

Structure and Bonding in Binuclear Metal Carbonyls from the Analysis of Domain Averaged Fermi Holes. I. $\text{Fe}_2(\text{CO})_9$ and $\text{Co}_2(\text{CO})_8$

ROBERT PONEC,¹ GYÖRGY LENDVAY,² JOAQUIN CHAVES³

¹*Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Prague 6, Suchbátarova 2,
165 02 Czech Republic*

²*Institute of Structural Chemistry, Chemical Research Center, Hungarian Academy of Sciences,
H-1525 Budapest, P.O. Box 17, Hungary*

³*Institute of Computational Chemistry, University of Girona, Campus Montilivi,
17071 Girona, Spain*

Received 12 September 2007; Accepted 12 November 2007

DOI 10.1002/jcc.20894

Published online 14 January 2008 in Wiley InterScience (www.interscience.wiley.com).

Abstract: The nature of the bonding in the above carbonyls was studied using the analysis of domain averaged Fermi holes (DAFH). The results straightforwardly confirm the conclusions of earlier theoretical studies in which the existence of direct metal–metal bond, anticipated for the above carbonyls on the basis of 18-electron rule, was questioned. In addition to indicating the lack of direct metal–metal bond, the DAFH analysis also allowed to characterize the nature of the electron pairs involved in the bonding of the bridging ligands. The analysis has shown that because the number of available electron pairs is not sufficient for the formation of ordinary localized 2c–2e bonds between terminal $\text{M}(\text{CO})_3$ fragments and the bridging ligands, the bonding in both carbonyls exhibits typical features of electron deficiency and one bonding electron pair is effectively involved in multicenter 3c–2e bonding. Because of the symmetry of the complexes the bridging ligands are not distinguishable and all M–C–M bridges have a partial 3c–2e nature via resonance of the localized structures.

© 2008 Wiley Periodicals, Inc. J Comput Chem 29: 1387–1398, 2008

Key words: domain averaged Fermi holes; chemical bond; bonding in metal carbonyls

Introduction

The chemistry of metal carbonyls represents an important and flowering field of transition metal organometallic chemistry. Besides the rapid expansion of synthetic aspects of transition metal carbonyl chemistry, increasing attention is also being paid to the elucidation of the structure of these species. In addition to experimental and computational studies primarily focused on the determination of reliable geometrical parameters,^{1–14} a lot of effort was also devoted to the development of theoretical models allowing one to describe and to understand the nature of the bonding interactions underlying the observed molecular structure in each particular case.^{15–27} The crudest models of the bonding in transition-metal carbonyls traditionally rely on the consideration of metal–metal distances and simple electron count exemplified by the 18-electron rule.²⁸ Based on this approach, the existence of Fe–Fe and Co–Co single bonds is frequently assumed in $\text{Fe}_2(\text{CO})_9$ and $\text{Co}_2(\text{CO})_8$. Although the predictions of this rule have received wide acceptance in the chemistry of metal carbonyls, some cautions concerning simplistic conclu-

sions about the metal–metal bonding have been stated in the literature.^{17–21,29–32} The relevance of such admonishments has received independent support from the analysis of orbital interactions^{17–20} and, more recently, also from the topological atoms-in-molecules (AIM) analysis of electron density in which no metal–metal bond path and the corresponding bond critical point (BCP) was detected in both $\text{Fe}_2(\text{CO})_9$ and $\text{Co}_2(\text{CO})_8$.^{27,33,34}

To contribute to the clarification of the complex interplay of the factors determining the final picture of the bonding in the title metal carbonyls, we report in this study the analysis of the bonding situation resulting from the general methodology known as the analysis of domain averaged Fermi holes (DAFH).^{35–39}

Correspondence to: R. Ponec; e-mail: rponec@icpf.cas.cz

Contract/grant sponsor: Grant Agency of Czech Academy of Sciences; contract/grant numbers: IAA 4072403

Contract/grant sponsor: Hungarian National Scientific Research Fund; contract/grant number: T34812

This analysis was repeatedly shown to provide a simple and chemically appealing picture of the bonding in various molecules with complicated bonding pattern including metal–metal bonds^{40–42} and it was thus of interest to see whether or to what extent it can help in revealing and clarifying the final picture of bonding in the most stable binuclear iron and cobalt carbonyls. In the remainder of the article we first briefly summarize the theory and the technical details of DAFH analysis, then present the results of the analysis of the electronic structure of $\text{Fe}_2(\text{CO})_9$ and of $\text{Co}_2(\text{CO})_8$, respectively.

Theoretical

DAFH introduced some time ago as a generalization of the original concept by Wigner and Seitz,⁴³ have proved to be a new efficient tool providing a simple and visually appealing insight into the nature of chemical bonding, and the applications reported recently have shown its usefulness for the elucidation of the picture of bonding in various molecules with nontrivial bonding pattern.^{39–42}

The most straightforward introduction of DAFH (originally called charge weighted Fermi holes in the studies^{35,36}) is via the definition eq. (1),

$$g_{\Omega}(r_1) = N_{\Omega}\rho(r_1) - 2 \int_{\Omega} \rho(r_1, r_2) dr_2 \quad (1)$$

in which $\rho(r_1, r_2)$ and $\rho(r_1)$ are the pair density and the first order density, respectively, and Ω denotes the integration domain over which the averaging is performed. The importance of these holes for structural investigations arises from the fact that the shape of the Fermi hole (1) depends on the shape and size of the domain Ω . The form of these domains is in principle quite arbitrary but in previous studies we have shown that especially useful and chemically relevant information can be obtained if the domains Ω are identified with the atomic domains resulting from Bader's virial partitioning of the electron density in the AIM theory.⁴⁴ The analysis of the Fermi holes consists in the diagonalization of the matrix representing the hole in the appropriate basis and in the subsequent visual inspection of the shape of the eigenvectors associated with the (essentially) nonzero eigenvalues of the corresponding hole. As the details of such an analysis are again sufficiently described in previous studies,^{35–42} we only recall that the analysis of the hole associated with the domain of a given single atom provides the information on the actual valence state of that atom in a molecule. Similarly, the Fermi holes associated with the more complex domains involving several atoms corresponding, e.g., to a certain molecular fragment, brings the information about the number and the nature of electron pairs (bonds) whose splitting is formally required to separate the given fragment from the original molecule as well as about the bonds and core and/or lone electron pairs which remain intact within the fragment. The nature of the electron pairs as well as the free valences is then straightforwardly revealed by the inspection of the corresponding eigenvectors.

Although the DAFH defined by eq. (1) are completely general and can be generated at any level of theory, most of the reported applications have so far been based on several simplifi-

ing approximations. One of them concerns the pair density which, in the most general case, should be derived from the correlated post-HF wave functions. Unfortunately, the extraction of the correlated pair density from existing quantum chemical programs is not a simple task and although the first example of the analysis of correlated DAFH was recently reported,⁴⁵ most of the applications have so far been restricted to the holes generated at the HF and/or density functional (DFT)^{46,47} level of theory. Here it is, of course, fair to say that the DFT extension, in which the pair density is formally constructed from Kohn-Sham orbitals using the Hartree-Fock-like formula, lacks strict theoretical justification and its success apparently relies only on the similarity of Hartree-Fock and Kohn-Sham orbitals. Nevertheless, as the results of such a formal generalization proved to provide reasonable and realistic description of other metal–metal bonds,^{40–42} we believe that the above approach can be accepted as a feasible alternative especially for applications in inorganic chemistry where DFT theory represents the contemporary computational standard.

In addition to the above simplification, yet another approximation, used also in previous studies of the bonding in transition metal complexes,^{40–42} was adopted in this study. This approximation concerns the determination of the integrals over the domain Ω and consists in replacing the integrals over real AIM domains by the Mulliken-like approximation according to which the electron is in the domain of a given atom, if it is in the orbital localized on that atom. In other words, instead of associating the atom with the domain in real 3D space, the atomic domain is identified with the subspace of the Hilbert space spanned by the atomic orbitals centered on an atom. The main reason for adopting this approximation is that it eliminates two important problems accompanying the use of the “exact” DAFH analysis especially for transition metal complexes. One of them is that the contemporary computational methods used for these molecules often rely on the use of basis sets of ECP type, which are known to produce electron densities, whose integration over real AIM domains is not always straightforward.^{48–50} Although it is true that such problems have been nicely overcome⁵¹ also on systems like those studied in the present article, there is yet another complicating factor whose impact on the applicability of DAFH analysis is also to be taken into account. This impact concerns the considerable computational demands of the integration over the real AIM domains. Irrespective of the type of the domain Ω , the analysis requires the knowledge of the AOM matrices for all the atoms in the molecule, and the computational demands required for their generation rapidly makes the “exact” DAFH analysis unfeasible for bigger systems. In such cases therefore the approximate form of the analysis can represent a real alternative and we believe that its use in our case is able to provide realistic and reliable insight into the structure of the studied carbonyl complexes similarly as in previous studies of other transition metal complexes.^{40–42} Such a belief is corroborated by the experience with comparing both approaches on smaller systems,^{38,39,45} which clearly suggest that the picture of bonding emerging from the “exact” and approximate DAFH analysis is generally very similar and especially at the level of the qualitative description, that is the aim of our study, no important differences are observed.

Table 1. Comparison of Calculated Geometrical Parameters of $\text{Fe}_2(\text{CO})_9$ with Available Experimental and Theoretical Data.

Parameter	Exp ²	B3LYP/DZP ⁹	B3LYP/LANL2DZ	B3LYP/SDD
$R_{\text{Fe-Fe}}$	2.523	2.525	2.524	2.517
$R_{(\text{Fe-C})\text{t}}$	1.838	1.829	1.810	1.810
$R_{(\text{Fe-C})\text{b}}$	2.016	2.008	2.008	1.990
$R_{(\text{C-O})\text{t}}$	1.156	1.152	1.150	1.170
$R_{(\text{C-O})\text{b}}$	1.176	1.176	1.190	1.190
$\angle \text{ClFeFe}$	120.9		120.4	120.4
$\angle \text{FeCbFe}$	77.6		78.1	78.3

Computations

The analysis of DAFH is a two step process, the first of which requires the generation of a reliable wave function for the studied molecules. For this purpose it is first necessary to perform the complete optimization of the geometry of the studied molecules at the appropriate level of the theory. In this study we focused on the analysis of the bonding in two isoelectronic binuclear carbonyls, $\text{Fe}_2(\text{CO})_9$ and $\text{Co}_2(\text{CO})_8$, which represent the most stable binuclear carbonyls of iron and cobalt and for which the optimized geometries can be compared with available experimental data.^{1,2,13,14} These calculations were performed using the Gaussian 98⁵² package at B3LYP/LANL2DZ and, for comparison, at the B3LYP/SDD level of theory. The resulting geometrical parameters are summarized, together with the available experimental and calculated data, in Tables 1 and 2. Our calculations with both basis sets reproduce very well the experimental geometry.

Based on the wave function obtained at the equilibrium geometry, the second step of the analysis consisted in the construction of the Fermi holes (1) for a chosen domain and in their subsequent analysis. As our analysis is focused above all on the elucidation of the nature of the bonding between the metal atoms and bridging carbonyl ligands and on the eventual presence of a direct metal-metal bond, the natural choice of the domain is the fragment $\text{M}(\text{CO})_x\text{M}$ involving both metal atoms and all bridging carbonyl ligands. The analysis was performed using our program WinFermi⁵³ which is available upon request. The

Table 2. Comparison of Calculated Geometrical Parameters of $\text{Co}_2(\text{CO})_8$ with Available Experimental Data.

Parameter	Exp ¹³	B3LYP/LANL2DZ	B3LYP/SDD
$R_{\text{Co-Co}}$	2.529	2.545	2.543
$R_{(\text{Co-C})\text{t}}$	1.837 _{eq}	1.821	1.810
	1.821 _{ax}	1.816	1.800
$R_{\text{Co-Cb}}$	1.946	1.950	1.940
$R_{(\text{C-O})\text{t}}$	1.138	1.150	1.170
$R_{(\text{C-O})\text{b}}$	1.165	1.190	1.190
$\angle \text{ClCoCo}$	112.7 _{eq}	110.3	110.8
	123.8 _{ax}	126.5	125.1
$\angle \text{CoCbCo}$	81.4	81.1	81.7

Table 3. Summary of the Results of the Analysis of the Fermi Hole Associated with $\text{Fe}(\text{CO})_3\text{Fe}$ Fragment of $\text{Fe}_2(\text{CO})_9$.

Eigenvalue	Degeneracy	Interpretation
2.00	3	(1s ²) electron pair on O
1.99	3	(1s ²) electron pair on C
1.99	8	Electron pairs of 3s and 3p inner shells on Fe
1.99	3	σ lone pair on bridging oxygen
1.99	3	Electron pair of bridging σ_{CO} bond
1.98	6	Electron pair of bridging π_{CO} bond
1.75	6	Occupied d orbitals on Fe
1.88	4	Electron pairs of bridging σ_{FeC} bond
1.91	1	3-center Fe-C _b -Fe bond
0.61	6	Broken valence of terminal Fe-C bonds

The data were generated at B3LYP/LANL2DZ level of the theory.

analysis was shown to be little sensitive to the choice of the basis set. The results summarized in Tables 3 and 4 and displayed in Figures 1–4 were obtained using the LANL2DZ basis.

Results and Discussion

Bonding in $\text{Fe}_2(\text{CO})_9$

Diiron nonacarbonyl, formed in the photochemical decomposition of $\text{Fe}(\text{CO})_5$ in organic solvents, was the first polynuclear metal carbonyl to be discovered.⁵⁴ Although the first X-ray study of its structure¹ was not accurate enough to provide reliable geometrical parameters, it revealed the presence of novel structural feature—the presence of the bridging carbonyl ligands whose existence was subsequently confirmed by a more recent study.² Consistent with the reported D_{3h} symmetry, the molecule

Table 4. Summary of the Results of the Analysis of the Fermi Hole Associated with $\text{Co}(\text{CO})_3\text{Co}$ Fragment of $\text{Co}_2(\text{CO})_8$.

Eigenvalue	Degeneracy	Interpretation
2.00	2	(1s ²) electron pair on O
1.99	2	(1s ²) electron pair on C
1.99	8	Electron pairs of 3s and 3p inner shells on Co
1.99	2	σ lone pair on bridging oxygen
1.99	2	Electron pair of bridging σ_{CoO} bond
1.98	4	Electron pair of bridging π_{CO} bond
1.76	4	Occupied d orbitals on Co
1.80	2	
1.90	2	Electron pairs of bridging σ_{CoC} bond
1.88	1	3-center Co-C _b -Co bond
1.84	2	Occupied d orbitals on Co
0.56	4	Broken valence of equatorial and
0.58	2	axial terminal Co-C bonds

The data were generated at B3LYP/LANL2DZ level of the theory.



Scheme 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

possesses three symmetrically placed bridging carbonyl ligands which keep together two $\text{Fe}(\text{CO})_3$ fragments (Scheme 1).

The nature of the bonding interactions between the terminal $\text{Fe}(\text{CO})_3$ fragments and bridging ligands was thoroughly discussed by Hoffmann and coworkers^{17–19} and although the analysis of symmetry constraints on the orbital interactions did indeed reveal a lot of interesting insights, the classification of the bonding using this approach is a bit complicated because of delocalized nature of the corresponding molecular orbitals, which prevents their straightforward association with particular bonds.

To eliminate the uncertainties left, we propose to analyse the nature of bonding in $\text{Fe}_2(\text{CO})_9$ from the new perspective provided by the analysis of domain averaged Fermi holes. The specific feature of this approach is that, instead of characterizing the bonding in terms of delocalized molecular orbitals and their interactions, it retains as much as possible the idea of localized chemical bonds and the picture of bonding it provides is thus close to classical chemical thinking.

Before reporting the results of the Fermi hole analysis of the bonding in the above carbonyl it is useful to recall the expectations of the isolobal analogy.^{24,25} According to this analogy, the $\text{Fe}(\text{CO})_3$ fragment is isolobal with CH^+ so that both terminal fragments possess two electrons available for the bonding with the bridging ligands. Taking now into account that each of these ligands contributes to the bonding by one electron pair, the total number of electron pairs that keep together the $\text{Fe}(\text{CO})_3$ fragments with three bridging CO ligands is five. This, of course, implies that the schematic formula 1, which assumes the existence of six localized (2c-2e) $\text{Fe}-\text{C}$ bonds between the metal atoms and bridging ligands, is not realistic and the picture of the bonding has to be slightly more complex.

As we are primarily interested in the bonding in the $\text{Fe}(\text{CO})_3\text{Fe}$ fragment, the natural choice for the analysis is the hole averaged over just that fragment.

The results of the analysis of the corresponding Fermi hole are summarized in Table 3 and Figures 1 and 2. As it is possible to see from the Table, the analysis yields 43 nonzero eigenvalues. The majority of them (26) is very close to 2, and the inspection of the corresponding eigenvectors shows that they correspond to core $1s^2$ electron pairs on O ($3\times$) and C ($3\times$) of the bridging ligands (Fig. 1a), the electron pairs of σ_{CO} ($3\times$) and π_{CO} ($6\times$) bonds (Figs. 1b and 1c), lone pairs of σ symmetry on the oxygen atoms of the bridging ligands ($3\times$), and the electron pairs of filled 4s and 4p shells on the two Fe atoms ($8\times$)

(Fig. 1d). In addition to these electron pairs, which are not involved in the bonding of the bridging ligands with the terminal $\text{Fe}(\text{CO})_3$ fragments, there is a set of six degenerate eigenvalues close to 1.75. The inspection of the corresponding eigenvectors (Fig. 1e) suggests that they correspond to nonbonding “ t_{2g} ” 3d orbitals on Fe, whose existence has been proposed for the $\text{Fe}(\text{CO})_3$ fragments on the basis of symmetry considerations.^{17–20} Consistent with the expectations of earlier theoretical analyses,^{17–20} these orbitals are not strictly nonbonding but the fact that the deviations of the corresponding occupation numbers from the ideal value of 2 are only slight suggest that the anticipated interactions with the ligand orbitals are weak and their importance for the bonding within the $\text{Fe}(\text{CO})_3\text{Fe}$ fragment is rather marginal.

The same is true of the group of six degenerate eigenvalues close to 0.62. The inspection of these eigenvectors shows that they correspond to free valences of six “dangling” terminal $\text{Fe}-\text{C}$ bonds, whose formal splitting is required in the DAFH analysis for the separation of the fragment from the rest of the molecule (Fig. 1f). This interpretation is corroborated by the inspection of the Fermi hole associated with one of the terminal CO ligands. In this case the analysis yields seven nonzero eigenvalues of which six, corresponding to a chemical bond and core and/or lone electron pairs within the ligand, are close to 2 and the remaining one equals 1.35. The inspection of the corresponding eigenvector shows that it is very reminiscent of the eigenvector of the free valence of terminal $\text{Fe}-\text{C}$ bond obtained from the analysis of the $\text{Fe}(\text{CO})_3\text{Fe}$ fragment. The close resemblance of the two eigenvectors together with the near complementarity of the corresponding eigenvalues ($0.62 + 1.35 \approx 2$) suggests that the terminal $\text{Fe}-\text{C}$ bonds have the character of more or less normal, albeit pretty polar 2c-2e bonds and the eigenvalues 0.62 and 1.35 can be regarded as the contributions of Fe and C to the shared electron pair of this bond.

The bonding with the bridging ligands is thus necessarily due to electron pairs associated with remaining five nonzero eigenvalues ranging between 1.88 and 1.91 and the elucidation of the nature of bonding in $\text{Fe}_2(\text{CO})_9$ thus relies on the interpretation of the eigenvectors associated with these five electron pairs. The form of these eigenvectors is displayed in Figures 2a–2e.

Before discussing the individual pictures it is useful to recall that the crucial step of the DAFH analysis is the isopycnic transformation⁵⁵ which transforms the original eigenvectors resulting from the diagonalization of the Fermi hole to localized functions reminiscent of classical chemical bonds. Although in most cases, the form of the resulting localized functions is straightforwardly consistent with the expectations based on the classical structural formula, the situation here is slightly more complex. The reason is that the number of available electron pairs (5) is not sufficient to form six localized 2c-2e $\text{Fe}-\text{C}_b$ bonds between the iron atoms and bridging ligands as required by the schematic formula 1 and at least some of the bonding electron pairs have to exhibit a certain degree of delocalization. This qualitative expectation is indeed confirmed by the results shown in Figure 2, in which the eigenvectors corresponding to the five bonding electron pairs are displayed. Based on this figure, the picture of the bonding can be characterized as follows. Four of the five electron pairs correspond to localized 2c-2e $\text{Fe}-\text{C}_b$ bonds between the metal atoms

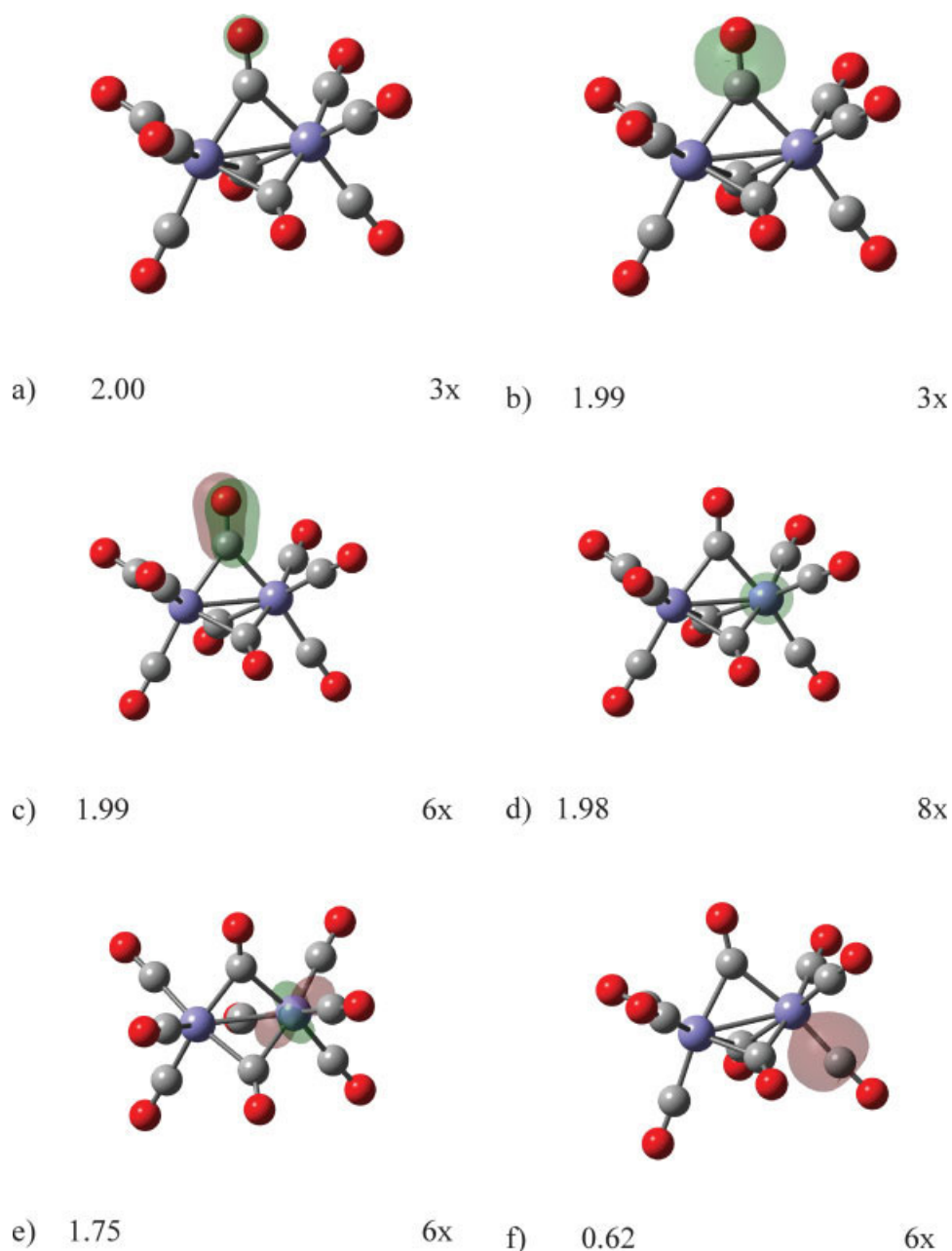


Figure 1. Graphical display of the eigenvectors of DAFH associated with the electron pairs retained in the $\text{Fe}(\text{CO})_3\text{Fe}$ fragment of $\text{Fe}_2(\text{CO})_9$. The pictures were generated at B3LYP/LANL2DZ level of the theory.

and two of the bridging ligands (Figs. 2a–2d). This implies that the delocalization should concern only the remaining single electron pair. As it can be seen from the Figure 2e this is indeed the case and the shape of this delocalized electron pair is identical to that typical for what is called multicenter 3c-2e bonding. The more detailed inspection of this multicenter bond shows that the corresponding electron pair is delocalized between the metal atoms and the carbonyl ligand not involved in 2c-2e bonding.

Based on this result, the distribution of the bonding electron pairs in $\text{Fe}_2(\text{CO})_9$ can be best described by the schematic formula 2 (Scheme 2).

In connection with such a straightforward transcription into the language of classical chemistry, one has to be aware of the fact that the localized picture of the bonding resulting from the DAFH analysis is not compatible with the threefold symmetry of the molecule. This inherent drawback of any localized

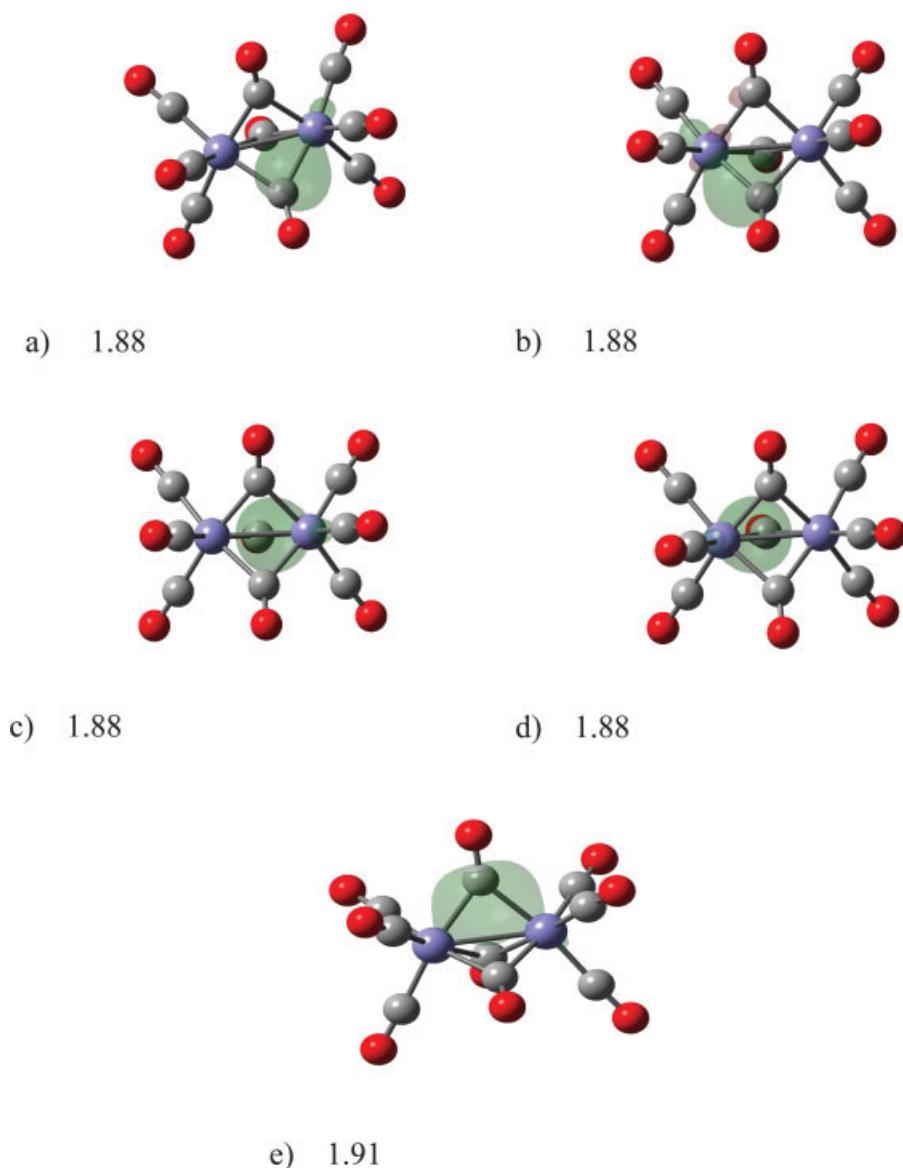


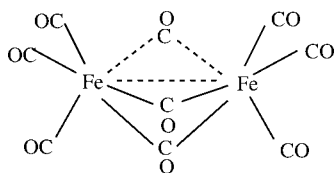
Figure 2. Graphical display of the eigenvectors of DAFH associated with five electron pairs involved in the bonding within the $\text{Fe}(\text{CO})_3\text{Fe}$ fragment of $\text{Fe}_2(\text{CO})_9$. The pictures were generated at B3LYP/LANL2DZ level of the theory. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

description can be, however, straightforwardly remedied by invoking the resonance of three symmetry equivalent resonance structures (Scheme 3).

As a consequence, each of the $\text{Fe}-\text{C}_b$ bonds loses slightly the character of localized 2c-2e bonds and the delocalized multi-center character of one bonding electron pair is uniformly distributed among all three $\text{Fe}-\text{C}_b-\text{Fe}$ bridges.

This result is very important not only because it confirms the delocalized nature of the bonding with the bridging ligands anticipated in previous studies,^{18,19,29–32} but also because it demonstrates that the bonding interactions between the metal atoms

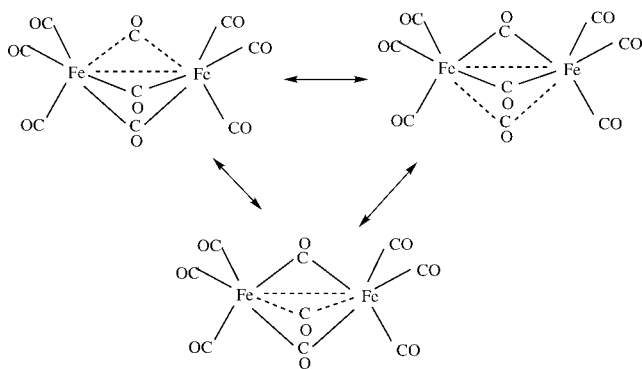
do not have the character of a direct $\text{Fe}-\text{Fe}$ bond anticipated on the basis of 18-electron rule. In this connection it is, however, necessary to be aware of the fact that the absence of direct $\text{Fe}-\text{Fe}$ bond does not necessarily imply the absence of any bonding interactions between the metal atoms. As it was shown in ref. 56, the existence of a 3c-2e bonding in an A-B-C fragment requires the existence of nonvanishing bond orders between all pairs of the atoms. This is also the case here and the calculated $\text{Fe}-\text{Fe}$ bond order (0.245) thus in fact represents the residual contribution associated with the partial multicenter character of the bonding between Fe atoms and bridging ligands.



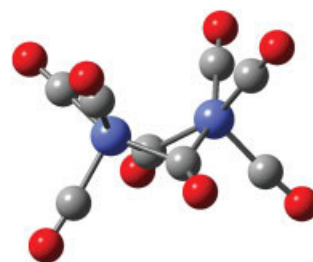
Scheme 2.

Such an interpretation is also straightforwardly corroborated by the values of the so-called multicenter bond indices. These indices were proposed some time ago as a tool for the straightforward detection of anticipated multicenter bonding in molecules like electron-deficient boranes simple atomic clusters, nonclassical carbon cations etc.,^{57–66} and the calculated values of these indices do indeed confirm the existence of delocalized 3c-2e bonding units in Fe—C—Fe fragments involving bridging ligands. The actual value of the corresponding bond indices is 0.060. Although this value is much lower than the ideal value 0.375 derived for 3c-2e bond from a simple analytical model of 3-center bond,⁶⁴ the observed discrepancy should not be regarded as indicating the marginal importance of multicenter character of the bonding with the bridging ligands. Instead, the low value of the index can straightforwardly be attributed the fact that due to the resonance required by the symmetry of the molecule, the single electron pair involved in 3c-2e bonding is evenly spread among three equivalent Fe—C_b—Fe bridges so that its multicenter character in individual fragments is in a sense “diluted.” Taking this into account, it seems reasonable to assume that the effective value of the bond index characterizing the “hypothetical” localized 3c-2e electron pair noninvolved in the resonance (Scheme 2) could be roughly equal to $3 \times 0.060 = 0.180$ which is much closer to the idealized standard value.

Here it is, of course, fair to remark that the nature of the metal–metal bonding in Fe₂(CO)₉, with the particular focus on the existence of direct Fe...Fe bond, was recently reconsidered in the study.⁶⁷ We completely agree with the authors that the main problem with the classification of the bonding in this molecule is that the electron density in the midpoint of Fe...Fe distance is extremely flat so that the presence and/or absence of the corresponding BCP critically depends on the quality of the computational methods used (mainly basis set) and, consequently,



Scheme 3.



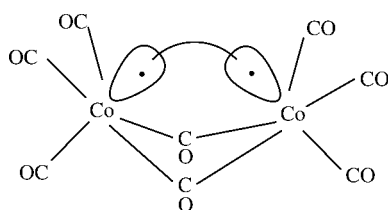
Scheme 4. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the presence and/or absence of bcp can hardly be taken as a criterion for the existence of direct Fe...Fe bond. We also agree with them that a weak bonding interaction between the two metals exists but we differ from them in the interpretation of this interaction. While our analysis implies that the interaction and nonzero Fe...Fe bond order originate from residual interactions associated with the multicenter 3c-2e character of the bonding with the bridging ligands, the authors of the study⁶⁷ characterize it as “some, albeit weak Fe...Fe bond.” In our opinion, such an interpretation is not, however, completely satisfactory as it completely ignores the fact that for any bonding interaction could be classified as a bond, it must be possible to associate it with an electron pair. An obvious choice to facilitate the above association is the use of localized instead of canonical molecular orbitals. The orbital localization shows, however, that there is no orbital (electron pair) corresponding to direct Fe...Fe bond and so the vague interpretation of residual Fe...Fe interactions as “some, albeit weak” bond is questionable. Moreover, we also feel a certain inconsistency in the fact that in the case of isoelectronic Co₂(CO)₈ the same authors using the same methodology concluded that there is no Co...Co bond,³³ while they find it in Fe₂(CO)₉.

Bonding in Co₂(CO)₈

The most stable arrangement of this molecule in the solid state^{13,14} corresponds to the structure of C_{2v} symmetry with two bridging carbonyl ligands shown in Scheme 4, a geometry very similar to that of Fe₂(CO)₉ except that one bridging carbonyl is missing. Although the 18-electron rule again predicts the existence of a direct metal–metal bond in this molecule, the relevance of such a structural assignment was seriously questioned by various theoretical studies^{27,28} which provide strong evidence that the bonding takes place exclusively through the bridging ligands.

The situation is thus quite similar to what was observed in the case of Fe₂(CO)₉ and it was thus of interest to see what picture of the bonding will emerge from the analysis of DAFH in this case. As the molecule is isoelectronic with Fe₂(CO)₉, the bonding that keeps together two Co(CO)₃ fragments with the bridging ligands again involves five electron pairs and the main goal of the analysis is the elucidation of the nature of these crucial electron pairs. As in the previous case, the natural choice for the analysis is the Fermi hole averaged over the Co(CO)₂Co fragment. The numerical results of the analysis are summarized in Table 4.



Scheme 5.

Before reporting the details of this analysis, it is useful to mention again some elementary considerations based on the isolobal analogy. According to this analogy, the $\text{Co}(\text{CO})_3$ fragment is isolobal with CH and each of the fragments thus contributes to the bonding by three electrons. Two of these electrons can be engaged in localized 2c-2e bonding with the bridging ligands and because of the absence of the third carbonyl ligand, the remaining unpaired electrons on the metal atoms could, in principle, be involved in the formation of direct bent Co—Co bond (Scheme 5).

This, however, is not the case and the actual picture of bonding is slightly more complex. The analysis of the Fermi hole averaged over $\text{Co}(\text{CO})_2\text{Co}$ fragment yields 37 (essentially) non-zero eigenvalues. Twenty of them are very close to 2 and the corresponding eigenvectors correspond to core $1s^2$ electron pairs on O ($2\times$) and C ($2\times$) of the bridging ligands, the electron pairs of σ_{CO} ($2\times$) and π_{CO} (4) bonds (Figs. 3a and 3b), σ -lone pairs on the oxygen atoms of the bridging ligands ($2\times$) (Fig. 3c), and the electron pairs of filled 3s and 3p shells on Co ($8\times$) (Fig. 3d). These electron pairs are not involved in bonding. There is a group of six eigenvalues ranging between 1.76 ($2\times$) and 1.80 ($4\times$) with eigenvectors corresponding to nonbonding 3d orbitals on Co whose existence can be expected for $\text{Co}(\text{CO})_3$ fragments on the basis of symmetry considerations¹⁷ (Fig. 3e). Similarly to the case of $\text{Fe}_2(\text{CO})_9$, these d orbitals are also somewhat involved in the interactions with the ligands but the fact that the deviations from the ideal value of 2 are again slight suggest that these interactions contribute to the bonding in $\text{Co}(\text{CO})_2\text{Co}$ fragment only marginally. The same is also true of eigenvectors associated with the group of six eigenvalues ranging between 0.56 ($4\times$) and 0.58 ($2\times$) which correspond to the free valences of six “broken” terminal Co—C bonds, whose splitting is required for the separation of the fragment from the terminal CO groups (Fig. 3f). The fact that in this case the eigenvalues significantly deviate from unity can again be attributed to the polarity of the terminal Co—C bonds which results in the uneven sharing of electron pairs. The observed values (0.56–0.58) can thus be regarded as the contribution of the Co atom to the shared electron pair of the terminal Co—C bond. The remaining roughly 1.4 electrons thus have to come from the contribution of the terminal carbon and this interpretation is supported by the analysis of the Fermi hole associated with one of the terminal carbonyl ligands.

The bonding with the bridging ligands is thus again due to electron pairs associated with the remaining five nonzero eigenvalues ranging between 1.88 and 1.91. The eigenvectors associated with these five crucial electron pairs are displayed in Figures 4a–4e.

Inspection of these eigenvectors shows that two of them, associated with the eigenvalue 1.90 correspond to electron pairs of two well localized 2c-2e Co—C bonds between the metal atoms and one of the bridging ligands (Figs. 4a and 4b). This result is very important since the existence of only two localized 2c-2e Co—C_b bonds clearly suggests the incompatibility of the actual picture of the bonding with the situation depicted in Scheme 5 and at the same time implies that at least some of the bonding electron pairs should display a certain degree of delocalization. The existence of such a delocalization is clearly evident on the form of the eigenvector associated with the eigenvalue 1.88, (Fig. 4e) which is very similar to the delocalized 3c-2e bond detected in the analysis of $\text{Fe}_2(\text{CO})_9$. This implies that similarly to diiron nonacarbonyl, the bonding of the bridging ligands cannot be described by the set of classical well localized 2c-2e Co—C_b bonds but that these bonds have to display again partial multicenter character.

To complete the picture of the bonding it is necessary to take into account only the remaining pair of degenerate eigenvalues close to 1.84. The inspection of the associated eigenvectors shows (Figs. 4c and 4d) that their shape is reminiscent of d_{z^2} orbitals on cobalt. To understand the presence of these two nonbonding electron pairs localized on metal atoms it is useful to refer to the traditional MO description of the bonding in $\text{Co}_2(\text{CO})_8$. The inspection of the occupied molecular orbitals of this carbonyls shows the presence of two molecular orbitals, HOMO (b_2) and HOMO-2 (a_1) whose shape is shown in Figures 5a and 5b.

The lower of these orbitals (a_1) evidently corresponds to a direct bent Co—Co bond but because the bonding contribution of this electron pair is cancelled by the antibonding contribution of the second (b_2) electron pair, the net result is the absence of Co—Co bond.^{27,33} The form of these two molecular orbitals can straightforwardly be derived from the orbital interaction diagram Scheme 6, which also clearly shows the complete equivalence of the delocalized MO description and the localized picture of two nonbonding electron pairs as it follows from the DAFH analysis.

With this in mind, the final picture of the bonding in $\text{Co}_2(\text{CO})_8$ can be described as follows. Two of five electron pairs involved in the bonding correspond to well localized 2c-2e bonds between the metal atoms and one of the bridging ligands. In addition to these two localized electron pairs, there are two other localized electron pairs, which can best be characterized as nonbonding pairs on the metal atoms. The bonding of the second carbonyl ligand thus necessarily involves only the remaining electron pair but because one electron pair is not enough to form two 2c-2e bonds with the second bridging ligand, the bonding of this ligand thus necessarily has to display the character of delocalized 3c-2e multicenter bond. The situation is thus quite similar to what was also observed in the case of $\text{Fe}_2(\text{CO})_9$ and similarly as in that case, the final picture of the bonding requires to invoke again the resonance of two limiting structures (Scheme 7).

As a consequence, each of the bridging Co—C bonds slightly looses the character of a localized 2c-2e bond and the delocalized multicenter character of one bonding electron pair is uniformly distributed among both Co—C_b—Co bridges. The existence of this delocalization is again corroborated by the values

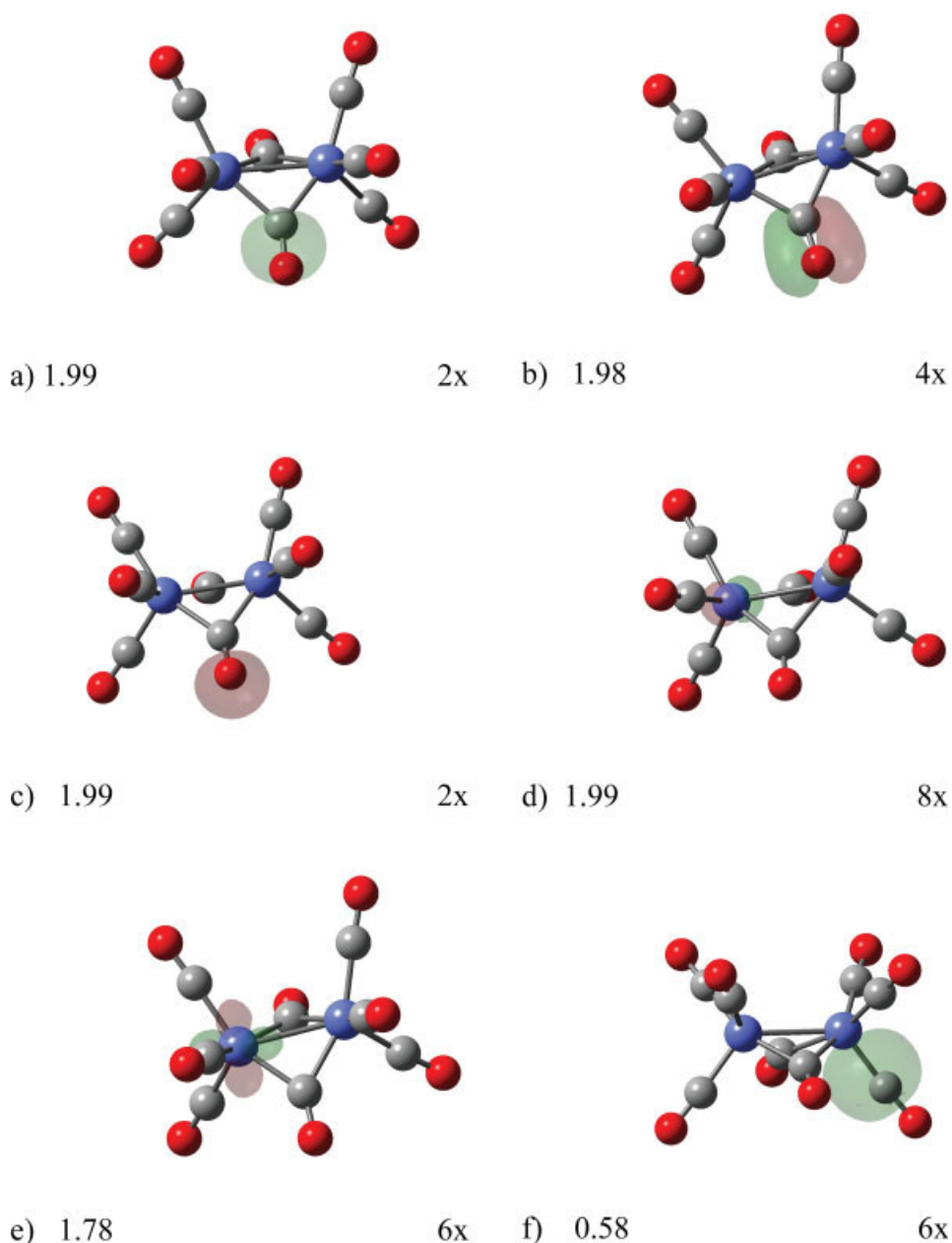


Figure 3. Graphical display of the eigenvectors of DAFH associated with the electron pairs retained in the $\text{Co(CO)}_2\text{Co}$ fragment of $\text{Co}_2(\text{CO})_8$. The pictures were generated at B3LYP/LANL2DZ level of the theory. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of calculated multicenter bond indices which indeed detect partial 3c-2e character in each of $\text{Co}-\text{C}_b-\text{Co}$ fragments. The actual value of the index for each of the fragments is 0.048 but taking into account that due to the resonance (Scheme 7) the single electron pair involved in 3c-2e bonding is uniformly spread between both $\text{Co}-\text{C}-\text{Co}$ bridges, the “hypothetical” 3-center bond index corresponding to the localized 3c-2e electron pair (Fig. 4e) should effectively be equal to 0.096. The decrease

of this value compared to the value 0.180 estimated for $\text{Fe}-\text{C}-\text{Fe}$ bonds can be attributed to the higher polarity of $\text{Co}-\text{C}$ bonds compared to $\text{Fe}-\text{C}$ bonds. At this place it is also interesting to remark that exactly the same picture of the bonding characterized by the lack of direct metal-metal bond and delocalized 3c-2e nature of the bonding of bridging ligands is observed also in the isoelectronic C_{2v} structure of $\text{Fe}_2(\text{CO})_8^{(2-)}$. The detailed DAFH analysis of the bonding in this carbonyl as

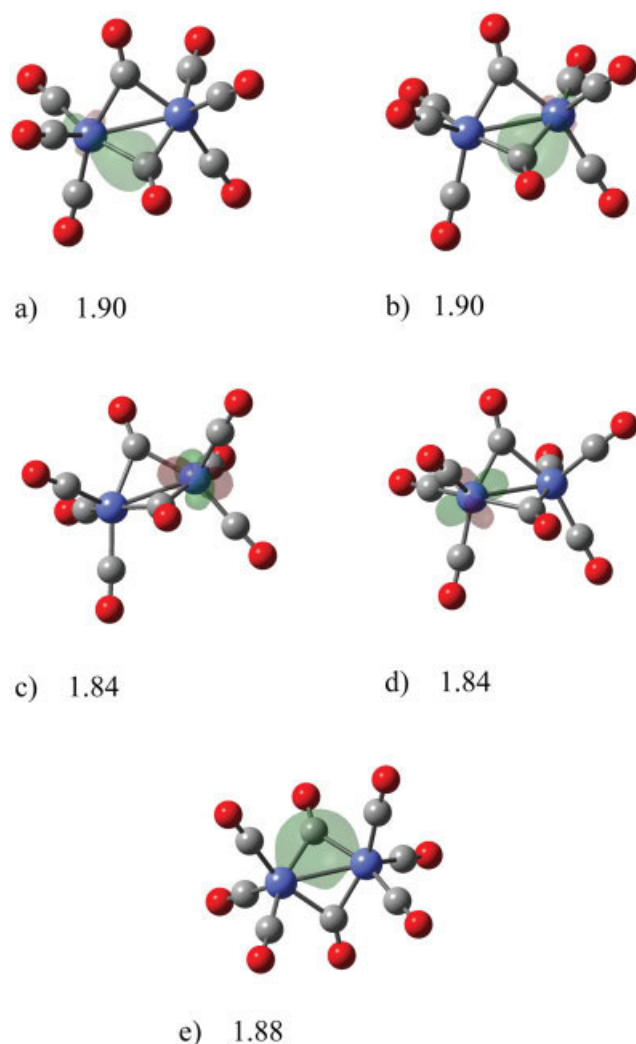


Figure 4. Graphical display of the eigenvectors of DAFH associated with five electron pairs involved in the bonding within the Co(CO)_2 Co fragment of $\text{Co}_2(\text{CO})_8$. The pictures were generated at B3LYP/LANL2DZ level of the theory.

well as in its other stable isomers of D_{2d} and D_{3d} symmetry will be reported in the intended forthcoming publication elsewhere (Ponec, R.; Lendvay, G., to be published).

Conclusions

The most interesting and surprising result of the reported analysis is that although the same number of electron pairs is available for the bonding of different number of bridging ligands, the actual picture of bonding in isoelectronic $\text{Fe}_2(\text{CO})_9$ and $\text{Co}_2(\text{CO})_8$ carbonyl complexes is in fact very similar. This concerns not only the absence of direct metal–metal bond anticipated for both carbonyls on the basis of 18-electron rule, but, above all, the existence of delocalized multicenter character of

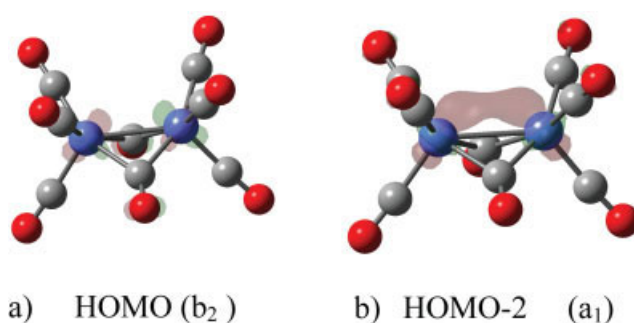
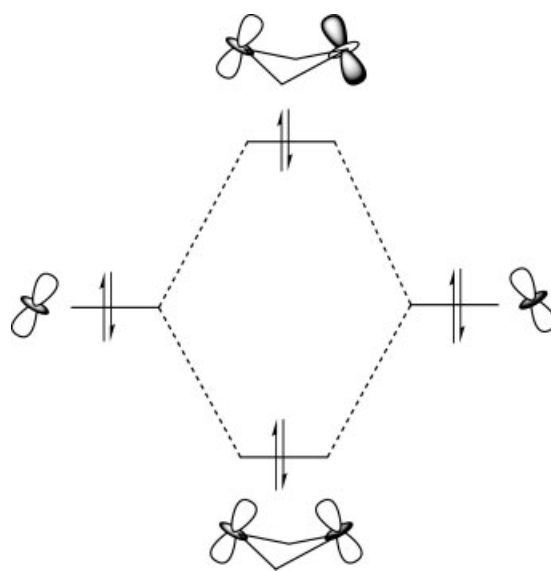


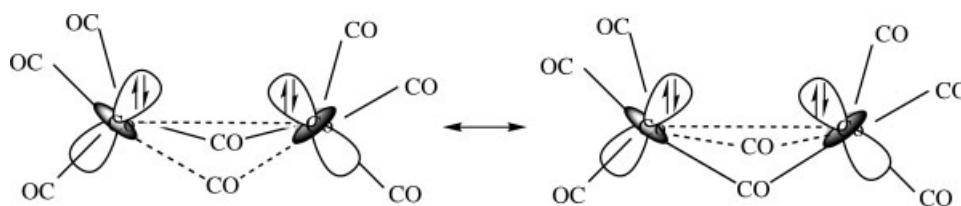
Figure 5. Graphical display of the two crucial molecular orbitals involved in metal–metal bonding in $\text{Co}_2(\text{CO})_9$.

one of the bonding electron pairs. This is not at all surprising in the case of $\text{Fe}_2(\text{CO})_9$, where five bonding electron pairs are not enough to form six localized $2c-2e$ $\text{Fe}-\text{C}_b$ bonds, but in the case of $\text{Co}_2(\text{CO})_8$, where at least the formal possibility of completely localized description cannot be ruled out, the existence of multicenter character of the bonding is a new phenomenon. Both molecules thus in some respect behave as electron deficient systems and the delocalized character of the bonding is thus nothing but the manifestation of the similarity with electron deficient system.

The above parallel with the electron deficient systems is also straightforwardly corroborated by the analysis of the bonding situation in closely related systems differing in the number of bonding electron pairs. Thus, e.g., in the case of dianion $\text{Fe}_2(\text{CO})_9^{(2-)}$, which we found to exist as the true minimum on the PE hypersurface (Ponec, R., unpublished results), the presence of the additional electron pair dramatically simplifies the bonding situation in the sense that six available bonding electron



Scheme 6.



Scheme 7.

pairs allows the formation of six localized Fe—C_b bonds and such a simple picture of bonding is indeed confirmed by the DAFH analysis.

Acknowledgments

The authors thank the undergraduate student I. Karpíšek who was involved in the study during his participation in the project of Czech Academy of Sciences “Open Science,” for the technical assistance with the DAFH analysis.

References

- Powel, H. M.; Ewens, R. V. *J Chem Soc* 1939, 286.
- Cotton, A.; Troup, J. M. *J Chem Soc Dalton Tans* 1974, 800.
- Farmery, K.; Kilner, M.; Greatrex, R.; Greenwood, N. N. *J Chem Soc A* 1969, 2339.
- Griffith, W. P.; Wickham, A. J. *J Chem Soc A* 1969, 834.
- Greatrex, R.; Greenwood, N. N. *Discuss Faraday Soc* 1969, 47, 126.
- Aullón, G.; Alvarez, S. *Organometallics* 2001, 20, 818.
- Fletcher, S. C.; Poliakoff, M.; Turner, J. J. *Inorg Chem* 1986, 25, 3597.
- Schaefer, H. F., III; King, R. B. *Pure Appl Chem* 2001, 73, 1059.
- Xie, Y.; Schaefer, H. F., III; King, R. B. *J Am Chem Soc* 2000, 123, 8746.
- Jang, J. H.; Lee, J. G.; Lee, H.; Xie, Y.; Schaefer, H. F., III. *J Phys Chem A* 1998, 102, 5298.
- Jakobsen, H.; Ziegler, T. *J Am Chem Soc* 1996, 118, 4631.
- Aullón, G.; Alvarez, S. *Eur J Inorg Chem* 2001, 3031.
- Leung, P.; Coppens, P. *Acta Crystallogr Sect B* 1983, 39, 535.
- Summer, G. G.; Klug, H. P.; Alexander, L. E. *Acta Crystallogr* 1964, 17, 732.
- Nyholm, R. S. *Proc Chem Soc* 1961, 273.
- Lewis, J.; *Pure Appl Chem* 1965, 10, 11.
- Elian, M.; Hoffmann, R. *Inorg Chem* 1975, 14, 1058.
- Summerville, R. H.; Hoffmann, R. *J Am Chem Soc* 1979, 101, 3821.
- Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J Am Chem Soc* 1976, 98, 3219.
- Jemmis, E. D.; Pinhas, A. R.; Hoffmann, R. *J Am Chem Soc* 1980, 102, 2576.
- Wade, K. *Chem Commun* 1971, 792.
- Mingos, D. M. P. *J Chem Soc Dalton Trans* 1977, 602.
- Mingos, D. M. P. *Adv Organomet Chem* 1977, 15, 1.
- Hoffmann, R. *Science* 1981, 211, 995.
- Hoffmann, R. *Angew Chem Int Ed Engl* 1982, 21, 711.
- Reinhold, J.; Barthel, A.; Mealli, C. *Coord Chem Rev* 2003, 238–239, 333.
- Macchi, P.; Sironi, A. *Coord Chem Rev* 2003, 238–239, 383.
- Shriver, D. F.; Atkins, P. W. *Inorganic Chemistry*, 3rd ed.; Oxford University Press: Oxford, 1999; p 541.
- Heijser, W.; Baerends, E. J.; Ros, P. *Faraday Symp* 1980, 14, 211.
- Bauschlicher, C. W. *J Chem Phys* 1986, 84, 872.
- Brateman, P. S. *Struct Bonding* 1971, 10, 57.
- Bénard, M. *J Am Chem Soc* 1978, 100, 7740.
- Kluge, O.; Finger, M.; Reinhold, J. *Inorg Chem* 2005, 44, 6494.
- Bo, C.; Sarasa, J. P.; Poblet, J. M. *J Phys Chem* 1993, 97, 6362.
- Ponec, R. *J Math Chem* 1997, 21, 323.
- Ponec, R. *J Math Chem* 1998, 23, 85.
- Ponec, R.; Duben, A. J. *J Comput Chem* 1999, 8, 760.
- Ponec, R.; Roithová, J. *Theor Chem Acc* 2001, 105, 383.
- Ponec, R.; Yuzhakov, G.; Cooper, D. L. *Theor Chem Acc* 2004, 112, 419.
- Ponec, R.; Yuzhakov, G.; Sundberg, M. R. *J Comput Chem* 2005, 26, 447.
- Ponec, R.; Yuzhakov, G.; Carbó-Dorca, R. *J Comput Chem* 2003, 24, 1829.
- Ponec, R.; Yuzhakov, G.; Gironés, X.; Frenking, G. *Organometallics* 2004, 23, 1790.
- Wigner, E.; Seitz, F. *Phys Rev* 1933, 43, 804.
- Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford University Press: Oxford, 1990.
- Ponec, R.; Cooper, D. L. *Faraday Discuss* 2007, 135, 31.
- Kohn, W.; Sham, J. *Phys Rev A* 1985, 140, 1133.
- Hohenberg, P.; Kohn, W. *Phys Rev B* 1964, 136, 864.
- Bo, C.; Costas, M.; Poblet, J. M. *J Phys Chem* 1995, 99, 5914.
- Vyboishchikov, S. F.; Sierraalta, A.; Frenking, G. *J Comput Chem* 1997, 18, 416.
- Lin, Z.; Bytheway, I. *Inorg Chem* 1996, 35, 594.
- Gatti, C.; Lasi, D. *Faraday Discuss* 2007, 135, 55.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, K. D.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian98, Revision A.9*; Gaussian: Pittsburgh, PA, 1998.
- Gironés, X.; Ponec, R.; Roithová, J. *Program WinFermi*, v. 2.0 Prague, Czech Republic, 2002.
- Dewar, J.; Jones, H. O. *Proc R Soc London* 1905, A76, 558.
- Cioslowski, J. *Int J Quantum Chem* 1990, S24, 15.
- Ponec, R.; Uhlík, F. *J Mol Struct (THEOCHEM)* 1997, 391, 159.
- Sannigrahi, A. B.; Kar, T. *Chem Phys Lett* 1990, 173, 569.

58. Giambiagi, M.; Giambiagi, M. S.; Mundim, K. C. *Struct Chem* 1990, 1, 123.
59. Marcos, E. S.; Karafiloglou, P.; Sanz, J. F. *J Phys Chem* 1990, 94, 2763.
60. Kar, T.; Nandi, P. K.; Sannigrahi, A. B. *Chem Phys Lett* 1994, 220, 133.
61. Sannigrahi, A. B.; Kar, T. *J Mol Struct (THEOCHEM)* 2000, 496, 1.
62. Sannigrahi, A. B.; Nandi, P. K.; Behera, L.; Kar, T. *J Mol Struct (THEOCHEM)* 1992, 276, 259.
63. Ponec, R.; Uhlík, F. *Croat Chem Acta* 1996, 69, 941.
64. Ponec, R.; Mayer, I. *J Phys Chem A* 1997, 101, 1738.
65. Ponec, R.; Yuzhakov, G.; Tantillo, D. J. *J Org Chem* 2004, 69, 2992.
66. Ponec, R.; Bultinck, P.; Gutta, P.; Tantillo, D. J. *J Phys Chem A* 2006, 110, 3785.
67. Reinhold, J.; Kluge, O.; Mealli, C. *Inorg Chem* 2007, 46, 7142.