

A Quantum Chemical Study of the Haptotropic Rearrangements of Cr(CO)₃ on Naphthalene and Phenanthrene Systems

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First-principles gradient-corrected density functional theory electronic structure calculations of the haptotropic rearrangement of a Cr(CO)₃ unit on naphthalene and phenanthrene derivatives are reported. Coupled-cluster calibration studies of Cr(CO)₃ complexes with benzene and naphthalene derivatives confirm the accuracy of the applied Becke exchange and Perdew correlation functionals. Characteristic points on the energy hypersurface (reactants, products, intermediates, and transition states) were located for various substituents on the aromatic skeleton. It is argued that a –OH/–O[–] substituent may provide a means to steer the haptotropic shift depending on the pH value, i.e., to construct a molecular switch. In addition, the mechanism of the [3 + 2 + 1] benzannulation of chromium pentacarbonyl naphthylcarbene complexes with alkynes was investigated, and the preference of the angular benzannulation leading to phenanthrene complexes of Cr(CO)₃ over the linear benzannulation leading to corresponding anthracene complexes is explained.

1. Introduction

The term “haptotropic” rearrangement or migration was first introduced by Hoffmann and co-workers¹ to refer to a process in which a ML_n unit (M = metal, L = coligand) changes its connectivity (hapto number) to a ligand with multicoordinate site possibilities. Haptotropic is thus an extension to “sigmatropic”, referring specifically to σ -bond shifts. Haptotropic shifts occur in many transition metal-catalyzed processes and considerable research efforts concentrated on the improvement of the understanding of the relevant mechanisms and the application of such metal shifts to selective synthesis.² Four decades ago Deubzer reported first on the reversible η^6 - η^6 -haptotropic rearrangement of both isomers of (η^6 -2,3-dimethylnaphthalene)-tricarbonylchromium.³ Encouraged by this work, a variety of arenes derived from fluorene, phenalene, anthracene, phenanthrene and other skeletons have been investigated. Recent studies of the rearrangement of these complexes include both experimental^{3–8} and theoretical^{9–11} investigations.

Albright et al.¹¹ proposed the pathway for the metal–coligand Cr(CO)₃ migration in the naphthalene system based on results of the semiempirical extended Hückel theory (EHT) method. They suggested that the migration of the metal–coligand unit through the least motion route from one ring to another via the center of the C_{4a}–C_{8a} bond is energetically very unfavorable (cf. Figure 1 for the numbering of the atoms). The metal–coligand unit rather migrates along the periphery of the naphthalene ligand with a Cr(CO)₃ η^4 -coordinated trimethylenemethane transition state complex; i.e., the Cr is approximately located above the C_{4a} (or C_{8a}) atom rather than above the center of the C_{4a}–C_{8a} bond (cf. Figure 2).

Later, Kirss et al.¹² reported a kinetic study of the haptotropic rearrangement for the dimethoxy naphthalene system. Based on

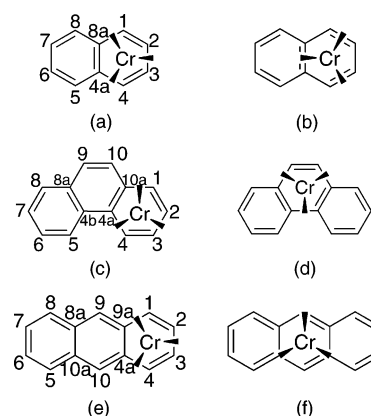


Figure 1. Structures of the selected regioisomers and corresponding most stable conformers of tricarbonylchromium naphthalene, phenanthrene, and anthracene complexes.

rate constant measurements they suggested that the methoxy groups only play a small role in the stabilization of the transition state. In 1999 Oprunenko et al.¹⁰ studied the kinetics of the η^6 - η^6 -haptotropic rearrangement for substituted naphthalene tricarbonylchromium complexes (substituents –D, –CH₃, –SnMe₃, –SiMe₃, and –Cl) and concluded that the reaction for mono-substituted complexes only slightly depends on the nature of the substituent group. Recently, we reported experimental and some preliminary theoretical results for the η^6 - η^6 -haptotropic rearrangement of Cr(CO)₃ on substituted phenanthrene systems.¹³

In the following report, we compare the structure and stabilities of the reactants, products, intermediate and transition state complexes and the details of reaction mechanisms of the haptotropic rearrangement of a Cr(CO)₃ fragment on naphthalene and phenanthrene as well as some of their derivatives based on results of a first-principles gradient-corrected density functional investigation. We also report the mechanistic and energetic

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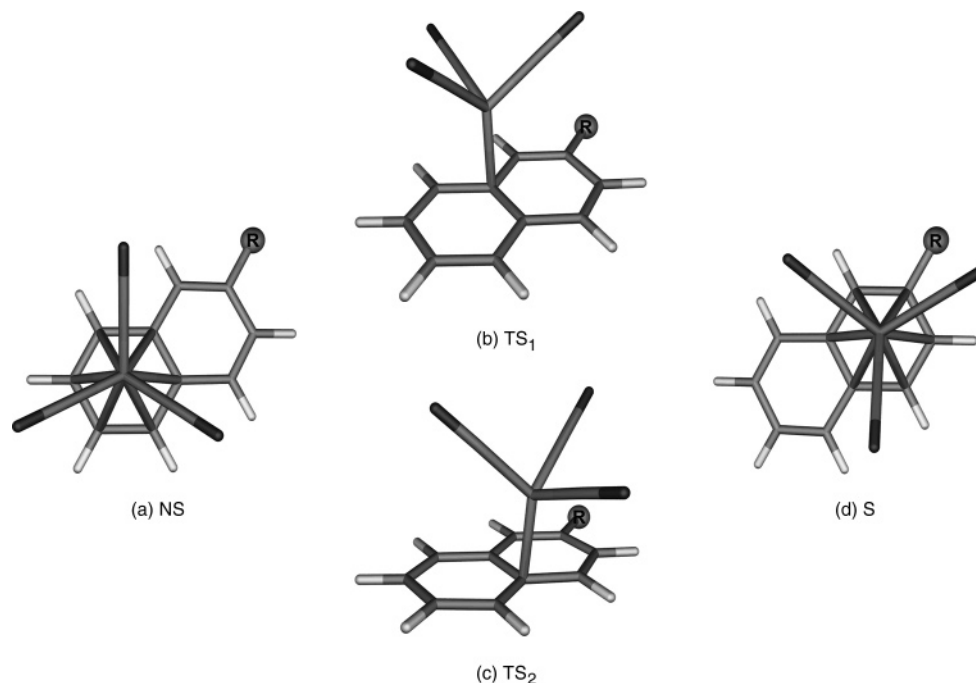


Figure 2. Equilibrium structures and transition state structures of chromium tricarbonyl naphthalene derivative complexes from DFT investigations: (a) complex with the nonsubstituted ring; (b) transition state 1; (c) transition state 2; (d) complex with the substituted ring.

aspects of the [3 + 2 + 1] benzannulation reaction leading from naphthalene Fischer-type carbene complexes to either anthracene or phenanthrene complexes with Cr(CO)₃ by linear or angular extension of the arene system. The latter study can be viewed as an extension of the theoretical investigation of Gleichmann et al.¹⁴ of the [3 + 2 + 1] benzannulation leading from benzene Fischer-type carbene complexes and alkynes to naphthalene complexes with Cr(CO)₃.

2. Computational Details

The majority of the reported calculations was performed with the TURBOMOLE program package^{15,16} in the framework of gradient-corrected density functional theory (DFT). Local Slater exchange and the local Vosko–Wilk–Nusair correlation energy density functional¹⁷ have been employed together with Becke's exchange¹⁸ and Perdew's correlation^{19,20} gradient corrections (BP86). The inner 1s²–2p⁶ shells (Ne core) of Cr were replaced by a scalar-relativistic energy-consistent ab initio pseudopotential (ECP-10-MDF).²¹ Similarly, Cl, Br, and I were treated as 7-valence electron atoms by means of pseudopotentials (ECP-*n*-MWB with *n* = 10, 28, and 46 for Cl, Br, and I, respectively).²² Unless otherwise noted, polarized split-valence (SVP) basis sets from the TURBOMOLE basis set library have been used for H, C, N, O, and F, i.e., (4s)/[2s] for H and (7s4p1d)/[3s2p1d] for C, N, O, and F. (8s7p6d)/[6s5p3d] and (6s6p1d)/[3s3p1d] valence basis sets were used for Cr and the heavy halogens (Cl, Br, and I), respectively. Besides these standard basis sets (basis A), a few DFT calculations were performed with polarized valence triple- ζ sets (TZVP). The determined equilibrium structures of starting materials, products, and intermediates as well as the transition states were confirmed and characterized by analyzing the eigenvalues of an approximate Hessian matrix obtained from a quasi-Newton–Raphson method. We note that a similar computational approach has successfully been used by Gleichmann et al.¹⁴ in their study of the [3 + 2 + 1] benzannulation of chromium pentacarbonyl phenylcarben complexes with an alkyne yielding Cr(CO)₃ complexes with naphthalene derivatives.

The influence of the solvent was estimated from calculations using a conductor like screening model (COSMO)^{23,24} assuming a dielectric constant $\epsilon = 2$, with default parameters as implemented in TURBOMOLE. Since the actual experimental studies are typically carried out in rather unpolar solvents, we expect that the real solvent effects are not considerably larger than those obtained in our studies.

Some additional ab initio calculations at the Hartree–Fock (HF), second-order Møller–Plesset (MP2) perturbation theory, singles and doubles coupled cluster (CCSD), including a perturbative estimate of triples (CCSD(T)) as well as complete active space self-consistent field (CASSCF) level of theory, have been performed with the MOLPRO program package²⁵ for calibration purposes. These calculations were performed at the BP86/SVP geometries, accounted for valence correlation only and, unless otherwise noted, applied polarized correlation consistent valence double- ζ basis sets (cc-pVDZ) of Dunning and co-workers²⁶ for H, C, N, O, and F. For Cr a (8s7p6d1f)/[6s5p3d1f] basis set, and for Cl, Br, and I, (6s6p1d)/[3s3p1d] basis sets have been used together with the pseudopotentials mentioned above. Besides these standard basis sets for wavefunction-based calculations (basis B) still larger basis sets have been applied in a few cases, e.g., polarized correlation consistent valence triple and quadruple- ζ basis sets (cc-pVnZ, *n* = T, Q) of Dunning and co-workers²⁶ for H, C and O as well as a 2f1g instead of the 1f polarization set for Cr, as will be described in more detail below.

3. Results and Discussion

The structural and energetic data of the most important compounds discussed in the following are available as Supporting Information. In most cases several conformers with differing orientation of the Cr(CO)₃ tripod with respect to the coordinated ring of the arene exist. Usually the associated energy differences are quite small, e.g., a few kilocalories per mole, except for the few cases where a direct bonding interaction between the arene substituent and the chromium atom is possible. Due to the nearly free rotation of the Cr(CO)₃ unit

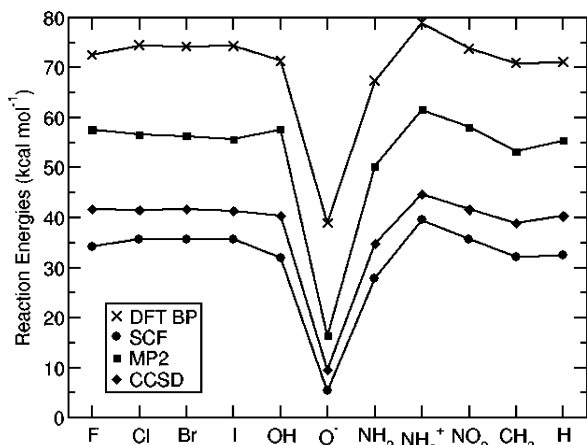


Figure 3. Reaction energies for $R-C_6H_5 + Cr(CO)_6 \rightarrow R-C_6H_5-Cr(CO)_3 + 3CO$ for various substituents R on benzene C_6H_6 . Positive values indicate an endothermic reaction.

around its local approximate C_{3v} axis we restrict ourselves to the energetically lowest conformers found in our studies, which are schematically represented for the unsubstituted arenes in Figure 1.

Benzene. Although a haptotropic migration cannot be observed in $\eta^6-Cr(CO)_3$ complexes with benzene derivatives, these systems exhibit essentially the same metal-ring bonding as the larger arenes, are still in the range of high level ab initio calculations and thus are suitable for calibration of the applied more approximate density functional methods. Historically $Cr(CO)_3$ complexes with arenes have been obtained by heating $Cr(CO)_6$ and the arene in inert solvents under exclusion of oxygen.^{27,28} Therefore, the underlying ligand exchange reaction



was used for benzene ($Ar = C_6H_5$) derivatives to calibrate the BP86 (basis A) approach against wavefunction-based ab initio methods such as Hartree–Fock (HF), second-order Moller–Plesset (MP2) and coupled cluster singles and doubles (CCSD) theory (basis B). The results for the reaction energies for various substituents $R = H, F, Cl, Br, I, OH, O^-, NH_2, NH_3^+,$ and NO_2 are shown in Figure 3. Excluding the substituent $-O^-$ for a moment it can be seen that the stability of the $Cr(CO)_3$ arene complexes depends only weakly on the substituents. The substituent pair $-NH_2/-NH_3^+$ yields the least/most endothermic reaction for all methods, differing by about 12 kcal mol⁻¹ for BP86 and MP2 as well as by about 10 kcal mol⁻¹ for CCSD. The substituent $-O^-$ clearly drops out and leads to significantly less endothermic reaction energies, i.e., decreases compared to $-OH$ of about 32, 41, and 31 kcal mol⁻¹ for BP86, MP2, and CCSD, respectively. We note that the substituent pairs $-NH_2/-NH_3^+$ and $-OH/-O^-$ thus exhibit a strongly pH-dependent complex stability and therefore in principle provide the possibility to construct a simple molecular switch.

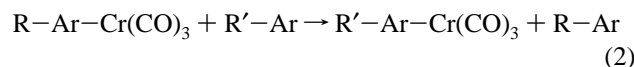
At first glance the DFT results of Figure 3 are in line with the ab initio data, but the relative stability of the $Cr(CO)_6$ complex compared to the $R-C_6H_5-Cr(CO)_3$ complexes is significantly higher. Since the convergence of the results with respect to the size of the basis set is much slower for the CCSD and MP2 approach than for HF or DFT, we investigated the effects of basis set extension in the cases $R = H, OH, O^-$. Some of the results are listed in Table 1. Augmenting the cc-pVDZ basis sets for H, C, and O changes the reaction energies by about 3 kcal mol⁻¹ for the unsubstituted case and by at most 1.5 kcal mol⁻¹ for the two substituted cases at all levels of

TABLE 1: Reaction Energies (kcal mol⁻¹) of the Ligand Exchange Reactions 1 and 2^a

method	H, C, O basis set	reaction 1			reaction 2
		Ar = C ₆ H ₅ R = H	Ar = C ₆ H ₅ R = OH	Ar = C ₆ H ₅ R = O ⁻	Ar = C ₆ H ₅ R = OH R' = O ⁻
MP2	cc-pVDZ	55.4	54.7	16.4	38.3
	aug-cc-pVDZ	52.4	55.1	17.2	37.9
	cc-pVTZ	55.1	58.5	18.2	40.3
CCSD	cc-pVQZ	55.5	59.4	19.8	39.6
	cc-pVDZ	40.3	39.2	9.5	29.7
	aug-cc-pVDZ	37.2	37.7	10.2	26.8
CCSD(T)	cc-pVTZ	39.4	40.5	10.8	29.7
	cc-pVQZ	39.7			
	cc-pVDZ	43.5	42.4	11.2	31.2
BP86	aug-cc-pVDZ	40.9	41.6	12.6	29.0
	cc-pVTZ	43.4	44.8	13.5	31.3
	SVP	71.1	70.5	38.9	31.6
	TZVP	66.1	66.0	35.9	30.1

^a Cr basis set (8s7p6d)/[6s5p3d] (for SVP, TZVP) plus 1f (for (aug-)cc-pVDZ) or 2f1g (for cc-pVNZ, N=T,Q) polarization functions. Positive values denote an endothermic reaction. MP2, CCSD and CCSD(T) results refer to B86/SVP geometries.

theory. Basis set extension from cc-pVDZ to cc-pVQZ quality at the MP2 level leads to an almost unchanged reaction energy, whereas for the cases $R = OH$ and O^- by 4.7 and 3.4 kcal mol⁻¹ more endothermic reaction energies result, respectively. A previous study of metal-ring binding energies of transition metal bis- η^6 -benzene complexes using pseudopotentials revealed that in case of Cr the CCSD(T) result (43.1 kcal mol⁻¹) is much closer to the experimental value (39 kcal mol⁻¹) than the BP86 result (27.0 kcal mol⁻¹) for medium sized basis sets, indicating that the arene–Cr bond might be too weak at the BP86 level.²⁹ This somewhat unpleasant finding fortunately does not have severe consequences for the study of the haptotropic rearrangement, since instead of their stability with respect to $Cr(CO)_6$ one should rather study the relative stability of different arene– $Cr(CO)_3$ complexes, e.g.:



The corresponding results for $Ar=C_6H_5$, $R = OH$ and $R' = O^-$ are also listed in Table 1. Correcting the cc-pVTZ CCSD(T) result of 31.3 kcal mol⁻¹ by -2.2 kcal mol⁻¹ for the neglect of diffuse basis functions, e.g., the difference of the aug-cc-pVDZ and cc-pVDZ CCSD(T) results, one arrives at an estimate of 29.1 kcal mol⁻¹ which is relatively close to the best BP86 result of 30.1 kcal mol⁻¹. We note that, at least as judged from the data compiled in Table 1, BP86 seems to be more reliable than MP2, which otherwise would be an alternative still feasible for larger systems. In view of the fact that it is unfeasible to use highly correlated wavefunction based methods such as CCSD(T) with the necessary extended basis sets for the larger systems studied in this contribution (the single-point aug-cc-pVDZ CCSD(T) calculation for $Cr(CO)_3C_6H_5OH$ required about 2 weeks of CPU time on a 1800 MHz Opteron PC), especially when minima and transition states have to be located, we restrict ourselves mainly to the BP86/SVP approach, supplemented by some cc-pVDZ MP2 and CCSD single point calculations, in the following.

Naphthalene. Complexes of naphthalene derivatives with $Cr(CO)_3$ are from the theoretical point of view among the most thoroughly investigated systems exhibiting haptotropic migrations.^{9–11} Our current work adds the first ab initio results obtained at the MP2 and CCSD level (basis B) as well as

TABLE 2: Comparison of the Calculated Bond Distances (in Å) of the Tricarbonyl Chromium Naphthalene Complex With Experimental Data from X-Ray Diffraction³⁰

bond	calculated	experimental	deviation
Cr—Cco	1.825	1.815–1.830	0.013
	1.843		
	1.841		
C—O	1.169, 1.172	1.167–1.147	0.005
Cr—C _(2,3)	2.215, 2.214	2.191, 2.213	0.023
Cr—C _(1,4)	2.216, 2.222	2.186, 2.214	0.030
Cr—C _(4a,8a)	2.345, 2.343	2.306, 2.337	0.037
C ₂ —C ₃	1.433	1.375	0.058
C ₁ —C ₂ , C ₃ —C ₄	1.412	1.389, 1.383	0.026
C ₄ —C _{4a} , C _{8a} —C ₁	1.448	1.447, 1.404	0.003
C _{4a} —C _{8a}	1.451	1.439	0.012

additional information from DFT calculations (basis A) considering a variety of ligands not studied so far and an estimate of solvent effects.

The Unsubstituted Naphthalene System. For unsubstituted naphthalene the reaction 1 was found to be endothermic by 75.3, 58.1, 41.8, and 44.7 kcal mol⁻¹ at the BP86, MP2, CCSD and CCSD(T) level, respectively, compared to values of 71.1, 55.4, 40.3, and 43.5 kcal mol⁻¹ for benzene. Our computational strategy further has been calibrated in calculations for the haptotropic rearrangement of chromium tricarbonyl on naphthalene as a model system. The gas phase activation energy of 30.1 kcal mol⁻¹ from BP86 was only slightly lowered to 29.1 kcal mol⁻¹ when zero-point energy corrections are included. Similarly the BP86 gas-phase result was slightly reduced from 30.1 kcal mol⁻¹ to 29.2 (27.5) kcal mol⁻¹ when solvent effects were approximated by means of the conductor like screening model (COSMO)^{23,24} assuming a dielectric constant $\epsilon = 2$ ($\epsilon = \infty$), indicating very small effects of noncomplexing solvents which are used in experimental studies. The BP86 gas-phase value was changed to 28.0 kcal mol⁻¹ when instead of SVP the larger TZVP basis sets were used for H, C, and O. The latter value was lowered only slightly to 27.6 kcal mol⁻¹, when instead of the BP86/ TZVP DFT treatment a wavefunction-based post-Hartree–Fock coupled cluster ab initio correlation treatment using the resolution of identity approximation (RI-CC2) as implemented in TURBOMOLE was applied using the same basis set. Finally, exploratory complete active space self-consistent field (CASSCF) calculations carried out with the MOLPRO program package²⁵ confirmed the single-reference character of starting materials, intermediates, products, and transition states for the Cr(CO)₃ complex with naphthalene and therefore support the application of single-reference techniques such as DFT.

For an unsubstituted naphthalene, a comparison of the calculated geometric parameters of the minimum complex with the X-ray crystal structure data³⁰ (Table 2) shows that our calculations correctly reproduce all experimental structural data, e.g., the deviations from the experimental Cr—C bond distances are at most 0.04 Å. A similar finding was previously obtained for phenanthrene with deviations of at most 0.03 Å from the experimental values.¹³ The rotation of the Cr(CO)₃ tripod by 60° about its local C₃ axis generates two possible conformations (Figure 1 a and b) for its regioisomer bearing a coordinated ring. Our calculations reveal that the conformer where the projection of the Cr(CO)₃ tripod on the naphthalene plane bisects the C₂—C₃, C₄—C_{4a}, and C_{8a}—C₁ bonds (**1a**) is more stable than the one with bisection of the C₁—C₂, C₃—C₄, and C_{4a}—C_{8a} bonds (**1b**) by about 4.5 kcal mol⁻¹. We attribute this to the fact that the three (empty) 3d_{4s} hybrid orbitals of the Cr(CO)₃ fragment available for metal ring bonding point directly to the more

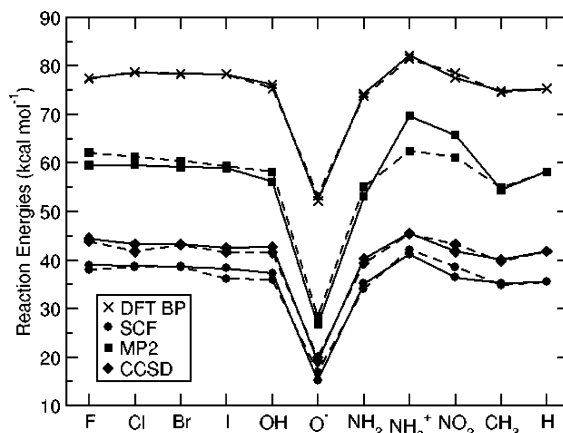


Figure 4. Reaction energies for R—C₁₀H₇ + Cr(CO)₆ → R—C₁₀H₇—Cr(CO)₃ + 3CO for various substituents R on naphthalene C₁₀H₈. Positive values indicate an endothermic reaction. Symbols connected by solid lines correspond to a substituent in position 1, the ones connected by dashed lines to those with a substituent in position 2.

electron rich C₁—C₂, C₃—C₄, and C_{4a}—C_{8a} bonds in the first case. The corresponding MP2, CCSD and CCSD(T) results of 4.4, 4.2, and 4.0 kcal mol⁻¹, respectively, obtained with cc-pVDZ basis sets agree very well with the DFT result. An analysis of the Hessian matrix indicates that structure **1b** in fact corresponds to a transition state rather than a local minimum.

A η⁴-trimethylenemethane-like complex was found as transition state of the haptotropic movement from one ring to the other in agreement with the finding in the pioneering semiempirical work of Albright et al.¹¹ However, the stationary point corresponding to an intermediate on the potential energy surface was not found, which is in agreement of the more recent nonrelativistic all-electron DFT results of Oprunenko et al.¹⁰ The calculated activation energy of 30.1 kcal mol⁻¹ is in the range of the experimental findings (27–30 kcal mol⁻¹)³ as well as the DFT results from literature (30.44 kcal mol⁻¹).¹⁰

The Monosubstituted Naphthalene System. Oprunenko and co-workers also studied the haptotropic migration of Cr(CO)₃, on various substituted naphthalene systems both experimentally and theoretically.¹⁰ The theoretical investigations considered singly substituted naphthalene with —CH₃, —Si(CH₃)₃, and —Cl in position 1 and 2. Selecting —Cl as a test system we found that the Cr(CO)₃ complexation at the substituted ring is by 2.3 and 2.4 kcal mol⁻¹ less favorable than at the unsubstituted ring for position 1 and 2, respectively. These values agree well with the corresponding results of 2.8 and 2.2 kcal mol⁻¹ of Oprunenko et al.¹⁰ despite the differences in the Hamiltonian (relativistic pseudopotential vs nonrelativistic all-electron treatment), the density functional (BP86 vs BLYP) and the basis sets (SVP vs TZVP). We further extended these studies to the ligand exchange reaction 1 (Ar = C₁₀H₇) for a variety of substituents R = H, F, Cl, Br, I, O⁻, OH, NH₂, NH₃⁺, NO₂, and CH₃ in positions 1 and 2 (Figure 4). The trend as well as the magnitude of the reaction energies is very similar to the one for the corresponding benzene complexes (Figure 3), however the naphthalene complexes are slightly less stable. We assume that the points concerning a comparison of DFT and wavefunction based correlation methods discussed there are also valid for the naphthalene complexes. It is noteworthy however that for some cases (e.g., NH₃⁺, NO₂) the MP2 results exhibit a much larger dependence on the substituent position than both BP86 and CCSD.

Our results for the relative stabilities of complexes with Cr(CO)₃ at the substituted and unsubstituted ring are summarized

TABLE 3: Relative Energies (kcal mol⁻¹) of 1,2,3,4,4a,8a- η^6 -Cr(CO)₃ Complexes (Complexation at the Substituted Ring) With Naphthalene Bearing a Single Substituent at Position p^a

substituent	p = 1			p = 2		
	BP86	MP2	CCSD	BP86	MP2	CCSD
-F	1.6	0.3	2.0	1.5	2.9	1.5
-Cl	2.3	0.9	1.2	2.3	1.4	0.6
-Br	2.0	0.8	1.0	2.0	1.0	0.5
-I	1.7	0.7	0.5	1.8	0.1	0.0
-OH	2.0	-0.4	2.1	1.6	1.8	0.8
-O ⁻	-3.0	-7.3	-4.8	-2.1	-5.4	-4.0
-NH ₂	1.5	-2.2	0.4	0.6	-1.8	-1.5
-NH ₃ ⁺	2.6	4.1	0.9	0.1	-4.1	-0.8
-NO ₂	0.8	6.6	-0.8	1.2	0.2	-0.2
-CH ₃	0.5	-1.4	-0.3	-0.3	-2.4	-1.4

^a The energy of the 4a,5,6,7,8,8a- η^6 -Cr(CO)₃ complexes (complexation to the unsubstituted ring) is set to zero.

TABLE 4: Relative Energies (kcal mol⁻¹) of the η^6 -Cr(CO)₃ Complexes With Monosubstituted Naphthalene at the Substituted (S) and Nonsubstituted (NS) Ring and the Transition States (TS₁ and TS₂), cf. Figure 2^a

p	substituent	S	NS	TS ₁	TS ₂
	H	0.0 (0.0)	0.0 (0.0)	30.1 (29.2)	
1	-O ⁻	0.0 (0.0)	3.0 (3.2)	24.3 (22.9)	23.4 (23.3)
1	-OH	2.0 (1.9)	0.0 (0.0)	28.7 (22.9)	32.3 (29.7)
1	-NH ₂	1.5 (1.3)	0.0 (0.0)	27.9 (25.4)	31.0 (28.8)
1	-NH ₃ ⁺	2.6 (2.4)	0.0 (0.0)	33.0 (28.2)	31.8 (30.1)
2	-O ⁻	0.0 (0.0)	2.1 (2.6)	29.2 (27.5)	20.4 (19.2)
2	-OH	1.6 (1.6)	0.0 (0.0)	30.9 (27.9)	27.0 (24.6)
2	-NH ₂	0.6 (0.8)	0.0 (0.0)	30.2 (27.3)	24.8 (22.3)
2	-NH ₃ ⁺	0.1 (1.8)	0.0 (0.0)	29.3 (30.1)	27.8 (29.4)

^a The results for including the effects of a solvent with a dielectric constant $\epsilon = 2$ (COSMO) are given in parentheses.

in Table 3. The relative stabilities are of the order of a few kcal mol⁻¹, several values are lower than the anticipated accuracy of our calculations of ~ 1 kcal mol⁻¹. The latter value is based on the calibration studies listed in Table 1 (reaction 2) and clearly results from error cancellations, since for systems as large as those reported in this work an absolute accuracy of 1 kcal mol⁻¹ cannot be achieved presently. Comparing two out of the three listed approaches BP86, MP2 and CCSD, we note that for all pairs out of ten cases given in Table 3 one to three contradictory results concerning the most stable complex are observed. The mean absolute deviation between BP86 and CCSD (1.2 kcal mol⁻¹) is lower than between BP86 and MP2 (2.2 kcal mol⁻¹) as well as MP2 and CCSD (1.6 kcal mol⁻¹), suggesting that here MP2 might be slightly less accurate than BP86.

It is obvious from Table 3 that in simple cases Cr(CO)₃ prefers the electron rich over the electron poor ring for coordination. It was of special interest to investigate in detail if the substituent pairs -OH/-O⁻ and -NH₂/-NH₃⁺ show reverse stabilities for the protonated and deprotonated case, i.e., if a simple pH-dependent molecular switch can be constructed. Therefore we extended our studies for these substituents by a determination of transition states and possible intermediates as well as a consideration of solvent effects. Due to the asymmetry of substituted naphthalene, the tricarbonylchromium group can migrate between the substituted (S) and the unsubstituted (NS) ring via two nonequivalent transition states (TS₁ and TS₂), cf. Figure 2. The corresponding calculated energies are listed in Table 4. The most interesting result is that at the BP86 level the relative stability of the complex at the substituted and unsubstituted ring can be reversed via deprotonation in case of

hydroxy naphthalene, whereas somewhat unexpectedly in the case of amino naphthalene, the protonation of the amino group does not change the order of stability of the complexes. A reason for the latter finding might be a favorable stabilizing hydrogen bond type interaction between the -NH₃⁺ group and one CO Cr-coligand present in 1- and 2-ammonium naphthalene substituted ring complexes as well as the 1-ammonium naphthalene unsubstituted ring complex. For both substituent pairs -OH/-O⁻ and -NH₂/-NH₃⁺ at least one transition state has a lower energy than in the unsubstituted naphthalene, i.e., in every case the haptotropic rearrangement should proceed more readily. It is noteworthy that in the case of deprotonated 2-hydroxy naphthalene (-O⁻) we were able to locate a η^3 -coordinated intermediate complex which was not found in the other cases. The Cr(CO)₃ fragment is coordinated to the carbon atoms 1, 8, and 8a. Energetically this intermediate (19.1 kcal mol⁻¹) is located significantly below the geometrically close transition state TS₁ (29.2 kcal mol⁻¹), but only slightly below transition state TS₂ (20.4 kcal mol⁻¹). In case of deprotonated 1-hydroxy naphthalene (-O⁻) a η^4 -coordinated intermediate complex was found, where besides the coordination to the carbon atoms 1, 8 and 8a the Cr(CO)₃ fragment is complexed by the -O⁻ substituent. Its relative energy (7.8 kcal mol⁻¹) is significantly lower than the energy of the transition states TS₁ (24.3 kcal mol⁻¹) and TS₂ (23.4 kcal mol⁻¹). Several other intermediates can be found, however they are from a geometrical point of view not relevant for the haptotropic rearrangement.

Table 4 also lists results for a solvent with a dielectric constant $\epsilon = 2$, which were obtained within the COSMO approach. Solvent effects contribute less than 3 kcal mol⁻¹ to the relative stabilities and less than 5 kcal mol⁻¹ to the activation energies. We assume that effects of similar magnitude apply to the other substituents listed in Table 3. The finding from gas-phase calculations that the pair -OH/-O⁻ in contrast to -NH₂/-NH₃⁺ possibly allows a steering of the Cr(CO)₃ haptotropic migration by a change of the pH-value is not altered by solvent effects. Zero-point energy corrections appear to have an even smaller influence on the reaction and activation energies, e.g., for the pair -OH/-O⁻ we found that the relative energies of the complexes with the substituted and unsubstituted rings are reduced by less than 0.2 kcal mol⁻¹ and the activation energies by about 1 kcal mol⁻¹. In view of the larger uncertainties arising from the applied density functional, finite basis sets and pseudopotentials we refrained from including zero-point corrections and solvent effects for the other systems studied here.

Phenanthrene. Recently we briefly summarized some theoretical results for haptotropic rearrangements of Cr(CO)₃ on phenanthrene as well as hydroxy and deprotonated hydroxy phenanthrene derivatives.¹³ In the following we discuss in more detail the possible migration processes and the influence of various other substituent groups on these processes.

The Unsubstituted Phenanthrene System. In case of unsubstituted phenanthrene, we found that the most stable structure is the complex of tricarbonylchromium at the terminal ring with a conformation resembling the one found for naphthalene (Figure 1c). The complexation of the metal-coligand unit at the middle ring is about 8.6 kcal mol⁻¹ less stable than the terminal ring complex. In the previous report, we also showed that the calculated equilibrium structure of the terminally coordinated phenanthrene is in good agreement with experimental data.¹³ The migration of the Cr(CO)₃ fragment from a terminal ring to the central ring proceeds along the ligand periphery with a η^4 -trimethylenemethane-like complex as transi-

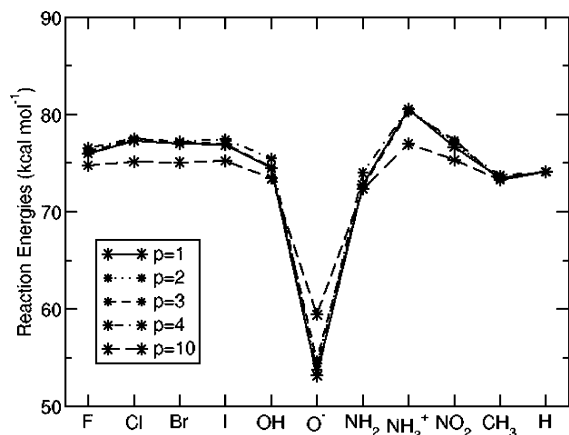


Figure 5. Reaction energies for $R-C_{14}H_9 + Cr(CO)_6 \rightarrow R-C_{14}H_9-Cr(CO)_3 + 3CO$ for various substituents R on naphthalene $C_{14}H_{10}$ from DFT BP86/SVP calculations. Positive values indicate an endothermic reaction.

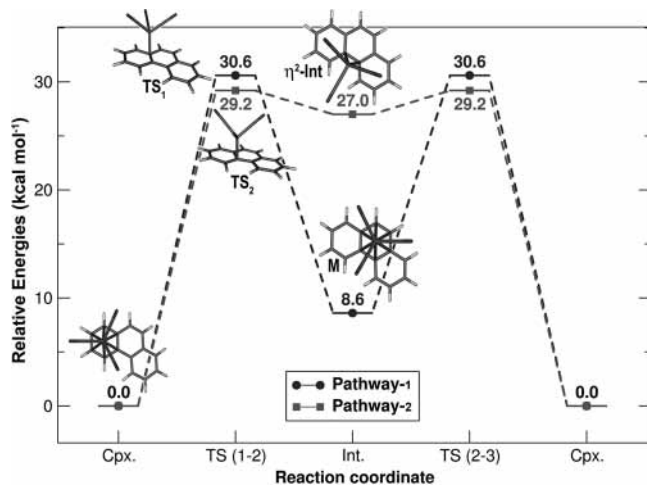


Figure 6. The reaction profile of the haptotropic rearrangement in the unsubstituted phenanthrene system.

tion state and exhibits great similarity to the naphthalene case. The haptotropic rearrangement of $Cr(CO)_3$ from one side ring to the other side ring mainly passes through two different pathways (Figure 6). We found that the longer pathway 1 along the outer periphery of the phenanthrene ligand has a slightly higher activation energy ($30.6 \text{ kcal mol}^{-1}$) than the shorter pathway 2 along the biphenyl axis linking the two terminal rings ($29.2 \text{ kcal mol}^{-1}$). For pathway 1 the $Cr(CO)_3$ shifts through transition state TS_1 to the η^6 -complexation of the central ring which we consider as the intermediate of this pathway ($8.6 \text{ kcal mol}^{-1}$). A η^2 -coordination complex with $Cr(CO)_3$ linked to the two C atoms defining the biphenyl axis was found as the intermediate of pathway 2 ($27.0 \text{ kcal mol}^{-1}$). The two intermediates are linked by a transition state at about $30.6 \text{ kcal mol}^{-1}$, with a geometry very close to the one of the η^2 -coordination complex. For both pathways $Cr(CO)_3$ crosses another transition state TS_2 (identical to TS_1 due to symmetry) to achieve complexation of the other terminal ring.

The Monosubstituted Phenanthrene System. The relative stabilities of $Cr(CO)_3$ complexes with monosubstituted phenanthrene were calculated for a variety of substituents $R = F, Cl, Br, I, CH_3, NO_2, OH, O^-, NH_2, NH_3^+$, and the results are listed in Table 5. All five possible substituent positions (1, 2, 3, and 4 on the side ring and 10 on the middle ring) as well as all three coordination sites for the $Cr(CO)_3$ fragment (side rings (T_1 and T_2) and middle ring (M)) were considered. In addition

TABLE 5: Relative Energies (kcal mol^{-1}) of $\eta^6-Cr(CO)_3$ Complexes With Phenanthrene Bearing a Single Substituent at Position p^a

p	-H		-CH ₃		-OCH ₃		-NO ₂	
	T_2	M	T_2	M	T_2	M	T_2	M
10	0.0	8.7	-0.4	8.7	2.5	11.0	-0.5	9.3
1	0.0	8.7	-0.5	7.6	0.9	7.3	1.4	8.4
2	0.0	8.7	-0.6	8.4	1.1	8.9	1.6	9.2
3	0.0	8.7	-0.5	8.5	1.1	9.0	1.7	8.9
4	0.0	8.7	-0.2	8.1	2.2	8.4	0.6	8.3

p	-OH		-O ⁻		-NH ₂		-NH ₃ ⁺	
	T_2	M	T_2	M	T_2	M	T_2	M
10	-2.5	8.2	3.1	8.8	0.0	9.6	-2.8	8.1
1	0.3	7.8	-8.9	3.6	-0.5	6.5	1.2	5.5
2	0.9	8.8	-6.7	6.7	-0.1	8.0	1.6	9.4
3	1.0	8.8	-6.9	4.8	0.0	8.4	1.8	9.8
4	2.3	8.7	-6.3	6.1	1.5	7.3	5.5	10.4

p	-F		-Cl		-Br		-I	
	T_2	M	T_2	M	T_2	M	T_2	M
10	0.3	10.4	0.2	10.9	0.1	10.5	0.2	10.3
1	1.5	8.7	2.5	8.9	2.2	8.8	2.0	8.9
2	1.9	8.8	2.8	9.0	2.4	9.0	2.2	9.0
3	1.7	8.9	2.7	9.0	2.3	8.9	2.2	8.9
4	2.3	9.2	2.9	9.2	2.7	9.3	2.9	9.6

^a The entries for unsubstituted phenanthrene are given as a reference. The energy T_1 of the $4b,5,6,7,8,8a-\eta^6-Cr(CO)_3$ terminal ring complex is set to zero. The energies given under T_2 and M denote the $1,2,3,4,4a,10a-\eta^6-Cr(CO)_3$ terminal ring and $4a,4b,8a,9,10,10a-\eta^6-Cr(CO)_3$ middle ring complexes, respectively.

to some deviations from the expected behavior due to direct interaction of the $Cr(CO)_3$ fragment with the substituent as observed already in the naphthalene case, one observes small changes due to nonplanar arene systems especially when larger substituents occupy ring position 4. Incorporation of a mainly electron-withdrawing substituent at a terminal ring favors metal coordination of the unsubstituted terminal ring over the substituted ring. An electron-donor substituent at a terminal ring reversed the situation, rendering the coordination of the substituted ring more stable than complexation of the unsubstituted one. The complexation of the central ring was found to be significantly less favorable (by $6-10 \text{ kcal mol}^{-1}$ for position 1, 2, 3, or 4, and $10-11 \text{ kcal mol}^{-1}$ for position 10) than the coordination of one of the terminal rings. We suggest that the stabilization and isolation of a middle ring complex of $Cr(CO)_3$ and phenanthrene is probably experimentally not feasible.

The energies of ligand exchange reaction 1 ($Ar = C_{14}H_9$) for various substituents R in positions 1, 2, 3, 4, and 10 of phenanthrene $C_{14}H_{10}$ were also investigated. For unsubstituted phenanthrene the reaction is found to be endothermic ($74.2 \text{ kcal mol}^{-1}$) as for benzene ($71.1 \text{ kcal mol}^{-1}$) and naphthalene ($75.3 \text{ kcal mol}^{-1}$). Similar to the previous discussion of this ligand exchange reaction for benzene the main interest is the relative stability of the three possible coordination sites for a given substituted arene. It is obvious that for $-O^-$ due to the increased electron density the complexation at the substituted ring is more than 5 kcal mol^{-1} more stable than at the unsubstituted ring. This stability is reversed for $-OH$; however, the energy difference is only of the order of 1 or 2 kcal mol^{-1} . Nevertheless, a pH-dependent steering of the $Cr(CO)_3$ motion over the arene might be a possibility to construct a molecular switch. Similar to the pair $-O^-/-OH$ one finds for the pair $-NH_2/-NH_3^+$ a reversal of the stabilities, although the energy differences are even smaller.

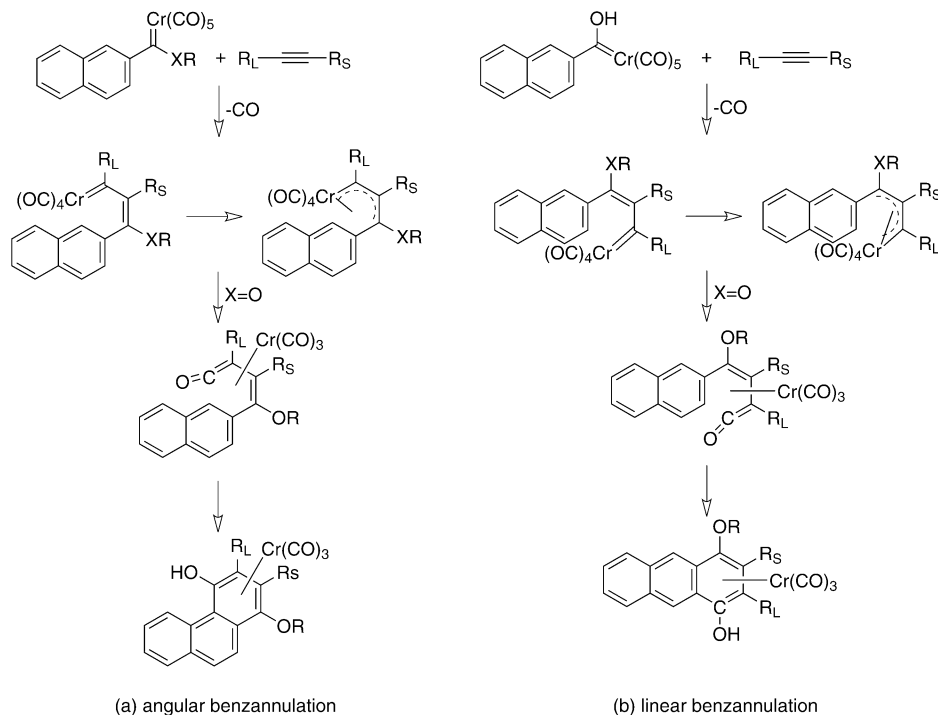


Figure 7. Simplified representation of the proposed mechanism of the [3 + 2 + 1] linear and angular benzannulation of pentacarbonyl chromium naphthyl hydroxy carbene complexes with alkynes.

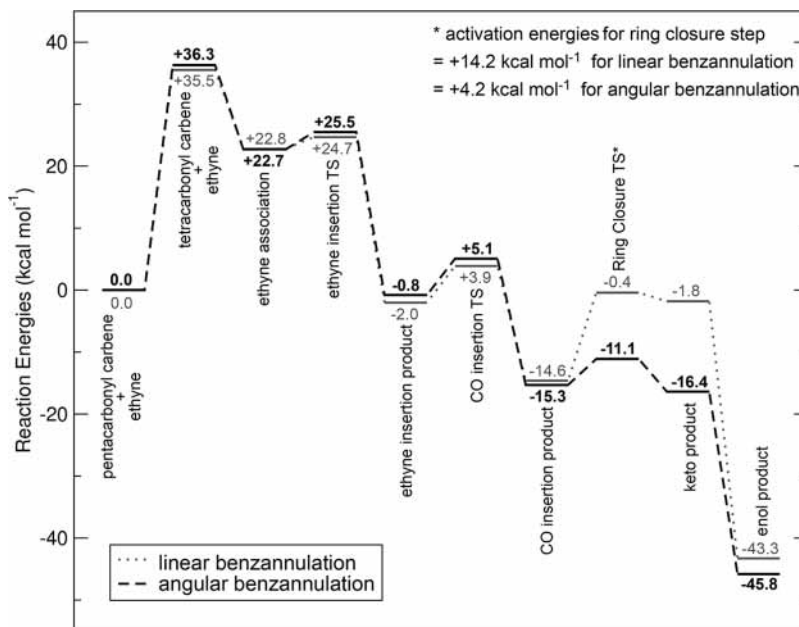


Figure 8. Reaction profiles for the [3 + 2 + 1] linear and angular benzannulation of pentacarbonyl chromium naphthyl hydroxy carbene complexes with alkynes.

Anthracene. We also studied the haptotropic rearrangement of $\text{Cr}(\text{CO})_3$ on unsubstituted anthracene, although the corresponding $\text{Cr}(\text{CO})_3$ complexes are less readily available, since the well-known Dötz reaction,³¹ i.e. the [3 + 2 + 1] benzannulation starting from a chromium pentacarbonyl naphthyl carbene complex with an alkyne, leads to the chromium tricarbonyl phenanthrene complex as the main product. The complexation of the anthracene side rings was found to be 6.0 kcal mol⁻¹ more favorable than the complexation at the middle ring compared to a corresponding value of 8.6 kcal mol⁻¹ for phenanthrene. Whereas for side-ring complexes the ligand exchange reaction 1 ($\text{Ar} = \text{C}_{14}\text{H}_{10}$) in case of anthracene is only slightly more endothermic (75.4 kcal mol⁻¹) than for phenanthrene (74.2 kcal mol⁻¹), the anthracene side ring complex with

$\text{Cr}(\text{CO})_3$ was found to be 5.8 kcal mol⁻¹ less stable than the phenanthrene side ring complex, thus partly explaining the preference of the latter as a product of the Dötz reaction.

[3 + 2 + 1] Benzannulation. Gleichmann et al.¹⁴ studied the [3 + 2 + 1] benzannulation of pentacarbonyl chromium phenyl carbene complexes with an alkyne. This reaction is known as Dötz reaction³¹ and leads to tricarbonyl chromium complexes with naphthalene, the simplest system in which a haptotropic $\text{Cr}(\text{CO})_3$ shift can be observed. A corresponding reaction starting from naphthalene can yield in principle $\text{Cr}(\text{CO})_3$ complexes with anthracene and phenanthrene; i.e., it can proceed as a linear and angular benzannulation, respectively (Figure 7). In experiments essentially only the latter case is observed. In order to explain this behavior we carried out studies

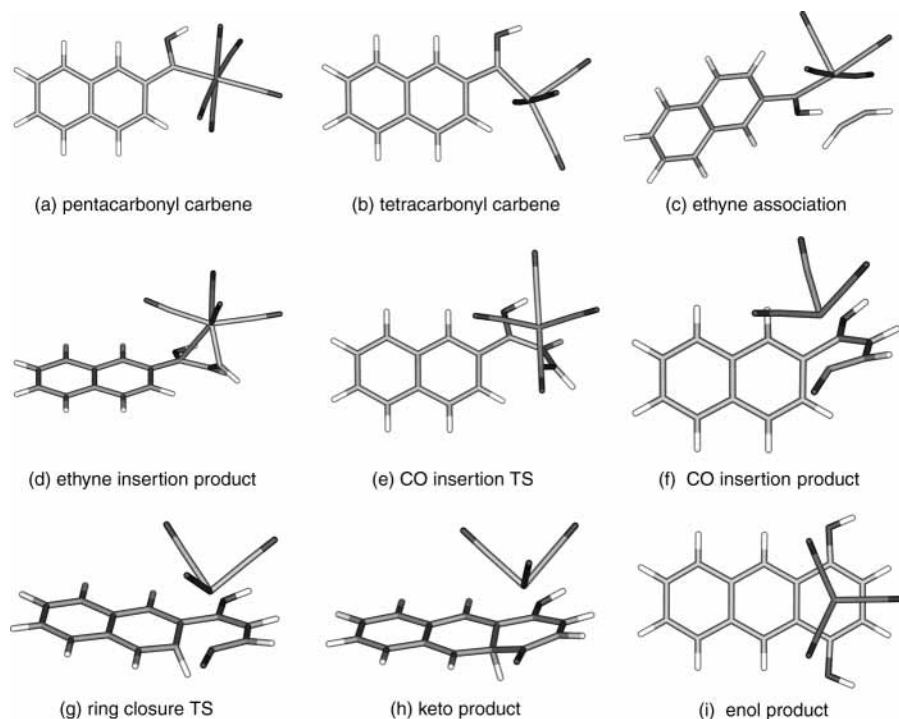


Figure 9. Structures of reactant, reaction intermediates and product of the [3 + 2 + 1] benzannulation of pentacarbonyl chromium naphthyl hydroxy carbene complexes via a linear benzannulation mechanism.

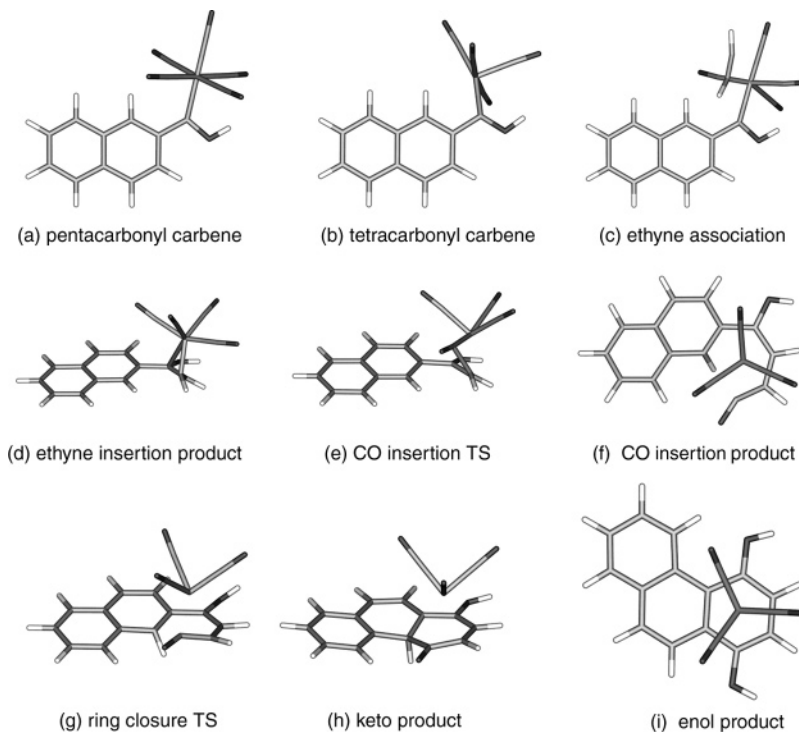


Figure 10. Structures of reactant, reaction intermediates and product of the [3 + 2 + 1] benzannulation of pentacarbonyl chromium naphthyl hydroxy carbene complexes via an angular benzannulation mechanism.

of the reaction mechanism similar to those performed by Gleichmann et al., paying special attention to the step in which the second C–C bond of the new ring is formed. The reaction energy profiles for the phenanthrene and anthracene formation are shown in Figure 8 and selected structures of interesting species (**9**, **10a–i**) occurring in the linear and angular benzannulation reactions are shown in Figure 9 and 10, respectively. The initial steps of the reaction mechanism occur in analogy to the mechanism found by Gleichmann et al. in the simpler case

of benzene and naphthalene formation. First the chromium pentacarbonyl carbene complex (**9**, **10a**) eliminates one cis-CO to yield a corresponding tetracarbonyl species (**9**, **10b**) with an about 36 kcal mol⁻¹ higher energy. The chromium tetracarbonyl carbene complex is the most unstable intermediate in the whole reaction mechanism. Then, the coordination site rendered available by the elimination is occupied by ethyne (**9**, **10c**). With a small activation energy of 3 kcal mol⁻¹ or less the ethyne is then inserted between the α -carbon atom and the

Cr center (**9**, **10d**). The following migratory insertion of one CO ligand has an activation energy of 5.8 kcal mol⁻¹ (**9**, **10e**) and yields a chromium tricarbonyl η^4 -vinylketene intermediate (**9**, **10f**).

Figure 8 reveals that the reaction and activation energies of all steps described so far agree within about 1 kcal mol⁻¹ for the cases of linear and angular benzannulation. However, the energy barriers between the intermediates of these two mechanisms appear to be quite large. Scans of the rotations about the relevant C–C–C–O dihedral angles yield barriers of about 7 and 10 kcal mol⁻¹ for the first and second intermediate (**9**, **10b,c**), respectively, as well as barriers of 100 kcal mol⁻¹ or more for the ethyne and CO insertion products (**9**, **10d,f**).

The chromium tricarbonyl η^4 -vinylketene intermediate (**9**, **10f**) is about 15 kcal mol⁻¹ lower in energy than the reactants (**9**, **10a**). The next and crucial step is the ring closure to a chromium tricarbonyl η^4 -cyclohexadienone intermediate (**9**, **10h**). For this step we found quite different energy barriers for the linear and angular benzannulations (**9**, **10g**), i.e. activation energies of 14.2 and 4.2 kcal mol⁻¹, respectively. The ring closure to the keto product (**9**, **10i**) is slightly exothermic for the angular benzannulation (–1.1 kcal mol⁻¹), but significantly endothermic for the linear alternative (+12.8 kcal mol⁻¹). The final keto–enol tautomerization from the chromium tricarbonyl η^4 -cyclohexadienone intermediate to the aromatic chromium tricarbonyl η^6 -phenol product is highly exothermic in both cases, leading to total reaction energies of –45.8 kcal mol⁻¹ in angular and –43.3 kcal mol⁻¹ in the linear case. These results reproduce well the experimental finding that a phenanthrene complex is the major product for the Dötz reaction.

4. Conclusions

The haptotropic rearrangement of Cr(CO)₃ on naphthalene and phenanthrene and some of their monosubstituted derivatives were investigated by means of gradient-corrected density functional theory and relativistic pseudopotentials for the heavy atoms. For monosubstituted naphthalene the ligand pair –OH/–O⁻ was shown to provide a possibility for a pH-value dependent steering of the haptotropic rearrangement, i.e., a simple molecular switch. In contrast to other ligands η^4 - and η^3 -coordinated intermediates were located for –O⁻ in 1- and 2-position, respectively. Two or more energetically close reactions pathways were found for un- and monosubstituted phenanthrene. In agreement with experimental evidence it was not possible to find substituents which render the middle ring complex more stable than the terminal ring complexes. As for the naphthalene case the ligand pair –OH/–O⁻ provides a possibility for steering the direction of the haptotropic Cr(CO)₃ migration. Finally, the experimentally observed preference of angular over linear products of the Dötz [3 + 2 + 1] benzannulation was explained by substantial differences in the activation and reaction energies of the ring closing step in the reaction mechanism leading from naphthalene to phenanthrene and anthracene.

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Supporting Information Available: Cartesian coordinates of optimized (BP86 density functional, SVP basis sets) structures, energies, and basis sets and pseudopotentials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Anh, N. T.; Elian, M.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 110–116.
- (2) Dötz, K. H.; Wenzel, B.; Jahr, H. C. *Top. Curr. Chem.* **2005**, *248*, 63–103.
- (3) Deubzer, B. Ph.D. thesis, Technische Hochschule München, Munich, Germany, 1966.
- (4) Oprunenko, Y.; Malyugina, S.; Nesterenko, P.; Mityuk, D.; Malyshev, O. *J. Organomet. Chem.* **2000**, *597*, 42–47.
- (5) Dötz, K. H.; Szesni, N.; Nieger, M.; Nattinen, K. *J. Organomet. Chem.* **2003**, *671*, 58–74.
- (6) Paetsch, D.; Dötz, K. H. *Tetrahedron Lett.* **1999**, *40*, 487–488.
- (7) Dötz, K. H.; Stinner, C. *Tetrahedron-Asymmetry* **1997**, *8*, 1751–1765.
- (8) Oprunenko, Y. F.; Malugina, S. G.; Ustyniuk, Y. A.; Ustyniuk, N. A.; Kravtsov, D. N. *J. Organomet. Chem.* **1988**, *338*, 357–368.
- (9) Glorizov, I. P.; Vasil'kov, A. Y.; Oprunenko, Y. F.; Ustyniuk, Y. A. *Russ. J. Phys. Chem.* **2004**, *78*, 244–248.
- (10) Oprunenko, Y. F.; Akhmedov, N. G.; Laikov, D. N.; Malyugina, S. G.; Mstislavsky, V. I.; Roznyatovsky, V. A.; Ustyniuk, Y. A.; Ustyniuk, N. A. *J. Organomet. Chem.* **1999**, *583*, 136–145.
- (11) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396–3411.
- (12) Kirss, R. U.; Treichel, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 853–855.
- (13) Dötz, K. H.; Stendel, J. Jr.; Müller, S.; Nieger, M.; Ketrat, S.; Dolg, M. *Organometallics* **2005**, *24*, 3219–3228.
- (14) Gleichmann, M. M.; Dötz, K. H.; Hess, B. A. *J. Am. Chem. Soc.* **1996**, *118*, 10551–10560.
- (15) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346–354.
- (16) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165–169.
- (17) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200–1211.
- (18) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- (19) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822–8824.
- (20) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.
- (21) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866–872.
- (22) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431–1441.
- (23) Klamt, A.; Schürmann, G. *J. Chem. Soc., Perkin Trans.* **1993**, *2*, 799–805.
- (24) Klamt, A. *J. Phys. Chem.* **1995**, *99*, 2224–2235.
- (25) Werner, H. J.; Knowles, P. J.; Schütz, M.; Lindh, R.; Celani, P.; Korona, T.; Rauhut, G.; Manby, F. R.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Lloyd, A. W.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. *Ab Initio Program MOLPRO 2002.1*; Universität Stuttgart: Stuttgart, Germany, 2002.
- (26) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (27) Fischer, E. O.; Öfele, K.; Essler, H.; Fröhlich, W.; Mortensen, J. P.; Semmlinger, W. *Z. Naturforsch.* **1958**, *13b*, 458.
- (28) Fischer, E. O.; Kriebitzsch, N.; Fischer, R. D. *Chem. Ber.* **1959**, *92*, 3214–3222.
- (29) Dolg, M. *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 18–21.
- (30) Kunz, V.; Nowacki, W. *Helv. Chim. Acta.* **1967**, *50*, 1052–1059.
- (31) Dötz, K. H. *Angew. Chem.* **1975**, *87*, 672–673. Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644–645.