making qualitative, physically oriented conclusions regarding the nature of the bonding in $Co(NH_3)_5NO^{2+}$. As the single configuration wave functions employed did faithfully reproduce the experimental structural tendencies, we feel that they were useful as a basis of qualitative discussions. We do not claim that the present results give quantitative energy separations. Indeed, the plethora of low-lying excited states—as suggested by the number of bound virtual orbitals as well as by the black color of the complex—would suggest that any attempts at a more quantitative treatment would necessitate inclusion of CI. Similarly, correlation effects would be critical if a description of the absorption spectrum of the complex were desired. These, however, were not the intent of the present study.

We feel that the insights provided by this work are both significant and typical of what might be attained by application of ab initio techniques to this type of problem. It should be noted that the energy analyses presented here are not possible with empirical wave functions. We also feel that the fractional charge simulation of dipolar ligands has proven itself as a useful qualitative tool in these types of problems.

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Registry No. $Co(NH_3)_5NO^{2+}$, 18222-60-1.

References and Notes

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(2) (a) D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Am. Chem. Soc.*, **90**, 4886 (1968); (b) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968); (c) B. A. Frenz and J. A. Ibers, *MTP Int. Rev. Sci.: Phys. Chem., Ser. One*, **11**, 33 (1972).

(3) C. S. Pratt, B. A. Coyle, and J. A. Ibers, *J. Chem. Soc. A*, 2146 (1971).

(4) N. V. Sidgwick and R. W. Bailey, *Proc. R. Soc. London, Ser. A*, **144**, 521 (1934). Many other workers have also implemented this idea; see, e.g., ref 5.

(5) (a) J. H. Enemark and R. D. Feltham, *J. Am. Chem. Soc.*, **96**, 5002 (1974); (b) R. D. Feltham and J. H. Enemark, *Theor. Chim. Acta*, **34**, 195 (1974); (c) J. H. Enemark and R. D. Feltham, *J. Am. Chem. Soc.*, **96**, 5004 (1974); (d) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974).

(6) (a) C. G. Pierpont and R. Eisenberg, *J. Am. Chem. Soc.*, **93**, 4905 (1971); (b) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **12**, 199 (1973); (c) D. M. P. Mingos and J. A. Ibers, *ibid.*, **10**, 1479 (1971); (d) D. M. P. Mingos, *ibid.*, **12**, 1209 (1973).

(7) (a) R. Hoffmann, M. M. L. Chen, M. Elian, A. R. Rossi, and D. M. P. Mingos, *Inorg. Chem.*, **13**, 2666 (1974); (b) R. Hoffmann, M. M. L. Chen, and D. L. Thorn, *ibid.*, **16**, 503 (1977).

(8) (a) K. Morokuma, *J. Chem. Phys.*, **55**, 1236 (1971); (b) K. Kitaura and K. Morokuma, *Int. J. Quantum Chem.*, **10**, 325 (1976).

(9) B. Roos, A. Veillard, and G. Vinot, *Theor. Chim. Acta*, **20**, 1 (1971).

(10) R. Ditchfield, M. D. Newton, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

(11) (a) J. O. Noell and K. Morokuma, *Chem. Phys. Lett.*, **36**, 465 (1975); (b) *J. Phys. Chem.*, **80**, 2675 (1976); (c) *ibid.*, **81**, 2295 (1977).

(12) J. Almlof, USIP Report 74-29, Univerity of Stockholm, 1974.

(13) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Poplee, GAUSSIAN 70, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., 1973.

(14) H. Umeyama, K. Morokuma, and S. Yamabe, *J. Am. Chem. Soc.*, **99**, 330 (1977).

(15) P. Kollman, *J. Am. Chem. Soc.*, **99**, 4875 (1977).

(16) D. A. Snyder and D. L. Weaver, *Inorg. Chem.*, **9**, 2760 (1970).

(17) R. McWeeney, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, **47**, 20 (1969).

(18) P. T. Manoharan and H. B. Gray, *Inorg. Chem.*, **5**, 823 (1966).

(19) (a) A. Tullberg and N. G. Vannerberg, *Acta Chem. Scand.*, **20**, 1180 (1966); (b) *ibid.*, **21**, 1462 (1967); (c) P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963); (d) D. F. Svedung and N. G. Vannerberg, *Acta Chem. Scand.*, **22**, 1551 (1968).

(20) (a) S. Z. Goldberg, C. Kubiak, C. D. Meyer, and R. Eisenberg, *Inorg. Chem.*, **15**, 1651 (1975); (b) W. R. Scheidt and J. L. Hoard, *J. Am. Chem. Soc.*, **95**, 8281 (1973); (c) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1035 (1971); (d) C. G. Pierpont, D. G. Van Derveer, W. Durland, and R. Eisenberg, *J. Am. Chem. Soc.*, **92**, 4670 (1970); (e) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968); (f) J. H. Enemark and R. D. Feltham, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 3534 (1972); (g) J. H. Enemark and R. D. Feltham, *J. Chem. Soc., Dalton Trans.*, 718 (1972).

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Molecular Orbital Analysis of the Metal–Metal Interaction in Some Carbonyl-Bridged Binuclear Complexes

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Molecular orbital calculations performed on *trans*-$[C_5H_5Fe(CO)_2]_2$ and the bridged form of $Fe_3(CO)_{12}$ show that there is apparently no net direct bonding between carbonyl-bridged iron atoms. The metal–metal interaction responsible for the short interatomic distance is better described in terms of multicentered linkages between the metal and the bridging carbonyl ligands. This description is supported by a recent experimental determination of differential electron density.

Introduction

The nature of the metal–metal interaction in diamagnetic binuclear complexes has for some years been the subject of numerous discussions, especially in the case of ligand-bridged systems.[1-3] When spin coupling between the metal atoms is required from the magnetic behavior of the complex, either a direct metal–metal bond[6] or a superexchange mechanism via the bridging ligands[8] can be invoked. However, qualitative considerations based upon molecular orbital symmetry have raised ambiguity about the nature of the metal–metal interaction since it was not possible according to these discussions to distinguish unequivocally between M–M direct bonding and indirect spin coupling through the bridging ligands.[1-3] It seems that these considerations have been already substantiated by a molecular orbital calculation on $Co_2(CO)_8$.[4] However, on the basis of structural data which associate the setting up of a spin-coupling interaction to a dramatic decrease of the M–M distance, Dahl et al.[6,7] were led to postulate the existence of a distinct metal–metal bond. These data were obtained on phosphorus-[6] and sulfur-bridged[7] complexes. Parameter-free molecular orbital calculations later performed on several P-, S-, N-, and As-bridged complexes with pseudobioctahedral

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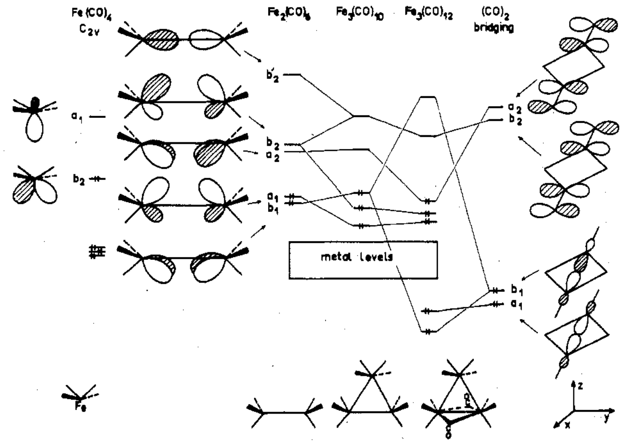

Figure 1. Orbital interaction diagram for $Fe_3(CO)_{12}$. The orbitals of $Fe_3(CO)_{12}$ are built up from those of one $Fe(CO)_4$ (left), one $Fe_2(CO)_6$ (center), and two bridging carbonyl (right) fragments.

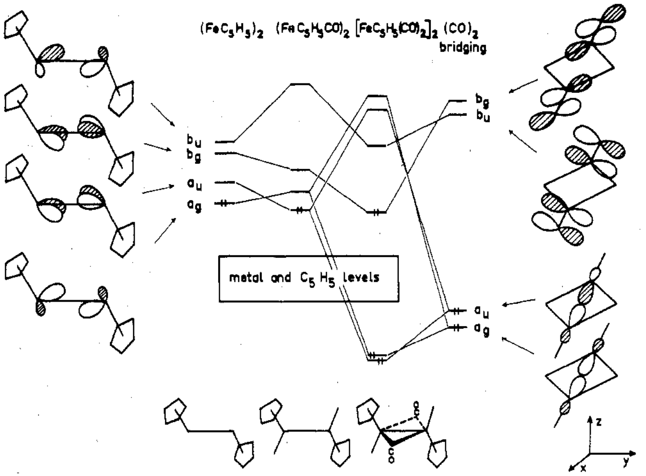

Figure 2. Orbital interaction diagram for *trans*-$[C_5H_5Fe(CO)_2]_2$. The orbitals of *trans*-$[C_5H_5Fe(CO)_2]_2$ are built up from those of one $(FeC_5H_5)_2$ (left), two terminal carbonyl, and two bridging carbonyl (right) fragments.

conformation[5,9] have substantiated the concept of a separate M–M bond in bridged binuclear complexes. Since then, this concept has gained general acceptance and has been applied in particular to carbonyl-bridged complexes in spite of the important differences in what concerns the metal–ligand interactions between CO and the ligands investigated by Dahl et al. Besides, it must be noted that structural data similar to those put forth by Dahl in favor of the separate metal–metal bond have apparently never been obtained for CO-bridged complexes. The recent experimental determination of the electronic density distribution in *trans*-$[C_5H_5Fe(CO)_2]_2$, indicating that the electron density gradient is small and generally insignificant between the two metal atoms, prompted us to investigate the nature of the metal–metal bonding in this class of carbonyl-bridged complexes by means of molecular orbital calculations. The calculations, of ab initio and extended Hückel types, were performed on the above mentioned trans isomer of bis(dicarbonyl-π-cyclopentadienyliron), $[C_5H_5Fe(CO)_2]_2$, and on the bridged form of triiron dodecacarbonyl, $Fe_3(CO)_{12}$.

Methods of Calculation

The wave functions for $[C_5H_5Fe(CO)_2]_2$ and $Fe_3(CO)_{12}$ have been obtained from ab initio calculations. These LCAO-MO-SCF calculations were carried out with the ASTERIX system of programs.[10] In $[C_5H_5Fe(CO)_2]_2$, the Gaussian basis sets used were 11, 7, and 5 for Fe, 8 and 4 for first-row atoms, and 4 for hydrogen contracted to basis sets minimal for the inner shells and the $(n + 1)$s and $(n + 1)$p of Fe but split for the valence shells. The geometry used for this complex corresponds to the most recent experimental determination.[11] For $Fe_3(CO)_{12}$, the Gaussian basis sets were 10, 6, and 4 and 7 and 3 contracted to minimal basis sets. The experimental structure of $Fe_3(CO)_{12}$ characterized by an asymmetrical disposition of the bridging carbonyls[12] has been idealized into a perfect C_{2v} system.[23] The bridged Fe–Fe bond lengths for these two complexes are respectively 2.539 and 2.558 Å.

Results

The results can be rationalized in terms of the molecular interaction diagrams displayed in Figures 1 and 2. Two intermediate steps based upon extended Hückel calculations[13] are considered in these diagrams. The orbital ordering and the trends of the Mulliken population analysis obtained from extended Hückel calculations performed on $Fe_3(CO)_{12}$ and $[C_5H_5Fe(CO)_2]_2$ were found to be qualitatively consistent with those obtained at the ab initio level.

Discussion

The interaction diagram for $Fe_3(CO)_{12}$ is based upon the $Fe_2(CO)_6$ fragment, the geometry of which is only slightly distorted from D_{3h} symmetry. Interaction with a $Fe(CO)_4$ fragment forms the metal triangle. The $Fe_3(CO)_{10}$ unit then interacts with two bridging carbonyls to give $Fe_3(CO)_{12}$. The metal triangle is located in the *YZ* plane and the *Y* axis is collinear with the bridged Fe–Fe line. The cyclic $Fe_2(CO)_2$ unit is slightly folded with a dihedral angle of 140°[12] so that the bridging carbonyls are pushed below the *XY* plane (Figure 1).

The $Fe_2(CO)_6$ fragment has been extensively studied by Thorn and Hoffmann on the basis of extended Hückel calculations.[14] In agreement with their results, a low-lying nest of six metal-type orbitals is found (not individually represented in the diagram) overtopped by a set of "valence" orbitals. Two of these orbitals, a_1 and b_1, present a metal–metal bonding character and are both occupied. The empty a_2 and b_2 orbitals form the corresponding antibonding combinations. Two orbitals of the $Fe(CO)_4$ unit are able to interact with these "valence" orbitals in order to form metal–metal bonds.[26,27] The $Fe(CO)_4$ empty orbital of a_1 symmetry, directed toward the center of the metal triangle, interacts with the $Fe_2(CO)_6$ orbital of the same symmetry. A three-center bonding orbital is obtained. The occupied b_2 sets up σ-type bonding combinations with each metal atom of $Fe_2(CO)_6$ and then stabilizes a combination which has some M–M antibonding character with respect to $Fe_2(CO)_6$.[27] The destabilized counterpart of this last interaction is contaminated by a high-lying b_2 orbital of $Fe_2(CO)_6$ and then becomes essentially σ antibonding with regard to the metal atoms of $Fe_2(CO)_6$. The bridging carbonyls display a set of six orbitals capable of interacting with the "valence" orbitals of the $Fe_3(CO)_{10}$ unit. Two of them of a_2 and b_2 symmetry represent the carbon σ lone pairs. Two pairs of π^*-acceptor orbitals are available, but only the ones of a_2 and b_2 symmetry with orbitals collinear to the *Y* axis can produce significant interactions. The other pair of a_1 and b_1 symmetry has not been represented on the diagram. It must be noted that there is practically no interaction between the occupied a_1 orbital of $Fe_3(CO)_{10}$ and the corresponding carbon lone-pair combination. Indeed, the $Fe_3(CO)_{10}$ a_1 orbital displays its maximal density in the central region of the Fe triangle, whereas the density of the carbon lone pairs is located below this triangle because of the folding of $Fe_2(CO)_2$[24] (Figure 1). However the geometrical disposition of orbitals is favorable for an interaction between the b_1 orbital of the complex and the corresponding lone-pair combination. This interaction destabilizes the M–M bonding "valence" orbital but forms a low-lying orbital having some metal–metal bonding character. This analysis of the interactions with lone-pair combinations resembles the scheme discussed by Thorn and Hoffmann for the bridged form of $Fe_2(CO)_8^{2-}$.[14] However the interactions of $Fe_3(CO)_{10}$ with the carbonyl π^* orbitals are different. The disposition of orbitals favors a strong interaction between the empty a_2 orbital of $Fe_3(CO)_{10}$ which has mainly d_{xy} character and the corresponding carbonyl π^* combination (Figure 1). This M–M antibonding combination is considerably stabilized and becomes the highest occupied molecular orbital (HOMO) of $Fe_3(CO)_{12}$ (Figure 3). The carbonyl b_2 acceptor does not interact significantly with the complex donor of same symmetry for geometrical reasons similar to those put forth in the a_1 symmetry case; the complex orbitals are directed inside the metal triangle and the projection of the carbonyl π^* of b_2 symmetry is located outside. However this same carbonyl π^* combination sets up a metal–ligand π-type bonding interaction with the empty M–M σ-antibonding orbital of the complex. This combination becomes the lowest unoccupied molecular orbital (LUMO) of $Fe_3(CO)_{12}$.

In the case of *trans*-$[C_5H_5Fe(CO)_2]_2$ (Figure 2) one can start from $(FeC_5H_5)_2$ which presents an isolobal analogy[15] with $Fe_2(CO)_6$. One must however take account first of the straightforward transformation of orbitals from C_{2v} into C_{2h} symmetry (Figure 2) and second of the fact that $(FeC_5H_5)_2$ considered as a fragment of $[C_5H_5Fe(CO)_2]_2$ resembles more than $Fe_2(CO)_6$ the "sawhorse" geometry described by Thorn and Hoffmann.[14] Thereby, the a_g and b_u orbitals of the "valence" set (corresponding respectively to the a_1 and b_2 orbitals of $Fe_2(CO)_6$) have a predominant σ character (Figure 2). The formal oxidation state of Fe is now 1+ so that only one orbital of the "valence" group, of a_g symmetry, is occupied. Adding two terminal carbonyls does not of course modify the occupancy of the "valence" orbitals, but the a_u orbital involved in back-bonding with the carbonyls is significantly stabilized.

In $[C_5H_5Fe(CO)_2]_2$, the spatial disposition of the bridged $Fe_2(CO)_2$ fragment is now planar, as required by C_{2h} symmetry. This geometrical conformation and the M–M σ-bonding character of the complex a_g acceptor orbital now justify an interaction with the carbonyl σ lone-pair combination of the same symmetry.[17] On the other hand, the interaction between the antisymmetric lone-pair combination (symmetry a_u) with the Fe–Fe combination of same symmetry is similar to what was observed in the C_{2v} system. These interactions lead to the formation of two low-lying orbitals presenting some metal–metal bonding character. However, as in the case of $Fe_3(CO)_{12}$, these orbitals cannot be considered as representing real metal–metal bonds, since their metal percentage does not exceed 15–18%.[16] Contrary to the case of the C_{2v} system, both pairs of carbonyl π^* orbitals share the same b_u–b_g symmetry. Consequently, their orientation is not fully determined by symmetry and the remaining degree of freedom is used in order to maximize the overlap with the orbitals of $[C_5H_5FeCO]_2$. For this reason, the interaction between the b_g orbitals is approximately as efficient as was the corresponding one in the C_{2v} system (symmetry a_2). Similarly, the resulting orbital becomes the HOMO of the $[FeC_5H_5(CO)_2]_2$ system, whereas the metal–metal σ-antibonding LUMO is obtained from a combination of the b_u orbitals.

It follows from this discussion that the electronic structures of $Fe_3(CO)_{12}$ and $[C_5H_5Fe(CO)_2]_2$ present some similarity. Taking account of the differences prescribed by symmetry, the HOMO's are both constructed from metal–metal antibonding combinations stabilized by a strong-bonding interaction with the bridging carbonyl π^* orbitals. The resemblance is strengthened by the similarity of the LUMO's which are σ antibonding with respect to the metal atoms but exhibit a π-type bonding interaction between the metal and the carbonyl orbitals. However the electronic structure considered from the point of view of the metal–metal interaction is rather different from what is currently postulated for spin-coupled binuclear complexes. If the two bridged iron atoms are isolated from the rest of the system, the metal–metal interaction cannot be described, as in the case of nonbridged binuclear systems, in terms of a *direct* metal–metal bond. However, if the metal atoms and the bridging carbonyls are not artificially separated, the nature of the interactions in the whole $M_2(CO)_2$ subsystem is unequivocally *bonding* and can be described in terms of a delocalized multicentered bond. These conculsions clearly appear from the discussion of the interaction diagrams and they are illustrated by a schematic in-plane representation of the HOMO (Figure 3, left).

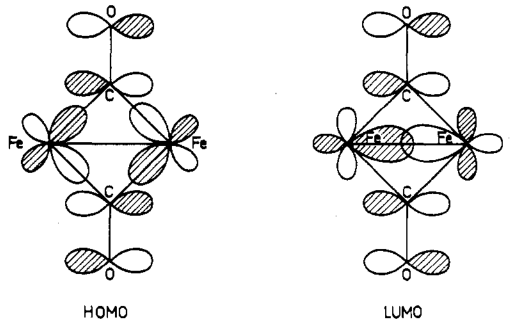

Figure 3. Schematic representation of orbital interactions in the HOMO (left) and in the LUMO (right) of $Fe_3(CO)_{12}$ and $[C_5H_5Fe(CO)_2]_2$.

Though overlap populations are not significant on an absolute scale, comparisons performed between closely related types of bonds generally give a correct trend. Keeping in mind this restriction, the above conclusions can be substantiated by a comparative examination of metal–metal and metal–carbonyl overlap populations. In the case of $Fe_3(CO)_{12}$, the overlap population (from the ab initio calculation) is +0.160 between nonbridged Fe atoms but −0.026 between the bridged atoms. For the same complex, the population between Fe and a terminal carbon is less than +0.08 but it is +0.18 for every Fe–C (bridging) bond. The corresponding overlap populations obtained for $[C_5H_5Fe(CO)_2]_2$ are −0.047, +0.161, and +0.152 for Fe–Fe, Fe–C (terminal), and Fe–C (bridging), respectively. The overlap population between Fe and C (bridging) is slightly smaller than between Fe and C (terminal) in the last case, but one must keep in mind that each bridging carbon contributes to two Fe–C bonds.

This metal–metal interaction scheme is fundamentally different from what is obtained when bridging carbonyls are replaced by three electron-donating ligands, such as PR_2 or NR_2 groups. As indicated by Teo et al. four orbitals are provided by the bridging ligands, representing the two symmetrized lone-pair-type orbitals and the π and π^* combinations.[5] These orbitals form low-lying combinations with the "valence" orbitals of the complex.[5,9] The same interactions also yield a set of four destabilized orbitals having a high metal weight. In the C_{2v} complexes of the type $Fe_2(CO)_6X_2$ for which the $Fe_2(CO)_6$ fragment assumes the "sawhorse" geometry, the HOMO is the lowest orbital of this set, i.e., the metal–metal σ-bonding orbital of a_1 symmetry. Orbitals b_1 and a_2 are pushed toward high energies so that the antibonding counterpart of orbital a_1, less destabilized, becomes the LUMO.[5]

Consequently, the four-centered linkage of bridging carbonyls to iron atoms displayed from the extended Hückel and ab initio wave functions has no equivalent in M_2X_2 bridged systems when X_2 denotes three-electron-donating ligands or, more generally, ligands presenting a π-donor character. A recent experimental determination of differential electron density in *trans*-$[C_5H_5Fe(CO)_2]_2$[11] substantiates this different orbital scheme proposed for carbonyl-bridged complexes or clusters. The differential electron-density maps obtained by Mitschler et al.[11] indicate that the residues between the iron

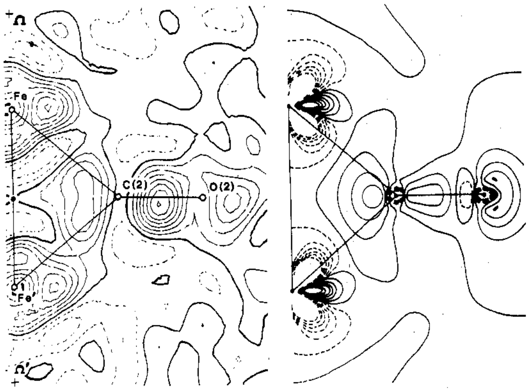

Figure 4. Section of the experimental (left) and of the computed (right) deformation density distributions of *trans*-$[C_5H_5Fe(CO)_2]_2$ in the plane containing the metal atoms and the bridging carbonyls. The contour intervals for the experimental and computed maps are 0.1 and 0.2 e A^{-3}, respectively. Dashed contours are for negative deformation density. The experimental map is reproduced by permission of A. Mitschler, B. Rees, and M. S. Lehmann.

atoms are small and generally insignificant, except at a short distance from the metal nucleus.[19] However a significant charge gradient is found along the lines Fe–C (bridging) with a large zone of charge accumulation close to the carbon atoms (Figure 4, left). A comparison of the electron density of the CO ligands with respect to the free carbon monoxide confirms that the configuration of the bridged carbonyls is more deeply altered than that of the terminal ones, in probable relation with the stronger bonding interaction with the iron atoms.[11] The ab initio wave function obtained for *trans*-$[C_5H_5Fe(CO)_2]_2$ has been used to set up theoretical electron-density maps which are in fair agreement with the experimental ones. Some details about this computed electronic deformation density distribution and its comparison with experiment have been reported in a preliminary account.[18] A section of this density distribution by the plane containing the metal atoms and the two bridging carbonyls is represented in Figure 4, compared to the corresponding experimental map obtained by Mitschler et al.[11] Both experimental and theoretical density maps display a large region of residual electronic density close to zero located along the basis of the Fe–C–Fe triangles. Another characteristic feature common to both maps is the large circular zone of density accumulation located all around the Fe_2C_2 bridged system.[21] These features are fully consistent with an important overlap between metal and carbon orbitals and with the bonding scheme depicted in the left part of Figure 3 from an analysis of the HOMO.

Conclusion

The wave functions obtained from ab initio and extended Hückel calculations performed on $Fe_3(CO)_{12}$ and *trans*-$[C_5H_5Fe(CO)_2]_2$ provide for these two carbonyl-bridged complexes a similar description which cannot be analyzed in terms of the currently postulated direct metal–metal bond. The consistency of the bonding interactions deduced from these wave functions with plane sections of the experimental deformation density distribution of *trans*-$[C_5H_5(CO)_2]_2$ suggests that the notion of multicentered delocalized bond[2-4] could provide in some cases a realistic description for the electronic structure of these complexes.

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Registry No. $[C_5H_5Fe(CO)_2]_2$, 32757-46-3; $Fe_3(CO)_{12}$, 17685-52-8.

References and Notes

(1) R. Mason and D. M. P. Mingos, *J. Organomet. Chem.*, **50**, 53 (1973).
(2) P. Chini, *Inorg. Chim. Acta, Rev.*, **2**, 31 (1968).
(3) P. S. Braterman, *Struct. Bonding (Berlin)*, **10**, 57 (1971).
(4) See note 19 in ref 5.
(5) B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *Inorg. Chem.*, **14**, 3103 (1975).
(6) J. M. Coleman and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 542 (1967).
(7) L. F. Dahl, E. R. De Gil, and R. D. Feltham, *J. Am. Chem. Soc.*, **91**, 1653 (1969).
(8) See for instance W. E. Hatfield and J. S. Paschal, *J. Am. Chem. Soc.*, **86**, 3888 (1964).
(9) B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *J. Organomet. Chem.*, **70**, 413 (1974).
(10) M. Bénard, A. Dedieu, J. Demuynck, M. -M. Rohmer, A. Strich, and A. Veillard, ASTERIX: a system of programs for the Univac 1110, unpublished work; M. Bénard, *J. Chim. Phys. Phys.-Chim. Biol.*, **73**, 413 (1976).
(11) A Mitschler, B. Rees, and M. S. Lehmann, *J. Am. Chem. Soc.*, **100**, 3390 (1978).
(12) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 4155 (1974).
(13) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. R. Lipscomb, **36**, 2179, 3489 (1962); **37**, 2872 (1962).
(14) D. L. Thorn and R. Hoffmann, *Inorg. Chem.*, **17**, 126 (1978).
(15) M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *Inorg. Chem.*, **15**, 1148 (1976).
(16) The metal percentage for the HOMO is 42%. These percentages are obtained from the ab initio wave function.
(17) A referee suggested that the stabilization of the carbonyl a_g orbital might be due to some extent to the influence of a high-lying a_g orbital of the Cp_2Fe_2 fragment. Such an influence cannot be ruled out but is probably negligible with respect to the interaction displayed in Figure 2, as it can be checked from the relatively high energy of the lowest unoccupied a_g orbital in $[C_5H_5Fe(CO)_2]_2$ which is the antibonding orbital resulting from this interaction. Though the lobes slightly deviate from the metal–metal axis in the a_g LUMO of Cp_2Fe_2 (Figure 2), the "sawhorse" configuration of this fragment allows some overlap around the center of the Fe–Fe line. This overlap could make possible the observed interaction with the carbonyl a_g orbitals.
(18) M. Bénard, *J. Am. Chem. Soc.*, **100**, 7740 (1978).
(19) An experimental determination of electron density has been performed in the case of $(\eta^5\text{-}C_5H_5Ni)_2C_2H_2$,[20] a complex for which the existence of a separate M–M bond has been confirmed by ab initio calculations.[18] Though in this case some disagreement persists between experimental and computed density maps,[18] both determinations agree to a significant charge gradient between the metal atoms.
(20) Y. Wang and P. Coppens, *Inorg. Chem.*, **15**, 1122 (1976).
(21) The comparison between experimental and computed density maps can only be made at a qualitative level. A quantitative comparison should allow for thermal motion and limited resolution which reduce the sharpest features in the experimental map.[22] As a matter of fact, both electron accumulations and deficiencies are found larger by the calculation than by the experiment. The negative zones are more extended in the computed map, especially in the vicinity of the metal nuclei, which is probably due to a small error in the experimental scale factor. The metal regions are very sensitive to such an error which changes the deformation density by an amount proportional to the total density.
(22) B. Rees and A. Mitschler, *J. Am. Chem. Soc.*, **98**, 7918 (1976).
(23) The wave function obtained from the asymmetrical geometry leads to a similar interpretation of the bonding.
(24) The term "ring puckering" has been coined by Pinhas and Hoffmann to designate this structural conformation. These authors have recently performed an extensive study of the orbital differences between planar and "puckered" conformations of the metal–ligand ring in a closely related class of dibridged complexes.[25]
(25) A. R. Pinhas and R. Hoffman, submitted for publication.
(26) M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975); J. K. Burdett, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1599 (1974); *Inorg. Chem.*, **14**, 375 (1975).
(27) B. E. R. Schilling and R. Hoffmann, submitted for publication.