Structural and Energetical Characterization of the Methylbutadiene–Fe(CO)$_3$ Isomers and Related Reactive Intermediates with Quantum Chemical Methods

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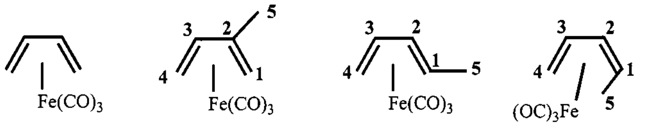
A theoretical investigation of isoprene–Fe(CO)$_3$ (**2**), (*E*)-1,3-pentadiene–Fe(CO)$_3$ (**3**), (*Z*)-1,3-pentadiene–Fe(CO)$_3$ (**4**), and reactive intermediates derived from these complexes was undertaken, employing the HF/DFT hybrid functional Becke3LYP, and the results are presented. Special emphasis is placed on cationic, anionic, and radical intermediates formally derived by abstraction of a hydride, a proton, or a hydrogen atom from the methyl group of the parent complexes. The geometry, energy, and electronic situation of the calculated species are discussed in the context of experimental facts. This leads to a better mechanistic understanding of the chemistry of acyclic butadiene–Fe(CO)$_3$ complexes, provides insights into structural details of the intermediates involved, and allows the evaluation of possible resonance formulae. The calculation of transition states of isomerization (or racemization) processes even permits a quantitative description of energy profiles. In this way, the configurational stability of relevant cationic, anionic and radical intermediates can be estimated.

Introduction

Acyclic 1,3-diene−Fe(CO)$_3$ complexes are well established as valuable intermediates in organic synthesis.[1] Besides the use of the Fe(CO)$_3$ fragment as a protecting group for the 1,3-diene unit, many synthetic applications are based on transformations that exploit the ability of the Fe(CO)$_3$ unit to stabilize positive[2] or negative[3] charge in a position adjacent to the complexed diene. Due to the steric bulk of the metal fragment, many reactions of such complexes additionally proceed with a high level of stereocontrol.[4]

While crystal structures of the parent η^4-butadiene−Fe(CO)$_3$ complex **1** and quite a large number of other neutral 1,3-diene−Fe(CO)$_3$ complexes are available,[5] very little is definitely known about the structure of the anionic and cationic intermediates.[6] In order to develop a deeper understanding of these systems and to improve the predictability of the chemistry of acyclic butadiene−Fe(CO)$_3$ complexes, it would be highly desirable to obtain information about structural and energetical details of reactive intermediates involved in this chemistry. As a follow-up to our previous theoretical investigation employing density functional theory of cationic, anionic, and radical reactive intermediates derived from toluene−Cr(CO)$_3$,[7] we provide in this paper a detailed and comprehensive picture of the computed structural and energetical features of η^4-methylbutadiene−Fe(CO)$_3$ isomers **2**, **3**, and **4**, as well as the corresponding cationic, anionic, and even radical species of type $(C_5H_7)Fe(CO)_3{}^{+/-/\bullet}$ derived from **2**, **3**, and **4** by formal abstraction of a proton, a hydride, or an H radical from the methyl group.



1 **2** **3** **4**

Scheme 1. The parent systems: 1,3-butadiene−Fe(CO)$_3$ (**1**), isoprene−Fe(CO)$_3$ (**2**) and the pentadiene−Fe(CO)$_3$ complexes **3** and **4**; please note the numbering system which is uniformly applied in this paper

Computational Details

In the work described in this paper we used the same computational strategy that we successfully applied in our previous work on reactive intermediates derived from η^6-toluene−Cr(CO)$_3$.[7] Therefore, a brief description of the computational strategy will suffice at this point. For further details the reader is referred to ref.[7] All calculations were carried out using the popular Becke3LYP hybrid density functional.[8] An all electron basis set, described by Wachters,[9] was extended by a set of f-functions for the iron atom and was applied while the standard D95* split valence basis set was chosen for C, H, and O. All calculations were performed employing Gaussian94[10] as implemented on our own IBM RS/6000 workstations and the CRAY J90 computer of the Konrad-Zuse-Zentrum für Informationstechnik Berlin. The electron density was analyzed through the *Natural Bond Orbital* (NBO) scheme introduced by Weinhold and co-workers.[11] The harmonic frequencies were calculated for all molecules considered in order to identify

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stationary points as minima or transition states and to estimate the zero point energies (ZPE) for which all energies are corrected. The calculations of the radical complexes all resulted in the expected S^2 value of 0.75 for a doublet.

Results and Discussion

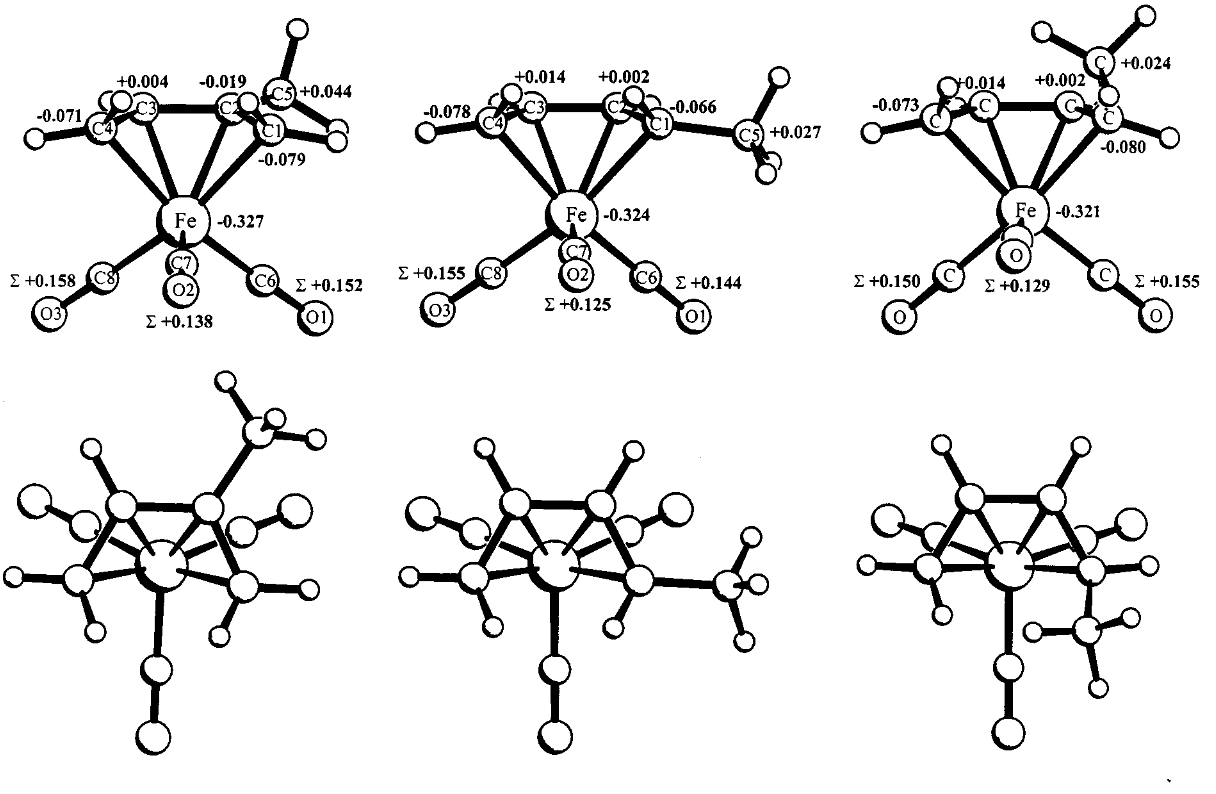
The Neutral $C_5H_8-Fe(CO)_3$ Complexes

We began our study with the neutral complexes **2**, **3**, and **4**, which are shown in Figure 1. These three neutral isomers serve as reference systems for the investigation of the related cationic, anionic, and radical intermediates discussed below. The complexes **3** and **4** can be considered as configurational isomers, which formally can be converted into each other by a simple rotation around the C1−C2 bond. The theoretically predicted structures of complexes **2**, **3**, and **4** are depicted in Figure 1.[12]

The neutral isoprene tricarbonyl iron complex **2** shows a regular arrangement of the η^4-diene ligand with a slightly shorter internal C2−C3 bond (1.423 Å) compared to the C1−C2 and the C3−C4 bonds (1.436 Å and 1.434 Å, respectively). The iron atom is positioned symmetrically below the plane of the butadiene fragment and the $Fe(CO)_3$-tripod assumes a conformation with one CO pointing towards the open side of the diene ligand. As in the case of previous theoretical studies on **1**,[13] the structure calculated for **2** is in good general accordance with X-ray crystal structures[5] of such complexes and with a microwave structure for **1**.[14] The barrier for the rotation of the $Fe(CO)_3$ moiety in **2** was computed to be 11.1 kcal mol^{-1}, which is considerably closer to the experimentally determined barrier (10.6 kcal mol^{-1}) than values from previous calculations.[15] It is interesting to note that this barrier is significantly higher than, for instance, that of the metal fragment in the neutral toluene $Cr(CO)_3$ complex, which amounts to only 0.8 kcal mol^{-1}.[7] In the rotational transition state **2′** (Figure 2), the C2−C3 bond is now *longer* than the bond lengths of the terminal C−C bonds by 0.017 Å. The calculation of the harmonic vibrational frequencies confirms that structure **2′** is indeed the transition state of the $Fe(CO)_3$ rotation and is characterized by an imaginary frequency of 82.4 cm^{-1}, connected to the expected transition mode.

In the other two isomers, **3** and **4** (Figure 1), the iron is also η^4 bonded to the organic ligand with Fe−C bond lengths of about 2.0 Å. The structures show that the methyl substituents do not visibly disturb the preferred geometry of the parent η^4-butadiene−$Fe(CO)_3$ substructure. Compound **3** is energetically more stable than its stereoisomer **4** by 8.9 kcal mol^{-1}. In all three complexes the $C-CH_3$ bond appears as a normal σ-bond with a typical bond length between 1.51 and 1.53 Å.

A view of the NBO analysis (see Figure 1) reveals a negative partial charge on the iron atom (≈ −0.32 |e|) in all three neutral complexes. The CO groups have positive charges of +0.125 |e| to +0.155 |e| (sum of the partial



2 **3** **4**

Figure 1. Ground-state structures of the neutral methylbutadiene complexes **2**, **3** and **4**; the charges of the hydrogen atoms are summed into the carbon atoms

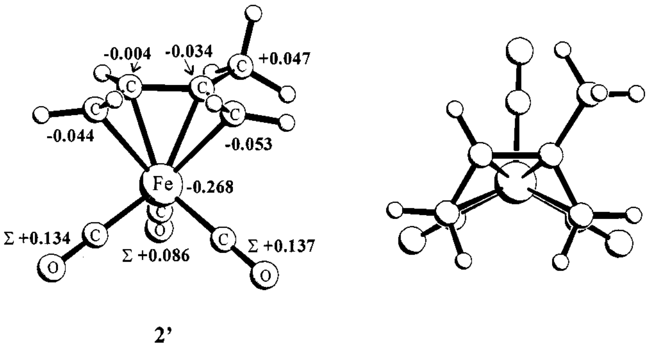
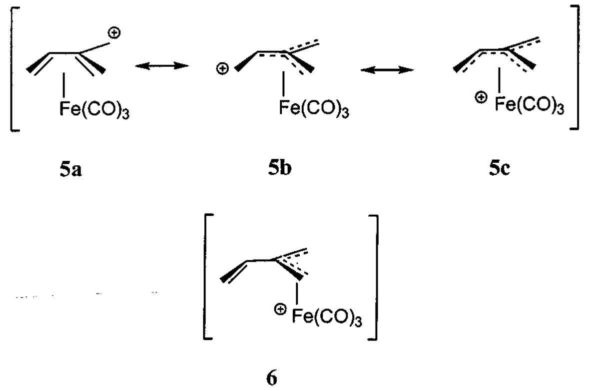


Figure 2. Calculated structure of the transition state (**2'**) for the rotation of the Fe(CO)$_3$ moiety in **2**



Scheme 2. Mesomeric structure of the cationic intermediates derived from the isoprene−Fe(CO)$_3$ complex **2**

charges of C and O). In all cases the CO group, which is pointing towards the open side of the butadiene ligand, carries the smallest positive charge. Therefore, the Fe(CO)$_3$ unit, which is characterized by total charges of at least +0.1 |e|, cannot be regarded as an electron-withdrawing group, in contrast to the metal fragment in arene−Cr(CO)$_3$ complexes,[7] where the Cr(CO)$_3$ moiety was negatively charged. Compared to C1 and C4, the inner carbon atoms (C2 and C3) have a slightly more positive partial charge. This is in accord with the experimental observation that under kinetic control the attack of nucleophiles occurs regioselectively at the inner carbon atoms.[16]

The geometrical parameters of the neutral complexes **2**, **3**, and **4** serve as a good indicator for the intepretation of the data obtained for the cationic, anionic and radical intermediates (see Table 1). The total energies and the zero point corrections for all calculated structures are collected in Table 2.

The Cationic $C_5H_7-Fe(CO)_3$ Complexes

Transformations of 1,3-diene−Fe(CO)$_3$ derivatives involving metal-stabilized cationic intermediates have been known for many years and have gained particular importance in organic syntheses.[1,2,17] Although some of the cationic intermediates have been characterized by spectroscopic methods,[18] data concerning structural and energetic features of these intermediates are very rare. At this point, modern theoretical methods open an ideal complementary avenue for obtaining far reaching insights into structural, energetical and, finally, mechanistic details of such species.

We commenced our investigation by first characterizing the cationic $C_5H_7-Fe(CO)_3^+$ complexes **5** and **6**, which were formally generated by abstraction of a hydride from the methyl group of the isoprene complex **2** (Scheme 2).

Our calculations suggest that only two minimum structures can be distinguished and these differ in the hapticity of the metal coordination. In the energetically most stable structure the metal coordinates to the ligand in an η^5 mode. This structure, which obeys the 18-valence electron (VE) rule, may be represented by the three mesomeric forms **5a**, **5b** and **5c** depicted in Scheme 2. The second structure, a formal 16 VE species that is energetically less favored by 7.4 kcal mol^{-1}, is perfectly described by formula **6**. In contrast to a previous picture based on a Frontier Orbital Analysis,[19] it is not possible to treat the two structures **5a** and **5b** as separate species. The calculated structures of species **5** and **6** are depicted in Figure 3 while the theoretically predicted bond lengths are collected in Table 1.

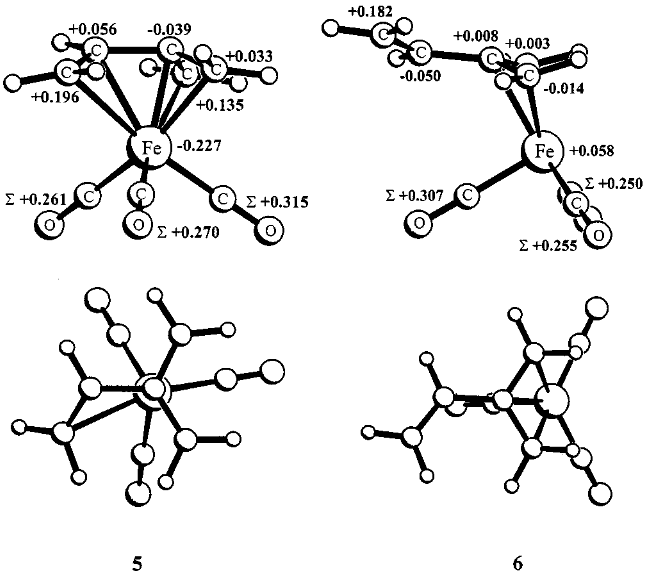


Figure 3. Structures of the two cationic complexes **5** and **6**

Compared to the neutral complex **2**, in structure **5** the iron tricarbonyl tripod has moved more closely to C2. This leads to a trimethylenemethane−Fe(CO)$_3$-type substructure involving the carbon atoms C1, C2, C3, and C5. As a result, the bond between Fe and C2 is shortened to 1.991 Å from 2.107 Å in **2** while C1, C3, and C4 have similar bond lengths to the iron (2.145, 2.197, and 2.266 Å, respectively). Whereas about 50% of the positive charge is localized on the metal carbonyl unit, in the organic ligand positive partial charges are mainly found at C4 (+0.196 |e|) and C5 (+0.135 |e|), a situation that is in accord with the mesomeric structures **5a** and **5b**. Taken together, all three mesomeric structures seem to contribute, but **5c** is probably the best formal representation of the calculated structure. In the η^3-isomer **6** the iron is bonded to C1, C2, and C5. This structure can be considered as a cationic η^3-allyl$-$Fe(CO)$_3$ complex bearing a vinyl side-chain. Two features of this structure are especially remarkable: Firstly, about 80% of the positive charge is now transferred to the iron carbonyl moiety. Secondly, the most electron deficient carbon atom is C4 (+0.182 |e|), which has no interaction with the Fe(CO)$_3$ group. It is further worth noting that the preferred conformation of the Fe(CO)$_3$ tripod has changed from fully staggered in **5** to eclipsed in **6** (Figure 3). Because the C2$-$C3 bond (1.48 Å) in **6** is a single bond, rotation around this bond should be possible. This would lead to a racemization of the planar chiral structure (**6** → *ent*-**6**). Calculation of the transition state of this process resulted in a barrier of $\Delta H^{\#} = 5.4$ kcal mol^{-1}. As **6** is energetically only 7.4 kcal mol^{-1} above **5**, the overall energy barrier for the racemization of the η^5 structure **5** amounts to 12.8 kcal mol^{-1}. This translates into a half life for **5** of ca. 10^{-3} s at 0°C and of ca. 14 s at -78°C.[20] The energy profile of the racemization of **5** is depicted in Figure 4.

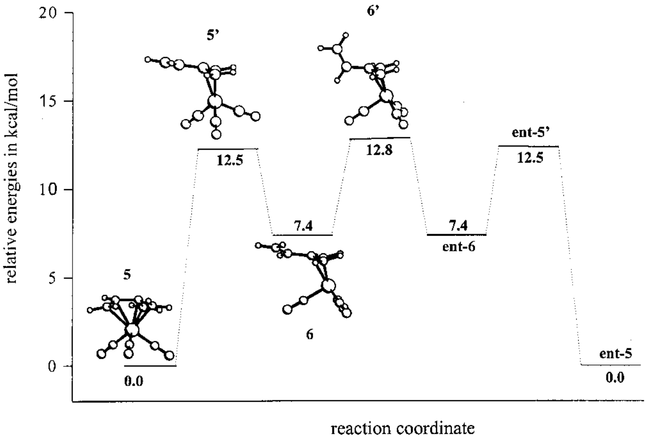
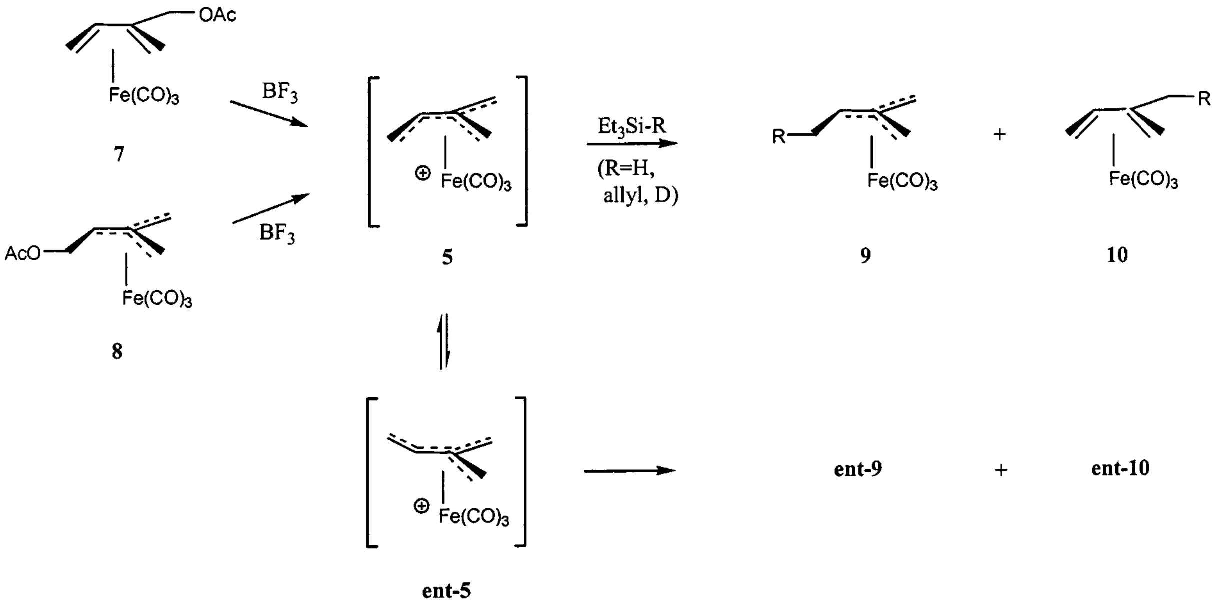


Figure 4. Energy profile of the racemization of **5** to *ent*-**5**

These results are in very good agreement with the qualitative picture that was derived by Gerlach,[21] Donaldson,[22] and Franck-Neumann[23] from experimental studies. These authors had shown that the intermediate cations **5**, generated from precursors **7** or **8** in the presence of Lewis acids, undergo reaction with (soft) nucleophiles to afford mixtures of products **9** and **10** (Scheme 3). The predominant formation of trimethylenemethane complexes **9** under kinetically-controlled conditions shows that the nucleophilic attack occurs preferentially at C4. This regioselectivity correlates nicely with the calculated partial charges in the intermediate **5** (Figure 3). The rather low barrier of racemization discussed above is also in good agreement with the experimental fact that a high degree of stereospecificity (retention of absolute stereochemical information) is only achieved when the reactions are performed at low temperatures (-78°C).[21]

The chemistry discussed above is often complicated by facile proton-catalyzed isomerization of **9** to **10**.[19–21] It was therefore interesting to calculate the relative energies of these two species (for R = H). The calculated structure (Figure 5) of the parent methyl-substituted trimethylenemethane (TMM)[24] complex **9** (R = H) reveals the expected coordination mode of the iron fragment to the ligand. This structure is in excellent agreement with X-ray crystal structures of TMM$-$Fe(CO)$_3$ derivatives. The maximum deviation of the bond lengths amounts to 0.03 Å and, in particular, the distances between iron and the TMM ligand are very well represented with deviations less than 0.02 Å.[25] In order to achieve a stronger coordination to the metal, the central carbon atom (C2) of the ligand is no longer planar but significantly pyramidalized ("umbrella-like").



Scheme 3. S$_N$1 reaction of substituted isoprene$-$Fe(CO)$_3$ complexes involving intermediates of type **5**

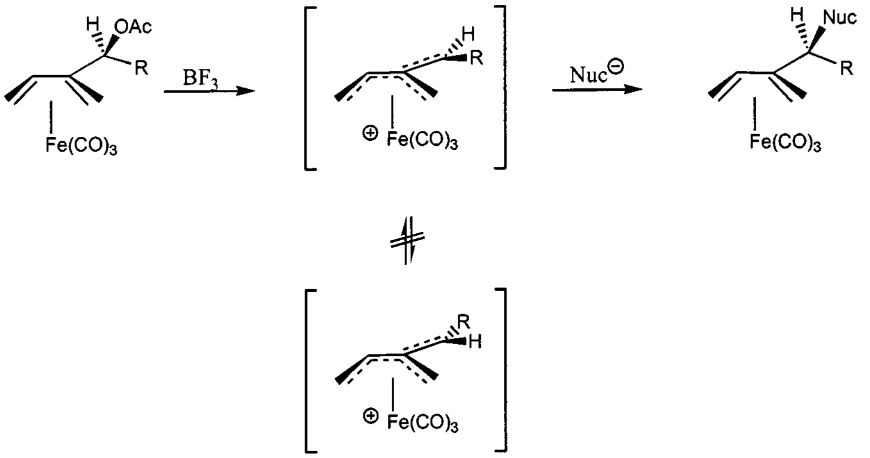
Table 1. Bond lengths for the complexes **2−24** in Å

	2	**2′**	**3**	**4**	**5**	**5ts**	**6**	**9**	**11**	**12**	**13**	**14**	**15**
C1−C2	1.436	1.423	1.428	1.442	1.428	1.475	1.437	1.436	1.476	1.430	1.493	1.496	1.437
C2−C3	1.423	1.439	1.422	1.420	1.474	1.427	1.478	1.438	1.411	1.430	1.412	1.475	1.468
C3−C4	1.434	1.421	1.433	1.433	1.377	1.411	1.353	1.514	1.430	1.408	1.425	1.432	1.354
C1−C5	–	–	1.515	1.525	–	–	1.432	–	1.367	1.407	1.345	–	–
C2−C5	1.511	1.511	–	–	1.414	1.425	–	1.439	–	–	–	1.359	1.442
Fe−C1	2.119	2.176	2.167	2.150	2.145	2.159	2.095	2.138	2.257	2.161	2.358	2.122	2.119
Fe−C2	2.107	2.108	2.093	2.082	1.991	2.029	2.203	1.957	2.088	2.155	2.082	2.537	2.023
Fe−C3	2.083	2.084	2.075	2.090	2.197	2.114	3.287	2.171	2.141	2.161	2.125	2.097	3.006
Fe−C4	2.112	2.170	2.121	2.125	2.467	2.166	4.256	3.239	2.150	2.228	2.136	2.090	4.042
Fe−C5	3.249	3.241	3.276	3.234	2.266	2.200	2.096	2.123	2.712	2.228	3.604	3.751	2.097
Fe−C6	1.798	1.793	1.797	1.798	1.818	1.830	1.837	1.798	1.852	1.839	1.865	1.777	1.775
Fe−C7	1.788	1.771	1.786	1.803	1.831	1.744	1.786	1.797	1.836	1.817	1.846	1.771	1.766
Fe−C8	1.799	1.772	1.797	1.784	1.854	1.657	1.840	1.797	1.813	1.838	1.805	1.776	1.769
C6−O1	1.159	1.160	1.159	1.158	1.144	1.147	1.163	1.157	1.146	1.144	1.143	1.173	1.177
C7−O2	1.158	1.162	1.159	1.158	1.145	1.146	1.164	1.157	1.145	1.145	1.143	1.174	1.177
C8−O3	1.158	1.162	1.158	1.159	1.144	1.145	1.163	1.157	1.145	1.144	1.144	1.174	1.176

	16	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**
C1−C2	1.491	1.463	1.477	1.432	1.462	1.423	1.472	1.414	1.481
C2−C3	1.402	1.434	1.437	1.468	1.450	1.483	1.415	1.476	1.419
C3−C4	1.359	1.432	1.430	1.354	1.411	1.347	1.422	1.347	1.417
C1−C5	–	1.356	1.354	1.429	–	–	1.351	1.414	1.349
C2−C5	1.364	–	–	–	1.407	1.421	–	–	–
Fe−C1	2.088	3.048	3.091	2.033	2.089	2.150	2.889	2.115	2.911
Fe−C2	2.828	2.186	2.150	2.187	2.189	2.081	2.204	2.182	2.172
Fe−C3	3.369	2.023	2.032	3.248	2.122	2.939	2.094	3.272	2.100
Fe−C4	3.396	2.122	2.130	4.056	2.184	3.911	2.126	4.205	2.144
Fe−C5	3.775	4.184	4.014	2.124	3.223	2.160	3.932	2.132	3.738
Fe−C6	1.759	1.764	1.765	1.780	1.807	1.845	1.801	1.800	1.801
Fe−C7	1.754	1.777	1.761	1.756	1.798	1.807	1.808	1.860	1.858
Fe−C8	1.765	1.760	1.781	1.779	1.809	1.805	1.847	1.804	1.804
C6−O1	1.180	1.177	1.179	1.178	1.157	1.157	1.158	1.159	1.159
C7−O2	1.182	1.177	1.179	1.179	1.158	1.158	1.159	1.157	1.158
C8−O3	1.177	1.179	1.176	1.176	1.158	1.159	1.158	1.159	1.158

The Fe(CO)$_3$ tripod prefers the fully staggered conformation. Compared to **10** (R = H; i.e. **2**), the isomer **9** (R = H) is less stable by 4.5 kcal mol^{-1}. This explains the almost complete disappearance of **9** in the equilibrium.

Another important point is the configurational stability of the intermediates of type **5** during S$_N$1-type transformations at C5 in the case of substituted substrates, which proceed with retention of configuration (Scheme 4).[21] This is reflected by our quantum chemical calculations, which predict a very high barrier of 44.2 kcal mol^{-1} for the rotation around the C2−C5 bond in the parent model compound **5**. In the transition structure **5ts** the positive charge is mostly localized at C5 and cannot be stabilized by interaction with the iron atom due to the orthogonal orientation of the formally empty p-orbital and the correspondingly vanishing overlap of C5 with potential donor orbitals from the metal.



Scheme 4. Retention of configuration in S$_N$1 transformations

Table 2. Total energies and zero point energy correction (ZPE) for structures **2**–**24**

	Total energies [Hartree]	ZPE [kcal mol^{-1}]
2	−1799.16467	89.3
2′	−1799.14649	89.0
3	−1799.16123	89.4
4	−1799.15141	89.5
5	−1798.28055	82.6
5′	−1798.08107	81.0
5ts	−1798.20612	80.1
6	−1798.26669	81.3
6′	−1798.07915	80.8
9	−1799.15757	89.4
11	−1798.27904	82.4
11ts	−1798.20070	79.1
12	−1798.29514	83.3
13	−1798.25954	81.1
14	−1798.57893	80.3
14ts	−1798.51141	78.1
15	−1798.59358	80.4
16	−1798.553277	79.7
17	−1798.59183	80.4
17ts	−1798.50744	78.7
18	−1798.58556	80.4
19	−1798.58831	80.2
20	−1798.51056	80.5
20ts	−1798.45038	76.8
21	−1798.52934	80.8
22	−1798.53662	80.9
22ts	−1798.48923	79.8
23	−1798.52441	81.0
24	−1798.52695	80.7

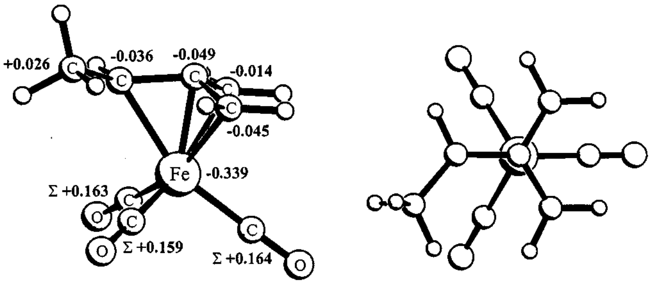


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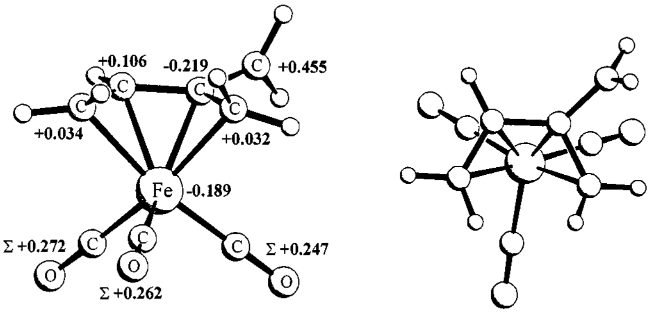
Figure 5. Structure of the neutral trimethylenemethane complex **9**

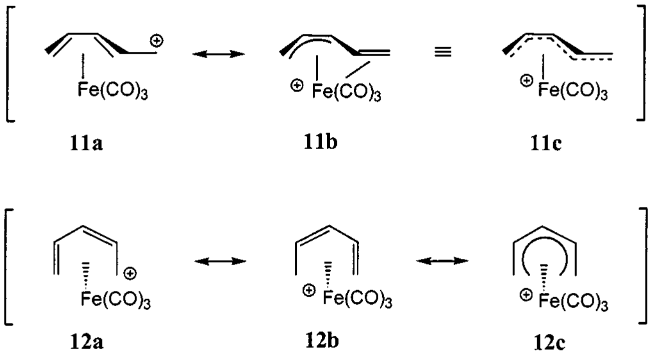
Because of this lack of interaction between the iron and the positive center C5, the transition structure **5ts** contains an almost undistorted diene–Fe(CO)$_3$ unit.



5ts

Figure 6. Transition state (**5ts**) for the rotation of the C5H$_2$ group around the bond between C2 and C5

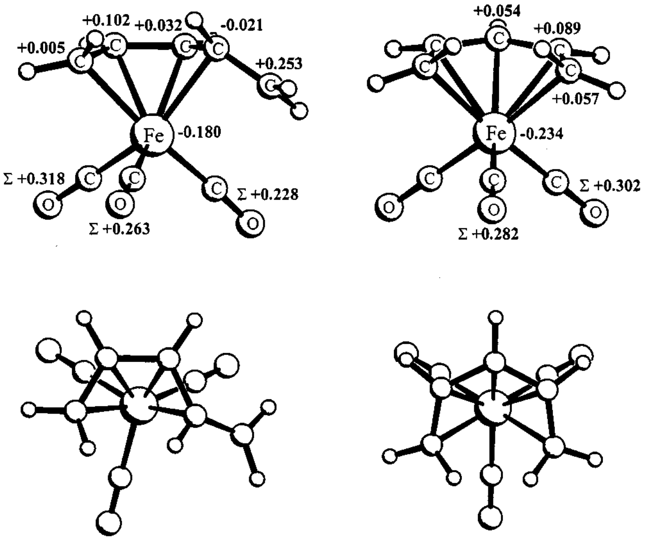
A second system, namely the cationic pentadienyl Fe(CO)$_3$ complexes, was also investigated. These species (**11** and **12**) formally result from abstraction of a hydride ion (H$^-$) from the methyl group of the neutral diene–Fe(CO)$_3$ complexes **3** and **4**, respectively (Scheme 5). Possible representations of the two configurational isomers **11** and **12** are shown in Scheme 5.



Scheme 5. Mesomeric forms of the cationic intermediates **11** and **12**

Our computational investigation of **11** and **12** led to the two minimum structures shown in Figure 7.[12] The calculated geometry of **11** indicates an η^4 coordination mode with an additional attractive interaction between Fe and C5. This becomes evident in a strong bending of C5 towards the metal. The clear double bond character of the C1–C5 bond (1.37 Å) emphasizes the contribution of the mesomeric form **11b**. About 50% of the positive charge is transferred to the Fe(CO)$_3$ group as expressed by formulae **11b** and **11c**. On the other hand, structure **11a** mirrors the charge distribution of the ligand. As expected, the calculated structure of complex **12** exhibits C_s symmetry with the organic ligand forming a totally delocalized π-system. The C–C bond lengths in the pentadienyl ligand are all in the same range of ca. 1.4 Å, which fits well with the experimental data of an X-ray diffraction analysis of [(2,4-dimethylpentadienyl)Fe(CO)$_3$]BF$_4$.[6] The Fe(CO)$_3$ tripod interacts with the pentadienyl ligand in an η^5-manner, which is also in full agreement with NMR spectroscopic results.[18a] All carbon atoms of the ligand in **12** have a similar, slightly positive, partial charge. Structure **12** is computed to be more stable than **11** by 9.2 kcal mol^{-1}.

The facile (reversible) isomerization of intermediates of type **11** to the more stable horseshoe isomers of type **12** is a well established experimental fact that has often been exploited in selective synthesis.[26] In this case an experimental value for the barrier of isomerization was available[27] and we therefore considered this system as being an ideal touchstone for the accuracy of our computational methodology. The isomerization of **11** to **12** can formally be regarded as a rotation around the C2–C3 bond. Our calculations predict an activation energy for this process, connected with the transition structure **13**, of 11.0 kcal mol^{-1} above that of **11**. In Figure 8 the energy profile for this process is displayed. The experimental value of 13 kcal mol^{-1} found by Sorensen et al. for the barrier of isomeriz-



11 **12**

Figure 7. Structures of the cationic pentadienyl$-$Fe(CO)$_3$ complexes **11** and **12**

ation is therefore in very good agreement with the computed barrier.[27]

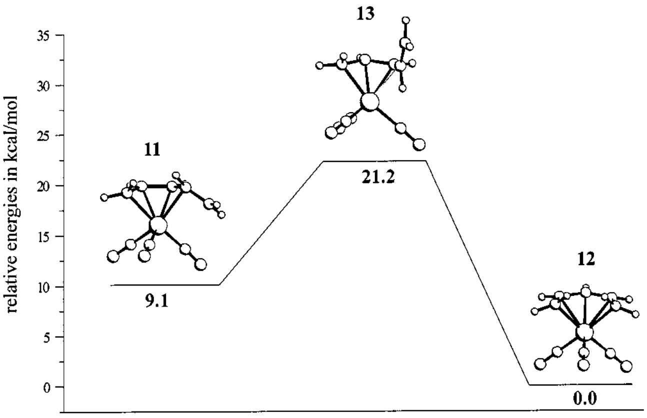
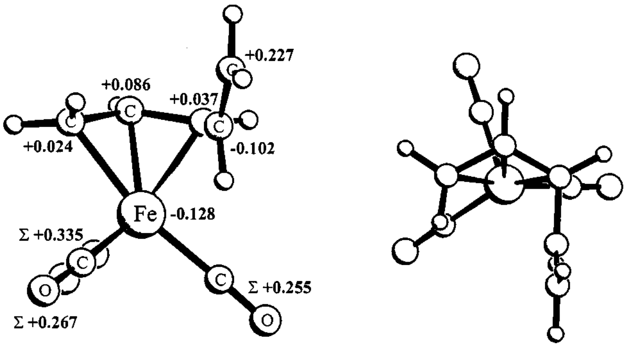


Figure 8. Energy profile for the isomerization of complexes **11** and **12**

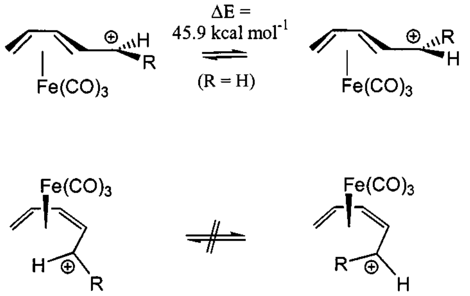
Analysis of the transition state structure **13** clearly shows only an η^3 coordination of the iron fragment to the ligand. This structure is a 16 VE cationic η^3 allyl complex in which the vinyl substituent is turned to the opposite side of the metal fragment by about 90° around the C2$-$C3 bond. It is interesting to note that all our attempts failed to locate the transition state structure for this rotation in the neutral complexes **3** and **4**. The reason for the much higher rotational barrier for the interconversion of these isomers is probably that any η^3 bonded intermediate (transition state) would correspond to a disfavored zwitterionic or diradical species.



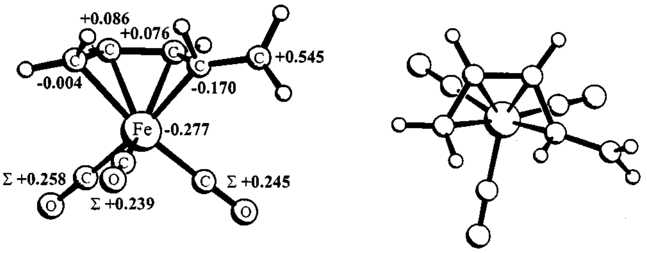
13

Figure 9. Structure of the transition state **13**, which is passed during the isomerization process shown in Figure 8

From the point of view of the synthetic chemist it is highly useful that S_N1-type reactions in the allylic position (at C5) of 1,3-pentadiene$-$Fe(CO)$_3$ complexes proceed with virtually complete retention of configuration.[28] We were interested to see if our calculations could quantify the obvious configurational stability of the cationic intermediates. In the case of the pentadienyl cation **11** we were able to determine a rotational barrier of 45.9 kcal mol^{-1} (Scheme 6). The corresponding transition structure **11ts** is depicted in Figure 10. In contrast, the transition state for the corresponding isomerization of **12** could not be localized. This indicates a very strong stabilization of the U-shaped pentadienyl cation by η^5-coordination to the metal. Therefore, the energy barrier for the rotation of a terminal CH_2 group in **12** should be extremely high and isomerization is not likely to take place.



Scheme 6. Rotation of the C5H$_2$ group around the bond between C1 and C2 of the cationic complexes **11** and **12**



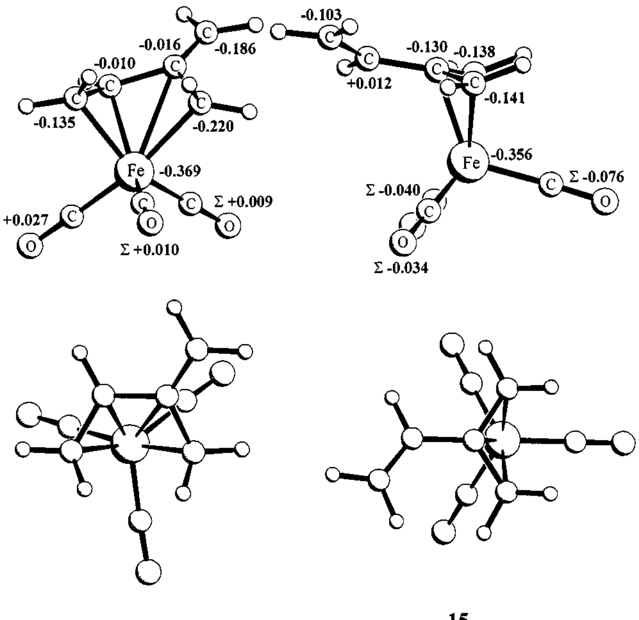
11ts

Figure 10. Transition structure **11ts** for the rotation of the C5H$_2$ group around the bond between C1 and C2 of the cationic complex **11**

The Anionic $C_5H_7-Fe(CO)_3$ Complexes

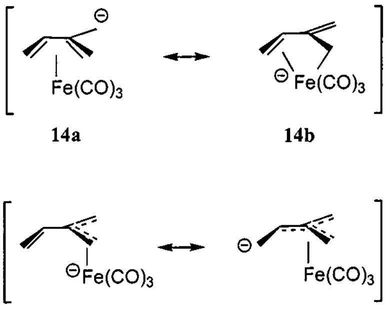
Compared to the cationic complexes discussed above, very little has been reported about the corresponding anionic iron complexes. While a few reactions involving such intermediates have been described,[3] virtually nothing is known about their geometry and electronic structures.

Firstly, we will present our results concerning the anionic system arising from proton abstraction from the methyl group of the isoprene complex **2**. The calculations revealed the two minimum structures **14** and **15** depicted in Figure 11. Both species formally count 18 VE and may be represented by two resonance formulae according to Scheme 7.



14 **15**

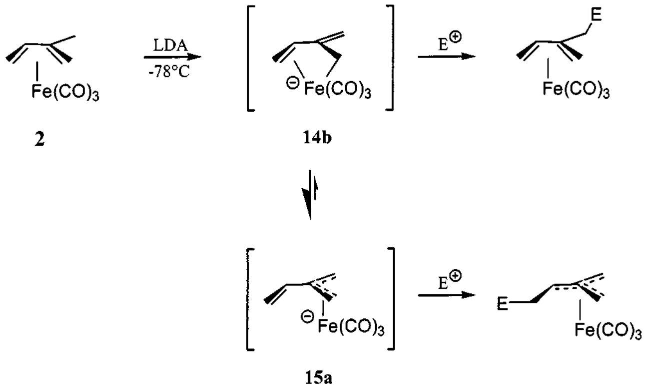
Figure 11. Structures of the anionic complexes **14** and **15**



Scheme 7. Mesomeric forms of the anionic complexes **14** and **15** derived from the isoprene$-Fe(CO)_3$ complex **2**

In structure **14** the deprotonated center (C5) has no contact with the iron. The C2−C5 bond has clear double bond character (bond length 1.36 Å) and is bent away to the opposite side of the $Fe(CO)_3$ moiety. The short Fe−C1 distance (2.12 Å) and a negative partial charge of −0.323 |e| of the $Fe(CO)_3$ fragment also indicate that **14b** is a better representation of this species than **14a**. In contrast to **14**, in the isomeric species **15** there is a strong interaction between the iron and C5. In fact, **15** is best regarded as a vinyl-substituted η^3-allyl complex as expressed by formula **15a**. Here the iron tricarbonyl group takes over 50% of the negative charge. It is interesting to note that this isomer is more stable than **14** by 9.2 kcal mol^{-1}. It is clear that the anionic intermediate prefers an η^3-allyl coordination mode (**15**) where more negative charge can be transferred to the metal fragment than in the mixed π/σ bonding in **14**. This is in accordance with the experimental observation that species **14**, which is initially formed through deprotonation of **2** at low temperatures, rearranges to a more stable isomer (**15**) on warming. While **14** gives 2-substituted butadiene$-Fe(CO)_3$ derivatives on reaction with electrophiles, **15** gives rise to TMM-type products (Scheme 8).[3a]

One should note that this situation is contrary to the one found for the cationic complexes **5** and **6**, where structure **5** is energetically more favored. However, this can easily be understood in terms of the 18-electron rule.



Scheme 8. Deprotonation reaction of the isoprene$-Fe(CO)_3$ complex **2** involving the anionic intermediates **14** and **15**, respectively

In order to gain a better understanding of this chemistry, the transition state for the interconversion of **14** to **15** was calculated. The relative energy of the resulting transition structure **16** was found to lie 15.4 kcal mol^{-1} above **14** and 24.6 kcal mol^{-1} above **15**. The energy profile for this process is shown in Figure 12.

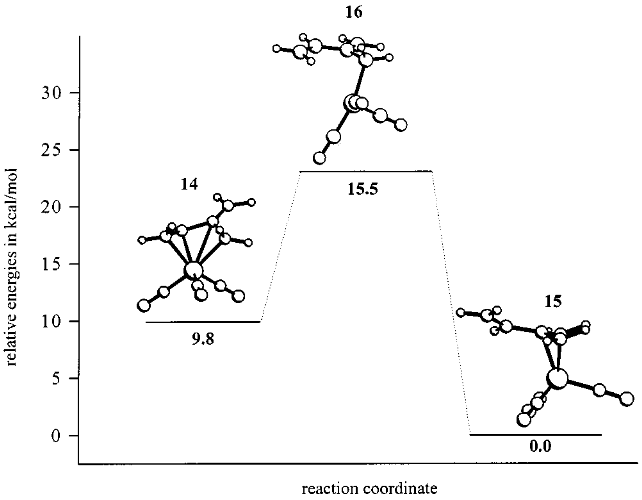
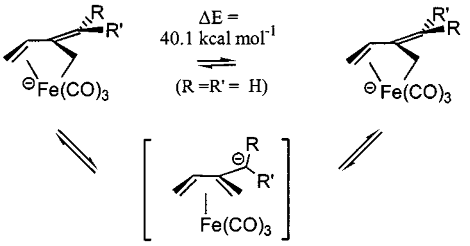


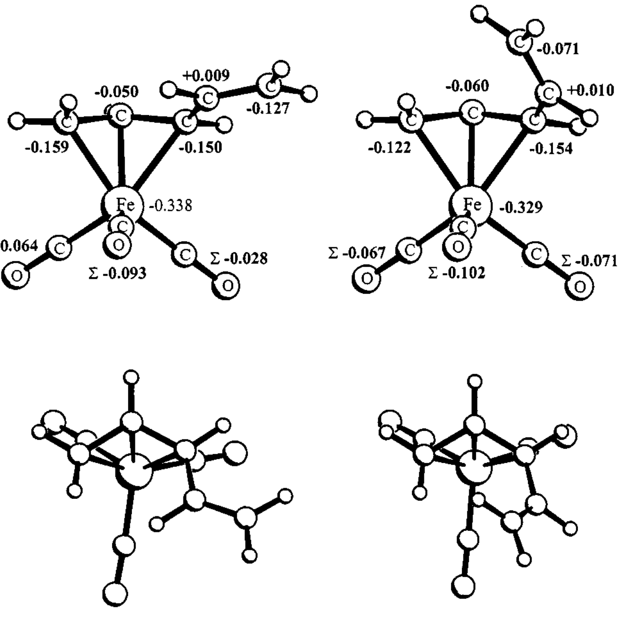
Figure 12. Energy profile for the isomerization of **14** and **15**

We further addressed the question as to whether a deprotonation/alkylation sequence at C5 of 5-substituted derivatives of **2** would proceed with stereochemical retention or not. In order to estimate the configurational stability of the corresponding intermediates, the barrier for the rotation around the C2−C5 bond in **14** was computed. A value of 40.1 kcal mol^{-1} was obtained and this shows that no isomerization should occur under common reaction conditions (Scheme 9). The high rotational barrier results from the fact that in the transition state the negative partial charge is not delocalized and is mainly located at C5 (−0.64 |e|) while the butadiene−$Fe(CO)_3$ substructure remains almost undisturbed.



Scheme 9. Rotation of the $C5H_2$ group around the bond between C2 and C5 of the anionic complex **14**

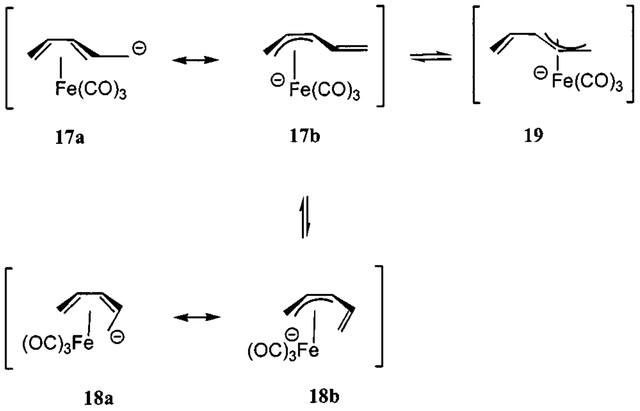
Very little has been reported about the generation and reactivity of the anionic pentadienyl $Fe(CO)_3$ complexes **17** and **18**.[29] Therefore, it is particularly interesting to look at the results of the optimized structures of these species (Figure 13).



17 **18**

Figure 13. Structures of the anionic complexes **17** and **18**

In both isomers, **17** and **18**, the bond between C1 and C5 is characterized as a double bond with bond lengths of 1.356 Å and 1.354 Å, respectively. The iron is η^3-bonded to the pentadienyl ligand and the $C_3H_4-Fe(CO)_3$ substructure has a local mirror symmetry with one CO group, the iron atom and C3 lying in the mirror plane. The three carbon atoms C2, C3, and C4 assume a delocalized π-allyl system with C−C bond lengths of 1.43 Å. The two anionic complexes **17** and **18** can be considered as being conformers by rotation around the C1−C2 single bond. It is important to note that **17** is more stable than the sterically congested isomer **18** by 5.6 kcal mol^{-1}. These results can be described in terms of the mesomeric structures depicted in Scheme 10.



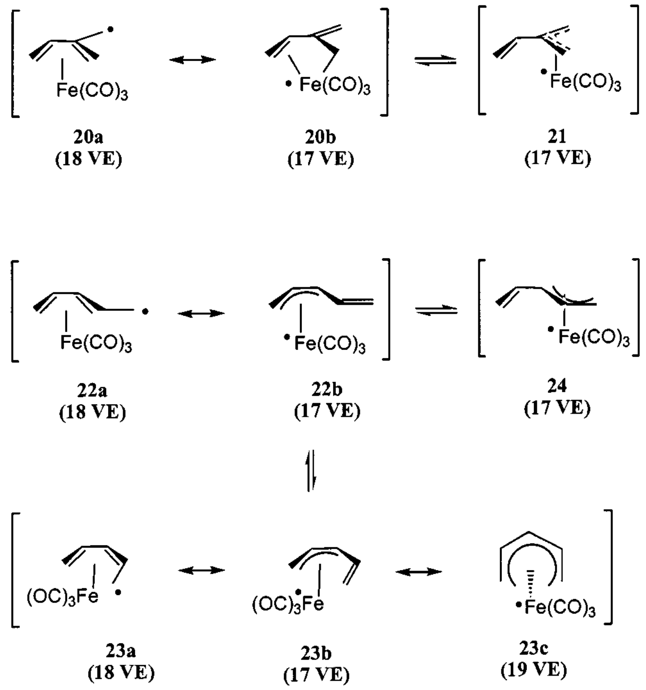
Scheme 10. Mesomeric forms of the anionic pentadienyl−$Fe(CO)_3$ complexes **17** and **18**

In accordance with the structural features discussed above, formulae **17b** and **18b** are unambiguously the better representations of these anionic intermediates. This becomes especially apparent by looking at the geometrical details (η^3 bonding mode) and the electron density distribution that is characterized by accumulating more than one half of the negative charge at the $Fe(CO)_3$ group. It should be briefly mentioned that the configurational stability at the deprotonated center in **17** is very high ($\Delta E^{\neq}$ = 52.9 kcal mol^{-1}) due to similar reasons as in the case of **14**. We also investigated the isomer **19**, a species that could possibly arise from **17** by haptotropic rearrangement of the metal fragment (Scheme 10). It was found that **19** is disfavored energetically by 3.7 kcal mol^{-1} compared to **17**. This suggests that, if anyone were to succeed in selectively deprotonating **3** at C5, the products of a subsequent reaction with an electrophile will be governed by the reactivity of the (most stable) anionic intermediate **17**. From the theoretical point of view there is no reason why this kind of transformation should not be feasible.

The Radical $C_5H_7-Fe(CO)_3$ Complex

To the best of our knowledge, very few radical reactions of butadiene $Fe(CO)_3$ complexes have ever been described.[30] Therefore, the investigation of possible radical intermediates with theoretical methods could help to evaluate potential preparative opportunities.

We will begin with a discussion of the radical complex **20**, which is formally derived by abstracting a hydrogen atom (H$^\bullet$) from the isoprene complex **2**. It is of interest to assess whether the unpaired electron is mainly located at C5 or delocalized to the $Fe(CO)_3$ moiety, corresponding to the mesomeric formulae **20a** and **20b**, respectively (Scheme 11). The calculated structure of this species (Figure 14) indicates that one third of the spin density is located at the iron and two thirds at C5. Regarding the geometry (the iron shows an η^4 bonding mode to the butadiene) as well as the fact that the main part of the spin density is located at C5, the mesomeric structure **20a** seems to be the better representation of this complex. On the other hand, the bond between C2 and C5 is shortened (1.407 Å) and part of the spin density is located at Fe, indicating a contribution of **20b** and suggesting an energetical barrier for the rotation around the C2−C5 bond. Indeed, a barrier of 11.3 kcal mol^{-1} was determined for this process.



Scheme 11. Mesomeric forms of the radical intermediates **20**−**24**

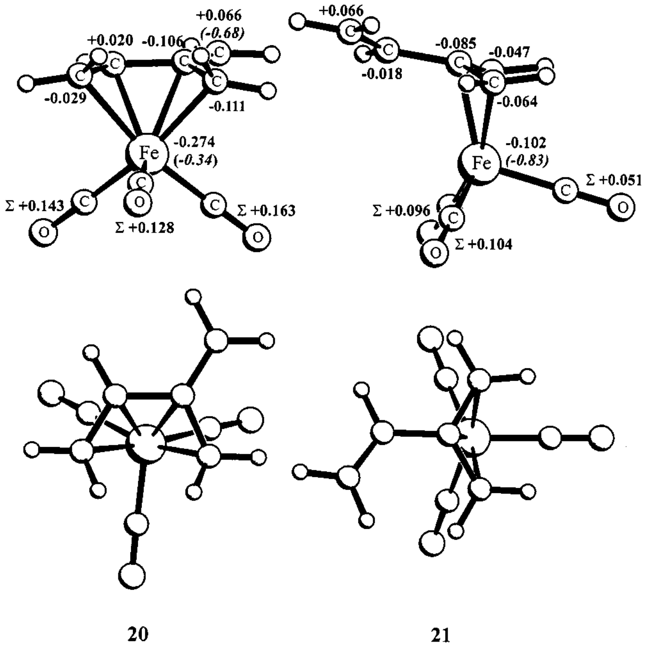
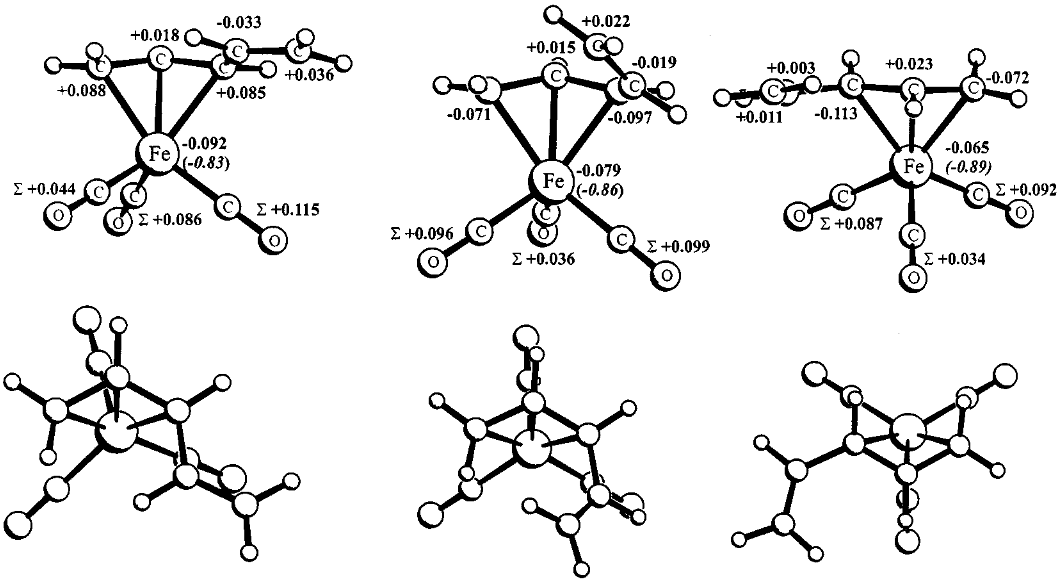


Figure 14. Structures of the radical complexes **20** and **21** formally derived by abstraction of a hydrogen atom from the neutral isoprene−$Fe(CO)_3$ complex **2**

Calculation of the isomeric structure **21** (Scheme 11) revealed that this isomer is energetically favored by 11.6 kcal mol^{-1} in comparison with **20**. In isomer **21** more than 80% of the spin density is localized at the iron center. Thus, it is not unlikely that trimethylenemethane derivatives with a substituent at C4 will be formed in reactions of such intermediates. The energetical difference between **20** and **21** is about 2 kcal mol^{-1} larger than that between the corresponding anionic complexes **14** and **15**, and it is therefore not improbable that a rapid isomerization of **20** to the more stable intermediate **21** will occur.

Finally, the radical pentadienyl complexes **22** and **23**, formally derived from **3** and **4**, respectively, will be discussed. These two species both show an η^3 bonding mode of the metal to the organic ligand (Figure 15) and a geometry akin to that of the anionic pentadienyl complexes **17** and **18**. In both complexes (**22** and **23**) the spin density is almost completely localized at the iron atom (-0.83 $|e|$ and -0.86 $|e|$, respectively). Therefore, the mesomeric formulae **22b** and **23b** (Scheme 11) perfectly describe the calculated structures. These species can thus be considered as conformers. The calculations revealed an energetical difference of 7.7 kcal mol^{-1} with **22** being the more stable conformer. The interconversion of **22** and **23** by rotation of the vinyl group can easily take place as it is associated with only a small barrier (11.7 kcal mol^{-1} from **22** to **23** and 4.0 kcal mol^{-1} from **23** to **22**). For complex **22** another isomer (**24**) must be considered that, according to our calculations, is energetically 6.4 kcal mol^{-1} disfavored in comparison with **22**. One can expect that the haptotropic isomerization of **22** to **24** should easily take place. It is interesting to note that all these open shell systems prefer a 17 VE configuration at the iron. The (formal) 18 VE structures **22a**/**23a** and especially the (η^5) 19 VE structure **23c**[30b] do not describe these complexes well.

These results nicely reflect the experimental observation that radicals of type **22**/**23** react with CBr_4 at the iron to form η^3-allyl−$Fe(CO)_3Br$ complexes.[30b] On the other hand, the small contribution of the mesomeric formulae **22a**/**23a** provides some spin density at C5, which explains the formation of C5−C5 dimers.[30b,c] Calculation of the transition state for the rotation of the $C5H_2$ group in **22** predicts an energy barrier of 28.6 kcal mol^{-1} for this process. Although this barrier is not as high as in the corresponding cationic or anionic complexes (**11** and **17**, respectively), the configurational stability at C5 should be sufficiently high to allow stereospecific transformations in the case of C5-substituted derivatives.



22 **23** **24**

Figure 15. Structures of the radical complexes **22**, **23** and **24** formally derived by abstraction of an hydrogen atom from the neutral pentadiene–Fe(CO)$_3$ complexes **3** and **4**, respectively

Conclusions

The quantum chemical investigation of acyclic 1,3-diene–Fe(CO)$_3$ complexes and their cationic, anionic, and radical intermediates with density functional methods gives a very clear and precise picture of the structures and the reactivity of such species. The high accuracy of the calculations becomes obvious in the few cases where the comparison with experimental data is possible. The calculated structures are used as a reliable basis for the evaluation of possible resonance formulae and for the subtle interpretation of the electronic and conformational situation in the various intermediates. Furthermore, the calculation of energy barriers even permits the rationalization of dynamic phenomena such as isomerization (and racemization) processes. In particular, the calculations predict a pronounced configurational stability of the different intermediates, challenging experimental exploitation. All in all, our computational study provides new insights into the chemistry of acylic 1,3-diene–Fe(CO)$_3$ complexes and experimental facts now appear in a much more lucid light.

Supporting Information available: Lists with the *x,y,z* coordinates for all calculated structures reported in this paper.

Acknowledgments

This work was financially supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. A generous amount of computer time and excellent service was provided by the Konrad-Zuse-Zentrum für Informationstechnik Berlin (Dr. T. Steinke) and the Zentraleinrichtung Rechenzentrum der TU Berlin.

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