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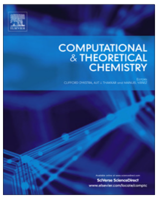

Structure and bonding in binuclear metal carbonyls. Classical paradigms vs. insights from modern theoretical calculations

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ABSTRACT

The nature of the bonding interactions in a series of bridged and unbridged binuclear metal carbonyls has been analyzed using the visual insights provided by the analysis of domain averaged Fermi holes (DAFH). Picture of the bonding emerging from this analysis has been confronted with the predictions anticipated in each particular case by the traditional bonding paradigms exemplified by the 18-electron rule and isolobal analogy. Such a confrontation has shown that the frequently observed inconsistencies, especially in what concerns the eventual existence and/or multiplicity of direct metal–metal bonds, are due to simplistic interpretation of 18-electron rule that primarily relies on formal electron count and qualitative consideration of metal–metal distances without taking into account the actual bonding capabilities of individual $M(CO)_n$ fragments. The systematic scrutiny of the results of DAFH analysis for the wide series of studied carbonyls allowed to reveal the shortcomings of the original simplistic interpretation and to propose a slight reinterpretation of 18-electron rule that makes its predictions consistent with the insights of moderns theoretical tools.

1. Introduction

Although the family of stable binuclear metal carbonyls involves only very few members, the complexity of the bonding interactions between the metal and bridging ligands as well as experimental studies reporting the possible existence of other related carbonyls as unstable transient species [1–8] initiated wider interest in the systematic scrutiny of the structure and stability of various possible isomers of homoleptic metal carbonyls. In past few years a number of extensive computational studies of such species with various stoichiometries was reported [9–20]. Besides interesting and valuable information about the relative stabilities and symmetries of various isomeric species, the resulting calculated molecular geometries were usually discussed and classified on the basis of speculations about the geometrical and electronic predispositions for the existence of direct metal–metal bonds. The key role in such speculations was usually attributed to traditional tools as the 18-electron rule [21], and based on that rule, combined with the comparison of interatomic distances, the existence of metal–metal bonds of various multiplicities was often anticipated. Despite undeniable and undisputable importance of this rule as a basic tool to predict the stability of molecules involving transition metals, the more systematic theoretical analyses of bonding interactions in various homoleptic metal carbonyls suggested that early original speculations about the possible existence of direct metal–metal bond in carbonyls like $Fe_2(CO)_9$ and $Co_2(CO)_8$, although occasionally corroborated by qualitative MO arguments [22], may be too simplistic. The relevance of such admonishments has independently received an additional support from various theoretical approaches such as the analysis of orbital interactions [23–25], or the topological atom-in-molecule (AIM) analysis of electron density [26–31].

Thus, e.g., although the 18-electron rule predicts in both carbonyls the existence of metal–metal single bond, the detailed QTAIM analysis of electron density [29–31], detected the absence of metal–metal bond path as well as the corresponding bond critical point. Similarly, the absence of direct metal–metal bond was reported in $Co_2(CO)_8$ using the orbital localization technique [32] that, instead, suggested the possibility of bonding of the bridging ligands via delocalized 3c–2e bonds. The possible existence of delocalized 3c–2e bonding has also recently found an independent theoretical support from the methodology known as the analysis of domain averaged Fermi holes [33,34]. In addition, the early predictions of metal–metal bond multiplicities in unbridged metal carbonyls were recently questioned and based on more detailed computational insights, the original high metal–metal bond multiplicities were considerably reduced [20,35].

Because of accumulating evidence of similar inconsistencies we decided to perform a detailed confrontation of traditional bonding paradigms such as the 18-electron rule and isolobal analogy [36],

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with modern theoretical insights provided by DAFH analysis for the extensive series of bridged and unbridged metal carbonyls so as to reveal the possible origin of the observed discrepancies.

2. Theoretical

The picture of the bonding in the studied series of binuclear carbonyls has primarily been analyzed using the analysis of domain averaged Fermi holes [37–40]. The most attractive feature of this analysis is that it provides highly appealing visual insights that proved to be especially useful in revealing the nature of the bonding interactions in other molecules with non-trivial bonding pattern like metal–metal bonding, multicenter bonding, hypervalence, etc. [33,34,41–46]. As the methodological background of this analysis has repeatedly been described in various earlier studies [37–40], we confine ourselves only to a brief recapitulation of the basic ideas to the extent necessary for the purpose of this study.

The domain averaged Fermi holes can most straightforwardly be introduced via the definition (Eq. (1))

$$g_\Omega(\mathbf{r}_1) = \rho(\mathbf{r}_1)\int_\Omega \rho(\mathbf{r}_2)d\mathbf{r}_2 - 2\int_\Omega \rho(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 = \rho(\mathbf{r}_1)N_\Omega - 2\int_\Omega \rho(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2, \quad (1)$$

where $\rho(\mathbf{r}_1)$ and $\rho(\mathbf{r}_1,\mathbf{r}_2)$ are the ordinary first order electron density and the pair density respectively and the integration is over the finite domain of the space Ω, N_Ω denotes the number of electrons in the domain Ω[1] (2)

$$N_\Omega = \int_\Omega \rho(\mathbf{r})d\mathbf{r} \quad (2)$$

In the case of the restricted Hartree–Fock and formally also the Kohn–Sham approximation, which is our case in this study, the general formula (1) reduces to (3)

$$g_\Omega(\mathbf{r}_1) = 2\sum_i^{occ}\sum_j^{occ}\langle i|j\rangle_\Omega \varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_1) \quad (3)$$

where $\langle i|j\rangle_\Omega$, defined by Eq. (4), denotes the element of the so-called atomic overlap matrix (AOM).

$$\langle i|j\rangle_\Omega = \int_\Omega \varphi_i(\mathbf{r})\varphi_j(\mathbf{r})d\mathbf{r} \quad (4)$$

Usefulness of domain averaged Fermi holes for structural investigation arises from the fact that their form depends on the actual choice of the domain in any particular case. In previous studies [39–46], we have shown that especially interesting and chemically relevant information can be extracted from the holes averaged over the domains resulting from any physically sound partitioning of electron density such as AIM [48], Hirschfeld [49] or Mulliken [50] into regions associated with individual atoms, but generated and analyzed can be also the holes averaged over more complex domains, formed by the union of several atomic domains corresponding to certain functional groups or interesting molecular fragments. In such a case the analysis provides the information about the electron pairs that remain intact in the fragment and about the broken or dangling valences created by formal splitting of the bond required to isolate the fragment from the rest of the molecule. As the analysis of the Fermi hole requires, irrespective of the size of the actual domain, the generation of AOM matrices for all the atoms in the molecule, which for the extensive set of the studied carbonyls can be extremely time consuming, we adopted a more feasible strategy based on the use of Mulliken-like approach to domain integration according to which an electron is considered to be in the domain of an atom A if it is in an orbital attached to that atom.

The DAFH analysis consists, in the first step, in the diagonalization of the matrix representing the hole in appropriate basis of atomic or molecular orbitals. The eigenvalues and eigenvectors resulting from this primary diagonalization are then, in the second step, subjected to the so-called isopycnic transformation [51] whose aim is to convert the original eigenvectors to more localized functions reminiscent of chemical bonds, core and/or valence lone pairs etc., which provide highly visually appealing picture of the bonding close to classical chemical thinking. The structural information is being extracted from the numerical eigenvalues, which allow to identify the bonds (and/or core and valence lone electron pairs) formed by shared electron pairs as well as broken or dangling valences resulting from the formal splitting of the bonds. The interpretation of the above numerical data is greatly facilitated by the visual inspection of the corresponding localized DAFH functions.

In addition, the picture of the bonding emerging from DAFH analysis was complemented by the calculation of Wiberg–Mayer bond indices [52,53] whose numerical values are often regarded as an indication of direct metal–metal bonding interactions.

3. Computations

The analysis of the bonding interactions in the studied metal carbonyls required to perform two types of calculations. First it was necessary to generate the reliable wave functions of the studied carbonyls. For this purpose we performed the complete optimization of molecular geometries of the wide series of 10 bridged and unbridged homoleptic metal carbonyls. These calculations were performed using Gaussian 03 program [54] at BP86 and B3LYP level of the theory using internally stored SDD and LANL2DZ bases. For all the studied molecules the resulting optimized geometries were subsequently subjected to vibrational analysis aiming at the specification of the nature of the corresponding structures on the PE hypersurface. The results of these calculations are summarized in Table 1.

The inspection of this table shows that although in most cases the calculated optimized structures do indeed correspond to true minima, for some of the species the vibrational analysis detected the existence of small imaginary frequencies. Such a situation was also reported in previous studies [11,12], and in keeping with the suggested interpretation, these imaginary frequencies were ignored and the structures regarded as genuine minima, or close to genuine minima. The resulting values of intermetallic $M\cdots M$ distance together with the $M\cdots M$ bond indices and the stretching vibrational frequencies ν_{MM} are summarized in Tables 2 and 3.

After having generated the wave functions for the studied molecules, the next step of the calculations involved the generation and subsequent analysis of the corresponding Fermi holes. As in the case of bridged carbonyls we were primarily interested in the nature of electron pairs involved in the bonding of the bridging ligands with the metals, the natural choice was to focus on the domains involving all these atoms. On the other hand, in case of unbridged carbonyls, where the main issue is the multiplicity of direct metal–metal bond, the DAFH analysis was performed for the domain involving metal atoms only.

The generation and the analysis of the holes was in each particular case performed using our program WinFermi that is available upon request. The program is interfaced with Gaussian and reads as an input the ordinary Gaussian output file generated using appropriate keywords.

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[1] For the sake of mathematical rigor it is possible to reformulate the whole approach in terms of density matrices instead of densities [47] although either formulation has no impact on the practical applicability of DAFH analysis.