Regioselective Electrophilic Substitution via Lithiation and Intramolecular Arene Exchange (Haptotropic Rearrangement) in (Naphthalene)tricarbonylchromium

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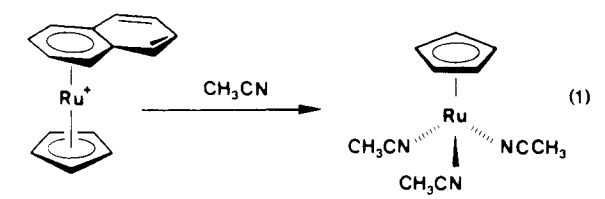
The sequential reaction of (η^6-naphthalene)tricarbonylchromium (1) with (tetramethylpiperidyl)lithium (TMPLi) and electrophiles (D^+, $ClSiMe_3$, CO_2, MeI, $EtOSO_2CF_3$) is highly regioselective and exclusively yields (2-substituted naphthalene)tricarbonylchromium complexes bearing the substituent in the coordinated ring. With *n*-BuLi, the same sequence gives mixtures of the 1- and 2-substituted naphthalene complexes in the ratio of 3:7. [1–4a,8a-η-1,3-$(SiMe_3)_2C_{10}H_6$]$Cr(CO)_3$ (**5**) is obtained in reactions with excess TMPLi and $ClSiMe_3$. The selectively labeled complexes (1–4a,8a-η-[2-D]naphthalene)$Cr(CO)_3$ (**3a**) and (1–4a,8a-η-[1,3-8-D_7]naphthalene)$Cr(CO)_3$ (**3b**) were used in a kinetic study of the haptotropic rearrangement of (naphthalene)tricarbonylchromium. The rate constants and activation parameters of the rearrangement in cyclohexane-d_{12} and in benzene were determined by ^1H and ^2H NMR methods. In cyclohexane, the activation parameters for the intramolecular rearrangement in **3b** were found to be $\Delta H^{\ddagger}$ = 20.4 kcal mol^{-1} and $\Delta S^{\ddagger}$ = –23 cal mol^{-1} K^{-1}. Haptotropic rearrangement was found to proceed by first-order kinetics and, within experimental error limits, at the same rate in benzene as in cyclohexane. Addition of THF accelerated intra- as well as intermolecular arene exchange. In benzene, at 100 °C, the intramolecular ring migration of **3b** is 9 times faster than arene exchange. (1–4a,8a-η-2-Methylnaphthalene)$Cr(CO)_3$ (**3e**) rearranges ($\Delta H^{\ddagger}$ = 26.2 kcal mol^{-1}) on heating in cyclohexane to an equilibrium mixture (65:35) of the two isomers, the major isomer being the one in which the metal is coordinated to the substituted ring.

Introduction

Complexes of polycyclic aromatic ligands occupy a special place among (arene)metal compounds. In contrast to the benzene analogues, complexes of condensed aromatic ligands often undergo very facile thermal arene displacement and exchange reactions.[1-11] Two recent examples for which kinetic data are available include eq 1 and 2.



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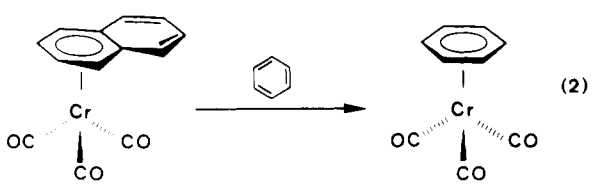

(2)

1

The thermal arene displacement reaction in eq 1 occurs readily at ambient temperature, but no reaction was observed when the analogous benzene complex was heated to reflux in acetonitrile.[11] The arene exchange reaction in eq 2 is almost 4 orders of magnitude faster than the displacement of *p*-xylene by benzene in (η^6-*p*-xylene)$Cr(CO)_3$.[4c,12] The lability in these and analogous systems appears to be associated with a slippage of the η^6-arene to an η^4- (or η^2-) arene ligand. This slippage is energetically more favorable in polycyclic aromatic ligands than in benzene because it is associated with an increase in aromaticity of the noncoordinated ring of the ligand. It has been suggested that the displacement of the metal away from the ring junction carbon atoms, observed in the ground-state structures of naphthalene complexes,[4c,13,14] is a consequence of the high potential encountered by the movement toward the central carbon–carbon bond.[14] The displacement can then be regarded as a first step in the slippage leading to dissociation. Alternatively, when taken together with the observation that a metal always coordinates to an end ring of a polycyclic aromatic system, it can be viewed as an indication of the maximum retention of aromaticity of the noncoordinated rings of the polyene.[14]

The facile displacement of the arene in (naphthalene)$Cr(CO)_3$ (**1a**) is of practical use. **1a** is an excellent catalyst precursor for the hydrogenation of conjugated dienes to *Z* monoolefins.[2b,15-17] It is also a good starting material for the synthesis, via $Cr(CO)_3$ transfer, of various (arene)$Cr(CO)_3$ complexes, which are difficult to obtain by other routes and so require mild synthesis.[4c,18]

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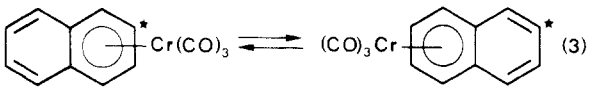
Table I. Regioselectivity of Electrophilic Aromatic Substitution via Lithiation in (Naphthalene)$Cr(CO)_3$ (1)

entry	RX	base	3	2	yield, %
1	D^+	*n*-BuLi	60–70[a]	40–30[a]	90
2	Me_3SiCl	*n*-BuLi	70	30	88
3	$EtOSO_2CF_3$	*n*-BuLi	63	37	65
4	D^+	TMPLi	≤98[b]	≥2[b]	93
5[c]	H^+	TMPLi	≤96[b,c]	≥4[b,c]	69[c]
6	Me_3SiCl	TMPLi	100		96
7	MeI	TMPLi	100		97
8	$EtOSO_2CF_3$	TMPLi	100		62
9	CO_2	TMPLi	100		68[d]
10	$ClCO_2Me$	TMPLi	100		67[e]

[a] A small variation of regioselectivity with reaction temperature (−80 to −60 °C) was noticed. [b] Limits of detection based on integration of ^1H NMR and ^2H NMR signals. [c] Starting complex, $(C_{10}D_8)Cr(CO)_3$ (98% naphthalene-d_8); product; $(C_{10}HD_7)Cr(CO)_3$ (**3b**). [d] Isolated as (1-4a,8a-η-2-carbomethoxynaphthalene)$Cr(CO)_3$ (**3f**) following reaction with CH_2N_2. [e] Isolated as methyl 2-naphthoate after decomplexation by acetone.

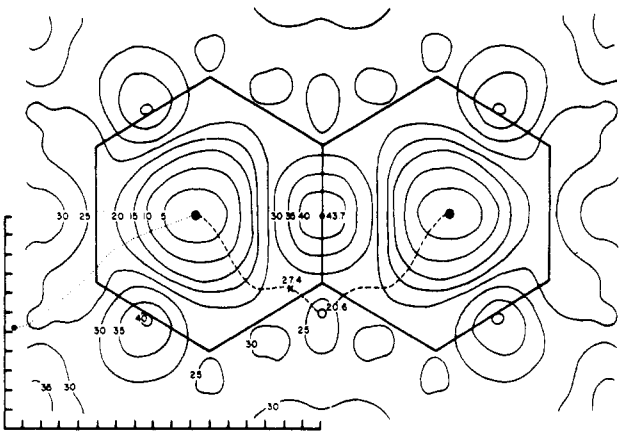
In the presence of strongly coordinating solvents (e.g. THF, CH_3CN, acetone, etc.) or other Lewis bases (e.g. PR_3, $P(OR)_3$, CO, etc.), arene displacement dominates the reactivity of the Cr–arene bond in **1a**.[2a,3,4b,c,6] In their absence, however, another pathway—migration of the $Cr(CO)_3$ fragment from one ring to the other—is feasible (eq 3).



(3)

It has been established previously that this degenerate rearrangement of **1a** occurs, if at all, only slowly. When **1a** is heated in dibutyl ether to 110 °C[19] or in decane to 140 °C[4c] (close to the decomposition temperature), no broadening of the ^1H NMR signals (2 AA'BB' systems for the hydrogens on the coordinated and noncoordinated rings) associated with **1a** is observed. There is considerable experimental evidence, however, that this rearrangement occurs in substituted naphthalene complexes. Kinetically formed isomers or isomers separated by fractional crystallization readily equilibrate to the thermodynamic mixtures on heating.[20–24] In contrast to the well-documented $\eta^6 \rightleftarrows \eta^5$ migration processes in indenyl and fluorenyl complexes[7,19,25–28] quantitative studies on the $\eta^6 \rightleftarrows \eta^6$ migration are scarce[29] and in naphthalene complexes are restricted to complexes bearing substituents on the arene. In the first study, Deubzer analyzed the rearrangement of

Scheme I. Calculated Minimum Energy Path (E_a = 27.4 kcal/mol) for Shifting the $Cr(CO)_3$ Group in Naphthalene $Cr(CO)_3$ (1)[a]



[a] Reprinted with permission from: Albright, T.; Hoffmann, P.; Hoffmann, R.; Lillya, C.; Dobosh, P. *J. Am. Chem. Soc.* **1983**, *105*, 3396. Copyright 1983, American Chemical Society.

(2,3-dimethylnaphthalene)$Cr(CO)_3$ in decane by IR and determined an activation energy (E_a) of 30 kcal/mol.[20] On the basis of detailed theoretical studies of haptotropic rearrangements of polyene–metal complexes, this value has subsequently been viewed as being associated with the intramolecular exchange reaction. The study by Albright et al. predicts a circuitous pathway via an exocyclic allyl intermediate for the haptotropic migration of the $Cr(CO)_3$ fragment from one ring to the other in **1a** (Scheme I).[30]

In a previous paper on arene exchange, we observed and briefly reported ring exchange (intramolecular arene exchange, haptotropic rearrangement) in **1a** in benzene to occur considerably faster than intermolecular arene exchange.[4c] Similar observations have been independently reported by Ustynyuk and collaborators.[31] Very recently, Kirss and Treichel, using ^1H NMR methods, obtained rate constants and activation parameters for the haptotropic rearrangement in two (methoxy-substituted naphthalene)$Cr(CO)_3$ complexes in toluene.[23]

In this paper we describe the full results of our kinetic study of haptotropic rearrangement in selectively labeled naphthalene $Cr(CO)_3$ complexes. The results are compared to the intermolecular arene exchange reactions described previously,[4c] and we show that lithiation of **1a** can be carried out with high regioselectivity in a reaction sequence

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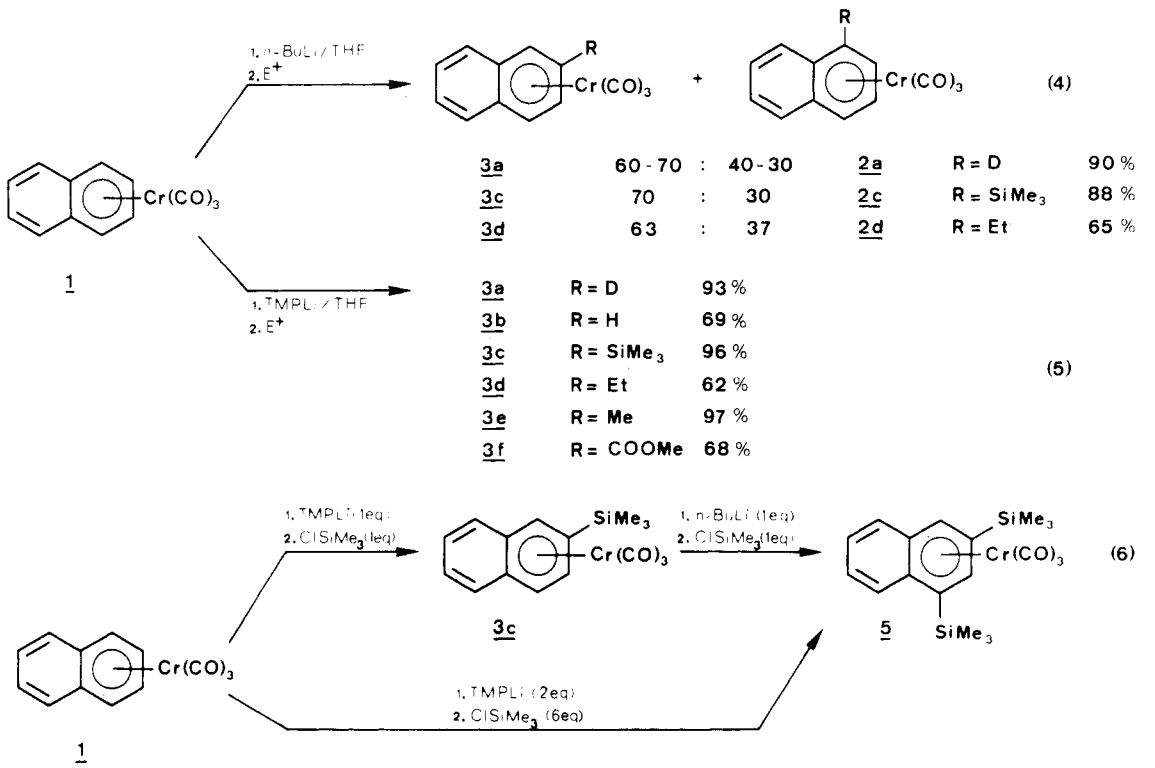

that gives access to 2-substituted naphthalene complexes bearing the substituent in the coordinated ring.

Results and Discussion

In order to investigate the degenerate reaction shown in eq 3, the ring selective introduction of a marker was required. Coordination of an arene to the tricarbonylchromium group enhances the kinetic acidity of the arene ring hydrogens, and we therefore chose lithiation of the complex followed by deuterium quench as the method by which to introduce a label in the coordinated naphthalene ring.

Regioselective Electrophilic Substitution of 1 via Lithiation. Treatment of **1a** with *n*-BuLi in THF at −78 °C followed by addition of methanol-d_4 gave (deuterionaphthalene)Cr(CO)$_3$. Although only one deuterium was incorporated in the ligand, ^{1}H and ^{2}H NMR indicated the product to be a mixture of the two possible isomers **2a** and **3a** containing D in the complexed ring (eq 4). Experiments with two other reactive electrophiles (Me_3SiCl and $EtOSO_2CF_3$) gave almost identical regioselectivity. The distribution of the isomers thus implies only a small discrimination of the 1- and 2-position in **1a** in the lithiation step. Change of reaction temperature and/or time did not improve the ratio of deuteriated products significantly, although a small variation was noted. The data are collected in Table I (entries 1–3).

Lithiation of naphthalene with *n*-BuLi occurs exclusively on the coordinated ring—albeit with low regioselectivity with respect to the 1- and 2-position (eq 4). This is in keeping with earlier reports on the lithiation of (arene)tricarbonylchromium complexes bearing substituents on the arene.[32,33] High selectivity in ring metalation in (arene)Cr(CO)$_3$ complexes generally requires the presence of directing groups[32–35] (e.g. OMe, F). Bulky silyl blocking groups have recently been used to divert the site of lithiation from the ortho to the meta position.[36,37]

When, instead of *n*-BuLi, a cold solution of TMPLi was slowly added to a cold solution of **1** (THF, −78 °C) and this was followed by the addition of the electrophile, complexes **3a–f** were obtained exclusively (Table I, entries 4–9) (eq 5). The position of the introduced substituent was established from ^{1}H NMR data. Characteristically the coordinated ring hydrogens exhibit a nearly first-order spectrum, allowing straightforward structure assignment. In these reactions the higher selectivity of the sterically encumbered base (tetramethylpiperidyl)lithium (TMPLi) is exploited. The formation of the naphthalene complexes substituted in the 2-position as sole products demonstrates the ring as well as site selective lithiation of **1** by TMPLi under kinetic conditions.

The reported yields of complexes **3a,b,d–g** are those obtained by using 2 equiv of TMPLi. Various modifications of this procedure, including addition of the complex (either as a solid or in solution) to the cold TMPLi solution or addition of 1 equiv of TMPLi (exception: Me_3SiCl) adversely affected the regioselectivity and/or the yield. The naphthyllithium intermediate is unstable in the reaction medium, and it was found to decompose rapidly with polymerization above −60 °C. Thus, when a solution of (1–4a,8a-η-2-Li$C_{10}H_7$)Cr(CO)$_3$ (prepared as described above) was allowed to warm up to −40 °C (15 min) prior to reaction (at −78 °C) with $ClSiMe_3$, the result was a brown insoluble residue from which only 5% product (**3c**) could be isolated. Interestingly, in reactions involving 2 equiv of TMPLi and an excess of $ClSiMe_3$ a highly regioselective double incorporation of the electrophile occurred. The only product isolated was [1–4a,8a-η-1,3-

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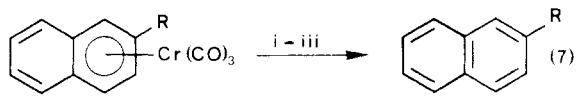
$(SiMe_3)_2C_{10}H_6]Cr(CO)_3$ (**5**) (83% yield (eq 6). The result suggests that the naphthyllithium complex reacts much faster with this electrophile than does TMPLi. The first addition was then followed by a second lithiation/electrophile addition sequence. The same product resulted when the two steps were carried out sequentially, using *n*-BuLi in the second lithiation step.

Decomplexation of the substituted naphthalenes with recovery of $Cr(CO)_6$ can be conveniently carried out by displacement of the arene by CO.[4a] Thus, on stirring a hexane solution of **3c** at 60 °C for 3 days in the presence of CO (4 atm), $Cr(CO)_6$ precipitated and $Me_3SiC_{10}H_7$ was recovered in 95% yield from the solution.[38] Alternatively, arene exchange of naphthalene for benzene to yield (benzene)$Cr(CO)_3$ occurs readily at 70 °C in a Lewis base promoted arene exchange reaction.[4c] If Cr(0) recovery is not important, simply dissolving a naphthalene $Cr(CO)_3$ complex in a coordinating solvent (e.g. acetone, pyridine, etc.) in the presence of O_2 yields the free ligand.[2a,3,4b,c,6] The reaction (eq 7) yielding methyl 2-naphthoate (Table I, entry 10) is one example of this very facile decomplexation.



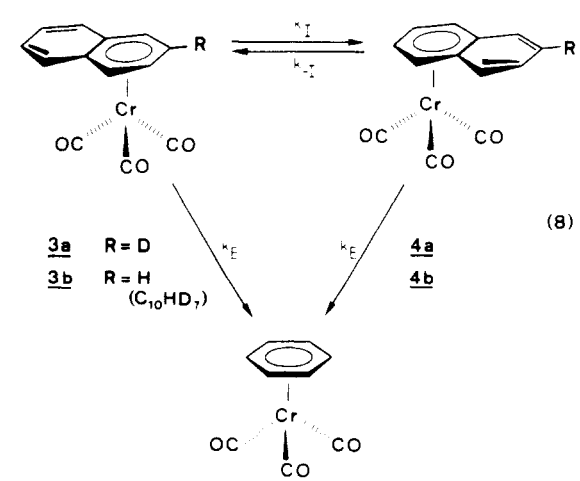
i R = $SiMe_3$: CO, 4 at, hexane, 95%

ii R = CO_2Me : acetone, 24 h, RT

iii R = H : benzene, ether/THF, 16 h, 70°

Haptotropic Rearrangement of (Naphthalene)Cr(CO)$_3$ in Benzene and Cyclohexane. The kinetic investigation of the intramolecular rearrangement shown in Scheme I was carried out with the selectively deuteriated (respectively protonated) complexes **3a** and **3b**. Progress of the exchange was followed by integration of the NMR signals of ^1H or ^2H nuclei on the coordinated and uncoordinated rings of the ligand. The exchange in most cases was followed for 2–3 half-lives of the reaction. Longer observation times, e.g. to total equilibration, posed problems because of the inaccuracy of integration of small signal intensity changes.

In benzene, intermolecular arene exchange of naphthalene for benzene is a competing side reaction (eq 8). The



extent of this was monitored by integration of the signals associated with free naphthalene. This did not turn out to be a serious problem as intermolecular exchange, even with the reaction partner being the solvent, is considerably slower. At 80 °C, the signal at 7.30 ppm arising from displaced naphthalene accounted for 14% of total naphthalene after 2 half-lives of the intermolecular reaction. It was noted, however, that small quantities of impurities (e.g. a few percent of decomposition of the complex arising from traces of air or water) could drastically accelerate intermolecular exchange.[39] Added cyclohexane provided the internal integration standard and mass balance in the reactions in benzene. Silylated NMR tubes were used in the kinetic experiments. This precaution was judged necessary following the observation of considerable and concentration-dependent rate acceleration of intermolecular arene exchange in unsilylated glass tubes.[4c] We blame this catalysis of naphthalene displacement on free OH groups on the glass wall. In the event, rate differences in the rates of the haptotropic rearrangement in silylated and non-silylated tubes were minor (within 8%) at complex concentrations above 0.15 M in benzene. On the other hand, erratic results were observed with more dilute solutions (10^{-2} M in cyclohexane) in nonsilylated tubes.

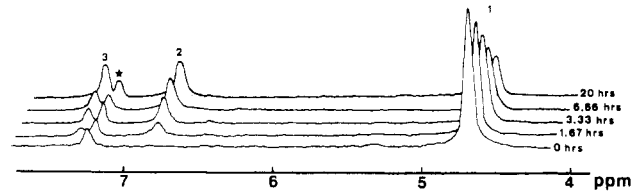


Figure 1. Aromatic region of the ^2H NMR spectra of a solution of 0.2 M ([2-D]naphthalene)$Cr(CO)_3$ (**3a**) in C_6H_6 (solvent) after heating to 87 °C for 0, 1.67, 3.33, 6.66, and 20 h: 1, D^2 in complex **3a**; 2, D^6 in **4a**; 3, D^2 in [2-D]naphthalene; *, solvent.

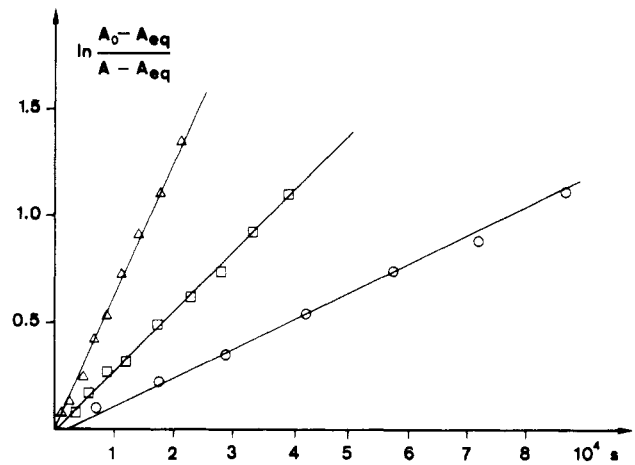


Figure 2. First-order kinetic plot for the haptotropic rearrangement of ([1,3–8-D_7]naphthalene)$Cr(CO)_3$ (**3b**) (eq 8) as measured by the disappearance of the ^1H NMR signal associated with H on the coordinated naphthalene ring: △, 87 °C; □, 80 °C; ○, 70 °C.

A first series of experiments was carried out with the monodeuterionaphthalene complex **3a** in C_6H_6. Figure 1 displays the ^2H NMR spectra of a solution of 0.2 M naphthalene complex **3a** in benzene (solvent) recorded after heating to 87 °C for 0, 1.67, 3.33, 6.66, and 20 h. The large amount of labeled complex required (115 mg of **3a** for each kinetic experiment) and the low solubility of naphthalene $Cr(CO)_3$ in cyclohexane (see below) made this approach impractical for the other runs. Subsequent kinetic measurements were therefore carried out by using

(38) In THF, decomplexation occurred under ambient pressure of CO. Hexane was used here for ease of separation of the arene from $Cr(CO)_6$. Higher CO pressure may be required in more substituted complexes, see: Dötz, K. H. *Angew. Chem.* **1984**, *96*, 573, and references therein.

(39) Arene exchange reactions catalyzed by iodine have recently been reported: Harrison, J. *J. Am. Chem. Soc.* **1984**, *106*, 1487.

Table II. Rate Constants and Activation Parameters for the Haptotropic Rearrangements in Selectively Deuteriated (Naphthalene)Cr(CO)$_3$ Complexes in Benzene and Cyclohexane

	$10^{-6}k_{obsd}$,[d] s^{-1}		
temp, °C	(2-$C_{10}H_7D$)-$Cr(CO)_3$[a]	(2-$C_{10}HD_7$)-$Cr(CO)_3$[b]	(2-$C_{10}HD_7$)-$Cr(CO)_3$[c]
60	2.0 ± 0.2		
70	6.5 ± 0.6	5.7 ± 0.6[e]	6.3 ± 0.6
80	13.6 ± 1.4	13.0 ± 1.3[e]	14.3 ± 1.4
87	25.0 ± 2.5	30.5 ± 3.0[e]	
90			28.7 ± 2.9
93		43.7 ± 4.4[e]	
100		86.5 ± 8.6[e]	81.1 ± 8.1
110			151 ± 15
E_a, kcal mol^{-1}	21.8 ± 1.5	23.3 ± 1.0	21.1 ± 1.0
$\Delta H^{\ddagger}$, kcal mol^{-1}	21.1 ± 1.5	22.6 ± 1.0	20.4 ± 1.0
$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}	−21 ± 4	−17 ± 3	−23 ± 3
$\Delta G^{\ddagger}$, kcal mol^{-1}[f]	28.9	28.9	29.0

[a] The rearrangement was followed by ^2H NMR. A 0.20 M solution of complex **3a** in C_6H_6. Cyclohexane-d_{12} served as internal integration standard. [b] The rearrangement was followed by ^1H NMR. A 0.15 M solution of complex **3b** in C_6D_6. [c] The rearrangement was followed by ^1H NMR. A 0.01 M solution of complex **3b** in cyclohexane-d_{12}. [d] Rate constants were calculated by using a least-squares program. First-order kinetics for the reversible degenerate reaction in eq 8 was assumed by using the equation $\ln (A_0 - A_{eq}/A - A_{eq}) = 2k_{obsd}t$. A minimum of seven data points defined each straight-line plot. Correlation was between 0.995 and 0.999 for all plots. The error limits for the rate constants represent 90% confidence limits. [e] Average of two determinations. [f] At 100 °C.

^1H NMR and the heptadeuterionaphthalene complex **3b**.

Rearrangement of **3b** in C_6D_6 (0.16 M) was followed by ^1H NMR by recording the growth of the signal at 6.82 ppm (H^6) and the concomitant decline in intensity of the signal at 4.75 ppm (H^2). First-order kinetics were observed for the rearrangement. Rates were determined at five temperatures in the range 70–100 °C; typical plots are shown in Figure 2. The rate constants for the haptotropic rearrangement in the two complexes **3a** and **3b** in benzene are listed in Table II together with the activation parameters determined from these data.

Addition of THF (1 mol equiv with respect to complex) to a 0.2 M solution of complex **3b** in benzene-d_6 resulted in a rate acceleration of a factor of ca. 2 of the rearrangement. Rate constants at 80, 87, and 100 °C were found to be 3.4, 5.8, and 15.7 × 10^{-5} s^{-1}, respectively ($\Delta H^{\ddagger}$ = 19.6 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −24 cal mol^{-1} K^{-1}). In parallel, and as expected from earlier results, intermolecular exchange of naphthalene for benzene-d_6 becomes a more important side reaction. This precluded a more thorough study of the Lewis base accelerated rearrangement as a function of THF concentration. After 1 half-life of the THF-catalyzed rearrangement at 80 °C, 20% of naphthalene had exchanged for benzene.

The results obtained in benzene for the rearrangement of **3a** and **3b** prompted us to expand our investigation to include cyclohexane as medium. The kinetic data, obtained with 10^{-2} M solutions of **3b** in cyclohexane-d_{12} are listed in Table II, column 3. As in the experiments described above, the sealed NMR tubes were heated at different temperatures (70–110 °C) and the ^1H NMR spectra were recorded at specific intervals. Rates were determined from the decay of the singlet associated with H^2 (5.24 ppm in cyclohexane-d_{12}) in **3b** and concurrent appearance and growth of the singlet at 7.23 ppm (H^6 in isomer **4b**). The residual solvent peak of cyclohexane (99.5% D) was suppressed by irradiation. The low solubility of the complex required long (ca. 90 min) accumulation times (Bruker 360-MHz spectrometer) for reliable integration. Examination of the data in Table II shows that within the limits of the accuracy of the experiments, the rates for haptotropic rearrangement of **3b** in cyclohexane are identical with those in benzene.

The mechanism of the haptotropic rearrangement is clearly intramolecular. The rate constants are independent of complex concentration; this argues against a bimolecular interchange process. In addition, the small amount of (irreversible) arene exchange in benzene excludes a dissociative mechanism. The presence of Lewis bases (OH groups on the glass wall, catalytic amounts of THF) accelerates the rearrangement and, in benzene, particularly the intermolecular arene exchange. This observation and the negative $\Delta S^{\ddagger}$ in benzene, unusual in intramolecular haptotropic rearrangements, initially suggested an associative mechanism. A reaction pathway in which benzene stabilizes a coordinatively unsaturated species was an attractive possibility, though it might be expected that if benzene participates in the rearrangement, arene exchange would be a more competitive reaction than was actually observed. The data obtained in cyclohexane, a noncoordinating solvent, are nearly identical with those obtained in benzene, and this ruled out a solvent-assisted mechanism.

The origin of the negative entropy of activation must lie elsewhere. The entropy change, indicative of a more ordered transition state, may indicate a loss of rotational freedom of the complex on the reaction pathway. We note, in this context, the negative activation entropy associated with a dissociative displacement of condensed aromatic ligands (naphthalene, pyrene) in $Cr(CO)_3$ complexes, a process that, not unlike the rearrangement discussed here, proceeds via a $\eta^6 \rightarrow \eta^n$ slippage of the $Cr(CO)_3$ fragment.[40] Although plausible, assuming the reaction pathway predicted by theory (Scheme I), our argument is speculative and still must be corroborated.

The data in Table II may be compared to those reported very recently by Kirss and Treichel for the haptotropic rearrangement in (3-deuterio-2,7-dimethoxynaphthalene)$Cr(CO)_3$ (**6**) and (3-deuterio-2,6-dimethoxynaphthalene)$Cr(CO)_3$ (**7**).[23] These compounds undergo rearrangement at a much faster rate. Extrapolation of their reported kinetic data to 100 °C shows rate increases (relative to **3b**) by factors of 14 for **6** and of 110 for **7**. The observed first-order kinetics exclude catalysis by the OMe_3 groups on the arenes. The trend may, as the authors pointed out, reflect stabilization of the transition state by the substituents. The selective rate acceleration of intramolecular exchange by the substituents would also explain the absence of competitive arene exchange under the conditions used in their study.

Haptotropic Rearrangement of (2-Methylnaphthalene)Cr(CO)$_3$ in Cyclohexane. Determination of rates and activation parameters in reversible reactions requires the accurate determination of the composition of the equilibrium mixture of the complexes under investigation. In the degenerate reaction in 1 this is obviously 1:1. In (2-methylnaphthalene)$Cr(CO)_3$, however, this is not the case. The equilibrium concentration of the two isomers (Cr coordinated to the substituted (**3e**), respectively, unsubstituted ring (**4e**)) was determined by two methods. The kinetic experiments were continued until no further changes were observed. At this point the ratio of **3e** to **4e** was 65:35. Thermal, THF-catalyzed exchange of naphthalene in **1a** by 2-methylnaphthalene in ether gave the two complexes in a ratio of 61.5:38.5, which changed on

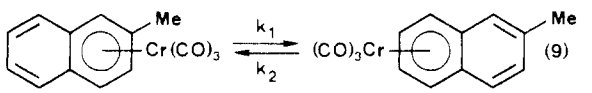
(40) Howell, J., University of Keele, UK, personal communication.

Table III. Rate Constants and Activation Parameters for the Haptotropic Rearrangement in (2-Methylnaphthalene)Cr(CO)$_3$[a]

temp, °C	$10^{-5}k_1$,[b] s^{-1}	$10^{-5}k_2$,[b] s^{-1}	activation parameters
80	0.64 ± 0.06	1.15 ± 0.1	
90	1.61 ± 0.2	2.87 ± 0.3	E_a = 26.9 ± 1.5 kcal mol^{-1}
100	6.40 ± 0.6	11.44 ± 1.1	$\Delta H^\ddagger$ = 26.2 ± 1.5 kcal mol^{-1}
105	7.68 ± 0.8	13.7 ± 1.4	$\Delta S^\ddagger$ = −8 ± 4 cal mol^{-1} K^{-1}[c]
110	13.4 ± 1.3	23.8 ± 2.4	$\Delta G^\ddagger$ = 29.2 kcal mol^{-1}[d]
115	19.2 ± 1.9	34.2 ± 3.4	

[a] The rearrangement was followed by ^{1}H NMR. A 0.025 M solution of complex **3e** in cyclohexane-d_{12}. At t = 0 complex **3e** was the only isomer in solution. [b] Rate constants were calculated by using a least-squares program. First-order kinetics for the reversible degenerate reaction in eq 9 was assumed with the equation ln $(A_0 - A_{eq}/A - A_{eq}) = (k_1 + k_2)t$ and the determined equilibrium $K_{eq} = k_1/k_2 = 0.56$. Seven data points defined each straight-line plot. Correlation was between 0.997 and 0.999 for all plots. The error limits for the rate constants represent 90% confidence limits. [c] Average value ($\Delta S^\ddagger_{k1}$ = −8.4 cal mol^{-1} K^{-1}, $\Delta S^\ddagger_{k2}$ = 7.3 cal mol^{-1} K^{-1}). [d] At 100 °C.

heating in cyclohexane to 63:37. The equilibrium of the mixture of complexes **3e** and **4e** in cyclohexane is thus 64:36 ± 1 (K_{eq} = 0.56 for the reaction in eq 9).



3e 4e

equilibrium : 64 : 36 (in cyclohexane)

$\Delta H^\ddagger$: 26.2 kcal/mole

With these data at hand, haptotropic rearrangement of **3e** was followed by ^{1}H NMR by integration of the methyl resonances. Rates and activation parameters were determined as described above. The results are summarized in Table III.

Intramolecular vs. Intermolecular Arene Exchange. The data presented in this paper expand our earlier observation, which indicated intramolecular exchange to be faster than intermolecular exchange of naphthalene for benzene under pseudo-first-order conditions.[4c] It is apparent that rate constants for the two processes in benzene cannot be compared directly. The rate expression for the intermolecular exchange is of the form

$$k_{obsd} = k_A[\text{complex}] + k_B[\text{complex}][\text{benzene}] \quad (10)$$

which, under pseudo-first-order conditions, reduces to

$$k'_{obsd} = (k_A + k_B')[\text{complex}] \text{ with } k_B' = k_B[\text{benzene}] \quad (11)$$

For $k_B \ll k_A$, the difference between the observed rates in eq 10 and 11 becomes small and the value of k_{obsd} approaches independence of benzene concentration. This is the case here. Extrapolation of the determined rates in benzene to 100 °C yields a rate (k'_{obsd}) of 9.6×10^{-6} s^{-1} for the intermolecular exchange.[4c] This value is 10 times smaller than that for intramolecular exchange (see Table II). Howell et al. recently reported kinetic data on naphthalene displacement in **1a** at low arene concentration.[6] They found the rate for naphthalene exchange for toluene to be 4.4×10^{-5} s^{-1} at 127.5°. It is of interest to note that this value is again ca. 10 times smaller than that found in this study for haptotropic rearrangement of deuterium labeled **1** in cyclohexane (extrapolated from the data in Table II). This implies that the rate of intermolecular arene exchange in an inert solvent depends very little on k_B. Furthermore, it shows that k_B[benzene] is small even in benzene. The mechanistic conclusion is that uncatalyzed naphthalene displacement in arene exchange reactions is essentially dissociative. This is in agreement with the early study of naphthalene exchange in **1a** by [^{14}C]-naphthalene carried out by Strohmeier et al.[1] as well as with the conclusions drawn from a recent study of arene exchange in (arene)tricarbonylchromium compounds by Traylor et al.[12]

Summary and Conclusion

Regioselective metalation of arenes in (arene)Cr(CO)$_3$ complexes is usually achieved via directing groups in the arene. A different approach, which makes use of steric requirements imposed by the reagent, is described in the first, synthetic, part of this paper. While metalation of (naphthalene)Cr(CO)$_3$ with *n*-BuLi occurs with low selectivity with respect to the 1- and 2-position, the more hindered TMPLi selectively reacts with the sterically more accessible hydrogen at C-2. Further applications of this approach are presently under study.

In the second part, rates and activation parameters of the intramolecular migration of the Cr(CO)$_3$ fragment from one ring to the other were determined. In benzene, this $\eta^6 \rightleftarrows \eta^6$ haptotropic rearrangement is roughly an order of magnitude faster than arene exchange. In the absence of Lewis bases, inter-ring equilibration in **1** is thus well advanced before intermolecular naphthalene exchange for benzene becomes noticeable. The Lewis base THF accelerates intermolecular arene exchange, a reaction that has found useful synthetic applications.[4c,18] THF also accelerates intramolecular arene exchange, but to a lesser extent than intermolecular exchange. In related work Traylor et al.[12] showed that even weak nucleophiles such as benzene and metal carbonyl groups efficiently catalyze arene exchange reactions in (arene)Cr(CO)$_3$ complexes. In reactions with (naphthalene)Cr(CO)$_3$, benzene only acts marginally, and metal carbonyl groups do not act at all in this capacity. We believe, however, this difference to be one of degree rather than of kind. It is most likely associated with the far greater facility of the fused arene ligands to undergo slippage by a dissociative mechanism. Consequently much milder reaction conditions are encountered in all reactions leading to arene–metal bond cleavage in this class of compounds compared to those of the benzene analogues.

Experimental Section

1. **General Data.** All manipulations were carried out under nitrogen or argon or under vacuum by using standard Schlenk techniques. Solvents and reagents were dried with CaH_2 (alkanes, TMPH), sodium benzophenone ketyl (ethers), or sodium (benzene, toluene) and distilled under nitrogen or in vacuo. ^{1}H and ^{2}H NMR spectra were recorded on a Bruker WM-360 spectrometer. Chemical shifts are given in parts per million relative to $SiMe_4$. IR spectra were recorded on a Perkin-Elmer 681 spectrometer. Mass spectra were measured on a Varian CH 4 or SM 1 spectrometer at 70 eV. Melting points were obtained in sealed capillaries on a Büchi 510 apparatus and are not corrected. Elemental analyses were performed by E. Thommen, Microanalytical Laboratory, University of Basel.

2. **Synthesis of Complexes.** **(η^6-$C_{10}H_8$)Cr(CO)$_3$ (1a)** was prepared according to published procedures from Cr(CO)$_6$ (Strem).[41,42]

(η^6-$C_{10}D_8$)Cr(CO)$_3$ (1b) was obtained analogously in 61% yield from $C_{10}D_8$ (Aldrich, 98% D) (1 g, 7.35 mmol) and Cr(CO)$_6$ (0.77

(41) Fischer, E. O.; Fritz, H. P. *J. Organomet. Chem.* **1967**, *7*, 121.
(42) Desobry, V.; Kündig, E. P. *Helv. Chim. Acta* **1981**, *64*, 1288.

g, 3.5 mmol) on heating for 23 h at 164 °C in a mixture of dibutyl ether (20 mL), hexane (2 mL), and THF (0.2 mL).

(1-4a,8a-η-2-$MeC_{10}H_7$)$Cr(CO)_3$ (3e) and (1-4a,8a-η-6-$MeC_{10}H_7$)$Cr(CO)_3$ (4e) were synthesized from **1a** via arene exchange:[4c] (2-methyl)naphthalene (426 mg, 3 mmol) and **1a** (264 mg, 1 mmol) were placed in a 5-mL heavy-wall glass tube equipped with an 8-mm O-ring tap (Youngs, UK). After addition of ether (1 mL) and THF (0.2 mL), the mixture was degassed by three freeze/pump/thaw cycles and then heated to 70 °C for 40 h in the closed system. Volatiles were removed in vacuo. ^1H NMR of the crude product indicated a mixture of **3e** and **4e** of 61.5:38.5. The mixture was taken up in cyclohexane (4 mL) and heated for 16 h at 80 °C. NMR analysis indicated the proportion of **3e** to **4e** to have changed slightly to 63:37. Crystallization from toluene/hexane (1:10) yielded 245 mg of orange crystals of **3e** and **4e** (88%).

(1-4a,8a-η-6-$MeC_{10}H_7$)$Cr(CO)_3$ (**4e**): ^1H NMR (C_6D_6) δ 4.73 (m, 2 H, $H^{6,7}$), 5.38 (m, 2 H, $H^{5,8}$), 6.73 (m, 3 H, $H^{1,3,4}$).

(1-4a,8a-η-2-$MeC_{10}H_7$)$Cr(CO)_3$ (**3e**): see below.

3. Reactions of (η^6-$C_{10}H_8$)$Cr(CO)_3$ (1a) with *n*-BuLi. (η^6-$C_{10}H_8$)$Cr(CO)_3$ (**1a**) (264 mg, 1 mmol) was added to 5 mL of cold (−30 °C) tetrahydrofuran. *n*-Butyllithium (0.63 mL of 1.6 M (1 mmol)) in hexane (fluka) was added dropwise to the stirred, cold solution (−78 °C) by syringe. The resulting solution was stirred at −78 °C for 20 min and then treated with the electrophiles a–c.

(a) CD_3COOD. CD_3COOD (0.455 mL, 10 mmol) was added in one portion. The reaction mixture was stripped of volatiles while warming up and the resulting residue extracted with toluene. The solution was filtered through Celite and the filtrate reduced in vacuo. Addition of hexane and cooling to −78 °C yielded an orange crystalline precipitate, which, by ^1H and ^2H NMR analysis, was found to consist of a mixture of (1-4a,8a-η-[1-D]$C_{10}H_8$)$Cr(CO)_3$ (**2a**) and (1-4a,8a-η-[2-D]$C_{10}H_8$)$Cr(CO)_3$ (**3a**) (90% yield) in the ratio of 3:7. No improvement of regioselectivity resulted when the lithiation/deuteriation sequence was carried out at −90 °C; on the other hand, the ratio **2a**:**3a** changed to 40:60 at −40 °C.

(b) $ClSiMe_3$. $ClSiMe_3$ (0.125 mL, 1 mmol) was added in one portion. The reaction mixture was stripped of volatiles while warming up and the resulting residue extracted with hexane. The solution was filtered through Cellite and the filtrate reduced in vacuo. Cooling to −78 °C yielded an orange crystalline precipitate, which, by ^1H NMR analysis and comparison to the spectrum of **3c**, was found to consist of a mixture of the two isomers (1-4a,8a-η-1-$SiMe_3C_{10}H_7$)$Cr(CO)_3$ (**2c**) and (1-4a,8a-η-2-$SiMe_3C_{10}H_7$)$Cr(CO)_3$ (**3c**) in the ratio of 3:7 (88% yield). ^1H NMR (C_6D_6) of **2c**: δ 0.41 (s, 9 H, $SiMe_3$), 4.64 (t, 1 H, $^3J_{ortho}$ = 6.5 Hz, H^3), 5.28 (dd, 1 H, $^3J_{ortho}$ = 6.5 Hz, $^4J_{meta}$ = 1.2 Hz, H^2), 5.67 (d br, 1 H, $^3J_{ortho}$ = 6.5 Hz, H^4), 6.86 (m, 2 H, $H^{6,7}$), 7.03 (m, 1 H, H^5), 7.58 (m, 1 H, H^8).

(1-4a,8a-η-2-$SiMe_3C_{10}H_7$)$Cr(CO)_3$ (**3c**): see below.

(c) $EtOSO_2CF_3$. $EtOSO_2CF_3$ (0.130 mL, 1 mmol) was added in one portion. The reaction mixture was stripped of volatiles while warming up. The resulting red-brown residue was taken up in hexane (40 mL) and toluene (10 mL) and the solution washed at 0 °C with N_2-saturated water. The organic phase was dried over $MgSO_4$, filtered, and taken to dryness in vacuo. The product was crystallized from hexane. ^1H NMR analysis and comparison to the spectrum of (1-4a,8a-η-2-$EtC_{10}H_7$)$Cr(CO)_3$ (**3d**) indicated the material to consist of a mixture of (1-4a,8a-η-1- and -2-$EtC_{10}H_7$)$Cr(CO)_3$ (**2d** and **3d**, 65% yield) in the ratio of 37:63. ^1H NMR (C_6D_6) of **2d**: δ 0.97 (3 H), 2.35 (1 H), 2.78 (1 H) (spin system [ABM_3], $^3J_{AM}$ = $^3J_{BM}$ = 8 Hz, $^2J_{AB}$ = 15 Hz), 4.70 (m, 1 H), 4.83 (m, 1 H), 5.83 (m, 1 H, H^4), 6.90 (m, 2 H, $H^{6,7}$), 7.03 (m, 2 H, $H^{5,8}$).

(1-4a,8a-η-2-$EtC_{10}H_7$)$Cr(CO)_3$ (**3d**): see below.

4. Reactions of (η^6-$C_{10}H_8$)$Cr(CO)_3$ (1a) and (η^6-$C_{10}D_8$)$Cr(CO)_3$ (1b) with (2,2,6,6-Tetramethylpiperidyl)lithium (TMPLi). A solution of TMPLi was prepared by addition of *n*-BuLi (2 mmol; 1.26 mL of 1.6 M solution in hexane) to a cold (−78 °C) solution of 2,2,6,6-tetramethylpiperidine (0.340 mL, 2 mmol) in 3 mL of THF.

After 10 min this solution was transferred to a double-jacketed dropping funnel maintained at −78 °C. The TMPLi solution was then added dropwise, over a period of 15 min, to a cold (−78 °C) solution of **1a** (264 mg, 1 mmol) (or **1b** (272 mg, 1 mmol)) in 7 mL of THF. (Note: it is important to prepare the solution of the complex in cold THF because of the lability of naphthalene in 1 in the presence of Lewis bases![2a]) During the addition, a color change from orange to deep red was observed. The solution was stirred a further 10 min at −78 °C and then treated with the electrophiles a–f.

(a) CD_3COOD. CD_3COOD (0.455 mL, 10 mmol) was added in one portion. The reaction mixture was brought to −40 °C over 20 min. A second, equivalent portion of acid was added, and this was followed by evaporation (in vacuo) of volatiles (excess acid was found to result in better separation of product from TMP). The crude product was taken up in toluene/hexane (1:2), filtered over Celite, and crystallized at −78 °C. Yield of (1-4a,8a-η-[2-D]$C_{10}H_8$)$Cr(CO)_3$ (**3a**): 246 mg, 93%. Mass spectrum (high resolution): calcd for $C_{13}H_7CrDO_3$ *m/z* 264.9940; obsd *m/z* 264.9986 ($M^{\bullet+}$, ^{52}Cr). IR (hexane): 1904, 1919, 1979 cm^{-1}. ^1H NMR (C_6D_6): δ 4.75 (d, 1 H, H^3), 5.37 (m, 2 H, $H^{1,4}$), 6.88 (m, 4 H, H^{5-8}). ^2H NMR (C_6H_6): δ 4.77 (br s, 1 D, D^2).

(b) CH_3OH. CH_3OH (0.400 mL, 10 mmol) was added at −78 °C to a solution of the lithiated complex prepared from ($\eta^6C_{10}D_8$)$Cr(CO)_3$ (**1b**) (544 mg, 2 mmol) as described above. At −50 °C 0.3 mL of HCOOH was added. Workup and purification as described for **3a** yielded (1-4a,8a-η-[1,3-8-D_7]$C_{10}H_8$)$Cr(CO)_3$ (**3b**) (375 mg, 69% yield). Mass spectrum (high resolution): calcd for $C_{13}HCrD_7O_3$ 271.034; obsd *m/z* 271.029 ($M^{\bullet+}$, ^{52}Cr). ^1H NMR (C_6D_6): δ 4.75 (s, 1 H, H^2). Anal. Calcd: C, 57.56; H, 5.57. Found: C, 57.42; H, 5.61.

(c) $ClSiMe_3$. 1. With 1 equiv of $ClSiMe_3$. ($C_{13}H_7Li$)$Cr(CO)_3$ was prepared as described above but by using only one 1 equiv of TMPLi. $ClSiMe_3$ (0.125 mL, 1 mmol) was added in one portion. The reaction mixture was stripped of volatiles while warming up and the resulting residue extracted with hexane. The solution was filtered through Celite and the filtrate reduced in vacuo. Crystallization at −78 °C yielded orange crystals of (1-4a,8a-η-2-$SiMe_3C_{10}H_7$)$Cr(CO)_3$ (**3c**) (309 mg, 92% yield), mp 132 °C. IR (hexane): 1977 (s), 1917 (s), 1900 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 0.30 (s, 9 H, $SiMe_3$), 5.11 (dd, 1 H, $^3J_{ortho}$ = 6.5 Hz, $^4J_{meta}$ = 1 Hz, H^3), 5.40 (d, 1 H, $^3J_{ortho}$ = 6.5 Hz, H^4), 5.89 (s br, 1 H, H^1), 6.90 (m, 2 H, $H^{6,7}$), 7.03 (m, 2 H, $H^{5,8}$). Anal. Calcd for $C_{16}H_{16}CrO_3Si$: C, 57.13; H, 4.79. Found: C, 56.97; H, 5.03.

Decomplexation. 3c (262 mg, 0.78 mmol) was taken up in hexane (40 mL) and the solution stirred for 48 h at 60 °C under an atmosphere of CO (4 atm). The now colorless solution was concentrated, cooled to −78 °C, decanted from the precipitated $Cr(CO)_6$, and taken to dryness. An oil (152 mg, 95%) identified as 2-(trimethylsilyl)naphthalene[43] was recovered. ^1H NMR ($CDCl_3$): δ 0.30 (s, 9 H, $SiMe_3$), 7.50 (m, 2 H), 7.63 (dd, 1 H, $^4J_{meta}$ = 1.5 Hz, $^3J_{ortho}$ = 8 Hz, H^3), 7.85 (m, 3 H), 8.03 (s br, 1 H, H^1).

2. TMPLi (2 equiv)/Excess of $ClSiMe_3$. $ClSiMe_3$ (0.750 mL, 6 mmol) was added in one portion at −78 °C. The temperature of the reaction mixture was gradually raised over a period of 1 h to 0 °C. Volatiles were removed at 10^{-2} torr and the resulting residue extracted with hexane. The solution was filtered through Celite and the filtrate reduced in vacuo. Crystallization at −78 °C yielded orange crystals of [1-4a,8a-η-(1,3-$SiMe_3$)$_2C_{10}H_6$]$Cr(CO)_3$ (**5**) (340 mg, 83% yield), mp 147 °C. IR (hexane): 1972 (s), 1912 (s), 1897 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 0.30 (s, 9 H, $SiMe_3$), 0.44 (s, 9 H, $SiMe_3$) 5.86 (d, 1 H, $^4J_{meta}$ = 1.5 Hz, H^2), 6.24 (m, 1 H, H^4), 6.82 (m, 1 H), 7.02 (m, 1 H), 7.12 (m, 1 H), 7.62 (m, 1 H). Anal. Calcd for $C_{19}H_{24}CrO_3Si_2$: C, 55.88; H, 5.88. Found: C, 55.77; H, 5.98.

(d) $EtOSO_2CF_3$. $EtOSO_2CF_3$ (0.386 mL, 3 mmol) was added in one portion. The reaction mixture was stripped of volatiles while warming up. The residue was taken up in hexane, filtered over Celite, and taken to dryness. Chromatography on silica gel (ether) followed by crystallization (hexane/ether, 5:1) yielded orange crystals of (1-4a,8a-η-2-ethylnaphthalene)$Cr(CO)_3$ (**3d**), mp 71–72 °C. Mass spectrum: *m/z* 292 (M^+, ^{52}Cr). IR (hexane): 1977 (s), 1916 (s), 1898 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 1.01 (3 H), 2.29 (1 H), 2.13 (1 H) (spin system [ABM_3], $^3J_{AM}$ = $^3J_{BM}$ = 7.6 Hz, $^2J_{AB}$ = 14.5 Hz), 4.76 (dd, 1 H, $^3J_{ortho}$ = 7 Hz, $^4J_{meta}$ = 1.5 Hz, H^3), 5.46 (s br, 1 H, H^1), 5.50 (d, 1 H, $^3J_{ortho}$ = 7 Hz, H^4), 6.96 (m,

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2 H, $H^{6,7}$), 7.03 (m, 2 H, $H^{5,8}$). Anal. Calcd for $C_{15}H_{12}CrO_3$: C, 61.42; H, 4.13. Found: C, 61.13; H, 4.29.

(e) MeI. MeI (0.315 mL, 5 mmol) was added in one portion at −78 °C. The reaction mixture was brought to −40 °C over 20 min and then stripped of volatiles under vacuum (10^{-2} mmHg). The crude product was taken up in ether, filtered over Celite, concentrated, and crystallized from ether/hexane (1:8) at −78 °C. Orange crystals of (1–4a,8a-η-2-methylnaphthalene)$Cr(CO)_3$ (**3e**): 269 mg, 97% yield; mp 125–126 °C.

Anal. Calcd for $C_{14}H_{10}CrO_3$: C, 60.43; H, 3.60. Found: C, 60.14; H, 3.73. Mass spectrum: m/z 278 ($M^{\bullet+}$, ^{52}Cr). IR (hexane): 1977 (s), 1899 (s), 1917 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 1.82 (s, 3 H), 4.68 (dd, 1 H, $^3J_{ortho}$ = 5 Hz, $^4J_{meta}$ = 1.5 Hz, H^3), 5.30 (s br, 1 H, H^1), 5.46 (d, 1 H, $^3J_{ortho}$ = 5 Hz, H^4), 6.86 (m, 2 H, $H^{6,7}$), 7.02 (m, 2 H, $H^{5,8}$).

(f) CO_2. Twenty milliliters of a cold (ca. −70 °C) saturated solution of CO_2 in ether was added rapidly. The reaction mixture was warmed up to 0 °C and treated successively with N_2-saturated aqueous 1 N HCl, H_2O, and brine. The organic phase was separated, dried over $MgSO_4$, filtered, and then treated with an ethereal solution of CH_2N_2 (1.1 mmol, 0 °C). The crude product was crystallized from hexane to give orange crystals of (1–4a,8a-η-2-carbomethoxynaphthalene)$Cr(CO)_3$ (**3f**), 219 mg, 68% yield. Mass spectrum: m/z 322 ($M^{\bullet+}$, ^{52}Cr). IR (CCl_4): 1984 (s), 1919 (s), 1739 (s, CO_2Me) cm^{-1}. ^1H NMR (C_6D_6): δ 3.52 (s, 3 H), 5.25 (d, 1 H, $^3J_{ortho}$ = 7 Hz, H^4), 5.90 (dd, 1 H, $^3J_{ortho}$ = 7 Hz, $^4J_{meta}$ = 1.5 Hz, H^3), 6.72 (s br, 1 H, H^1), 6.78 (m, 2 H, $H^{6,7}$), 6.93 (m, 2 H, $H^{5,8}$).

(g) $ClCO_2Me$. $ClCO_2Me$ (0.25 mL, 3 mmol) was added in one portion at −78 °C. The reaction mixture was brought to −40 °C over 20 min and then stripped of volatiles under vacuum (10^{-2} mmHg). The crude product was taken up in warm hexane, filtered over Celite, taken to dryness, and reacted with acetone (10 mL) in the presence of air. After stirring at ambient temperature for 1 day, the Cr residues were filtered off. Treatment of a hexane solution of the product with active charcoal, followed by chromatography on silica gel (ether/hexane, 3:2), yielded 125 mg of colorless crystals (67%) of methyl 2-naphthoate.

Reaction of (1–4a,8a-η-2-$SiMe_3C_{10}H_7$)$Cr(CO)_3$ (**3c**) with *n*-BuLi/$ClSiMe_3$. *n*-BuLi (0.75 mmol, 0.47 mL of a 1.6 M solution in hexane) was added to a cold (−78 °C) solution of **3c** (250 mg, 0.74 mmol) in THF (5 mL). The mixture was maintained at that temperature for 2 h and then treated with $ClSiMe_3$ (0.10 mL, 0.80 mmol). The reaction mixture was stripped of volatiles while warming up and the resulting residue extracted with hexane. The solution was filtered through Celite and the filtrate reduced in vacuo. Crystallization at −78 °C yielded orange crystals of [1–4a,8a-η-(1,3-$SiMe_3)_2C_{10}H_6$]$Cr(CO)_3$ (**5**) (275 mg, 90% yield). For spectroscopic data see above.

5. Kinetics of Haptotropic Rearrangement in (1–4a,8a-η-[2-D]$C_{10}H_8$)$Cr(CO)_3$ (3a), (1–4a,8a-η-[1,3-8-D_7]$C_{10}H_8$)$Cr(CO)_3$ (3b), and (η-$MeC_{10}H_7$)$Cr(CO)_3$ (3e and 4e). Sample Preparation. The NMR tubes were silylated with a 5% solution of *N,O*-bis(trimethylsilyl)acetamide in ether. A weighed amount of naphthalene complex was placed into the tube, and traces of air were removed on a vacuum line. The solvent, and where necessary, integrating standard (cyclohexane) were degassed by three freeze/pump/thaw cycles and then added via syringe under nitrogen to the sample. The NMR tube was then sealed under vacuum. Care was taken to protect the tubes from light throughout the experiment.

Rate Constant Determination. Each sealed tube was immersed in a 1-L oil bath kept at a specific temperature in the range 60–115 °C. Temperature constancy was ±0.2 °C. The rearrangement was quenched by removing the tubes from the hot baths and immersing them in a cold water bath. Progress of the rearrangement was monitored by integration of the NMR signals of ^2H or ^1H nuclei on the coordinated and uncoordinated ring or, where applicable, on the methyl group of the ligand. Mass balance or an internal standard was used in some of the experiments to convert integrations into concentrations. The accuracy of integral determination was estimated to be ±3%. All rearrangements exhibited normal first-order kinetics over the 38–75% exchange examined. At least seven data points defined each straight-line plot. First-order rate constants were determined by a least-squares analysis[44] of a plot of $\ln (A_0 - A_{eq}/A - A_{eq}) = (k_1 + k_2)\cdot t$. For the reaction in eq 8: $k_1 = k_2$; for the reaction in eq 9: $k_1 = 0.56\ k_2$. Least-squares analysis gave standard deviations of 1–4% for all determined rate constants. Repetitions of several kinetic experiments indicated data deviation to be somewhat higher (≤10%). A confidence value of 90% was therefore assigned to all k_{obsd} and used in the determination of the activation parameters. A least-squares fit yielded the values of the activation parameters with the standard deviation as the confidence limit.

Complex 3a in C_6H_6. NMR tubes (10 mm in diameter) containing 115 mg of **3a** and 2,3 mL of a 0.15% solution of C_6D_{12} (Ciba-Geigy, 99.5% D) in C_6H_6 (Merck 99.7%) were prepared as described above (0.2 M solution). In the ^2H NMR spectra the signals assigned to D^2 (coordinated ring) at 4.68 ppm, D^6 (uncoordinated ring) at 6.80 ppm, D^2 (decomplexed naphthalene) at 7.33 ppm, and D^{1-12} (cyclohexane) were carefully integrated. Rates were determined at four temperatures (60, 70, 80, 87 °C), and the rearrangement was followed for 2 half-lives of the reaction.

Complex 3b in C_6D_6. NMR tubes (5 mm in diameter) containing 20 mg of **3b** in 0.45 mL of C_6D_6 (Ciba-Geigy, 99.95% D) were prepared as described above (0.16 M solution). In the ^1H NMR spectra the signals assigned to H^2 (coordinated ring) at 4.75 ppm, H^6 (uncoordinated ring) at 6.82 ppm, and H^2 (decomplexed naphthalene) at 7.10 ppm were carefully integrated. The rearrangement was followed for 1.5 half-lives at 93 °C and 2 half-lives at 70, 80, 87, and 100 °C.

Complex 3b in C_6D_6/THF. NMR tubes (5 mm in diameter, unsilylated) containing 25 mg of **3b**, 6.7 mg of THF (1 equiv with respect to the complex), and 0.45 mL of C_6D_6 (Ciba-Geigy, 99.95% D) were prepared as described above (0.2 M solution). The rearrangement was followed for 1 half-life at 80 °C and 1.5 half-lives at 87 and 100 °C.

Complex 3b in C_6D_{12}. NMR tubes (5 mm in diameter) containing 1.3 mg of **3b** in 0.45 mL of C_6D_{12} (Ciba-Geigy, 99.5% D) were prepared as described above (saturated solution, 0.01 M). The ^1H NMR spectra were recorded with suppression of the solvent peak (0.5% H) by irradiation. The low-solubility of the complex necessitated accumulation times of 60–90 min (5–800 scans). The signals assigned to H^2 (coordinated ring) at 5.24 ppm, H^6 (uncoordinated ring) at 7.23 ppm, and H^2 (decomplexed naphthalene) at 7.33 ppm were carefully integrated. The rearrangement was followed for 1.5 half-lives at 70 °C, 2 half-lives at 80, 90, and 100 °C, and 3 half-lives at 110 °C.

Complex 3e in C_6D_{12}. NMR tubes (5 mm in diameter) containing 3.3 mg of **3e** in 0.45 mL of C_6D_{12} (Ciba-Geigy, 99.5% D) were prepared as described above (saturated solution, 0.025 M). The ^1H NMR spectra were recorded, and the methyl signals assigned to $CH_3(2)$ (coordinated ring) at 2.24 ppm, $CH_3(6)$ (uncoordinated ring) at 2.38 ppm, and $CH_3(2)$ (decomplexed naphthalene) at 2.45 ppm were carefully integrated. The rearrangement was followed for 1.5 half-lives at 80 °C, for 2 half-lives at 90, 105, and 115 °C, and to within 1% of the equilibrium (see above) at 100 and 110 °C.

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Note Added in Proof. We draw attention to another, recently published study on metalation of fused polycyclic aromatic ligands in (arene)tricarbonylchromium complexes.[45]

Registry No. **1a**, 12110-37-1; **1b**, 107847-71-2; **2a**, 95386-57-5; **2c**, 105063-46-5; **2d**, 107847-70-1; **3a**, 95386-58-6; **3b**, 107847-73-4; **3c**, 105063-52-3; **3d**, 107847-72-3; **3e**, 96858-08-1; **3f**, 107847-75-6; **4e**, 103837-14-5; **5**, 107847-74-5; $Cr(CO)_6$, 13007-92-6; $C_{10}D_8$, 1146-65-2; CD_3COOD, 1186-52-3; $ClSiMe_3$, 75-77-4; $EtOSO_2CF_3$, 425-75-2; 2-methylnaphthalene, 91-57-6; 2-trimethylsilylnaphthalene, 18052-85-2; methyl 2-naphthoate, 2459-25-8.

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