

Spectroscopic and Computational Assessment of the Rotational Barrier of a Ferrocenyl-Stabilized Cyclopentadienyl Cation: Evidence for the First Hydroxyfulvalene Ligand

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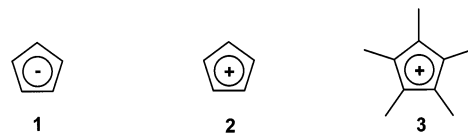
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Protonation of 3-ferrocenyl-2,4,5-triphenylcyclopentadienone with trifluoroacetic acid results in the formation of the first hydroxyfulvalene complex. The dramatic deshielding and decoalescence of the ¹H and ¹³C NMR signals in the ferrocenyl region offer evidence for the participation of the metal in the stabilization of the positive charge, which results in restricted rotation of the ferrocenyl group. As determined by NMR spectroscopy, the maximum barrier to rotation in the neutral species is ca. 9 kcal mol⁻¹, whereas the minimum barrier in the cation considerably exceeds 13 kcal mol⁻¹. The difference in rotational barriers for the neutral and protonated species is rationalized by using DFT calculations.

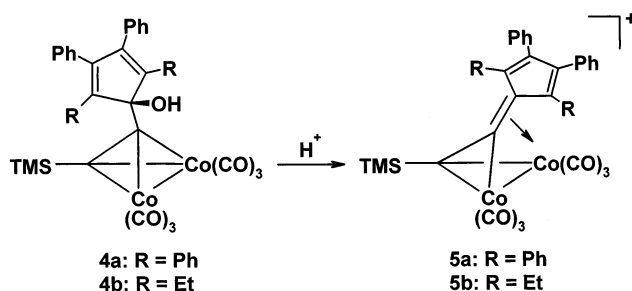
Introduction

The ease with which the aromatic cyclopentadienide anion (**1**) can be generated and characterized¹ is in stark contrast to that of the antiaromatic cyclopentadienyl cation (**2**). The observation of antiaromatic cations has been the subject of recent interest, with the initial report² and subsequent refutation³ of evidence for the formation of the pentamethylcyclopentadienyl cation (**3**) (Chart 1). We have a long-standing interest in such short-lived species, particularly the use of transition metals in their stabilization and characterization.⁴ Examples include cobalt-coordinated fluorenyl, indenyl, and cyclopentadienyl cations, such as molecules **5a** and **5b**, which are formed by the protonation of the corresponding alcohols **4** (Scheme 1).⁵ In these instances, the electron deficiency is relieved by the direct overlap of a vacant orbital at the cationic site with a filled metal orbital, as evidenced by the pronounced tilting of the cation toward the metal center.^{6–11} This electronic

Chart 1. Aromatic (1) and Antiaromatic (2, 3) Cyclopentadienyl Ions



Scheme 1. Cobalt-Stabilized Cyclopentadienyl Cations



stabilization imparts conformational rigidity, which offers application in stereoselective nucleophilic addition reactions,^{6,12} and is manifested in the restricted rotation of the exocyclic bond, as observed by NMR spectroscopy.^{7,13–19}

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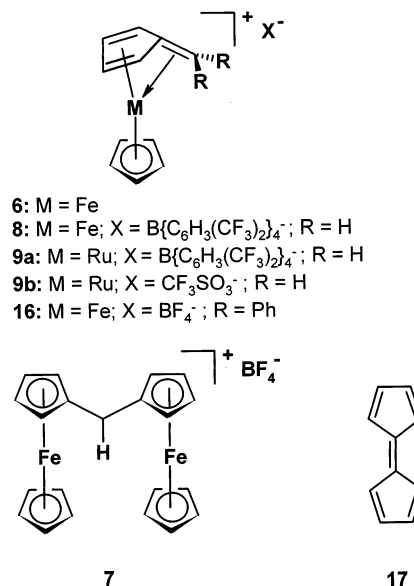
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The extension of this concept to ferrocenyl systems is straightforward, as the stabilization of carbocations in the α -position is well established. There are numerous examples in the literature of the use of ferrocene to stabilize cations that are otherwise not isolable: for instance, allenyl^{7,20} and allyl²¹ systems and vinyl²² and cyclopropyl²³ cations, as well as norbornan-2-yl²⁴ and azuleny²⁵ derivatives. The structure and bonding of ferrocenyl carbenium ions has been the subject of discussion and debate, and several structures were described in the early literature to account for the unique properties of these complexes.^{16,26} More recently, the combination of physical methods and calculations has affirmed the fulvenoid structure **6**, in which the steric and electronic nature of the substituents R dictates the extent to which the exocyclic double bond leans toward the metal.^{7,13} Cais reported the X-ray crystal structure of the α,α -diferochenylmethylmethyl tetrafluoroborate complex (**7**) and asserted that the geometric flexibility of the cation allows it to maximize metal–ligand interactions and determines the stability of the complex.²⁷ These observations have been manifested in other structures,^{8–11} including the recent reports of the first crystal structure of the primary ferrocenyl carbocation **8**,⁹ and of the ruthenocenylmethylmethyl cations **9**¹⁰ (Chart 2).

The preparation of the 3-ferrocenyl-2,4,5-triphenylcyclopentadienone complex (**10**) has already been described,²⁸ and protonation of this species might be expected to yield a stabilized cyclopentadienyl cation. We now report NMR investigations of the protonation of **10** at low temperature, as well as the use of DFT calculations to rationalize the observed rotational barriers and to evaluate the structures of the neutral molecule and the resulting cation.

Chart 2. Iron and Ruthenium-Stabilized Cations (6–9, 16) and Pentafulvalene (17)



Results and Discussion

NMR Spectroscopic Results. The ¹H and ¹³C NMR spectra of the neutral cyclopentadienone **10** exhibited no decoalescence behavior and were consistent with rapid rotation of the phenyl groups and ferrocenyl substituent, on the NMR time scale, to temperatures as low as –80 °C. The protonation study was conducted by cooling a solution of the cyclopentadienone in CD₂Cl₂ to –78 °C in an NMR tube, followed by the addition of trifluoroacetic acid and acquisition of the NMR spectra at –80 °C. The appearance of a new peak in the proton NMR at 4.41 ppm was accompanied by the splitting of the ferrocenyl C₅H₄ peaks at 3.88 and 4.27 ppm into four peaks (4.09–6.37 ppm), revealing their nonequivalence (Figure 1a). These findings are mirrored in the ¹³C spectrum (Figure 1b) and are attributable to restricted rotation of the ferrocenyl group relative to the central ring. Figure 2 presents the 2-D ¹H–¹H COSY NMR spectrum obtained at –20 °C, clearly outlining the assignment of the four ferrocenyl resonances and the new hydroxy proton; the assignments were unambiguously defined on the basis of the ¹H–¹³C HSQC and HMBC as well as the ¹H–¹H COSY experiments. The signal at lowest frequency is assigned to proton 7, as it lies in the shielding region of the most hindered phenyl group on the cyclopentadienone ring (protons are numbered according to the carbon to which they are attached; Scheme 2). Proton 10 is in a similar environment, but the corresponding phenyl group is in a less hindered locale and thus is not restricted to a perpendicular conformation. As a result, this proton resonates at a higher frequency (lower field); the assignment of the remaining protons follows accordingly.

Restricted rotation of the ferrocenyl group is consistent with the formation of the cation **11**, in which the Cp–Fe⁺ fragment is coordinated to a fulvalenoid system (Scheme 2). The delocalization of the positive charge onto the ferrocenyl ring is clear from the dramatic deshielding of the proton and carbon resonances compared to the shifts observed in the neutral cyclopentadienone and related compounds (Table 1).

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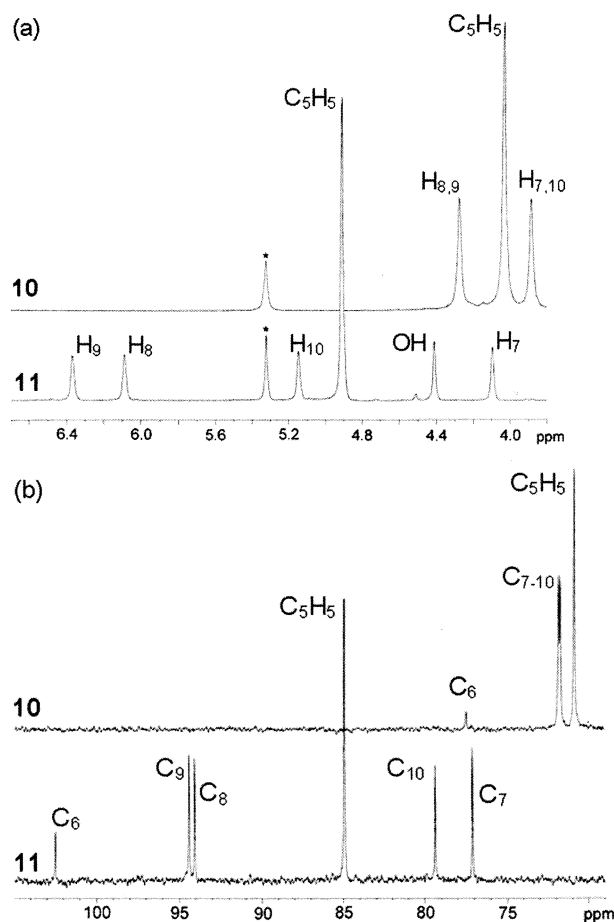


Figure 1. 500 MHz ^1H (a) and 125 MHz ^{13}C (b) NMR spectra of 3-ferrocenyl-2,4,5-triphenylcyclopentadienone (**10**) and its protonation product, **11**. The dichloromethane solvent resonance is marked with an asterisk.

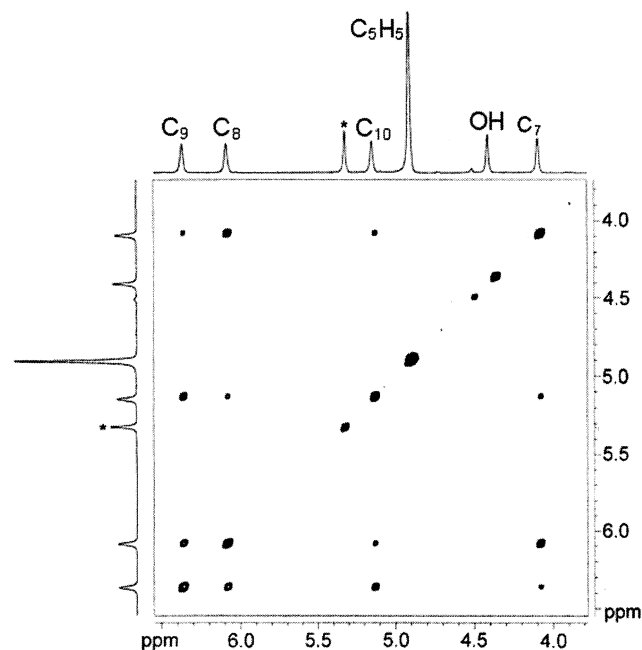


Figure 2. ^1H - ^1H COSY NMR spectrum of the protonated molecule **11**, showing correlations between pairs of protons in the C_5H_4 ring.

These findings are in agreement with an early study by Cais on the proton NMR of a variety of ferrocenyl carbenium ions,²⁹ in which a "metal participation" model

Scheme 2. Protonation of **10** To Give the Fulvenoid Cation **11**

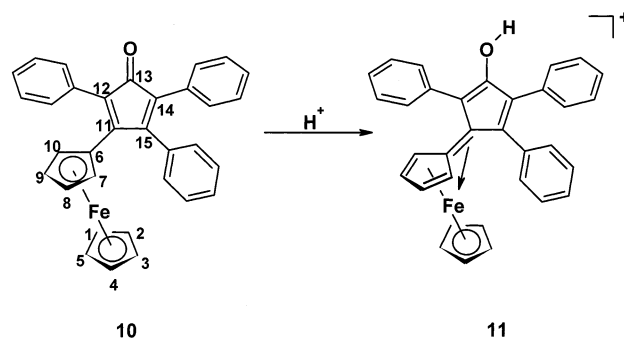


Table 1. NMR Spectral Data^a

atom	10	10 ·Fe(CO) ₃ ^b	10 ·Rh(acac) ^b	11
^1H				
H ₇	3.88	3.57	4.03	4.09
H ₈	4.27	4.1	4.18	6.08
H ₉	4.27	4.1	4.18	6.37
H ₁₀	3.88	3.50	3.77	5.14
C ₅ H ₅	4.02	3.92	3.92	4.91
^{13}C				
C ₆	77.44			102.47
C ₇	71.72	69.25	70.42	77.09
C ₈	71.83	70.74	70.66	94.05
C ₉	71.83	70.74	72.60	94.39
C ₁₀	71.72	69.25	71.12	79.36
C ₅ H ₅	70.87	70.34	69.99	84.92

^a Chemical shifts in ppm. ^b Reference 31.

was invoked to explain the experimental data. It was suggested that the metal moved closer to the cationic center than in the neutral analogue, thus increasing the electron density at protons 7 and 10 relative to protons 8 and 9, resulting in a noticeable deshielding of the latter protons. Substituting the cationic carbon with electron-donating groups minimized the geometric perturbation of the iron, thus diminishing the effect. Moreover, the induced field attributable to the magnetic anisotropy of the iron was described as a major contributor to the shielding of protons 7 and 10, as confirmed by the substitution of alkyl groups with aryl substituents. As the positive charge was delocalized onto the aryl rings, the movement of the iron was reduced and the affected protons experienced less shielding. Complementary work by Dannenberg and co-workers achieved the same result.¹⁶ In agreement with these analyses, there have been several similar studies performed on the ^{13}C NMR spectra of ferrocenyl-stabilized cations.^{15,30} In each case, the marked deshielding of the cationic carbon and the shielding influence of electron-donating substituents have been explained in terms of the delocalization of the positive charge throughout the ferrocenyl group and the fulvenoid structure of the substituted cyclopentadienyl ring. The trends evident in the spectra of the present study echo these results and the analogous structural interpretations. Thus, we

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Table 2. Computed Structural Details^a

distance	8 ^b	9a ^c	12	13	14	15	16 ^d	17 ^e	literature ^f
Fe–C ₆	1.97	2.080	2.10	2.08	2.07	2.06	2.009		2.517, 2.070
Fe–C ₇	2.05	2.177	2.08	2.08	2.08	2.08	2.060		2.142, 2.217
Fe–C ₈	2.12	2.245	2.09	2.13	2.09	2.12	2.095		2.060, 2.243
Fe–C ₉	2.14	2.235	2.09	2.13	2.09	2.12	2.085		2.060, 2.213
Fe–C ₁₀	2.05	2.175	2.07	2.10	2.08	2.08	2.018		2.142, 2.162
C ₆ –C ₇	1.45	1.458	1.45	1.46	1.44	1.45	1.438	1.476	1.477
C ₆ –C ₁₀	1.42	1.459	1.45	1.46	1.44	1.45	1.445	1.476	1.477
C ₇ –C ₈	1.38	1.413	1.43	1.42	1.43	1.43	1.413	1.333	1.414
C ₈ –C ₉	1.46	1.429	1.43	1.43	1.43	1.43	1.425	1.479	1.399
C ₉ –C ₁₀	1.42	1.412	1.43	1.42	1.43	1.43	1.402	1.333	1.414
C ₆ –C ₁₁	1.37	1.405	1.45	1.41	1.47	1.46	1.416	1.339	1.357, 1.446
C ₁₁ –C ₁₂			1.37	1.42	1.35	1.38		1.476	
C ₁₁ –C ₁₅			1.51	1.50	1.52	1.51		1.476	
C ₁₂ –C ₁₃			1.48	1.39	1.50	1.35		1.333	
C ₁₃ –C ₁₄			1.52	1.48	1.51	1.46		1.479	
C ₁₄ –C ₁₅			1.34	1.48	1.51	1.46		1.333	
C ₁₃ –O			1.23	1.33	1.23	1.32			

angle	8 ^b	9a ^c	12	13	14	15	16 ^d	lit.
α	4.7	7.1	1.6	7.9	1.2	0.6	11.4	4–5, ^g 4.2, ^h 5.7 ^h
β	23.6	42.6°	0.4	8.4	3.0 ^j	5.9 ^j	20.7	28.9, ^f 10–20 ^g
γ			5.4	6.3	89.7	83.4		1.22–7.57 ⁱ

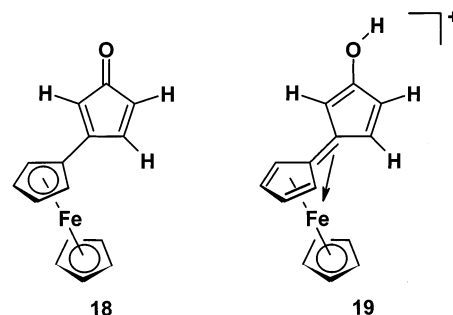
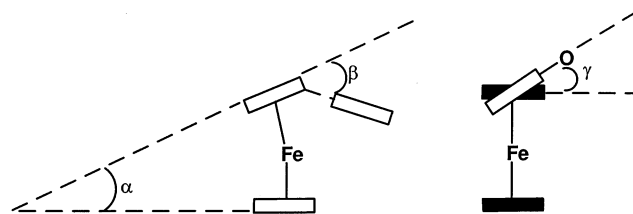
^a All bond lengths in Å and angles in deg. ^b Reference 9. ^c Reference 10. ^d Reference 8. ^e Reference 35. ^f References 11b and 32b. ^g Reference 7. ^h Reference 27. ⁱ Reference 32. ^j Bent away from Fe; all others are bent toward Fe.

anticipate a complex in which the iron has moved closer to the cationic center, resulting in the formation of the first organometallic hydroxyfulvalene complex.

The removal of the degeneracy of the ferrocenyl C₅H₄ protons as the cation is generated is also an important feature of the NMR spectra. There is no evidence for decoalescence of these protons at –80 °C in the neutral species; however, it is apparent that, on the NMR time scale, the ferrocenyl group is not rotating in the cation. If the signals of the ferrocenyl protons of the cation had coalesced at 0 °C, this would have corresponded to a rotational barrier of 13 kcal mol^{–1}; the true barrier is evidently greater than this minimum value. Furthermore, if, for simplicity, the assumption is made that the chemical shift differences in the neutral molecule are the same as those displayed by the protonated species, and if the onset of decoalescence had been observed at –80 °C, the barrier to rotation would have been approximately 9 kcal mol^{–1}; apparently the actual barrier is less!

Finally, the protonation of the carbonyl oxygen and formation of a hydroxyl group have also been confirmed by in situ IR spectroscopy, as the C=O peak at 1694 cm^{–1} gradually disappears under the same reaction conditions described above. All attempts to obtain X-ray-quality crystals were thwarted by the slow decomposition of the sample.

Computational Modeling. To rationalize the observed difference in energy barriers associated with rotation about the ferrocenyl–carbon bond in the neutral and protonated species (**10** and **11**), computational studies were performed using DFT. Models **12** and **13** were built by replacing phenyl groups with hydrogen atoms to mimic compounds **10** and **11**, and their ground-state structures were fully optimized without any symmetry constraints. Selected structural features of the neutral and protonated models, as well as their rotational transition states, are summarized in Table 2. Each of the computed Fe–C, C–C, C–O, and C–H bond lengths correspond to literature values of related com-

Chart 3. Localized (18) and Delocalized (19) Bonding Structures for the Neutral Molecule and Cation**Chart 4. Definition of Angles for Structural Analysis**

pounds, including **8**, **9a**, **16**, and **17**, within 0.05 Å, and the analogous bond angles are within 0.1°.

The Fe–C distances in the C₅H₄R ring of the ground-state neutral molecule 3-ferrocenylcyclopentadienone (**12**) are comparable and range from 2.07 to 2.10 Å. Moreover, the cyclopentadienone C–C bond lengths of **12** are consistent with the localized structure **18** (Chart 3), with a C=O bond length of 1.23 Å (literature³¹ 1.216–(11), 1.226(3) Å). The cyclopentadienone ring is slightly rotated (twisted) out of the plane of the C₅H₄ ring (γ) and bent toward the metal atom (β) (Chart 4). The two possible twist orientations were considered as initial points in the optimization, leading to two different

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minima; the dihedral angle (γ) in the resulting lowest energy structure is 5.4° , which is within the range of values ($1.2\text{--}7.6^\circ$) found in related structures in the literature.³² As a consequence of the position of the cyclopentadienone group, the ferrocenyl cyclopentadienyl rings adopt a staggered orientation to minimize steric interactions.

The protonated molecule (**13**) exhibits a slightly greater range of Fe–C distances than the neutral analogue, from 2.08 Å (C_6) to 2.13 Å (C_8 , C_9). This elongation of bond lengths suggests a slight shift in the position of the metal from the center of the cyclopentadienyl ring toward the cationic center. Similar behavior has been seen in the X-ray crystal structures of molecules **8**⁹ and **9a**,¹⁰ as well as the cation **16**⁸ (Chart 2). This effect is also consistent with the NMR spectroscopic properties of the cation and similar compounds,^{15,16,29,30} in which the change in the position of the metal is manifested in the deshielding of the proton and carbon atoms relative to the chemical shifts in their neutral analogues.

In the protonated molecule, the C–O bond length increases to 1.33 Å, intermediate between normal C=O and C–O distances (1.21 and 1.42 Å, respectively).³³ The C–C bond lengths in these structures suggest greater delocalization, such as in molecule **19** depicted in Chart 3. Furthermore, there is a tilt (α) of 7.8° between the cyclopentadienyl rings of the ferrocenyl group (Chart 4). Lukasser⁷ has estimated a range of $4\text{--}5^\circ$ for the tilt of the cyclopentadienyl rings in other protonated structures as a consequence of the participation of the iron atom in the delocalization of the positive charge. This trend is also apparent in related structures, with angles of 4.7 , 7.1 , and 11.4° for cations **8**,⁹ **9a**,¹⁰ and **16**.⁸ As noted by Cais,³⁹ the molecule must be sufficiently flexible to allow for favorable orbital overlap and adequate stabilization of the cation.

The cationic species also exhibits the twist (γ) and bend (β) predicted for the neutral molecule. Again, both twist directions were considered and, in this case, the optimizations converged to essentially the same geometry in which the oxygen is pointed toward the metal.

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A twist angle of 6.3° is found for **13**, which is very similar to that for the neutral analogue; however, an even larger β value of 8.4° is computed. Lukasser has estimated values between 10 and 20° for the bend in protonated structures,⁷ and larger angles of 20.7° (**16**),⁸ 23.6° (**8**),⁹ and 42.6° (**9a**)¹⁰ have been observed crystallographically. As anticipated, the ring is tilted toward the metal to allow for the necessary electronic stabilization, resulting in a hydroxyfulvalene ligand.

The initial structures of the transition states were obtained by rotating the external ring relative to the ferrocenyl group and were fully optimized without restrictions. Though there has been some discussion in the literature regarding the multiplicity of cyclopentadienyl cations,³⁴ the transition states must be singlets and were treated as such. The computed bond lengths in the transition state, **14**, of the neutral molecule were very similar to those in the ground state, and no major geometric reorganization occurred upon rotation. One feature of note is the bend angle (β) of the external ring: in this case 3.0° away from the metal as a result of steric interactions with the C_5H_5 ring.

The transition state, **15**, of the cation exhibits the same elongation of Fe–C bond lengths observed in the ground state, from 2.06 Å (C_6) to 2.12 Å (C_8 , C_9), confirming the same minor movement of the metal closer to the cationic center. However, in this case, the $C_6\text{--}C_{11}$ bond distance is significantly longer, and the protonated ring has experienced a structural reorganization, as evidenced by changes in bond lengths. The tilt in the ground state of the cation is no longer present in the transition state; the angle between the cyclopentadienyl rings of the ferrocene is only 0.6° . This geometric reorganization results in a structure in which the ferrocenyl group does not participate in charge stabilization. The protonated ring is bent away from the metal, in this case by 5.9° , as a result of the steric interaction of the OH and the C_5H_5 ring.

Figure 3 portrays a potential energy diagram outlining the possible rotamers, the transition states, and their relative energies. The minimum barrier to rotation of the ferrocenyl group relative to the cyclopentadienone ring in the neutral species was found to be 7.2 kcal mol^{-1} . This is in agreement with the experimental NMR data, which suggest a maximum barrier of 9 kcal mol^{-1} . Moreover, the minimum barrier to rotation in the protonated version was calculated to be $17.1\text{ kcal mol}^{-1}$, again in correspondence with the NMR behavior of the cation, which suggests a barrier considerably in excess of 13 kcal mol^{-1} . In examining the structural parameters of the neutral molecule, there is no significant geometrical reorganization or charge relocation upon rotation to the transition state, as would be anticipated, since there is no need for charge stabilization within the ferrocenyl group. Conversely, in the cation, the ground-state charge distribution involves both the fulvalene rings and the remainder of the ferrocenyl group. Upon rotation, the molecule undergoes structural reorganization and electron density redistribution, as the ferrocenyl group can no longer stabilize the positive charge; the most notable consequence is the migration of the positive charge from C_{11} to C_{13} (Table 3). Overall,

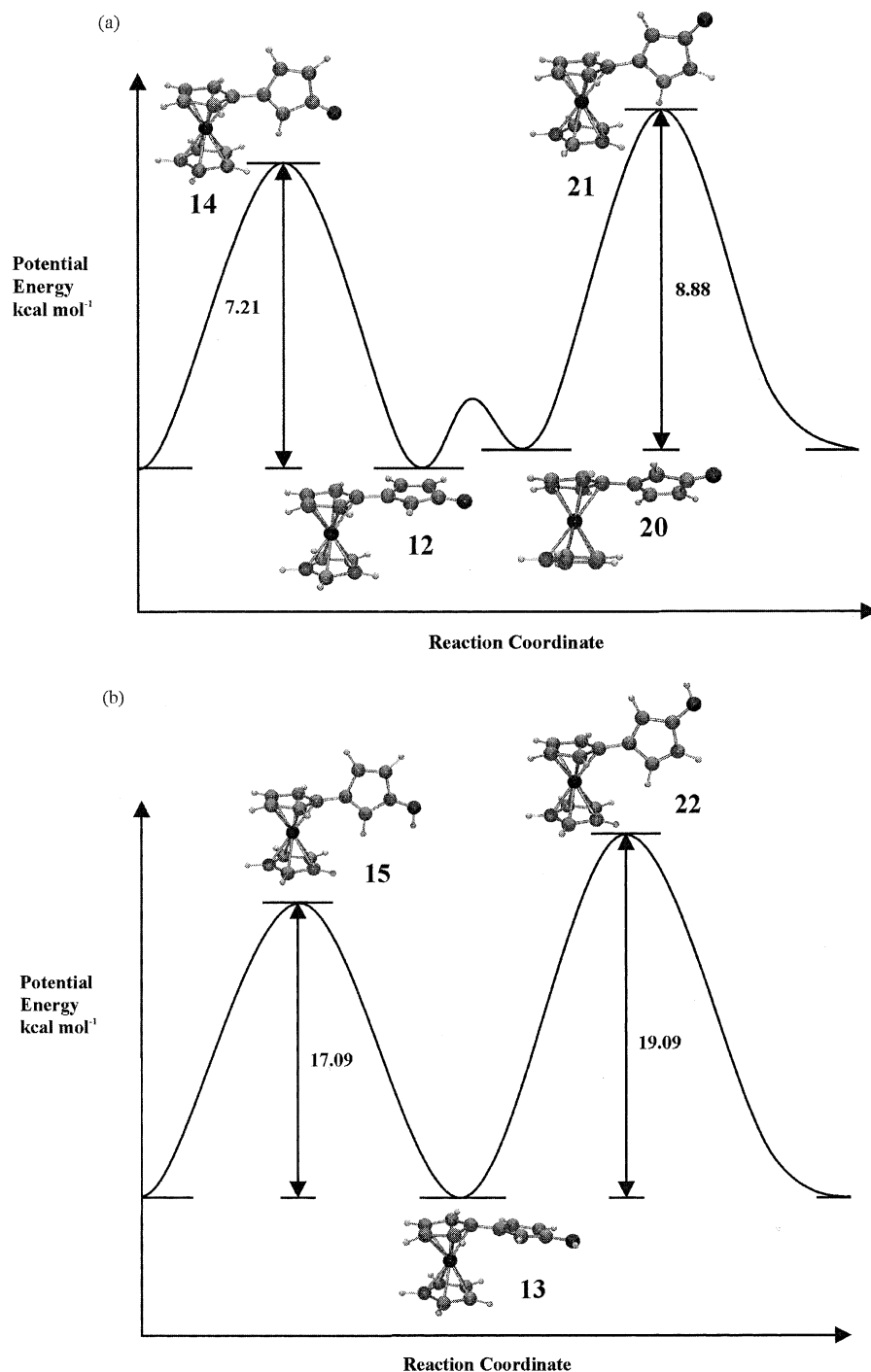


Figure 3. Potential energy diagrams for the neutral (a) and cationic (b) species.

Table 3. Charge Distribution

atom	12	13	14	15
Fe	0.0558	0.0559	0.0559	0.0214
C ₁ –C ₅ (av)	0.2324	0.2691	0.2239	0.2551
C ₆	0.0995	0.0549	0.0473	0.0422
C ₇ –C ₁₀ (av)	0.2207	0.2571	0.2180	0.2482
C ₁₁	0.1709	0.2095	0.1135	0.1382
C ₁₂	0.1003	0.0942	0.1417	0.1206
C ₁₃	0.4870	0.4752	0.5003	0.5104
C ₁₄	0.0957	0.1439	0.0930	0.1354
C ₁₅	0.2077	0.2174	0.2185	0.2353
O	-0.5390	-0.4637	-0.5234	-0.4298

these changes result in a much higher barrier to rotation for the protonated molecule. There are several examples of the observation of restricted rotation in

ferrocenyl carbenium ions;^{7,13–18} however, we are aware of only one experimental estimate of the barrier (20 kcal mol⁻¹).¹⁷

Conclusions

Treatment of 3-ferrocenyl-2,4,5-triphenylcyclopentadienone (**10**) with trifluoroacetic acid results in the formation of the hydroxyfulvalene cation **11**. Proton and carbon NMR spectra of **11** display restricted rotation of the ferrocenyl group relative to the protonated ring; this observation may be rationalized in terms of the geometric reorganization required to stabilize the positive charge in the transition state. The deshielding of the ferrocenyl proton and carbon NMR chemical shifts

in **11**, relative to **10**, confirms the participation of the iron in the stabilization of the positive charge. The computed barriers to rotation in the neutral and protonated models are 7.2 and 17.1 kcal mol⁻¹, respectively.

Experimental Section

General Methods. Trifluoroacetic acid was used as received from commercial sources. ¹H and ¹³C NMR spectra were obtained on a Bruker Avance DRX-500 spectrometer at 500.13 and 125.76 MHz, respectively, and were referenced to the residual proton signal, or ¹³C signal, of the solvent. Assignments were based on ¹H–¹H COSY and ¹H–¹³C HSQC and HMBC two-dimensional techniques. In situ infrared spectra were recorded on an ASI Applied Systems ReactIR 1000 with a SiComp probe. Compound **10** was prepared as previously described.²⁸

Protonation of 10. 3-Ferrocenyl-2,4,5-triphenylcyclopentadienone (**10**; 30 mg) was dissolved in CD₂Cl₂ in an NMR tube and cooled to -78 °C; 2 drops of trifluoroacetic acid were added, and the tube was shaken. The NMR spectra were subsequently recorded over the range -80 to -20 °C. The improved resolution at -20 °C assisted in the interpretation of the spectra; thus, peak assignments refer to this temperature. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.69 (1H, s, phenyl *p*-H), 7.61 (1H, s, phenyl *para*-H), 7.55–7.40 (8H, m, phenyl *o*-H, *m*-H), 7.29 (2H, d, *J*(HH) = 6.6 Hz, phenyl *o*-H, *m*-H), 7.21 (2H, d, *J*(HH) = 6.2 Hz, phenyl *o*-H, *m*-H), 7.04 (1H, d, *J*(HH) = 5.4 Hz, phenyl *p*-H), 6.37 (1H, s, H₉), 6.08 (1H, s, H₈), 5.14 (1H, s, H₁₀), 4.91 (5H, s, C₅H₅), 4.41 (1H, s, OH), 4.09 (1H, s, H₇). ¹³C NMR (125 MHz, CD₂Cl₂): δ 166.7, 148.3, 147.2, 135.2 (C_{11,12,14,15}), 131.8 (phenyl CH), 131.6 (phenyl CH), 131.3 (phenyl C), 130.6 (phenyl C), 130.4 (phenyl CH), 130.3 (phenyl CH), 130.0 (phenyl CH), 129.7 (phenyl C), 129.6, 129.4, 127.9, 127.3 (phenyl CH), 102.5 (C₆), 94.9 (C₉), 94.1 (C₈), 84.9 (C₅H₅), 79.4 (C₁₀), 77.1 (C₇), 60.2 (C₁₃).

Computational Details. Optimization of model geometries has been performed using ADF 2002.01,³⁷ with gradient-corrected density functional theory (DFT) with Becke's exchange functional³⁸ and Perdew's correlation functional³⁹ (BP86). All basis functions have triple-ζ quality and are composed of uncontracted Slater-type orbitals (STOs).⁴⁰ The (1s)² core electrons of C and O and the (1s2s2p)¹⁰ core electrons of Fe have been treated with the frozen-core approximation.⁴¹ In each SCF cycle, an auxiliary basis set of s, p, d, f, and g STOs has been used to fit the molecular densities and to represent the Coulomb and exchange potentials. The barriers to rotation have not been corrected for zero-point energies.

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Supporting Information Available: A full table of geometric parameters of **12–15** and comparison to related structures in the literature, as well as enlarged diagrams of the optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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