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A Helicoid Ferrocene

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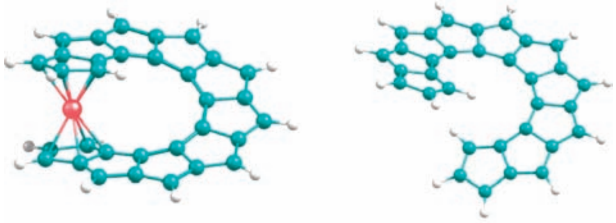
Here, we address the problem of stabilizing a new helicoid ferrocene. Of course, to obtain a helical complex, it is essential to design suitable organic ligands. The ligands should possess the correct symmetry to match the geometrical requirement of the metal center. We propose in silico a beautiful helix that consists of one polycyclic hydrocarbon composed of 10 fused cyclopentadiene rings bound on opposite sides of an iron atom. The nature of the metal−ligand interactions between Fe^{2+} and the ligand was investigated with energy decomposition analysis. Our results provide strong evidence for the viability of the hitherto unknown helicoid ferrocene as a target for synthesis.

Ferrocene is the first and prototypal member of metallocenes, one of the most important families of organometallic compounds. The synthesis of ferrocene, published by Kealy and Pauson[1] 50 years ago, is considered to be a milestone event in organometallic chemistry.[2,3] Beyond its attractive structure and bonding, ferrocene has several applications in the field of material science, asymmetric catalysis,[4] large-scale olefin polymerization,[5] and luminescent materials.[6,7]

In our group, a series of novel metallocenes have been proposed in silico.[8−10] Usually, molecules with nonclassical structures excite the attention of chemists because they are often a sign of unusual bonding.[11−13] Here, we address the problem of stabilizing a new helicoid ferrocene. Of course, to obtain a helical complex, it is essential to design suitable organic ligands. The ligands should possess the correct symmetry to match the geometrical requirement of the metal center. We propose the beautiful helix **1**, which consists of one polycyclic hydrocarbon composed of 10 fused cyclopentadiene rings (**2**) bound on opposite sides of an iron atom. Molecular structures with well-defined helicity are of particular theoretical and practical importance to chemistry.[14−19]



1 **2**

The general interest in helical structures stems in part from the occurrence of screwlike motifs in important biomolecules, such as proteins, nucleic acids, or polysaccharides. The self-

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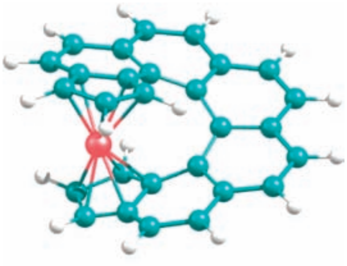
assembly of helical superstructures observed in these systems has been mimicked in a variety of artificial supramolecular assemblies. In this Communication, we examine the structure and bonding of **1** and compare them with the parent complex ferrocene. There are obvious similarities in the electronic structure of **1** and ferrocene, and there are interesting differences as well.

The geometries have been optimized using the BP86[20,21] functional in conjunction with two different basis sets: DZVP[22] and TZ2P.[23] We use *Gaussian 03*[24] for calculations at the BP86/DZVP level and *ADF 2007*[25,26] for those at the BP86/TZ2P level. Our Gaussian values are based on the GTO basis and the ADF values on the STO basis. Geometries have been computed with both variants (results are very similar), and we do all energetics and analyses based on the ADF computations. The nature of the stationary points was examined by calculating the Hessian matrix at the BP86/DZVP level. Particularly, the BP86/TZ2P level includes relativistic effects by the ZORA approximation.[27]

The organic helical backbone **2** consists of one polycyclic hydrocarbon composed of 10 fused cyclopentadiene rings. The steric effects in **2** enforce a helical structure. Note that two terminal cyclopentadienyl rings in the dianion **2** are almost superimposed. Thus, if a metal atom interacts with the inside faces of the single fully π-conjugated chain, the beautiful helix **1** emerges. In 1982, Katz and Pesti reported the intriguing structure **3**.[28−30] This molecule possesses two cyclopentadiene rings linked by five benzene rings. Both **1** and **3** represent conjugated arrays with a helical and chiral structure that might display chiroptical activity and also electricity conducting properties.



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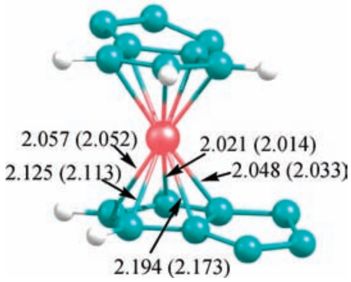

Figure 1. Fe−C bond lengths (in Å) of **1**, calculated at BP86/TZ2P and, in parentheses, at BP86/DZVP.

The geometry of **1** has been optimized in C_2 symmetry. This symmetry automatically induces chirality. Clearly, the BP86/TZ2P and BP86/DZVP calculations give very similar values for the bond lengths (see Figure 1). Thus, in the following, we focus on the results provided by the BP86/TZ2P level. The structure of the title compound consists of an iron atom bound in an η^5 fashion by each of the two cyclopentadienyl rings at either extremity of the helicene **2**. The dihedral angle between the terminal cyclopentadienyl rings, or tilt angle, is 40.6°. As a result of this tilt, the Fe−C bond lengths range from 2.021 to 2.194 Å, whose average is close to the Fe−C bond distances (2.055 Å) in ferrocene[31] calculated at the same level. The vibrational analysis of structure **1** shows that it is a local energy minimum on the corresponding potential energy surface.

The highest occupied molecular orbital (HOMO)−lowest unoccupied molecular orbital (LUMO) gap of 0.37 eV for **1** is clearly smaller than that in ferrocene, which amounts to 2.81 eV. This is a consequence of the more extended conjugation in the former. Interestingly, in recent years, molecules with exceptionally small HOMO−LUMO gaps (<0.5 eV), such as **1**, have become synthetically achievable targets.[32] A variety of unusual optoelectronic properties and electron-transfer phenomena have already been demonstrated for these compounds, making **1** a very desirable target for further physical studies and electronics applications.

The iron atomic charge in **1** is small (+0.057 and −0.046 au using Hirshfeld and VDD methods, respectively) and not much different from that in ferrocene (+0.041 and −0.063 au, respectively).[33] This suggests strong donor−acceptor bonding in either complex. We recall, however, that atomic charges depend in a delicate manner on the methods used to evaluate them as well as on the precise geometry of a system.[33]

Thus, in order to achieve a better and more precise understanding of the similarities and differences in metal−ligand bonding, we have analyzed the bonding mechanism between Fe^{2+} and the ligand, i.e., $\mathbf{2}^{2-}$ in **1** and $(Cp_2)^{2-}$ in ferrocene, in the framework of quantitative Kohn−Sham molecular orbital theory, using an energy decomposition scheme originally introduced in the context of density functional theory by Ziegler and Rauk.[34−36] The valence state of Fe^{2+} is $(3d_{a_{1g}})^2(3d_{e_{2g}})^4(3d_{e_{1g}})^0$, while that of the dianionic ligands

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Table 1. Energy Decomposition Analysis (in kcal·mol^{-1}) of the Fe−Ligand Coordination Bond between Fe^{2+} and the Dianionic Ligand in **1** and Ferrocene[a]

	1	ferrocene
ΔE_{Pauli}	266.0	282.0
ΔV_{elstat}	−445.7 (41%)	−600.5 (51%)
ΔE_{oi}	−628.9 (59%)	−577.6 (49%)
ΔE_{int}	−808.6	−896.0
ΔE_{prep}	34.7	93.8
ΔE	−773.9	−802.3

[a] Computed at BP86/TZ2P. $\Delta E = \Delta E_{\text{prep}} + \Delta E_{\text{int}}$; the latter two terms correspond to steps a and b, respectively, in eqs 1 and 2; $\Delta E_{\text{int}} = \Delta E_{\text{Pauli}} + \Delta V_{\text{elstat}} + \Delta E_{\text{oi}}$ (see ref 28).

corresponds in both cases to their ground states. Table 1 shows how the bond energy ΔE, corresponding to reactions 1 and 2, respectively, is constituted by the various energy terms; the fictitious intermediate step of deforming (eq 1a) or forming (eq 2a) the dianionic ligand is used, later on

$$\mathrm{Fe}^{2+} + \mathbf{2}^{2-} \rightarrow \mathrm{Fe}^{2+} + [\mathbf{2}]_{\mathrm{prep}}{}^{2-} \tag{1a}$$

$$\mathrm{Fe}^{2+} + [\mathbf{2}]_{\mathrm{prep}}{}^{2-} \rightarrow \mathbf{1} \tag{1b}$$

$$\mathrm{Fe}^{2+} + 2\mathrm{Cp}^{-} \rightarrow \mathrm{Fe}^{2+} + [\mathrm{Cp}]_{2}{}^{-} \tag{2a}$$

$$\mathrm{Fe}^{2+} + [\mathrm{Cp}]_{2}{}^{-} \rightarrow \text{ferrocene} \tag{2b}$$

In the first place, we note that equilibrium structure **1** is bound relative to Fe^{2+} and **2**$^{2-}$ (eq 1) by the substantial amount of −774 kcal·mol^{-1} (see Table 1). Thermodynamically, it is therefore a viable target. However, the small HOMO−LUMO gap of **1** is likely to cause a higher bimolecular reactivity as compared to ferrocene (vide supra).

Furthermore, we note that the heterolytic bond energy ΔE of **1** (−774 kcal·mol^{-1} for eq 1) is less stabilizing than that in ferrocene (−802 kcal·mol^{-1} for eq 2). As can be seen in Table 1, this is so because of a substantially weaker electrostatic attraction ΔV_{elstat} (−446 and −601 kcal·mol^{-1} in **1** and ferrocene, respectively), which, in turn, can be ascribed to the more spread-out charge in the conjugated helical ligand **2**$^{2-}$ as compared to that of the [Cp$_2$]$^{2-}$ fragment. Indeed, the combined charge on the two coordinating C$_5$ rings is in the former only −0.756 and −0.706 au (according to Hirshfeld and VDD, respectively) and in the latter substantial −1.638 and −1.280 au in the [(C$_5$H$_3$)$_2$]$^{2-}$ fragment of ferrocene.

All other components in the bonding mechanism are more favorable for **1** than for ferrocene. The deformation or preparation energy ΔE_{prep} of **1** (34.7 kcal·mol^{-1}) is nearly 3 times smaller than that of ferrocene (93.8 kcal·mol^{-1}) because it corresponds to "only" a deformation of ligand **2**$^{2-}$ in the former (eq 1a), whereas in the latter (eq 2a), it is brought about by pushing two separate and negatively charged Cp^{-} rings from infinity together to their positions in ferrocene.

Finally, ligand **2**$^{2-}$ has a smaller HOMO−LUMO gap than [Cp$_2$]$^{2-}$ and enters into somewhat stronger donor−acceptor interactions with Fe^{2+}. Both in **1** and in ferrocene this yields a practically neutral iron atom (vide supra), but the relative importance of the orbital interactions ΔE_{oi} increases from 49% (of all bonding contributions, i.e., $\Delta E_{\text{oi}} + \Delta V_{\text{elstat}}$) in the latter to 59% in the former (see Table 1).[37]

In conclusion, our results provide strong evidence that the hitherto unknown helicoid ferrocene **1** may be a viable target for synthesis. Further explorations of the nature and viability[13] of this and other helicoid metallocenes are underway in our group.

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