Structural and Energetical Characterization of Reactive Intermediates Derived from Toluene – $Cr(CO)_3$

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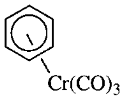
Abstract: In order to gain a deeper understanding of the specific reactivity of arene – $Cr(CO)_3$ complexes, the structures and energies of the reactive intermediates formally generated by abstraction of a proton (H^+), a hydride (H^-), or a hydrogen atom ($H^\bullet$) from the methyl group of toluene – $Cr(CO)_3$ (**2**) were computationally investigated by using density functional theory based quantum chemical techniques. The solid-state structure of the parent complex (**2**) was determined by low-temperature X-ray crystallography and this confirmed the high accuracy of the computational methods. Besides calculating the geometry of the lowest energy conformation, particular emphasis was laid on the rotational barrier of the $Cr(CO)_3$ group as well as on that of the exocyclic carbon – carbon bond which exhibited a significant amount of double-bond character in all of the reactive intermediates investigated. The results are put into broader perspective by discussing their relevance for the rationalization and prediction of the selectivity of synthetically relevant reactions of arene chromium tricarbonyl complexes.

Keywords: chromium · conformation analysis · density functional calculations · organometallic chemistry · reactive intermediates · stereoelectronic effects

Introduction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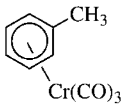
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Since their discovery 40 years ago,[1] arene – chromium tricarbonyl complexes (e.g. **1** and **2**) have enjoyed an ever growing popularity among synthetic chemists.[2] Amid the most important effects of the complexation with $Cr(CO)_3$ is the significant transfer of electron density from the aromatic ring to the metal tricarbonyl moiety resulting in an increased reactivity towards nucleophiles.[3] Concomitantly, the acidity of the arene ring[4] as well as of benzylic hydrogen atoms[5] is enhanced. Furthermore, the $Cr(CO)_3$ group also stabilizes positive charge in the benzylic position allowing S_N1 type transformations in the side chain.[6] Very recently, reactions involving $Cr(CO)_3$ complexed benzylic radicals have been described which also show a promising potential for synthetic exploitation.[7] Because the $Cr(CO)_3$ tripod effectively shields one of the two π faces of the aromatic ligand, all these reactions usually proceed with an excellent degree of stereoselectivity, opening a large variety of synthetically important avenues which are not possible with nonactivated arene compounds.[8]

In spite of the fact that arene – chromium complexes are frequently employed in syntheses, several aspects of the underlying mechanistic details that govern the course of their reactions are still not understood to a satisfying degree. For instance, the regioselectivity of nucleophilic addition or of deprotonation reactions is sometimes difficult to predict, especially in cases where no obvious electronic or steric effects apply. Experimentally it has been established that the regioselectivity of such reactions correlates with the preferred orientation (conformation) of the $Cr(CO)_3$ tripod in the starting complexes.[9, 10] However, as the $Cr(CO)_3$ tripod can be regarded as a nearly unhindered internal rotor (the barrier of rotation being generally $\leq 1\ kcal\,mol^{-1}$),[11] the Curtin – Hammet principle[12] must apply, and it does not make very much sense to explain the observed selectivities by simply regarding the favored ground state conformation of the substrates. What actually would be needed for a conclusive interpretation of the experimental facts is a detailed knowl-

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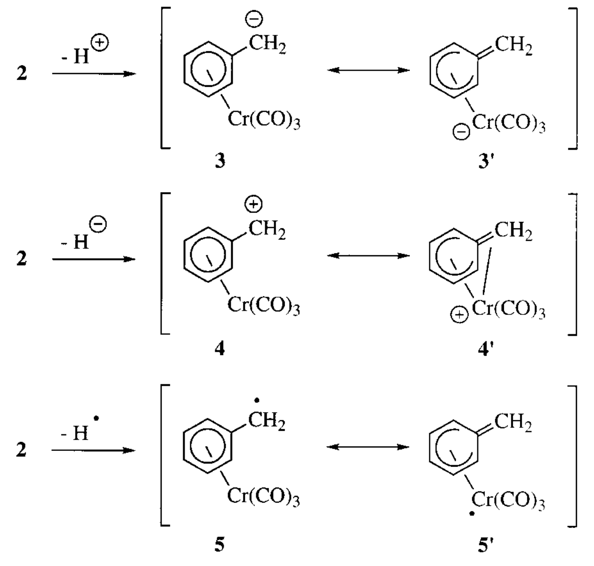
edge about energy, structure, and conformational preferences of the *reactive intermediates*. This would also allow the prediction of the configurational stability of such species and lead to a deeper understanding of the electronic origins of the unique stereoelectronic effects guiding their selective generation.

While many neutral η^6-arene – Cr(CO)$_3$ complexes have been characterized by X-ray crystallography, no reliable structural information is available for the corresponding benzylic anions, cations, or radicals because these reactive intermediates have never been obtained in crystalline form. Only a few NMR investigations on Cr(CO)$_3$-complexed benzylic anions[13] and cations[14] have revealed some structural details.

Quantum chemical calculations in principle offer a complementary source of information. Unfortunately, theoretical studies on these systems are scarce due to the size of arene – chromium tricarbonyl complexes which render such studies rather demanding from the computational point of view.[15] However, in recent years quantum chemical methods and computer hardware have evolved to a point, where a promising investigation of such problems is in reach. In particular the advent of computational strategies based on approximate density functional theory has given new impetus to the computational approach, even for species containing complicated electronic structures such as transition metal containing compounds.[16]

In this contribution we will employ such modern quantum chemical techniques in order to shed more light onto the reactivity of arene – Cr(CO)$_3$ complexes. We focus our investigation on reactive intermediates formally derived from the parent toluene – chromium tricarbonyl complex (**2**, Scheme 1). These include the anionic $C_6H_5CH_2^-$ – Cr(CO)$_3$ species (**3**), which results from deprotonation in the benzylic position, further the corresponding cationic species $C_6H_5CH_2^+$ – Cr(CO)$_3$ (**4**) which occurs as reactive intermediate in solvolysis reactions, and finally the open-shell $C_6H_5CH_2^{\bullet}$ – Cr(CO)$_3$ radical (**5**). The latter species, which is of particular relevance due to the recent interest in transformations involving Cr(CO)$_3$ complexed benzylic radicals,[7] has never been investigated before neither experimentally nor theoretically.

We report the structural and energetic properties of these species, such as the equilibrium geometries, the barriers for rotation of the chromium tricarbonyl tripod and of the exocyclic CH$_2$ group, the charge distribution, and—in the case of radicals—the spin density. At this point, we would like to add a *caveat*. Our calculations do not account for any effects brought about by a solvent, counterions in the case of charged species, or influences of the surrounding of any kind. Rather, they refer to isolated molecules and model vacuum gas-phase chemistry, since for the time being the computational techniques available to us do not allow for a rigorous treatment of these effects. While certainly of importance for a quantitative description, we believe that the current results—which neglect the surrounding—still offer valuable insights into the intrinsic properties of our target species.



Scheme 1. Resonance structures of reactive intermediates formally derived from toluene – Cr(CO)$_3$.

Computational Strategy

All structures presented in the following sections were fully optimized in the respective point group symmetry by employing analytical gradient techniques and the popular hybrid density functional method B3LYP[17] as implemented in Gaussian94.[18] The one-particle description for the chromium atom was a (14s11p6d) → [8*s*6p4d] all-electron basis set introduced by Wachters,[19] supplemented with three primitive f-type polarization functions contracted into two. For carbon, hydrogen, and oxygen we employed Dunning's standard split valence D95* basis set,[20] which includes a set of d-type functions on C and O. Spherical harmonic polarization functions (i.e., 5d and 7f components) were used throughout. For the calculations on the anionic complexes, the basis was augmented with a set of standard diffuse s and p functions on carbon and oxygen (D95 + *) and with diffuse s, p, and d functions on chromium.[21] Harmonic frequencies were computed analytically in order to estimate the zero-point vibrational energies (ZPE) and to identify a stationary point as minimum (only real frequencies) or transition structure (one and only one imaginary frequency). However, to keep the computational demand at a reasonable level, in these calculations the polarization functions had to be discarded and consequently the frequencies are based on geometries optimized by using this smaller basis set. However, the influence of the polarization functions on the equilibrium structures was found to be only marginal. Thus, all relative energies given in the following are based on the B3LYP results with the larger, polarized basis sets corrected for ZPE contributions obtained with the smaller set, as described above. The electronic wave functions[22] were analyzed in terms of partial charges, bond orders, orbital hybridization, etc., by employing the natural bond orbital (NBO) scheme as developed by Weinhold and co-workers.[23] All calculations were carried out on either IBM RS/6000 workstations at the TU Berlin or the CRAY J90 computer at the Konrad-Zuse-Zentrum Berlin.

Results and Discussion

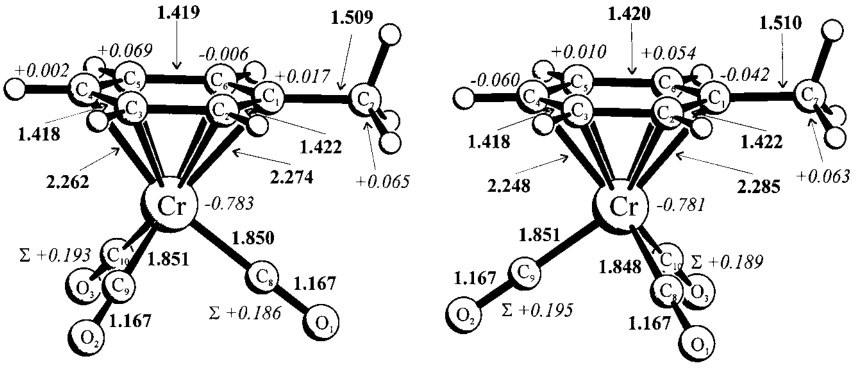
The toluene – chromium tricarbonyl complex (2): The toluene – chromium tricarbonyl complex is the smallest arene – Cr(CO)$_3$ complex which offers in addition to the aromatic positions a side chain as site of attack in a chemical transformation. It is therefore ideally suited as a prototype molecule to study the details of deprotonation and solvolysis reactions at the benzylic positions, which lead to anionic, cationic, and radical $C_6H_5CH_2$ – Cr(CO)$_3$ species (**3**, **4**, and **5**, respectively) as reactive intermediates, respectively. Before we proceed with an indepth discussion of the properties of these short-lived intermediates, we present our results for the neutral, closed-shell parent system, that is, the toluene–chromium tricarbonyl complex (**2**).

First of all, of the two possible orientations of the Cr(CO)$_3$ group with respect to the methyl substituent of the benzene ring, the eclipsed conformation (**2e**) is favored. The calculations, after correction for ZPE, place **2e** 0.6 kcal mol^{-1} below the alternative structure, in which the CH$_3$ group is staggered with respect to the carbonyl groups (**2s**) (Figure 1 and Table 1). The latter species was identified as being the saddlepoint for the Cr(CO)$_3$ rotation by an, albeit very small imaginary frequency of 18 wavenumbers. The normal mode connected to this frequency indeed shows the expected rotation of the tripod with respect to the toluene unit. An NMR study established a ΔG_0 of 0.5 kcal mol^{-1} between **2e** and **2s**, in full harmony with our computed result.[24] Thus, as in the case of benzene–Cr(CO)$_3$ (**1**) (which prefers a staggered conformation) the barrier for rotation is almost negligible.

Table 2. Calculated and experimental geometric parameters for toluene–Cr(CO)$_3$(**2e**). Bond lengths in Å, angles in degrees.

Parameters	Calculated	Experimental[25]	Experimental[a, b]
C_1-C_2	1.422	1.390, 1.426	1.42(1)
C_2-C_3	1.419	1.370, 1.375	1.413(1)
C_3-C_4	1.418	1.377, 1.387	1.412(1)
C_1-C_7	1.509	1.501	1.506(1)
$Cr-C_1$	2.274	2.236	2.248(1)
$Cr-C_4$	2.262	2.217	2.234(1)
$Cr-C_8$	1.850	1.823	1.842(1)
$Cr-C_9$	1.851	1.817, 1.833	1.846(1)
C_8-O_1	1.167	1.156	1.160(1)
C_9-O_2	1.167	1.154, 1.142	1.162(1)
C_1-C_2-C_3	120.34	121.2, 119.6	120.2(1)
C_2-C_1-C_7	120.56	120.9, 121.5	120.5(1)
Cr-C_8-O_1		178.83	179.3
179.2(1)			
Cr-C_9-O_2	179.03	178.9, 179.3	179.2(1)
C_8-Cr-C_9	86.82	89.9, 87.7	88.6(1)
C_9-Cr-C_{10}	88.76	88.9	88.87(4)

[a] Including libration correction. [b] This work.



2e **2s**

Figure 1. Optimized geometries (distances in Å, angles in degrees) and natural charges of toluene–Cr(CO)$_3$ (**2**). The charges of the hydrogen atoms are summed into the carbon atoms.

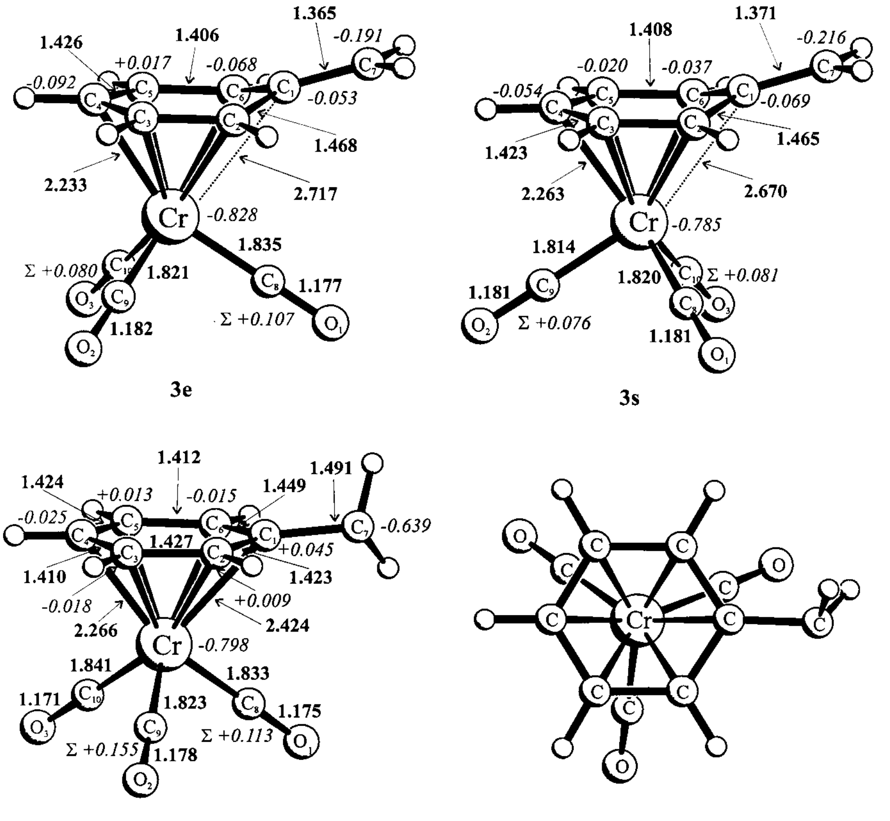
Table 1. Total energies, zero point energy correction (ZPE), and relative energies for structures **2**–**5**.

Structure	Total energies (Hartree)	ZPE [kcal mol^{-1}]	Rel. energies [kcal mol^{-1}]
2e	– 1656.18075	97.7	0.0
2s	– 1656.17963	97.6	0.6
2ts	– 1656.17922	97.5	0.8
3e[a]	– 1655.62631	88.8	0.0
3s[a]	– 1655.61656	88.6	5.9
3ts[a]	– 1655.56302	86.5	37.4
4s	– 1655.29303	90.8	0.0
4e	– 1655.27478	90.5	11.2
4ts	– 1655.21643	88.1	45.4
5s	– 1655.52930	89.3	0.0
5e	– 1655.52461	89.1	2.8
5ts	– 1655.50685	88.2	12.3

[a] Diffuse functions included.

Table 2 contains the computationally predicted geometric parameters in comparison with experimental structural information for this species. When we started our investigation, only an X-ray structure reported more than 20 years ago by van Meurs and van Koningsveld[25] was available. The agreement between the computed and the experimental structural data[25] is, however, significantly less satisfactory than for the benzene complex **1**.[26] For example, the computationally predicted structure has a mirror plane (C_s symmetry), while experimentally only C_1 symmetry was identified. Furthermore, atypically large deviations of up to 0.04 Å are found for the C–C distances in the aromatic ring. Thus, we decided to carry out a new X-ray investigation of this complex. The resulting structure[27] is now indeed in excellent agreement with the computed one (Table 2) and fully supports the reliability of our computed data. The deviations for the carbon–carbon bond lengths amount to less than 0.007 Å, similarly the distances between the chromium atom and the carbonyl groups differ by less than a hundredth of an Ångstrom. Hence, our theoretical predictions led to a revision of the previous experimental data, providing another beautiful example for the fruitful interplay between theory and experiment.

Next, we turned to the results of the NBO analysis. The electron withdrawal from the toluene ligand by the Cr(CO)$_3$ unit amounts to 0.21 $|e|$. Within the ligand, the variations of the partial charges are small but show certain systematics in that those carbon atoms which are directly above a carbonyl ligand show the higher electron deficit. This applies also to the comparison between the two rotamers of **2**. In **2s** the *ipso*-carbon atom C_1, which is in between two CO groups, is even slightly negatively charged (-0.042 $|e|$), whereas in **2e**, C_1 is eclipsed to one carbonyl group and carries a small positive charge of $+0.017$ $|e|$. This result is in line with the experimental observation that in systems with more than one benzylic position, those positions with an eclipsed CO ligand are the favored site of deprotonation.[10] However, one should be careful not to overinterpret this pattern because the variations of the charge density are very small. In addition, the barrier for the rotation of the exocyclic methyl group in the toluene complex is computed to be well below 1 kcal mol^{-1}. As elaborated further below, the height of both barriers for rotation will rise significantly in the $C_6H_5CH_2^{+/-/\bullet}$-chromium tricarbonyl complexes, pointing to the origin of some of the peculiar aspects of the chemistry of arene-chromium tricarbonyl complexes.



3e

3s

3ts

3ts

Figure 2. Optimized geometries (distances in Å, angles in degrees) and natural charges of the $C_6H_5CH_2^-$-$Cr(CO)_3$ ion (**3**). The charges of the hydrogen atoms are summed into the carbon atoms.

The anionic $C_6H_5CH_2^-$-chromium tricarbonyl complex (3): One of the major effects brought about by the $Cr(CO)_3$ fragment in toluene is the significantly enhanced acidity of the methyl protons. The absolute gas-phase acidity of toluene itself, that is, the heat of reaction for the process $C_6H_5CH_3 \rightarrow C_6H_5CH_2^- + H^+$, is experimentally determined as 382.3 ± 0.3 kcal mol^{-1}.[28] Our calculations, which use the diffuse function augmented basis set and include a finite temperature correction based on the harmonic frequencies and one RT (= 0.6 kcal mol^{-1}) for the pressure-volume term, are in excellent agreement, resulting in $\Delta H_{\text{acid}} = 382.0$ kcal mol^{-1}.[29] The deprotonation of the toluene-chromium tricarbonyl complex at the benzylic position leads to the anionic intermediate **3**. Unfortunately, no experimental data for the gas-phase acidity of this complex are known to us, however, the computationally predicted ΔH_{acid} value for the energetically more stable eclipsed form **3e** is indeed some 33 kcal mol^{-1} smaller than that found for toluene, amounting to 349.4 kcal mol^{-1}. Thus, the gas-phase acidity of the CH_3 protons is now comparable to that of typical weak acids such as HCN ($\Delta H_{\text{acid}} = 351.4 \pm 0.5$ kcal mol^{-1})[30] or H_2S ($\Delta H_{\text{acid}} = 351.1 \pm 2.0$ kcal mol^{-1}).[30]

To a first approximation, the stabilization of the negative charge can be attributed to a delocalization onto the metal as indicated by the resonance structure **3'** in Scheme 1. The structure **3'** represents an anionic η^5 complex, which would still obey the 18-electron rule. Indeed, as the computed equilibrium structure shown in Figure 2 indicates, the ring loses its planarity and partially breaks its delocalized aromatic system. The exocyclic CH_2 group is bent by 18° to the *exo* π face opposite to the $Cr(CO)_3$ moiety. The Cr-C_1 distance has increased from 2.274 Å in the neutral complex to 2.717 Å, and the Cr-arene mode of bonding has changed from η^6 to η^5. Concomitantly, the bond length between C_1 and C_7 has decreased dramatically and amounts to only 1.365 Å as compared to 1.509 Å in **2e** indicating the formation of a double bond (the C-C distance in ethylene at this level of theory amounts to 1.341 Å), while the bond lengths between C_1 and its neighbor C_2 has increased to 1.468 Å, resembling more a carbon-carbon single bond. The NBO analysis indicates that the negative excess electron is almost evenly shared between the $Cr(CO)_3$—which carries a partial charge of −0.56 |e|—and the $C_6H_5CH_2$ units. Within the ring the usual pattern with *ortho* and *para* positions more negative than *meta* and *ipso* positions is realized. Most of the negative charge—almost 0.2 |e|—is still localized on the CH_2 group at C_7.

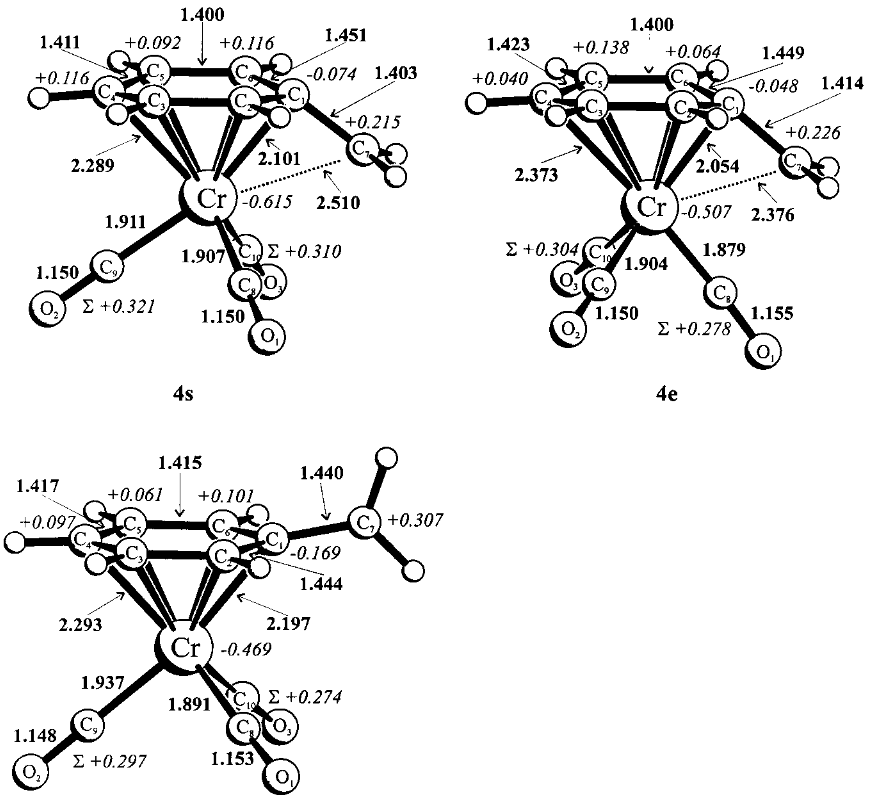
The deprotonation has also a decisive effect on the barrier for rotation of the chromium tricarbonyl. While in the neutral toluene complex this barrier was well below 1 kcal mol^{-1} (see above), this barrier amounts to 5.9 kcal mol^{-1} in the present, anionic species. Like in the neutral system the saddlepoint corresponds to the staggered conformation (**3s**) of the CH_2 unit with regard to the carbonyls. It is characterized by an imaginary frequency of 45 cm^{-1} which is connected with the expected transition mode. This comparably large rotational barrier of the $Cr(CO)_3$ tripod in the anionic species **3** offers now a much better explanation for the experimentally observed regioselectivity of benzylic deprotonation in more complex substrates.[10a] Even if we assume virtually unhindered rotation in **2**, the deprotonation reaction indeed clearly favors the formation of the eclipsed conformation **3e** of the anionic intermediate and thus, the methyl protons in **2e** are more acidic than those in **2s** by 6 kcal mol^{-1}.

Also the rotation of the exocyclic CH$_2$ group of **3e** is connected with a substantial barrier of 37.4 kcal mol^{-1}. Thus, once the anion is formed, the stereochemistry of the exocyclic CRR′ group is frozen, and attack of an electrophile occurs from the *exo* π face, that is, opposite to the metal, leading to a well-defined stereochemistry. The configurational stability of such anions becomes evident in enantioselective benzylic deprotonation/alkylation reactions.[31] Let us now take a closer look at the geometry of the saddlepoint connected with this rotation, **3ts**, where several aspects deserve further comments. Most importantly, the rotation breaks the π overlap between the methylene group and the aromatic system and thus interrupts the charge transfer onto the ring and further towards the chromium tricarbonyl moiety. The negative charge is now mostly located in the CH$_2$ group as indicated by the large partial charge of -0.64 |e| (as compared to -0.2 |e| in **3e**). This accumulation of excess charge is also evident from the significant pyramidalization of the RCH$_2$ unit which is now very akin to a regular methyl anion derivative. The loss of planarity of the CH$_2$ unit evidently leads also to a reduction in point group symmetry from C_s to C_1. In contrast to the systems discussed so far the Cr(CO)$_3$ tripod assumes a fully staggered conformation in **3ts** with no carbonyl ligand positioned directly below a carbon atom of the aromatic ring. In addition, the decoupling of the anionic group and the remaining part of the molecule is mirrored in the large bond length between C$_1$ and C$_7$ which is only 0.018 Å shorter than in the parent toluene complex **2e** and the almost undisturbed structure of the aromatic ring.

The cationic C$_6$H$_5$CH$_2$$^+$–chromium tricarbonyl complex (4): The chromium tricarbonyl fragment not only enhances the stability of benzylic anions, it also exerts a significant stabilizing effect on a positive charge at a benzylic position.[6] Thus, it facilitates S$_N$1-type solvolysis reactions, for example, of complexed benzylic alcohol derivatives. The central intermediate in such a reaction is the cationic C$_6$H$_5$CH$_2$$^+$–chromium tricarbonyl complex **4**. The stabilizing effect is ascribed to a neighboring group participation of the chromium center, that is, a charge donation from occupied Cr(CO)$_3$ orbitals into the formally empty p-atomic like orbital at the methylene carbon C$_7$ as shown in the resonance structure **4′** in Scheme 1. In order to still correspond to a formal 18-electron species the bonding between the metal and the arene should become η^7. From this bonding picture it is expected that these cations incorporate a substantial amount of exocyclic double-bond character which in turn implies a significant barrier for the rotation around the C$_1$–C$_7$ bond. Similar to the anionic species discussed above, also the cations, once formed, are configurationally stable. As a consequence, if the leaving group was expulsed whilst positioned *anti* to the chromium center and nucleophilic attack occurs from the *exo* face, a double inversion mechanism takes place resulting in an overall retention of configuration.[6]

Again, our calculations unravel significant structural differences between the neutral toluene chromium tricarbonyl complex **2** and the corresponding cationic complex **4** (Figure 3). First of all, the lowest energy conformer is now characterized by a staggered arrangement of the CH$_2$ group and the CO ligands. The barrier for rotation in **4** was found to be almost twice as large as in the anionic complex **3** amounting to 11.2 kcal mol^{-1}.[32] The transition mode connected with the imaginary frequency of 57 cm^{-1} is again indicative of the Cr(CO)$_3$ tripod rotation, confirming the assignment.

The structure of the staggered minimum **4s** fully corroborates the assumption of a η^7 binding between the arene ligand and the transition metal. The methylene unit is with 37°



4s

4e

4ts

Figure 3. Optimized geometries (distances in Å, angles in degrees) and natural charges of the C$_6$H$_5$CH$_2$$^+$–Cr(CO)$_3$ ion (**4**). The charges of the hydrogen atoms are summed into the carbon atoms.

significantly bent downwards towards the chromium and concomitantly the Cr–C_7 distance has decreased to only 2.510 Å. On the other hand, the C_1–C_7 bond length (1.403 Å) is not as short as in the anionic complex discussed above pointing to a somewhat less pronounced double-bond character of this bond. A further indication for the direct interaction between occupied metal orbitals and the formally empty orbital at the cationic site is the onset of a pyramidalization on the CH_2 group. The charge distribution shows that the positive charge has been delocalized over the whole complex. About one third ($+0.326$ $|e|$) has been transferred onto the chromium tricarbonyl moiety. However, the metal still carries a substantial negative partial charge of -0.615 $|e|$ (as compared to -0.78 $|e|$ in the parent toluene complex) and the electron deficiency is mainly located on the three CO ligands (weaker backbonding). In the arene ligand it is C_7, which bears the most cationic character with a partial charge of $+0.215$ $|e|$.

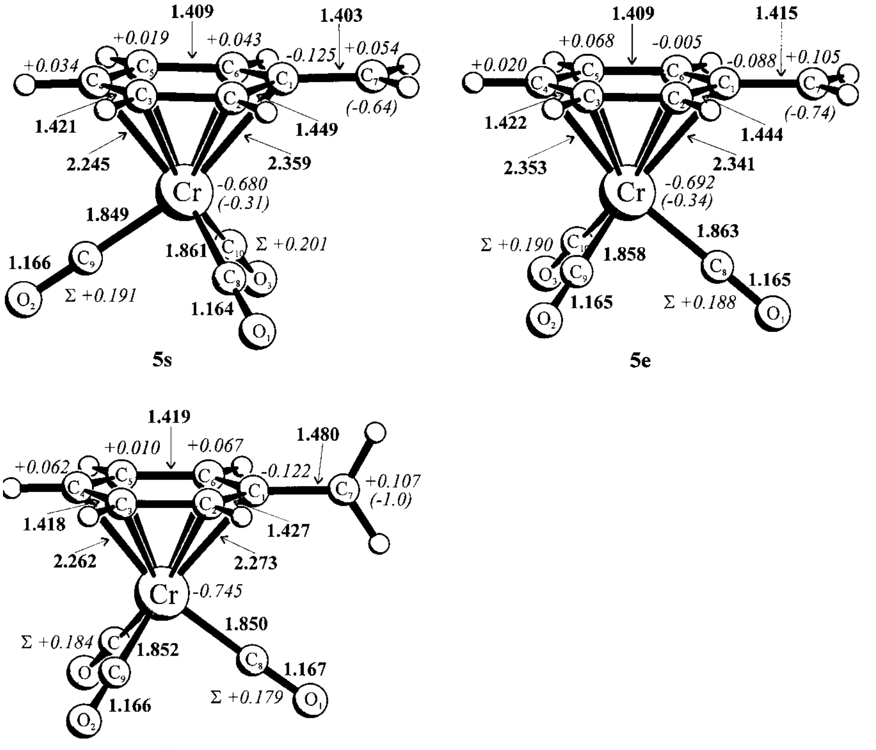
Not only is the energy difference of 11.2 kcal mol^{-1} between the staggered minimum and the eclipsed saddlepoint structure significant, the two conformers also differ considerably in their structures. In the eclipsed form (**4e**) the interaction between the methylene group and the chromium center seems to be even more pronounced. This is indicated in the larger bending angle of the methylene group which amounts to 42°, and the shorter C_7–Cr contact of only 2.379 Å, which is in the similar to the distance between C_4 and the metal (2.373 Å). For comparison, in **4s**, these two distances are 2.510 and 2.289 Å, respectively. From a different point of view these structural data show that the chromium center has moved from its position from beneath the center of the six-membered ring towards the exocyclic methylene group when comparing **4s** and **4e**. Also the charge distribution mirrors the stronger interaction between the chromium and the formal cationic center in the eclipsed conformation, the positive partial charge on the $Cr(CO)_3$ moiety has increased by more than 0.05 $|e|$ with respect to **4s** and amounts to 0.380 $|e|$. In particular the metal itself has lost some 0.1 $|e|$ in **4e** as compared to **4s** (q[Cr] = -0.51 $|e|$).

Let us finally turn to the question of the configurational stability of the cationic complexes with respect to rotation around the C_1–CH_2 bond. In agreement with the experimental experience[6] we find a rather large barrier for this process. It amounts to 45.4 kcal mol^{-1}. Somewhat counterintuitively, despite the fact that the C_1–C_7 bond in **4s** is longer than that in **3e**, the barrier is even more pronounced than in the anionic case. In any case, the barrier is substantial and results in a strong configurational stability of the exocyclic group fully confirming the likelihood of a double inversion mechanism with overall retention of configuration in solvolysis reactions.

The $C_6H_5CH_2^{\bullet}$–chromium tricarbonyl radical (5): The final reactive intermediate which was investigated results from toluene–chromium tricarbonyl by a formal homolytic cleavage of a benzylic C–H bond. It is the radical $C_6H_5CH_2^{\bullet}$-chromium tricarbonyl complex **5** (Figure 4). In contrast to its anionic and cationic relatives **3** and **4**, respectively, radicals of type **5** have not received much attention in preparative chemistry.[7] To the best of our knowledge, there are no experimental or computational data on the structure and configurative stability of such species.

As a result of our computations, the most stable rotamer of **5** is, like in the cationic complex **4**, the staggered conformer, **5s**. However, the eclipsed alternative **5e** is only 2.8 kcal mol^{-1} disfavored energetically, resembling more the parent, neutral complex **2**. The geometry of **5s** in many respects is similar to the structure of **4s**. While the arene ligand is almost planar, there is nevertheless a slight bending of some 3° towards the metal akin to that found for the cationic complexes. The other geometric features of the C_7H_7 unit are similar as well. For example, the bond length predicted for the exocyclic C–C bond between C_7 and C_1 is identical (1.403 Å) to the one computed for **4s** and the alternations of distances within the ring do also hardly differ.

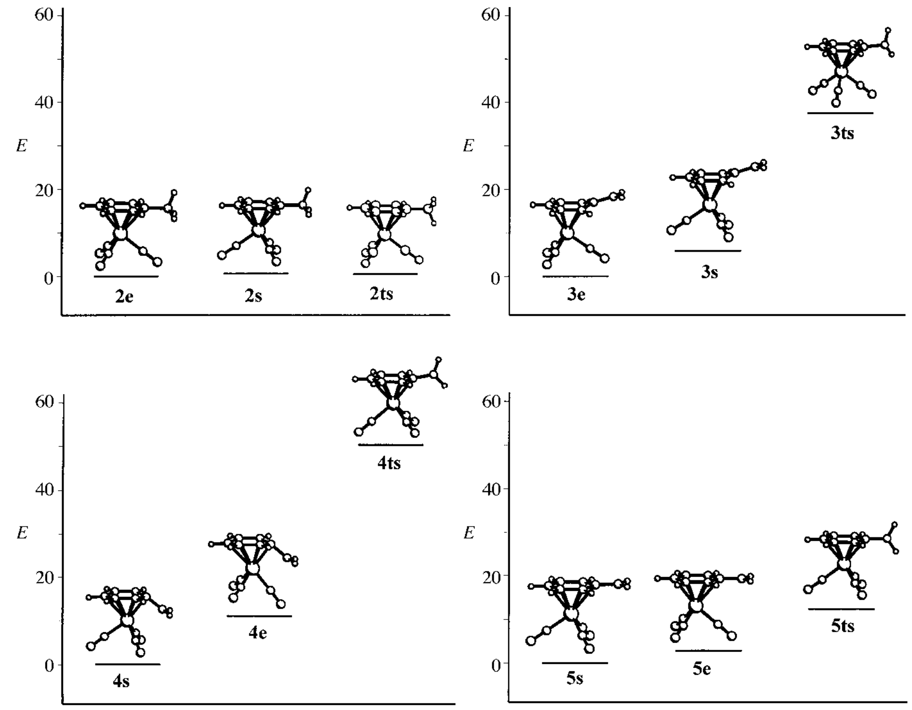
One of the most important aspects of this open shell intermediate is, however, the spin density. Is the unpaired electron mainly localized on the exocyclic CH_2 group or has a



5s **5e** **5ts**

Figure 4. Optimized geometries (distances in Å, angles in degrees) and natural charges of the $C_6H_5CH_2^{\bullet}$–$Cr(CO)_3$ radical (**5**). The charges of the hydrogen atoms are summed into the carbon atoms.

delocalization to the metal taken place, which would formally result in a 17-electron complex? These two extreme cases are depicted in the corresponding resonance structures (**5** and **5′**) in Scheme 1. According to our calculations the real picture is in between, about 2/3 of the excess α spin is on C_7 however, 0.31 $|e|$ is now localized on the Cr atom. The spin density on the other atoms is negligible. Interestingly, compared to the neutral toluene complex, where the Cr(CO)$_3$ group exerted a significant electron-withdrawing effect on the aromatic ligand, in **5s** the chromium tricarbonyl unit has an excess charge of only -0.09 $|e|$.



Scheme 2. Summary of relative energetics of **2**, **3**, **4** and **5**. E = relative energy in kcal mol^{-1}.

The barrier for rotation of the exocyclic CH$_2$ is much smaller than in the charged reactive intermediates and is computationally predicted as 12.3 kcal mol^{-1}. Nevertheless, this barrier might be large enough to provide configurational stability also for this (short-lived) intermediate. The most eye-catching feature of the corresponding saddlepoint **5ts** is the complete localization of the unpaired electron at C_7. In other words, unlike in **5s** neither the chromium tricarbonyl nor the aromatic ring participate in a delocalization and thus stabilization of the radical. The structural parameters follow this conclusion and are very similar to those obtained for the parent system **2**, including even the energetical preference for the eclipsed conformation (the staggered form is, however, only 0.5 kcal mol^{-1} higher in energy), in contrast to the minimum structure of the radical which adopts a staggered conformation.

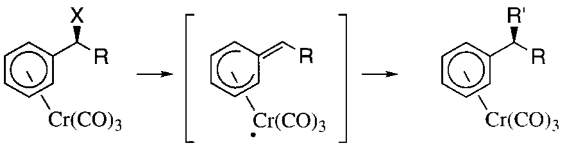
Summary and Conclusion

Employing modern quantum chemical techniques using the B3LYP Hartree–Fock/density functional hybrid approach combined with adequately sized basis sets we have studied the prototype toluene–chromium tricarbonyl complex **2** and the anionic, cationic, and radical reactive intermediates **3**, **4**, and **5**, respectively. The calculations unraveled important structural details such as the energy differences and the corresponding barriers between competing conformations concerning both the orientation of the Cr(CO)$_3$ tripod and the rotation around the exocyclic C–C bond. This knowledge paves the way for a deeper understanding of the effects governing the selectivity of synthetically important reactions of arene–Cr(CO)$_3$ complexes. A graphical summary of these data is given in Scheme 2.

In the charged intermediates **3** and **4** a significant delocalization of the positive or negative charge takes place, resulting in eminent structural changes and a variation in the hapticity of the metal–arene ligand binding: While the parent toluene complex realizes the expected η^6 interaction with the metal, η^5 and η^7 modes of bonding are computed for **3** and **4**, respectively. Also for the radical (**5**), a significant part of the spin density is delocalized to the chromium center. According to the common picture, which was earlier established based on indirect arguments, the calculations unequivocally demonstrate that the resonance structures **3′** and **4′** (see Scheme 1) better represent the electronic structure of these intermediates than formulas **3** and **4**. In addition, our results suggest that even the radical species **5** is best represented by the resonance structure **5′**.

An important consequence is the double-bond character of the exocyclic C–C bond in **3**, **4**, and **5** which results in substantial barriers for the rotation around this bond. This is the origin for the well-known configurational stability of the anionic and cationic species. Compared to **4** and **5**, the double-bond character of the exocyclic bond in the radical intermediate **5** is considerably less pronounced. However, the calculations suggest that the configurational stability of Cr(CO)$_3$-complexed benzylic radicals should be high enough to allow transformations of the type shown in Scheme 3.

If the abstraction of an atom X from an optically active substrate **6** would occur with anchimeric assistance of the



6 **7** **8**

Scheme 3. Schematical description of a radical reaction with retention of configuration.

metal to form the delocalized radical **7** (which represents a planar chiral structure) the stereospecific formation of the chiral product **8** would be achieved with an overall retention of configuration. This general possibility of achieving stereocontrolled radical substitution reactions at the benzylic position of complexed arenes is currently under investigation in our laboratory.

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