Haptotropic migration of M(CO)$_3$ (M = Cr, Mo, W) on substituted phenanthrene

Anja Pfletschinger, Michael Dolg *

Institut für Theoretische Chemie, Universität zu Köln, Greinstr. 4, D-50939 Köln, Germany

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ABSTRACT

The haptotropic migration of Cr(CO)$_3$, Mo(CO)$_3$ and W(CO)$_3$ moieties on a substituted phenanthrene has been studied theoretically using gradient-corrected density functional theory. The stationary points (minima and transition states) on the energy hypersurface characterizing the migrating process of the metal fragment over the aromatic system have been located. Furthermore, the energetic and structural differences between complexes of the three metals Cr, Mo and W and the effect of a high substitution of one arene ring on the reaction energy profile have been analyzed. The possibility to design a molecular switch based on the substituent pair R = O$^-$/OH is investigated. It is concluded that the Mo and W complexes undergo a haptotropic migration more easily than the corresponding Cr system.

1. Introduction

The haptotropic migration [1] of a metal fragment over aromatic systems has been subject of many experimental and theoretical studies [2–5]. Most theoretical research focused on the η^6-η^6-rearrangements of Cr(CO)$_3$ on naphthalene complexes [6], but the investigations have also been extended to larger aromatic systems such as phenanthrene [7] and other polycyclic aromatic hydrocarbons with up to four fused six-membered rings [8]. The haptotropic migration of Cr(CO)$_3$ over a (6, 0) carbon nanotube sidewall was also studied by static and dynamical density functional theory [9] The most prominent metal moiety undergoing haptotropic migration is the chromium tricarbonyl unit, however, coligands other than CO such as PR$_3$ (R = Me, OMe, Ph, OPh) have also been investigated [10]. Besides the arene unit and its specific substitution pattern as well as the coligands the metal itself certainly has a significant influence on the energy profile of haptotropic migrations. Although the heavier chromium homologues molybdenum and tungsten are known to give e.g. stable naphthalene tricarbonyl complexes [11], little is known about their ability to migrate over an aromatic system. Experimentally it has been found that the ligand-M(CO)$_3$ bond strength increases significantly when going from Cr over Mo to W [12]. It is therefore of interest how the metal influences the energetic course of the rearrangement and if possibly other metals than Cr are more suitable to construct a molecular switch based on haptotropic metal migration [13]. Thermally induced haptotropic migrations of a MoH(PMe$_3$)$_3^+$

group over an indolyl anion as well as of a Mo(PMe$_3$)$_3$ group over a quinoline unit were already experimentally observed [14]. In the first case the starting compound even could be recovered by photolysis, although not quantitatively.

To the best of our knowledge no experimental or computational study of the influence of the substitution of Cr by its heavier homologues Mo or W exists. In this theoretical study we therefore present the results of gradient-corrected density functional calculations of the haptotropic rearrangement of M(CO)$_3$ (M = Cr, Mo, W) on a phenanthrene derivative. The substitution pattern of one terminal ring of the phenanthrene was chosen similar to the product of the [3+2+1] benzannulation of a pentacarbonyl chromium naphthyl carbene with an alkyne [15], which makes systems as the one studied here experimentally readily available in the case of Cr. This so-called Dötz reaction was investigated by quantum chemical methods similar to the ones used here previously [4,16]. Carbon monoxide CO was chosen as the most simple coligand on the metal, although experimental and computational evidence exists that e.g. trialkyl phosphine PR$_3$ coligands might even allow haptotropic migrations under milder conditions [10]. Fig. 1 schematically shows the possible reactions pathways and characteristic points on the energy hypersurface which have been calculated for all three metals Cr, Mo and W for the phenanthrene derivatives studied here.

2. Computational details

All calculations have been performed using the program package TURBOMOLE (Version 5.10) [17]. The optimizations have been done using gradient-corrected density functional theory (Becke/

* Corresponding author. Tel.: +49 221 470 6893; fax: +49 221 470 6896.
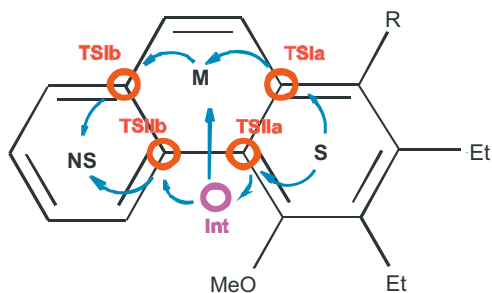 *E-mail address:* m.dolg@uni-koeln.de (M. Dolg).

Fig. 1. Schematic representation of the pathways I and II for the migration of a $M(CO)_3$ fragment on a substituted phenanthrene. NS: $M(CO)_3$ η^6-coordination to the non-substituted ring, S: $M(CO)_3$ η^6-coordination to the substituted ring, Int: intermediate, η^2-coordination of $M(CO)_3$, M: $M(CO)_3$ η^6-coordination to the middle ring, TS: transition states, η^4-coordination of $M(CO)_3$.

Perdew 1988/1986 exchange–correlation–functional) [18,19]. Scalar-relativistic contributions arising from the presence of the heavy transition metals were taken into account by energy-consistent small-core pseudopotentials for the transition metals Cr (ecp-10-mdf) [20], Mo (ecp-28-mwb) [21] and W (ecp-60-mwb) [11] together with the appropriate polarized valence triple-zeta (TZVP) basis sets. For C, H, O and P polarized split-valence (SV(P)) basis sets were used as implemented in TURBOMOLE. All stationary points of interest on the energy hypersurface were confirmed and characterized by analyzing the Hessian matrix. In order to take the presence of a solvent into account, for all structures a single-point calculation has been performed with a conductor-like screening model (COSMO) [22] assuming a dielectric constant $\varepsilon = 2$, with default parameters as implemented in TURBOMOLE, except for W, for which the radius of 2.22 Å was used [23].

3. Results and discussion

Some of the trends along the series Cr–Mo–W which will be discussed in the following can partially already be rationalized on the basis of atomic data. Figs. 2 and 3 show radial expectation values and orbital energies, respectively, for the valence s and d orbitals of the three metals from state-averaged fully relativistic multi-configuration Dirac–Hartree–Fock calculations using a Dirac–Coulomb point nucleus Hamiltonian as well as the corresponding results for the nonrelativistic limit [24]. Relativistic contributions increase as Cr < Mo < W and lead to a contraction and stabilization of the valence s shells, whereas the valence d shells undergo a slight expan-
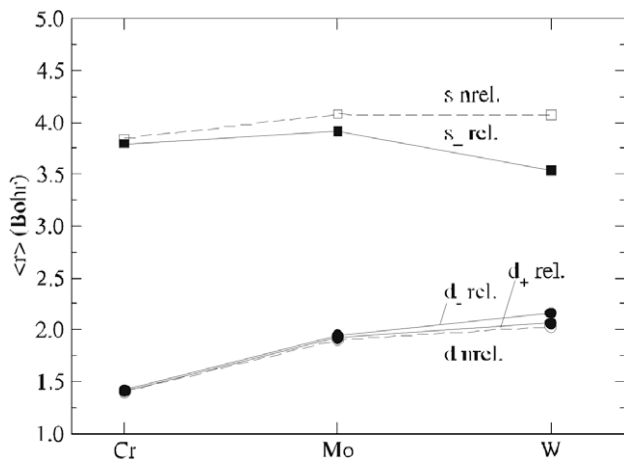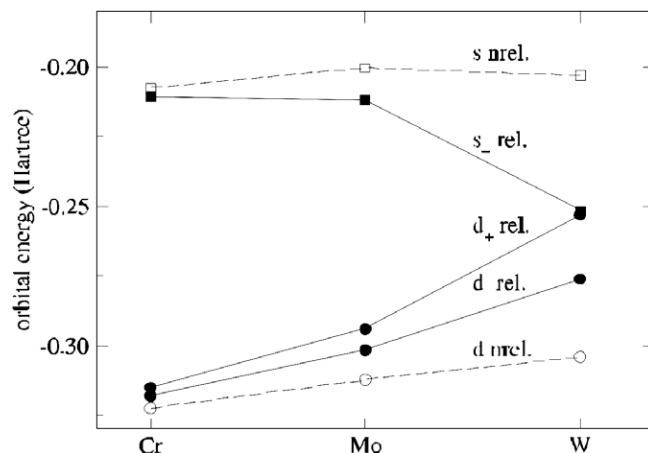

Fig. 3. Orbital energies of the metals Cr, Mo and W.

sion and destabilization. The need to include relativistic effects is especially apparent for W, where the relativistic s and d valence shells are nearly degenerate, whereas their nonrelativistic counterparts are energetically well separated. It has to be noted however, that relativistic contributions and shell structure effects always occur together, their definition is model-dependent and their contributions are often not simply additive [25]. Based on the atomic data one might expect that both from an energetic (orbital energies) as well as a spatial (radial expectation values) point of view the Mo 4d and W 5d orbitals are more suitable for haptotropic interactions with arenes than the energetically low-lying and spatially quite compact Cr 3d orbitals.

In order to evaluate the quality of the applied gradient-corrected correlation and exchange density functional BP86 as well as the used pseudopotentials and basis sets for this study, a comparison of some structural parameters of a calculated and an experimentally obtained structure was carried out at the beginning (Table 1). The molybdenum complex 1 was chosen because of the lack of experience in treating ML₃-complexes of the higher homologues of chromium theoretically. Additionally, the hybrid density functional B3LYP [26] has been used to calculate the minimum structure of the molybdenum complex 1 since this approach is frequently used for studies of transition metal-π-complexes. To the best of our knowledge only a few crystal structures of molybdenum(0) arene complexes are available from the literature, and therefore a naphthalene molybdenum complex with three trimethylphosphite coligands has been calculated. Table 1 reveals that the distances within the arene ring are better represented when using the B3LYP functional, whereas the bond lengths between the chromium and the ring carbons are in better agreement with the experimental results for the BP86 functional. Since for the haptotropic rearrangement the coordination of the metal to the arene ring atoms is especially important, the computationally simpler non-hybrid BP86 functional is an expedient choice, representing very well the experimental structure.

In order to model the experimentally used arenes, on which the haptotropic migration takes place, as good as possible, we decided to calculate the potential energy surface for a highly substituted system similar to the ones accessible with the Dötz reaction [15]. In a previous study we worked out the effects of different single substituents at various positions of the arene [3]. It was found that in case of R = O⁻ the coordination of the chromium tricarbonyl moiety to the substituted ring is clearly energetically favored, which is in contrast to most other substituents (e.g. OH, OMe or NH₂), for which the coordination to the unsubstituted ring is thermodynamically favored. For that reason the substituents R = O⁻

Fig. 2. Radial expectation values for the three metals Cr, Mo and W.

Table 1
Comparison of selected calculated structure parameters (in Å) with X-ray data for naphthalene Mo(POMe)$_3$.

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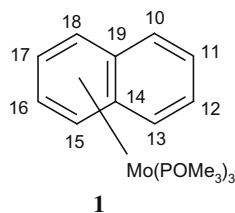
Bond lengths	Exp.[30]	Calc. BP86	Calc. B3LYP	Deviation calc. (BP86) – exp.	Deviation calc. (B3LYP) – exp.
Mo–P1	2.350	2.375	2.388	0.025	0.038
Mo–P2	2.362	2.382	2.396	0.020	0.034
Mo–P3	2.325	2.317	2.328	−0.008	0.003
Mo–C14	2.417	2.504	2.527	0.087	0.110
Mo–C15	2.314	2.324	2.340	0.010	0.026
Mo–C16	2.297	2.328	2.342	0.031	0.045
Mo–C17	2.314	2.312	2.326	−0.002	0.012
Mo–C18	2.291	2.335	2.349	0.044	0.058
Mo–C19	2.407	2.506	2.528	0.099	0.121
C14–C15	1.446	1.456	1.451	0.010	0.005
C15–C16	1.397	1.418	1.409	0.021	0.012
C16–C17	1.416	1.435	1.428	0.019	0.012
C17–C18	1.420	1.421	1.413	0.001	−0.007
C18–C19	1.413	1.452	1.448	0.039	0.035
C19–C14	1.445	1.451	1.440	0.006	−0.005

and R = OH have been calculated in position 1 of the phenanthrene species (cf. R in Fig. 1). Furthermore, this system would open up the possibility to design a molecular switch, which is tuned by the pH-value.

In Table 2 relative energies of the most important characteristic points on the energy hypersurface for the haptotropic rearrangement are collected. The values have to be discussed in different perspectives: firstly, the common influence of the four substituents on one terminal phenanthrene ring on the energetic course of the haptotropic migration has to be analyzed. Secondly, the differences of the substituent pair R = O⁻/OH have to be discussed in view of a possible switchable system. Finally, the differences due to the three metals Cr, Mo and W have to be considered.

With respect to the first point, restricting the discussion to the Cr systems, it can be stated that the energy profiles of the substituted systems tend to be more flat than for the unsubstituted one, i.e. the relative energies of the middle ring complex (**M**), the intermediate (**Int**) and almost all transition states (**TS**) are lower. Studies of singly substituted phenanthrene systems led to the conclusion that for R = O⁻ the substituted terminal ring is more electron rich and thus can more strongly bind the Cr(CO)$_3$ fragment, whereas for R = OH a complexation at the unsubstituted terminal ring is favoured [4]. Concerning the second point this general

feature remains valid also for the multiply substituted phenanthene, with R = O⁻ leading to a much more drastic flattening of the energy profile than R = OH. For the haptotropic migration from the substituted terminal ring to the middle ring the transition states are lowered by up to ∼10 kcal/mol, whereas the effects are much smaller for the transition states of the migration from the middle ring to the unsubstituted ring. This means that the haptotropic shift of the M(CO)$_3$ group proceeds more easily comparing a substituted phenanthrene to an unsubstituted one.

The third point concerns the substitution of Cr by Mo or W and is the central topic of this contribution. It is clear from the data compiled in Table 2 that the energy profiles for Mo and W are significantly more flat than the ones of the Cr cases. The change from Cr to Mo (W) causes a significant reduction of the energy barriers of 0.4 (1.7) kcal/mol up to 6.0 (6.9) kcal/mol for R = O⁻ and of 1.6 (1.2) kcal/mol up to 6.1 (4.3) kcal/mol for R = OH. The energy of the middle ring complex **M** (relative to the non-substituted ring complex **NS**) is slightly decreased and amounts in case of Mo (W) to only 1.4 (2.4) kcal/mol for R = O⁻ and 5.2 (7.0) kcal/mol for R = OH. This means that the substitution of Cr by Mo or W definitely reduces the effort to initiate a slippage of the M(CO)$_3$ group along an aromatic system. We assume that this finding also remains for moderately differing substitution patterns on the arene

Table 2
Relative energies in kcal/mol for the haptotropic migration of M(CO)$_3$ over a phenanthrene derivative, with the substituents R = O⁻ and OH in position 1, respectively (cf. Fig. 1; **TS-X** denotes the **TS** between **M** and **Int**). Optimizations with TURBOMOLE and single-point calculations with the solvent model COSMO.

Metal/conformer	Unsubstituted phenanthrene [5]	R = O⁻			R = OH		
	Cr	Cr	Mo	W	Cr	Mo	W
NS	0.0	2.1	3.6	1.9	0.0	0.0	0.0
S	0.0	0.0	0.0	0.0	2.9	3.2	4.6
M	8.6	6.0	5.0	4.3	8.4	5.2	7.0
Int	27.0	18.0	15.1	14.0	25.8	20.8	21.2
TSIa	30.6	19.4	19.0	17.5	27.2	23.6	24.0
TSIIa	29.2	18.4	15.5	14.2	25.9	24.3	24.7
TSIb	30.6	26.8	20.8	19.9	29.3	23.2	25.5
TSIIb	29.2	29.2	24.3	23.5	29.8	24.9	25.5
TS-X	30.7	24.9	20.0	19.4	27.4	21.7	22.5

system. If other commonly used coligands on the metal, e.g. trialkylphosphine groups PR_3, will lead to the same trends with respect to an exchange of the metal remains to be investigated, however, it might be expected that for slightly modified groups such as $M(CO)_2PR_3$ this actually might be the case.

Another effect of the substituents can be found in the calculated structures (Fig. 4). For example the intermediate **Int**, which is located symmetrically in a η^2-bonding mode between the carbon atoms 4a and 4b in the phenanthrene complex without any substituents, is now shifted closer to the substituted ring and coordinates in a η^3-bonding mode to C4, C4a and C4b. According to standard notation C4 denotes the carbon atom bearing the OMe substituent, whereas C4a and C4b are the atoms of the substituted and unsubstituted terminal ring, respectively, which are directly bonded to each other (cf. Fig. 1). The energy difference between **Int** and **TSIIa** decreased in all cases (i.e. $R = O^-/OH$ and M = Cr, Mo or W), the intermediate being between 0.1 and 3.5 kcal/mol more stable than **TSIIa**. A slight structural change can also be found in some of the transition states where the ideal methylene-methane structure is not adopted.

Concerning the possibility to obtain a pH-value dependent molecular switch based on the haptotropic migration one can state the following. For all three metals the substituted ring complex **S** is lowest for $R = O^-$, whereas the unsubstituted ring complex **NS** is lowest for R = OH. The sum of the energy differences between **S** and **NS** for $R = O^-$ and **NS** and **S** for R = OH is 5.0, 6.8 and

Table 3
Partial charges of the $M(CO)_3$ metal fragment obtained by summing up the partial charges of the atoms obtained by the NBO analysis.

	|e| $Cr(CO)_3$	|e| $Mo(CO)_3$	|e| $W(CO)_3$
S ($R = O^-$/OH)	−0.36/−0.18	−0.32/−0.13	−0.24/−0.04
M ($R = O^-$/OH)	−0.26/−0.12	−0.23/−0.08	−0.17/−0.02
NS ($R = O^-$/OH)	−0.27/−0.14	−0.22/−0.10	−0.15/0.00

6.5 kcal/mol for Cr, Mo and W, respectively. Thus for a given ligand R the equilibrium is shifted more clearly to one side for Mo and W compared to Cr. In view of the significantly lower activation barriers for complexes of these two metals compared to the ones of chromium one may conclude that not only the haptotropic migration is easier for Mo and W complexes, but also the design of a molecular switch might be more successful. In addition, experimental and theoretical studies of bis-benzene complexes imply that the metal-arene binding is significantly stronger for Mo and W than for Cr [27]. Thus the preference of the desired intramolecular reaction over a possible intermolecular one should be larger for Mo and W than for Cr.

A look to the NBO (Natural Bond Orbital) analysis [28] given in Table 3 shows that for the case of $R = O^-$ the negative charge on the $M(CO)_3$ fragment decreases as Cr > Mo > W for the metals and $S > M \cong NS$ for the complexation position. This trend is also followed for R = OH, however, the charges are in general by 0.1–0.2 units less negative than for $R = O^-$ and almost vanish in case of the complexation of $W(CO)_3$ to the middle and the non-substituted rings.

The lower tendency of the heavier metal fragments to accept electron density from the arene is probably mainly related to the strongly increasing relativistic destabilization of the valence d shell in the order Cr < Mo < W, which significantly increases the destabilization due to shell structure effects occurring at the nonrelativistic level (Fig. 3). The increase of the radial extension of the metal valence d shell in the order Cr < Mo < W and its related better availability to form bonds to the extended arene π-electron system occurs already at the nonrelativistic level, with a small relativistic enhancement, and is thus more related to shell structure effects (Fig. 2). The especially compact nature of the Cr 3d shell compared to the Mo 4d and W 5d shells is due to the missing orthogonality requirements to inner shells of the same angular symmetry in case of Cr, an effect which was termed missing primogenic repulsion [29]. The spatially less compact and energetically more accessible Mo 4d and W 5d orbitals are not only more suitable for haptotropic bonding to arenes, but also allow at the same time an easier rearrangement of the electrons during the course of the haptotropic shift and thus lead to lower energy barriers than in case of Cr 3d systems.

4. Conclusions

The haptotropic migration of three different metal tricarbonyl moieties, containing either chromium, molybdenum or tungsten, has been calculated using gradient-corrected density functional theory. The results reveal that the change of the metal has a significant effect on the relative energies of the barriers for the migrating process. The activation energies decrease by up to $\sim$7 kcal/mol when going from Cr to Mo or W. Thus the haptotropic migration from the substituted to the unsubstituted ring induced by heating should proceed under milder conditions for $Mo(CO)_3$ and $W(CO)_3$ than for $Cr(CO)_3$. It is further suggested that the $Mo(CO)_3$ and $W(CO)_3$ arene complexes might be more suitable than the corresponding $Cr(CO)_3$ systems to design a molecular switch based on the haptotropic rearrangement. Finally, the chances to isolate a so far experimentally not found middle ring phenanthrene
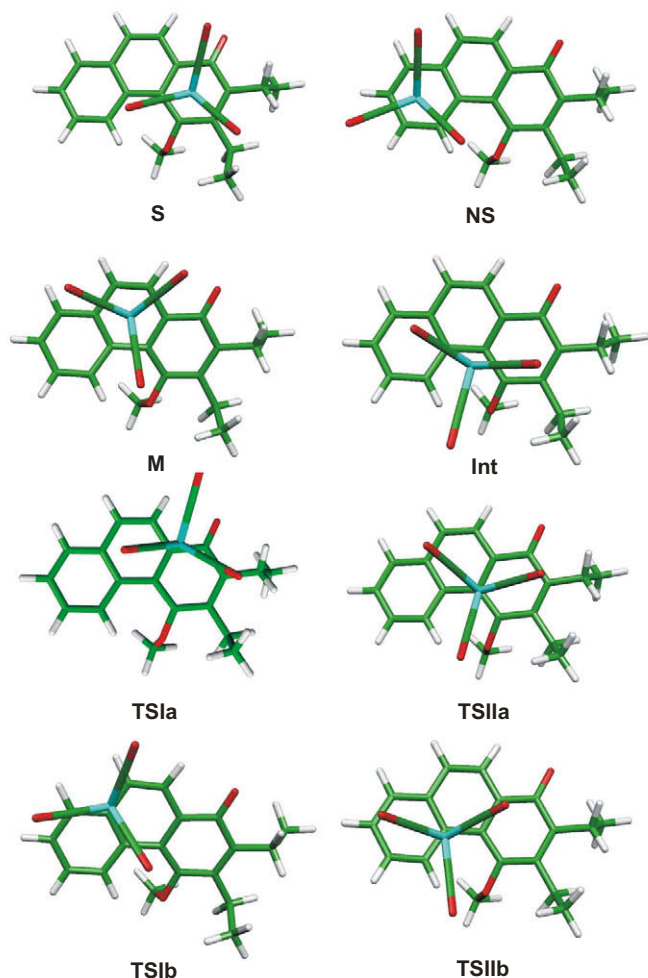

Fig. 4. Calculated structures for the haptotropic migration of $Mo(CO)_3$ on a substituted phenanthrene ($R = O^-$ in Fig. 1).

M(CO)$_3$ complex appear to be higher for the Mo and W systems studied here, especially in presence of a strongly electron donating R = O$^-$ arene substituent.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.05.039.

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