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# Fullerene based endohedral metallocenes

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In this study, the density functional theory (DFT)-based Becke's three parameter hybrid exchange functional and Lee–Yang–Parr correlation functional (B3LYP) and dispersion corrected B3LYP (B3LYP-D) calculations have been performed to predict the structure and stability of fullerene based endohedral sandwich complexes. The role of confinement on the structure of half-sandwich complex (i.e. ($\eta^5$-Cp)Fe$^+$ (Cp = cyclopentadienyl anion)) has also been probed using energy decomposition analysis. The standard redox potential has been calculated to understand the electrochemical property of newly designed endohedral sandwich complexes. Results have been compared with exohedral sandwich complexes and ferrocene.

## 1. Introduction

The first prototypical member of the metallocene family was discovered by Kealy and Pauson in 1951 and christened as ferrocene [1]. Discovery of ferrocene has kindled further research activities in transition metal organometallic chemistry. Beyond its attractive (sandwich) structure and bonding, the ferrocene and its derivatives have several applications in the field of material science, asymmetric catalysis, large scale olefin polymerization, electrochemical, biochemical and luminescent materials [2–18]. Ferrocene and other molecules of the same class (i.e. metallocenes) have been extensively studied for the last six decades by both experimental and theoretical methods [4,7,19]. Herein, some of the important literature survey on the structure of the ferrocene has been presented.

In 1968, Haaland and Nilsson have measured the metal ligand distance as 1.66 Å using electron diffraction technique [20]. Luthi et al. have calculated the same distance as 1.88 Å using Hartree-Fock theory [21]. Subsequently, several theoretical studies have been carried out to investigate the structure of ferrocene by various investigators like Klopper, Koch, Jørgensen, and Helgaker [22–24]. The structural investigation unveiled that the hybrid density functional (B3LYP) method yields the equilibrium structure with significantly smaller deviation at affordable computational cost when compared to other methods [24].

Numerous experimental and theoretical investigations have been carried out to understand the functions of metallocenes [2–18,20–28]. Among various studies, Merino and coworkers have made significant contributions to the theoretical understanding of a variety of metallocenes [25–28]. Different donor–acceptor heteroleptic open sandwiches of the form, CpM–M′Pyl (where M = B, Al, Ga; M′ = Li, Na; Pyl = pentadienyl) have been studied using density functional theory. They have also probed the structures and stabilities of $Cp_2M_n$ (where $n = 2–5$; M = Be, Mg, Ca and Zn) compounds [26]. The geometries and metal–ligand bond dissociation energies of $(E\text{-Cp-}E')^+$ (where $E$ and $E'$ = group 13 elements) have been calculated using DFT based BP86/TZ2P method [25]. It is found that heteroleptic complexes are less stable than those of homoleptic complexes. A new helicoid ferrocene has been designed with the help of suitable organic ligand [27].

Hitherto, a variety of metallocenes has been explored. Jemmis et al. have studied exohedral fullerene based metallocene [29]. They have investigated various model systems of fullerene based metallocene using different carbon clusters employing PM3(tm), HF and B3LYP level of theories [29]. Furthermore, they have proposed $\eta^6$-hapticity of the fullerene in metallocene employing energies of isodesmic reaction [29]. Subsequently, Nakamura and coworkers have experimentally synthesized the fullerene based metallocenes with $\eta^5$-hapticity [30]. In their subsequent work, they have also synthesized fullerene based half-sandwich complexes [31].

Several experimental studies have been carried out on the preparation of various fullerenes and their endohedral complexes [32–36]. To the best of our knowledge, the first report on molecular surgery of fullerene appeared in 1997 [37]. Fullerene molecular surgery can be completed in three steps. They are: (i) creation of a hole on the fullerene surface by cage opening, (ii) increasing the size of the hole until guest molecule can be inserted at high pressure and temperature, and (iii) closing the hole to reform the fullerene host with an incarcerated guest molecule.

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Prompted by the advancements in the fullerene chemistry and preparation techniques, the possibility of design of endohedral sandwich complexes using DFT based method has been attempted in this investigation. In this context, $C_{60}$, $C_{80}$, and $C_{180}$ based fullerenes have been taken as the host molecules. The synthesis and stability of half-sandwich complex (($\eta^5$-cyclopentadienyl anion ($\eta^5$-Cp)Fe$^+$) has already been reported [38]. Thus, above-mentioned half-sandwich complex has been chosen as a guest molecule to design the endohedral sandwich complexes. This half-sandwich complex is denoted as ($\eta^5$-Cp)Fe$^+$ in the remaining part of the text. The structures and energies of various endohedral sandwich complexes have been predicted using DFT based method. The properties of $C_{60}$ based endohedral sandwich complex have been compared with its exohedral counterpart.

## 2. Models and symbols

Schematically, the endohedral and exohedral metallocenes considered in this study are depicted in Scheme 1. Since ferrocene can be found in two conformers, both eclipsed and staggered conformations were investigated. The eclipsed and staggered exohedral metallocene complexes were also built from $C_{60}$. They are represented as E-($\eta^5$-Cp)Fe$^+$($\eta^5$-$C_{60}$) and S-($\eta^5$-Cp$^-$)Fe$^+$($\eta^5$-$C_{60}$), respectively. Both eclipsed and staggered endohedral complexes of $C_{60}$ are referred to as E-($\eta^5$-Cp)Fe$^+$@($\eta^5$-$C_{60}$) and S-($\eta^5$-Cp)Fe$^+$@($\eta^5$-$C_{60}$), respectively. The complexes formed by the encapsulation of ($\eta^5$-Cp)Fe$^+$ in $C_{80}$ and $C_{180}$ are represented as E-($\eta^5$-Cp)Fe$^+$@($\eta^5$-$C_{80}$) (eclipsed), S-($\eta^5$-Cp)Fe$^+$@($\eta^5$-$C_{80}$) (staggered), E-($\eta^5$-Cp)Fe$^+$@($\eta^5$-$C_{180}$) (eclipsed) and S-($\eta^5$-Cp)Fe$^+$@($\eta^5$-$C_{180}$) (staggered).

## 3. Computational methods

The geometries of all the metallocenes considered in the study were optimized without any geometrical constrains using DFT based B3LYP method employing 6-31G* basis set [39,40]. Due to the computational cost, the harmonic frequency analysis was carried out only for $C_{60}$ based metallocenes at the same level of theory. The complexation energy ($\Delta E$) was calculated using B3LYP/6-311+G*//B3LYP/6-31G* level employing supermolecule approach:

$$\Delta E = E_{Complex} - (E_{Fullerene} + E_{HS}) \quad (1)$$

where $E_{Complex}$, $E_{Fullerene}$, and $E_{HS}$ are the total energies, complex, fullerene and half-sandwich complex ($\eta^5$-Cp)Fe$^+$, respectively. The monomer (i.e. fullerene and half-sandwich complex) energies were calculated from the respective monomer geometries in the complexes (i.e. fullerene…half-sandwich complexes). The calculated $\Delta E$s were corrected for the basis set superposition error (BSSE) using the counterpoise method suggested by Boys and Bernardi [41].

The standard redox potentials were evaluated by computing the molecular energies for the oxidized and reduced forms in acetonitrile (MeCN) solvent employing the following equation: [42]:

$$E^0_{redox} = \frac{[-(E_{red} - E_{ox}) - V^0]}{n} \quad (2)$$

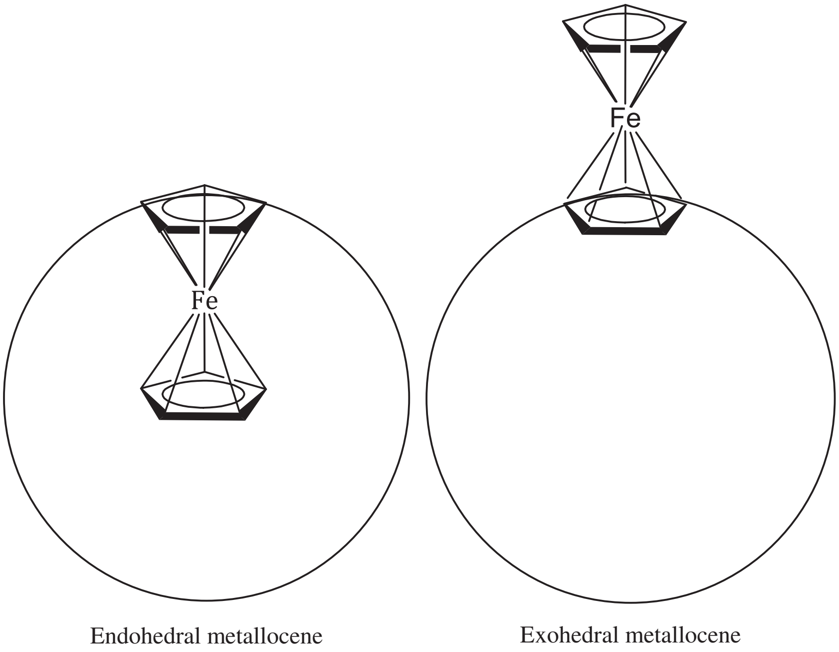
where $E_{red}$ and $E_{ox}$ are energies (in eV) of the reduced and oxidized species including solvation, $V^0$ is absolute potential of reference electrode, and $n$ is the number of electrons. In this study, standard hydrogen electrode (SHE) was considered as reference electrode. The solvent effects were included using the polarizable continuum model (PCM). All these energies were calculated using B3LYP/6-31G* level of theory. The Gaussian 03 suite of program was utilized for the calculations [43].

To understand the nature of interaction, the energy decomposition analysis was carried out employing the Ziegler–Morokuma energy decomposition analysis scheme [44–47]. These calculations were performed using the B3LYP-D/DZP level of theory. The Amsterdam density functional (ADF) theory software package was used for the decomposition analysis [48].

## 4. Results and discussions

### 4.1. Geometry

The geometrical parameters of free fullerenes were calculated at B3LYP/6-31G* level of theory. The calculated average diameters of pristine $C_{60}$, $C_{80}$, and $C_{180}$ are 6.83, 7.94, and 12.38 Å, respectively. Thus calculated average cage volumes of these fullerenes are 166.74, 261.96, and 992.98 Å$^3$, respectively. It is found from



**Scheme 1.** Sandwich complexes (endohedral and exohedral in/on fullerene cages) considered in the study.