Mendeleev Commun., 2003, 13(5), 209–211

Topological analysis of the electron density distribution functions of neutral 3*d* metal metallocenes

Konstantin A. Lyssenko,*[a] Denis G. Golovanov[a,b] and Mikhail Yu. Antipin[a]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 135 5085; e-mail: kostya@xrlab.ineos.ac.ru*

[b] *Higher Chemical College, Russian Academy of Sciences, 125047 Moscow, Russian Federation. E-mail: spyros@ineos.ac.ru*

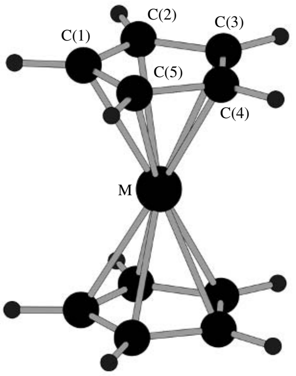
10.1070/MC2003v013n05ABEH001836

Topological analysis of the electron density distribution functions for 3*d* metal neutral metallocenes $M(C_5H_5)_2$ (M = V, Cr, Mn, Fe, Co and Ni) on the basis of DFT calculation [B3PW91 functional and 6-311+G(d,p) basis set] has revealed that the chemical bonding pattern in the Fe, Ni, V, and Mn complexes corresponds to the η^5-type coordination of C_5H_5 ligands, while Co and Cr metallocenes are characterised by η^1, η^2 and η^3-coordination types, respectively.

Despite of more than 50 years since the dicovery of $Fe(C_5H_5)_2$,[1] this class of compounds still attracts both theoretical and practical attention.[2] Modern computational methods make it possible to reproduce not only the experimental geometry but also the barriers to rotation of cyclopentadienyl ligands (Cp), vibrational frequencies and bond energies.[3,4] Recent studies of the electronic structure of neutral 3*d* metallocenes $M(Cp)_2$ (M = V, Cr, Mn, Fe, Co and Ni) within the B3LYP/DZP calculations have revealed that D_{5h} symmetry is usually a genuine minimum, but for $CrCp_2$ and $CoCp_2$ the D_{5h} structure distorts forwards to the C_{2v} symmetry due to Jahn–Teller effects.[3] The symmetry distortion in the latter complexes also leads to nonequivalence of C–C bond lengths in Cp ligands, which might indicate that chemical bonding in $CrCp_2$ and $CoCp_2$ differs from that of the symmetrical complexes.

During the last decade the estimation of the atom···atom interaction nature and an experimental or theoretical analysis of electron density distribution function $\rho(r)$ within Bader's 'Atom in Molecule' theory (AIM) were commonly used.[5] In spite of the validity of analysis of the $\rho(r)$ within AIM for weak interaction was debated,[6] recent comparison of the $\rho(r)$ topology and potential energy density distribution function $\nu(r)$ have resolved this controversy.[7] Bader has demonstrated that each bond path in the electron density is mirrored by the virial path, a line of maximum potential energy density, what in turn indicates that presence of the bond path or critical point (3, –1) between the pair of atoms in question is the 'universal indicator of bonding between atoms'.[7]

Note that despite of advantages of this method for organometallic compounds (for example, transition metal carbonyl clusters[8]) no systematic analysis of the $\rho(r)$ topology in metallocenes is available. Up to date, such investigations are limited to experimental analysis of the deformation electron density function in crystals of VCp_2,[9] $CpM(C_7H_7)$ (M = Ti, V or Cr)[10] and $(C_8H_8)Ti(C_7H_7)$.[10]



M	C–C/Å	M–C/Å	M–Cp$_{cent}$/Å
V	1.419	2.282	1.937
Mn	1.419	2.394	2.067
Fe	1.424	2.052	1.655
Ni	1.420	2.199	1.837

Figure 1 The general view and principle geometry of the $M(C_5H_5)_2$ (M = V, Mn, Fe and Ni) complexes.

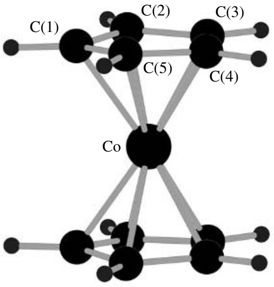


Figure 2 The general view of the $Co(C_5H_5)_2$ complex. Bond lengths (Å): C(1)–C(2) 1.429, C(2)–C(3) 1.407, C(3)–C(4) 1.441, Co–C(1) 2.076, Co–C(2) 2.144, Co–C(3) 2.110, Co–Cp$_{cent}$ 1.737; the C(1) atom is shifted from the C(2)–C(5) plane by 0.088 Å towards the Co atom.

To analyze the chemical bonding in metallocenes, we report the results of a topological analysis of $\rho(r)$ in neutral $M(C_5H_5)_2$ (M = V, Cr, Mn, Fe, Co and Ni) complexes. In this study, we used density functional theory (DFT) calculations to perform geometry optimization of $FeCp_2$, $NiCp_2$, VCp_2 and $MnCp_2$ with the D_{5h} symmetry constrain, and of $CoCp_2$ and $CrCp_2$ molecules within C_{2v} symmetry point group according to ref. 2. DFT calculations were used to include an electron correlation effect, which is widely recommended as an effective computational tool for organometallic compounds.[1,2,11] For our quantum chemical calculations, we used B3PW91 DFT for $FeCp_2$ and unrestricted B3PW91 methods for rest open shell systems with the 6-311+G** basis set. All calculations were carried out with the use of the Gaussian 98 program package,[12] in which fine grid (75302) is the default for evaluating integrals numerically and the (10^{-8} hartree) disignation is the default for the SCF convergence. As a convergence criteria, threshold limits of 1.5×10^{-5} and 6×10^{-5} a.u. were used for maximum force and displacement, respectively.

The geometry of complexes obtained within the B3PW91/6-311+G(d,p) calculations (Figures 1–3) is close to B3LYP/DZ

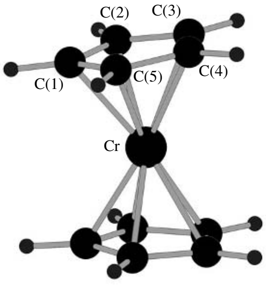


Figure 3 The general view of $Cr(C_5H_5)_2$. Bond lengths (Å): C(1)–C(2) 1.433, C(2)–C(3) 1.422, C(3)–C(4) 1.418, Cr–C(1) 2.110, Cr–C(2) 2.151, Cr–C(3) 2.218, Cr–Cp$_{cent}$ 1.800; the dihedral angle between Cp rings is equal to 9.3°.

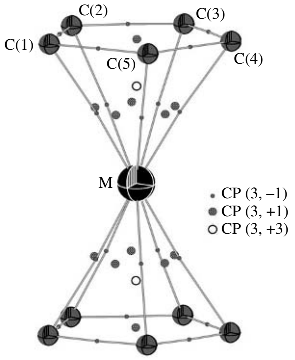


Figure 4 The characteristic set of critical points in $M(C_5H_5)_2$ (M = V, Mn, Fe and Ni) complexes.

data and experimental values.[2] The M–C distances vary in the range 1.655–2.067 Å with the minimum and maximum values observed for ferrocene and manganacene, respectively. Note that, in spite of such a variation, the C–C bond lengths in complexes with D_{5h} symmetry remain practically the same (Figure 1). In contrast, in $CoCp_2$ and $CrCp_2$, the bond lengths in the Cp ligand are much more sensitive to variation in the M–C bond lengths (Figures 2, 3). Thus, in Cp_2Co the variation of M–C distances within the range 2.076–2.144 Å leads to consequent alternation of the C–C bonds from 1.407 to 1.441 Å. In addition to C–C bond alternation the symmetry lowering due to an odd number of 3*d* electrons at a double degenerate orbital is also manifested in an envelope conformation of the Cp ligand [C(1) atom is deviated by 0.088 Å toward the metal] in $CrCp_2$ and in the nonplanarity (dihedral angle is 9.3°) of Cp ligands in $CoCp_2$.

The topological analysis of $\rho(r)$ was performed using the AIMPAC program package.[13] The critical point (CP) search for $\rho(r)$ function has revealed that characteristic sets for metallocenes are dependent not only on the symmetry point group of the complex but also on the metal nature.

In all Cp_2M (M = Fe, Ni, V and Mn) complexes with D_{5h} symmetry, the molecular graph obtained from the topological analysis of $\rho(r)$ corresponds to the η^5-type coordination of the Cp ligands, *i.e.*, CP's (3, –1) were found for all M–C, as well as C–C and C–H, bonds. Taking into account that such a geometry leads to the formation of ten three-membered rings in addition to Cp rings and two polyhedrons (pentagonal pyramid), the characteristic set also contains 12 ring CP (3, +1) and two cage CP (3, +3) in accordance with the Puancare–Hoph relationship[5] (Figure 4). Unfortunately, in the case of Cp_2Fe, the Puancare-Hoph relationship is not satisfied, namely, the CP (3, +1) of the Cp ring and the cage CP(3, +3) due to their proximity cannot be located unambiguously. This clearly arises from the fact that both of these critical points are located at the five-fold axis, and a local minimum [CP (3, +3)] is situated between a local maximum corresponding to nonbonding dz^2-orbital (a_{1g}) and saddle point (3, +1). Thus, in the case of $FeCp^2$, in which the distance from the metal atom to the centroid of the Cp ring is only 1.655 Å, and the a_{1g} orbital is fully occupied, the curvatures of the $\rho(r)$ function and thus the signature of the CP cannot be estimated within the necessary accuracy.

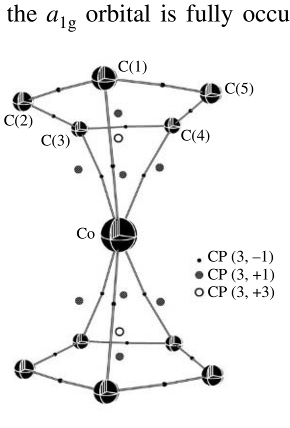


Figure 5 The characteristic set of critical points in $Co(C_5H_5)_2$.

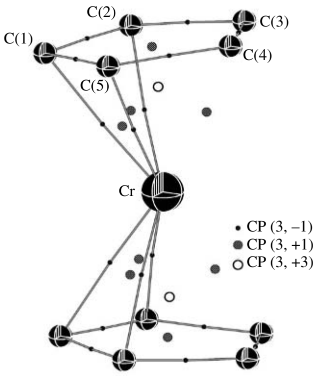


Figure 6 The characteristic set of critical points in $Cr(C_5H_5)_2$.

In the Cp_2Co and Cp_2Cr complexes, although the molecular symmetry is the same (C_{2v}), the characteristic set of CP's and, as a result, the type of Cp ligand coordination are drastically different. In both complexes, only three of carbon atoms of each Cp ligand form a chemical bond with the metal atom. In the $CoCp_2$ complex in the Co–C(2) and Co–C(5) interatomic areas instead of CP (3, –1) the ring critical points (3, +1) were located thus indicating the formation of four-membered rings (Figure 5). The values of positive principle curvatures of the electron density in the CP (3, +1) for C(1)C(2)C(3)Co ring (0.20 and 6.625 eÅ^{-5}) are essential for unambiguous determination of its type. As the result, the characteristic set for Cp_2Co complex instead of 10 CP's (3, +1) for three-membered CCM rings includes 4 CP (3, +1) for four-membered CCCM rings and 2 for three-membered MCC rings. Note that the value of the $\rho(r)$ function in CP (3, +1) for CCCM ring (0.420 eÅ^{-3}) is significantly smaller than $\rho(r)$ for CP (3, –1) of M–C bonds (0.495–0.542 eÅ^{-3}) and to the corresponding value in CP (3, +1) for CCM ring (0.492 eÅ^{-3}). This characteristic set is in line with a significant elongation of Co(1)–C(2) and Co(1)–C(5) bonds up to 2.218 Å in comparison with the rest ones (2.110–2.151 Å), as well as with the nonplanarity of Cp rings and finally with the alternation of C–C bonds. Thus, from both the geometry and topological analysis of the $\rho(r)$ function, the type of coordination of Cp rings in $CoCp_2$ complexes corresponds to the η^1,η^2 type.

In $CrCp_2$, while there are also only three chemical bonds between chromium and carbon atoms of each of the Cp ligand instead of four-membered CCCM rings, the five-membered C(2)C(3)C(4)C(5)Cr ring was found (Figure 6). As in $CoCp_2$, in the Cr–C(3) and Cr–C(4) interatomic areas no CP (3, –1) are located. The positive principle curvatures of the $\rho(r)$ in the CP (3, +1) for five-membered CCCCM rings are also essential for the determination of critical point signature and are equal to 0.30 and 7.81 eÅ^{-5}, respectively. The values of the $\rho(r)$ function

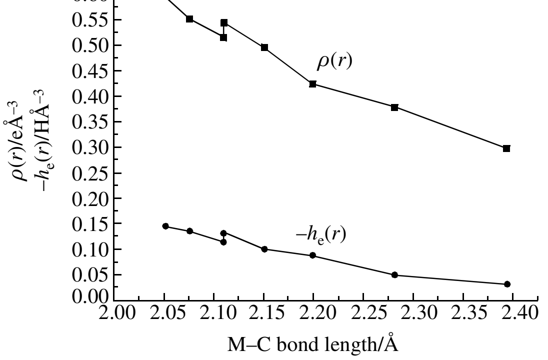


Figure 7 Correlations between the M–C bond length and electron density and energy density functions at critical point (3, –1) of the M–C bonds in $M(C_5H_5)_2$ (M = V, Cr, Mn, Fe, Co and Ni) complexes.

in the latter CP (3, +1) is 0.483 eÅ^{-3}, which is significantly smaller than the corresponding value for CP (3, –1) of M–C bonds (0.514–0.550 eÅ^{-3}). Thus, in the case of CrCp$_2$, the type of Cp-ring coordination can be described as the η^3 type.

Despite of the above drastic differences in characteristic sets, there are some general features of M–C chemical bonding in the 3*d* metallocenes studied. First, while the Laplacian of the electron density $\nabla^2\rho(r)$ in CP's (3, –1) of M–C bonds is positive (3.479–7.167 eÅ^{-5}), the values of the electron energy density $h_e(r)$ are negative (–0.030 to –0.144 HÅ^{-3}); thus, regardless of bond lengths, all M–C bonds correspond to the intermediate type of interatomic interactions.[7] It should be noted that a significant decrease in the $h_e(r)$ function upon the occupation of antibonding e_{1g} orbitals in MnCp$_2$ (–0.030 HÅ^{-3}) indicate that the covalent component in this complex is essentially smaller. In contrast, C–C and C–H bonds are characterised by expected negative values of $\nabla^2\rho(r)$ in CP (3, –1), which is characteristic of the shared type of interatomic interactions.

Taking into account that both $\rho(r)$ and $h_e(r)$ values in the CP's (3, –1) for M–C bonds ideally correlate with their lengths (Figure 7), we can expect that these values obtained from either theoretical or experimental electron density functions can be used for estimating the energy of these interactions as it was previously done for boron donor–acceptor complexes[14] and hydrogen bonds.[15]

This work was supported by the Russian Foundation for Basic Research (grant no. 03-03-32214) and the Support of Leading Schools of the President of the Russian Federation (1060.2003.3 and MK-1209.2003.03).

References

1 T. J. Kealy and P. L. Pauson, *Nature*, 1951, **168**, 1039.

2 N. J. Long, *Metallocenes: An Introduction to Sandwich Complexes*, Blackwell Science Ltd., Oxford, 1998.

3 Zhen-Feng Xu, Yaoming Xie, Wen-Lin Feng and H. F. Shaffer III, *J. Phys. Chem. A*, 2003, **107**, 2716.

4 N. Fey, *J. Chem. Tech. Biotech.*, 1999, **74**, 852.

5 R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendron Press, Oxford, 1990.

6 (*a*) J. Cioslowski, S. T. Mixon and W. D. Edwards, *J. Am. Chem. Soc.*, 1991, **113**, 1083; (*b*) J. Cioslowski, P. B. O'Connor and E. D. Fleischmann, *J. Am. Chem. Soc.*, 1991, **113**, 1086; (*c*) J. Cioslowski and S. T. Mixon, *J. Am. Chem. Soc.*, 1992, **114**, 4382; (*d*) J. Cioslowski, L. Edginton and B. B. Stefanov, *J. Am. Chem. Soc.*, 1995, **117**, 10381.

7 R. F. W. Bader, *J. Chem. Phys. A*, 1998, **102**, 7314.

8 P. Macchi and A. Sironi, *Coord. Chem. Rev.*, 2003, **238–239**, 383.

9 M. Yu. Antipin, K. A. Lyssenko and R. Boese, *J. Organomet. Chem.*, 1996, **508**, 259.

10 K. A. Lyssenko, M. Yu. Antipin and S. Yu. Ketkov, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 125 (*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 130).

11 T. Ziegler, *Can. J. Chem.*, 1995, **73**, 743.

12 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98, Revision A.9*, Gaussian, Inc., Pittsburgh PA, 1998.

13 J. Cheeseman, T. A. Keith and R. W. F. Bader, *AIMPAC Program Package*, McMaster University, Hamilton, Ontario (Canada), 1992.

14 E. Espinosa, E. Molins and C. Lecomte, *Chem. Phys. Lett.*, 1998, **285**, 170.

15 V. Jonas, G. Freking and M. Reetz, *J. Am. Chem. Soc.*, 1994, **116**, 8741.

Received: 21st July 2003; Com. 03/2162