

Research Article

Electronic Structure of Ferrocene-Substituted Cavitannds: A QTAIM and NBO Study

Tímea R. Kégl, László Kollár, and Tamás Kégl

Department of Inorganic Chemistry and János Szentágothai Research Center, University of Pécs,
MTA-TKI Research Group for Selective Chemical Syntheses, Ifjúság Útja 6, Pécs 7624, Hungary

Correspondence should be addressed to Tamás Kégl; tkegl@gamma.ttk.pte.hu

Received 1 November 2013; Accepted 24 December 2013; Published 10 February 2014

Academic Editor: Anton Kokalj

Copyright © 2014 Tímea R. Kégl et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Ferrocene-substituted tetrakis(methyl)resorcin[4]arenes have been investigated by means of DFT calculations employing the gradient-corrected PBEPBE functional. In comparison with ferrocene and simple *ansa*-ferrocenes containing 2–4 bridging methylene groups, it was found that the tilt angle of the functionalized cyclopentadienyl (Cp) rings strongly influences the electron density distribution of the ferrocenyl moieties. According to NBO analyses, the iron atoms in the cavitannds are more positive in comparison to those in ferrocene, whereas they are less positive in *ansa*-ferrocenes. The partial charges of carbon atoms belonging to Cp rings show some correlation with the tilt angle.

1. Introduction

Metallocenes are among the first known organometallic compounds. Since the discovery of ferrocene [1] and the elucidation of its bispentahapto sandwich structure, biscyclopentadienyl-transition metal complexes have been in the focus of many important developments in modern organometallic chemistry.

In biscyclopentadienyl-transition metal complexes, the cyclopentadienyl (Cp) rings are relatively inert moieties in most reactions. The Cp rings can function as scaffolding of the upper and lower frames and define the reaction space of the attached metal. Moreover, the Cp ring can be varied in an almost unlimited number of ways in order to modify the steric properties of the complex and the electronic properties of the metal. A commonly used alteration to the metallocene ligand framework is the inclusion of a linking group between the two Cp rings called an interannular bridge. Complexes of this class were originally called metallocenophanes; however, the term “*ansa*-metallocene” is now more commonly used [2]. The Latin prefix *ansa* (meaning “handle”) was introduced by Smith et al. [3], referring to the bent handle functional group connecting to the two Cp rings at both ends. *Ansa*-metallocenes became very popular in the polymer industry

as, for example, an excellent catalyst in the synthesis of highly isotactic polypropylene [4].

The amount of distortion from the normal metallocene geometry that is caused by the bridging group X is depicted in Scheme 1. Several geometrical parameters can be defined describing the geometries of *ansa*-metallocenes [2], from which we will focus on two fundamental values within this study. The degree of ring tilt is represented by angle α , whereas angle β denotes the deviation of the X-C_{ipso} axis from the ring plane.

The reactivity of metallocenes can substantially be influenced by the bridge. Lentzner and Watts studied the effect of the bridge on the reactivity of ferrocenophanes [5]. The tetramethylene bridge enforces some bending of the Cp rings and enhances the Lewis basicity of the iron center in comparison to that in Cp₂Fe but makes the aromatic rings resistant to Friedel-Crafts acylation and to lithiation by Wilkinson et al. [6].

The introduction of an ethylene bridge between Cp rings has a strong effect on the chromocene system [7]. Whereas the carbonyl complex Cp₂CrCO cannot be isolated due to the reversible binding of CO by chromocene [8], various *ansa*-chromocenes were prepared and crystallographically characterized [9, 10]. DFT calculations indicated that

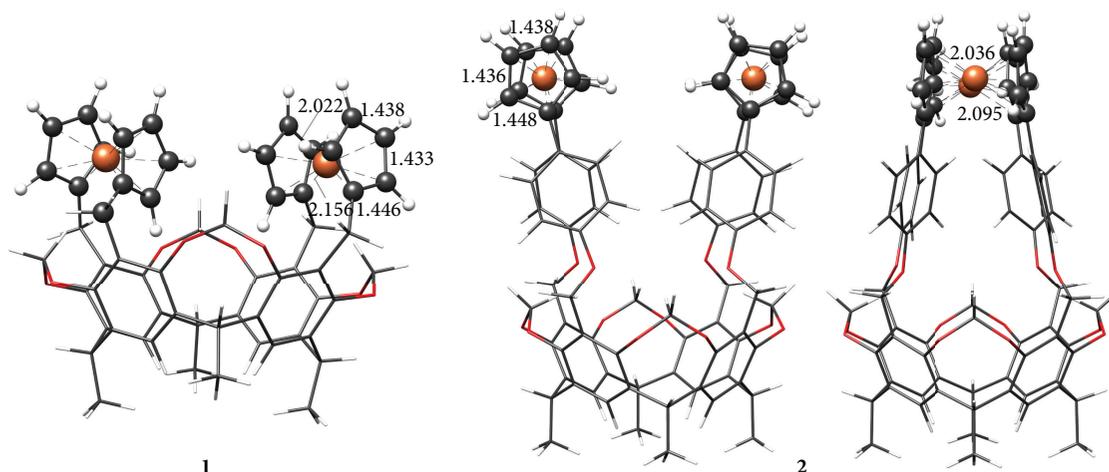
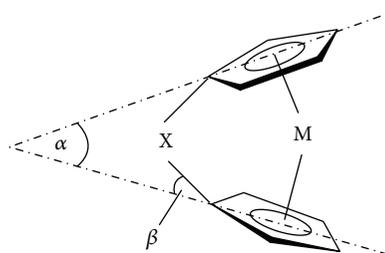


FIGURE 1: Computed structures of complexes 1 and 2 (from two viewpoints). Bond lengths are given in Å.



SCHEME 1

the stabilization of the CO complex of *ansa*-chromocene is the consequence of the stability of the triplet metallocene product. However, in the *ansa*-bridged free chromocene the rings are unable to relax to a near parallel structure, therefore the triplet state is of less advantage [11].

The resorcin[4]arenes and the related cavitands are macrocyclic compounds consisting of multiple aromatic rings connected by different linkers [12]. Cavitands are known to offer excellent points of departure for the construction of large bowl-shaped molecular entities possessing a well-formed hydrophobic cavity. Therefore, cavitands and similar structures show promise with potential applications as gas sensors, nanoreactors, and drug delivery systems. Cavitands have also found a wide application in the preparation of capsule-like self-assemblies. Ferrocene-substituted resorcinarenes were found to be redox-switchable dynamic systems, in which the ferrocene moieties serve as electroactive hydrophobic fragments [13]. Moreover, decamethylruthenocene was found to act as template for the self-assembly of a C-methylcalix[4]resorcinarene/bipyridine/decamethylruthenocene supramolecular crystal [14].

The first goal of this study is to describe the geometry and electronic structure of tetrakis(methyl)resorcin[4]arene (1) and tetrakis(phenoxy)methylresorcin[4]arene (2) containing ferrocene moieties. The ferrocenyl groups provide some prediction for their stability and applicability by the functionalization of cavitands with cyclopentadiene followed

by deprotonation and metallocene formation by the addition of Fe(II) salts. The second purpose of this paper is to give some details for the electron density distribution of ferrocene-substituted cavitands in comparison to simple *ansa*-ferrocenes containing 2–4 bridging methylene groups, as model compounds.

2. Computational Details

For all the calculations the PBE gradient-corrected functional by Perdew et al. [15] was selected using the Gaussian 09 suite of programs [16]. For iron, the triple-zeta basis set by Schaefer and coworkers was applied and denoted as TZVP [17], whereas the 6-31G(d,p) basis set [18] was employed for every other atom. Local minima were identified by the absence of the negative eigenvalues in the vibrational frequency analyses, whereas the Hessian matrix of transition states has only one negative eigenvalue. For the NBO calculations the GENNBO 5.0 program was utilized [19]. For the QTAIM studies the AIMAll software was employed [20].

3. Results and Discussion

The functionalization of resorcin[4]arenes with ferrocenes is predicted to result in well-organized structures with symmetries very close to C_2 . The computed geometries of ferrocene-substituted tetrakis(methyl)resorcin[4]arene (1) and tetrakis(phenoxy)methylresorcin[4]arene (2) are depicted in Figure 1. For a better visibility, complex 2 is shown from two viewpoints emphasizing its peculiar structure arranged by the closure of Cp rings around the iron centers forming formally a dimer of *ansa*-ferrocenes.

For comparison, the geometries of ferrocene and simple *ansa*-ferrocenes, containing bridges formed from 2–4 CH_2 groups, have been computed as well and illustrated in Figure 2. The unsubstituted ferrocene is denoted as 3, whereas *ansa*-ferrocenes with ethylene, 1,3-propylene, and 1,4-butylene bridges are denoted as 4, 5, and 6, respectively. For ferrocene the eclipsed D_{5h} structure was found as global minimum at

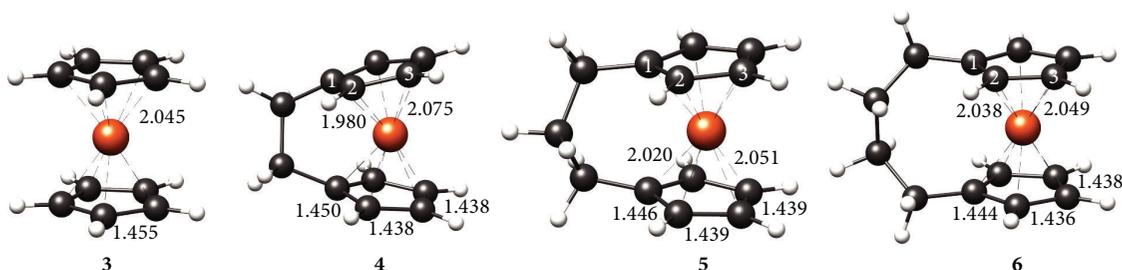


FIGURE 2: Computed structures of complexes 3 through 6. Bond lengths are given in Å.

the PBE/PBE level, in accord with the studies of Salzner [21]. In all *ansa*-complexes, the presence of the bridge breaks the symmetry of the Cp ring leading to contracted C–C bonds in comparison to those in ferrocene. The C1–C2 bonds, in the neighboring position with respect to the bridge, are the least elongated, while the C2–C3 and C3–C3' bonds are somewhat shorter. According to bond lengths, the same tendency can be observed for the cavitands **1** and **2**. As expected, the lengths of Fe–C bonds strongly depend on the bridge, resulting in very short Fe–C1 distance in complex **4**. In complex **6**, however, with the more flexible 1,4-butylene group, the Fe–C distances are quite close to those in ferrocene. It is remarkable that the Fe–C distances in cavitands are somewhat longer compared to *ansa*-ferrocenes. For instance, in complex **1**, the Fe–C3 distance is 2.156 Å, notably longer than that in complex **4**, with somewhat comparable tilt angle (see Table 1).

In Table 1, the results of natural population analysis have been collected as well. The NPA charges of iron centers show distinct values for cavitands and *ansa*-ferrocenes. In complexes **1** and **2**, the iron atoms are more positive than those in ferrocene. In contrast, in complexes **4**–**6** the metal center is more negative. As expected, the charge distribution in the Cp rings strongly depends on the relative position of the bridge; the partial charges increase gradually from the *ipso*-carbons to the C3 carbons. The electron density distribution of the Cp rings in cavitands reveals similarity with that of complexes **4**–**6**, especially for **2**, which presumably possesses a less rigid structure compared to complex **1**.

The electronic structure around the iron central atom has been elucidated within the framework of the quantum theory of atoms in molecules developed by Bader. One of the three QTAIM descriptors taken into account is the electron density at bond critical points (ρ_{BCP}), which is somewhat related bond strengths. The delocalization index $\delta(A,B)$, which is introduced by Bader and Stephens [22], describes the number of electron pairs delocalized between two atomic basins. The $\delta(A,B)$ is somewhat related to formal bond orders for an equally shared pair between two atoms in a polyatomic molecule; however, it is usually less than that due to delocalization over the other atoms in the molecule. The ellipticity (ε) calculated from two negative eigenvalues (λ_1 and λ_2) of the Hessian matrix of the electron density function $\rho(\mathbf{r})$ at the BCP is a measure of the deviation of the charge density from the axial symmetry of a chemical bond and is defined as $\varepsilon = \lambda_1/\lambda_2 - 1$. Values close to zero indicate cylindrical character, whereas values greater than

TABLE 1: Structural parameters (in degrees, see Scheme 1) and selected NPA charges of complexes 1–6.

Complex	α	β	$Q(\text{Fe})$	$Q(\text{C1})$	$Q(\text{C2})$	$Q(\text{C3})$
1	–14.1	–9.7	0.178	–0.072	–0.259	–0.263
2	–6.6	–4.6	0.176	–0.080	–0.270	–0.271
3	0	n.a.	0.141	–0.281	n.a.	n.a.
4	21.0	14.8	0.124	–0.043	–0.261	–0.297
5	8.4	4.4	0.120	–0.061	–0.269	–0.283
6	1.8	–2.4	0.128	–0.065	–0.273	–0.277

zero may indicate partial π -character of a bond. The ρ_{BCP} and ε values for complexes 1–6 are compiled in Table 2, whereas delocalization indices $\delta(A,B)$ are presented in Table 3.

The introduction of a bridge causes changes in Fe–C bond strengths due to the distortion of the metallocene structure. For the cavitand-based complexes, the interaction between the iron center and the Cp rings is somewhat weaker in comparison to ferrocene. In *ansa*-metallocenes, however, the strength of this interaction strongly depends on the bridge size: in the more strained complex **4**, the Fe–C1 and Fe–C2 bonds become stronger, while the Fe–C3 bond is weaker in terms of delocalization indices, as well as ρ_{BCP} values. As expected, the smallest change in the strength of Fe–C interactions can be observed for the least strained *ansa*-ferrocene **6**.

Inspecting, however, the changes in electron density distribution of the Cp rings, it can be observed that the C–C bond strengths, in terms of delocalization indices, are expected to be increased upon the introduction of the *ansa*-bridge for complexes **1** and **5** in β -position, whereas almost no change is predicted for complexes **2**, **4**, and **6**. For the C1–C2 bonds, a decrease can be expected in all cases according to the ρ_{BCP} and $\delta(A,B)$ values. The bond ellipticities follow the distortion of the metallocene structure as well. Upon decreasing the distance between the analogous carbon atoms in the Cp rings, the double bond character is increased, whereas it is decreased for the carbon atoms on the opening parts in the rings. That is, in complexes **1** and **2**, the C2–C3 bond is expected to behave with a somewhat increased double bond character, which may result in a change of the reactivity of the rings on that site.

It is concluded that the synthesis of ferrocene-substituted tetrakis(methyl)resorcin[4]arene (**1**) and tetrakis(phenoxy)methyl)resorcin[4]arene (**2**) is likely to lead to success.

TABLE 2: Electron densities and bond ellipticities in bond critical points ρ_{BCP} for selected bonds in complexes 1–6.

Complex	$\rho_{\text{BCP}}(\text{Fe}, \text{C1})$	$\rho_{\text{BCP}}(\text{Fe}, \text{C2})$	$\rho_{\text{BCP}}(\text{Fe}, \text{C3})$	$\rho_{\text{BCP}}(\text{C1}, \text{C2})$	$\epsilon(\text{C1}, \text{C2})$	$\rho_{\text{BCP}}(\text{C2}, \text{C3})$	$\epsilon(\text{C2}, \text{C3})$
1	0.080	0.083	0.091	0.279	0.220	0.282	0.235
2	0.081	0.089	0.090	0.277	0.221	0.282	0.245
3	0.089	n.a.	n.a.	0.281	0.244	n.a.	n.a.
4	0.103	0.094	0.086	0.276	0.264	0.279	0.243
5	0.094	0.091	0.088	0.278	0.253	0.282	0.244
6	0.090	0.090	0.088	0.279	0.239	0.281	0.244

TABLE 3: Delocalization indices $\delta(\text{A}, \text{B})$ in complexes 1–6.

Complex	$\delta(\text{Fe}, \text{C1})$	$\delta(\text{Fe}, \text{C2})$	$\delta(\text{Fe}, \text{C3})$	$\delta(\text{C1}, \text{C2})$	$\delta(\text{C2}, \text{C3})$
1	0.467	0.501	0.503	1.189	1.223
2	0.437	0.501	0.502	1.171	1.211
3	0.503	n.a.	n.a.	1.211	n.a.
4	0.517	0.510	0.491	1.172	1.210
5	0.492	0.508	0.497	1.178	1.215
6	0.491	0.505	0.501	1.182	1.211

These complexes, with presumably somewhat activated ferrocene moieties, are possible candidates for further transformations. The increased electron density on the β -position of cyclopentadienyl rings makes them possible candidates for following functionalization.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

- [1] T. J. Kealy and P. L. Pauson, "A new type of organo-iron compound," *Nature*, vol. 168, no. 4285, pp. 1039–1040, 1951.
- [2] P. J. Shapiro, "The evolution of the *ansa*-bridge and its effect on the scope of metallocene chemistry," *Coordination Chemistry Reviews*, vol. 231, no. 1-2, pp. 67–81, 2002.
- [3] J. A. Smith, J. von Seyerl, G. Huttner, and H. H. Brintzinger, "*ansa*-Metallocene derivatives. Molecular structure and proton magnetic resonance spectra or methylene- and ethylene-bridged dicyclopentadienyltitanium compounds," *Journal of Organometallic Chemistry*, vol. 173, no. 2, pp. 175–185, 1979.
- [4] W. Kaminsky, K. K ulper, H. H. Brintzinger, and F. R. W. P. Wild, "Polymerization of propene and butene with a chiral zirconocene and methylalumoxane as cocatalyst," *Angewandte Chemie International Edition in English*, vol. 204, no. 6, pp. 507–508, 1985.
- [5] H. L. Lentzner and W. E. Watts, "Bridged ferrocenes-VII. The preparation and properties of [2]ferrocenophanes," *Tetrahedron*, vol. 27, no. 18, pp. 4343–4351, 1971.
- [6] G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, "The structure of iron bis-cyclopentadienyl," *Journal of the American Chemical Society*, vol. 74, no. 8, pp. 2125–2126, 1952.
- [7] H. Schwemlein, L. Zsolnai, G. Huttner, and H. H. Brintzinger, "*ansa*-metallocene derivatives. VI. Synthesis and molecular structure of a stable tetramethylethylene-bridged chromocene carbonyl complex, $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})$," *Journal of Organometallic Chemistry*, vol. 256, no. 2, pp. 285–289, 1983.
- [8] K. L. T. Wong and H. H. Brintzinger, "Reactivity patterns of chromocene, molybdenocene, and tungstenocene reaction systems. I. Carbonyl complex formation as a probe of coordinative unsaturation," *Journal of the American Chemical Society*, vol. 97, no. 18, pp. 5143–5146, 1975.
- [9] F. Schaper, M. Rentsch, M.-H. Prosen, U. Rief, K. Schmidt, and H.-H. Brintzinger, "*ansa*-Metallocene derivatives XXXVI. Dimethylsilyl-bridged permethyl chromocene carbonyl complexes—syntheses, crystal structures and interconversion reactions," *Journal of Organometallic Chemistry*, vol. 534, no. 1-2, pp. 67–79, 1997.
- [10] G. J. Matare, D. M. Foo, K. M. Kane et al., "*ansa*-Chromocene complexes. I. Synthesis and characterization of Cr(II) carbonyl and tert-butyl isocyanide complexes," *Organometallics*, vol. 19, no. 8, pp. 1534–1539, 2000.
- [11] J. C. Green and C. N. Jardine, "Thermal stability of Group 6 bis(cyclopentadienyl) and ethylene bridged bis(cyclopentadienyl) monocarbonyl complexes; a theoretical study," *Journal of the Chemical Society, Dalton Transactions*, pp. 3767–3770, 1999.
- [12] Z. Cs ok, T. K egl, Y. Li et al., "Synthesis of elongated cavitands via click reactions and their use as chemosensors," *Tetrahedron*, vol. 69, no. 38, pp. 8186–8190, 2013.
- [13] D. E. Korshin, N. V. Nastapova, S. V. Kharlamov et al., "Electroswitchable self-assembly of tetraferrocene-resorcinarene," *Mendeleev Communications*, vol. 23, no. 2, pp. 71–73, 2013.
- [14] Y. Zhang, C. D. Kim, and P. Coppens, "Does *C*-methylcalix[4]resorcinarene always adopt the crown shape conformation? A resorcinarene/bipyridine/decamethylruthenocene supramolecular clathrate with a novel framework structure," *Chemical Communications*, pp. 2299–2300, 2000.
- [15] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Physical Review Letters*, vol. 77, no. 18, pp. 3865–3868, 1996.
- [16] M. J. Frisch et al., *Gaussian 09 Revision C. 01*, Gaussian, Wallingford, Conn, USA, 2009.
- [17] A. Schaefer, C. Huber, and R. Ahlrichs, "Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr," *Journal of Chemical Physics*, vol. 100, p. 5829, 1994.

- [18] R. Ditchfield, W. J. Hehre, and J. A. Pople, "Self-consistent molecular-orbital methods. IX. An extended Gaussian-type basis for molecular-orbital studies of organic molecules," *Journal of Chemical Physics*, vol. 54, p. 724, 1971.
- [19] NBO 5.0., E. D. Glendening, K. Badenhoop et al., Theoretical Chemistry Institute, University of Wisconsin, Madison, Wis, USA, 2001.
- [20] AIMAll (Version 13.05.06), A. Todd, and T. K. Keith, *Gristmill Software*, Overland Park, Kan, USA, 2013.
- [21] U. Salzner, "Quantitatively correct UV-vis spectrum of ferrocene with TDB3LYP," *Journal of Chemical Theory and Computation*, vol. 9, no. 9, pp. 4064–4073, 2013.
- [22] R. F. W. Bader and M. E. Stephens, "Spatial localization of the electronic pair and number distributions in molecules," *Journal of the American Chemical Society*, vol. 97, no. 26, pp. 7391–7399, 1975.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

