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Stereospecific Side Chain Activation in Cyclobutadiene–Fe(CO)$_3$ Chemistry: A Theoretical and Experimental Study on the Structure and Configurational Stability of Cationic, Radical and Anionic Intermediates

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Dedicated to Professor Štefan Toma on the occasion of his 70th birthday

Keywords: Organoiron compounds / π Complexes / Density functional calculations / Reactive intermediates / Stereospecificity / S$_N$1 reactions

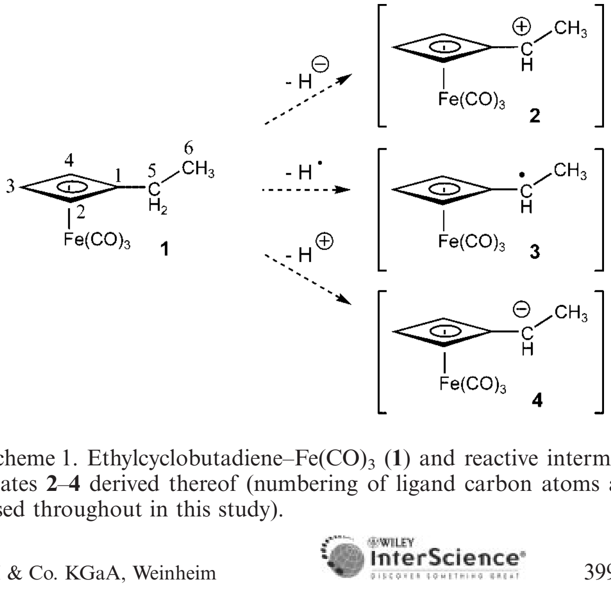
The configurational stability of reactive intermediates (cation, radical and anion) derived from ethylcyclobutadiene–Fe(CO)$_3$ by formal abstraction of a hydride, a hydrogen atom or a proton from the pseudobenzylic position was investigated. Density functional calculations (Becke3lyp) predicted that all these reactive intermediates can be regarded as planar chiral structures having a significant configurational stability. The racemization barriers were calculated to be 38.8 kcal mol^{-1} for the cationic, 16.9 kcal mol^{-1} for the radical and 44.8 kcal mol^{-1} for the anionic intermediate. In an experimental part of the study, derivatives of the 1-hydroxyethyl-substituted complex, which was enantioselectively prepared by CBS reduction of the acetyl complex, were subjected to S$_N$1-type as well as single-electron-transfer-driven umpolung reactions. The observed stereospecificity of these transformations (retention of configuration) is in accordance with the predicted configurational stability of the involved reactive intermediates.

Introduction

The discovery of cyclobutadiene–Fe(CO)$_3$ has been of outstanding importance for the development of organometallic chemistry as an early example for the stabilization of otherwise unstable molecules by metal complexation.[1] Following the theoretical prediction by Longuet-Higgins and Orgel concerning "the possible existence of transition-metal complexes of cyclobutadiene",[2] Pettit and coworkers succeeded in 1965 to prepare the parent (unsubstituted) cyclobutadiene–Fe(CO)$_3$ complex.[3]

From a synthetic point of view, cyclobutadiene–Fe(CO)$_3$ complexes are of particular value as precursors of free cyclobutadienes, which are released upon oxidative decomplexation and usually trapped in situ by cycloaddition chemistry.[3–5] Another characteristic feature of cyclobutadiene–Fe(CO)$_3$ is its ability to undergo electrophilic substitution (e.g. Friedel–Crafts acylation),[6] similar to ferrocene and some other π complexes. While the ability of the Fe(CO)$_3$ unit to stabilize cationic intermediates in the pseudobenzylic position is known, side chain activation by the Fe(CO)$_3$ moiety in general has only been scarcely explored and exploited so far.[7] In a theoretical study, Creary predicted a particularly high radical stabilizing ability of a cyclobutadieneiron tricarbonyl group.[8]

In the context of our research program on the use of transition-metal π complexes as building blocks for the stereoselective synthesis of bioactive compounds,[9] we previously used theoretical methods to gain deeper insights into the structural and energy-related features (e.g. configurational stability) of reactive intermediates derived from



Scheme 1. Ethylcyclobutadiene–Fe(CO)$_3$ (**1**) and reactive intermediates **2**–**4** derived thereof (numbering of ligand carbon atoms as used throughout in this study).

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toluene–$Cr(CO)_3$,[10] methylbutadiene–$Fe(CO)_3$[11] and alkyne–$Co_2(CO)_6$.[12]

We herein report the results of a quantum chemical and experimental investigation of reactive intermediates derived from ethylcyclobutadiene–$Fe(CO)_3$ (**1**). In particular, we studied the configurational stability of the pseudobenzylic cationic, radical and anionic intermediates **2**–**4**, formally derived from **1** by abstraction of a hydride ion, a H radical, or a proton, respectively (Scheme 1).

Computational Details

All calculated structures presented in the following sections were fully optimized in the respective point group symmetry employing analytical gradient techniques and the hybrid density functional method B3LYP[13] as implemented in Gaussian 03.[14] The one-particle description for the metal atom was a (14s11p6d)→(8s6p4d) all-electron basis set introduced by Wachters,[15] supplemented with three primitive f-type polarization functions contracted into one for the metal atom. For carbon, hydrogen and oxygen, Dunning's standard split-valence D_95^* basis set was employed,[16] which includes a set of d-type functions on C and O. The electronic wave functions[17] were analyzed in terms of partial charges, bond orders, orbital hybridization, etc., employing the natural bond orbital (NBO) scheme as developed by Weinhold and coworkers.[18] The nature of stationary points was determined by frequency calculations, and zero-point energy corrections were performed throughout.

Results and Discussion

Theoretical Studies

The Neutral Ethylcyclobutadiene–Fe(CO)$_3$ Complex

We started our theoretical investigation with the neutral parent system **1**. The optimized minimum structure shows the expected η^4 coordination mode with a planar cyclobutadiene ring. The calculations revealed that the eclipsed conformer **1e** (one CO ligand eclipsed to the ethyl substituent) and the staggered conformer **1s** are virtually equal in energy (Table 1). In structure **1s**, which is actually the transition state for the rotation of the $Fe(CO)_3$ tripod, one carbonyl group is eclipsed to C3. The negligible barrier (<0.1 kcal mol^{-1}) suggests a more or less unhindered rotation of the $Fe(CO)_3$ group comparable to the neutral toluene–$Cr(CO)_3$ complex (rotational barrier of 0.6 kcal mol^{-1}).

Table 1. Total energies, zero-point energy correction (ZPE) and relative energies for structures **1**–**4**.

Structure	Total energies (hartree)	ZPE [kcal mol^{-1}]	Relative energies [kcal mol^{-1}]
1e	–1837.23782	92.46	0.0
1s	–1837.23771	92.47	< 0.1
2s	–1836.37322	85.49	0.0
2e	–1836.35674	84.85	9.7
2ts	–1836.30778	83.22	38.8
3s	–1836.60162	83.65	0.0
3e	–1836.59711	83.49	2.7
3ts	–1836.57338	82.85	16.9
4e	–1836.66223	83.29	0.0
4s	–1836.65203	83.27	6.4
4ts	–1836.58811	81.60	44.8

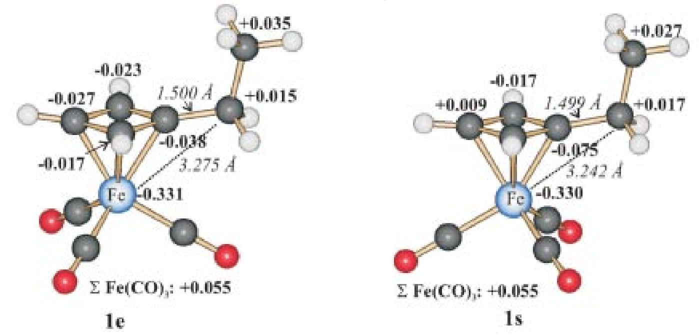
The calculated geometries of the conformers **1e** and **1s** of the parent system **1** as well as the partial charges are displayed in Figure 1. Both structures have a C_s symmetry with the ethyl carbons lying in the mirror plane. A slight distortion of the cyclobutadiene ring is revealed by two pairs of C–C bonds with different lengths (1.453 Å for C1–C2 and C1–C4 and 1.468 Å for C2–C3 and C3–C4). The single bond between C1 and C5 has a length of 1.50 Å.[19] Remarkably, the ethyl substituent is significantly bent out of the ring plane by ca. 11° in **1e** and 16° in **1s**. The NBO analysis of the partial charges shows that the $Fe(CO)_3$ moiety in **1e** is nearly neutral [Σ $Fe(CO)_3 = +0.055$ |e|]. Thus, as in the case of acyclic 1,3-diene–$Fe(CO)_3$ complexes[11] [and in contrast to arene–$Cr(CO)_3$ complexes][10a] the metal tricarbonyl moiety in cyclobutadiene–$Fe(CO)_3$ does not act as an electron withdrawing group. Accordingly, the carbon atoms of the cyclobutadiene ring and the pseudobenzylic carbon C5 are nearly neutral. The iron atom itself carries a negative partial charge of –0.331 |e|.

The accuracy of the computational method was probed by calculating the structure of complex **5** for which we succeeded to obtain reliable X-ray crystal structural data (Figure 2). Comparison of the bond lengths calculated for this complex with the data from the X-ray crystal structure analysis shows good agreement (Table 2) with a maximum deviation of 0.05 Å between the calculated and the experimental bond lengths. As often found for density functional methods, the calculated bond lengths tend to be a bit too long.[20] It should be mentioned that two independent molecules of complex **5** appear in the unit cell, differing in their conformation along the C1–C5 bond. The data presented in Table 2 refer only to the conformer with an *anti-periplanar* orientation of the OH group with respect to the Fe atom.

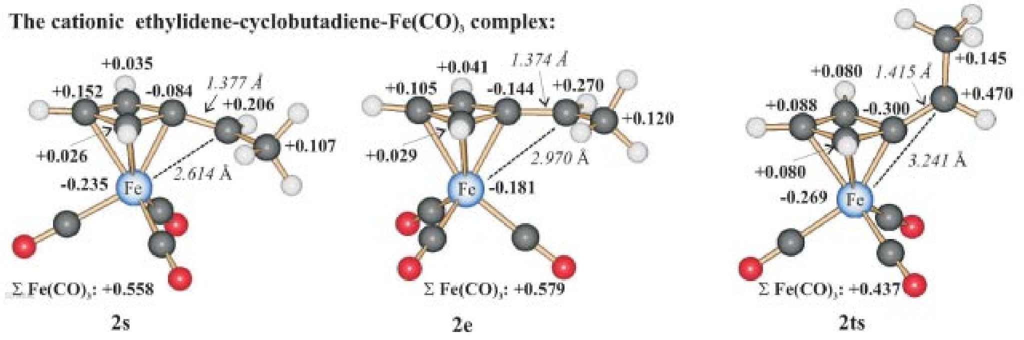
The Cationic C_6H_7–$Fe(CO)_3^+$ Complex

The formal abstraction of a hydride ion from the pseudobenzylic position of **1** (i.e. at C5) leads to cation **2** (Figure 1). Experimentally, this species would, for instance, occur as an intermediate in solvolysis reactions. The calculated minimum structure **2s** for this system shows that C5 (i.e. the pseudobenzylic carbon) is strongly bent towards the metal centre (the Fe–C5 distance is shortened to 2.614 Å relative to 3.275 Å in **1**) and the $Fe(CO)_3$ tripod prefers a staggered conformation with respect to the ethylidene substituent (Figure 2). The bond length C1–C5 of 1.377 Å indicates a double bond. The distances C1–C2 and C1–C4 (1.494 Å) correspond to slightly shortened single bonds, in contrast to C2–C3 and C3–C4 (1.437 Å), which have a bond order of about 1.5 (allylic system). The rotation of the

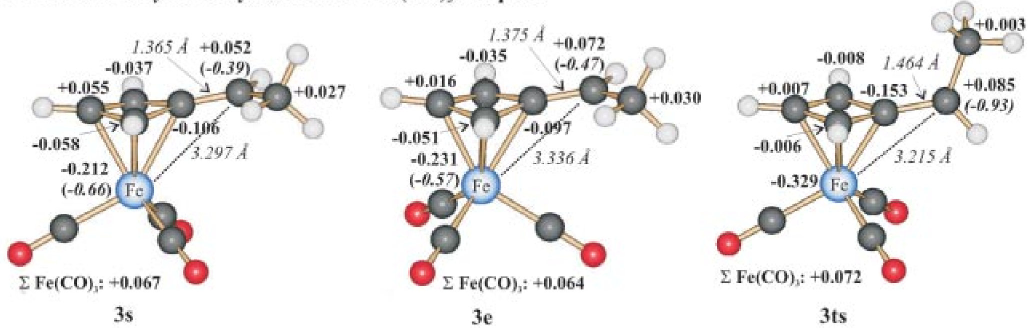
The neutral ethyl-cyclobutadiene-Fe(CO)$_3$ complex:



The cationic ethylidene-cyclobutadiene-Fe(CO)$_3$ complex:



The radical ethylidene-cyclobutadiene-Fe(CO)$_3$ complex:



The anionic ethylidene-cyclobutadiene-Fe(CO)$_3$ complex:

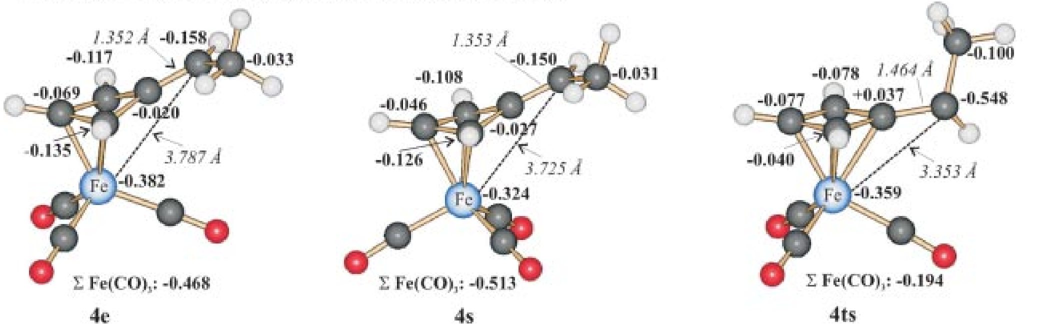


Figure 1. Calculated structures of the neutral ethylcyclobutadiene–Fe(CO)$_3$ complex **1** in the eclipsed (**1e**) and the staggered (**1s**) conformations. Calculated structures of the cationic (**2**), the radical (**3**) and the anionic (**4**) intermediates [ethylidenecyclobutadiene–Fe(CO)$_3$ species] derived from **1** by formal abstraction of a hydride, an H-atom, or a proton. In all cases, the minimum structures are shown on the left (**1e**, **2s**, **3s**, **4e**) and it should be noted that the other conformers (**1s**, **2e**, **3e** and **4s**) correspond to the transition states connected to the rotation of the Fe(CO)$_3$ tripod. On the right, the transition states for the rotation around the exocyclic bonds (**2ts**, **3ts**, **4ts**) are depicted. Partial charges are shown in bold letters and the bond lengths in italic. For the radical complexes, the spin density is given in parentheses.

Fe(CO)$_3$ group in the cationic intermediate **2** is much more hindered than in the neutral complex **1**. The eclipsed conformer **2e** was identified to be the transition state for this rotation connected to an imaginary frequency of 72 wavenumbers. Conformer **2e** is disfavoured by 9.7 kcal mol^{-1} relative to **2s**.

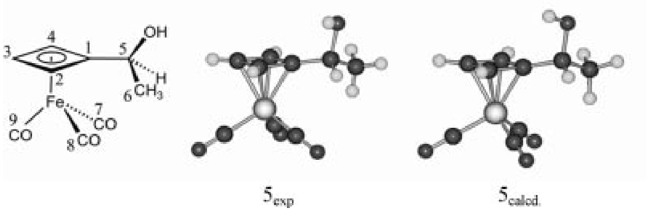
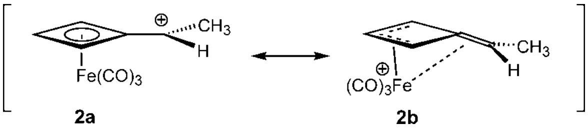


Figure 2. Structure of complex **5**: Comparison of the experimental ($\mathbf{5}_{exp}$) and calculated ($\mathbf{5}_{calcd.}$) geometry.

Table 2. Calculated bond lengths (in Å) for 1-hydroxyethylcyclobutadiene–$Fe(CO)_3$ (**5**) compared to the experimental data obtained by X-ray crystal analysis of **5**.

Parameters	Calculated	Experimental
C1–C2	1.478	1.468
C1–C4	1.466	1.465
C1–C5	1.504	1.492
C2–C3	1.454	1.454
C3–C4	1.445	1.433
C5–C6	1.527	1.514
Fe–C1	2.038	2.049
Fe–C2	2.045	2.043
Fe–C3	2.080	2.072
Fe–C4	2.073	2.062
Fe–C7	1.787	1.782
Fe–C8	1.790	1.799
Fe–C9	1.795	1.807
O–C5	1.440	1.436
O–C7	1.158	1.164
O–C8	1.158	1.135
O–C9	1.158	1.134
Fe–C5	3.249	3.195

The geometrical features found for the minimum structure **2s** clearly suggest that the cation **2** is best represented by the resonance structure **2b** (Scheme 2). In accordance, the NBO analysis for **2s** reveals that more than one half of the positive charge is delocalized to the $Fe(CO)_3$ moiety, whereas C5 carries only a small positive partial charge of +0.206 |e|.



2a **2b**

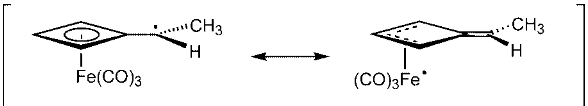
Scheme 2. Resonance structures for the cationic ethylcyclobutadiene–$Fe(CO)_3$ complex **2**.

The calculated minimum geometry of **2** (Figure 1) also indicates that this species represents a planar chiral structure.[21] Therefore, it was of interest to calculate the barrier of rotation around the formal C1–C5 double bond in **2b**, which would lead to racemization. The relative energy of the transition state **2ts** is 38.8 kcal mol^{-1} (compared to **2s**) and reveals a very high barrier for this process and, hence, suggests the possibility of stereospecific (S_N1-type) reactions.[22] Interestingly, in the transition state **2ts** the ethylidene group is bent away from the $Fe(CO)_3$ moiety and a reduced delocalization of the positive charge to the $Fe(CO)_3$ group is observed, as also reflected by an increased C1–C5 distance (1.415 Å).

The Radical C_6H_7–$Fe(CO)_3^{\cdot}$ Complex

In the minimum geometry of the radical intermediate **3s** (Figure 1), the carbonyl ligands are arranged staggered to the ethylidene group, which is slightly bent out of the ring plane away from the $Fe(CO)_3$ moiety as reflected by a Fe–C5 distance of 3.297 Å (compared to 3.275 Å in **1e**). In **3s**, the C1–C5 bond clearly has double bond character (1.365 Å as compared to 1.50 Å in **1**), and the metal fragment takes over most of the spin density. Only about one third of the spin density remains at C5. The eclipsed conformer **3e** was identified as being the saddle point for the $Fe(CO)_3$ rotation connected to an imaginary frequency of 44 wavenumbers. In **3e** the transfer of the spin density to the iron is less pronounced (Fe = –0.57 |e|, C5 = –0.47 |e|), but nevertheless the barrier for the rotation of the $Fe(CO)_3$ tripod is rather small (2.7 kcal mol^{-1}).

These results suggest that the electronic and geometric features of the radical intermediate **3** are best represented by the resonance structure **3b** (Scheme 3).



3a **3b**

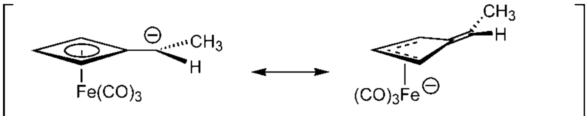
Scheme 3. Two resonance structures for the radical complex **3**.

To evaluate the configurational stability, the transition state **3ts** for the rotation of the exocyclic C1–C5 bond was also calculated (Figure 1). It was found that the length of the exocyclic C1–C5 bond increases to 1.464 Å (single bond character) during the rotation and the main part of the spin density is located at C5 (–0.93 |e|) in the transition structure **3ts**. All this is mirrored by a significant rotational barrier of 16.9 kcal mol^{-1}, which is higher than that of the corresponding ethylbenzene–$Cr(CO)_3$ derived radical.[10b] Thus, it is predicted that stereospecific reactions involving radical intermediates of type 3 should be feasible.

The Anionic C_6H_7–$Fe(CO)_3^{-}$ Complex

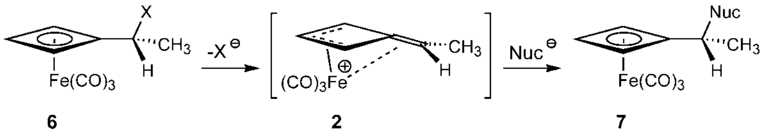
The third reactive intermediate to be discussed is the anionic ethylidenecyclobutadiene–$Fe(CO)_3$ complex **4**, formally derived from **1** by deprotonation at the pseudobenzylic position (Scheme 1).

The most pronounced feature of the anionic intermediate **4** is a distorted structure in which the ethylidene group is strongly bent away from the $Fe(CO)_3$ moiety (24° with respect to the plane defined by the ring carbons C2, C3 and C4) with a long Fe–C5 distance of 3.787 Å (Scheme 4). In calculated conformers **4e** and **4s** the found geometry indicates a η^3 coordination mode of the anionic $Fe(CO)_3$ moiety to an π-allyl system defined by C2, C3 and C4. This



4a **4b**

Scheme 4. Resonance structures of the anionic intermediate **4**.



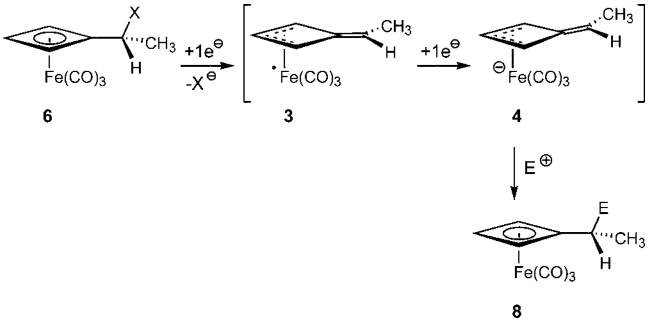
Scheme 5. S$_N$1-type reaction.

picture is also supported by a pronounced localization of the negative charge at the Fe(CO)$_3$ fragment (e.g. –0.467 |e| in **4e**) whereas only a small negative charge (–0.158 |e| in **4e**) remains at the pseudobenzylic centre. Therefore, the anionic intermediate **4** must also be considered as a planar chiral species best represented by the resonance structure **4b**.

The calculation of the transition state **4ts** for the racemization of **4** through rotation around the exocyclic C1–C5 bond of **4** revealed a barrier of 44.8 kcal mol^{-1} and thus a high configurational stability of this type of anionic intermediate. In the transition state **4ts** (Figure 1) the charge delocalization towards the metal fragment is significantly reduced.

Experimental Investigations

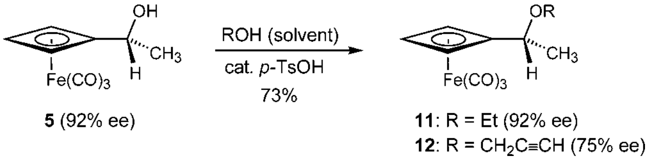
To probe the configurational stability of the reactive intermediates of type **2**, **3** and **4** predicted by the calculations (vide supra), we decided to also carry out an experimental study focusing on two general types of transformations: (1) A S$_N$1-type reaction as sketched in Scheme 5 should proceed with retention of configuration, as the planar chiral cationic intermediate **2**, generated by Fe-assisted expulsion of the leaving group X from substrate **6** should be attacked by a nucleophile from the *exo*-face to give product **7**.[22] (2) The second process (Scheme 6) to be explored concerns the transformation of a substrate of type **6** into **8** by means of an electron-transfer-driven umpolung reaction. Here, the predicted configurational stability of the radical **3** and the anionic intermediate **4** would ensure stereospecificity (overall retention) after *exo*-alkylation of **4** with an electrophile, in analogy to the corresponding transformations in the arene–Cr(CO)$_3$ series.[9d,10b]



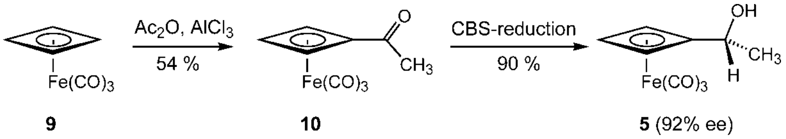
Scheme 6. Stereospecific benzylic alkylation of **6** by an electron-transfer-driven umpolung reaction.

As a nonracemic starting material for the planned experiments we prepared the alcohol **5** from the parent cyclobutadiene–Fe(CO)$_3$ complex **9**[23] by Friedel–Crafts acylation[24] and subsequent oxazaborolidin-catalyzed borane reduction (CBS-reduction)[25] of the acetyl derivative **10** (Scheme 7). The enantiomeric excess of **5** (92%*ee*) was determined by HPLC analysis and considered to be sufficiently high for the planned experiments. The absolute configuration of **5**, as confirmed by X-ray crystal structure analysis (compare Figure 2), was in accordance with the configuration predicted by applying the model of Corey.[25c] In addition, a sample of *rac*-**5** was prepared (by NaBH$_4$ reduction of **10**) to provide racemic references for the enantiomeric analysis.

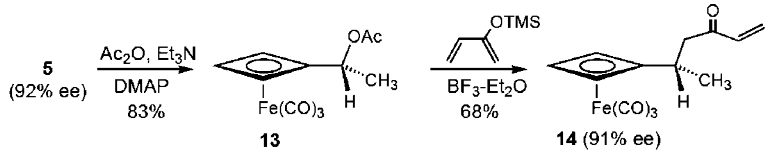
On treatment of a solution of **5** in either ethanol or propargylic alcohol with catalytic amounts of *p*-TsOH solvolysis afforded the ethers **11** and **12** (Scheme 8). In both cases an optically active product was obtained, indicating the stereospecificity of the transformation. Whereas virtually no racemization was observed for the reaction with ethanol, a significant loss of stereochemical information (from 92 to 75%*ee*) was found for the reaction with propargylic alcohol. Nevertheless, these experiments clearly underline a pronounced configurational stability of the cationic intermediate **2** in these reactions (Scheme 5).



Scheme 8. Stereospecific solvolysis of **5** by an S$_N$1-type pathway.



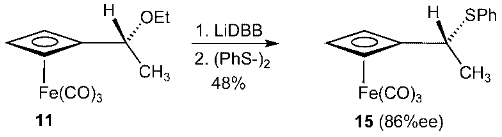
Scheme 7. Synthesis of the nonracemic complex **5**.



Scheme 9. Another stereospecific S_N1-type transformation in the pseudobenzylic position of a cyclobutadiene–Fe(CO)$_3$ complex.

As an additional example for such a stereospecific S_N1 reaction, the conversion of **5** into the enone **14** was achieved by reaction with 2-trimethylsiloxy-1,3-butadiene in the presence of boron trifluoride–diethyl ether (Scheme 9).

In analogy to our previous experiments using arene–Cr(CO)$_3$ complexes[10b] we also probed the possibility to achieve a stereospecific benzylic alkylation of the anionic intermediate **4** obtained by an electron-transfer-driven umpolung reaction according to Scheme 6. Indeed, when **11** was treated with an excess of the single-electron reducing agent LIDBB[26] followed by the addition of diphenyl disulfide, the nonracemic product **15** (86%*ee*) was isolated in at least 48% yield (Scheme 10). Attempts to employ other electrophiles (such as TMSCl, 4-methoxybenzylbromide and MOMCl) failed. Nevertheless, the formation of **15** with only little loss of stereochemical information supports the predicted configurational stability of both the radical and the anionic intermediates. As the product **15** could not be crystallized, its absolute configuration was not directly proven. Nevertheless, we assume retention of configuration in agreement with the proposed mechanism (Scheme 6) and in analogy to our earlier experiments.[10b] It also would be hard to imagine any mechanism leading to a specific inversion of configuration.



Scheme 10. LiDBB-mediated electron-transfer-driven umpolung/sulfination of **11**.

Conclusions

The application of transition-metal π complexes in stereoselective synthesis greatly benefits from a detailed knowledge and understanding of reactive intermediates. Against this background, reactive intermediates formally derived from ethylcyclobutadiene–Fe(CO)$_3$ were investigated in a combined theoretical and experimental study. By using density functional theory, the pseudobenzylic cation, radical and anion were characterized. Besides structural features, the energetics for the rotation of the Fe(CO)$_3$ tripod and the *exo*-ethylidene group were calculated. The predicted significant configurative stability of the reactive intermediates (38.8 kcal mol^{-1} for the cationic, 16.9 kcal mol^{-1}for the radical, and 44.8 kcal mol^{-1} for the anion) was then experimentally probed. Indeed, by using nonracemic complexes **5** and **11** as substrates, both S_N1-type reactions, as well as an electron-transfer-driven umpolung reaction could be performed with retention of stereochemical information. The fact that chiral cyclobutadiene–Fe(CO)$_3$ complexes can be transformed in a stereospecific fashion may promote their future application in enantioselective organic synthesis.

Experimental Section

η^4-(1-Acetyl-1,3-cyclobutadiene)tricarbonyliron (10): To a solution of 1.48 g (7.72 mmol) of the parent cyclobutadiene–Fe(CO)$_3$ complex (**9**)[24] in anhydrous dichloromethane (15 mL) was added acetic anhydride (766 µL, 8.1 mmol), and the reaction mixture was cooled to –20 °C. Then, AlCl$_3$ (2.16 g, 16.2 mmol) was added in portions and stirring was continued until TLC indicated complete conversion. The mixture was poured into aqueous NaHCO$_3$ (5%, 25 mL) and extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried with Na$_2$SO$_4$, and the solvent was removed under reduced pressure. Column chromatography on silica gel (cyclohexane/EtOAc, 4:1) afforded **10** (986 mg, 54%) as a yellow oil. R_f = 0.21 (cyclohexane/EtOAc, 4:1). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.00 (s, 3 H, CH$_3$), 4.42 (s, 1 H), 4.55 (s, 2 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 25.2 (q, C-6), 64.9 (d, C-2/C-4), 69.4 (d, C-3), 70.1 (s, C-1), 197.2 (s, C-5), 211.8 (s, CO) ppm. IR: ṽ = 3096 (w), 2360 (w), 2050 (s, CO), 1964 (s, CO), 1665 (s, CO), 1430 (m), 1352 (w), 1309 (w), 1161 (m), 927 (w) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 234 (1) [M]$^+$, 206 (19) [M – CO]$^+$, 178 (7) [M – 2 CO]$^+$, 150 (69) [M – 3 CO]$^+$, 124 (100), 96 (24), 84 (21), 82 (31), 81 (59), 56 (94) [Fe]. HRMS (EI, 70 eV): calcd. for $C_{20}H_{26}O_4$ [M]$^+$ 233.9615; found 233.962.

(*R*,*S*)-Tricarbonyl-η^4-[(1-hydroxyethyl)-1,3-cyclobutadiene]iron (*rac*-5): A solution of complex **10** (391 mg, 1.24 mmol) in EtOH/1,4-dioxane (4:1, 15 mL) was cooled to 0 °C and NaBH$_4$ (260 mg 6.8 mmol, 5 equiv.) was added. The reaction mixture was stirred for 3 h and then quenched by the addition of ice. After extraction with EtOAc (3 × 15 mL), the combined organic solutions were washed with saturated aqueous NaCl (25 mL), dried with Na$_2$SO$_4$ and the solvent was removed in vacuo. The product was purified by chromatography on silica gel (cyclohexane/EtOAc, 2:1) to afford *rac*-**5** (251 mg, 78%) as a yellowish, low melting solid. R_f = 0.26 (cyclohexane/EtOAc, 2:1). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.24 (d, ^3J = 6.5 Hz, 3 H, CH$_3$), 1.34 (d, ^3J = 5.5 Hz, 1 H, OH), 4.07 (s, 2 H, 2-H & 4-H), 4.17 (s, 1 H, 3-H), 4.30 (ψquin, ^3J = 6 Hz, 1 H, C*H*OH) ppm. ^{13}C NMR (63 MHz, CDCl$_3$): δ = 22.6 (q, C-6), 61.9 (d, C-5), 62.4 (d, C-2/C-4), 62.6 (d, C-2/C-4), 63.5 (d, C-3), 89.9 (s, C-1), 214.4 (s, CO) ppm. IR: ṽ = 3325 (m, OH), 2972 (w, CH$_2$), 2340 (w), 2037 (s, CO), 1943 (s, CO), 1371, (w), 1296 (w), 1130 (w), 1102 (w), 1056 (w), 876 (w) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 236 (17) [M]$^+$, 208 (65) [M – CO]$^+$, 180 (47) [M – 2 CO]$^+$, 152 (79) [M – 3 CO]$^+$, 134 (76), 126 (64), 108 (100), 81 (14), 73 (13), 56 (32) [Fe]. HRMS (EI, 70 eV): calcd. for $C_9H_8FeO_4$ [M]$^+$ 235.977; found 235.977.

(*R*)-Tricarbonyl-η^4-[(1-hydroxyethyl)-1,3-cyclobutadiene]iron (5): A solution of the oxazaborolidine catalyst [prepared from (*S*)-diphenylprolinol and methylboronic acid] (130 mg, 0.35 mmol) and complex **10** (986 mg, 4.2 mmol) in THF (10 mL) was cooled to 0 °C. Then, $BH_3{\cdot}SMe_2$ (2 M in THF, 0.75 mL) was added and stirring was continued for 5 min before additional $BH_3{\cdot}SMe_2$ (1.56 mL) was added dropwise. After 1 h, the reaction was quenched by the addition of methanol (3 mL). After 1 h, the solution was concentrated in vacuo, and the crude product was purified by column chromatography on silica gel (cyclohexane/EtOAc, 3:1) to afford **5** (734 mg, 90%) as a yellow solid. $[\alpha]_{589} = +2.2$ (c = 0.963, $CHCl_3$, 20 °C). HPLC [Chiralcel OJ, *n*-hexane/*i*PrOH (95:5), $v = 0.5\ mL\,min^{-1}$, $\lambda = 254$ nm]: $t_{(S)} = 20.1$ min; $t_{(R)} = 22.2$ min; 92%*ee*. The spectroscopic data were identical to those reported above for *rac*-**5**.

(*R*)-Tricarbonyl-η⁴-[(1-ethoxyethyl)-1,3-cyclobutadiene]iron (11): A solution of **5** (173 mg, 0.66 mmol) in ethanol (8 mL) was cooled to 0 °C. After the addition of *p*-TsOH (19 mg, 15 mol-%), the mixture was warmed to room temp. and left to stir overnight. The solution was then diluted with dichloromethane (20 mL)and extracted with a saturated aqueous solution of $NaHCO_3$ (1 × 15 mL). The aqueous layer was extracted once with dichloromethane, and the combined organic solutions were dried with Na_2SO_4 and concentrated under reduced pressure. After column chromatography on silica (cyclohexane/EtOAc, 6:1), **11** (134 mg, 74%) was obtained as a yellow oil. $R_f = 0.53$ (cyclohexane/EtOAc, 4:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.16 (d, ^3J = 6.6 Hz, 3 H, CH_3), 1.18 (t, ^3J = 6.7 Hz, 3 H), 3.37–3.63 (m, 2 H), 3.82 (q, ^3J = 6.5 Hz, 1 H), 4.00 (d, ^3J = 9.0 Hz, 1 H), 4.12 (d, ^3J = 7.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4 (q, C-8), 19.6 (q, C-6), 62.5 (d, C-3), 62.9 (d, C-2/C-4), 63.0 (d, C-2/C-4), 64.3 (t, C-7), 70.8 (d, C-5), 86.5 (s, C-1), 214.5 (s, CO) ppm. IR: $\tilde{\nu}$ = 2974 (m, CH), 2928 (w, CH), 2866 (w, CH), 2036 (s, CO), 1961 (s, CO), 1481, (w), 1446, (w), 1317 (m), 1299 (w), 1129 (m), 1098 (m), 1082 (m), 935 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 264 (1) $[M]^+$, 236 (18) $[M - CO]^+$, 208 (25) $[M - 2\ CO]^+$, 180 (18) $[M - 3\ CO]^+$, 136 (100), 134 (52), 110 (29), 81 (10), 56 (32) [Fe]. $[\alpha]_{589} = +36.9$, $[\alpha]_{546} = +43.0$, $[\alpha]_{405} = +67.1$ (c = 1.117, $CHCl_3$, 20 °C). HPLC [Chiralpak AD-H, *n*-hexane/*i*PrOH (97:3), $v = 0.5\ mL\,min^{-1}$, $\lambda = 254$ nm]: $t_{(S\text{-ent})} = 6.9$ min; $t_{(R\text{-ent})}$ = 7.6 min; 92%*ee*.

(*R*)-Tricarbonyl-[η⁴-(1-prop-2-inyloxyethyl)-1,3-cyclobutadiene]iron (12): A solution of alcohol **5** (39 mg, 0.16 mmol, 92%*ee*) in propargylic alcohol (5 mL) was cooled to 0 °C and *p*-TsOH (0.016 mmol, 3.2 mg, 0.1 equiv.) was added. While stirring for 1 h the mixture was warmed to room temp. The solution was then diluted with dichloromethane (20 mL) and washed with a saturated $NaHCO_3$ solution (2 × 10 mL) followed by saturated aqueous NaCl (1 × 10 mL). After drying over Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/EtOAc, 6:1) to afford **12** (33 mg, 73%, 75%*ee*) as an oil. $R_f = 0.35$ (cyclohexane/EtOAc, 6:1). $[\alpha]_{589}$ = +30.9, $[\alpha]_{546} = +34.6$ (c = 0.718, $CHCl_3$, 20 °C, 75%*ee*). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.19 (d, ^3J = 6.5 Hz, 3 H), 2.41 (t, ^4J = 2.5 Hz, 1 H), 4.04 (d, ^3J = 9.3 Hz, 1 H), 4.10 (q, ^3J = 6.5 Hz, 1 H), 4.13 (s, 1 H), 4.16 (d, ^3J = 9.3 Hz, 1 H), 4.21 (dd, ^2J = 6.5 Hz, ^4J = 2.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 (q, C-6), 55.7 (t, C-7), 63.0 (d, C-2/C-4), 63.2 (d, C-2/C-4), 69.8 (d, C-3), 74.6 (d, C-9), 79.6 (d, C-5), 84.6 (s, C-8), 92.0 (s, C-1), 214.2 (s, CO) ppm. IR: $\tilde{\nu}$ = 3302 (m), 2978 (w, CH), 2933 (w, CH), 2856 (w, CH), 2039 (s, CO), 1961 (s, CO), 1445 (m), 1375 (m), 1319 (w), 1300 (w), 1119 (m), 1074 (s), 1030 (m), 827 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 274 (<1) $[M]^+$, 246 (<1) $[M - CO]^+$, 218 (20) $[M - 2\ CO]^+$, 190 (24) $[M - 3\ CO]^+$, 158 (37), 134 (58), 81 (44), 56 (100) [Fe]. HRMS (EI, 70 eV): calcd. for $C_8H_8FeO_3$ $[M - CO]^+$ 245.9979; found 245.998. HPLC [Chiralpak AD-H, *n*-hexane/*i*PrOH (97:3), $v = 0.5\ mL\,min^{-1}$, $\lambda = 254$ nm]: $t_{(S)} = 9.0$ min; $t_{(R)}$ = 10.2 min; 75%*ee*.

(*R*)-Tricarbonyl-[η⁴-(1-acetoxyethyl)-1,3-cyclobutadiene]iron (13): A solution of **5** (135 mg, 0.57 mmol, 93%*ee*) in dichloromethane (8 mL) was cooled to 0 °C and acetic anhydride (270 µL, 2.86 mmol, 5 equiv.), triethylamine (2.86 mmol, 397 µL, 5 equiv.) and a catalytic amount of DMAP (ca. 5 mol-%) were added. The mixture was warmed to room temp. and stirred overnight. The solution was then concentrated in vacuo and purified by column chromatography on silica gel (cyclohexane/EtOAc, 4:1) to afford **13** (139 mg, 83%) as a yellow oil. $R_f = 0.22$ (cyclohexane/EtOAc, 4:1). $[\alpha]_{589} = +81.4$, $[\alpha]_{546} = +97.3$ (c = 0.588, $CHCl_3$, 20 °C). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.22 (d, ^3J = 6.5 Hz, 3 H, CH_3), 2.03 (s, 3 H, $COCH_3$), 4.05 (s, 2 H), 4.14 (s, 1 H), 5.32 (q, ^3J = 6.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.6 (q, C-6), 21.0 (q, $COCH_3$), 62.5 (d), 63.4 (d), 63.5 (d), 65.8 (d), 84.0 (s, C-1), 170.2 (s, $COCH_3$), 214.1 (s, CO) ppm. IR: $\tilde{\nu}$ = 3109 (w, CH), 2984 (w, CH), 2936 (w, CH), 2040 (s, CO), 1960 (s, CO), 1733 (s, CO), 1450 (w), 1370 (m), 1320 (w), 1233 (s), 1045 (m), 938 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 250 (4) $[M - CO]^+$, 222 (10) $[M - 2\ CO]^+$, 194 (45) $[M - 3\ CO]^+$, 168 (97), 134 (38), 115 (21), 108 (57), 81 (35), 56 (100) [Fe].

(*R*)-Tricarbonyl-[η⁴-(1-methyl-3-oxopent-4-enyl)-1,3-cyclobutadiene]iron (14): A solution of acetate **13** (54 mg, 0.18 mmol, 92%*ee*) and 2-trimethylsilyloxy-1,3-butadiene (33 mg, 0.24 mmol) in dichloromethane (1 mL) was cooled to 0 °C and $BF_3{\cdot}Et_2O$ (25.3 µL, 0.2 mmol, 1.1 equiv.) was added dropwise under vigorous stirring. Once TLC had indicated complete conversion (ca. 1 h), the reaction was quenched by the addition of a saturated $NaHCO_3$ solution (2 mL). The aqueous layer was extracted with dichloromethane (2 × 1 mL), and the combined organic phases were washed with saturated aqueous NaCl (1 mL), dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc, 6:1) to give **14** (36 mg, 68%) as an oil. $R_f = 0.19$ (cyclohexane/EtOAc, 6:1). $[\alpha]_{589} = +9.4$, $[\alpha]_{546} = +9.2$ (c = 1.123, $CHCl_3$, 20 °C). ^1H NMR (250 MHz, $CDCl_3$): δ = 0.94 (d, ^3J = 6.5 Hz, 3 H), 2.56 (dd, ^2J = 16.8 Hz, ^3J = 6.6 Hz, 2 H), 2.86 (ψhept, ^3J = 7 Hz, 1 H), 3.89 (d, ^4J = 9.3 Hz, 1 H), 4.96 (d, ^4J = 9.0 Hz, 1 H), 4.05 (s, 1 H), 5.84 (dd, ^2J = 1.5 Hz, ^3J = 10.0 Hz, 1 H), 6.19 (dd, ^2J = 1.5 Hz, ^3J = 17.8 Hz, 1 H), 6.33 (dd, $^3J_1$ = 10 Hz, $^3J_2$ = 17.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9 (q, C-6), 26.9 (d, C-5), 46.5 (t, CH_2), 60.9 (d, C-2/3/4), 62.4 (d, C-2/3/4), 62.8 (d, C-2/3/4), 93.1 (s, C-1), 128.6 (t,$=CH_2$), 136.5 (d, $CH{=}CH_2$), 198.6 (s, CH_2-CO), 214.9 (s, CO) ppm. IR: $\tilde{\nu}$ = 2968 (w, CH), 2931 (w, CH), 2034 (s, CO), 1942 (s, CO), 1699 (m), 1680 (s, CO), 1399 (m), 1374 (w), 1358 (m), 1080 (w), 984 (m), 959 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 260 (7) $[M - CO]^+$, 232 (27) $[M - 2\ CO]^+$, 204 (40) $[M - 3\ CO]^+$, 178 (100), 148 (18), 134 (27), 121 (16), 108 (18), 84 (32), 56 (37) [Fe]. HRMS (EI, 70 eV): calcd. for $C_8H_8FeO_3$ $[M - CO]^+$ 260.0136; found 260.013. HPLC [Chiralpak AS, *n*-hexane/*i*PrOH (97:3), $v = 0.5\ mL\,min^{-1}$, λ = 254 nm]: $t_{(R)} = 14.2$ min; $t_{(S)} = 22.2$ min; 91%*ee*.

(*R*)-Tricarbonyl-[η⁴-1-(1-thiophenylethyl)-1,3-cyclobutadiene]iron (15): Under an atmosphere of dry argon, a solution of 4,4′-di-*tert*-butyldiphenyl (186 mg, 0.7 mmol) in THF (15 mL) was cooled to 0 °C and a large excess (ca. 20 equiv.) of lithium metal was added. After stirring for 4 h the resulting blue solution was transferred by a cannular into a long-necked Schlenk flask and cooled to –78 °C. To the LiDBB solution was then added a solution of **11** (46 mg, 0.17 mmol) in THF(2 mL). The mixture was stirred for 30 min and diphenyl disulfide (95 mg, 0.44 mmol) was added to the (meanwhile brown) mixture. After 1 h, the mixture was poured into water

(30 mL). After extraction with MTB/diethyl ether (3 × 15 mL) the combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. Column chromatography on silica gel (cyclohexane) afforded **15** (29 mg, 48 %). R_f = 0.77 (cyclohexane). $[\alpha]_{589}$ = +5.6, $[\alpha]_{546}$ = +1.5, $[\alpha]_{405}$ = –123.3 (c = 0.642, $CHCl_3$, 20 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.27 (d, ^3J = 6.8 Hz, 3 H), 3.57 (d, ^3J = 9.0 Hz, 1 H), 3.64 (q, ^3J = 6.8 Hz, 1 H), 4.01 (s, 1 H), 4.07 (d, ^4J = 9.0 Hz, 1 H), 7.29–7.49 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.5 (C-6), 41.7 (C-5), 61.8 (C-2/C-4), 61.9 (C-2/C-4), 63.6 (C-3), 88.4 (C-1), 100.8 (C-7), 128.0 (C_{Ar}), 128.9 (C_{Ar}), 133.8 (C_{Ar}), 214.5 (CO) ppm. IR: $\tilde{\nu}$ = 3070 (w, CH), 2970 (w, CH), 2922 (w, CH), 2036 (s, CO), 1985 (s, CO), 1581 (s), 1476 (m), 1436 (m), 1372 (w), 1087 (w), 1022 (m), 748 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 328 (2) $[M]^+$, 300 (22) $[M - CO]^+$, 272 (4) $[M - 2\,CO]^+$, 244 (60) $[M - 3\,CO]^+$, 210 (30), 207 (65), 166 (21), 134 (30), 111(25), 109 (100), 83 (29), 56 (18) [Fe], 55 (59). HRMS (EI, 70 eV): calcd. for $C_8H_8FeO_3$ $[M - CO]^+$ 327.9857; found 327.983. HPLC (Chiralcel OD-H, n-hexane, v = 0.3 mL min–1, λ = 254 nm): $t_{(S)}$ = 39.5 min; $t_{(R)}$ = 58.4 min; 86 % *ee*.

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