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Bond Shift Isomerization in Cyclic and Acyclic (triene)Fe(CO)$_3$ Complexes. A Density Functional Study

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The 1,3-metal shift process has been studied for several conjugated cyclic and acyclic (η^4-triene)Fe(CO)$_3$ systems. In all cases the transition state of the process corresponds to (η^2-triene)Fe(CO)$_3$ structures. The computed energy barriers are notably higher for acyclic complexes than for the cyclic ones, in good agreement with the experimental observations. The analysis of the energy barriers shows that this is due to the different orientations of the triene ligand in the transition states, which leads to more efficient stabilizing metal−ligand orbital interactions for the cyclic systems.

Introduction

(Polyene)iron tricarbonyl complexes are important intermediates in organic synthesis.[1−8] The structure and conformational equilibrium of (butadiene)Fe(CO)$_3$ has been the subject of several theoretical studies.[9−14] In particular, the Fe−butadiene bond dissociation energy and the energy barrier for the turnstile rotation computed from density functional calculations are in excellent agreement with the experimental values.[12] More recently, the conformational equilibrium in several carbonyl- and olefin-substituted derivatives of (butadiene)Fe(CO)$_3$ has also been studied.[15]

When the polyene has more than two conjugated C−C double bonds, the corresponding complexes can present different bond shift isomers, depending on the site of attachment of the metal group. The interconversion between these structures is possible in solution. Experimental studies have shown that this bond shift isomerization is much faster for complexes of cyclic polyenes than for acyclic derivatives.[16−23]

Whitlock et al.[17] have studied this process for the acyclic (1-phenyl-6-tolyl-1,3,5-hexatriene)Fe(CO)$_3$ complex, obtaining an activation energy of 33 kcal mol^{-1}. They have postulated a mechanism involving the formation of a coordinatively unsaturated intermediate, with a η^2 coordination of the triene ligand. According to these authors, the process is slower for acyclic systems because the metal atom has to move along a longer distance than for cyclic systems.

Karel et al.[18] have extensively studied the fluxionality in (cycloheptatriene)iron tricarbonyl complexes from ^{1}H NMR spin saturation transfer experiments, obtaining an activation Gibbs energy of 22.3 kcal mol^{-1} for the parent compound. Theoretical calculations using the extended Hückel method were consistent with a mechanism involving the formation of coordinatively unsaturated (η^2-cycloheptatriene)Fe(CO)$_3$ species. A similar activation Gibbs energy has been obtained by Tajiri et al.[19] for the racemization of the (tropone)Fe(CO)$_3$ complex.

Substituted derivatives of (tropone)Fe(CO)$_3$ have also been studied.[20,22] In particular, Banwell and Schuhbauer[22] have studied the interconversion of several regioisomeric (bromotropone)Fe(CO)$_3$ complexes. For the 4-bromotropone complex, the bond shift isomerization takes place with an activation enthalpy of 22.9 kcal mol^{-1} at 323.15 K. On the other hand, the isomerization was not observed for the corresponding 3-bromotropone complex.

Given that the mechanisms for the bond shift isomerization of cyclic and acyclic (triene)Fe(CO)$_3$ complexes seem to be similar, the question of the different reaction rates arises. In this paper we present a theoretical study

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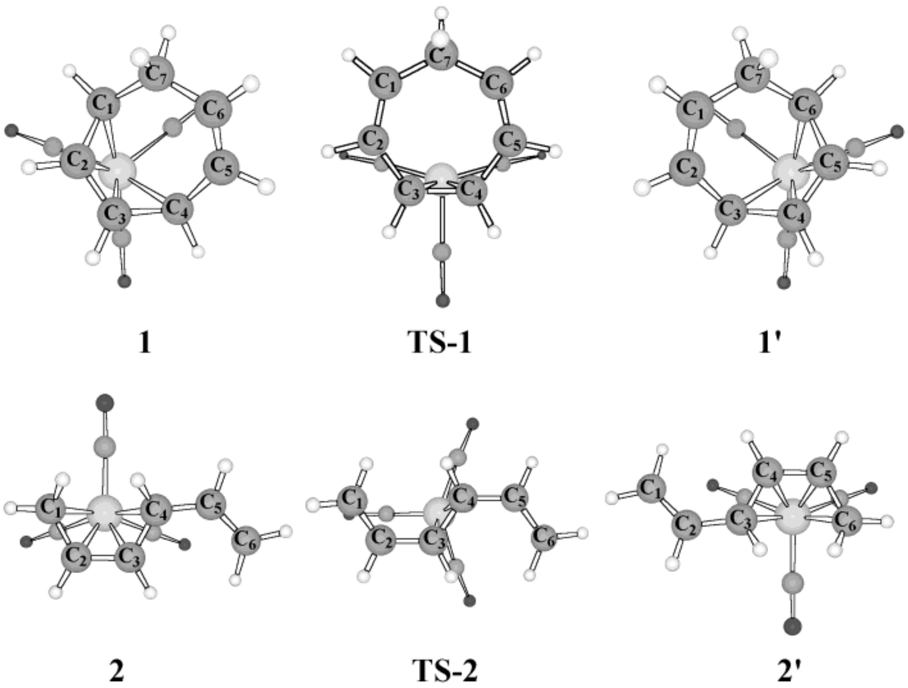

Figure 1. Optimized structures for the minima and the transition states of complexes **1** and **2**.

of this process in the acyclic (hexatriene)Fe(CO)$_3$ complex as well as in the cyclic cycloheptatriene, tropone, and bromotropone complexes.

Computational Details

Molecular geometries have been fully optimized at the generalized gradient approximation (GGA) level of calculation using Becke's exchange potential[24] and the correlation potential of Perdew[25] (BP86) implemented in the Gaussian-98 program.[26] For Fe we have used the effective core potentials of Hay and Wadt[27] for the inner shells (up to 2p) and a valence double-ζ basis set. For the remaining atoms we have used the D95 basis set[28] supplemented with a set of 3d polarization functions for C and O. All structures have been characterized as energy minima or transition states through the calculation of the harmonic vibrational frequencies. Energies have been recalculated from single-point calculations with the ADF program[29−31] using an uncontracted triple-ζ basis set of Slater type orbitals[32] supplemented with a set of 3d (C and O) and 2p (H) polarization functions. The 1s shell of C and O and the 1s2s2p shell of Fe have been treated by the frozen-core approximation.[30] All the reported energies correspond to the ADF calculations, whereas thermodynamic corrections have been calculated from Gaussian-98 harmonic frequencies.

Table 1. Selected Geometry Parameters[a] for 1,3,5-Cycloheptatriene, 1,3,5-Hexatriene and Their Complexes with Fe(CO)$_3$

	cyclohepta-triene	**1**	**TS-1**	hexa-triene	**2**	**TS-2**
Fe−C$_1$		2.147			2.117	
Fe−C$_2$		2.072	2.643		2.069	2.835
Fe−C$_3$		2.070	2.028		2.094	2.122
Fe−C$_4$		2.181	2.028		2.208	2.101
Fe−C$_5$			2.643			2.707
C$_1$−C$_2$	1.372	1.448	1.377	1.363	1.441	1.366
C$_2$−C$_3$	1.451	1.426	1.460	1.467	1.429	1.472
C$_3$−C$_4$	1.387	1.449	1.455	1.371	1.439	1.421
C$_4$−C$_5$	1.451	1.478	1.460	1.467	1.475	1.474
C$_5$−C$_6$	1.372	1.356	1.377	1.363	1.359	1.369
C$_6$−C$_7$	1.515	1.502	1.499			
C$_7$−C$_1$	1.515	1.524	1.499			

[a] Interatomic distances are given in angstroms. See Figure 1 for atom numbering.

Results and Discussion

We will first present the results corresponding to (cycloheptatriene)Fe(CO)$_3$ (**1**) and to (1,3,5-hexatriene)-Fe(CO)$_3$ (**2**). The optimized geometries of these complexes are represented in Figure 1. **1** has two enantiomeric structures (**1** and **1′**) which are connected through a transition state of C_s symmetry (**TS-1**). For **2** we present two equivalent structures (**2** and **2′**) with an *s-cis* arrangement of all C−C single bonds, since it is mandatory for Fe to be able to coordinate to both butadiene moieties of the triene. However, it should be taken into account that these *s-cis*/*s-cis* structures are not the absolute energy minima[15] but the intermediates directly linked with the bond shift transition state (**TS-2**). Selected geometry parameters obtained for all these structures, as well as for the isolated trienes, are presented in Table 1.

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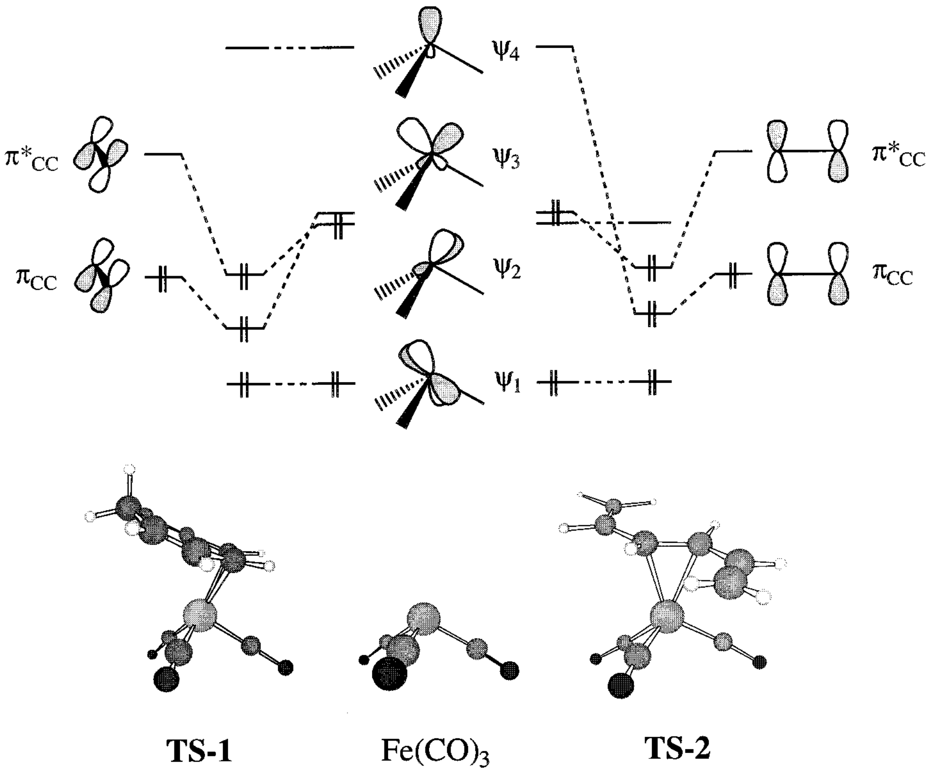

Figure 2. Schematic orbital interaction diagram between Fe(CO)$_3$[35] and an olefin with the relative orientations corresponding to **TS-1** and **TS-2**.

A (η^4-butadiene)Fe(CO)$_3$ complex can be viewed as a square pyramid in which one of the CO ligands is in the apical position, whereas the other two CO groups and the C−C double bonds of butadiene occupy the basal positions. In **1** the coordinated butadiene moiety (C_1−C_2−C_3−C_4) is oriented in such a way that the central C_2−C_3 bond is staggered with the apical CO ligand. The obtained Fe−C and C−C bond distances are similar to those previously reported for (η^4-butadiene)Fe(CO)$_2$L complexes.[12] The internal carbon atoms of the coordinated butadiene moiety (C_2 and C_3) are slightly closer to the metal than the external ones (C_1 and C_4). The Fe−C_1 distance is slightly smaller than the Fe−C_4 distance. With regard to the C−C bond distances, Table 1 shows that the C_1−C_2 and C_3−C_4 bonds are longer than the C_2−C_3 bond, so that their ordering is reversed with respect to the isolated cycloheptatriene.

The racemization process can be viewed as the metal shifting between the C_1−C_2−C_3−C_4 and the C_3−C_4−C_5−C_6 butadiene moieties. The transition state is halfway along this path and presents C_s symmetry. In the racemization transition state **TS-1** the cycloheptatriene ligand is η^2-coordinated to the metal. The computed potential energy barrier for this process is 18.1 kcal mol^{-1}. The inclusion of the zero-point energy, thermal corrections, and entropy leads to an activation Gibbs energy at 1 atm and 298 K of 16.3 kcal mol^{-1}, slightly lower than the experimental value of 22.3 kcal mol^{-1} reported by Karel et al.[18]

The structure of **2** is very similar to those previously reported for the (butadiene)Fe(CO)$_3$ complex[12] and several C_4-substituted complexes.[15] The bond-shift process between **2** and **2′** involves a rotation of the Fe(CO)$_3$ group around its pseudo-C_3 axis. In the transition state **TS-2** the triene ligand is η^2-coordinated. The computed potential energy barrier for this process is 31.8 kcal mol^{-1}, notably higher than the value computed for **1**. This fact is in good agreement with the experimental observation that the metal shift reaction for open-chain trienes is slower than for cyclic ones.

Table 2. Decomposition of the Metal−Triene Binding Energies[a] for 1 and 2

	1	2	TS-1	TS-2
E_{prep}				
Fe(CO)$_3$	22.0	20.6	20.7	11.2
triene	44.0	35.3	14.1	13.9
total	66.0	55.9	34.8	25.1
E_{elstat}	−124.7	−117.5	−119.3	−80.7
E_{Pauli}	177.9	170.2	178.1	111.6
E_{orb}	−172.1	−162.7	−128.4	−77.9
BE	52.9	54.1	34.8	21.9

[a] Values in kcal mol^{-1}. See text for definitions.

At this point, our goal was to analyze the origin of the difference between the metal shift barriers for **1** and **2**. According to the extended transition state method developed by Ziegler and Rauk,[33,34] the binding energy (BE) between a triene ligand and an Fe(CO)$_3$ fragment can be decomposed into several contributions, as

$$\text{BE} = -(E_{\text{prep}} + E_{\text{elstat}} + E_{\text{Pauli}} + E_{\text{orb}})$$

E_{prep} is the preparation energy term, i.e., the energy needed to convert the fragments from their ground-state equilibrium geometries to the geometry and electronic state involved in the formation of the complex. E_{elstat} represents the electrostatic interaction between the

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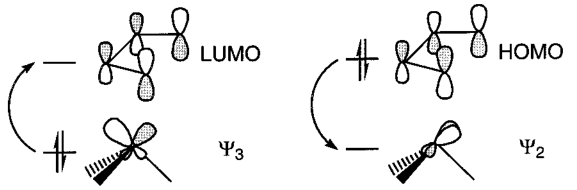
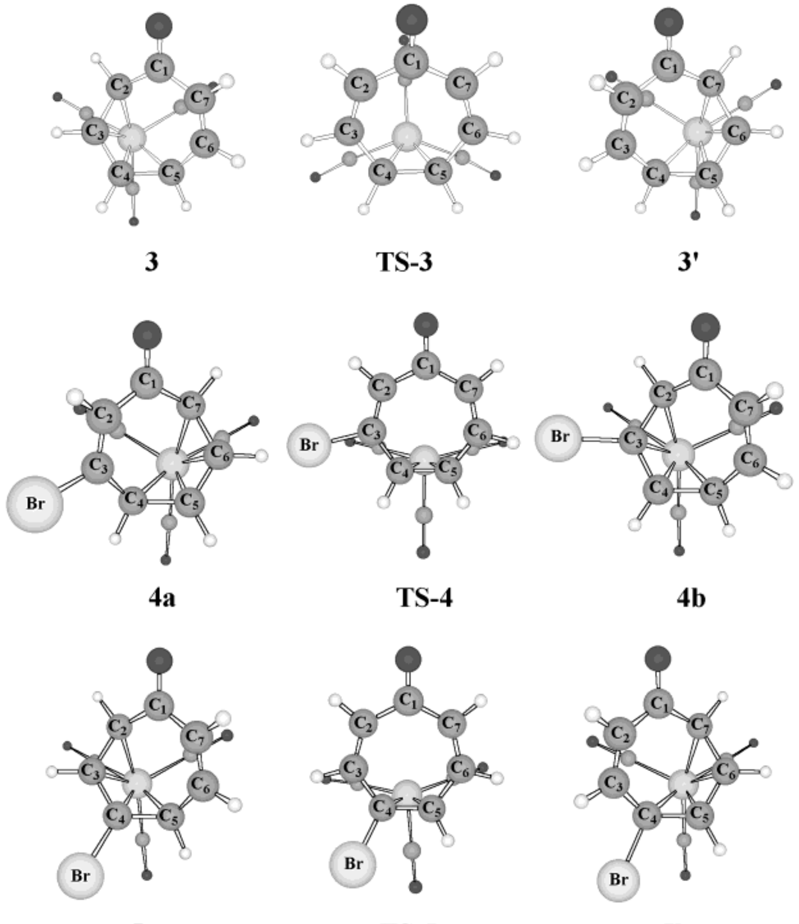
Chart 1



prepared fragments with the electron densities that each fragment would have in the absence of the other fragment. E_{Pauli} arises from the orthonormalization of the occupied fragment orbitals to obtain an antisymmetrized product and takes into account the four-electron destabilizing interactions between the fragments. Finally, the orbital interaction term, E_{orb}, represents the stabilization produced when the electron density is allowed to relax. This term comes from the two-orbital−two-electron stabilizing interactions between both fragments. Table 2 presents the results obtained in the analysis of the bonding energy in **1** and **2**. In both cases the contributions of the different terms are similar and lead to very similar binding energies. The slight differences in individual terms can be related to differences in the Fe−C bond lengths. These bonds are shorter for **1**, thus involving both larger stabilizing and repulsive interactions. Since the metal−ligand binding energy is almost the same in the energy minima of both systems, the differences in the bond-shift energy barriers must be due to differences in the interaction energies at the transition states.

Figure 2 shows that the relative orientations of the triene fragments with respect to $Fe(CO)_3$ in the transition states **TS-1** and **TS-2** are different. In **TS-1** the orientation of the $C_3{-}C_4$ double bond of cycloheptatriene allows efficient interactions between the π_{CC} and $\pi_{CC}{}^*$ orbitals and the corresponding d orbitals of Fe (ψ_2 and ψ_3). The same kind of arrangement is not favorable for **TS-2**, since it would involve important steric hindrance between one of the vinyl groups and the CO ligands. In the alternative arrangement, the $C_3{-}C_4$ double bond of hexatriene is placed along the pseudo-C_3 axis of $Fe(CO)_3$. Back-donation to the $\pi_{CC}{}^*$ orbital involves the ψ_3 orbital of $Fe(CO)_3$, whereas the π_{CC} orbital interacts with ψ_4. As a result, the metal−ligand interaction is less efficient than the one corresponding to **TS-1**.

The partition of the metal−ligand binding energy in the transition states has also been included in Table 2. It should be noted that for the cycloheptatriene complex there is a change in the orbital occupation of the $Fe(CO)_3$ fragment on going from the minimum to the transition state. In a η^4-butadiene complex,[12] the main metal−ligand interactions involve electron donation from the HOMO of the diene ligand to ψ_2 of $Fe(CO)_3$ and back-donation from ψ_3 to the LUMO of butadiene, as shown in Chart 1. Therefore, in the energy partition the occupations of the $Fe(CO)_3$ fragment are $(\psi_3)^2(\psi_2)^0$.



3 **TS-3** **3'**

4a **TS-4** **4b**

5a **TS-5** **5b**

Figure 3. Optimized structures for the minima and the transition states of the tropone (**3**) and bromotropone (**4** and **5**) complexes.

Table 3. Selected Geometry Parameters[a] for Isolated Tropone, 3- and 4-Bromotropone, and Their Complexes with Fe(CO)$_3$

	tropone	**3**	**TS-3**	3-bromotropone	**4a**	**TS-4**	**4b**	4-bromotropone	**5a**	**TS-5**	**5b**
Fe−C$_2$		2.151					2.140		2.141		
Fe−C$_3$		2.081	2.715			2.698	2.087		2.088	2.726	
Fe−C$_4$		2.071	2.046		2.135	2.035	2.074		2.070	2.032	2.167
Fe−C$_5$		2.160	2.046		2.071	2.042	2.147		2.139	2.034	2.080
Fe−C$_6$			2.715		2.084	2.777				2.678	2.074
Fe−C$_7$					2.143						2.145
C$_1$−C$_2$	1.451	1.510	1.484	1.452	1.478	1.490	1.516	1.453	1.510	1.486	1.478
C$_2$−C$_3$	1.353	1.451	1.379	1.359	1.362	1.379	1.450	1.351	1.452	1.376	1.361
C$_3$−C$_4$	1.415	1.420	1.455	1.416	1.479	1.456	1.420	1.416	1.420	1.459	1.481
C$_4$−C$_5$	1.357	1.454	1.456	1.354	1.457	1.460	1.455	1.355	1.455	1.460	1.453
C$_5$−C$_6$	1.415	1.475	1.455	1.416	1.420	1.456	1.475	1.413	1.478	1.454	1.421
C$_6$−C$_7$	1.353	1.364	1.379	1.351	1.451	1.375	1.364	1.353	1.363	1.379	1.452
C$_7$−C$_1$	1.451	1.476	1.484	1.450	1.508	1.479	1.475	1.447	1.477	1.480	1.505

[a] Interatomic distances are given in angstroms. See Figure 3 for atom numbering.

Table 4. Relative Energies and Thermodynamic Parameters Corresponding to the Bond Shift Isomerization of 3−5

structure	ΔE^a	$\Delta H_{298}°^a$	$\Delta S_{298}°^b$	$\Delta G_{298}°^a$
3	0.0	0.0	0.0	0.0
TS-3	21.2	20.5	2.2	19.8
4a	0.0	0.0	0.0	0.0
TS-4	23.6	22.5	2.1	21.9
4b	3.3	3.1	−0.1	3.1
5a	0.0	0.0	0.0	0.0
TS-5	23.2	22.3	1.3	21.9
5b	1.3	1.0	−0.4	1.1

[a] Values in kcal mol^{-1}. [b] Values in cal K^{-1} mol^{-1}.

These occupations are reversed in the transition state **TS-1** (see Figure 2), where the ligand is η^2-coordinated. In contrast, for hexatriene the occupations of the Fe(CO)$_3$ fragment do not change on going from the minimum to the transition state **TS-2**.

The analysis of the metal−ligand binding energy of the transition states shows that the preparation energy and Pauli repulsion terms are lower for **TS-2** than for **TS-1**, whereas the electrostatic and orbital interaction terms are more stabilizing for **TS-1**. The difference between metal−ligand binding energies for **TS-1** and **TS-2** are almost coincident with the difference in bond-shift energy barriers. The largest contribution to this result comes from the orbital interaction term, in good agreement with the orbital interaction diagram shown in Figure 2.

To complement the results obtained for the cycloheptatriene complex **1**, we have also studied the bond shift process in tropone, **3**, and in two bromo-substituted derivatives of tropone, **4** and **5**. Figure 3 presents the optimized structures for the bond-shift isomers and for the corresponding transition states. For tropone we show the two enantiomeric structures **3** and **3′** and the racemization transition state **TS-3**. For the bromotropone complexes we have optimized the geometries of the two bond-shift isomers, **4a**/**4b** and **5a**/**5b**, and we have located the corresponding transition states, **TS-4** and **TS-5**. The most relevant structural parameters corresponding to these structures are presented in Table 3, along with those corresponding to the isolated tropone ligands.

Table 4 presents the relative energies and thermodynamic parameters calculated for the bond shift isomerization of **3**−**5**. We can observe that the energy barriers corresponding to these systems are similar to one another and are also similar to the value computed for **1** (vide supra). The activation enthalpies computed for **3** and for **5** are in good agreement with the experimental values of 25.1 kcal mol^{-1} [19] and 22.9 kcal mol^{-1},[22] respectively. With regard to the activation entropy, the computed values are positive, whereas the experimental estimates for **3** and **5** are negative. This leads to a larger discrepancy between the computed and the experimental activation Gibbs energies. From a qualitative point of view, a positive activation entropy seems reasonable, since the energy minima show more ordered structures (η^4 coordination) than the transition states (η^2 coordination).

As we have mentioned in the Introduction, the interconversion between **5a** and **5b** has been experimentally observed, whereas the **4a** → **4b** isomerization does not take place.[22] However, Table 4 shows that the computed barriers for both processes are very similar, so that the different behaviors of both systems does not seem to be due to kinetic factors. On the other hand, the computed Gibbs energy difference between **4a** and **4b** is larger than the value corresponding to **5a** → **5b** (see Table 4). According to these results, the isomerization process **4a** → **4b** would be thermodynamically unfavorable and the predicted equilibrium population ratio at 298 K would be 222:1. On the other hand, for **5a** → **5b** the computed ΔG value predicts an equilibrium population ratio of 6:1 at 298 K. The equilibrium constant of this process has been experimentally determined in different solvents at 323.15 K.[22] The obtained values range between 0.688 in acetic-d_4 acid and 1.355 in CDCl$_3$. The latter value would qualitatively agree with the computed ΔG value, but the calculated value is overestimated.

Concluding Remarks

The 1,3-metal shift process has been studied for several conjugated (η^4-triene)Fe(CO)$_3$ systems. In all cases the transition states correspond to (η^2-triene)Fe(CO)$_3$ structures, and the computed energy barriers are in good agreement with the experimental observation that the process is slower for acyclic complexes. An analysis of the energy barriers shows that this different behavior is due to differences in the metal−ligand stabilizing interactions at the transition states caused by the different relative orientations of the triene and the $Fe(CO)_3$ moieties, depending on the cyclic or acyclic nature of the ligand. For the 3- and 4-bromotropone complexes, the computed energy barriers are not significantly dependent on the position of the Br atom, so that the different experimental behaviors of both systems may be due to the different relative stabilities of both bond-shift isomers.

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