1.11 (0.09)	0.724 (0.016)
			1.0	6.6	5.87		
			1.0	5.6	4.85		
			1.0	3.8	3.97		
			1.0	2.4	3.15		
			1.0	0.76	1.48		
			2.0	0.76	1.35[b]		
			0.5	0.76	1.60[b]		
			1.0	0.19	0.880[b]		
			1.0	0.10	0.785[b]		
			1.0	0.03	0.662[b]		
(2,5-dimethylthiophene)Cr(CO)$_3$/decalin	C$_6$H$_5$Me	170	1.0[a]	7.6	22.6	3.00 (0.27)	2.63 (0.05
				6.6	20.2		
				5.6	18.4		
				3.8	13.7		
				2.4	9.10		
				0.76	4.63		
(pyrene)Cr(CO)$_3$/decalin	C$_6$H$_5$Bu^t	150	1.0[a]	7.6	22.6	2.37 (0.41)	7.55 (0.13)
				3.50	29.1		
				2.60	21.5		
				1.50	13.7		
				0.52	6.36		
	m-C$_6$H$_4$Me$_2$	150	1.0[a]	5.0	33.0	3.13 (0.31)	5.92 (0.09)
				4.0	26.4		
				3.0	20.3		
				2.0	15.4		
				1.0	9.10		
	C$_6$Me$_6$	150	1.0[a]	0.5	9.97	5.4 (2.5)	19.1 (0.75)
				0.25	5.62		
				0.10	2.26		
	C$_6$H$_5$CF$_3$	150	1.0[a]	6.6	5.62	1.67 (0.14)	0.558 (0.032)
				5.0	3.75		
				3.3	3.28		
				1.7	2.75		
				0.4	1.96		
	C$_7$H$_8$	150	1.0[a]	0.76	53.1	1.69 (0.96)	68.1 (2.1)
				0.50	35.5		
				0.25	22.0		
				0.10	7.35		
(pyrene)Cr(CO)$_3$/cyclooctane	C$_6$H$_5$Me	115	1.0[a]	6.6	2.52	0.336 (0.027)	0.320 (0.006)
				5.3	1.91		
				3.8	1.60		
				2.4	1.11		
				0.76	0.58		
(pyrene)Cr(CO)$_3$/cyclooctane	C$_6$H$_5$Me	130	1.0[a]	6.6	7.17	1.03 (0.060)	0.955 (0.014)
				5.3	6.16		
				3.8	4.90		
				2.4	3.30		
				0.76	1.65		
		140	1.0[a]	6.6	17.4	2.52 (0.010)	2.29 (0.023)
				5.3	15.0		
				3.8	11.4		
				2.4	7.91		
				0.76	4.20		
		150	1.0[a]	6.6	35.6	5.51 (0.21)	4.52 (0.049)
				5.3	29.3		
				3.8	21.9		
				2.4	16.7		
				0.76	9.04		
(naphthalene)Cr(CO)$_3$/cyclooctane	C$_6$H$_5$Me	130	1.0[a]	6.6	0.87		
				3.8	0.72		
				2.4	0.55		
				0.76	0.38		
		145	1.0[a]	6.6	3.11	0.980 (0.034)	0.316 (0.007)

Table II (Continued)

solvent/substrate	incoming arene	temp/°C	$10^3[S]/$ mol dm^{-3}	[arene]/ mol dm^{-3}	$10^5k_{obs}/s^{-1}$	$10^5k_A/s^{-1}$	$10^5k_B/$ mol^{-1} dm^3 s^{-1}
(naphthalene)Cr(CO)₃/cyclooctane	C₆H₅Me	145	1.0^a	5.3	2.65		
				3.8	2.15		
				2.4	1.67		
				0.76	1.29		
		160	1.0^a	6.6	11.3	3.38 (0.13)	1.19 (0.029)
				5.3	9.60		
				3.8	7.85		
				2.4	6.35		
				0.76	4.26		
(naphthalene)Cr(CO)₃/cyclooctane	C₆H₅Me	175	1.0^a	6.6	30.7	11.0 (0.39)	2.88 (0.09)
				5.3	25.2		
				3.8	22.3		
				2.4	17.5		
				0.76	13.5		
(2,6-dimethylpyridine)Cr(CO)₃/cyclooctane	C₆H₅Me	115	1.0	6.6	16.1	5.18 (0.15)	1.68 (0.05)
			1.0	5.3	14.0		
			1.0	3.8	11.8		
			1.0	2.4	8.16		
			0.5	0.76	6.07		

^{a} All runs within this group were at the same substrate concentration. ^{b} Runs not used in calculation of k_A and k_B.

Table III. Activation Parameters Found for the Exchange Reaction Using Toluene as the Entering Ligand^a

substrate	$\Delta H^{\ddagger}_A/$ kcal mol^{-1}	$\Delta S^{\ddagger}_A/$cal K^{-1} mol^{-1}	$\Delta H^{\ddagger}_B/$ kcal mol^{-1}	$\Delta S^{\ddagger}_B/$cal K^{-1} mol^{-1}
(naphthalene)Cr(CO)₃	28 (1)	−14 (2)	26 (1)	−23 (3)
(pyrene)Cr(CO)₃	25 (1)	−19 (3)	24 (1)	−22 (2)

^{a} The standard deviations are given in parentheses. Subscripts A and B refer to eq 3.

cycloheptatriene. Measurements of relative rates at a single arene concentration in the xylene series show a reactivity order ortho (1.0) = meta (1.0) < para (1.2). These kinetic results are in keeping with the very small difference in thermodynamic stability observed between the three (xylene)Mo(CO)₃ isomers.[19c] Exchange between (pyrene)Cr(CO)₃ and arenes such as C₆H₅CH₂CO₂Me containing Lewis base donor sites is complete within a few minutes at 150 °C. The above ordering is the same as that qualitatively observed for the reaction of Mo(CO)₆ with these arenes and cycloheptatriene.[21] At least for the arenes, there is a direct correlation between increasing reaction rate and the increasing thermodynamic stability of the product complex resulting from increased methyl substitution.[19] Cycloheptatriene is different; although it exhibits the highest k_B value, recent results place its M-polyene ground state bond enthalpy contribution between Cr–toluene and Cr–mesitylene.[19a] Such a reversal of ordering is not unknown; although *cis*-2-pentene reacts more rapidly than 1-pentene with W(CO)₅(acetone), the terminal alkene forms the more thermodynamically stable W-(CO)₅(alkene) complex.[22]

Mechanistic Discussion. The $k_B[S][arene']$ term of rate law (3) is typical of substitution reactions of arene and cycloheptatriene complexes of both Mo and Cr by group 15 ligands.[14,23] In common with these reactions, this term

may be interpreted as either a dissociative slippage (i.e., a discrete (η^x-arene)Cr(CO)₃ intermediate) or an associative pathway (probably I$_d$) in which slippage and attack of entering ligand are concerted, as shown in Scheme I.

Interpretation of the $k_A[S]$ term requires some comment, since at least three interpretations different from that presented in Scheme I have been discussed in the literature.

(a) As in Strohmeier's original postulate, it may represent a dissociative to Cr(CO)₃ followed by rapid coordination of arene'.[6c] Following Traylor,[8b] we have sought to examine the potential viability of a Cr(CO)₃ intermediate by application of the three-phase test[24] in the following reaction:

(dvb–2-vn)Cr(CO)₃ + dvb–st →
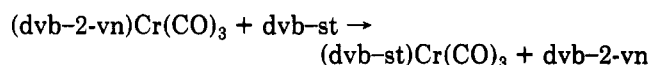
(dvb–st)Cr(CO)₃ + dvb–2-vn

where dvb–2-vn = copoly(divinylbenzene-2-vinyl-naphthalene) and dvb–st = copoly(divinylbenzene–styrene). Red (dvb–2-vn)Cr(CO)₃ of about 8% Cr content may be prepared by the complexation method used for (naphthalene)Cr(CO)₃. The naphthalene-bound chromium may be determined and differentiated from chromium bound to monocyclic rings and from any chromium deposited through decomposition by extraction of the polymer with either toluene to give (toluene)Cr(CO)₃ or P-(OMe)₃ to give *fac*-Cr(CO)₃[P(OMe)₃]₃, both under conditions where (dvb–st)Cr(CO)₃ is unreactive. The chromium-bound naphthalene may thus be estimated as 1% by weight (about one-eighth of the total chromium content). Polymeric complexes recovered after extraction by toluene or P(OMe)₃ are yellow and exhibit infrared spectra that are indistinguishable in the CO stretching region from (dvb–st)Cr(CO)₃. In common with (naphthalene)Cr(CO)₃, the (dvb–2-vn)Cr(CO)₃ complex undergoes thermal decomposition in the absence of ligand to produce about a 30% yield of Cr(CO)₆ under conditions where (dvb–st)-Cr(CO)₃ is unreactive.

Catalyzed bead-to-bead exchange may be accomplished, the most efficient catalyst being 2,6-dimethylnaphthalene. Thus, reaction of (dvb–2-vn)Cr(CO)₃ with copoly(divinylbenzene–styrene) in the presence of 2,6-dimethyl-naphthalene initially develops a red solution due to (2,6-dimethylnaphthalene)Cr(CO)₃, which fades with time to

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(23) (a) Zingales, F.; Chiesa, A.; Basolo, F. *J. Am. Chem. Soc.* 1966, *88*, 2707. (b) Pidcock, A.; Smith, J. D.; Taylor, B. W. *J. Chem. Soc. A* 1967, 872. (c) Pidcock, A.; Smith, J. D.; Taylor, B. W. *Ibid.* 1969, 1604. (d) Gower, M.; Kane-Maguire, L. A. P. *Inorg. Chim. Acta* 1979, *37*, 79. (e) Yagupsky, G.; Cais, M. *Inorg. Chim. Acta* 1975, *12*, L27. (f) Butler, I. S.; Ismail, A. A. *Inorg. Chem.* 1986, *25*, 3910.

(24) Rebek, J.; Gavina, F. *J. Am. Chem. Soc.* 1975, *97*, 3453.

yield yellow beads and a transparent solution containing no $Cr(CO)_6$. In contrast, attempts at *uncatalyzed* bead-to-bead exchange result only in the liberation of $Cr(CO)_6$ in an amount equivalent to that formed from the thermolysis of $(dvb-2-vn)Cr(CO)_3$ in the absence of copoly-(divinylbenzene–styrene). The results suggest that any "$Cr(CO)_3$" intermediate produced by Cr–naphthalene bond scission has too short a lifetime to allow diffusion to another arene site before decomposition to "Cr" and CO.

Additionally, the substantial negative $\Delta S^\ddagger$ values associated with k_A (Table III) are not consistent with such a dissociative process. The values imply a substantially more ordered nature for the slipped η^y intermediate.

(b) As originally postulated by Pauson,[4a] the k_A term may represent rate-determining CO dissociation, followed by rapid arene exchange and recoordination of CO. We have not been able to examine the influence of external CO on the rate of arene exchange because of rapid formation of $Cr(CO)_6$. The results of Traylor[8] on monocyclic arene complexes are not consistent with this mechanism, and there is no spectroscopic or crystallographic indication that in our more ring-labile complexes, the M–CO bonds are also more labile. A decreasing value for the highest frequency ν_{CO} band has been taken as a measure of increasing M–CO back-bonding, and, therefore, increasing M–CO bond strength.[25] All of the substrates used in this work show ν_{CO} values that lie within ± 13 cm^{-1} of the 1977 cm^{-1} position of $(toluene)Cr(CO)_3$. Indeed, the effect of changing the substituent in the monocyclic series is more substantial (e.g., $C_6H_5CF_3$ 1994 cm^{-1}; C_6Me_6 1952 cm^{-1}).

(c) The k_A term may represent a bimolecular catalysis of the exchange by substrate arene complex, product arene complex, or both. Recently,[8b] the exchange reaction

$(benzene)Cr(CO)_3$ + mesitylene $\rightarrow$
$\qquad\qquad$ $(mesitylene)Cr(CO)_3$ + benzene
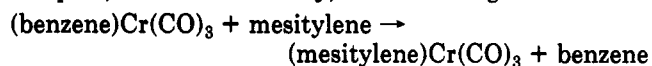
in cyclohexane at 170 °C has also been shown to obey rate law (3). While the values of k_A and k_B (3.7 × 10^{-7} s^{-1} and 2.5 × 10^{-7} mol^{-1} dm^3 s^{-1}) are about 100 times less than our results for pyrene/toluene exchange at 150 °C, the k_A:k_B ratio is comparable.

Combined with the demonstration that $(C_6Me_6)Cr(CO)_3$ functions as a catalyst for arene exchange without undergoing exchange itself, the implication of this recent work is that the $k_A[S]^2$ term of Strohmeier may better be represented as

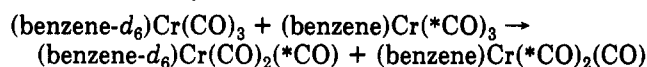$$d[S]/dt = k_A[S]\{[S] + [(\text{arene}')Cr(CO)_3]\} \qquad (5)$$

where [S] + [(arene$'$)$Cr(CO)_3$] represents the *total* (arene)$Cr(CO)_3$ concentration and is constant. Catalysis is postulated to occur through formation of an intermediate such as **1a**, which undergoes rapid exchange of the η^4-ring,

1a　　　　　　　**1b**
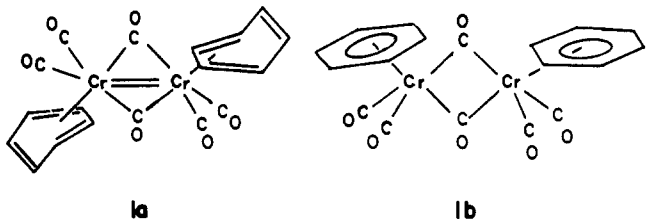
with both substrate and product being catalytically active. As written, eq 5 implies an equal catalytic activity for both substrate and product and, while this is almost certainly true for the isotopic exchange results of Strohmeier, it would be coincidental in the benzene/mesitylene reaction above.

If the substrate is a much better catalyst than a product, the reaction should exhibit a second-order dependence on the concentration of substrate. If the product is a much better catalyst, the rate of reaction should increase with time and should be sensitive to product complex added at the start of the reaction. We find neither; the reactions of the pyrene, naphthalene, and pyridine complexes with toluene are all first order in substrate concentration at low concentrations of toluene where the k_A term predominates and, in the case of exchange of $(pyrene)Cr(CO)_3$ with $C_6H_5Bu^t$, the reaction rate is not increased by introduction of a 10-fold molar excess of $(C_6H_5Bu^t)Cr(CO)_3$ at the start of the reaction. The pyrene/$C_6H_5Bu^t$ exchange at 150 °C *can* be catalyzed, strongly by tetrahydrofuran (10:1 molar excess, reaction complete within minutes in 8 mol dm^{-3} toluene)[26] or weakly by $(C_6Me_6)Cr(CO)_3$ (10:1 molar excess, rate enhancement of about 1.5 in the same solvent). However, we have no evidence for catalytic activity by substrate or product in any of the other complexes used in our work.

A recent study[8c] of the reaction

$(benzene-d_6)Cr(CO)_3$ + $(benzene)Cr(*CO)_3$ $\rightarrow$
$\qquad$ $(benzene-d_6)Cr(CO)_2(*CO)$ + $(benzene)Cr(*CO)_2(CO)$

where $*CO$ is ^{13}CO shows that CO exchange, which is *non*dissociative, occurs at a rate which is 1 order of magnitude faster than arene exchange. Thus, if arene exchange is catalyzed bimolecularly, intermediate **1a** must lie at a significantly higher energy than the bridged species **1b**, postulated to be an intermediate in the CO exchange.

Theoretical Discussion

The remaining key questions, then, concern the viability of the proposed reaction mechanism in Scheme I along with the values of x and y. For this, we turn to molecular orbital calculations at the extended Hückel level. The bonding in $(\eta^6\text{-arene})Cr(CO)_3$ complexes has been extensively discussed elsewhere,[17,27] and thus, our focus will be on the dynamics of slippage in $Cr(CO)_3$ complexes of benzene, naphthalene, and pyrene. Our basic working approach is to first obtain a crude overview of the entire potential energy surface. To do this we have chosen benzene, naphthalene, and pyrene–MnCp. A MnCp group is isolobal[28] to $Cr(CO)_3$; the overall form of the potential energy surface in a qualitative sense is insensitive to this substitution.[27d] The reason this replacement was made centers around the orientational dependence of the Cr(CO)$_3$ group, which is absent in MnCp.[17] Allowing an extra dimension for $Cr(CO)_3$ rotation is prohibitive for the construction of a full potential energy surface as large as that for $(pyrene)Cr(CO)_3$. The critical regions of the MnCp surfaces were then recalculated for the $(arene)Cr(CO)_3$ complexes, and additional geometrical optimizations were performed as indicated. We have *not* refined (allowed for additional geometric flexibility) the arene–MnCp surfaces. As we shall see, there are artifacts created by the geometrical constraints used in the construction of them. Nevertheless, they are useful to make qualitative comparisons

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(28) (a) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; John Wiley: New York, 1984. (b) Hoffmann, R. *Angew. Chem.* **1982**, *94*, 725; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.
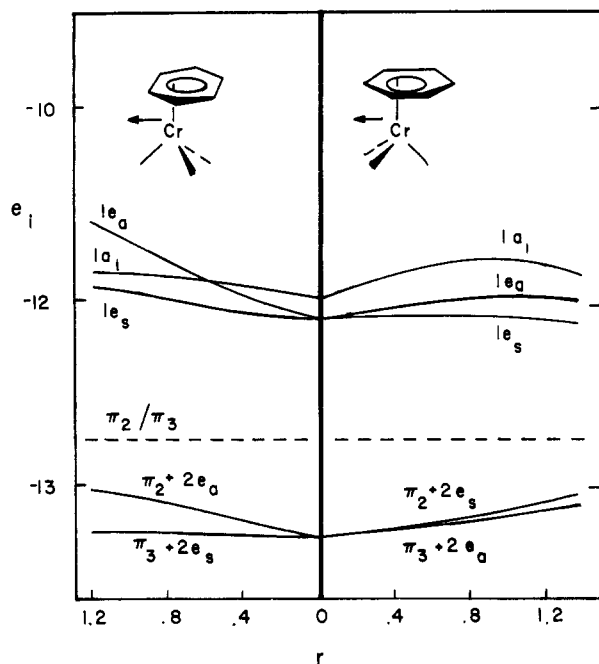
Figure 3. Potential energy surface for slipping the MnCp group in benzene–MnCp. The distance scale on the lower left is plotted in 0.2-Å intervals, and the energy contours are in kilocalories per mole. The ground state is given by the large solid circle, a minimum by an open circle, and a transition state by a cross. The energies for these points relative to the ground state are explicitly given. The distance of the MnCp group to the benzene plane was held constant at 1.73 Å. The dimensions of the benzene ligand are provided for reference.

about how the potential changes with the substitution of benzo units.

The full potential energy surface for benzene–MnCp is shown in Figure 3. The distance scale, at the lower left corner of Figure 3 is plotted in 0.2-Å intervals. The energy contours are given in kilocalories per mole relative to the η^6 ground state, symbolized by a large solid circle. The distance between the plane of the benzene ligand and the Mn was held fixed at 1.73 Å. The potential around the η^6 ground state is nearly circular and quite steep until the MnCp unit reaches the periphery of the benzene ring. Notice that there is *absolutely no evidence for the intervention of a discrete η^4 intermediate*. Slippage of the MnCp group by 0.5 Å to an η^4 position requires 10.1 kcal mol⁻¹ (9.6 kcal mol⁻¹ for the Cr(CO)₃ derivative). However, as pointed out elsewhere,[27d] steric and electronic reasons demand that the uncoordinated portion of the benzene ligand bend up, out of the plane to facilitate attack by the approaching arene′. Given a reasonable value of 25° for this bend, the energy required to attain a hypothetical η^4 species now becomes 24.7 kcal mol⁻¹ (24.3 kcal mol⁻¹ for the Cr(CO)₃ derivative). The absence of an η^4 *intermediate* is not likely to be an artifact of the computational method. Optimization of benzene–MnCp²⁻ yielded a ground-state structure where the MnCp unit is slipped 0.55 Å from η^6 and the uncomplexed olefinic group is bent 24° out of the plane of the remaining carbon atoms. This is in reasonable agreement with arene–ML₃ and arene–MCp molecules at this electron count.[29] In fact, the η^4 ground state is com-

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Figure 4. Orbital interaction diagram for (benzene)Cr(CO)₃ at the η^6 ground state.

puted to lie 45.7 kcal mol⁻¹ lower in energy than an η^6 structure with a flat benzene ligand!

The potential continues to climb for an excursion toward η^1 in Figure 3 until a transition state is reached at a relative energy of 28.5 kcal mol⁻¹ (33.4 kcal mol⁻¹ for the Cr(CO)₃ derivative). This feature is symbolized by a cross on the potential energy surface. Continuing along the reaction path leads to an intermediate, given by an open circle, at 25.2 kcal mol⁻¹ (30.0 kcal mol⁻¹ for the Cr(CO)₃ complex). Although this might be labeled an "η^1" species since the metal atom lies almost directly below a carbon atom, substantial bonding still exists to the two flanking carbons. For example, in (benzene)Cr(CO)₃ at this point the Cr–C overlap population to the carbon directly above Cr was 0.283 while that to the two adjacent carbons was 0.082. Let us make a slight diversion, before we pursue this point further, and examine the specific electronic details for the $\eta^6 \rightarrow$ "η^1" transit.

An orbital interaction diagram for (benzene)Cr(CO)₃ at the η^6 geometry is given in Figure 4. The six valence orbitals of Cr(CO)₃[28a] are shown on the right side. The three filled levels, 1e + 1a₁, are remnants of the octahedral t_{2g} set. At higher energy are three empty orbitals, 2a₁ + 2e. On the left side are the three filled π orbitals of benzene. The 2a₁ fragment orbital on Cr(CO)₃ interacts with and stabilizes π_1. Likewise, the 2e set stabilizes π_2 and π_3. With the particular orientation shown at the top of the Figure, the 2e_s component interacts with π_2 and 2e_a, with π_3. Finally, 1a₁ and the 1e set remain predominantly nonbonding. It is convenient to view the 1a₁ + 1e set as three lone pairs that are directed between the CO ligands. Not much overlap between 2a₁ and π_1 is lost upon slipping toward η^1; thus, the energy of the π_1 + 2a₁ molecular orbital remains nearly constant.[30] The energetic variation of the

Figure 5. Walsh diagram for shifting the $Cr(CO)_3$ group from η^6 to η^2 (left) and η^6 to η^1 (right) in (benzene)$Cr(CO)_3$. The energy scale is given in electrovolts and r represents the amount of slippage in Å from the η^6 position. The Cr–benzene plane distance was fixed at 1.73 Å. The horizontal, dashed line indicates the energy of the π_2/π_3 (e_{1g}) set on benzene in the absence of interaction with $Cr(CO)_3$ orbitals.

remaining molecular orbitals is presented on the right side of Figure 5. π_2 and, to a lesser extent, π_3 lose overlap with the 2e set. This is reflected by the rise in energy of π_2 + $2e_s$ and π_3 + $2e_a$. The dashed, horizontal line in Figure 5 indicates the energy of π_2 and π_3 for an isolated benzene molecule. Notice that significant stabilization of especially π_3 persists at the "η^1" intermediate. The $1e_a$ and $1a_1$ molecular orbitals are also destabilized along the reaction path. Repulsion between them and benzene σ orbitals increases. Near the geometry for the intermediate, the $2a_1$ acceptor level on $Cr(CO)_3$ mixes appreciably into molecular $1a_1$, which causes this molecular orbital to become stabilized upon further slippage. It is this feature which creates the shallow minimum in the potential energy surface shown in Figure 3. There is a strong conformational preference at work for the $Cr(CO)_3$ complex at this geometry. Notice that the $2e_a$ orbital is titled[17,27] away from the xz plane in Figure 4. The overlap then between π_3 and $2e_a$, shown in **2a**, is larger than that when the $Cr(CO)_3$

2a   **2b**
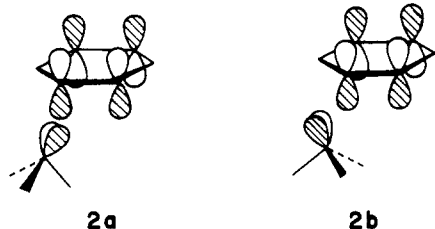
group is rotated by 60°; see **2b**. Furthermore, repulsive interactions between π_3 and $1e_a$ are minimized at a geometry that corresponds to **2a**. The barrier for rigid rotation was computed to be 10.0 kcal mol⁻¹. It is the interaction in **2a** which leads to residual bonding between Cr and the

two flanking carbon atoms in the benzene ligand.

Returning to Figure 3, the potential rises sharply along a path from η^6 to η^2. A maximum is reached at η^2 with a relative energy of 40.2 kcal mol⁻¹ (34.7 kcal mol⁻¹ for the $Cr(CO)_3$ complex). A Walsh diagram for this transit is shown on the left side of Figure 5. With the particular conformation indicated at the top of this Figure, π_3 now interacts with $2e_a$ (see Figure 4 for the orbital notations). Not much overlap is lost along the reaction path. The same is true for the interaction between π_1 and $2a_1$. On the other hand, the overlap of π_2 with $2e_a$ is greatly diminished and repulsions between $1e_a$ and the lower benzene-centered orbitals are greatly increased. Thus, both molecular orbitals are significantly destabilized.

The maximum encountered at η^2 is, in reality, an artifact of the geometrical constraints that we have imposed. (Benzene)$Cr(CO)_3$ at η^2 ($r_1 = 1.22$ Å in **3**) was optimized further by allowing the distance of Cr to the benzene lig-

3   **4**
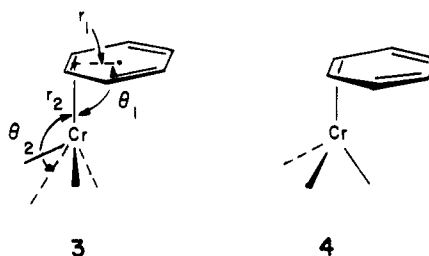
and, r_2, to vary along with tilting the benzene ligand, θ_1, and reorienting the local 3-fold axis of the $Cr(CO)_3$ unit, θ_2. A structure at $r_2 = 1.98$ Å, $\theta_1 = 92°$, and $\theta_2 = 162°$ was found with a relative energy of 32 kcal mol⁻¹. An approximate position for the transition state was located at $r_1 = 1.00$ Å, $r_2 = 1.98$ Å, $\theta_1 = 90°$, and $\theta_2 = 165°$ with a relative energy of 35 kcal mol⁻¹. Further evidence that **3** represents a genuine intermediate is given by the optimization of an η^2 structure, **4**, where the $Cr(CO)_3$ group was rotated by 60°. Independent variation of r_2, θ_1, and θ_2 resulted in collapse back to the η^6 ground state with no activation energy. There is considerable intermixing of $2a_1$ and $2e_a$ in **3** so that the LUMO becomes hybridized in the direction shown by **5**. The spatial disposition of the

5   **6**
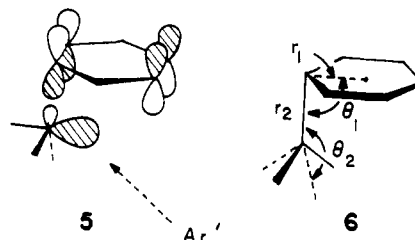
LUMO is ideal for attack by an external arene' ligand. The HOMO of the arene' ligand (π_3 in Figure 4) will maximize its overlap with **5** in the direction indicated by the dashed arrow. This approach also minimizes repulsions between the filled π orbitals on arene' and the filled $1a_1$ + $1e$ set on $Cr(CO)_3$.

Further optimization of the "η^1" intermediate, **6**, with r_1 at 1.60 Å and r_2 fixed at 2.05 Å[31] yielded $\theta_1 = 180°$ and $\theta_2 = 95°$ with a relative energy of 29 kcal mol⁻¹ and an associated transition state ($r_1 = 1.00$ Å) at 32 kcal mol⁻¹. Thus, the $\eta^6 \rightarrow \eta^1$ route is computed to be energetically competitive with an $\eta^6 \rightarrow \eta^2$ slippage ($E_a = 35$ kcal mol⁻¹).

(30) This is identical with the situation found for slipping $Mn(CO)_3$ across the face of the cyclopentadienyl ligand; see: Anh, N. T.; Elian, M.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 110.

(31) The optimized value of r_2 tends to collapse to an unreasonable value of ∼1.70 Å in all calculations of "η^1" species, primarily due to the neglect of internuclear repulsion at the extended Hückel level; for a discussion of this point and one possible resolution, see, for example: Calzaferri, G.; Forss, L.; Kamber, I. *J. Phys. Chem.* **1989**, *93*, 5366.
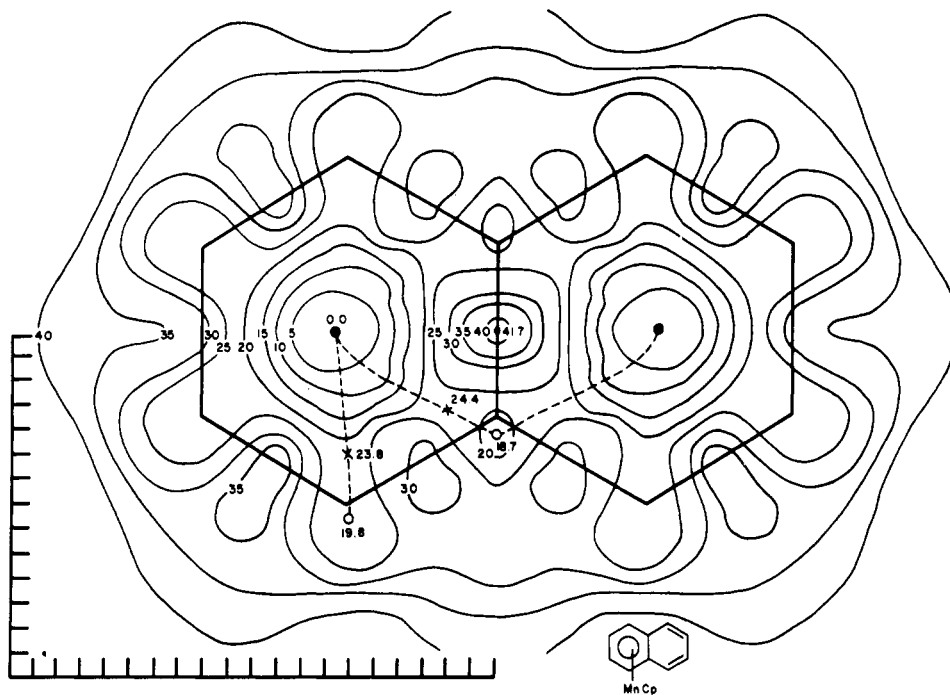
Figure 6. Potential energy surface for naphthalene–MnCp. The details displayed are the same as those in Figure 3.

We emphasize again that no evidence for a discrete η^4 intermediate was found.

Reliable experimental data are lacking for the uncatalyzed exchange reaction of (benzene)Cr(CO)₃. In Strohmeier's classic work on the isotopic exchange of [¹⁴C]-benzene with (benzene)Cr(CO)₃,[6] the rate law contains the second and third terms of eq 1. Traylor[8a] has interpreted the third term as being *first* order in [S]. On this basis, the activation parameters[6b] are $\Delta H^{\ddagger}$ = 28.8 (2.6) kcal mol⁻¹ and $\Delta S^{\ddagger}$ = –9.5 (6) cal K⁻¹ mol⁻¹. However, Willeford and co-workers[4b] have found that $\Delta H^{\ddagger}$ = 28.6 (1.9) kcal mol⁻¹ and $\Delta S^{\ddagger}$ = 5.9 (5.2) cal K⁻¹ mol⁻¹ for the cyclohexanone *catalyzed* exchange reaction (the raw rate constants from the original papers were reprocessed by us to avoid any difference in data analysis). The activation parameters are identical within experimental error, thus casting some doubt on the former values. In a later paper,[6d] Strohmeier reported rate constants for the same reaction that are approximately 100 times smaller than the original values. If one assumes that the value of $\Delta S^{\ddagger}$ is not unreasonable, then a more probable value of $\Delta H^{\ddagger}$ for the uncatalyzed exchange reaction is in the region of 32–33 kcal mol⁻¹. The agreement between experiment and theory is excellent; but, there is a clear need for more accurate experimental data.

The patterns that we have highlighted in (benzene)Cr-(CO)₃ are also found in (naphthalene)- and (pyrene)Cr-(CO)₃. Figure 6 shows the global potential energy surface for naphthalene–MnCp. The interested reader should compare this with Figure 3 in ref 26d, which displays an analogous surface for (naphthalene)Cr(CO)₃. The shapes of the two surfaces are nearly identical. There are two unique exit channels for slippage to η^1, one of which is shown by a dashed line in Figure 6. The potential is considerably lower for slippage away from the central C₉–C₁₀ bond in naphthalene, toward the C₂–C₃ bond, compared to that for benzene–MnCp. It requires 30.0 kcal mol⁻¹ to form this η^2 species in naphthalene–MnCp (25.0 kcal mol⁻¹ for the Cr(CO)₃ derivative). Part of this difference can be traced to a smaller binding energy computed for the naphthalene complex compared to that of benzene. For example, the binding energy of benzene to Cr(CO)₃

(at the ground-state geometry) is calculated to be 50 kcal mol⁻¹, whereas it is 46 kcal mol⁻¹ for (naphthalene)Cr(CO)₃. Experimentally, a value of 43 ± 3 kcal mol⁻¹ has been established[32] in (benzene)Cr(CO)₃. Furthermore, the arene–Cr(CO)₃ bond enthalpy in (naphthalene)Cr(CO)₃ was found[33] to be 6 ± 2 kcal mol⁻¹ *less* than that in (benzene)Cr(CO)₃. However, another general feature is evident in the potential energy surface shown in Figure 6. A gigantic mountain is encountered when the MnCp unit is shifted under the central, C₉–C₁₀ bond of naphthalene. The least motion transit from one η^6 ground state to the other is symmetry forbidden;[27d] the primary source of bonding between naphthalene and the metal is lost midway along the reaction path. Consequently, the global minimum, given by a solid circle in Figure 6, is shifted away from an idealized η^6 position, toward the C₂–C₃ bond. Furthermore, the potential for slippage in this direction is markedly reduced. Notice that, here again, there is absolutely no evidence for a discrete η^4 intermediate.

A top view of the two highest occupied π orbitals in naphthalene are given in 7.
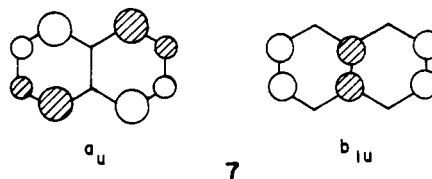
Experimentally,[34] the a_u orbital is 0.73 eV higher in energy than b_{1u} (0.61 eV in our calculations). Consequently, the interaction between $2e_a$ (see Figure 4) and a_u

(32) Brown, D. L. S.; Connor, J. A.; Demain, C. P.; Zafarani-Moattar, M. T. *J. Organomet. Chem.* **1977**, *142*, 321. Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71.

(33) Al-Takhin, G.; Connor, J. A.; Skinner, H. A.; Zafarani-Moattar, M. T. *J. Organomet. Chem.* **1984**, *260*, 189.

(34) (a) Clark, P. A.; Brogli, F.; Heilbronner, E. *Helv. Chim. Acta* **1972**, *55*, 1415. (b) Boschi, R.; Schmidt, W. *Tetrahedron Lett.* **1972**, 2577.

(35) (a) Kündig, E. P.; Desobry, V.; Grivet, C.; Rudolph, B.; Spichiger, S. *Organometallics* **1987**, *6*, 1173. (b) Kriss, R. U.; Treichel, P. M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 853. (c) Oprunenko, Yu. F.; Malugina, S. G.; Ustynyuk, Yu. A.; Ustynyuk, N. A.; Kravtsov, D. N. *J. Organometallic Chem.* **1988**, *338*, 357.
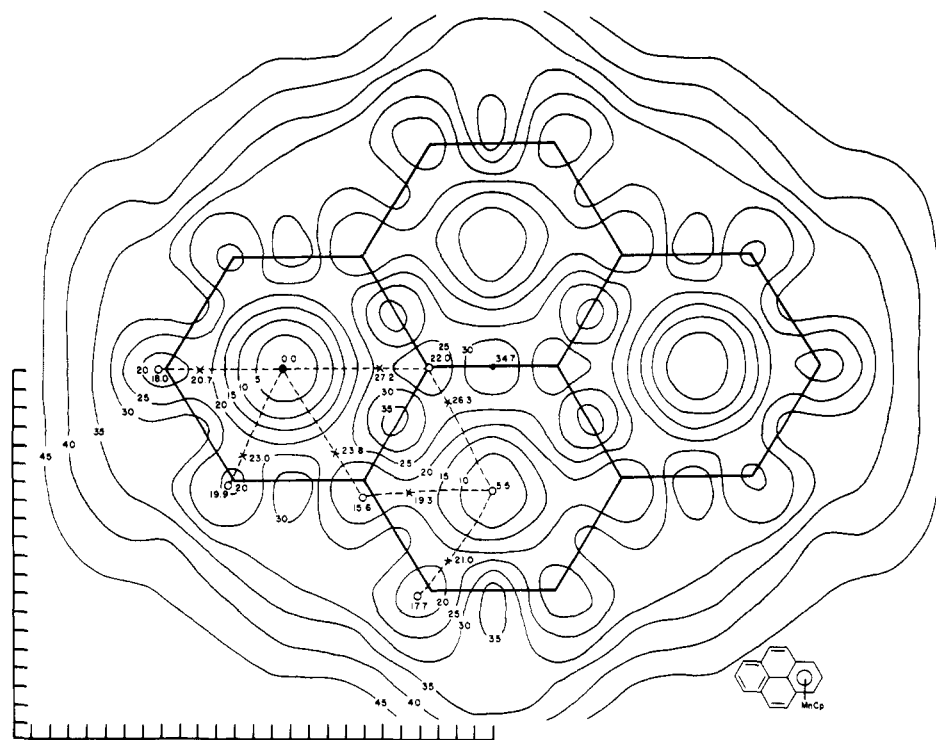
Figure 7. Potential energy surface for pyrene–MnCp. The details displayed are the same as those in Figure 3.

is slightly larger than that between $2e_a$ and b_{1u}. This, in turn, sets the optimal conformational preference for the $Cr(CO)_3$ group at the η^2 geometry. The tilting of the $2e_a$ function creates a greater overlap between $2e_a$ and a_{2u} in **8** than that in **9** where the $Cr(CO)_3$ group has been rotated by 60°. Further optimization of **8** yielded an intermediate
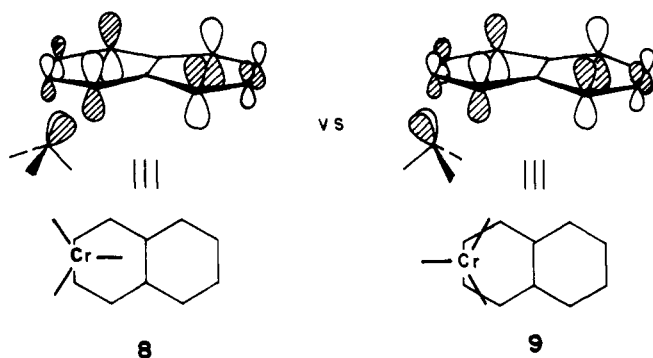
at a relative energy of 22 kcal mol^{-1} with $r_1 = 1.22$ Å, $r_2 = 1.95$ Å, $\theta_1 = 85°$, and $\theta_2 = 165°$ (the variables are defined in **3** and an associated transition state ($r_1 = 1.18$ Å) at 25 kcal mol^{-1}. The alternative conformation, shown in **9**, simply collapsed back to the η^6 ground state upon further optimization. This also occurred for both possible conformations in **10**. The two "η^1" species, **11** and **12**, were
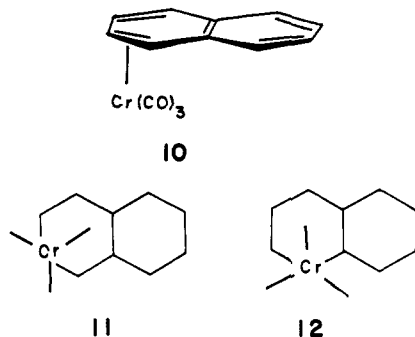
also reoptimized. With the variables defined in **6**, $r_1 = 1.60$ Å, $r_2 = 2.05$ Å,[31] $\theta_1 = 92°$, and $\theta_2 = 180°$ for the geometry shown in **11**, which had a relative energy of 23 kcal mol^{-1}. The optimal structure for **12** ($r_1 = 1.51$ Å, $r_2 = 2.05$ Å, $\theta_1 = 96°$, $\theta_2 = 177°$) was computed to be at a slightly higher relative energy, 24 kcal mol^{-1}. The associated transition state for **11** ($r_1 = 1.25$ Å) was found to lie at 26 kcal mol^{-1}, while that for **12** ($r_1 = 1.20$ Å) was found to be 28 kcal mol^{-1}.

As mentioned previously, the least motion path for haptotropic exchange between η^6 ground states is symmetry forbidden for (naphthalene)$Cr(CO)_3$ and –MnCp. However, a circuitous reaction path does exist, as indicated by the dashed line in Figure 6. An η^3 intermediate where the Mn is bonded to C_1, C_8, and C_9[27d] was found to lie at a relative energy of 18.7 kcal mol^{-1} and the associated transition state was 24.4 kcal mol^{-1}. For the $Cr(CO)_3$ complex, reoptimization using the parameters defined in **6** produced an η^3 intermediate at $r_1 = 1.57$ Å, $r_2 = 1.86$ Å, $\theta_1 = 89°$, and $\theta_2 = 172°$ with a relative energy of 20 kcal mol^{-1}. Haptotropic exchange has been experimentally studied for a number of substituted (naphthalene)$Cr(CO)_3$ complexes. We compute the transition state ($r_1 = 1.15$ Å, $r_2 = 1.95$ Å, $\theta_1 = 90°$, $\theta_2 = 180°$) to be at 27 kcal mol^{-1}, in excellent agreement with experiment.[36] Our concern here is the possibility that the η^3 intermediate may serve also as a shuttle for the arene–exchange reaction, i.e., the (η^y-Ar)M species in Scheme I. It is known that THF,[35a] for example, accelerates the intramolecular, haptotropic rearrangement. The strongest argument against this scenario comes from the competition experiments by Kündig and co-workers.[35a] A deuterium-substituted (naphthalene)$Cr(CO)_3$ complex in benzene at 100 °C was found to undergo the haptotropic rearrangement 9 times faster than arene exchange. This mandates the existence of two discrete intermediates. Since no other minimum was located in the vicinity of the η^3 structure, the most

(36) Values for $\Delta G^{\ast}$ at 100 °C in deuterium substituted complexes are in the range 26–29 kcal mol^{-1}.[35]

probable hypothesis is that arene exchange occurs via the η^2 intermediate 8. It should be noted that our computations do not correctly order the energetics for arene exchange versus haptotropic rearrangement. The activation energy for the former was computed to be 25 kcal mol⁻¹ (the experimental value for the arene' independent route is 28 kcal mol⁻¹, see Table III), whereas that for the latter was 27 kcal mol⁻¹.

The global potential energy surface for pyrene–MnCp is displayed in Figure 7. Many of the features in the naphthalene surface are evident here. There are, however, two subtle differences concerning the $\eta^6 \rightarrow \eta^2$ and $\eta^6 \rightarrow \eta^1$ routes, which we think are important. The most meaningful comparisons can be made directly from the potentials in Figures 6 and 7. The minimum energy required to attain an η^2 structure is 32.8 kcal mol⁻¹ for the pyrene complex compared to the lower value of 30.0 kcal mol⁻¹ in the naphthalene system. The situation is reversed for the $\eta^6 \rightarrow \eta^1$ path. Activation energies of 20.7 and 23.8 kcal mol⁻¹ are required for the pyrene and naphthalene cases, respectively. These tendencies are even reflected in the ground-state geometries. As indicated previously, the global minimum in Figure 6 is shifted away from an idealized η^6 position, toward the C_2–C_3 bond. In Figure 7 it is shifted toward the C_2 atom, along the $\eta^6 \rightarrow \eta^1$ path. For (naphthalene)Cr(CO)₃ the amount of slippage is computed to be 0.12 Å, which is in the range found for complexes of this sort.[26,27b,c] For (pyrene)Cr(CO)₃ the slippage corresponds to 0.13 Å. Unfortunately, no structural data on (pyrene)Cr(CO)₃ exists to check this point. Our working hypothesis then is that the $\eta^6 \rightarrow \eta^1$ exit channel is used for the arene-exchange reaction in (pyrene)Cr(CO)₃.

The two highest occupied π orbitals of pyrene are shown in 13. The b_{3g} orbital lies 0.85 eV higher in energy than b_{2g}[34b] (0.71 eV in our calculations). From the nodal structure in b_{3g}, it is easy to see why coordination of Cr-

13

14
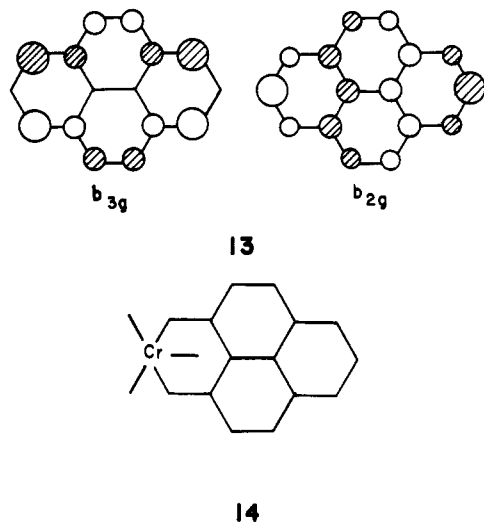
(CO)₃ or MnCp to the outer ring is preferred over that to the central ring.[37] The nodal structure of b_{3g} also determines the optimal orientation of the Cr(CO)₃ at the η^1 geometry shown in 14. We find that 14 is 15 kcal mol⁻¹ higher in energy than the ground-state structure with r_1 = 1.46 Å, r_2 = 2.05 Å, θ_1 = 105°, and θ_2 = 175°. The transition state corresponding to this reaction path (r_1 =

1.8 Å) was computed to be at a relative energy of 18 kcal mol⁻¹. Experimentally ΔH^*_A (for the arene'-independent route) is 25 kcal mol⁻¹; see Table III. The calculations correctly predict that ΔH^*_A should be smaller for (pyrene)Cr(CO)₃ than that for (naphthalene)Cr(CO)₃; however, the experimental difference (3 kcal mol⁻¹) is less than the computed one (7 kcal mol⁻¹). Therefore, it is most probable that extended Hückel theory systematically underestimates the potential required for the $\eta^6 \rightarrow \eta^1$ excursion in all of the cases we have studied. Nevertheless, we do feel that the $\eta^6 \rightarrow \eta^1$ route for (pyrene)Cr(CO)₃ is particularly viable for the arene'-independent route because of the nodal structure exhibited by the two highest occupied π orbitals in pyrene (13).

Information provided by (2,6-dimethylpyridine)Cr(CO)₃ is also consistent with this hypothesis. It is certainly much more reactive in the arene-exchange reaction than (m-xylene)Cr(CO)₃. In cyclooctane at 115 °C, k_A for (2,6-dimethylpyridine)Cr(CO)₃ is over 40 times larger than even that for (naphthalene)Cr(CO)₃ (see Table II). Yet the arene–Cr(CO)₃ binding energy should be very close for the two molecules. The binding energy in (pyridine)Cr(CO)₃ was calculated to be 44 kcal mol⁻¹, and that number should be increased by 2–3 kcal mol⁻¹ by the introduction of two methyl groups, based on the analogous trend in methyl-substituted (benzene)Cr(CO)₃[32] and (benzene)Mo(CO)₃[19] complexes. Slippage of the Cr(CO)₃ group to 15 should

15

16
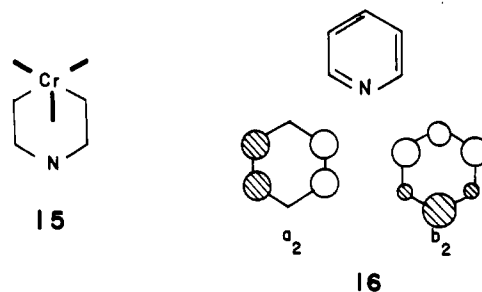
be particularly favored over that in (benzene)Cr(CO)₃. The replacement in benzene of a more electronegative N atom for a CH group splits the degeneracy of π_2 and π_3 (see Figure 4). Specifically, the b_2 orbital in 16 is lowered in energy by this perturbation.[38] Therefore, its stabilization by 2e_s on Cr(CO)₃ is decreased and this also implies that b_2 will be destabilized less for an $\eta^6 \rightarrow \eta1$ path than that in the benzene system. In addition, there is an intermixing of π and π^* levels in pyridine, which increases electron density on C_3 and C_5.[38] This will also lead to a preference for 15. It is difficult to understand why (2,3-dimethylpyridine)Cr(CO)₃ should be so labile if an $\eta^6 \rightarrow \eta^4$ or $\eta^6 \rightarrow \eta^2$ pathway was used.

Returning to (pyrene)Cr(CO)₃, the imposition of two symmetry-forbidden barriers for slipping the metal in a least motion sense from the ground state to an η^6 position under either of the central rings[27d] lowers the potential for slippage in the *opposite* direction. Hence, an $\eta^6 \rightarrow \eta^1$ path is preferred. There is one least motion, symmetry-forbidden barrier in (naphthalene)Cr(CO)₃, so an $\eta^6 \rightarrow \eta^2$ exit channel in the opposite direction is favored.[39] From this model, the increased substitutional lability of (η^6-arene)-Ru(C₅R₅)⁺ where arene = naphthalene, anthracene, pyrene, chrysene, and azulene[40] and indenyl-ML$_n$[41] complexes can

(37) For the same reason electrophiles attack C_1, see: Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley: New York, 1976; pp 170–172. Valence bond-resonance structure arguments come to the same conclusion: Nicholson, B. *J. J. Am. Chem. Soc.* **1966**, *88*, 5156. Herndon, W. C. Unpublished results.

(38) See ref 28a, p 84.

(39) These arguments are derived from a simple application of Thornton's rules or the Hammond postulate; see: Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; pp 212–220.

(40) McNair, A. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 2519.

be easily understood. In all cases, the least motion haptotropic shift is symmetry forbidden.[27d] Recovery of the full aromatic stabilization in a benzo unit has been frequently cited for the "indenyl effect". We prefer the rationale given here since the extraordinary reactivity of $(azulene)Ru(C_5R_5)^+$ compared to the other $(arene)Ru(C_5R_5)^+$ complexes[40] is difficult to understand on the basis of the recovery of aromatic stabilization[42] and the sense of slippage in $(pyrene)Cr(CO)_3$ would be $\eta^6 \rightarrow \eta^2$ in contrast to what we have found.

Conclusions

In summary, we believe that Scheme I represents a more reasonable mechanistic scenario for the uncatalyzed arene-exchange reaction. No spectroscopic or theoretical evidence has been found for a prior $\eta^6 \rightarrow \eta^4$ equilibrium step. The putative $(\eta^y\text{-arene})M$ intermediate for the arene'-independent route is computed to be $y = 2$ for naphthalene and $y = 1$ for pyrene. The $(\eta^y\text{-arene})M$ species might be stabilized further by interaction with the solvent. The reaction paths and associated energetics are determined primarily by the nodal structure and changes in overlap between the arene and $Cr(CO)_3$ units. We are less secure about the exact details in the arene-dependent route, given by the left branch in Scheme I. We have

attempted to examine the details of the $(\eta^x\text{-arene})M(\eta^{6-x}\text{-arene}')$ intermediate at the ab initio level of theory by using $(\eta^4\text{-benzene})Cr(CO)_3(\eta^2\text{-ethene})$ as a model.[45] Unfortunately, this structure collapsed to $(\eta^6\text{-benzene})\text{-}Cr(CO)_3$ and free ethene with no activation energy; i.e., no intermediate was found. It is possible that ethene is more weakly bound to $Cr(CO)_3$ than an η^2-benzene ligand (the π orbital of ethene lies lower in energy than the e_{1g}, π_2/π_3 set in benzene; ionization potentials of 10.51 and 9.24 eV, respectively, have been measured for these molecules[46]). It is reasonable to assume that the favored path will be the one which requires the least expenditure of energy for ring slippage. Therefore, the $(\eta^x\text{-arene})M(\eta^{6-x}\text{-arene}')$ intermediate would be represented by $x = 4$ for naphthalene and $x = 3$ for pyrene. The ΔH^*_B and ΔS^*_B terms in Table III represent the *net* enthalpy and entropy difference at the transition state between slippage to $\sim\eta^x$ (including any required bending of arene or distortion of the $Cr(CO)_3$ moiety) and bond formation between the metal and incoming arene'. For slippage only, it is clear from a comparison of Figures 6 and 7 that the calculations suggest a lower barrier for $(\eta^4\text{-naphthalene})M$, whereas the ΔH^*_B values are in the reverse order. However, as previously indicated, calculations on $(benzene)Cr(CO)_3$ suggest that the energy required to bend the uncomplexed part of the arene and to distort the $Cr(CO)_3$ group to accommodate the incoming arene' ligand[27c] exceeds the energy required for slippage to η^4. The reversed order of ΔH^*_B for the naphthalene and pyrene systems may, therefore, reflect differences in this energy term. It is our intention to examine more closely the interaction between slippage, metal–incoming ligand bond formation, and molecular distortion at the transition state for particularly the left branch of Scheme I in this complicated reaction.

(41) See, for example: Habib, A.; Tanke, R. S.; Holt, E. M.; Crabtree, R. H. *Organometallics* 1989, 8, 1225. Rerek, M. E.; Basolo, F. *Ibid.* 1983, 2, 372. Yang, G. K.; Bergman, R. G. *Ibid.* 1985, 4, 129. Basolo, F.; Schuster, H. G. *J. Am. Chem. Soc.* 1966, 88, 1657. Rest, A. J.; Whitwell, J.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Chem. Commun.* 1984, 624.

(42) Slippage in azulene would release the resonance stabilization of the tropylium cation whereas that in naphthalene generates the stabilization in a benzene unit. All estimates[43] put the resonance energy of the tropylium cation to be less than that of benzene; however, $(azulene)Ru(C_5R_5)^+$ is much more labile than $(naphthalene)Ru(C_5R_5)^+$. This argument would also predict that anthracene complexes should be less reactive than naphthalene complexes since benzoannelation reduces aromatic stabilization.[44] In fact, $(anthracene)Ru(C_5H_5)^+$ is over 4 orders of magnitude more reactive for acetonitrile substitution than $(naphthalene)Ru(C_5H_5)^+$. Furthermore, this argument presupposes that an ML_n unit when coordinated to a polycyclic hydrocarbon somehow destroys aromaticity, i.e., cyclic conjugation. There is no theoretical reason of which we are aware which mandates this. In fact, a recent NMR study has concluded that $(benzene)Cr(CO)_3$ has about 1.3 times the resonance energy of benzene! See: Mitchell, R. H.; Zhou, P.; Venugopalan, S.; Dingle, T. W. *J. Am. Chem. Soc.* 1990, 112, 7812.

(43) See, for example: Haddon, R. C. *J. Am. Chem. Soc.* 1979, 101, 1722 and references therein.

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