Haptotropic Metal Migration in Densely Substituted Hydroquinoid Phenanthrene $Cr(CO)_3$ Complexes[1]

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A series of densely substituted hydroquinoid phenanthrene tricarbonyl chromium complexes prepared via benzannulation of naphthyl carbene complexes have been subjected to haptotropic metal migration. The rearrangements were monitored by IR and NMR spectrometry using dibutyl ether, hexafluorobenzene, and/or octafluorotoluene as solvents, respectively. In mildly coordinating dibutyl ether the phenanthrene complexes **8**−**14** were reacted in preparative scale at 90 and 120 °C, affording the haptotropic migration products **15**−**21** in up to 90% yield. All rearrangements led to thermodynamically stable phenanthrene chromium tricarbonyl complexes in which the organometallic fragment is attached to the less substituted terminal ring. The transformation of phenanthrene complex **11** at 90 °C also afforded bis-tricarbonyl chromium complex **22** as a low-yield byproduct. Kinetic studies of the rearrangement of complexes **8**, **9**, and **11**−**13** performed in either hexafluorobenzene or octafluorotoluene afforded the rate constants k and the free activation enthalpies $\Delta G^{\ddagger}$ for the metal migration. Reaction of bromo- and fluorophenanthrene complexes **10** and **14** under the standard conditions resulted in decomposition of the starting material. The studies reveal that the haptotropic migration of the $Cr(CO)_3$ fragment along the phenanthrene π-face obeys first-order kinetics and is faster than in analogous naphthalene complexes. Quantum chemical first-principles calculations of the haptotropic rearrangement of chromium tricarbonyl naphthalene and phenanthrene model complexes support these findings.

Introduction

The change of the metal coordination site in π-coordinated mono-, bi-, or oligocyclic fused arene complexes is referred to as haptotropic rearrangement or haptotropic migration.[3] The metal fragment is considered as the movable functional group that is shifted between two nonequivalent rings of an oligocyclic ligand. This kind of transformation has been and continues to be an active field of research focusing on $\eta^6-\eta^6$ metal shifts, with naphthalene chromium tricarbonyl derivatives frequently used. Recent studies of the rearrangement of these complexes include both experimental[4] and theoretical[5] investigations. Theoretical studies indicated that a metal migration along the periphery of the naphthalene ligand with a η^4-coordinated trimethylenemethane complex as transition state is favored over the least motion pathway across the carbon−carbon bond common to both six-membered rings. This pathway has also been suggested in a recent theoretical investigation of the haptotropic rearrangement in chromium tricarbonyl complexed sidewalls in carbon nanotubes.[6] Here, Car−Parrinello simulations[7] reveal that the haptotropic metal migration trajectory between the rings in a naphthalene subunit is characterized by two transition states in which the $Cr(CO)_3$ fragment is coordinated in

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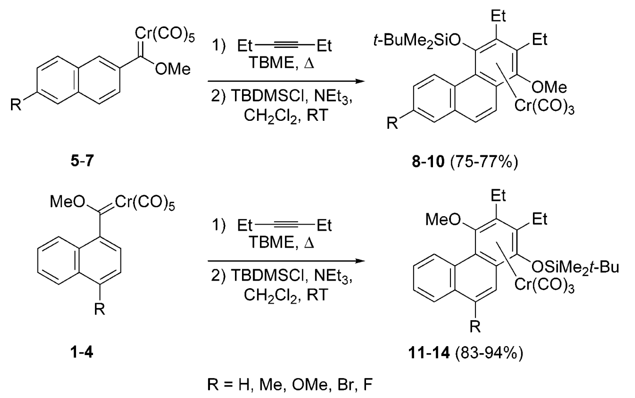
10.1021/om0500570 CCC: $30.25

a η^2-fashion via two short linkages to the bridgehead carbons followed by a η^4-trimethylenemethane transition state. Experimental efforts devoted to naphthalene complexes recently culminated in the development of a reversible stereoselective chiral thermo-optical organometallic switch.[3b,8]

The application of oligocyclic arene complexes to haptotropic metal migration requires a regioselective access to both haptotropomers. The benzannulation reaction of aryl carbene complexes with alkynes turned out to be the method of choice for the synthesis of the kinetically stable isomers of fused hydroquinoid complexes.[9] On warming a solution of the benzannulation products, a metal migration to the less substituted terminal ring is observed. The migration is considered *intramolecular* (i.e., the metal fragment is shifted along the same π-face of the hydrocarbon ligand) if solvents of poor coordinating ability (fluorinated aromatic compounds[5b] or selected ethers such as dibutyl ether)[4d] are utilized. On the other hand, the use of coordinating solvents such as tetrahydrofuran or the presence of free arenes may alter the rearrangement to occur in an *intermolecular* fashion; moreover, increased temperatures (>120 °C) also account for an intermolecular course of the haptotropic migration.

The rearrangement in $Cr(CO)_3$ complexes of distorted hydroquinoid naphthobenzofurans and -thiophenes[10] and further extended benzenoid heterocycles[11] occurs along a helical platform. In the metal migration along these π-systems the heterocyclic ring does not act as a stopper for the chromium tricarbonyl fragment. Instead, the metal shift proceeds from the hydroquinoid ring across the heterocycle to the other terminal benzene ring. For a closer investigation of the influence of the helical distortion on the rearrangement, phenanthrenes as the simplest hydrocarbons with a helical distortion represent a particularly attractive target. Prior to our study reported here, (cyclopenta-fused) phenanthrene derivatives had been addressed only marginally to investigate $\eta^6-\eta^5$ rearrangements.[12] $\eta^6-\eta^6$ rearrangements were reported by Oprunenko et al., who used 9,10-dihydro-10,10-dimethyl-9-oxa-10-silaphenanthrene chromium tricarbonyl complexes as targets.[13] These transformations were carried out at temperatures >130 °C in decanes and were considered to occur intramolecularly. As an extension of our studies on phenanthrene chromium tricarbonyl complexes,[14a] we now report our experimental results obtained on the haptotropic $\eta^6-\eta^6$ rearrangement of densely substituted hydroquinoid chromium phenanthrenes. In addition, we summarize the results of first-principles quantum chemical calculations on model $Cr(CO)_3$ complexes with unsubstituted and monosubstituted phenanthrenes.

Scheme 1



Results and Discussion

The kinetically stable hydroquinoid phenanthrene $Cr(CO)_3$ complexes **8**−**14** have been subjected to thermal haptotropic metal migration. Their synthesis (Scheme 1), which will be described in detail elsewhere,[14a] starts from Fischer chromium 1- and 2-naphthyl carbene complexes **1**−**7** (accessible from commercially available bromo naphthalenes), which were benzannulated with 3-hexyne. After chromatographic purification the target compounds **8**−**14** were isolated in yields between 52 and 90%. Two of these phenanthrene complexes bear a persubstituted and an unsubstituted terminal ring (**8**, **11**). To study the effect of additional substituents on the rearrangement, complexes carrying a substituent at the less substituted terminal (**9** and **10**) or the central ring (**12**−**14**) were included. The location of the substituent at the less substituted terminal ring was chosen to evaluate its effect on the site of coordination in the rearranged phenanthrene complex. The substituents at the central phenanthrene ring are placed along the path of the haptotropic migration and therefore are thought to exert a more direct influence on the metal shift.[15] It was expected that in the products of the haptotropic migration the chromium fragment is coordinated to one of the terminal rings and the complexation of the central ring of the phenanthrene ligand is unfavored. This can be rationalized by the fact that with the attachment of the metal template to the central ring of the phenanthrene ligand no aromatic electron sextet remains in the

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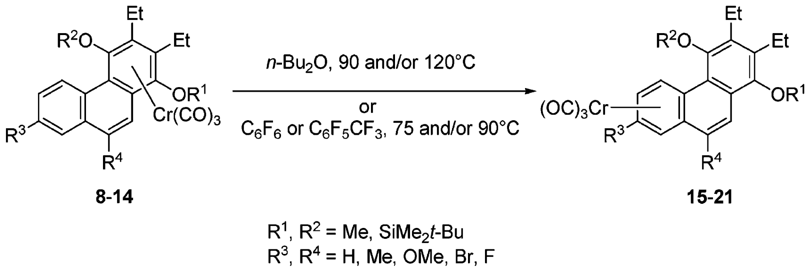
(15) The impact of substituents on haptotropic metal migrations in naphthalene chromium tricarbonyl complexes has been investigated. Details are found in refs 3b, 4a, 5b, and 8b.

Scheme 2



two noncoordinated rings and that the $Cr(CO)_3$ moiety is usually linked to one of the two terminal rings which retain the highest aromatic character. Accordingly, reports dealing with complexes in which a central benzene ring in an unsaturated polycyclic hydrocarbon is η^6-coordinated to the metal are very rare.[16] Additionally, recent theoretical investigations in the framework of gradient-corrected density functional theory (DFT) on preferred coordination sites in monosubstituted η^6-coordinated phenanthrene chromium tricarbonyl derivatives have shown that over a wide range of substituents (i.e., halogen, nitro, oxy and hydroxy, methyl, amino, and ammonium) the terminal rings are favored for coordination over the central ring.[17]

Haptotropic rearrangements in dibutyl ether were performed at 90 and 120 °C and monitored by IR spectroscopy. Independently, the metal migration was studied at 75 and 90 °C in hexafluorobenzene and/or octafluorotoluene by ^{1}H NMR spectroscopy to obtain kinetic data of the rearrangement.

Haptotropic Metal Migration in Phenanthrene Chromium Tricarbonyl Complexes. 1. IR-Monitored Chromium Shifts in Dibutyl Ether. The kinetic benzannulation products **8**−**14** (0.9−4.1 mmol) were dissolved in 60−80 mL of dibutyl ether and warmed to 90 and 120 °C, respectively. The reaction was quenched after IR spectroscopy indicated complete conversion of the kinetically stable phenanthrene complexes to the thermodynamic haptotropomers **15**, **16**, **18**, and **19** or, in the case of starting materials **10**, **13**, and **14**, until decomposition in the reaction mixture started to dominate. After removal of the solvent and other volatiles the reaction mixtures were submitted to chromatographic workup using petroleum ether/dichloromethane mixtures as eluent (Scheme 2).

The kinetic phenanthrene complexes bearing no additional substituents except those at the persubstituted terminal ring (**8** and **11**) undergo complete haptotropic metal migration in dibutyl ether to give the thermodynamically stable benzannulation products in which the unsubstituted terminal rings are coordinated to the chromium fragment. The ^{1}H NMR spectra of **15** and **16** reveal an upfield shift of 1−1.5 ppm for the hydrogen atoms H5−H8, whereas the hydroquinoid carbon atoms in the ^{13}C NMR spectra are shifted downfield by 10−15 ppm. The metal migration in the 4-*tert*-butyldimethylsilyloxy (TBDMSO)-substituted phenanthrene complex **8** proceeded significantly more slowly compared to its 1-TBDMSO protected isomer **11**, indicating that increasing helical distortion—as evidenced by X-ray crystallographic data[14a] for **8** and **11** (torsion angles (C4−C4a−C4b−C5) of 19.9° and 8.1°, respectively)—hampers the rearrangement.[14b] This stereochemical implication also results in increasing decomplexation, as reflected in the considerably lower yield of **15** (19%) compared to that of **18** (90%) (Table 1, entries 1 and 4). The extended reaction time required for metal migration in phenanthrene complex **11** at 90 °C (13 h) favored the formation of bis-tricarbonylchromium complex **22** as byproduct (6%). The efficiency of the haptotropic migration is enhanced by electron-releasing substitution of the less substituted terminal ring as demonstrated for the methoxy series (**9** → **16**); comparable good yields of rearrangement product **16** have been obtained irrespective of slightly modified reaction conditions (90 °C/6 h: 70% vs 120 °C/1.5 h: 75%, Table 1, entry 2). Moderate electron donation to the central phenanthrene ring by methyl substitution accelerates the metal rearrangement, as demonstrated by comparison of the parent complex **11** and its methyl congener **12**, which allowed for a slightly increased yield even in considerably reduced reaction time (Table 1, entries 4 and 5).

Incorporation of halogens both in the less substituted terminal and the central ring render the metal shift distinctly less efficient. The metal migration reaction **10** → **17** is severely slowed by the bromo substituent in the terminal ring and had to be stopped after 1 h as a result of major decomposition, affording a yield of only 19% of rearrangement product (entry 3). A similar deactivation of the phenanthrene skeleton for haptotropic metal migration by halogen substitution has been observed for the central ring. While the metal shift proceeds readily in the parent complex **11** and its methyl analogue **12**, the yields of rearrangement products decrease dramatically upon incorporation of a bromo or fluoro substituent (Table 1, entries 4−7). These results reflect the established decreased tendency of halogenated arenes for metal coordination and may also indicate a substituent-dependent destabilization of the relevant trimethylenemethane transition states along the metal migration trajectory.

2. ^{1}H NMR-Monitored Chromium Migration in Hexafluorobenzene and Octafluorotoluene. To gain further insight into the mechanism of the haptotropic migration, a kinetic NMR study was performed. Perfluorinated benzene derivatives were applied as solvents to guarantee an intramolecular course of the reaction.[5b,18] Depending on the substitution pattern of the phenanthrene skeleton, the reactions were run in perfluorobenzene or perfluorotoluene with the latter used preferentially for phenanthrene complexes bearing the deactivating halogeno substituents. The quantitative analysis of the

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Table 1. Reaction Conditions and Yields of the Haptotropic Rearrangements of Chromium Tricarbonyl Complexes 8−14 in Dibutyl Ether (for the structure of the compounds refer to Scheme 2)

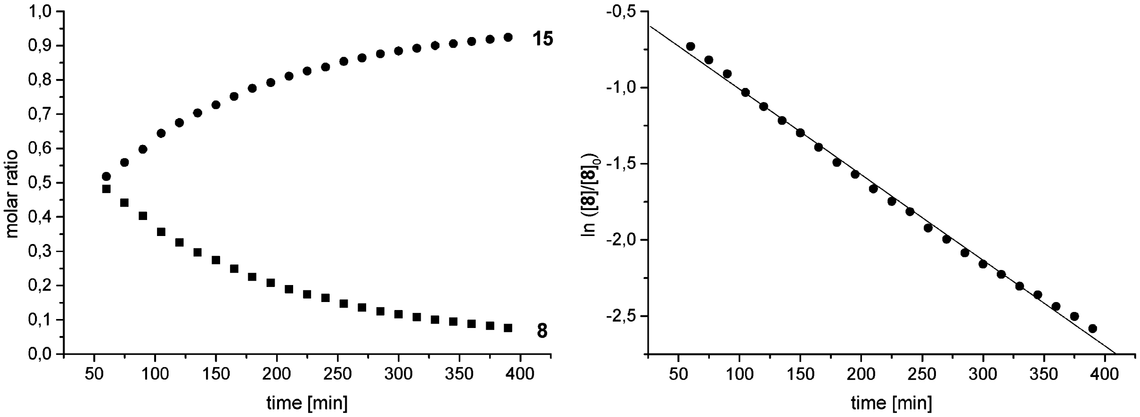
entry	reactants		R^1	R^2	R^3	R^4	temperature (°C)	time (h)	yield (%)
1	**8**	**15**	Me	TBDMS	H	H	90	7	19
2	**9**	**16**	Me	TBDMS	OMe	H	90	6	70
							120	1.5	75
3	**10**	**17**	Me	TBDMS	Br	H	120	1	19[a]
4	**11**	**18**	TBDMS	Me	H	H	90	13	90[b]
							120	4	70
5	**12**	**19**	TBDMS	Me	H	Me	120	1	80
6	**13**	**20**	TBDMS	Me	H	Br	90	3.5[c]	7
							120	1.75	40[d]
7	**14**	**21**	TBDMS	Me	H	F	90	5	5[e]

[a] Additional isolation of 4% of starting material **10** and 6% of complex **15**. [b] Additional isolation of 6% of phenanthrene bistricarbonylchromium complex **22**. [c] Reaction terminated after 3.5 h due to major decomposition. [d] Reisolation of 5% of starting material **13**. [e]Reisolation of 7% of starting material **14**.

Table 2. Kinetic Data of the Haptotropic Rearrangements of Phenanthrene Chromium Tricarbonyl Complexes 8, 9, and 11−13 Measured at 75 and 90 °C, Respectively (for the structure of the compounds refer to Scheme 2)

entry	reactants		R^1	R^2	R^3	R^4	T (°C)	k (s^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})
1	**8**	**15**	Me	TBDMS	H	H	75	$(5.6 \pm 0.6) \times 10^{-3}$	100.7 ± 0.3
2	**9**	**16**	Me	TBDMS	OMe	H	90	$(1.7 \pm 0.2) \times 10^{-3}$	109.5 ± 0.3
3	**11**	**18**	TBDMS	Me	H	H	75	$(1.6 \pm 0.2) \times 10^{-3}$	104.3 ± 0.3
4	**12**	**19**	TBDMS	Me	H	Me	90	$(1.2 \pm 0.1) \times 10^{-2}$	102.8 ± 0.3
5	**13**	**20**	TBDMS	Me	H	Br	90	$(2.0 \pm 0.2) \times 10^{-3}$	108.3 ± 0.3

Chart 1. Kinetic Plots of the Haptotropic Rearrangement of 1-Methoxyphenanthrene Chromium Tricarbonyl 8 to the Isomer 15 at 348 K (75 °C)



NMR spectra was based on the signal(s) of the methyl groups linked to the silicon atom of the TBDMSO group.

Kinetic data could be obtained for all metal rearrangements except for the reaction of the 7-bromo- and 9-fluoro-phenanthrene complexes **10** and **14** due to decomposition. The rate constants k and the free activation enthalpies for the transition states $\Delta G^{\ddagger}$ are summarized in Table 2. Kinetic plots are given in Charts 1−5.

The rate constants obtained for the parent phenanthrene chromium tricarbonyl complexes **8** and **11** in hexafluorobenzene at 75 °C demonstrate that the metal migration in these compounds is 13 and 3 times, respectively, faster than in their 2,3-diethyl-4-methoxy-1-[(*tert*-butyl)dimethylsilyloxy]naphthalene $Cr(CO)_3$ complex analogue.[3b,4a,8b]

The impact of helical distortion on the haptotropic migration is obvious from a comparison of the parent phenanthrene complexes **8** and **11**. As is pointed out above, their solid state structures have been established by X-ray crystallography and reveal an increased dihedral angle (C4−C4a−C4b−C5) of 19.9° for **8** compared to that of 8.1° for **11**.[14a] The increased helical distortion in complex **8** weakens metal coordination to the hydroquinoid ring and results in a considerably lower activation barrier for the metal shift, which at 75 °C occurs 3.5 times faster in 4-*tert*-butyldimethylsilyl-protected phenanthrenol complex **8** than in its 4-methoxy isomer **11** (entries 1 and 4). A comparative study carried out

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(18) π-Complexes containing η^6-coordinated electron-deficient benzenes that bear more than three electron-withdrawing substituents cannot be synthesized via ligand exchange in the liquid phase. For ligands containing more than three electron-withdrawing groups other techniques have to be applied: (a) $[C_6H_4(1,4\text{-}F_2)]Cr(CO)_3]$ and $[C_6H_4(1,4\text{-}Cl_2)]Cr(CO)_3]$: Strohmeier, W. *Z. Naturforsch. B* **1962**, *17*, 627−628. (b) $[C_6H_4(1,3\text{-}F_2)]Cr(CO)_3$: Fletcher, J. L.; McGlinchey, M. J. *Can. J. Chem.* **1975**, *53*, 1525−1529. (c) $[C_6H_4(1,2\text{-}\{COOMe\}_2)]Cr(CO)_3$, $[C_6H_4(1,3\text{-}\{COOMe\}_2)]Cr(CO)_3$, and $[C_6H_4(1,4\text{-}\{COOMe\}_2)]Cr(CO)_3$: Klopman, G.; Calderazzo, F. *Inorg. Chem.* **1967**, *6*, 977−981. (d) $[C_6Cl_6]Cr(CO)_3$, prepared by stepwise hydrogen−chlorine exchange starting from $[C_6H_5Cl]Cr(CO)_3$: Gassman, P. G.; Deck, P. A. *Organometallics* **1994**, *13*, 1934−1939. (e) $[C_6H_3(1,3,5\text{-}\{COOMe\}_3)]Cr(CO)_3$: Hunter, A. D.; Mozol, V.; Tsai, S. D. *Organometallics* **1992**, *11*, 2251−2262. (f) $[C_6F_6]Cr(PF_3)_3$, prepared by the metal atom-ligand-co-condensation technique: Middleton, R.; Hull, J. R.; Simpson, S. R.; Tomlinson, C. H.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1973**, 120−124. For similar compounds, see pp 74−76 in: Timms, P. L.; Turney, T. W. *Adv. Organomet. Chem.* **1977**, *15*, 53−112. (g) The synthesis of $[(2,4,6\text{-}\{NO_2\}_3)C_6H_2Me]Cr(CO)_3$ in the liquid phase has been published, but the isolation of this complex is questionable based on the missing IR absorptions of the $Cr(CO)_3$ fragment, the nonreported ^{13}C NMR shifts of the CO ligands, and the fact that even $[C_6H_5NO_2]Cr(CO)_3$ has not been isolated yet: Azam, K. A.; Kabir, S. E.; Kazi, A. B.; Molla, A. H.; Ullah, S. S. *J. Bangl. Acad. Sci.* **1987**, *11*, 239−241.

Chart 2. Kinetic Plots of the Haptotropic Rearrangement of 1,7-Dimethoxyphenanthrene Chromium Tricarbonyl 9 to the Isomer 16 at 363 K (90 °C)

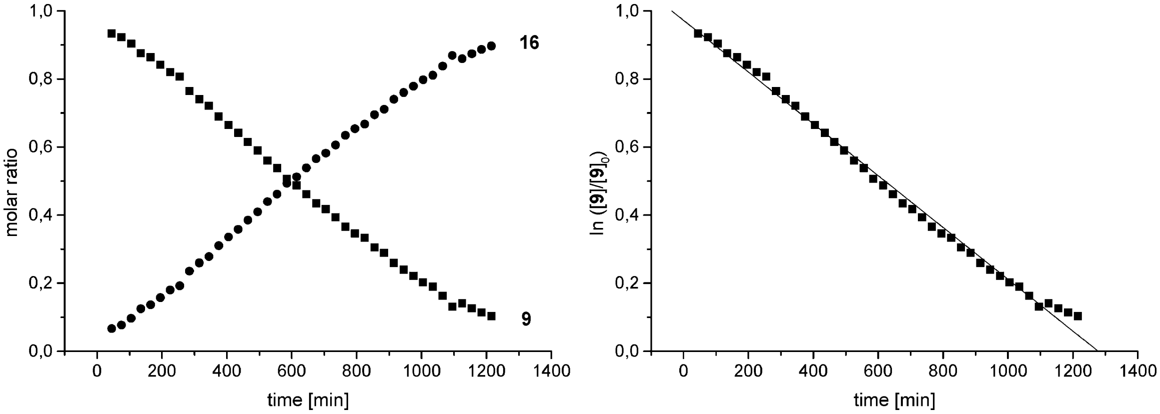


Chart 3. Kinetic Plots of the Haptotropic Rearrangement of 4-Methoxyphenanthrene Chromium Tricarbonyl 11 to the Isomer 18 at 348 K (75 °C)

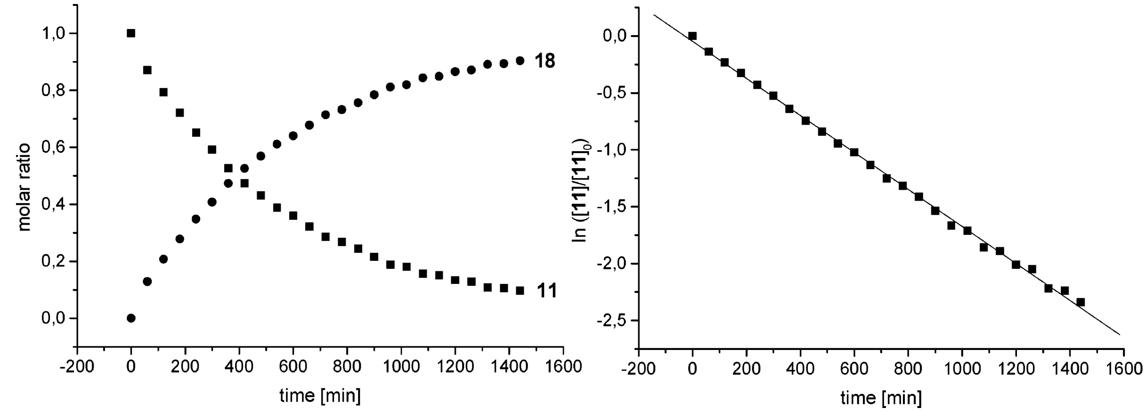
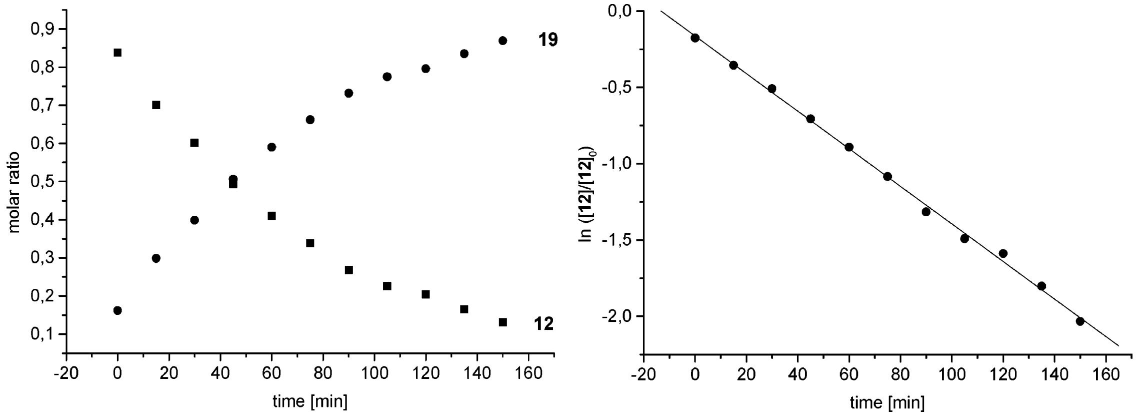


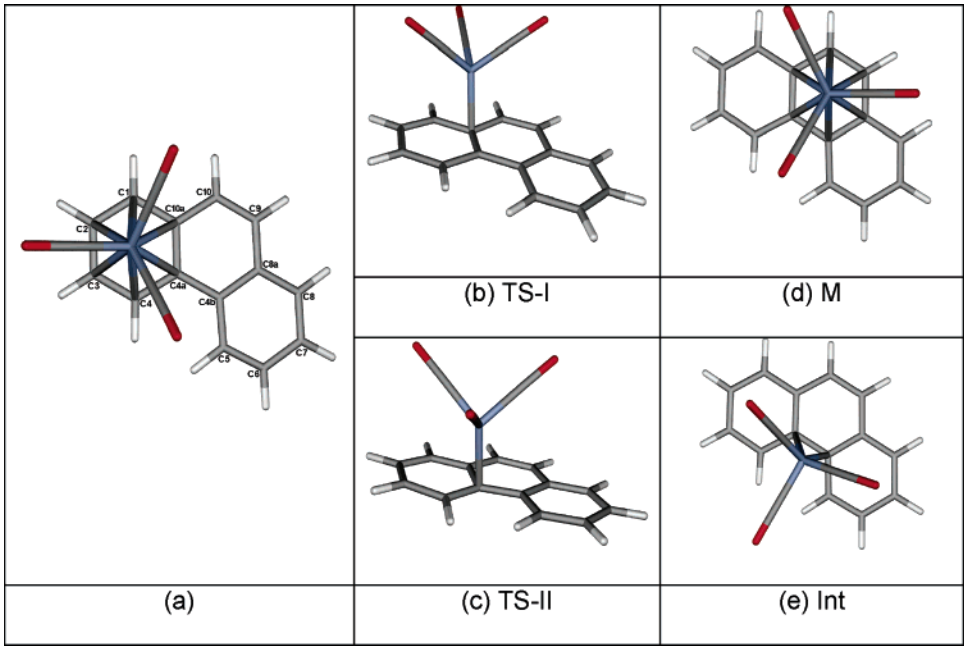
Chart 4. Kinetic Plots of the Haptotropic Rearrangement of 9-Methyl-4-methoxyphenanthrene Chromium Tricarbonyl 12 to the Isomer 19 at 363 K (90 °C)



at 90 °C indicates that monosubstitution of the central or the non-hydroquinoid terminal ring by a bromo, methoxy, or methyl group influences the rate constant by an order of magnitude. Incorporation of the methyl substituent at the central ring (**12**, entry 5) enhances the metal rearrangement by a factor of 7 compared to that observed for a methoxy substitution of the non-hydroquinoid terminal ring (**9**, entry 2). The metal shift of 9-methyl-substituted phenanthrene complex **12** is 6 times faster than in the 9-bromo complex **13** (entry 6).

The methyl substitution of the central ring leads to only a slight decrease (1.5 kJ mol^{-1}) of the free activation enthalpy (entries 4 and 5), while incorporation of the methoxy substituent in position 7 or of the bromo substituent in position 9 has a more pronounced effect and increases $\Delta G^{\ddagger}$ by 4.5−9 kJ mol^{-1} (entries 1−2, 4, and 6).

Quantum Chemical Calculations. The experimental studies were accompanied by quantum chemical investigations of the haptotropic rearrangement of naphthalene and phenanthrene chromium tricarbonyl complexes using gradient-corrected density functional theory. In case of unsubstituted phenanthrene the complexation of the central ring is 35.9 kJ mol^{-1} less favorable than the complexation of one of the terminal rings. We found that the chromium tricarbonyl tripod



(a)

(b) TS-I

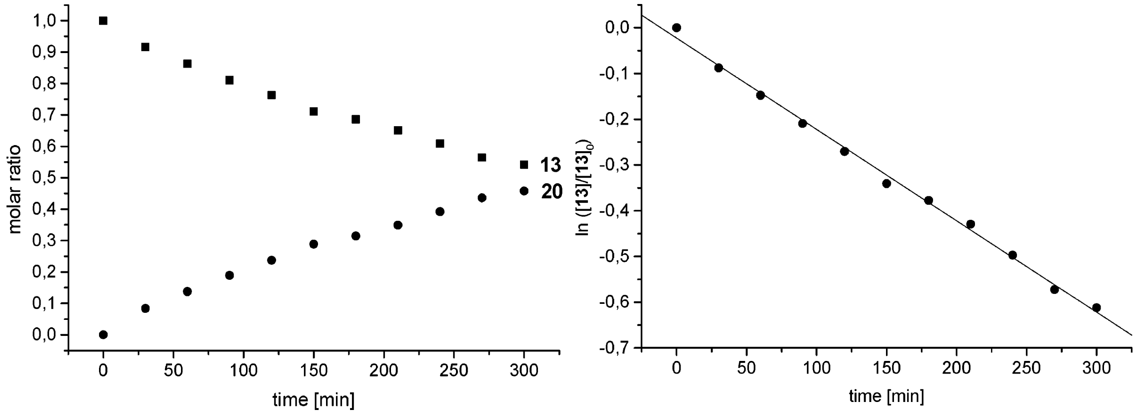
(c) TS-II

(d) M

(e) Int

Figure 1. Equilibrium structures and transition state structures of chromium tricarbonyl phenanthrene complexes from DFT calculations: (a) side ring complex; (b) transition state pathway I; (c) transition state pathway II; (d) intermediate pathway I, middle ring complex; (e) intermediate pathway II.

Chart 5. Kinetic Plots of the Haptotropic Rearrangement of 9-Bromo-4-methoxyphenanthrene Chromium Tricarbonyl 13 to the Isomer 20 at 363 K (90 °C)



when coordinated to the terminal ring can almost rotate freely around its axis, whereas two energetically distinct conformations are found for its regioisomer bearing a coordinated central ring. The most stable conformer is depicted in Figure 1d; rotation of the chromium tricarbonyl tripod by 60° about its axis generates a conformer that has two carbonyl ligands staggered with the terminal benzene rings and, thus, is about 30.9 kJ mol^{-1} less stable. The calculated equilibrium structure of the terminally coordinated phenanthrene is in good agreement with experimental data from X-ray diffraction (Table 3).

As previously reported for naphthalene $Cr(CO)_3$,[5] the migration of the chromium fragment from a terminal ring to the central ring does not take a least motion pathway crossing the middle of the carbon−carbon bond common to two fused six-membered rings, but rather proceeds along the ligand periphery with a η^4-trimethylenemethane-like complex as transition state (Figure 2). In analogy with the naphthalene chromium tricarbonyl complex one might expect four possible transition states (chromium above the C atom 4b, 8a, 4a, or 10a) associated with the metal migration from the terminal to the central ring of the phenanthrene skeleton. We found that the longer pathway (I) along the outer periphery of the phenanthrene ligand has a slightly higher activation energy (127.9 kJ mol^{-1}) than the shorter pathway (II) along the biphenyl axis linking the

Table 3. Comparison of the Calculated Bond Distances (in Å) of the Phenanthrene Chromium Tricarbonyl Complex with Experimental Data from X-ray Diffraction

bond	calculated	experimental[a]	deviation
Cr−C1	2.220	2.212	0.008
Cr−C2	2.220	2.210	0.010
Cr−C3	2.215	2.206	0.009
Cr−C4	2.213	2.208	0.005
Cr−C4a	2.319	2.289	0.030
Cr−C10a	2.312	2.289	0.023
Cr−Cco	1.830	1.828	0.002
Cr−Cco	1.842	1.844	−0.002
Cr−Cco	1.842	1.857	−0.015
C−O	1.172 1.170	1.136−1.165	0.034

[a] Muir, K. W.; Ferguson, G.; Sim, G. A. *J. Chem. Soc. B* **1968**, 467−475.

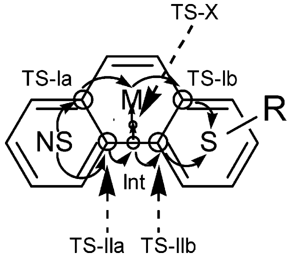


Figure 2. Reaction pathways I (NS−TS-Ia−M−TS-Ib−S) and II (NS−TS-IIa−Int−TS-IIb−S) considered for the haptotropic rearrangement of chromium tricarbonyl phenanthrene complexes. "NS" and "S" denote the complexes of chromium tricarbonyl with the nonsubstituted and substituted terminal rings, respectively, whereas "M" stands for the complex with the middle ring. "Int" refers to the η^2-coordinated intermediate of pathway II. "TS-I" and "TS-II" denote transition states for pathways I and II, respectively, and "TS-X" stands for the transition state between the intermediates of pathways I and II.

two terminal rings (122.1 kJ mol^{-1}). The activation energy calculated for the haptotropic migration of Cr(CO)$_3$ on naphthalene (125.8 kJ mol^{-1}) is slightly higher than that obtained for pathway II of phenanthrene. This result is in line with the experimental finding that the haptotropic metal migration occurs more readily along the phenanthrene than the naphthalene platform.

However, whereas pathway I along the outer periphery leads to an expected intermediate with η^6-complexation of the central ring (35.9 kJ mol^{-1}), an energetically substantially higher η^2-coordinated intermediate is found for pathway II (112.9 kJ mol^{-1}). We base the hapto-numbers 6 and 2 mainly on the calculated bond distances. For the "central ring complex" originating from pathway I Cr−C bond distances of 2.21 Å (Cr−C9, Cr−C10), 2.33 Å (Cr−C8a, Cr−C10a), and 2.35 Å (Cr−C4a, Cr−C4b) were obtained, which are very similar to the Cr−C distances obtained for the coordination of the terminal ring (cf. Table 3). The η^2-intermediate of pathway II reveals only two short Cr−C distances of 2.24 Å (Cr−C4a, Cr−C4b), whereas all others are equal or even longer than 2.54 Å (Cr−C8a, Cr−C10a). The situation is more complex since pathway II, which is actually the least motion pathway linking the two terminal ring complexes, and pathway I are connected by a transition state (128.3 kcal mol^{-1}) between the η^2-coordinated intermediate and the η^6-complex with the middle ring. The structure of this transition state is nearly identical with that of the η^2-complex. The calculated minimum and transition state structures are displayed in Figure 1; the corresponding relative energies for pathways I and II are listed in Table 4.

Table 4. Relative Energies (kJ mol^{-1}) of Phenanthrene and Phenanthrene Derivative Chromium Tricarbonyl Complexes for Reaction Pathways I and II[a]

Arene		Complex				
			TS-Ia	M	TS-Ib	
		NS		TS-X		S
			TS-IIa	Int.	TS-IIb	
Phenanthrene			127.91	35.95	127.91	
		0.00		128.30		0.00
			122.06	112.86	122.06	
Phenanthrenol anion	1-O^-		137.77	52.79	124.61	
		37.12		130.10		0.00
			144.75	96.43	98.40	
	2-O^-		141.74	56.51	88.32	
		27.92		123.88		0.00
			129.41	115.16	130.08	
	3-O^-		125.65	49.87	121.93	
		29.22		129.72		0.00
			140.49	89.37	93.92	
	4-O^-		138.07	51.96	92.38	
		26.79		127.46		0.00
			133.26	42.85	129.45	
Phenanthrenol	1-OH		126.11	32.56	133.93	
		0.00		124.99		4.18
			121.51	107.47	113.15	
	2-OH		129.08	36.99	118.34	
		0.00		124.41		4.14
			119.17	111.65	123.69	
	3-OH		125.44	35.95	129.62	
		0.00		125.21		5.02
			120.84	101.74	112.07	
	4-OH		127.87	36.28	121.60	
		0.00		125.56		9.11
			125.23	123.65	133.64	

[a] "NS" and "S" denote the η^6-complexation of the unsubstituted and substituted terminal ring, respectively. "M" stands for the η^6-complexation of the middle ring (pathway I), and "Int." denotes the η^2-coordinated intermediate (pathway II). "TS-Ia", "TS-Ib" and "TS-IIa", "TS-IIb" correspond to the transition states on pathways I and II, respectively, between the intermediates listed in the columns to the right and left. Finally, "TS-X" is the transition state between the intermediates "M" and "Int." linking the two pathways. (Note that for convenience the layout of this table was designed according to Figure 2.)

The relative stabilities of Cr(CO)$_3$ complexes of monosubstituted phenanthrene were calculated for the complexation of the terminal substituted and unsubstituted rings.[17] Incorporation of an mainly electron-withdrawing substituent at a terminal ring favors metal coordination of the unsubstituted ring over the substituted ring (−F, −OH: 4−8 kJ mol^{-1}; −NO$_2$: 4−12 kJ mol^{-1}; −Cl, −Br, −I: 8−12 kJ mol^{-1}; −NH$_3^+$: 4−25 kJ mol^{-1}). For substitution in positions 1, 2, and 3 the energy differences are identical within 4 kJ mol^{-1} and are close to the lower value, whereas the upper value holds for substitution in position 4. Mono-donor substitution at a terminal ring reverses the situation, rendering coordination of the substituted ring more stable than complexation of the unsubstituted one (−CH$_3$, −NH$_2$: ≤4 kJ mol^{-1}; −O$^-$: 25−37 kJ mol^{-1}). Only marginal effects (less than 4 kJ mol^{-1}) on the relative stabilities are observed for nearly all these substituents at the central ring. Exceptions are −O$^-$ and −NH$_3^+$, which destabilize (−O$^-$) or stabilize (−NH$_3^+$) coordination of the terminal ring closer to the substituent by 12 kJ mol^{-1}, respectively.

The complexation of the central ring was found to be significantly disfavored over coordination of one of the terminal rings. For a variety of substituents (−F, −Cl, −Br, −I, −OH, −NH$_2$, −NH$_3^+$, −NO$_2$, −CH$_3$) coordination of the central ring is destabilized by 25−41 kJ mol^{-1} for position 1, 2, 3, or 4, and 41−46 kJ mol^{-1} for position 9. Again, the most significant effect is observed for −O$^-$, which renders coordination of the central ring less stable by 50−58 kJ mol^{-1} upon substitution in positions 1, 2, 3, and 4 and by 37 kJ mol^{-1} upon substitution in the 9-position.

On the basis of these results as well as on previous calculations on naphthalene $Cr(CO)_3$ complexes the corresponding Brønsted acid−base pair $-OH/-O^-$ appeared most promising for the design of a pH-controlled metal migration toward an organometallic molecular switch. Thus, the influence of these substituents on all intermediates and transition states of pathways I and II was investigated in more detail, and we focused on the four possible substituent positions on one of the terminal rings. The results are listed in Table 4 for both pathways. In general, hydroxy substitution slightly favors (by 4−9 kJ mol^{-1}) the coordination of the unsubstituted over the substituted terminal ring, whereas the relative stabilities are reversed upon deprotonation of the phenolic hydroxy substituent, which renders complexation of the substituted terminal ring considerably more stable (by 27−37 kJ mol^{-1}). Whereas an only marginal influence of the position of the −OH substituent on the relative stability of phenanthrenol coordinated over the central ring is observed, the "central ring complex" is distinctly destabilized by 16−24 kJ mol^{-1} upon *O*-deprotonation to the phenanthrenolate complex. In comparison with the deprotonated "central ring complexes" the coordination of the unsubstituted and the oxygenated terminal rings is stabilized by 16−29 and 50−57 kJ mol^{-1}, respectively.

The situation is more complicated for the η^2-coordinated intermediate (pathway II). In principle, on the basis of the possible resonance structures, similar electronic effects mediated by the π-system should be expected for substitution in positions 1 and 3 as well as in 2 and 4. However, due to the vicinity of the 4-oxy substituent to the chromium atom in the η^2-coordinated intermediate, more drastic effects dominate. In case of a $-O^-$ substitution at C4 the intermediate is significantly stabilized (by 70 kJ mol^{-1}) by direct coordination of the oxygen to the chromium fragment, whereas a small destabilization (by 11 kJ mol^{-1}) due to steric effects results for −OH. For both −OH and $-O^-$ substitution in position 1 or 3 a weak stabilization of the intermediate is observed (by 5−11 and 16−24 kJ mol^{-1}, respectively), whereas no significant change in the relative stability can be discerned for position 2.

The data collected in Table 4 for $-O^-$ substitution follows quite clearly a pattern that can be explained by considering mesomeric charge donation to the aromatic π-system, whereas the effects are smaller and less obvious for −OH substitution. The relative energies of the transition states TS-I/IIa are less affected by substituents in the positions 1−4 than those of the transition states TS−I/IIb. For the latter, a significant stabilization results from resonance structures that allow for a localization of a negative charge on (one of) the three methylene carbon atoms in the trimethylenemethane-like unit η^4-complexing the chromium tricarbonyl fragment, i.e., TS-Ib for substituent positions 2, 4 and TS-IIb for substituent positions 1, 3. The increase of negative charges on the three methylene carbon atoms provides a better donation into the three empty hybrid orbitals of the $Cr(CO)_3$ tripod which formally result from the removal of three CO ligands from the octahedral $Cr(CO)_6$ complex. If TS-I/IIb are stabilized, TS-I/IIa are usually destabilized, since the negative charge on the central carbon atom of the trimethylenemethane unit repels the chromium tricarbonyl fragment.

According to the results discussed above, a single substituent obviously cannot significantly lower both transition states of a pathway. Our calculations also indicate that a transition state with low energy (124−130 kJ mol^{-1} for the systems listed in Table 4) between the "central ring complex" intermediate of pathway I and the η^2-coordinated intermediate of pathway II always exists. Therefore, in some systems the calculated least energy pathway is a combination of pathways I and II (e.g., for $-O^-$ in position 2 or −OH in position 4). Moreover, in other systems the transition states are energetically so close to each other that the reaction may actually proceed via two competing pathways (e.g., for $-O^-$ in position 4).

The $-OH/-O^-$-monosubstituted phenanthrene $Cr(CO)_3$ complex provides a readily available pair of complexes, which are expected to allow for a reversal of relative stabilities upon complexation of the substituted and unsubstituted terminal ring by a deprotonation−reprotonation sequence.

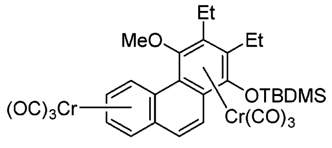
Conclusion

The haptotropic metal migration in a series of multiply substituted hydroquinoid phenanthrene $Cr(CO)_3$ complexes investigated in a preparative scale in dibutyl ether as a mildly coordinating solvent and in hexafluorobenzene and octafluorotoluene as noncoordinating solvents was characterized as a first-order process based on a kinetic NMR study in fluorinated aromatic solvents. The metal shift proceeds from the hydroquinoid to the other terminal ring with a rate that depends on the arene substitution pattern. The free activation enthalpy for this process increases upon incorporation of bromo and methoxy substituents into the central and the other terminal ring, respectively, but is decreased with increasing helical distortion of the phenanthrene platform, which, however, favors decomplexation. DFT calculations disfavor least motion pathways between adjacent rings and suggest alternative pathways along the inner and/or outer π-periphery, with a preference for the former occurring along the central biphenyl axis. These shifts are characterized by a η^2-coordinated complex intermediate or a "central ring complex" intermediate, respectively, and proceed via η^4-trimethylenemethane-like complex transition states. The calculations are in line with experimental results that a final coordination of the central ring cannot compete with a complexation of either the hydroquinoid or the less substituted terminal ring. They further suggest that a deprotonation−reprotonation sequence might be applied to induce a reversible metal migration toward a novel organometallic switch.

Experimental Section

All operations involving organometallic compounds were carried out under argon using round-bottom flasks (rearrangement of tricarbonylchromium complexes at preparative scale). Solvents were predistilled, dried using standard methods, saturated, and stored under argon. The solvents used for the NMR monitoring of the haptotropic rearrangements (hexafluorobenzene, Aldrich; octafluorotoluene, Acros) were stirred for 1 day over calcium hydride at ambient temperature followed by distillation and one cycle of freeze, pump, and thaw. Macherey Nagel silica gel MN 60 (0.015−0.025 mm) was used

Scheme 3



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for chromatographic purification. Given yields refer to pure products. ^{1}H and ^{13}C NMR: Bruker DRX-300, -400, and -500, using Me$_4$Si as an internal standard. NMR spectra of the purified complexes were recorded in CDCl$_3$ at 25 °C (298 K). FT-IR: Nicolet Magna 550. MS (EI): Kratos MS 50. All IR spectra were measured in petroleum ether (PE).

General Procedure for the Haptotropic Rearrangement of the Phenanthrene Complexes. Monitoring by IR Spectroscopy. A saturated solution of the starting phenanthrene complex **8**−**14**, respectively, in 50−75 mL of *n*-dibutyl ether was transferred to a round-bottom flask and immersed into a preheated oil bath maintained at 90 and 120 °C, respectively. After the reaction was completed (indicated by complete consumption of the starting material or by decomposition indicated by the strong IR absorption of hexacarbonyl chromium) the solvent and volatiles were removed under high vacuum at room temperature. Workup by column chromatography applying petroleum ether/dichloromethane mixtures (**15**, **16**, **18**, **19**, **22**: 2:1, **17**, **20**, **21**: 3:1) afforded the pure rearrangement products.

Monitoring by NMR Spectroscopy. A suspension of ca. 10^{-6}−10^{-5} mmol of phenanthrene complex **8**−**13**, respectively, in 0.5 mL of the fluorinated solvent was filtered through a pad of Celite, and the filtrate was transferred into a NMR tube. The NMR measurement was performed in the presence of an external standard (dimethyl sulfoxide-d_6 or dioxane-d_8, Merck) at either 75 °C (348 K) or 90 °C (363 K) with a Bruker DRX-500 NMR spectrometer.

Tricarbonyl-{η^6-4b,5,6,7,8,8a-(2,3-diethyl-1-methoxy-4-[(*tert*-butyl)dimethylsilyloxy]phenanthrene)}chromium (15). Chromatography yielded 0.15 g (2.83 mmol, 19%) of **15** after performing the rearrangement of **8** (0.79 g, 1.49 mmol) at 90 °C for 7 h as a yellow-orange solid. R_f = 0.25 (2:1 petroleum ether/CH$_2$Cl$_2$). ^{1}H NMR (300 MHz): δ −0.24 (s, 3H, SiCH$_3$), −0.06 (s, 3H, SiCH$_3$), 1.17 (s, 9H, SiC(CH$_3$)$_3$, 1.20 (t, ^3J = 7.34 Hz, 3H, CH$_2$C*H*$_3$), 1.26 (t, ^3J = 7.49 Hz, 3H, CH$_2$C*H*$_3$), 2.59−2.79 (m, 2H, C*H*$_2$CH$_3$), 2.93−3.12 (m, 2H, C*H*$_2$CH$_3$), 3.88 (s, 3H, OCH$_3$), 5.42 (ddd, ^3J = 6.91 Hz,^3J = 6.03 Hz, ^3J = 1.32 Hz, 1H, Ar H), 5.49 (ddd, ^3J = 7.50 Hz,^3J = 6.03 Hz, ^3J = 1.13 Hz, 1H, Ar H), 5.99 (dd, ^3J = 6.94 Hz, ^4J = 1.41 Hz, 1H, Ar H), 7.24 (d, ^3J = 9.04 Hz, 1H, Ar H), 7.69 (d, ^3J = 6.97 Hz, 1H, Ar H), 7.77 (d, ^3J = 9.04 Hz, 1H, Ar H). ^{13}C NMR (75 MHz): δ −4.90 (SiCH$_3$), −2.83 (SiCH$_3$), 15.10 (CH$_2$*C*H$_3$), 15.57 (CH$_2$*C*H$_3$), 18.38 (Si*C*(CH$_3$)$_3$), 20.24 (*C*H$_2$CH$_3$), 21.06 (*C*H$_2$CH$_3$), 25.95 (SiC(*C*H$_3$)$_3$), 62.91 (OCH$_3$), 90.00 (Ar CH), 91.43 (Ar CH), 91.64 (Ar CH), 92.88 (Ar CH), 101.97 (Ar C), 105.52 (Ar C), 120.74 (Ar C), 123.43 (Ar CH), 125.15 (Ar C), 125.43 (Ar CH), 136.33 (Ar C), 136.47 (Ar C), 146.73 (Ar C), 149.50 (Ar C), 232.69 (CO). FT-IR (cm^{-1}, PE): ν_{CO} 1972 (m, A$_1$), 1913, 1903 (s, "E"). MS (EI): (M$^+$) *m*/*z* (%) 530 (8), 474 (8), 446 (100), 394 (48), 379 (24), 379 (30). HR-MS: calcd for C$_{28}$H$_{34}$CrO$_5$Si 530.1580, found 530.1586.

Tricarbonyl-{η^6-4b,5,6,7,8,8a-(2,3-diethyl-1,7-dimethoxy-4-[(*tert*-butyl)dimethylsilyloxy]phenanthrene)}chromium (16). Chromatography yielded 0.56 g (1.00 mmol, 70%) and 0.60 g (1.07 mmol, 75%) of **16** after performing the rearrangement of **9** (0.80 g, 1.43 mmol) at 90 and 120 °C for 6 and 1.5 h, respectively, as a yellow-orange solid. R_f = 0.35 (2:1 petroleum ether/CH$_2$Cl$_2$). ^{1}H NMR (300 MHz): δ −0.20 ppm (s, 3H, SiC*H*$_3$); −0.05 (s, 3H, SiC*H*$_3$); 1.16 (s, 9H, SiC(CH$_3$)$_3$); 1.20 (t, ^3J = 7.30 Hz, 3H, CH$_2$C*H*$_3$); 1.26 (t, ^3J = 7.50 Hz, 3H, CH$_2$C*H*$_3$); 2.57−2.76 (m, 2H, C*H*$_2$CH$_3$); 2.89−3.10 (m, 2H, C*H*$_2$-CH$_3$); 3.84 (s, 3H, OCH$_3$); 3.87 (s, 3H, OCH$_3$); 5.32 (dd, ^3J = 6.53 Hz, ^4J = 2.64 Hz, 1H, Ar H); 5.68 (d, ^4J = 2.55 Hz, 1H, Ar H); 7.23 (d, ^3J = 9.23 Hz, 1H, Ar H); 7.83 (d, ^3J = 9.23 Hz, 1H, Ar H); 7.90 (d, ^3J = 7.54 Hz, 1H, Ar H). ^{13}C NMR (75 MHz): δ −4.89 (C, SiCH$_3$); −2.71 (SiCH$_3$); 15.08 (CH$_2$*C*H$_3$); 15.56 (CH$_2$*C*H$_3$); 18.36 (Si*C*(CH$_3$)$_3$); 20.12 (*C*H$_2$CH$_3$); 21.05 (*C*H$_2$CH$_3$); 25.92 (SiC(*C*H$_3$)$_3$); 55.67 (OCH$_3$); 62.83 (OCH$_3$); 74.99 (Ar CH); 78.85 (Ar CH); 93.19 (Ar CH); 99.15 (Ar C); 103.06 (Ar C); 121.16 (Ar C); 124.37 (Ar C); 124.48 (Ar CH); 125.53 (Ar CH); 135.57 (Ar CH); 136.49 (Ar C); 141.81 (Ar C); 146.08 (Ar C); 149.58 (Ar C); 233.16 (CO). FT-IR (cm^{-1}, PE): ν_{CO} 1969 (m, A$_1$); 1906, 1897 (s, "E"). MS (EI): (M$^+$) *m*/*z* (%) 560 (10), 504 (1), 476 (100), 424 (48), 420 (40), 409 (10). HR-MS: calcd for C$_{29}$H$_{36}$CrO$_6$Si 560.1686, found 560.1684.

Tricarbonyl-{η^6-4b,5,6,7,8,8a-(7-bromo-2,3-diethyl-1-methoxy-4-[(*tert*-butyl)dimethylsilyloxy]phenanthrene)}-chromium (17). Chromatography yielded 0.17 g (0.28 mmol, 19%) of **17** after performing the rearrangement of **10** (0.91 g, 1.50 mmol) at 120 °C for 1 h as a yellow-orange solid. R_f = 0.50 (3:1 petroleum ether/CH$_2$Cl$_2$). ^{1}H NMR (300 MHz): δ −0.21 ppm (s, 3H, SiCH$_3$); −0.06 (s, 3H, SiCH$_3$); 1.16 (s, 9H, SiC(CH$_3$)$_3$); 1.17 (t, ^3J = 7.34 Hz, 3H, CH$_2$C*H*$_3$); 1.20 (t, ^3J = 7.49 Hz, 3H, CH$_2$C*H*$_3$); 2.58−2.76 (m, 2H, C*H*$_2$CH$_3$); 2.87−3.10 (m, 2H, C*H*$_2$CH$_3$); 3.86 (s, 3H, OCH$_3$); 5.90 (dd, ^3J = 7.16 Hz, ^4J = 1.88 Hz, 1H, Ar H); 6.21 (d, ^4J = 1.89 Hz, 1H, Ar H); 7.23 (d, ^3J = 9.23 Hz, 1H, Ar H); 7.72 (d, ^3J = 7.35 Hz, 1H, Ar H); 7.82 (d, ^3J = 9.05 Hz, 1H, Ar H). ^{13}C NMR (75 MHz): δ −4.92 (SiCH$_3$); −2.71 (Si*C*H$_3$); 15.04 (CH$_2$*C*H$_3$); 15.53 (CH$_2$*C*H$_3$); 18.37 (Si*C*(CH$_3$)$_3$); 20.21 (*C*H$_2$CH$_3$); 21.05 (*C*H$_2$CH$_3$); 25.91 (SiC(*C*H$_3$)$_3$); 62.91 (OCH$_3$); 91.23 (Ar CH); 91.47 (Ar CH); 92.68 (Ar CH); 97.00 (Ar C); 101.98 (Ar C); 103.83 (Ar C); 120.95 (Ar C); 124.48 (Ar CH); 124.78 (Ar CH); 130.80 (Ar CH); 136.47 (Ar C); 136.87 (Ar C); 146.44 (Ar C); 149.62 (Ar C); 231.57 (CO). FT-IR (cm^{-1}, PE): ν_{CO} 1978 (m, A$_1$); 1920, 1914 (s, "E"). MS (EI): (M$^+$) *m*/*z* (%) 608 (8), 554 (5), 526 (100), 474 (20). HR-MS: calcd for C$_{28}$H$_{33}$BrCrO$_5$Si 608.0685, found: 608.0699.

Tricarbonyl-{η^6-4b,5,6,7,8,8a-(2,3-diethyl-4-methoxy-1-[(*tert*-butyl)dimethylsilyloxy]phenanthrene)}chromium (18). Chromatography yielded 1.53 g (2.89 mmol, 90%) and 1.19 g (2.24 mmol, 70%) of **18** after performing the rearrangement of **11** (1.70 g, 0.90 mmol) at 90 and 120 °C for 13 and 4 h, respectively, as a yellow-orange solid. R_f = 0.52 (2:1 petroleum ether/CH$_2$Cl$_2$). ^{1}H NMR (300 MHz): δ 0.16 ppm (s, 3H, SiCH$_3$); 0.19 (s, 3H, SiCH$_3$); 1.07 (s, 9H, SiC(CH$_3$)$_3$); 1.19 (t, ^3J = 7.33 Hz, 3H, CH$_2$C*H*$_3$); 1.29 (t, ^3J = 7.33 Hz, 3H, CH$_2$C*H*$_3$); 2.73−2.99 (m, 2H, C*H*$_2$CH$_3$); 3.85 (s, 3H, OCH$_3$); 5.49−5.53 (m, 2H, Ar H); 5.96−6.01 (m, 1H, Ar H); 7.17 (d, ^3J = 9.05 Hz, 1H, Ar H); 7.78 (dd, ^3J = 6.97 Hz, ^4J = 1.14 Hz, 1H, Ar H); 7.83 (d, ^3J = 9.23 Hz, 1H, Ar H). ^{13}C NMR (75 MHz): δ −3.31 (SiCH$_3$); −3.21 (SiCH$_3$); 14.59 (CH$_2$*C*H$_3$); 15.81 (CH$_2$*C*H$_3$); 18.70 (Si*C*(CH$_3$)$_3$); 20.41 (*C*H$_2$CH$_3$); 20.83 (*C*H$_2$CH$_3$); 26.04 (SiC(*C*H$_3$)$_3$); 61.52 (OCH$_3$); 90.55 (Ar CH); 91.86 (Ar CH); 91.96 (Ar CH); 92.56 (Ar CH); 103.01 (Ar C); 103.27 (Ar C); 121.03 (Ar C); 124.05 (Ar CH); 124.89 (Ar C); 125.29 (Ar CH); 134.56 (Ar C); 137.94 (Ar C); 146.52 (Ar C); 151.40 (Ar C); 232.92 (CO). FT-IR (cm^{-1}, PE): ν_{CO} 1972 (m, A$_1$); 1913, 1903 (s, "E"). MS (EI): (M$^+$) *m*/*z* (%) 530 (10), 474 (3), 446 (100), 394 (50), 390 (41). HR-MS: calcd for C$_{28}$H$_{34}$CrO$_5$Si 530.1850, found 530.1852.

Tricarbonyl-{η^6-4b,5,6,7,8,8a-(2,3-diethyl-4-methoxy-9-methyl-1-[(*tert*-butyl)dimethylsilyloxy]phenanthrene)}-chromium (19). Chromatography yielded 2.39 g (4.39 mmol, 80%) of **19** after performing the rearrangement of **12** (1.63 g, 2.99 mmol) at 120 °C for 1 h as a yellow-orange solid. R_f = 0.32 (2:1 petroleum ether/CH$_2$Cl$_2$). ^{1}H NMR (300 MHz): δ 0.17 (s, 3H, SiCH$_3$); 0.20 (s, 3H, SiCH$_3$); 1.09 (s, 9H, SiC(CH$_3$)$_3$); 1.20 (t, ^3J = 7.35 Hz, 3H, CH$_2$C*H*$_3$); 1.29 (t, ^3J = 7.34 Hz, 3H, CH$_2$C*H*$_3$); 2.56 (s, 3H, C9-CH$_3$); 2.74−2.94 (m, 4H, 2×C*H*$_2$CH$_3$); 3.83 (s, 3H, OCH$_3$); 5.54−5.57 (m, 2H, Ar H); 6.07−6.10 (m, 1H, Ar H); 7.70 (s, 1H, Ar H); 7.86−7.88 (m, 1H, Ar H). ^{13}C NMR (75 MHz): δ −3.37 (SiCH$_3$); −3.21 (SiCH$_3$); 14.59 (CH$_2$*C*H$_3$); 15.85 (CH$_2$*C*H$_3$); 18.77 (Si*C*(CH$_3$)$_3$); 19.58 (CH$_3$); 20.34 (*C*H$_2$CH$_3$); 20.82 (*C*H$_2$CH$_3$); 26.08 (SiC(*C*H$_3$)$_3$); 61.42

$(\mathrm{OCH_3})$; 88.28 (Ar CH); 90.91 (Ar CH); 91.74 (Ar CH); 92.43 (Ar CH); 103.12 (Ar C); 103.88 (Ar C); 120.07 (Ar C); 124.15 (Ar CH); 124.92 (Ar C); 129.71 (Ar CH); 134.38 (Ar C); 136.78 (Ar C); 145.84 (Ar C); 151.22 (Ar C); 232.90 (CO). FT-IR ($\mathrm{cm^{-1}}$, PE): ν_{CO} 1970 (m, $\mathrm{A_1}$); 1911, 1901 (s, "E"). MS (EI): ($\mathrm{M^+}$) *m/z* (%) 544 (7), 488 (3), 460 (100), 408 (18), 393 (5). HR-MS: calcd for $\mathrm{C_{29}H_{36}CrO_5Si}$ 544.1737, found 544.1735.

Tricarbonyl-{η^6-4b,5,6,7,8,8a-(9-bromo-2,3-diethyl-4-methoxy-1-[(*tert*-butyl)dimethylsilyloxy]phenanthrene)}-chromium (20). Chromatography yielded 0.17 g (0.28 mmol, 7%) and 1 g (1.64 mmol, 40%) of **20** after performing the rearrangement of **13** (2.50 g, 4.11 mmol) at 90 and 120 °C for 3.5 and 1.75 h, respectively, as a yellow-orange solid. $R_f = 0.52$ (3:1 petroleum ether/$\mathrm{CH_2Cl_2}$). ^{1}H NMR (300 MHz): δ 0.21 ppm (s, 3H, $\mathrm{SiCH_3}$); 0.25 (s, 3H, $\mathrm{SiCH_3}$); 1.12 (s, 9H, $\mathrm{SiC(CH_3)_3}$); 1.23−1.38 (m, 6H, $2\times\mathrm{CH_2CH_3}$); 2.79−2.97 (m, 4H, $2\times\mathrm{CH_2CH_3}$); 3.83 (s, 3H, $\mathrm{OCH_3}$); 5.26−5.31 (m, 2H, Ar H); 6.23 (d, ^3J = 6.21 Hz, 1H, Ar H); 7.59 (s, 1H, Ar H); 7.78 (d, ^3J = 6.78 Hz, 1H, Ar H). ^{13}C NMR (75 MHz): δ −3.51 ($\mathrm{SiCH_3}$); −3.36 ($\mathrm{SiCH_3}$); 14.48 ($\mathrm{CH_2}C\mathrm{H_3}$); 15.66 ($\mathrm{CH_2}C\mathrm{H_3}$); 18.70 ($\mathrm{Si}C\mathrm{(CH_3)_3}$); 20.45 ($C\mathrm{H_2CH_3}$); 20.80 ($C\mathrm{H_2CH_3}$); 25.99 ($\mathrm{SiC(}C\mathrm{H_3)_3}$); 61.48 ($\mathrm{OCH_3}$); 89.45 (Ar CH); 90.96 (Ar CH); 91.81 (Ar CH); 92.07 (Ar CH); 100.62 (Ar C); 104.13 (Ar C); 120.08 (Ar C); 127.96 (Ar CH); 125.14 (Ar C); 132.20 (Ar C); 134.92 (Ar C); 138.50 (Ar C); 145.80 (Ar C); 151.17 (Ar C); 231.85 (CO). FT-IR ($\mathrm{cm^{-1}}$, PE): ν_{CO} 1976 (m, $\mathrm{A_1}$); 1916, 1910 (s, "E"). MS (EI): ($\mathrm{M^+}$) *m/z* (%) 610 (8), 554 (5), 526 (100), 474 (33). HR-MS: calcd for $\mathrm{C_{28}H_{33}BrCrO_5Si}$ 608.0685, found 608.0695.

Tricarbonyl-{η^6-4b,5,6,7,8,8a-(2,3-diethyl-9-fluoro-4-methoxy-9-methyl-1-[(*tert*-butyl)dimethylsilyloxy]phenanthrene)}chromium (21). Chromatography yielded 0.08 g (0.15 mmol, 5%) of **21** after performing the rearrangement of **14** (1.64 g; 1.00 mmol) at 90 °C for 5 h as a yellow-orange solid. $R_f = 0.48$ (3:1 petroleum ether/$\mathrm{CH_2Cl_2}$). ^{1}H NMR (300 MHz): δ 0.08 ppm (s, 3H, $\mathrm{SiCH_3}$); 0.17 (s, 3H, $\mathrm{SiCH_3}$); 1.16 (s, 9H, $\mathrm{SiC(CH_3)_3}$); 1.34 (t, ^3J = 7.45 Hz, 3H, $\mathrm{CH_2C}H_3$); 1.37 (t, ^3J = 7.46 Hz, 3H, $\mathrm{CH_2C}H_3$); 2.70−2.89 (m, 4H, $\mathrm{C}H_2\mathrm{CH_3}$); 3.84 (s, 3H, $\mathrm{OC}H_3$); 5.53−5.55 (m, 2H, Ar H); 6.27−6.29 (m, 1H, Ar H); 7.43 (s, 1H, Ar H); 7.74 (d, ^3J = 7.07 Hz, 1H, Ar H). ^{13}C NMR (75 MHz): δ −3.10 ($\mathrm{SiCH_3}$); −2.09 ($\mathrm{SiCH_3}$); 14.57 ($\mathrm{CH_2}C\mathrm{H_3}$); 15.81 ($\mathrm{CH_2}C\mathrm{H_3}$); 18.73 ($\mathrm{Si}C\mathrm{(CH_3)_3}$); 20.33 ($C\mathrm{H_2CH_3}$); 20.93 ($C\mathrm{H_2CH_3}$); 25.97 ($\mathrm{SiC(}C\mathrm{H_3)_3}$); 61.59 ($\mathrm{OCH_3}$); 84.74 (D, J_{CF} = 7.99 Hz, Ar CH); 89.80 (D, J_{CF} = 2.00 Hz, Ar CH); 91.34 (Ar C); 94.51 (D, J_{CF} = 22.37 Hz, Ar C); 103.71 (Ar C); 104.95 (D, J_{CF} = 21.17 Hz, Ar CH); 118.58 (Ar C); 124.52 (D, J_{CF} = 18.39 Hz, Ar C); 124.97 (Ar C); 134.94 (Ar C); 136.82 (D, J_{CF} = 2.39 Hz, Ar C); 146.13 (D, J_{CF} = 5.59 Hz, Ar C); 152.30 (D, J_{CF} = 150.99 Hz, Ar C); 155.56 (Ar C); 231.96 (CO). FT-IR ($\mathrm{cm^{-1}}$, PE): ν_{CO} 1976 (m, $\mathrm{A_1}$); 1920, 1912 (s, "E"). MS (EI): ($\mathrm{M^+}$) *m/z* (%) 548 (9), 496 (4), 468 (100), 416 (31). HR-MS: calcd for $\mathrm{C_{28}H_{33}CrFO_5Si}$ 548.1468, found 548.1477.

Hexacarbonyl-{η^6,η^6-1,2,3,4,4a,4b,5,6,7,8,8a,10a-(2,3-diethyl-4-methoxy-1-[(*tert*-butyl)dimethylsilyloxy]phenanthrene)}bischromium (22). Chromatography yielded 0.04 g (0.06 mmol, 6%) of **22** after performing the rearrangement of **11** (1.70 g, 0.90 mmol) at 90 °C as an orange solid. $R_f = 0.21$ (2:1 petroleum ether/$\mathrm{CH_2Cl_2}$). ^{1}H NMR (300 MHz): δ 0.27 ppm (s, 3H, $\mathrm{SiCH_3}$); 0.29 (s, 3H, $\mathrm{SiCH_3}$); 1.05 (s, 9H, $\mathrm{SiC(CH_3)_3}$); 1.33 (t, ^3J = 7.53 Hz, 3H, $\mathrm{CH_2C}H_3$); 1.35 (t, ^3J = 7.35 Hz, 3H, $\mathrm{CH_2C}H_3$); 2.38−2.70, 2.81−2.90 (m, 4H, $2\times\mathrm{C}H_2\mathrm{CH_3}$); 3.90 (s, 3H, $\mathrm{OCH_3}$); 5.46 (ddd, ^3J = 7.07 Hz, ^3J = 6.45 Hz, ^4J = 1.22 Hz, 1H, Ar H); 5.56 (ddd, ^3J = 6.31 Hz, ^3J = 6.22 Hz, ^4J = 0.96 Hz, 1H, Ar H); 5.99 (dd, ^3J = 6.41 Hz, ^4J = 1.32 Hz, 1H, Ar H); 6.87 ppm (d, ^3J = 9.39 Hz, 1H, Ar H); 7.29 (d, ^3J = 6.97 Hz, 1H, Ar H); 7.43 (d, ^3J = 9.61 Hz, 1H, Ar H). ^{13}C NMR (75 MHz): δ −2.94 ($\mathrm{SiCH_3}$); −2.73 ($\mathrm{SiCH_3}$); 15.20 ($\mathrm{CH_2}C\mathrm{H_3}$); 17.73 ($\mathrm{CH_2}C\mathrm{H_3}$); 18.87 ($\mathrm{Si}C\mathrm{(CH_3)_3}$); 19.80 ($C\mathrm{H_2CH_3}$); 21.41 ($C\mathrm{H_2CH_3}$); 25.93 ($\mathrm{SiC(}C\mathrm{H_3)_3}$); 66.74 ($\mathrm{OCH_3}$); 90.26 (Ar C); 90.61 (Ar CH); 91.29 (Ar CH); 91.58 (Ar CH); 93.22 (Ar CH); 93.24 (Ar CH); 100.00 (Ar C); 102.88 (Ar C); 104.82 (Ar C); 112.96 (Ar C); 123.89 (Ar C); 126.12 (Ar CH); 130.45 (Ar C); 134.73 (Ar C); 232.07, 233.84 (2xCO). FT-IR ($\mathrm{cm^{-1}}$, PE): ν_{CO} 1969 (m, $\mathrm{A_1}$); 1911, 1900 (s, "E"). MS (EI): ($\mathrm{M^+}$) *m/z* (%) 666 (1), 582 (30), 554 (16), 526 (45), 498 (44), 446 (100), 394 (26), 390 (28). HR-MS: calcd for $\mathrm{C_{31}H_{34}Cr_2O_8Si}$ 666.0833, found 666.0827.

Details of Quantum Chemical Calculations. The quantum chemical first-principles calculations reported here were carried out with the TURBOMOLE program package[19] in the framework of gradient-corrected density functional theory.[20] The local Slater exchange and Vosko−Wilk−Nusair correlation[21] energy functionals were applied together with the Becke exchange[22] and Perdew correlation[23] energy gradient corrections (BP). The inner $1s^2{-}2p^6$ shells (Ne core) of Cr were replaced by a scalar relativistic energy-consistent ab initio pseudopotential.[24] Similarly, Cl, Br, and I were treated as 7-valence electron atoms by means of pseudopotentials.[25] Polarized split-valence (SVP) basis sets from the TURBOMOLE basis set library[26] have been used for H, C, N, O, and F. (8s7p6d)/[6s5p3d] and (6s6p1d)/[3s3p1d] valence basis sets were used for Cr and the heavy halogenes Cl, Br, and I, respectively. The determined equilibrium structures of starting materials, products, and intermediates and the transition states were confirmed by analyzing the eigenvalues of the Hessian matrix.

Our computational strategy has been calibrated in calculations for the haptotropic rearrangement of chromium tricarbonyl on naphthalene as a model system. Here, the gas phase activation energy of 30.1 kcal $\mathrm{mol^{-1}}$ from BP/SVP was only slightly lowered to 122.1 kJ $\mathrm{mol^{-1}}$ when solvent effects were approximated by means of the conductor-like screening model (COSMO)[27] assuming an infinite dielectric constant, indicating very small effects of noncomplexing solvents. The BP/SVP gas phase value was changed to 117.0 kJ $\mathrm{mol^{-1}}$ for the larger polarized valence triple-ζ (TZVP) basis sets. The latter value was lowered only slightly to 115.4 kJ $\mathrm{mol^{-1}}$, when instead of the BP DFT treatment a wave function-based post-Hartree−Fock coupled-cluster correlation treatment[28] using the resolution of identity approximation (RI-CC2)[29] was applied for the TZVP basis set. Finally, complete active space self-consistent field calculations (CASSCF) confirmed the single-reference character of starting materials, intermediates, products, and transition states and therefore support the application of single-reference schemes such as DFT.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **15**−**20** and **22** are included in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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