

Internet Electronic Journal of Molecular Design

May 2004, Volume 3, Number 5, Pages 222–232

Editor: Ovidiu Ivanciuc

Special issue dedicated to Professor Nenad Trinajstić on the occasion of the 65th birthday
Part 11

Guest Editor: Douglas J. Klein

η^5 - and η^6 -Coordinations Revisited: An ELF Study of Ferrocene and Dibenzenechromium

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Received: October 7, 2003; Accepted: March 17, 2004; Published: May 31, 2004

Citation of the article:

G. Frison and A. Sevin, η^5 - and η^6 -Coordinations Revisited: An ELF Study of Ferrocene and Dibenzenechromium, *Internet Electron. J. Mol. Des.* **2004**, *3*, 222–232, <http://www.biochempress.com>.

η^5 - and η^6 -Coordinations Revisited: An ELF Study of Ferrocene and Dibenzenechromium[#]

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Internet Electron. J. Mol. Des. 2004, 3 (5), 222–232

Abstract

Motivation. The chemistry of five-membered and six-membered conjugated cyclic ligands complexes belongs to the most important classes of organometallic compounds. The determination of the precise nature of the metal–ligand bond is of great importance for the synthesis of new compounds and understanding of their reactivity. We propose here a topological ELF analysis of the metal–ligand interaction with a comparative model study of η^5 - and η^6 -coordination respectively in ferrocene and dibenzenechromium.

Method. Electron Localization Function (ELF) offers a reliable measure of electron pairing and localization. An ELF calculation partitions molecular space in terms of attractors and basins. Each basin, located around an attractor, could be clearly identify into series, each of them having a precise significance (core, lone pair, two-center bond, three-center bond, ...).

Results. This work shows that both η^5 - and η^6 -coordinations could be decomposed in a sum of η^1 - and η^2 -interactions, the latter being predominant. The bonding description is in agreement with the classical resonance scheme.

Conclusions. The topological analysis of the ELF function provides a basis for interpreting and visualization of the bonding scheme in model sandwich molecules.

Availability. TopMoD package is available free of charge at http://www.lct.jussieu.fr/silvi/topmod_english.html.

Keywords. Density Functional Theory (DFT) calculation; metallocenes; sandwich compounds; bond theory; Electron Localization Function (ELF); metal–ligand interaction.

1 INTRODUCTION

The theoretical study of metal–ligand interactions is well developed [1]. Among the variety of ligands, five-membered and six-membered highly conjugated cyclic ligands are widely found in transition metal complexes. The former correspond to metallocenes, sandwich and half-sandwich

[#] Dedicated to Professor Nenad Trinajstić on the occasion of the 65th birthday.

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complexes for which simplest example is given by ferrocene [Fe(Cp)₂] (Cp⁻, cyclopentadiene anion, C₅H₅⁻) and the latter to arene complexes best exemplified by dibenzenechromium [Cr(Bz)₂] (Bz, benzene, C₆H₆). Since the first synthesis of these compounds [2–4], the chemistry of metallocene and arene complexes now belongs to the most important classes of organometallic compounds which are very important for synthetic and industrial applications [5–7].

Two kinds of approaches are currently used in bonding interaction studies. The first one is based on the examination of the wavefunction and includes molecular orbital theory [8] as well as valence bond methods [9,10] whereas the second one is based on the electronic density [11]. Methods based on the molecular orbital theory are the most popular and among them we find the natural bond orbital (NBO) method [12], the charge distribution analysis (CDA) [13] and the energy decomposition analysis (EDA) [14] which is very similar to the extended transition state method (ETS) [15]. They have proven to be extremely useful in bond description and to compute quantitative bond energy [16]. The bonding remains however mostly described with an approximate localized formalism and generally requires an arbitrary choice of fragments. Topological analysis of the electronic density, as the Atoms in Molecules (AIM) theory [17], or the Electron Localization Function (ELF) built from the electron density [18,19] (see Materials and Methods) offers other interesting possibilities. These methods complement nicely approximate MO models since they permit an easily understanding and picturing of the bonding situation on the entire system. Furthermore, they could be applied to experimental density.

The bonding situation in metal–cyclic conjugated ligands complexes has already been analyzed with quantum chemical calculations in earlier theoretical work [20,21]. Recent MO studies on metallocenes and arenes complexes focus on cyclopentadienyl–main–group metal bond [22–24], on heterocyclopentadienyl–transition metal bond [25–29], on heterocyclopentadienyl–main–group metal bond [30], and on heterobenzene–transition metal bond [31]. They give interesting trends in structure stabilities and bond energies depending on the nature of the conjugated ring and on the central atom. The binding interactions in ferrocene and dibenzenechromium have been also recently analyzed [32] with orbital and energy decomposition analyses. Topological analyses on metallocenes and arenes complexes are less abundant. AIM theory has been used for analyzing the bonding in metallocenes [33–35] as well as in arene complexes [36,37], in which various types of bond paths are located between the metal center and the conjugated ring. However, no systematic topological study has been done to give a general description of metal–cyclic conjugated ligand bond.

We have recently explored the η^5 -coordination mode of azaferrocene and phosphoferrocene with the ELF method and shown that η^5 -coordination is characterized by both η^1 - and η^2 -interactions [38]. We propose here an extension of this previous work with a comparative model study of η^5 - and η^6 -coordination respectively in ferrocene **1** and dibenzenechromium **2** (Figure 1). It is shown

that in both complexes the dominant π -type bonding with the ring is accompanied by σ -type contributions, in agreement with the classical resonance scheme which is thus clearly visualized.

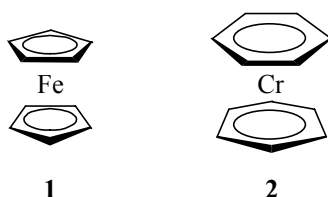


Figure 1. Molecules studied in this investigation.

2 MATERIALS AND METHODS

2.1 Chemical Data

We performed calculations on ferrocene **1** and dibenzenechromium **2** (Figure 1). Both eclipsed and staggered conformations of the cyclopentadienyl units in **1** (respectively of D_{5h} and D_{5d} symmetry) and of the arene units in **2** (respectively of D_{6h} and D_{6d} symmetry) were explored in the geometry optimization. A vibrational analysis was performed at each stationary point. In each case, one almost-zero frequency corresponding to the free rotation of the rings was found. The difference between the eclipsed and staggered structures is negligible for compounds **1** and **2**. Therefore, for the sake of conciseness, only data obtained for eclipsed structures are presented here.

2.2 Computer Software

Geometry optimizations of all compounds studied were performed with the Gaussian 98 [39] suite of program. Becke's hybrid three-parameter exchange functional and Lee, Yang, and Parr's nonlocal correlation functional (B3LYP) [40,41] have been used in conjugation with the 6-31G* basis set containing six cartesian d function.

In each case, following the optimization runs, the topological analysis of the Electron Localization Function (ELF) was made with the TopMoD program [42, 43]. The first approach in the field of electronic topology was made by Richard Bader in his theory of Atoms in Molecules, in which he applied topological concepts to the electronic density $\rho(\vec{r})$ [17]. More recently, the basis-independent ELF method, proposed by Becke and Edgecombe has proved to be very versatile in determining static and dynamic properties of electronic densities, in a great variety of molecules [18]. This function is:

$$\eta(\vec{r}) = \frac{1}{1 + \left(\frac{D(\vec{r})}{D_0(\vec{r})} \right)^2}$$

In this equation $D(\vec{r})$ is given by the following formula:

$$D(\vec{r}) = \frac{1}{2} \sum_i |\vec{\nabla} \Phi_i(\vec{r})|^2 - \frac{1}{8} \frac{|\vec{\nabla} \rho(\vec{r})|^2}{\rho(\vec{r})}$$

This is the excess of local kinetic energy density, due to Pauli repulsion [44].

$D_0(\vec{r}) = C_F \rho(\vec{r})^{5/3}$ is the Thomas–Fermi kinetic energy density which acts as a renormalization factor, and C_F is the Fermi constant ($C_F = 2.871 \text{ \AA}$). The range of values of η is $0 \leq \eta \leq 1$. For a single pair of electrons with antiparallel spins, $\eta = 1$, while for the uniform gas of electrons, by construction, $\eta = 0.5$.

Recently, Silvi and Savin [19] applied these concepts to a new theory of bonding, in which a partition of the molecular space into basins located around an attractor having a clear signification is obtained. Core basins, labeled C(X) and located around the heavy atoms, are typical of the K shell for C atoms and K, L and M shells for Fe and Cr atoms. A given valence basin will be labeled as one of the following: (i) V(X) when it only shares a boundary with a core basin and thus contains electrons that are not involved in a bonding process. This monosynaptic basin corresponds to the usual Lewis language for nonbonding electrons. In this case, the ideal count of electrons is 2 for a “lone pair” or 1 for an “odd electron”, depending on the actual cases. (ii) V(X, Y) when the basin shares a boundary with the cores of two atoms X and Y. Such a basin is typical of a bond between X and Y and is called a disynaptic (bicentric) basin. It has been shown in previous studies that its population may vary significantly, according to the actual nature of the bond [45–48]. Though the classical MO language distinguishes σ and π contributions to bonding, the ELF analysis, which is based on the total electronic density, characterizes basins and attractors without separating these types of contribution. For example, when dealing with alkenes, two V(C, C) basins are observed at the usual standard bond length, separately lying above and below the double–bond local plane. (iii) V(X, Y, Z) when the basin shares a boundary with the cores of three atoms X, Y and Z. Such a basin is typical of a three center bond and is called a trisynaptic (tricentric) basin.

The TopMoD program uses as input the wfn file generated by Gaussian 98, with natural orbital population. The calculations are then carried out in four steps: (i) evaluation of the ELF function over a 3D grid; (ii) identification of the various basins and assignment of the corresponding grid points; (iii) location of the critical points of the ELF function; (iv) integration of charge density over the basins.

3 RESULTS AND DISCUSSION

Table 1 displays the most important geometrical parameters for **1** and **2** that have been calculated at the B3LYP/6–31G* level of theory. The calculated metal–ligand and C–C distances are in very good agreement with the experimental data and do not deserve special comment.

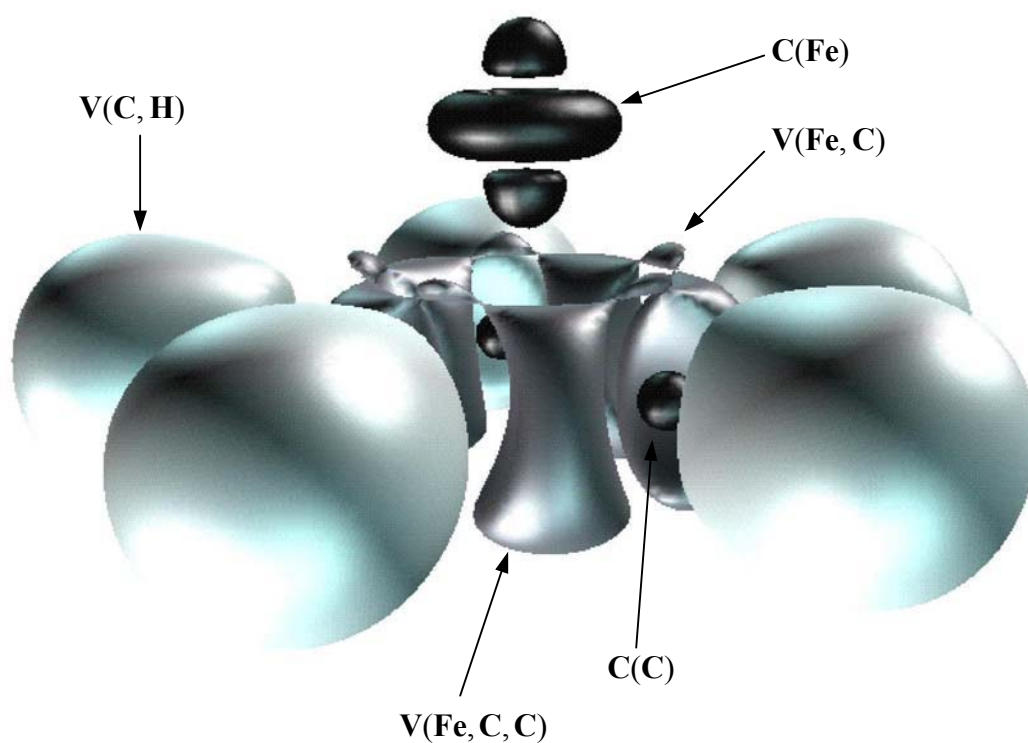
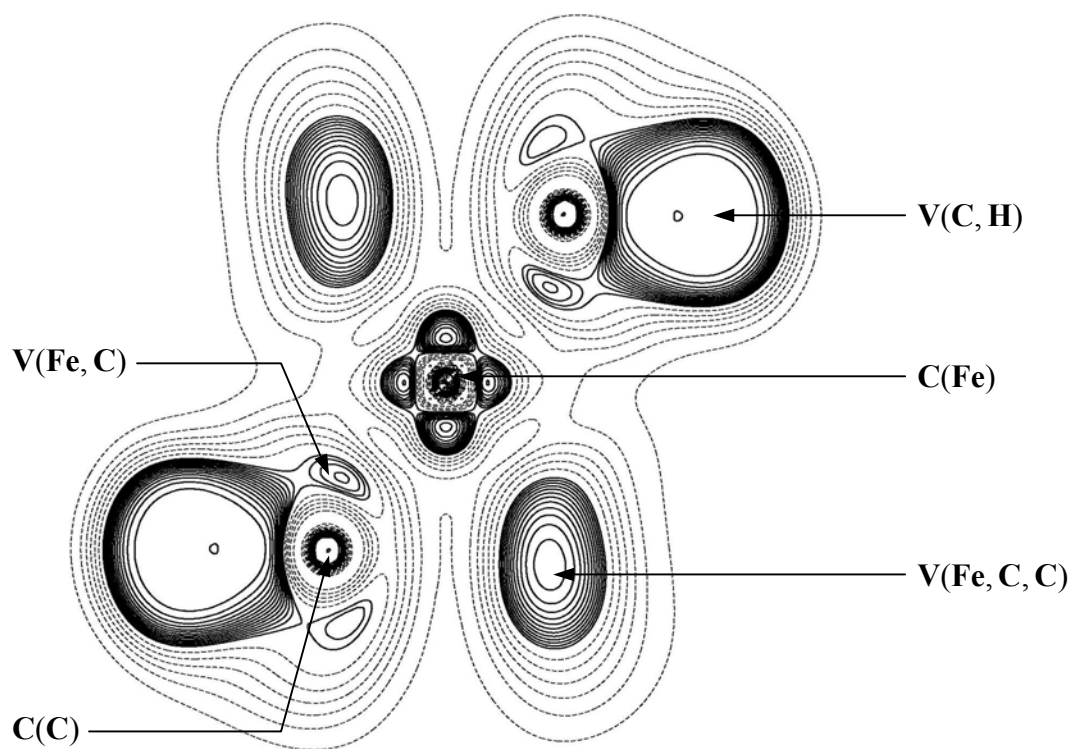


Figure 2. *Upper part.* Contours of the ELF in a plane containing a CH bond of each cycle in **1**. *Lower part.* ELF picture of the bonding between one ring and iron atom in **1**.

Table 1. Theoretical and Experimental Geometry Parameters for **1** and **2**

	Symmetry	M	C–M	C–C	M–X ^a
1	D_{5h}	Fe	2.052	1.428	1.655
1 ^b	D_{5h}	Fe	2.064	1.440	1.661
2	D_{6h}	Cr	2.155	1.419	1.621
2 ^c	D_{6h}	Cr	2.150	1.423	1.613

Bond lengths in Å

^a X designates the center of the conjugated rings

^b Gas phase electron diffraction study [49]

^c Electron diffraction data [50]

Table 2. Electron Population for the Various Basins of **1** and **2**

	Symmetry	M	C(M)	C(C)	V(C, H)	V(M, C)	V(M, C, C)	V(M)
1	D_{5h}	Fe	24.15	2.09	2.16	0.39	2.54	–
2	D_{6h}	Cr	21.93	2.09	2.14	0.25	2.66	0.06

The calculated results for the ELF analysis based on the optimized geometry of **1** and **2** are given in Table 2. Let us first consider the data of **1** more closely (Figure 2).

The ELF calculation yields the core basins of the Fe and C atoms, with respectively 24.15 and 2.09 e. The calculated population of C(Fe) corresponds to the $(1s)^2(2s,p)^8(3s,p)^8(3d)^6$ sequence of electrons expected for a Fe(II) oxidative state. Furthermore, the shape of C(Fe) shows clearly (Figure 2) that electrons are located mainly just above and below, and in the plan parallel to Cp rings around the metal center, which correspond to the extension of the three occupied d orbital of a_{1g} and e_{2g} symmetry. This shows that the d electrons of Fe^{2+} which are not involved in bonding remain close to the positive nucleus atom and are not differentiated from other core electrons. The inclusion of d electron in C(Fe) induces a large volume of the iron core basin in comparison to the one of carbon atom, with a ratio of 1 to 42. The C–H bonds are depicted by the ten V(C, H) bonding basins, populated each by 2.16 e.

The bonding between Fe and each cycle occurs through *two* distinct type of basins, depicted with striking difference in Figure 2: (i) five disynaptic basins, noted V(Fe, C), each with a population of 0.39 e. They correspond to η^1 -interactions between each carbon and the metal center. (ii) five trisynaptic basins, noted V(Fe, C, C), each with a population of 2.54 e. They correspond to η^2 -interactions between each CC bond and the metal center

As seen above, C(Fe) is much bulkier than C(C). This explains that C(Fe) possesses the ability of forming ten bonds with each cycle. V(Fe, C, C) basins are mainly located between the two carbon atoms even if they possess a border with C(Fe). These basins come from the CC bond in isolated Cp^- ring. On the contrary, V(Fe, C) basins do not fit with any basin of isolated Cp^- ring and result directly from the interaction with iron. The V(Fe, C, C) basin has a population (2.54 e), smaller than that of CC bond in isolated Cp^- (2.94 e. B3LYP/6–31+G*). The rest of the electrons attributed to the CC bonds ($2.94 - 2.54 = 0.40$ e) forms almost exactly the population of the V(Fe, C) basins.

Cp–iron interaction could be written as a combination of 5 equivalent resonance forms as illustrated in Figure 3. In this localized description, η^5 –coordination is composed of a σ –bond between the carbon atom bearing the negative charge and the metal center and of two π –bond between CC double bond and the iron atom.

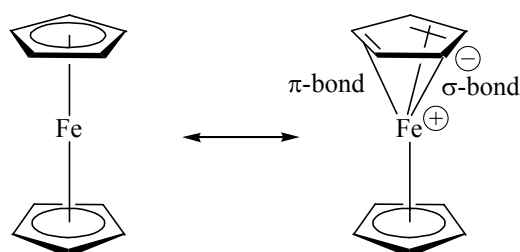


Figure 3. Resonance forms of the η^5 –coordination.

According to the Dewar–Chatt–Duncanson model [51,52], π metal–ethylene bond is described by a ligand to metal donation from the π_{CC} MO and a metal to ligand back–donation in the π^*_{CC} MO (Figure 4).

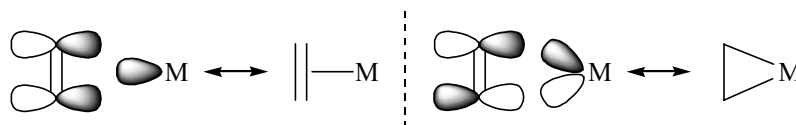


Figure 4. Dewar–Chatt–Duncanson model of the interaction between a CC double bond and a metal center M.

This description of a double bond–metal interaction finds a parallel in AIM theory [53]. In the case of ELF analysis, the donation and back–donation (Figure 4, left and right respectively) will correspond to a trisynaptic basin and to two disynaptic basins respectively.

From the above analysis, it emerges that: (i) $V(\text{Fe}, \text{C}, \text{C})$ basins correspond to the CC double bond to metal donation, (ii) $V(\text{Fe}, \text{C})$ basins could mix metal to CC double bond back–donation and σ –bond between the carbon atom and the metal center. If we considered the charged species Fe^{2+} and Cp^- as interacting fragments, we have seen that the electronic population of the $V(\text{Fe}, \text{C}, \text{C})$ and $V(\text{Fe}, \text{C})$ basins comes exclusively from Cp^- rings. This shows that in this decomposition scheme, the $V(\text{Fe}, \text{C})$ basin does not come from metal to ligand back–donation. η^5 –coordination in ferrocene could thus be described by a combination of η^2 – and η^1 –interaction. Furthermore, if the choice of interacting fragments is Fe^{2+} and Cp^- , the interaction corresponds to dative ligand to metal bond of respectively π and σ –type.

We will now compare the result of the ELF analysis of dibenzenechromium **2** (Table 2) with those obtained for the ferrocene **1**. $C(\text{C})$ and $V(\text{C}, \text{H})$ are the same in **2** as they are in **1** and do not deserve comment. The population of $C(\text{Cr})$ (21.93 e) is in agreement with the $(1s)^2(2s,p)^8(3s,p)^8(3d)^4$ sequence of electrons expected for a $\text{Cr}(0)$ oxidative state. Six very small

basins $V(\text{Cr})$ populated each by 0.06 e are located in the neighborhood of the border of $C(\text{Cr})$, in the plane parallel to the Bz ring and including the metal center. They correspond to excess of electron coming from the metal center, which do not participate to the bonding but which cannot be accommodated into the core. The population of $C(\text{Cr})$ and $V(\text{Cr})$ indicates that the metal center has lost $24 - 21.93 - 6 \times 0.06 = 1.71$ electron to form bonds with both cycles, contrary to the case of dicationic iron which gives no electron to the bonds in ferrocene.

The ELF analysis indicates that each cycle is bound to the metal through 6 $V(\text{Cr}, \text{C})$ basins and 6 $V(\text{Cr}, \text{C}, \text{C})$ basins, by analogy with the preceding compound. As when dealing with **1**, the η^6 -coordination of **2** is actually composed of two contributions via η^1 - and η^2 -interaction modes. Each $V(\text{Cr}, \text{C})$ basins is populated by 0.25 e, which give a total of $12 \times 0.25 = 3.00$ e for the η^1 -interaction in **2**. This shows that both the metal and the cycle give electrons to $V(\text{Cr}, \text{C})$, basins which, as for Cp^- , did not exist in free benzene. The $V(\text{Cr}, \text{C}, \text{C})$ basins are each populated by 2.66 e which is slightly less than the population of a CC bond in benzene (2.80 e). This analysis lead to the description of the η^6 -coordination as depicted in Figure 5.

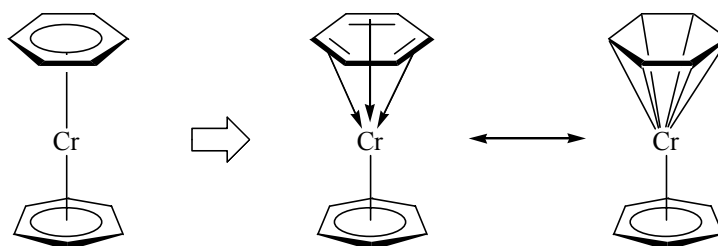


Figure 5. Schematic representation of the η^6 -coordination in **2**.

The last question we address is the respective weight of three center and two center interaction form in η^5 - and η^6 -coordination. This may be given by the respective population of each kind of basin. However, $V(\text{M}, \text{C}, \text{C})$ basin includes both σ and π electrons and we have thus to subtract the σ electrons in order not to overestimate the weight of the η^2 -interaction. The $V(\text{C}, \text{C})$ basin in the single CC bond of ethane is populated by 1.79 e. We can thus estimate that $2.54 - 1.79 = 0.75$ e ($2.66 - 1.79 = 0.87$ e) of $V(\text{Fe}, \text{C}, \text{C})$ ($V(\text{Cr}, \text{C}, \text{C})$ respectively) participate in the three center interaction of **1** (**2** respectively) whereas 0.39 e (0.25 e respectively) participate in the two center interaction of **1** (**2** respectively). These results give a percentage of 66% and 78% of η^2 -interaction respectively in ferrocene and dibenzenechromium. They show that η^1 -interaction remains relatively weak in each case, which is consistent with the aromaticity of the cycle.

4 CONCLUSIONS

This work shows that both η^5 - and η^6 -coordination may be decomposed in a sum of η^1 - and η^2 -interactions, the latter being predominant. This shows that the ELF analysis provides a helpful

qualitative and quantitative view of bonding in delocalized systems and could be used to bring information about the electronic properties of various ligands whose actual nature remains to be established and compared to cyclic aromatic ligands [54,55].

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