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Erratum

Erratum to "Complementarity of QTAIM and MO theory" [Coord. Chem. Rev. 249 (2005) 633]☆

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Professor Dunitz of ETH has drawn my attention to a miss-interpretation of a statement made by Moffitt [1] regarding the number of electrons participating in the bonding between Fe and the carbon atoms of the Cp rings in ferrocene that appears in the papers "Complementarity of QTAIM and MO theory in the study of bonding in donor–acceptor complexes" [2] and in "Where to draw the line in defining a molecular structure" [3]. The error arose from the incorrect identification of Moffitt's "number of electrons" with the "number of electron pairs" participating in the bonding. Moffitt's statement is: "Four electrons are therefore involved, two for each Cp–Fe bond", rather than the "two pairs of electrons" per Cp ring as stated in [2] on page 639 and the participation of "two Lewis pairs" stated in [3] on page 6257. The value of the delocalization index δ(M,C) provides a count of the number of electrons shared, that is, exchanged, between a metal atom M and a carbon of the Cp ring and when used in this manner rather than tying it to the Lewis pair model, one finds qualitative agreement with Moffitt's model of the involvement of two electrons per Cp ring: the value of δ(Fe,C) in ferrocene predicts a sharing of 4.5 electrons between the Fe and the two Cp rings [2] while the value of δ(Mn,C) in the adduct $Cl_3SiHMnCp(CO)_2$ predicts a sharing of 1.9 electrons with the single Cp ring [3].

Professor Dunitz also drew my attention to a paper he published along with Professor Orgel in 1953 that anticipates the MO description of the bonding in ferrocene given by Moffit, one that clearly identifies the e_{1g} set of orbitals as the primary source of bonding of Fe with the Cp rings [4]. Their paper also points out the possibility of donation of electrons from the e_{2g} orbitals of Fe with the corresponding vacant antibonding orbitals on the Cp rings, a possibility borne out by the analysis presented in [2] showing that 0.6 e of the four electrons in the e_{2g} orbitals reside on the Cp rings. This is to be contrasted with 3.5 e of the four electrons in the bonding e_{1g} set that reside on the Cp rings, resulting in a negative charge on each Cp ring [2], as also predicted by their analysis [4].

References

[1] W. Moffitt, J. Am. Chem. Soc. 76 (1954) 3386.
[2] F. Cortés-Guzmán, R.F.W. Bader, Coord. Chem. Rev. 249 (2005) 633.
[3] R.F.W. Bader, C.F. Matta, F. Cortés-Guzmán, Organometallics 23 (2004) 6253.
[4] J.D. Dunitz, L.E. Orgel, Nature 171 (1953) 121.

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