

Arene Hapticity in $(C_6H_6)Cr(CO)_n$ ($n = 1–5$) Complexes: A DFT Study of Singlet and Triplet Energy Surfaces

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DFT calculations were employed to investigate the mechanism of formation and the interconversion of reduced-hapticity $(\eta^x-C_6H_6)Cr(CO)_n$ complexes ($n = 1–5$, $x = 1–6$) on both singlet and triplet energy surfaces. A variety of functionals (mPW1k, B3LYP, B97-1, and BP86) and basis sets (SDD, SDB-cc-pVDZ, and LANL2DZ+P) were used. The same structures were consistently found for all functional/basis set combinations. The structures of the different singlet and triplet complexes and comparisons between their energies are described. On the basis of the structures and energies of the intermediates and the transition states found for singlet reduced-hapticity complexes, a mechanism for the decomposition of the $(\eta^6-C_6H_6)Cr(CO)_3$ complex to $Cr(CO)_6$ is suggested. This mechanism, which is closely related to the arene exchange reaction mechanism, involves the formation of $(\eta^1-C_6H_6)Cr(CO)_4$ and $(\eta^2-C_6H_6)Cr(CO)_5$ complexes as ring-slippage intermediates along the pathway for the complete replacement of the benzene ring by carbonyl ligands. The barriers found for the ring-slippage process are accessible under mild conditions. Triplet reduced-hapticity complexes have different structures; however, they are similar in energy to the analogous singlet complexes. Formation of triplet reduced-hapticity complexes might take place in reactions of $(\eta^6-C_6H_6)Cr(CO)_3$ initiated by photolysis, which have been reported to show no observable decomposition to $Cr(CO)_6$.

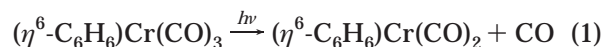
Introduction

Activation of arenes by complexation with metals through the π -system is important in several processes, such as arene hydrogenation, functionalization, and various coupling processes.¹ In particular, functionalization of arenes using (arene) $Cr(CO)_3$ complexes is an important process, which has been extensively studied.²

In 1966 Basolo et al.³ proposed ring-slippage species as possible intermediates in arene exchange reactions. For more than 30 years, this area has been intensively studied because of fundamental interest in these novel intermediates and their relevance to arene exchange and activation reactions.⁴

Nevertheless, reduced arene hapticity in chromium carbonyl complexes is still a controversial matter. Infrared spectroscopic studies of the solvolysis of a naphthalene complex in THF have been cited as evidence for $(\eta^4$ -naphthalene) $Cr(CO)_3$ (THF).⁵ However, in 1991, Howell et al.⁶ found no evidence for a discrete η^4

intermediate in this and related systems but suggested stable η^1 and η^2 intermediates based on molecular orbital calculations at the extended Hückel level. In 1994 Basolo et al. reported⁷ that they found no direct evidence for an η^4 intermediate of the type $(\eta^4$ -naphthalene) $Cr(CO)_3$ (THF). However, interestingly, the dianion complex $[(\eta^4-C_6H_6)Cr(CO)_3]^{2-}$ is known⁸ and other stable η^4 -naphthalene complexes were recently prepared and characterized for several metals, but not for $Cr(0)$.^{9,10} Photoinduced ring slippage in (arene) $Cr(CO)_3$ and related systems has also been investigated. There have been reports on the photochemistry of $(\eta^6-C_6H_6)Cr(CO)_3$ that date back to 1963.¹¹ CO loss (reaction 1) is reported to be the dominant photoinduced process in low-temperature matrices,¹² room-temperature solutions,^{12,13} and the gas phase.¹⁴



On the basis of indirect evidence, McGrath suggested that an additional photoproduct, possibly one involving

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a haptotropic, or “ring-slippage”, process may also be formed during photolysis of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$.¹⁵ Furthermore, a photoinduced “ring-slippage” product, $(\eta^1\text{-C}_5\text{H}_5\text{N})\text{Cr}(\text{CO})_5$, was observed in both low-temperature matrices and in room-temperature solution studies of the $(\eta^6\text{-C}_5\text{H}_5\text{N})\text{Cr}(\text{CO})_3$ complex.¹⁶ Despite these recent reports of ring-slipped intermediates, little insight has been obtained for the arene ring-slippage mechanism.⁶

It was suggested that the ring-slippage process in arene exchange involves the gradual change in hapticity $\eta^6 \rightarrow \eta^4 \rightarrow \eta^2$ during the reaction;¹⁷ however, no direct evidence was provided. It is highly desirable to understand the nature of reduced-hapticity complexes in the arene exchange reaction, as well as their structure, relative stability, and interconversion, especially in (arene)Cr(CO)₃ type complexes, which represent important reagents for aromatic ring functionalization.²

The reactivity of (arene)Cr(CO)₃ type complexes varies as a function of the experimental conditions for the activation reaction. In general, thermochemical¹⁸ and steady-state photolysis^{16,19} reactions result in the decomposition of (arene)Cr(CO)₃ to Cr(CO)₆ when excess CO is present. However, under most circumstances laser flash photolysis has been reported to result in the regeneration of the parent complex, (arene)Cr(CO)₃ (even when a large excess of CO is present).^{13c,14} Both thermochemical^{16,17} and photochemical^{15,16} reactions, however, were suggested to involve formation of reduced-hapticity complexes. Photoinduced reactions might promote spin-flip transitions as a result of formation of excited states, and these spin-flip transitions might account for part of the reactivity observed in photochemical reactions. There have been laser flash photolysis studies on the reactivity of (arene)Cr(CO)₃ which suggest the involvement of spin-flip transitions.^{14a} However, theoretical studies considering high-spin intermediates of (arene)Cr(CO)₃ type complexes reactions are scarce.²⁰

Here we report a density functional theory (DFT) study on the reduced-hapticity intermediates involved in the decomposition of (arene)Cr(CO)₃. The mechanism

of their formation and interconversion was also investigated. To the best of our knowledge, these are the first investigations of reduced-hapticity complexes (arene)Cr(CO)₃ for both singlet and triplet energy surfaces.

Results

DFT by means of the Gaussian98 program package²¹ was employed to calculate the structure and relative stability of the unsaturated complexes that could be formed during activation of the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ complex. Both reduced-hapticity complexes and ligand dissociation complexes were considered and thoroughly searched for, and the relative stabilities of the resulting complexes and their geometries were compared. Both singlet and triplet multiplicity surfaces were investigated.

I. Singlet Complexes. Four different functionals and three different basis sets were used for geometry optimizations and energy calculations: functionals, mPW1k, B3LYP, BP86 and BP97-1; basis sets, SDD, SDB-cc-pVDZ, and LANL2DZ+P (for details see Computational Methods). The results for all functionals/basis sets were qualitatively similar and are summarized in Figures 1 and 2.

The known complex **1**, $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$,²² was found and taken as a zero energy reference point for all other compounds.

(a) Carbonyl Dissociation Complexes. In general, for all the complexes, the more saturated, the more energetically stable. Thus, dissociation of CO from the (arene)Cr(CO)₃ complex results in the formation of unsaturated compounds that are expected to be highly reactive. Two complexes involving CO loss, $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$ (**2**) and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})$ (**3**), were searched for and found as local minima.²³ Their relative energies were found to be ~40 and ~80 kcal/mol higher, respectively, than that of the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ complex **1**. These values, which represent bond dissociation enthalpies, are similar to those reported in previous experimental and theoretical studies.²⁴ The structures (Figure 3) and relative energies of **2** and **3** were similar for all functional/basis set levels of theory (Figures 1 and 2). The Cr–CO and the C–O bond distances increased slightly in **3** compared to **1**. Thus, the Cr–CO bond distance in **3** (1.183 Å) was longer than that in complex **1** (1.181 Å), and the C–O bond distance in **3** (1.178 Å) was longer than the analogous bond in **1** (1.172 Å). This might be explained by a larger π -back-donation per CO

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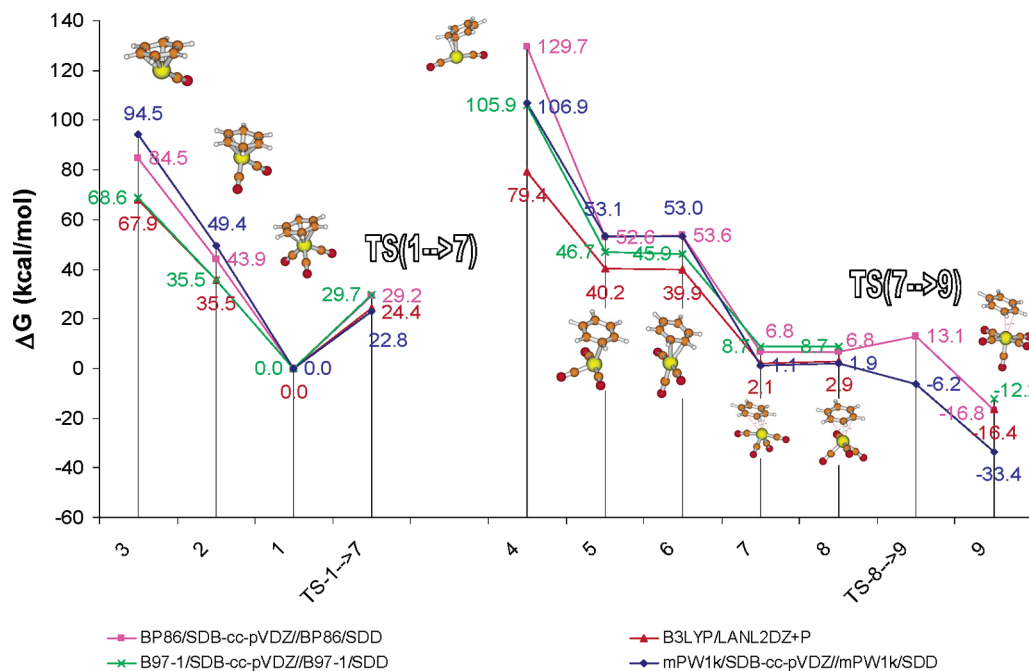


Figure 1. Relative ΔG_{298} (kcal/mol) values for the various singlet spin intermediates and transition states found for $(\eta^x-C_6H_6)Cr(CO)_y$ complexes.

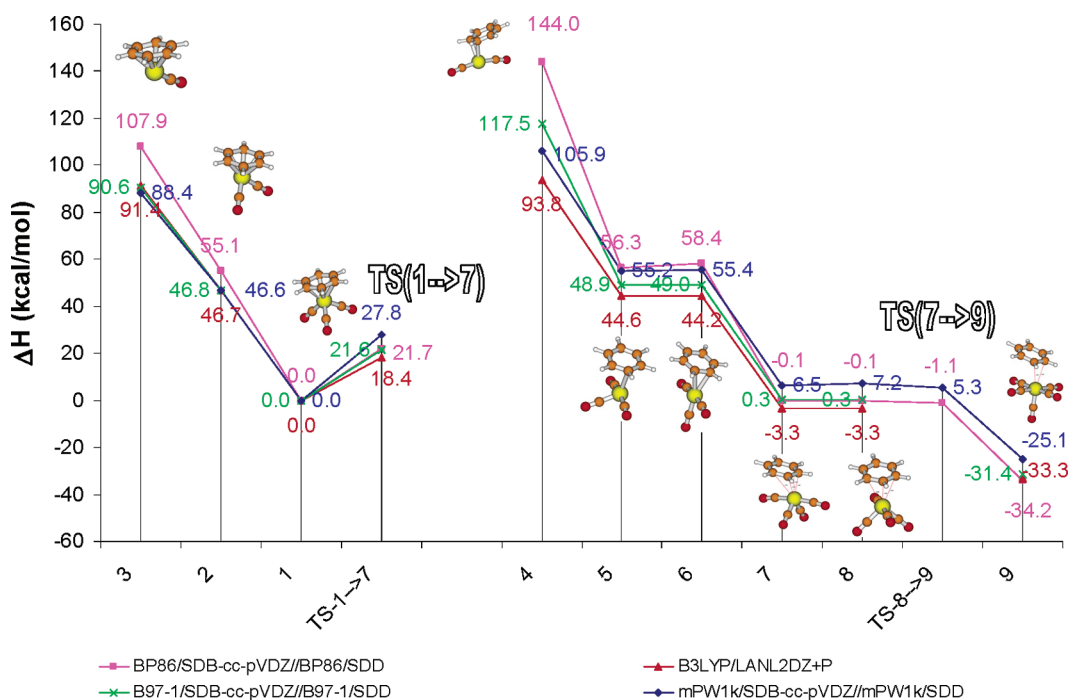


Figure 2. Relative ΔH_{298} (kcal/mol) values for the various singlet spin intermediates and transition states found for $(\eta^x-C_6H_6)Cr(CO)_y$ complexes.

ligand in **3** in comparison to **1**, resulting in a larger C–O bond distance. No TS was found for CO ligand dissociation processes.²⁵

(b) Reduced Hapticity Complexes. The reduced-hapticity complexes found for the $(\eta^x-C_6H_6)Cr(CO)_n$ ($x = 1-4$; $n = 2-5$) system are described by going from the most unsaturated (arene)Cr(CO)₂ configuration considered here²⁶ to the saturated (arene)Cr(CO)₅ com-

plex (Figure 3). The hapticity suggested for the observed complex structures was verified by comparing bond lengths and Wiberg indices obtained from NBO calculations (for natural population analysis (NPA) Wiberg bond orders, see the Supporting Information).

The search for reduced hapticity in (arene)Cr(CO)₂ complexes resulted in the exclusive convergence to the η^2 -arene complex $(\eta^2-C_6H_6)Cr(CO)_2$ (**4**). This formally 12-electron complex was found to be ~100 kcal/mol less

(25) Transition states are normally difficult to find for association and dissociation of ligands, since that process mostly involves entropic contributions, which cannot then be calculated using the a bottom-of-the-well energy surface.

(26) The (arene)Cr(CO) and (arene)Cr configurations were not considered, due to their expected high instability and low probability to be produced in most of the reactions.

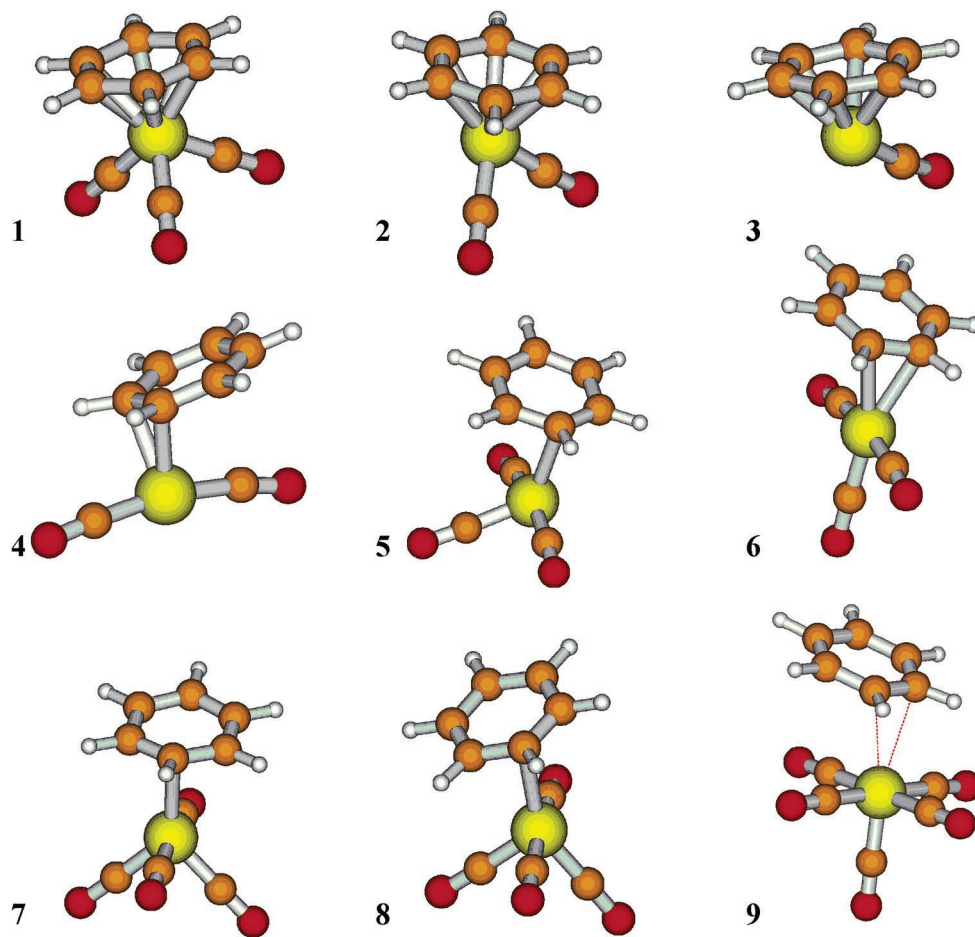


Figure 3. Structures of the singlet complexes found at the mPW1k/SDD level of theory.

stable than the parent ($\eta^6\text{-C}_6\text{H}_6$)Cr(CO)₃ complex **1**. Its stability is comparable to that of the highly unsaturated complex **3**. The structure of complex **4** is distorted trigonal, as shown in Figure 3. It involves a rather short Cr–C_{arene} bond of 2.2 Å and a reduced aromaticity of the benzene ring, as indicated by the 13° H–C–C–H dihedral angle (0° in fully aromatic benzene). No other reduced-hapticity complexes were found with two carbonyl ligands.

For the ($\eta^x\text{-C}_6\text{H}_6$)Cr(CO)₃ group of complexes, two slipped species were found, the ($\eta^1\text{-C}_6\text{H}_6$)- and ($\eta^2\text{-C}_6\text{H}_6$)-Cr(CO)₃ complexes. The ($\eta^1\text{-C}_6\text{H}_6$)Cr(CO)₃ complex (**5**) is distorted tetrahedral, and the ($\eta^2\text{-C}_6\text{H}_6$)Cr(CO)₃ complex (**6**) is square planar (Figure 3). Both complexes have comparable energies that are ~45 kcal/mol higher than that of the reference complex, ($\eta^6\text{-C}_6\text{H}_6$)Cr(CO)₃. The barrier for their interconversion was found to be low ($\Delta G_{5-6}^\ddagger \approx 1.5$ kcal/mol). Both are formally 14-electron complexes and thus should be highly reactive. A square-planar geometry for d⁶ 14-electron complexes, as in **6**, is very unusual; we are aware of only one example of a stable d⁶ 14-electron square-planar complex of Ru.²⁷ The geometry of the η^1 -arene complex **5** demonstrates an aromatic ring more distorted than that in the η^2 -arene complex **6**, as indicated by a 10° H–C–C–H dihedral angle in **5** compared to 7° in **6**. The Cr–C_{arene} bond distance is shorter in the η^1 complex **5** (2.28

vs 2.42 Å in **6**). On the basis of natural population analysis (NPA) calculations, apparently the arene is twice as positively charged in complex **6** as in **5** (+0.131 vs +0.065 in **5**). This is probably due to the coordination to Cr through two carbons in **6** rather than through one carbon in **5**. η^1 coordination in (arene)Cr(CO)₃ complexes was found in the extended Hückel studies of Howell et al.⁶ It should be noted that the $\eta^1(\text{C}-\text{Cr})$ Wiberg bond order in complex **5** is relatively low (0.17). The bond lengths, bond angles, and natural charges in the arene ring of **5** suggest largely aromatic character. Significantly, the distortion from planarity in the $\eta^1(\text{C})$ -coordinated arene in complex **5** is small (10°, compared to 40° distortion in other reported arenium complexes²⁸). Thus, complex **5** cannot be considered a true arenium compound.²⁹ The search for an η^4 -arene coordination mode resulted in convergence to η^1 - and η^2 -arene complexes. Remarkably, we found η^4 -arene coordination in the case of the [η^4 -arene]Cr(CO)₃²⁻ complex (experimentally suggested to exist);⁸ however, when the charge was removed, the η^4 coordination converged to η^1 . The existence of η^4 -arene coordination in the dianion [η^4 -arene]Cr(CO)₃²⁻ can be explained by π -back-donation from the electron-rich chromium center to the arene, resulting in a stronger Cr–arene bond. This back-donation compensates for the significant loss of aromaticity resulting from η^4 -arene coordination.

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A search for reduced-hapticity $(\eta^x-C_6H_6)Cr(CO)_4$ ($x = 1-4$) configurations revealed two η^1 -arene complexes. Both have very similar geometry regarding bond distances and angles; however, the $(\eta^1-C_6H_6)Cr(CO)_4$ complex **7** is symmetric along the Cr–C_{arene} bond and complex **8** is not (Figure 3). Both complexes have similar energies, which are ~ 5 kcal/mol higher than for the $(\eta^6-C_6H_6)Cr(CO)_3$ complex. Accordingly, the stability of the η^1 species, albeit unsaturated, with a formal 16-electron count, is only slightly lower than for the saturated complex **1** $(\eta^6-C_6H_6)Cr(CO)_3$. This could suggest that, in the presence of an excess of CO, such slipped species can be formed and can be relatively stable. As in the case of $(\eta^1-C_6H_6)Cr(CO)_3$, here the η^1 -arene complexes show some distortion in the aromatic ring. In the symmetric complex **7**, the ring is more distorted than in **8**, as indicated by the H–C–C–H angle, which is 10° in **7** and only 5° in **8**. The Cr–C_{arene} bond distance is shorter in **7** than in **8** (2.35 vs 2.41 Å in **8**). Thus, as the Cr–C_{arene} bond is shorter, the aromaticity loss is larger, as was indicated for **4–8**. On the basis of the natural population analysis (NPA) calculation, the coordinated arene in complexes **7** and **8** is slightly positively charged (0.15+), whereas the Cr center is negatively charged (0.73–). However, the coordinated benzene cannot be regarded as a true arenium complex, since the distortion from the aromatic benzene structure is negligible, as indicated by its bond lengths, angles, and natural charges. An $(\eta^4-C_6H_6)Cr(CO)_4$ complex was never found as a local minimum, despite a thorough search. Attempts to find $\eta^4-C_6H_6$ complexes in different functionals or basis sets resulted in the convergence to $\eta^1-C_6H_6$ for all functional/basis set levels of theory.

The last ring-slippage complex found in the singlet case is the saturated $(\eta^2-C_6H_6)Cr(CO)_5$ complex **9**. In this complex the η^2 -arene coordination is rather weak, with a Cr–C_{arene} bond distance of 2.71 Å (compared to 2.35 Å in **7** and 2.41 Å in **8**). This formally 18e octahedral complex was found to be ~ 20 kcal/mol more stable than complex **1**. It is known that in the presence of excess CO this complex rapidly decomposes to form the more stable $Cr(CO)_6$ complex.³⁰

To understand the mechanism involved in the ring-slippage process in this system, we searched for barriers between the different complexes. The transition state **TS(1–8)** for the simultaneous association of one CO ligand and ring slippage from $\eta^6-C_6H_6$ coordination in **1** to $\eta^1-C_6H_6$ in **8** was located. The barrier for this concurrent slippage and ligand association was found to be ~ 25 kcal/mol. We could not locate a transition state for ring slippage without concurrent CO association: i.e., from **1** to either **5** or **6**. However, such a transition state cannot be ruled out. In any case, the barrier **TS(1–5,6)** is expected to be much higher in energy than that for **TS(1–8)**, due to the larger energy difference between **1** and **5** or **6** ($\Delta G \approx 45$ kcal/mol) than between **1** and **7** or **8** ($\Delta G \approx 5$ kcal/mol). Thus, such a transition state is probably not involved in the ring-slippage mechanism in the $(C_6H_6)Cr(CO)_3$ system.

Following an extensive search for a transition state connecting complex **8** (or **7**) with complex **9**, it was found

at two out of four functional/basis set levels of theory considered.³¹ The transition state was found to be low ($\sim 0-13$ kcal/mol), suggesting a facile coordination of a CO ligand concurrent with slippage from an η^1 - to an $\eta^2-C_6H_6$ coordination mode. Thus, in the presence of an excess of CO such an intermediate (**9**) is expected to be formed and to rapidly decompose to form the $Cr(CO)_6$ complex, in agreement with experimental reports.³⁰

Decomposition of $(\eta^6-C_6H_6)Cr(CO)_3$ to $Cr(CO)_6$ was reported, and a proposed mechanism including a ring slippage process was suggested.^{17,32} However, only limited information regarding the reduced hapticity intermediates of this reaction was provided.⁶ Here we suggest the energetically feasible pathway (**1** \rightarrow **7** \rightarrow **9** \rightarrow $Cr(CO)_6$) for decomposition of $(\eta^6-C_6H_6)Cr(CO)_3$ to $Cr(CO)_6$ through the formation of reduced-hapticity complexes such as $(\eta^1-C_6H_6)Cr(CO)_4$ and $(\eta^2-C_6H_6)Cr(CO)_5$. A graphic presentation of the mechanism proposed for decomposition of $(\eta^6-C_6H_6)Cr(CO)_3$ to $Cr(CO)_6$, including barriers for such transitions, is presented in Figure 4.

II. Triplet Complexes. In some cases, decomposition of $(\eta^6-C_6H_6)Cr(CO)_3$ does not produce $Cr(CO)_6$. In photoinduced reactions in the gas phase, activation of $(\eta^6-C_6H_6)Cr(CO)_3$ generates transient species, which eventually convert to the parent complex, $(\eta^6-C_6H_6)Cr(CO)_3$.^{13c,14} This suggests that a different mechanism may be involved in photoinduced reactions. This could result from spin-flip transitions suggested to take place in photoinduced metal carbonyl reactions.³⁴ If as a result of excitation a spin flip is involved, generation of triplet spin reduced-hapticity complexes is possible. Generation of high-spin (arene)chromium carbonyl complexes in the gas phase was suggested.^{14,20}

As in the case of reduced-hapticity singlet spin complexes we seek analogous triplet complexes which can be compared in terms of their stability and structures to the singlets. It is known that electronically unsaturated, open-shell configurations tend to be more common for early first-row transition metals (usually in a high oxidation state), such as chromium. Less mixing of spin states would be expected for lighter transition metals.³⁵ Thus, the effect of spin on a chemical reaction is best probed in complexes of these metals. In addition, photoinduced reactions are more likely to promote spin-forbidden transitions, due to the involvement of excited states.³⁶

The triplet complexes were found and compared using various functional/basis set levels of theory. The geometries and energies of the different triplet complexes are

(31) This could result from a very shallow PES for this transition state search, which could be located for one functional but not for another. Ligand dissociation and hapticity changes involve large entropic contributions, which cannot then be calculated using the bottom-of-the-well energy surface.

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(33) The transition state leading to **9** appears to rest below the intermediate, **7** ($\Delta G^\ddagger = -7.3$ kcal/mol). It should be noted that using the mPW1k/SDD optimized geometry for the mPW1k/SDB-cc-pVDZ energy profile is an approximation that can lead to errors, especially in cases of small energy differences. Furthermore, the correction to the energy used to calculate G_{298} is based upon the rigid-rotor-harmonic-oscillator approximation. At the mPW1k/SDD level of calculation the energy value for this transition state is $\Delta G^\ddagger = 4.7$ kcal/mol.

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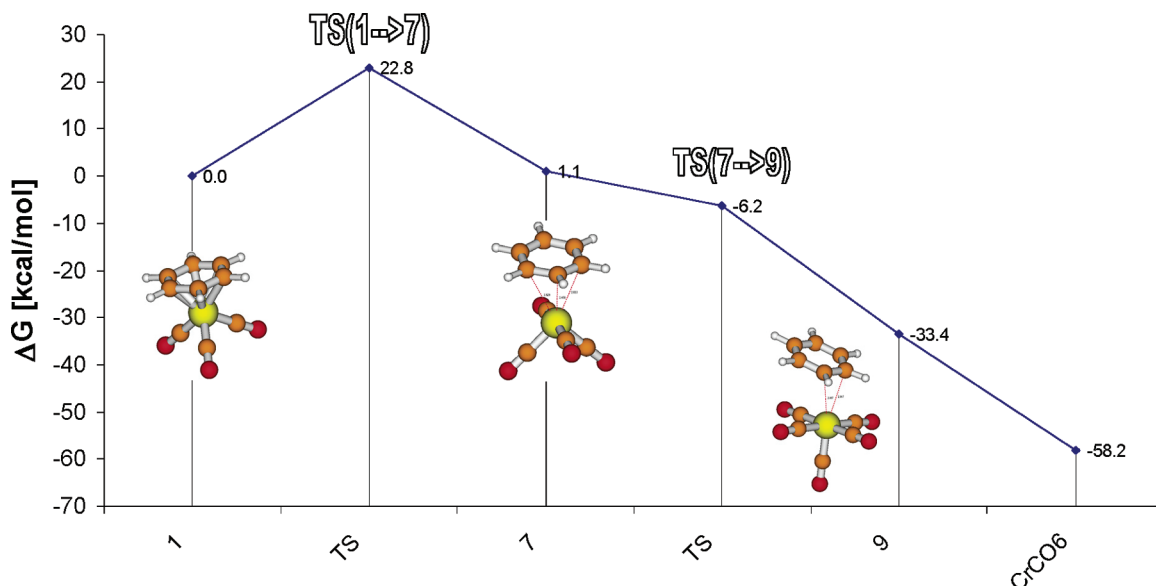


Figure 4. Proposed mechanism for decomposition of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ to $\text{Cr}(\text{CO})_6$ and relative ΔG_{298} (kcal/mol) energies at the mPW1k/SDB-cc-pVDZ//mPW1k/SDD level of theory.³³

qualitatively comparable for all functional/basis set combinations. The hapticity suggested for the observed complex structures was verified by comparing bond lengths and Wiberg indices obtained from NBO calculations (for NPA Wiberg bond orders, see the Supporting Information). A summary of these results is presented in Figure 5.

Triplet spin 16-electron complexes are the “saturated” analogues of the 18-electron singlet spin complexes, since an empty orbital is needed to accommodate an unpaired electron. However, these complexes also resemble diradicals and thus would be expected to be more reactive than their singlet saturated analogues. Thus, $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ (complex **1**) and $(\eta^2\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_5$

(complex **9**), which are formally 18-electron saturated complexes, cannot exist as triplets and were not found in our calculations. Reduced-hapticity complexes, similar to those found as singlets, were found as triplets with slightly different geometries and energies. Some additional reduced-hapticity complexes were found as well. Variation of the functional did not significantly change the energy or the geometry of the triplet compounds. The structures of the different complexes are illustrated in Figure 6.

(a) Ligand Dissociation Complexes. The CO dissociation products $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$ (**10**) and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})$ (**11**) were found as triplets. The geometry of the triplet complex **10** is more symmetric than that for the

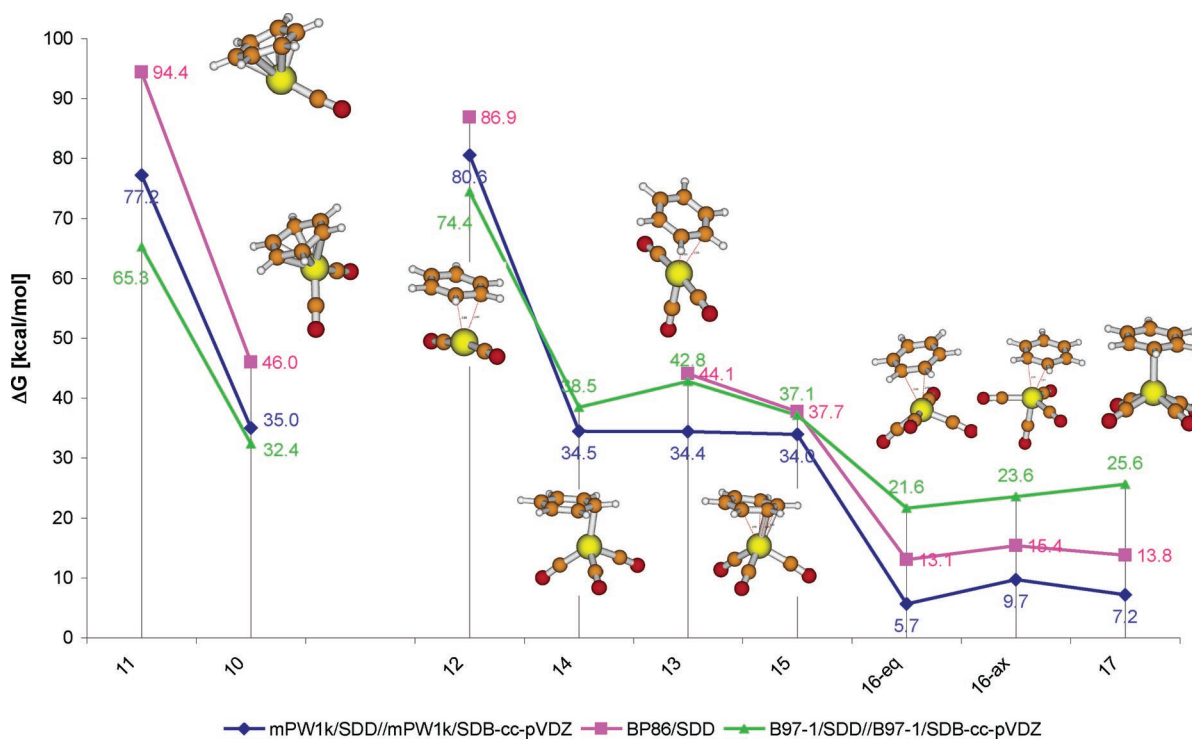


Figure 5. Relative ΔG_{298} (kcal/mol) values for the various triplet spin intermediates found for $(\eta^x\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_y$ complexes. Energy values are compared to $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ as a zero energy reference point.

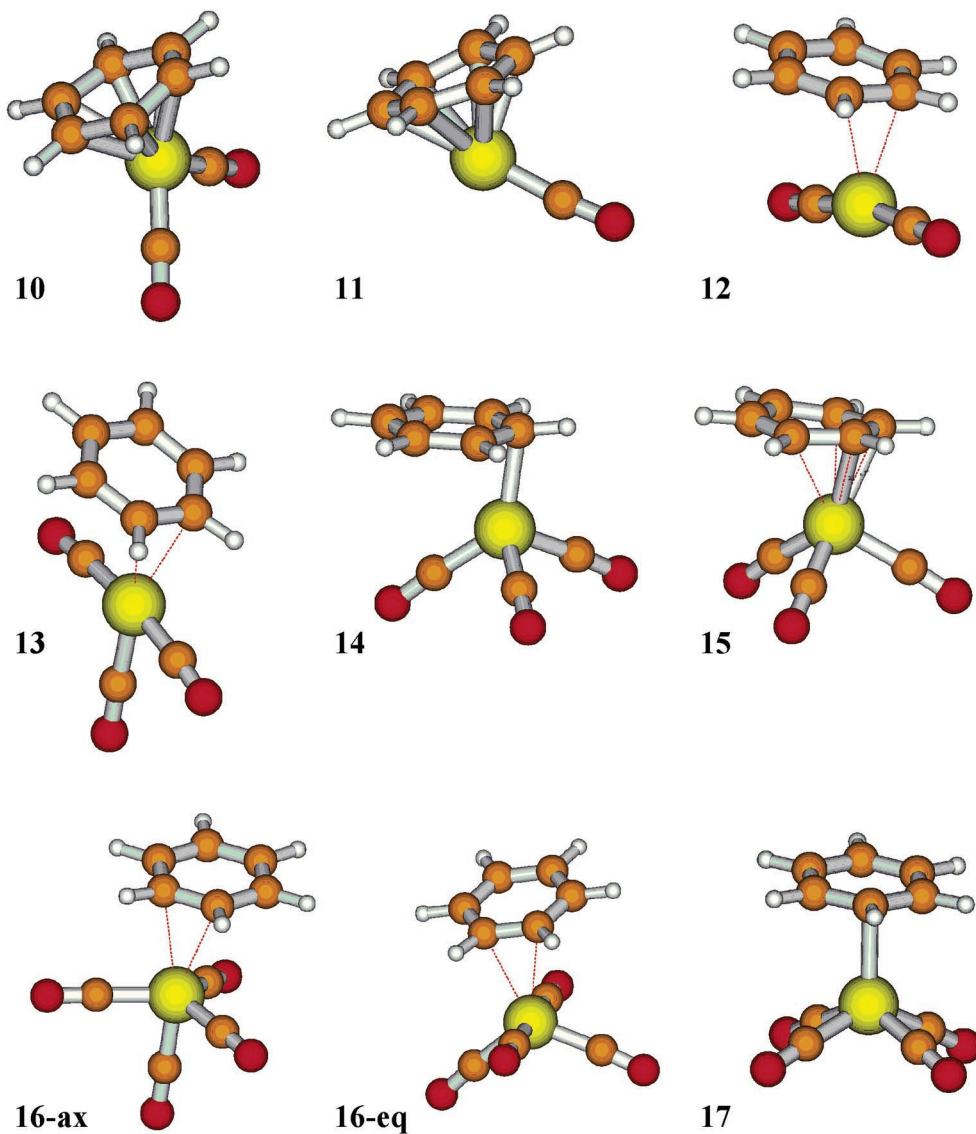


Figure 6. Structures of the triplet complexes found at the mPW1k/SDD level of theory.

singlet complex **2** (Figure 5). Thus, complex **10** has a symmetric trigonal geometry, while **2** has a largely distorted one. The different symmetry found for the computed triplet vs singlet CO dissociation complexes $(arene)Cr(CO)_x$ was discussed elsewhere.²⁰ The stabilities of **10** and **11** are comparable to those for the analogous singlet species **2** and **3**. Thus, complex **10** is less stable than **1** by 30–45 kcal/mol and complex **11** is destabilized in comparison to **1** by 60–95 kcal/mol (depending on the functional/basis set used) (Figure 5).

(b) Reduced-Hapticity Complexes. The following reduced-hapticity complexes were found. For the $(\eta^x-C_6H_6)Cr(CO)_2$ configuration, only one local minimum was found: a slipped $(\eta^2-C_6H_6)Cr(CO)_2$ complex (**12**) with a geometry similar to that of the analogous singlet species **4**. The energy of this complex is, however, much lower than that of the singlet complex **4** (by 15–40 kcal/mol depending on the functional/basis set level of theory used). The Cr–C_{arene} bond distance in **12**, however, is much longer than that in **4** (2.5 vs 2.2 Å in **4**), and the aromaticity of the benzene is also much less influenced by the η^2 coordination than that in **4**, as indicated by an H–C–C–H dihedral angle of 6° vs 13° (**4**).

For the $(\eta^x-C_6H_6)Cr(CO)_3$ configuration, three different slipped triplet complexes were found. (1) The first was the complex $(\eta^2-C_6H_6)Cr(CO)_3$ (**13**), which has a geometry similar to that of the corresponding singlet complex **6**. The stability of this triplet complex is higher than that of **6** (by 10–20 kcal/mol depending on the functional used). The Cr–C_{arene} bond in complex **13** is longer than the analogous Cr–C_{arene} bond in **6** (2.5 vs 2.4 Å in **6**), and for complex **12**, the aromaticity of the benzene is less affected by the coordination, as indicated by a smaller H–C–C–H dihedral angle of 4° vs 7° in **6**. (2) A second complex, $(\eta^1-C_6H_6)Cr(CO)_3$ (**14**), is tetrahedral³⁷ (found only in the hybrid functionals mPW1k and B97-1) and has a geometry very different from that of the η^1 singlet complex **5**. However, the Cr–C_{arene} bond distance in **14** (2.3 Å) is comparable to the analogous bond distance in **5**. Both the η^1 and η^2 triplet complexes are formally 14-electron complexes that have different geometries but are of comparable stability. (3) An $(\eta^4-C_6H_6)Cr(CO)_3$ complex (**15**) was also found.³⁸ This

(37) Complex **14** can be also regarded as an η^3 -arene, due to the relatively short Cr–C_{arene} distances of 2.6 Å to the two carbons adjacent to the coordinated one.

is the only η^4 complex found so far for the $(\eta^x\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_n$ system. The aromatic ring in **15** is distorted from planarity. However, the distortion is not as large as would typically be expected for an η^4 -arene coordination, as indicated by the relatively small C–C–C dihedral angle in the benzene ring.^{10b} Surprisingly, although **15** is formally “saturated” (16e complex), its energy is very similar to that for the unsaturated (14e) $(\eta^2\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ and $(\eta^1\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ complexes **13** and **14**, respectively. Consequently, the energy differences between the η^2 , η^1 , and η^4 complexes **13**, **14**, and **15** are small.

Three different geometries were found for the $(\eta^x\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_4$ configuration complexes. Two have a trigonal-bipyramidal geometry: (1) $(\eta^2\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_4$ (**16-eq**), in which the benzene is coordinated in an equatorial position, and (2) the analogous complex **16-ax**, in which the benzene is coordinated in an axial position (*trans* to CO). Complex **16-eq** is more stable (by 2–3 kcal/mol) than **16-ax** for all functionals, probably due to a stronger *trans* effect of the arene ligand as compared to the CO ligand. (3) The $(\eta^1\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_4$ complex (**17**) has a distorted-square-pyramidal geometry in which the benzene is coordinated *trans* to an empty coordination site. The Cr–C_{arene} bond distance in this complex is 2.3 Å, which is shorter than the Cr–C_{arene} bond distance in **16** (2.6 Å in both **16-eq** and **16-ax**). These three complexes, although different in geometry, have comparable stabilities, and they all are 10–15 kcal/mol higher in energy than the reference $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ complex **1**.

III. Comparison between Singlets and Triplets.

Finding transition states connecting triplet and singlet surfaces is beyond the scope of this work. A search for a spin-flip transition barrier should involve a special calculation of the minimum energy crossing points between the energy surfaces involved in singlet and triplet pathways.³⁵ A summary of the free energy results including both singlets and triplets is shown in Figure 7.

From the figure it can be seen that the relative energies of triplets and singlets are qualitatively similar. Before the singlet and triplet potential energy surfaces can be compared, several issues of computational accuracy should be considered. It is known that the local spin density (LDA) DFT functional tends to exaggerate the stability of low spin states (singlets in this case), gradient-corrected functionals (GGA) (such as BP86) give an intermediate behavior, although still weakly biased toward singlet states, and hybrid functionals (such as mPW1k, B3LYP, and B97-1) tend to increase the relative stability of the high-spin states (triplets in this case), as the proportion of HF exchange is increased above 15%.^{35,39,40} Thus, in mPW1k and B97-1 results, the stability of the triplets is probably exaggerated (this is more pronounced in mPW1k results, since the proportion of HF is larger in this case), whereas BP86 results are somewhat biased toward the singlets.

When the accuracy is taken into account, on comparison of the stabilities of the singlets and the triplets for

the same functional, it can be seen that, in general, as the complex becomes less saturated, the stability of the triplets relative to the singlets is higher, and as the complex is more saturated, the stability of the singlets rises. This is qualitatively consistent for all functionals. Consequently, both for the BP86 functional (GGA type) and for mPW1k or B97-1 (hybrid type) the $(\eta^x\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$, $(\eta^x\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$, and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})$ triplet complexes are more stable than the analogous singlets and the $(\eta^x\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_4$ singlets are more stable than the analogous triplets.

However, the energy differences between singlet and triplet spin complexes are not significant. Thus, according to our computational results, depending on the ability of the specific experimental system to undergo a spin-flip transition, either singlet or triplet reduced-hapticity complexes can be formed. The formation of some of the complexes also depends on the amount of free CO present in the reaction mixture. When a large excess is present, reduced-hapticity complexes such as **7–9** and **15–17** could form from unsaturated species.

Discussion

The different behaviors of the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ complex under different reaction conditions are not completely understood. Varied evidence for its reactivity/decomposition has been reported. Thus, in thermal reactions heated in solution or in a matrix,¹⁸ or for continuous photolysis in the UV range,¹⁹ the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ complex decomposes to the $\text{Cr}(\text{CO})_6$ complex. However, in gas-phase flash photolysis experiments in the UV range, transient intermediates are formed, but no significant decomposition to the $\text{Cr}(\text{CO})_6$ has been reported, and regeneration of the parent complex $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ is observed.^{13c,14} This suggests different mechanisms for the thermal chemistry vs the photochemistry of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$. Possible explanations for the different reactivities observed under different reaction conditions could be the ability of high-energy UV irradiation to promote spin-flip transitions among excited states of the complex, which are less likely to take place in thermal reactions.

Thus, in thermal reactions only singlet spin complexes may be involved. In this case, decomposition of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ to $\text{Cr}(\text{CO})_6$ appears to involve reduced-hapticity complexes. On the basis of our computational DFT results it can be seen that formation of $(\eta^1\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_4$ is easily accessible with a small barrier (of ~20 kcal/mol) from the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ complex. After its formation, in the presence of CO, the $(\eta^2\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_5$ complex can be formed with a low barrier. Similarly, another CO can substitute for the η^2 arene, resulting in the formation of the thermodynamically most stable product, $\text{Cr}(\text{CO})_6$. A general mechanism for $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ decomposition was suggested by Traylor et al.¹⁷ This mechanism proceeds by a stepwise ring displacement by CO with the help of increasing slippage: $\eta^6\text{-arene} \rightarrow \eta^4\text{-arene} \rightarrow \eta^2\text{-arene}$. This mechanism was also used to describe the arene exchange reaction mechanism (by displacement with arene instead of CO). Later, a more general mechanism for the arene exchange was suggested by Howell et al.⁶ on the basis of extended

(38) Complex **15** can be also regarded as a η^2 -arene, due to the longer Cr–C_{arene} distances of 2.6 Å to the two carbons adjacent to the coordinated ones.

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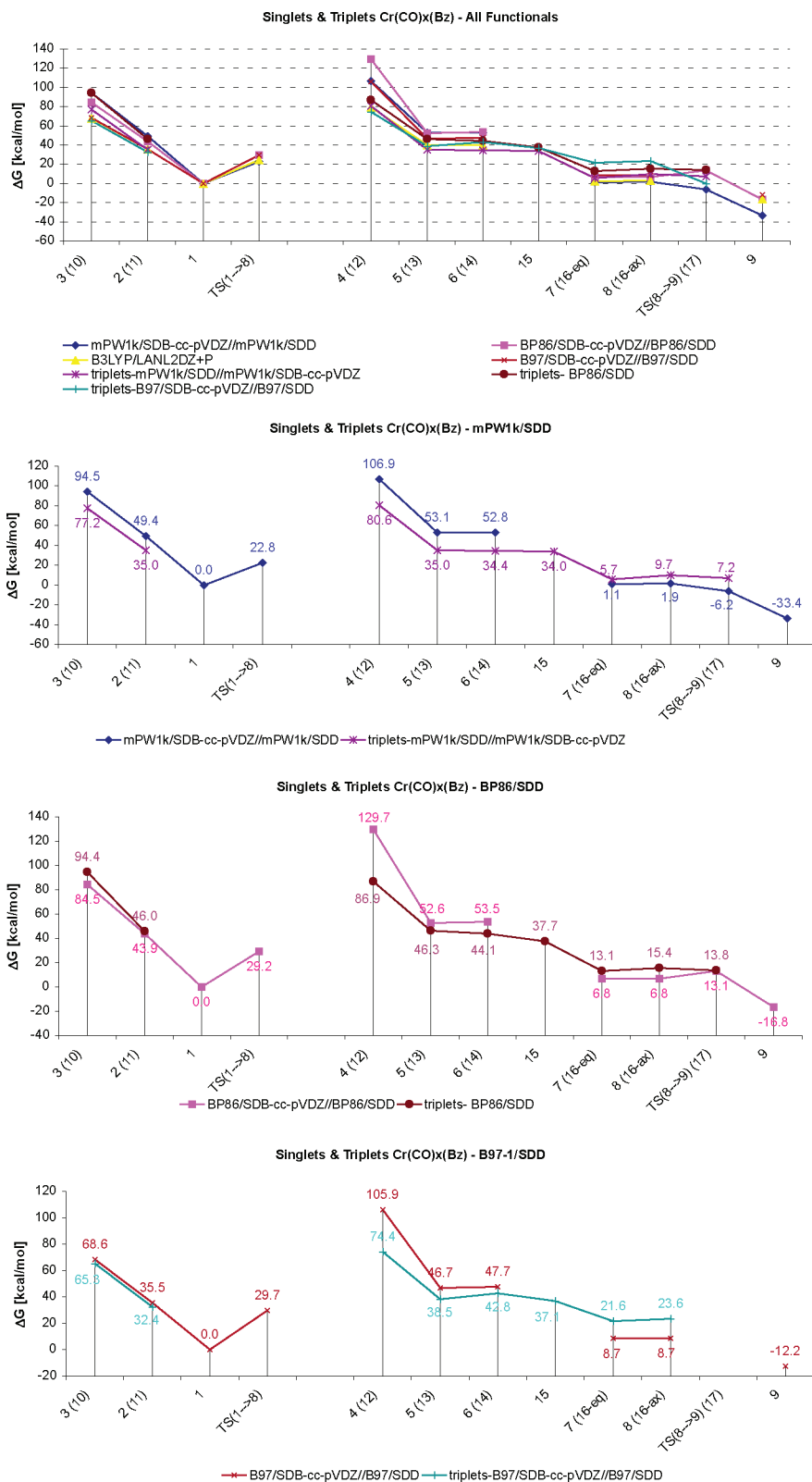


Figure 7. Relative ΔG_{298} (kcal/mol) values for the various singlet and triplet intermediates found for $(\eta^x-C_6H_6)Cr(CO)_y$ complexes.

Hückel calculations. This mechanism involves a step-wise arene displacement without specifying the exact reduced hapticity of the complexes. Our computational picture of transition states connecting the initial complex $(\eta^6-C_6H_6)Cr(CO)_3$ (**1**), the slipped complex $(\eta^1-C_6H_6)Cr(CO)_4$ (**8**), and the octahedral complex $(\eta^2-C_6H_6)Cr(CO)_5$ supports the mechanism proposed by Howell et

al. and extends it by specifying the reduced hapticity, geometries, and energies of the complexes involved. Decomposition of $(\eta^2-C_6H_6)Cr(CO)_5$ to $Cr(CO)_6$ is well-known and has been documented in solution and matrices.^{16,18,19} As suggested by Traylor et al.,¹⁷ this decomposition mechanism is closely related to the arene exchange reaction mechanism (exchanging CO and

arene). Thus, the arene exchange reaction, taking place in the functionalization of arenes by $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes, might also involve the formation of η^1 - and η^2 -arene reduced-hapticity intermediates, as found in our DFT studies.

In some cases, activation of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ does not lead to its decomposition to $\text{Cr}(\text{CO})_6$, even when a large excess of CO is present. On the basis of the computational results, reduced-hapticity triplet complexes are also relatively stable compared to the parent complex **1**; therefore, they might be formed if a spin-flip transition is involved in the activation of the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ complex. If a spin-forbidden process is involved in $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ activation and triplet species are being formed, decomposition of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ to $\text{Cr}(\text{CO})_6$ might not take place. In this case, the barrier to form the singlet complex **9** (which rapidly decomposes to $\text{Cr}(\text{CO})_6$) from any reduced-hapticity triplet complex depends on the barrier for a spin-forbidden CO association reaction to occur. Regeneration of the singlet spin $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ from any given reduced-hapticity triplet complex (such as $(\eta^x\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ or $(\eta^x\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_4$) is a spin-forbidden reaction. However, it might be more accessible than the reactions resulting in decomposition to $\text{Cr}(\text{CO})_6$. Thus, if a spin-flip transition is involved, although reduced-hapticity complexes could be formed, decomposition to $\text{Cr}(\text{CO})_6$ might not take place and regenerating the parent complex **1** from triplet slipped species might be easier, as observed in several experimental studies.^{13c,14} To verify this suggestion, accurate calculations of the minimum-energy crossing points between the different energy surfaces involved for singlet and triplet pathways should be conducted.

Conclusion

We have carried out a theoretical investigation of the relative energies and structures of the reduced-hapticity intermediates which can be formed in the decomposition (thermal and photochemical) of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$. A variety of functionals and basis sets were used for the calculations. Our calculations show that the reduced-hapticity complexes of the type $(\eta^x\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_y$ can be formed either as singlets or as triplets. A mechanism for the decomposition of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ to $\text{Cr}(\text{CO})_6$ based on ring-slippage processes for singlet spin complexes is proposed. We suggested an alternative scheme involving the formation of triplet spin complexes, for flash photolysis reactions, in which no such decomposition is observed.

Computational Methods

All calculations were carried out using the Gaussian 98 program revision A.11²¹ running on a mini-farm of Pentium IV Xeon 1.7/2.0 GHz PC's running Red Hat Linux 7.2 in our group in the Weizmann Institute of Science and on the Faculty of Chemistry Linux PC Farm at the Weizmann Institute of Science.

The mPW1k (modified Perdew–Wang 1-parameter for kinetics) exchange–correlation functional of Truhlar and co-workers⁴¹ and the BP86 and B97-1 exchange correlation functionals were employed in conjunction with the SDD and SDB-cc-pVDZ basis sets (see below). The mPW1k functional was very recently shown^{41–43} to yield more reliable reaction

barrier heights than other exchange–correlation functionals. The Becke97-1 (B97-1) DFT functional was used in the calculations,⁴⁴ as it has been shown that in some instances this functional is more suitable than, for example, B3LYP for determining molecular equilibrium properties.⁴⁵ BP86, Becke's 1988⁴⁶ functional for exchange and Perdew's 1986⁴⁷ functional for correlation, was shown to reproduce better experimental bond enthalpies than the B3LYP functional in systems similar to those studied in the present paper.⁴⁸

The SDD basis set is the combination of the Huzinaga–Dunning double- ζ basis set on lighter elements with the Stuttgart–Dresden basis set–relativistic effective core potential (RECP) combination⁴⁹ on the transition metals. The SDB-cc-pVDZ basis set combines the Dunning cc-pVDZ basis set⁵⁰ on the main-group elements with the Stuttgart–Dresden basis set–RECP combination⁴⁹ on the transition metals, with an f-type polarization exponent taken as the geometric average of the two f-exponents given in the Appendix to ref 51.

The energetics for our final reaction profiles, obtained from BP86, mPW1k, and B97-1 functionals with SDD basis set, were validated by single-point energy calculations, using the SDD reference geometries, with the extended SDB-cc-pVDZ basis set. The B3LYP⁵² exchange correlation functional together with the Los Alamos National Laboratory double- ζ (LANL2DZ+P) basis set–RECP combination was used,⁵³ where the “+P” stands for the addition of polarization functions with exponents taken from ref 54.

Geometry optimizations for minima were carried out using the standard Schlegel algorithm⁵⁵ in redundant internal coordinates, until in the neighborhood of the solution, and then continued using analytical second derivatives.⁵⁶ Optimizations for transition states were carried out with an initial guess for the transition state being generated from manual manipulation of the geometry using MOLDEN.⁵⁷ In cases where this approach failed to converge, we used analytical second derivatives at every step.

Zero-point and RRHO (rigid rotor–harmonic oscillator) thermal corrections (to obtain ΔS and ΔG values) were obtained from the unscaled computed frequencies.

Where necessary, the Grid = UltraFine combination, i.e., a pruned (99 × 590) grid in the integration and gradient steps

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and a pruned (50×194) grid in the CPKS (coupled perturbed Kohn–Sham) steps, was used as recommended in ref 58.

For interpretative purposes, atomic partial charges and Wiberg bond indices⁵⁹ were obtained by means of a Natural Population Analysis (NPA)⁶⁰ at the mPW1k/SDD level.

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Supporting Information Available: Tables giving XYZ coordinates of all computed structures and figures giving NPA Wiberg bond orders for complexes **4–9**, **12–15**, **16-ex**, **16-ax**, and **17**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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