Theoretical Study of the $[\{Fe(CO)_2Cp\}_3(\mu_3\text{-}C_3)]^+$ Tricarbido Cation

Nazzareno Re and Antonio Sgamellotti*

Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto 8, I-06100 Perugia, Italy

Carlo Floriani

Institut de Chimie Minérale et Analytique, BCH, Université de Lausanne,
CH-1015 Lausanne, Switzerland

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Density functional calculations have been carried out on a trinuclear $[\{Fe(CO)_2Cp\}_3(\mu_3\text{-}C_3)]^+$ cation, and on related $C_3H_3^+$ and $C_3(NH_2)_3^+$ molecules in order to study the electronic structure and the bonding of the C_3^+ unit to the metal fragments in this complex. An analysis of the MOs and of the Mulliken populations has been performed in order to understand the extent of the relative σ and π interactions between the C_3^+ and the $Fe(CO)_2Cp$ fragments. The results show that the iron−cyclopropenyl bond is mainly of σ character with a smaller, but important, π contribution. DFT calculations were also performed on the hypothetical mononuclear $[Fe(CO)_2Cp(C_3H_2)]^+$ complex to study the relative stabilities of the possible orientations of the $Fe(CO)_2Cp$ fragments with respect to the C_3^+ ring and to study its rotation about the Fe−C bond.

Introduction

Organometallic compounds in which small carbon fragments are stabilized by transition metal complexes have recently received much interest.[1−3] Indeed, they constitute a first step in the synthesis of carbon forms stabilized by transition metal complexes. Several complexes are known in which two transition metal atoms are bound by μ-C_2 bridges,[4−8] and more recently complexes in which two metal fragments are connected by linear C_3, C_4, C_5, C_6, and C_8 chains have been reported.[3,9−13]

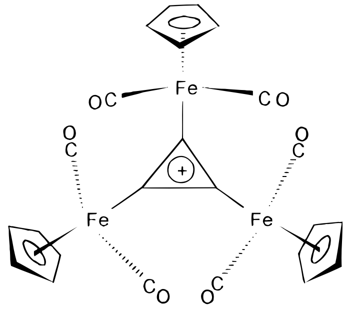

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Figure 1. Symmetrized structure of the $[\{Fe(CO)_2(Cp)\}_3\text{-}(\mu_3\text{-}C_3)]^+$ complex used in the calculations.

In this context, a $[\{Fe(CO)_2Cp\}_3(\mu_3\text{-}C_3)][SbF_6]$ complex, **1**, has been recently synthesized,[14] which represents the first example of a trimetallic *cyclo*-C_3 complex. The X-ray crystal structure of **1** has shown a nearly equilateral C_3 ring with an iron center bonded to each vertex. This is represented in Figure 1, which shows a slightly symmetrized model. The C−C bond lengths in the ring are almost equal, with an average value of 1.39 Å. The average Fe−C_{ring} bond length is 1.92 Å, which is shorter than typical Fe−C_{sp^3} or Fe−C_{sp^2} single bonds (2.0−2.1 Å)[15] but similar to Fe−C_{sp} bonds (1.9 Å)[16,17] and longer than Fe−C bonds to strong π acceptors like CCl_2 in $[Cp(CO)_2Fe{=}CCl_2]$.[18] It has been suggested[14] that in compound **1** the Fe to cyclopropenyl ring π donation is of minor importance. This is because in 18 electron $[Cp(CO)_2M{=}CR_2]$ complexes with a high degree of M to CR_2 π donation, as in $[Cp(CO)_2Fe{=}CCl_2]$, the carbene ligand lies in the $[M(CO)_2Cp]$ symmety plane with Cp(centroid)−M−C−R torsion angles of 0 and 180°,

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* To whom correspondence should be addressed.

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while in compound **1** the cyclopentadienyl rings lie above or below the C_3 plane with Cp(centroid)−Fe−C_α−C_β torsion angles close to 90°. Moreover, ^1H and ^{13}C NMR spectra show a single [Fe(CO)$_2$Cp] environment from room temperature to −80 °C, which implies a small barrier to the rotation about the Fe−C bonds and could substantiate the hypothesis of a small π contribution to the Fe−C bonds.

A few theoretical investigations have been recently performed on μ-C_2-bridged dinuclear complexes and show the possibility of strong M → C_2 π donation.[19] In this paper we have performed LCAO density functional calculations on the $[\{Fe(CO)_2Cp\}_3(\mu_3\text{-}C_3)]^+$ cation in order to study the effect of the coordinated metal fragments upon the stability of the C_3^+ unit and to determine the extent of the metal to cyclopropenyl ring π donation. In an attempt to discuss the importance of the σ/π contribution to the C_3^+ unit, we have considered also the cyclopropenyl cation, $C_3H_3^+$. This species is the smallest aromatic hydrocarbon but, because of its high ring strain, is highly unstable, and only cyclopropenyl ions with strongly stabilizing substituents, like phenyl or dimethylamino, have been prepared.[20]

As $N(CH_3)_2$ is known to be a strong π donor, a high degree of π donation to the C_3^+ ring is expected in the tris(dimethylamino)cyclopropenyl cation, $C_3(N(CH_3)_2)_3^+$. We have therefore performed density functional calculations on the cyclopropenyl cation $C_3H_3^+$, **2**, and tris(amino)cyclopropenyl cation $C_3(NH_2)_3$+, **3**, to compare the bonding between the ring carbon and H, NH_2, or the transition metal fragments.

Computational Details

The calculations reported in this paper have been performed by the Gaussian 94 program package[21] and were done on IBM RISC/6000 workstations. The LDA exchange correlation potential and energy was used, together with the Vosko−Wilk−Nusair parametrization for homogeneous electron gas correlation,[22] including Becke's nonlocal correction to the local exchange expression[23] and the Perdew's nonlocal correction to the local expression of correlation energy (NLDA).[24]

It has been demonstrated that excellent metal−metal and ligand−metal bond energies are obtained from this density functional based approach.[25] The Fe basis set is a [8s4p3d] contraction[26] of the (14s9p5d) primitive set of Watchers.[27] A 6-31G* basis set was used for the carbon atoms of the C_3^+ ring, while a 6-31G basis was used for the carbon, oxygen, and hydrogen atoms of the CO and Cp ligands. A 6-31G** basis set was used for all the atoms in the cyclopropenyl cation **2** and tris(amino)cyclopropenyl cation **3**.

In the calculations on **1**, the geometry of the complex was idealized to a C_s symmetry with the cyclopropenyl ring perfectly equilateral, two cyclopentadienyl groups lying above and one below the C_3 plane with Cp(centroid)−Fe−C_α−C_β torsion angles of 90°. The remaining geometrical parameters of the [Fe(CO)$_2$Cp] fragments were taken from the crystal structure of **1** and slightly adjusted to an ideal C_s geometry. The coordinate system has been chosen so that the z axis is in the C−Fe (unique) direction and the planar C_3^+ unit lies in the yz plane (see Figure 1). Complete geometry optimizations were performed on complexes **2** and **3** in the D_{3h} symmetry.

Table 1. Valence Energy Levels and Net Fragment Orbital Population for $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)]^+$

		fragment pop.	
level	energy (eV)	C_3^+	Fe(CO)$_2$Cp
49a′	−15.4	0.99	0.01
59a″	−9.4	0.02	0.98
73a′	−8.3	0.42	0.58
60a″	−8.0	0.40	0.60
74a′	−7.8	0.01	0.99
61a″	−7.7	0.14	0.86
75a′	−7.6	0.01	0.99
62a″	−7.4	0.02	0.98
76a′	−7.2	0.06	0.94
63a″	−7.1	0.10	0.90
77a′	−7.0	0.08	0.92
64a″	−6.9	0.19	0.81
78a′ HOMO	−6.8	0.21	0.79
79a′ LUMO	−5.5	0.22	0.78
80a′	−5.3	0.18	0.82
65a″	−5.1	0.15	0.85
81a′	−5.0	0.39	0.61
93a′	−2.1	0.91	0.09
94a′	−2.0	0.92	0.08

Results

The results of the DFT calculations on the model complex **1** (Figure 1) are illustrated in Table 1, where we report the computed energy levels, labeled according to the C_s symmetry, together with the net fragment population. To discuss the results it is convenient to consider a fragment approach in which three [Fe(CO)$_2$Cp] fragments interact with a C_3^+ moiety.

The C_3^+ molecule has been considered with an ideal D_{3h} geometry, in the $^4A_1'$ state corresponding to the valence state suitable for bonding with the three substituents. Its main valence orbitals are depicted on the left in Figure 2. The singly occupied $3a_1'$ and $3e'$ are made up by sp hybrids and are of the right symmetry to interact with the metal d_σ orbitals. The highest doubly occupied MO $1a_2''$ and the LUMO $1e''$ correspond, respectively, to the bonding and the two degenerate antibonding orbitals of the three-member cyclic π system; see Chart 1.

The [Fe(CO)$_2$Cp] fragment has been considered in the pseudo-pyramidal structure it presents in the complex, with a C_s symmetry, and the main frontier orbitals are reported on the right of Figure 2. The main frontier orbitals reported for the [Fe(CO)$_2$Cp] fragment consist of the three highest bioccupied orbitals (26a′, 17a″, and 27a′), the singly occupied 28a′, and the lowest unoccupied 18a″ which are essentially of metal d character. The 26a′ is mainly a $d_{x^2-y^2}$ slightly mixed with d_{z^2}. The almost degenerate 17a″ and 27a′ are essentially comprised of d_{xz} and d_{yz} orbitals, respectively, and are responsible for the Fe to cyclopropenyl π-donation. The SOMO 28a′ is mainly a d_{z^2} slightly mixed with $d_{x^2-y^2}$ while the LUMO 18a″ is an almost pure d_{xy}. Lower in energy we report few occupied MOs which describe essentially the highest cyclopentadienyl π orbitals. It

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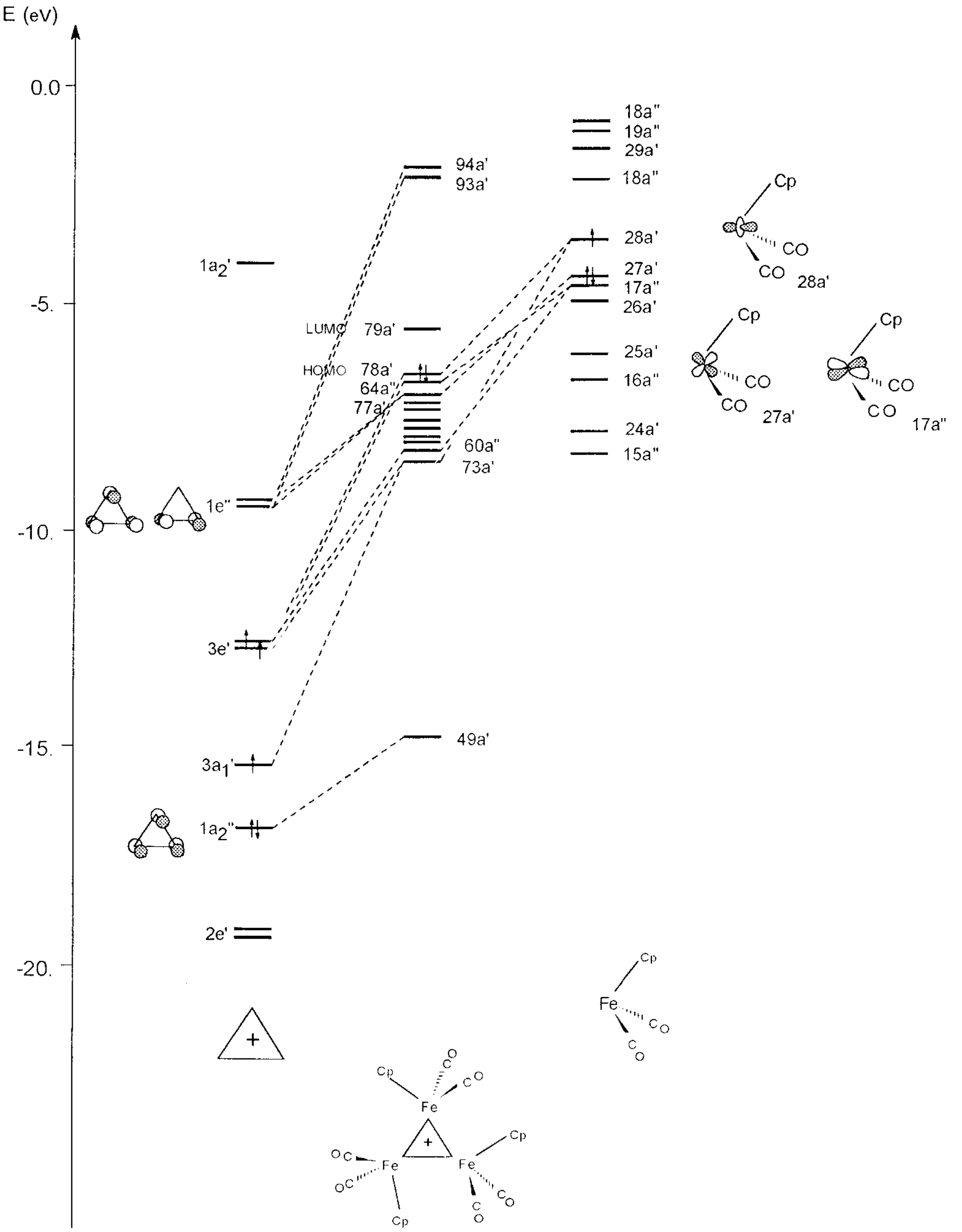
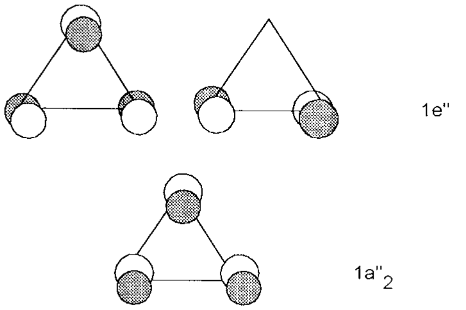


Figure 2. Molecular orbital diagram for the $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)]^+$ complex in the ${}^1A'$ state.

Chart 1



is worth noting that the ordering of the energy levels obtained for the $[Fe(CO)_2Cp]$ fragment is significantly different from that obtained in earlier extended Hückel calculations on similar systems.[28]

In particular, the results of those calculations indicated the 17a″ above the 27a′. These two orbitals are responsible for the π-bonding capability of the fragment, in the symmetry plane bisecting the CO−Fe−CO angle ($\sigma_{\|}$) and the perpendicular one ($\sigma_{\perp}$), respectively, for a′ and a″ symmetries. When the bonding of the $[Fe(CO)_2Cp]$ fragment with a CH_2 unit was considered,[28] the π interaction in the $\sigma_{\perp}$ plane, corresponding to interaction of the π orbital of CH_2 unit with the higher a″ fragment orbital, was found stronger leading to the CH_2 ligand lying in the bisecting $\sigma_{\|}$ plane; see Chart 2. In our calculations the 17a″ and 27a′ orbitals are essentially degenerate, with the 27a′ slightly above. This almost degeneracy suggests a near equivalence between the two possible orientations of the $[Fe(CO)_2Cp]$ fragment, indicating that an almost free rotation around the Fe−C(ring) bond may be consistent with an important degree of Fe−C π bond character.

Figure 2 shows the MOs for the three $[Fe(CO)_2Cp]$

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Chart 2

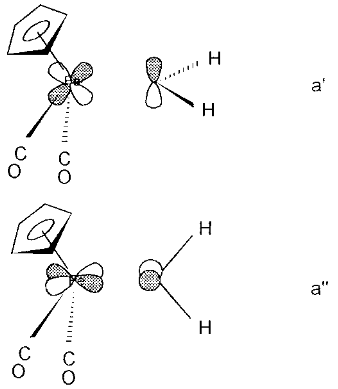


Table 2. Symmetry Properties of the C_3^+ (D_{3h} Group) and $Fe(CO)_2Cp$ (C_s Group) Orbitals in the C_s Group of the Trimeric Complex

C_3^+		$Fe(CO)_2Cp$	
a_1'	a′	a′	a′ + a′ + a′
a_2'	a″	a″	a″ + a″ + a″
e′	a′ + a″		
a_1''	a″		
a_2''	a′		
e″	a′ + a″		

fragments interacting with the MOs of the bridging C_3^+ unit to reproduce the energy levels of the upper valence region of complex **1** most relevant to metal−carbon bonding. On the right of Figure 2 we report the energy levels for the three $[Fe(CO)_2Cp]$ fragments at the same positions observed in the whole complex. Due to the distance among the three fragments (~5 Å) and their extremely small interactions, these levels consist in the proper combinations of a′ or a″ symmetry of the levels for the single fragment. Each level of the single fragment gives rise to three essentially degenerate orbitals which are not distinguished for sake of simplicity. On the left of Figure 2 we report also the main valence orbitals of the C_3^+ molecule, described above. The analysis of Figure 2 is facilitated by Table 2, which reports the irreducible representations spanned by the combinations of three iron fragment orbitals (C_s) and those to which the orbitals of the C_3^+ unit (D_{3h}) correlate in the C_s symmetry group of the whole trinuclear complex.

The bonding in this system arises mainly from the interaction of the two combinations of a′ symmetry (in the C_s group) of the singly occupied 28a′ orbital and the combination of a″ symmetry of the doubly occupied 17a″ orbital of a single iron fragment with the singly occupied $3a_1'$ and 3e′ orbitals (of a′ and a′ + a″ symmetries, respectively, in the C_s group) of the C_3^+ unit. These two types of interactions correspond to the σ and to the π bonding in the plane of the C_3^+ ring; they will be referred to as σ interactions to distinguish them from the π bonding out of the C_3^+ ring plane with the cyclopropenyl π system. The biggest contribution to this metal−carbon σ bonding comes from the two highest occupied 64a″ and 78a′ orbitals and from the two lower 73a′ and 60a″, although many frontier MOs give a small contribution.

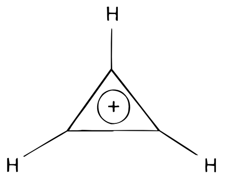
A second contribution to the carbon−iron bonding is due to the interaction between the appropriate combinations of the 27a′ orbitals (with d_π character) of the iron fragments with the π sistem of the C_3^+ unit. This contribution describes the metal−carbon π bond and is smaller than the σ contibution. It is also widely spread over many MOs, but the most important contribution comes from the 77a′ orbital.

Table 3. Mulliken Absolute Charges and Population Changes for Various Orbitals of the $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)]^+$ Complex

	charge	pop. change	charge	pop. change
C_3^+	+0.50	−0.50	Fe d_σ	+0.17
C_3^+ σ		+0.29	Fe d_π	+0.10
C_3^+ π		+0.21	CO	+0.05
Fe	+0.02	-0.48	Cp	+0.53
Fe d		+0.27		

Table 3 shows the changes of the main Mulliken populations and the Mulliken charges of the C_3^+ fragment, the iron atoms, and the CO and Cp ligands in the complex. According to Table 3 the π population of C_3^+ increases by 0.21 units on interaction with the metal framents, indicating that the M → C_3^+ back-donation is fairly small but not neglegible. This suggests a small but significant metal−carbon double-bond character, which is compatible with the experimental evidence.[14] Table 3 shows also that the Mulliken population of the σ orbitals of the C_3^+ increases by 0.29 e indicating that the Fe−C σ bond is polarized toward the carbon atoms. Finally, we see that the C_3 unit bears only a charge of +0.50; an analysis of the Mulliken population changes on the ligands of the metallic fragments (0.05 and 0.53 e lost by the CO and Cp ligands, respectively) shows that the positive charge is mainly delocalized on these ligands which act as electron buffers.

Chart 3



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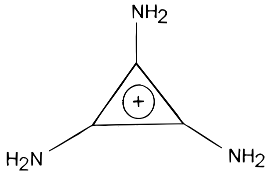

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Table 4. Optimized Geometrical Parameters for the Three Considered Molecules

	$C_3H_3^+$	$C_3(NH_2)_3^+$
C−C	1.37	1.40
C−H	1.09	
C−N		1.34
N−H		1.01

DFT calculations were carried out on the cyclopropenyl cation $C_3H_3^+$ (**2**) and tris(amino)cyclopropenyl cation $C_3(NH_2)_3^+$ (**3**), see Chart 3.

Complete geometrical optimizations were performed in the D_{3h} symmetry, and the computed bond distances and angles are reported in Table 4. The calculated C−C bond lengths are in fairly good agreement with the experimental values for derivative compounds[20] and previous accurate calculations.[29] The geometrical changes within the ring can be understood in terms of orbital interactions between the ring and the substituents. Indeed, the lowest unoccupied orbitals of the π system for the cyclopropenyl ring are the doubly degenerate 1e″ of antibonding character between the carbon

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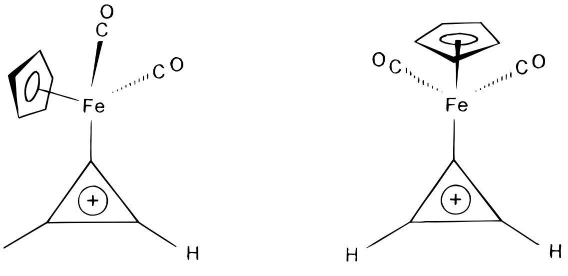
Table 5. Mulliken Population Changes for Various Orbitals of the C_3^+ Unit in the Three Considered Molecules

	$C_3H_3^+$	$C_3(NH_2)_3^+$	$C_3(Fp)_3^+$
C_3^+	−0.70	−0.15	−0.50
$C_3^+\ \sigma$	+0.68	−0.84	+0.29
$C_3^+\ \pi$	+0.02	+0.69	+0.21

atoms, and π donation from the substituents into them will result in an increase in bond length within the ring. The longer C−C bond length in the triamino derivative **3**, 1.40 Å to be compared with 1.37 Å in **2**, is consistent with a high degree of π donation from nitrogen to the antibonding 1e″ orbital of the cyclopropenyl ring. Therefore, the C−C bond length experimentally observed for complex **1**, 1.39 Å, would suggest a significant π donation from the iron fragment. Table 5 shows the changes of the main Mulliken populations of the C_3^+ moiety for the three considered complexes. According to Table 5 the π population of C_3^+ unit remains almost unchanged in the cyclopropenyl ion **2** while increasing by 0.69 units in the triamino-substituted cyclopropenyl. This reflects the absence of π-donation by the hydrogen in $C_3H_3^+$ and the strong π donor character of the amino substituent, respectively. Compared to these values, the gain of 0.21 unit in the π population of C_3^+ calculated for complex **1** is about one-third of that observed for **3** and therefore indicates a significant π-donation from the iron fragment. This result is quite different from that recently obtained by Hall et al. in a calculation on a related dinuclear 1,4-C_6H_4FeCp$(CO)_{22}$ complex in which two FeCp$(CO)_2$ metal fragments substitute two ortho-hydrogens of benzene.[30] Indeed, they found a neglegible π donation from the metal fragments to the benzene ring without any significant quinone-like resonance character. However, this difference could be due to the higher energy of the lowest unoccupied π level of the C_6H_4 fragment with respect to that of the cyclopropenyl cation, the latter being much closer to the low-lying d_π levels of the metal fragments.

Further DFT calculations were performed on the hypothetical [Fe$(CO)_2$Cp $(C_3H_2)]^+$ complex **4** (see Figure 3) to elucidate the relative stabilities of the possible orientations of the [Fe$(CO)_2$Cp] fragments with respect to the cyclopropenyl ring and to study its rotation about the Fe−C bond. Indeed, complex **4** is constituted by the cyclopropenyl cation **2** in which only one hydrogen atom has been substituted by a [Fe$(CO)_2$Cp] fragment. Single point DFT calculations have been carried out for Cp(centroid)−M−C_α−C_β torsion angles of 0°, **4a**, and 90°, **4b**, and for a few intermediate values, keeping fixed all the others geometrical parameters, taken from the crystal structure of **1** or from the optimized value of **2** (the C_{ring}−H bond length). The results show that (i) the orientation corresponding to the cyclopropenyl ring lying in the symmetry plane of the [Fe$(CO)_2$Cp] fragment (with a Cp(centroid)−M−C_α−C_β torsion angles of 0°) is more stable, although by only 1.8 kcal mol^{-1} and (ii) there is no energy barrier between the two limiting orientations. Moreover a Mulliken population analysis shows that the π population of the C_3^+ unit increases by 0.09 e for both orientations, suggesting that the M → C_3^+ π donation is essentially not affected by the Cp(centroid)−M−C_α −C_β torsion angle. The two limiting orientations are therefore almost isoenergetic, and the Cp(centroid)−M−C_α−C_β torsion angles close to 90° observed by the X-ray analysis could be determined by crystal packing effects. These results are also in good agreement with the almost free rotation of the metal fragments around the Fe−C_{ring} bonds, deduced by NMR data in solution.[14]



4a **4b**

Figure 3. Geometries of the two limiting orientations of the $[Fe(CO)_2Cp(C_3H_2)]^+$ complex in the $^1A'$ ground state.

Conclusions

This theoretical study has shown that the iron−cyclopropenyl bond in the considered $[\{Fe(CO)_2Cp\}_3(\mu_3\text{-}C_3)]^+$ cation is mainly of σ character with a smaller, but important, π contribution. Moreover, we have found that the two possible orientations of the [Fe$(CO)_2$Cp] fragment (with the symmetry plane parallel or perpendicular to the C_3^+ ring plane) have essentially the same energy and are separated by no energy barrier. This latter result indicates that an almost free rotation around the Fe−C(ring) bond may be consistent with a significant Fe−C π bond character.

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