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Ligand Stereochemistry of Metal Carbonyl Clusters: Steric vs Electronic Effects[1]

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The homogeneous spreading of valence electrons and free charges in metal carbonyl clusters is not ensured by the best steric disposition of the ligands; this is the major pitfall of all the theories of ligand stereochemistry based on purely steric arguments. In order to compute local formal charges, which are essentially a mathematical device for taking into account the distribution of local valence electrons and free charges, the electrons donated by a (η^1-C) carbonyl ligand have been partitioned between adjacent metal atoms, according to a "bond valence" approach. Cotton's charge equalization principle has been formulated quantitatively and used in molecular mechanics computations of metal carbonyl clusters which have been modeled as if they were mainly under the influence of (i) valence forces, constraining the CO to float on the equipotential surface maintaining the CO vector approximately perpendicular to the surface, (ii) van der Waals interactions, conveying both the (few) strong repulsions responsible for nonpenetrability of bodies and the (many) weakly attractive interactions, and (iii) local charge interactions, addressing the fulfilments of the local electron bookkeeping but also favoring the conformations associated with the better spread of the total charge on the cluster. The performance of the method has been discussed by comparing the experimental and computed stereochemistries of a series of metal carbonyl species ($[FeCo(CO)_8]^-$, $Fe_2(CO)_9$, $Fe_2(CO)_7(bipy)$, $CrOs(CO)_{10}$, $Fe_2(CO)_4Cp_2$, $MnRh(CO)_4Cp_2$, $CrNi(CO)_4Cp_2$, $V_2(CO)_5(Cp)_2$, $[Fe_3(CO)_{11}]^{2-}$) deliberately chosen to assess local charge effects, which are relevant (and visible) whenever the best steric conformation of carbonyl ligands does not correspond to a reasonable distribution of local valence electrons and/or charges.

Many observations suggest that the ligand stereochemistry of metal carbonyl clusters depends on small interactions and that their potential energy surface (PES) is quite soft with respect to ligand mobility. For instance, in a few cases, two isomers of the same metal carbonyl cluster, differing only in the ligand disposition, have been structurally characterized in the solid state.[2] The stereochemical flexibility in solution, as well as the presence of two or more isomers in solution, is well documented for many metal clusters;[3] in addition, there are examples of a fluxional behavior even in the solid state.[4]

The "reaction" trajectory for terminal/μ_2-bridge/terminal carbonyl exchange between two iron atoms has been obtained by Crabtree and Lavin,[5] using the structure correlation method,[6] thus demonstrating the earlier suggestion by Cotton that there is a smooth continuum which encompasses terminal, bent semibridging, and symmetrically bridging CO groups.[7] With the same method, the CO exchange process on a triangular M_3 face has been mapped out by Orpen, who has shown that the terminal/μ_2-bridge/μ_3-bridge path is more likely than the terminal/μ_3-bridge one, which however is not forbidden.[8]

Even if there is no general theory for rationalizing the overall observed behavior, carbonyl mobility around the cluster surface has always been related to this group's ability to act as a two-electron donor in all its coordination environments, whenever carbon is the only donor atom, and to the similarity of the binding energies of μ_1, μ_2, and μ_3 carbonyls.[9] Indeed the variety of the CO bonding capabilities and the multitude of cluster orbitals available for metal−metal and metal−ligand bonding allows the stabilization of conceivable transition states and the lowering of the fluxionality barriers.

The flatness of the potential energy surface of metal carbonyl clusters makes the task of foreseeing their stereochemistry difficult. However, a favorable packing of the CO ligands about the cluster core[10] and charge equalization over all the metal atoms[7,11,12] are widely recognized as prerequisites for any reasonable ligand stereochemistry.

Packing of the CO ligands about the cluster core was qualitatively,[13] and later (semi)quantitatively,[14] investigated by Johnson *et al.*, who tried to find the best fit between the metal

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(2) $Ir_6(CO)_{16}$: Garlaschelli, L.; Martinengo, S.; Bellon, P. L.; Demartin, F.; Manassero, M.; Chiang, M. Y.; Wei, C.; Bau, R. *J. Am. Chem. Soc.* **1984**, *106*, 6664. $[Ru_6C(CO)_{16}]^{2-}$ (C_{2v}-$[AsPh_4]^+$ salt): Johnson, B. F. G.; Lewis, J.; Sankey, S. W.; Wong, K.; McPartlin, M.; Nelson, W. J. H. *J. Organomet. Chem.* **1980**, *191*, C3. $[Ru_6C(CO)_{16}]^{2-}$ (C_s-$[NEt_4]^+$ salt): Bradley, J. S.; Ansell, G. B.; Hill, E. W. *J. Organomet. Chem.* **1980**, *184*, C33. Ansell, G. B.; Bradley, J. S. *Acta Crystallogr.* **1980**, *B36*, 726. $H_3Ru_4(CO)_{13}$: McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Dalton Trans.* **1986**, 1557 and references therein. $[Rh_{11}(CO)_{23}]^{3-}$: Fumagalli, A.; Martinengo, S.; Ciani, G.; Sironi, A.; Heaton, B. T. *J. Chem. Soc., Dalton Trans.* **1988**, 163. $[Fe_4(CO)_{13}]^{2-}$ ($[Fe(Py)_6]^{2+}$ salt): Doedens, R. J.; Dahl, L. F. *J. Am. Chem. Soc.* **1966**, *88*, 4847. $[Fe_4(CO)_{13}]^{2-}$ ($[PPN]^+$ salt): van Buskirk, G.; Knobler, C. B.; Kaesz, H. D. *Organometallics* **1985**, *4*, 149. $Ru_6C(CO)_{17}$: Braga, D.; Grepioni, F.; Dyson, P. J.; Johnson, B. F. G.; Frediani, P.; Bianchi, M.; Piacenti, F. *J. Chem. Soc., Dalton. Trans.* **1992**, 2565 and references therein. $[Fe_5N(CO)_{14}]^-$: Hourihane, R.; Spalding, T. R.; Ferguson, G.; Deeney, T.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1993**, 43.

(3) Johnson, B. F. G.; Benfield, R. E. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980; p 471.

(4) Braga, D.; Anson, C. E.; Bott, A.; Johnson, B. F. G.; Marselia, E. *J. Chem. Soc., Dalton Trans.* **1990**, 3517.

(5) Crabtree, R. H.; Lavin, M. *Inorg. Chem.* **1986**, *25*, 805.

(6) Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153.

(7) Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1.

(8) Orpen, A. G. *Chem. Soc. Rev.* **1993**, 191.

(9) Connor, J. A. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980; p 345.

(10) Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 1351.

(11) Churchill, M. R.; Veidis, M. V. *J. Chem. Soc. A* **1971**, 2170, 2995.

(12) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 1233.

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cluster and the optimum[15] ligand polyhedron and eventually formulated what is actually known as the ligand polyhedral model (LPM).[16] The most powerful method for evaluating ligand crowding and the relative steric energy of different conformers is, however, *molecular mechanics* (MM). The first attempts to use a sort of MM in the cluster field have been made by Clare *et al.*[17] and by Horwitz *et al.*,[18] but it is only with the work of Lauher[19] that MM has been really employed for rationalizing the stereochemistry of binary carbonyl metal clusters (BCMC). Lauher's key idea was to describe in a unified way all the intermediate conformations of the concerted motion of some of the CO ligands about the metal frame assuming that the carbonyls are globally connected to the metal cage but dropping the ideas of a definite coordination geometry around each atom and of an individual metal−carbon connectivity (which, indeed, is not conserved when carbonyls scramble). In other words, all carbon atoms are free to float on a surface (maintaining the C−O vector normal to that surface) which is named the *equal potential surface* (EPS) since all the carbonyls feel the same (metal-centered) potential in all the surface points. In spite of the simplicity of this idea, its inclusion in a preexistent MM program is a rather complex task since the atom−atom connectivity is a central assumption of all the MM computations.[20] We recently showed that an EPS can be derived by maintaining a *weakened* concept of connectivity, *i.e.* assuming that the carbonyls were only *locally connected*.[21] The assumption that the carbonyls are connected during each minimization cycle (but periodically redetermining their connectivity, on the basis of their actual coordinates until convergence) eventually allowed the implementation[21] of the EPS algorithm in Allinger's MM2 program[22] with full retention of all its features.[23]

The role of charge equalization in determining ligand stereochemistry was recognized early by Cotton when he accounted for the presence of *semibridging carbonyl groups*[24] in terms of their role in mitigating charge imbalance between two (or more) metal atoms.[7] It is worth noting that, according to Cotton, charge imbalance must be avoided because of Pauling's electroneutrality principle and that the role of charge equalization in determining the ligand stereochemistry around inherently different metal atoms (carrying opposite formal charges) derives from the ability of the metals to perturb adjacent CO groups through d→π^* interactions. In the case of $[FeCo(CO)_8]^-$,[25] for instance, the attainment of 18-electron configurations on both metal atoms leads to a highly polarized structure (with a negative charge on the Fe atom) when all the CO's are terminal and the semibridging CO group (which is principally bonded to the Co atom) acts to mitigate this by receiving some electron density from a filled Fe d orbital (Figure 1). Moreover, a structure with a completely symmetric CO bridge is also unsatisfactory in terms of charge distribution, since it places a full formal negative charge on the Co atom. A complementary view is to assume that the two electrons donated by the semibridging CO group are (somehow) partitioned between Fe (δ) and Co ($2-\delta$) atoms; for $\delta = 0.5$, the charge would be equally spread over the metal atoms.

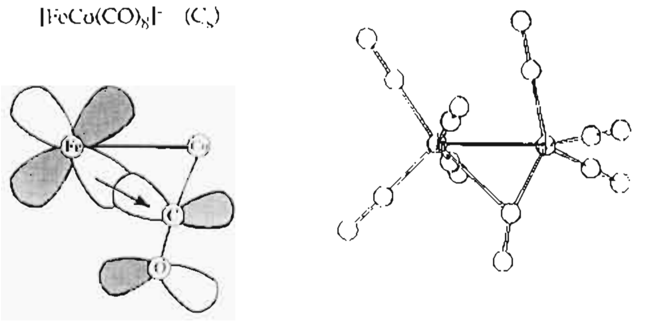

Figure 1. The structure of $[FeCo(CO)_8]^-$. Without the semibridging CO, the attainment of 18-electron configurations on both metal atoms leads to a highly polarized structure (with a negative charge on the Fe atom). It can be noted that a structure with a completely symmetric CO bridge is also unsatisfactory in terms of charge distribution, since it places a full formal negative charge on the Co atom. According to Cotton, the semibridging CO group acts to mitigate the charge imbalance through electron density transfer from a filled Fe d orbital to an empty π^* orbital of the semibridging CO group (which is principally bonded to the Co atom). A complementary view is to assume that the two electrons donated by the semibridging CO group are (somehow) partitioned between the Fe (δ) and Co ($2-\delta$) atoms; for $\delta = 0.5$, the charge would be equally spread about the metal atoms.

Following this complementary but fully equivalent point of view, we propose in this paper a quantitative formulation of Cotton's qualitative arguments, that is, a partition, between the adjacent metal atoms, of the electrons donated by a carbonyl ligand. This allows (i) the quantification of the electron flux associated with the bending of CO ligands, (ii) the assignment of the proper formal charge to each metal atom, and (iii) the inclusion in our MM force field for metal carbonyl clusters[21] of a force accounting for the tendency of the formal charges to smear and of the metal atoms to fulfill their "ideal" effective atomic number (EAN).

Molecular Mechanics of Metal Carbonyl Clusters

The Need for Control of Local Electron Bookkeeping. We have shown previously[21] that, as long as metal carbonyls are modeled within the local connectivity approach, by considering explicitly the 1,3-nonbonded interactions[26] and avoiding any assumption regarding the C−M−C (and torsional) angles, the major contribution to the computed steric energies arises from the nonbonding interactions.[27] As a consequence, we were able

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(13) Johnson, B. F. G. *J. Chem. Soc., Chem. Commun.* **1976**, 211.

(14) (a) Benfield, R. E.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1980**, 1743. (b) Johnson, B. F. G.; Benfield, R. E. *Top. Stereochem.* **1981**, *12*, 253.

(15) The best ligand polyhedra were determined (and ranked) using a "point on a sphere" repulsion model.

(16) Johnson, B. F. G.; Roberts, Y. V. *Polyhedron* **1993**, *12*, 977.

(17) (a) Clare, B. W.; Favas, M. C.; Kepert, D. L.; May, A. S. In *Advances in Dynamic Stereochemistry*; Gielen, M. F., Ed.; Freund Publishing House Ltd.: London, 1985, p 1. (b) Clare, B. W.; Favas, M. C.; Kepert, D. L.; May, A. S.; Taylor, N. R. *J. Organomet. Chem.* **1994**, *478*, 111.

(18) Horwitz, C. P.; Holt, E. M.; Shriver, D. F. *Inorg. Chem.* **1984**, *23*, 2491.

(19) Lauher, J. W. *J. Am. Chem. Soc.* **1986**, *108*, 1521.

(20) Lauher has realized a rather unsophisticated program which alternates direct search with Newton−Raphson energy minimization and constrains the metal framework to rigidity.

(21) Sironi, A. *Inorg. Chem.* **1992**, *31*, 2467.

(22) Allinger, N. L.; Yuh, Y. H. *QCPE* **1987**. Program No. 395.

(23) The metal framework can be optimized together with the ligand geometry, symmetry constraints can be imposed, and the cluster stereochemistry can be straightforwardly studied in the presence of other "organic" ligands.

(24) Cotton recognized the existence of two broad classes of unsymmetrical bridging carbonyl groups: *compensating sets*, which are distributed in a cyclic fashion over two or more equivalent metal atoms, and *semibridging carbonyl groups*, which connect nonequivalent metal atoms.

(25) Chin, H. B.; Smith, M. B.; Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1974**, *96*, 5285.

(26) (a) Hambley, T. W.; Hawkins, C. J.; Palmer, J. A.; Snow, M. R. *Aust. J. Chem.* **1981**, *34*, 45. (b) Ferguson, D. M.; Raber, D. J. *J. Comput. Chem.* **1990**, *11*, 1061.

(27) The valence forces maintain the carbonyl ligands on the EPS without a substantial contribution to the steric energy because of the lack of bending and torsional terms. Moreover, the globularity of many carbonyl clusters makes dipolar interactions rather insensitive to the CO geometry.

to model a carbonyl cluster *as if it were under the influence of the (intramolecular) van der Waals forces only*[28] and, by comparison between modeled and experimental structures, to verify whether or not intramolecular steric interactions are the predominant factor affecting carbonyl ligands in the choice of their local coordination geometry. The analysis of octahedral metal carbonyl cluster stereogeometries has clearly shown that "real" structures are only occasionally found in the global minimum of the "steric" PES; more frequently they are close to a local minimum if not somewhere along the valley connecting a minimum to a saddle point. Accordingly, *intramolecular steric interactions were recognized not to be the leading term in determining BCMC stereogeometries.*

This implies the presence of "other" forces at work which should be added to the force field in order to enhance the performances of the MM approach. In particular, we think that the most important improvement to the force field will arise from the parametrization of the electron flow correlated to the floating of the carbonyl ligands on the EPS. In a conventional MM study, the connectivity of the atoms is exactly defined (and it is not allowed to change during the minimization), and as a consequence, the number of valence electrons of each atom is also strictly controlled. On the contrary, within the EPS formalism, allowing for a variable connectivity of the metals, we lose the control of the local number of valence electrons on each metal center. This is the major pitfall of the EPS approach, and we think that *it is chemically sound to allow for a variable M−CO connectivity only if a new component of the force field accounts for the tendency of a homogeneous spreading of valence electrons.* Indeed, the smearing of valence electrons is not ensured by the best steric disposition of the ligands, particularly when one is dealing with mixed-metal clusters.

A "Bond Valence" Approach to Local Electron Bookkeeping in Metal Carbonyl Clusters. A μ_n carbonyl ligand ($n = 1-3$), when symmetrically bound to n metal atoms, donates $2/n$ electrons to each metal. However, in all the intermediate (semibridging) situations, the number of electrons donated by a CO ligand to each bonded metal has not yet been defined. We propose to use the "bond valence" method for partitioning the two electrons donated by a (η^1-C) carbonyl ligand between each metal of the cluster.

The so called *valence sum rule*,[29] which is closely related to Pauling's electrostatic valence rule,[30] states that the sum of bond valence (v_{ij}) at each atom (i) is equal to its atomic valence (V_i)

$$\sum_j v_{ij} = V_i$$

(the sum being extended to all the atoms j bonded to atoms i). The most commonly adopted empirical expression correlating bond length (d_{ij}) with bond valence is

$$v_{ij} = \exp[(D_{\text{ref}} - d_{ij})/b]$$

where b is commonly taken to be a "universal" constant equal to 0.37 Å,[31] even if, in his pioneering discussion of C−C bonds, Pauling used a value of $b = 0.31$.[32] The parameter D_{ref}, in a formal sense, is the length of a single bond.

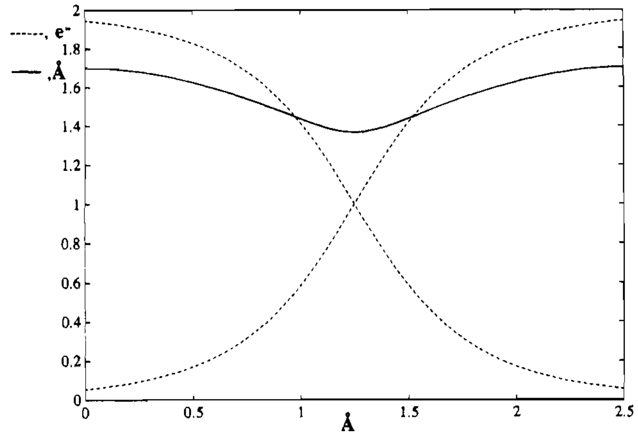

Figure 2. Continous line: terminal/μ_2/terminal carbon atom reaction path computed according to formulas 1a and 1b of ref 21 (using M−M, M−C_t, and M−$C_{\mu 2}$ values of 2.50, 1.70, and 1.85 Å, respectively; the metal atoms are in the bottom corners). Dashed lines: electrons donated by the CO ligand to the metals along the terminal/μ_2/terminal reaction path, according to the proposed "bond valence" partition. Note that the dashed lines do not reach 0.0 and 2.0; that is, even a terminal CO ligand donates a small fraction of its valence electrons to the adjacent metals.

In the case of a carbonyl bound to a cluster, we may assume $D_{\text{ref}} = R_{\mu 2}$ ($R_{\mu 2}$ being the reference M−$C_{\mu 2}$ bond distance) and that the following relation should roughly hold for each carbon atom

$$\sum_j \exp[(R_{\mu 2} - d_{ij})/b] = K_i \approx \text{constant}$$

(the sum being extended to all the metals j adjacent to the carbon i). K_i is not constant since ν_{CO} depends on the CO coordination mode; accordingly, the EPS is not an "M−C isovalent surface". However, we are interested only in the partitioning of valence electrons and not in a detailed correlation of M−CO bond distances; therefore, we can use K_i as a normalization factor and assume that the electrons (e_{ij}) donated by carbonyl i to the metal j are

$$e_{ij} = 2(\exp[(R_{\mu 2} - d_{ij})/b])/K_i$$

The following will obviously hold:

$$\sum_j e_{ij} = 2$$

Within this electron partition scheme, all the nearby metals are considered to interact with a given carbon atom; hence, even "true" terminal CO ligands appear to donate a small fraction of their valence electrons to the adjacent metals, as shown in Figure 2. Apart from any physical meaning (which will not be discussed here), this will be a useful feature of the model, as we shall see later.

Local Formal Charge Equalization. At the beginning of the 1970s, it became apparent that the structures of transition metal and main group clusters could be described in terms of a set of electron-counting rules, analogous to those developed for mononuclear compounds, which, given the shape of the metal cage, permitted the prediction of the number of cluster valence electrons (CVE). In the case of BCMC, the CVE number is simply computed from the relation

$$\text{CVE} = E + E_{\text{C}} - Q$$

where E is the number of electrons deriving from the metal, E_{C}

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[28] In other words, BCMC's stereochemistry has been modeled as being determined by the packing of ligands around the surface of the metal core, rather than by the sum of the structures about the individual metal atoms.

[29] Brown, I. D. In *Structure and Bonding in Crystals*; O'Keeffe, M., Navrotsky, A., Eds.; Academic: New York, 1981; Vol. 2, p 1.

[30] Pauling, L. *J. Am. Chem. Soc.* **1929**, *51*, 1010.

[31] Brown, L. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

[32] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell: Ithaca, NY, 1960.

is the number of electrons donated by the carbonyl ligands, and Q is the charge of the cluster.

Stable metal clusters require, however, not only an opportune CVE number but also a similar number of local valence electrons (LVE) on each metal center. *The CVE number strongly determines the stoichiometry and the cluster shape. On the contrary, the correct LVE distribution influences the ligand conformation.* The number of LVE of metal j can be computed as follows

$$\mathrm{LVE}_j = E_j + E_{j\mathrm{M}} + E_{j\mathrm{C}} - Q_j \qquad (1)$$

where E_j is the number of electrons of the metal, $E_{j\mathrm{M}}$ is the number of electrons obtained from the M$-$M bonds, $E_{j\mathrm{C}}$ is the number of electrons donated by the M$-$C bonds, and Q_j is the local charge. Obviously

$$\sum_j E_j = E; \quad \sum_j E_{j\mathrm{C}} = E_{\mathrm{C}}; \quad \sum_j Q_j = Q$$

In order to normalize the average LVE count to 18 electrons, we assume that the formal number of electrons shared in a M$-$M bond is $a = (18N - \mathrm{CVE})/n_{\mathrm{M}}$ (N is the number of metals, and n_{M} the number of M$-$M bonds, as determined from the connectivity). a normally has a value close to 2, and it is exactly equal to 2 electrons when the cluster follows the EAN rule. On each metal center, $E_{j\mathrm{M}} = an_{j\mathrm{M}}/2$ ($n_{j\mathrm{M}}$ is the number of M$_j$$-$M bonds). Obviously

$$\sum_j E_{j\mathrm{M}} = an_{\mathrm{M}}; \quad \sum_j \mathrm{LVE}_j = 18N$$

Now the average LVE number is 18 and we know how to compute $E_{j\mathrm{M}}$ and $E_{j\mathrm{C}}$ (from the electron partition scheme of the previous section); hence we may use eq 1 for defining (and computing Q_j

$$Q_j = E_j + E_{j\mathrm{M}} + E_{j\mathrm{C}} - 18$$

which we call *formal local charge* and, as follows from the above equation, is *the charge a metal would have in order to reach the average LVE count* (18).

Note that LVE$_j$ and Q_j are correlated.[33] This implies that the tendency to charge equalization and that to equidistribution to the valence electrons will appear as a unique effect.

These formal local charges are not "true" charges; i.e., they do not interact through Coulomb's law, but rather they are only a mathematical device for taking into account the local valence electron distribution. Now, because we know experimentally the validity of Pauling's electroneutrality principle, we assume the following energy expression as a new component of our force field

$$E_{\mathrm{lc}} = \sum_j K_{\mathrm{lc}}(Q_j - Q_{\mathrm{av}})^2$$

where E_{lc} is the energy associated with a particular local charge distribution, K_{lc} a force constant (here tentatively 3.0 kcal/(mol e^2), and Q_{av} the average charge per metal atom. E_{lc} is a nonnegative quantity having a minimum for a totally delocalized ($Q_j = Q_{\mathrm{av}}$, for all j) formal local charge. Moreover, because E_{lc} is defined with respect to Q_{av}, it will be possible to compare relative energies of charged and uncharged species.

Table 1

Stretching and Bending Parameters

K$_s$ surface$-$C	3.0 mdyn/Å	K$_b$ surface$-$C$-$O	0.05 mdyn/deg
K$_s$ C$-$O	12.0 mdyn/Å	cubic stretch term	$-$2.0 mdyn/Å^2
K$_s$ M$-$M	2.0 mdyn/Å		

Charge Interaction Parameters

CO dipole moment	0.552 D[a]	dielectric constant	1.5

Bond Length Parameters (Å)[b]

metal	R_{M}	M$-$C$_{\mathrm{t}}$	M$-$C$_{\mu2}$	M$-$C$_{\mu3}$
Ni	1.20	1.771	1.882	1.931
Co	1.25	1.780	1.914	1.950
Fe	1.30	1.782	1.941	2.002
Mn	1.35	1.808	1.940	2.09
Cr	1.40	1.866	2.00	2.15
V	1.45	1.946	2.05	2.20
Ru	1.45	1.896	2.072	2.171
Rh	1.40	1.847	2.040	2.170
Re	1.50	1.936	2.073	2.20
Os	1.45	1.902	2.081	2.20
Ir	1.40	1.870	2.065	2.15
Pt	1.35	1.853	2.044	2.10

[a] Corresponding to a charge separation of 0.1e at 1.15 Å. [b] The values reported with three figures are from ref 35.

Computational Details. All the computations have been made with the MM3 program,[34] adapted for dealing with metal carbonyls as was previously carried out for MM2.[21] The adopted force field parameters are reported in Table 1. They are the parameters of the usual stretching, bending, and dipole$-$dipole interaction equations adopted in MM3. The reported M$-$C reference values, which are used to compute the EPS, concern terminal and symmetric bridging (μ_2 and μ_3) carbonyl ligands and have been mainly taken from the compilations of organometallic bond distances given by Orpen *et al.*[35] Note that in the minimum energy conformation the M$-$C interactions are normally 0.02$-$0.03 Å longer than the chosen reference values. In fact, the optimized geometry is a compromise between different effects and, in particular, the 1.3 vdW interactions actuate an inflation of the molecule. As a matter of personal choice, the reported M$-$C values in Table 1 are those found in the literature but the program will automatically use values 0.02 Å shorter in order to obtain optimized geometries closer to reality.

The computed energies have little meaning outside the context of the present paper and should be used only to compare different conformers. This is not a serious limitation because the term "conformer", within the EPS formalism, is comprehensive also of all the stereoisomers which, differing in metal$-$carbonyl connectivity, would normally be considered *constitutional isomers*. Hereafter we will attribute essentially the same meaning to the terms "conformer" and "isomer", and we will use them, indifferently, to address different stereogeometries of the M$_m$(CO)$_n$ manifold.

As previously stated, it is possible to deal with "normal" and locally connected ligands at the same time. In the following computations, for instance, we will consider metal carbonyl clusters containing cyclopentadienyls (Cp) or 2,2′-bipyridyl as extra ligands. It is not the aim of the present study to parametrize ligands other than CO. We have roughly assumed a M$-$C reference bond distance for Cp close to that found experimentally in the species to be modeled and a M$-$C force constant of 1.0 mdyn/Å. On the contrary, 2,2′-bipyridyl has

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(33) A local deficit of valence electrons (LVE$_j$ < 18) appears as a negative local charge (if the cluster is neutral).

(34) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551.

(35) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

been treated as a free organic molecule constrained into the experimental conformation by restraining the coordinates of the two Fe atoms and the N−C−C−N moiety. In this way, the only bipyridyl/metal-cluster interactions are the nonbonding ones and all eventual "electronic" interactions are not considered. Note, however, that in order to compute formal local charges, these ligands have been considered to donate five and four σ valence electrons, respectively.

Results and Discussion

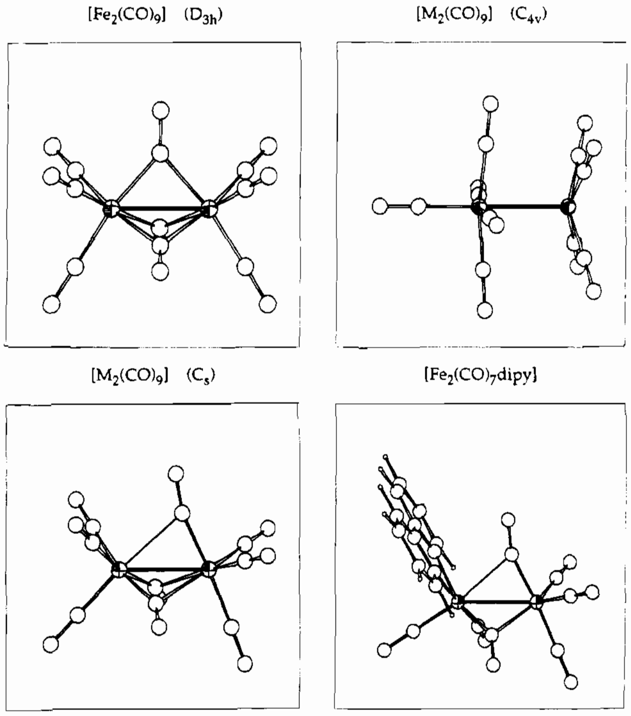
We will discuss a few simple examples where local charge equalization plays a significant role in order to test the performance of our approach. We will only demonstrate the ability of the model to correctly reproduce the essential geometrical features of such molecules. However, we think that the relative energies of the different conformers should also be meaningful; hence our computations could be useful in the interpretation of dynamic behavior.

$[FeCo(CO)_8]^-$. The structure of $[FeCo(CO)_8]^-$,[25] of idealized C_s symmetry, is closely related to that of the lowest energy $M_2(CO)_8$ isomer (which has D_{2d} symmetry) but does not correspond to a minimum of the PES computed *via* steric forces alone.[36] As a matter of fact, the sterically favored D_{2d} structure, when the metals contribute different numbers of valence electrons, is highly polarized and some proper distortion must occur in order to partially quench charge polarization (Figure 1).

The addition to the force field of the local charge component E_{lc} makes the absolute minimum of the PES close to the experimental structure. However, this is not enough to correctly reproduce the solid state structures of $Co_2(CO)_8$,[37] $[Ru_2(CO)_8]^{2-}$,[38] and $[RuFe(CO)_8]^{2-}$.[39] This can be considered, rather than a pitfall of the method, an indication that packing effects and/or the tendency of certain metals for a definite local ligand stereogeometry can be relevant in determining the actual geometry of a given carbonyl cluster. Work is in progress in order to deal with such aspects of BCMC's stereochemistry.[40,41]

$Fe_2(CO)_9$. The most relevant $M_2(CO)_9$ stereogeometries are reported in Figure 3. When steric forces alone are taken into account, the low-energy conformer has C_{4v} symmetry and a really odd distribution of valence electrons. The introduction of E_{lc} favors a C_s conformer, with one heavily and two slightly asymmetric (semi)bridging CO's, which is closely related to the experimental structure of D_{3h} symmetry,[42] with three symmetric μ-CO's. The relative energies of the different conformers depend upon the geometrical reference values chosen for the Fe−C and Fe−Fe bond distances (see Table 2). In particular, when the experimental data for $Fe_2(CO)_9$[42] are used, the minimized D_{3h} and C_s conformers become closer in energy (and shape). Since the use of the actual experimental bond distances favors the observed $Fe_2(CO)_9$ conformation, we think that the present force field can be further improved by introducing some *general* dependence of the M−C and M−M interactions on the actual local geometry into each metal center. It is well-known, for instance, that CO-bridged M−M bond lengths are systematically shorter than the unbridged ones[43] and that M−CO interactions *trans* to an M−M bond are shorter than those *trans* to an M−CO bond.

The conformation of the C_s isomer is also closely related to that of $Fe_2(CO)_7(2,2'$-bipyridyl), where one of the two slightly


$[Fe_2(CO)_9]$ (D_{3h})

$[M_2(CO)_9]$ (C_{4v})

$[M_2(CO)_9]$ (C_s)

$[Fe_2(CO)_7dipy]$

Figure 3. $Fe_2(CO)_9$ and related stereoisomers.

Table 2. Steric Energies (kcal mol^{-1}) of Selected Stereoisomers[a]

isomer	E_{ster}	E^*_{ster}	E_{lc}
$[Fe_2(CO)_9]$, C_{4v}	28.8	24.7	4.1
	23.6[b]	19.8[b]	3.8[b]
$[Fe_2(CO)_9]$, D_{3h}	29.5	29.5	0.0
	21.9[b]	21.9[b]	0.0[b]
$[Fe_2(CO)_9]$, C_s	26.3	26.1	0.2
	21.1[b]	20.9[b]	0.2[b]
$[V_2Cp_2(CO)_5]$, C_s	10.3	10.1	0.2
$[V_2Cp_2(CO)_5]$, *cis* C_{2v}	24.8	24.8	0.0
$[V_2Cp_2(CO)_5]$, *trans* C_s	19.6	19.6	0.0
$[Fe_3(CO)_{11}]^{2-}$, A	24.3	24.3	0.04
$[Fe_3(CO)_{11}]^{2-}$, B	25.2	23.9	1.3
$[Fe_3(CO)_{11}]^{2-}$, C	26.6	26.6	0.0

[a] E_{ster} is the total steric energy; E_{lc} is the energy due to the local charge distribution; $E^*_{ster} = E_{ster} - E_{lc}$. [b] Energy-minimized using Fe−C and Fe−Fe reference values equal to those found in $[Fe_2(CO)_9]$.[42]

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(36) Lauher, in order to force the calculation toward the experimental stereogeometry, had to constrain the Fe−Co−C angle of the semibridging carbonyl group to its experimental value.[19]

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(40) The tendency for a definite stereochemistry about a selected metal atom can be partially restored by considering explicitly the proper C−M−C bending interactions. The geometric preferences expressed by such bending interactions will smoothly add to those of the EPS even if some care is needed because of the strong correlation between bending and 1,3 interactions. In fact, within the local connectivity approach, the shape of the EPS is controlled by a careful use of M−C and M−C−O interactions while the local geometry on each metal center is controlled by the 1,3 interactions only.

(41) Minimization of the molecular conformation within the crystal lattice is presently under implementation: Sironi, A.; Moret, M. To be published.

(42) Cotton, F. A.; Troup, J. M. *J. Chem. Soc., Dalton Trans.* **1974**, 800.

(43) $[Fe_4(CO)_{13}]^{2-}$ for instance has been characterized either as the hexakis(pyridine)iron(II) salt or as the PPN$^+$ salt.[1] The stereochemistries of the anions in the two different salts differ mainly in the degree of semibridging of three equatorial CO ligands in the basal plane. In the hexakis(pyridine)iron(II) salt, where the CO's are strongly semibridging, the (bridged) Fe−Fe bonds are 2.50 Å long, while in the PPN$^+$ salt, where the CO's are only weakly semibridging, the corresponding Fe−Fe bonds are 2.55 Å long.

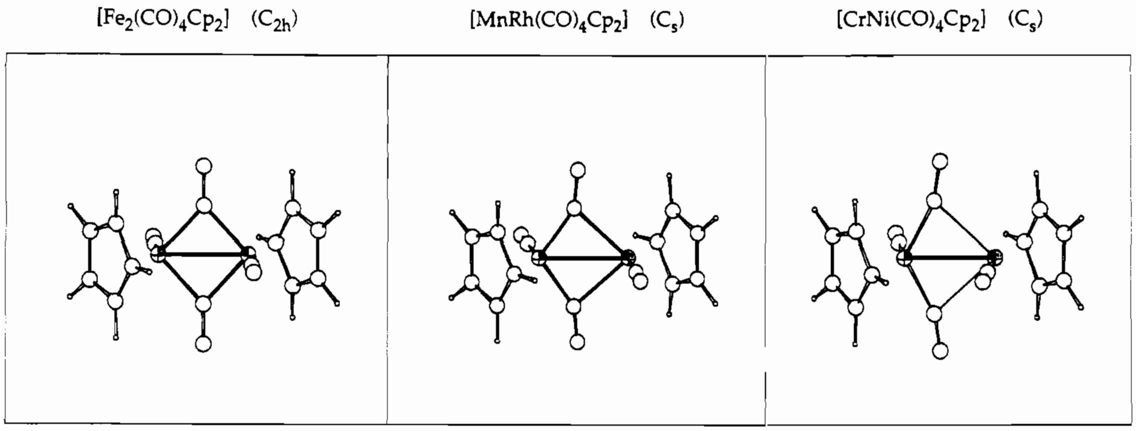

Figure 4. The structures of *trans*-$MM'(CO)_4(Cp)_2$ complexes.

semibridging CO's has become almost terminal.[44] The experimental structure of $Fe_2(CO)_7$(2,2′-bipyridyl) is reproduced well in the present computations by altering the formal bookkeeping of σ electrons on the Fe atom which carries the bipyridyl ligand, *i.e.* by considering such a ligand to contribute 3.4 rather than 4 electrons. This procedure, even if a little anomalous, is only a short cut for considering a ligand which, being less π acidic than CO, does not dissipate efficiently the excess of σ electrons (*i.e* allows a buildup of negative local charge) through $d \rightarrow \pi^*$ interactions. In fact, as stated above, LVE_j and Q_j correlate and a local deficit of valence electrons ($LVE_j < 18$) appears as a negative local charge (if the cluster is neutral).

$M_2(CO)_{10}$. Most $M_2(CO)_{10}$ derivatives are built up from two staggered $M(CO)_5$ fragments and have an idealized D_{4d} symmetry. Such a conformation is the low-energy one, and the only relevant stereochemical feature to discuss here is the value of the $M-M-C_{eq}$ angle. The bending of the equatorial CO ligands toward the adjacent metal atom has been rationalized by Bau *et al.* in terms of long-range $d \rightarrow \pi^*$ interactions.[45] They have clearly shown that such bending cannot be due to steric repulsions alone. In the present computations, since we allow the $M-C_{ax}$ to be substantially shorter than the $M-C_{eq}$ distances (as is experimentally found), we partially account (on steric grounds) for the bending but we still cannot handle the small attractions due to long range $d \rightarrow \pi^*$ interactions (e).[46] Accordingly, in the case of $[Cr_2(CO)_{10}]^{2-}$, we foresee $M-M-C_{eq}$ angles (87.0°) larger than those found experimentally (average value 85.5°).[47] It is, however, rewarding to analyze $CrOs(CO)_{10}$, where the different numbers of electrons contributed by the two metal atoms determine an uneven distribution of the formal local charge. In fact, the current view about $CrOs(CO)_{10}$ assumes the presence of a dative (semipolar) $(CO)_5Os \rightarrow Cr(CO)_5$ bond which determines the presence of a formal charge of $+1$ and -1 on the Os and Cr atoms, respectively. The structure of $CrOs(CO)_{10}$ has not yet been determined; however, Pomeroy and co-workers have extensively studied complexes with unbridged dative bonds between osmium and a group 6 element. They have invariably found that there is an inward leaning of the equatorial CO's on the donor half of the molecule ($M-Os-C_{eq} < 90°$) while such inward leaning is not present in the equatorial carbonyls of the acceptor half of the molecule ($Os-M-C_{eq}$ = ca. 90°).[48] This feature is well reproduced by our computations even if we do account only for the charge transfer and not for the net attraction due to long-range $d \rightarrow \pi^*$ interactions.[46] Accordingly, we compute $Cr-Os-C_{eq}$ and $Os-Cr-C_{eq}$ angles of 85.7 and 88.5°, respectively, to be compared, for instance, with those found in $(Me_3P)(CO)_4OsCr(CO)_5$, which average to 84.1 and 89.2°, respectively.[49]

Table 3. Comparison between Calculated and (Observed) Local Geometries of Bridging Carbonyl ligands in *trans*-$MM'(CO)_4Cp_2$

	FeFe	MnRh	CrNi
$M-C_{\mu 2}$, Å	1.94 (1.92)	1.85 (1.87)	1.88 (1.88)
$M'-C_{\mu 2}$, Å	1.94 (1.92)	2.24 (2.17)	2.45 (2.43)
$M-C_{\mu 2}-O$, deg	137 (138)	150 (153)	161 (168)
$M'-C_{\mu 2}-O$, deg	137 (138)	126 (123)	124 (118)
local charges, *e*	0/0	$-0.19/+0.19$	$-0.46/+0.46$

$MM'(CO)_4Cp_2$. In Figure 4 the structures of *trans*-$MM'(CO)_4Cp_2$ for the couples of metal atoms Fe/Fe,[50] Mn/Rh,[51] and Cr/Ni[52] are reported. The major stereochemical change, on varying the relative number of the electrons contributed by the metals, is the polarization of the two μ_2-bridging CO's toward the most electron-demanding metal. This feature is reproduced well in our computations (Table 3). According to conventional electron bookkeeping, there is a normal covalent bonding (between two 17-electron fragments) in the Fe/Fe and Cr/Ni derivatives while, in the Mn/Rh one, the 18-electron $MnCp(CO)_3$ fragment is supposed to donate an electron pair datively to the 16-electron RhCp(CO) fragment. The close relationship between dative bonding and semibridging carbonyls has been discussed previously by others,[53] and apparently, in the Mn/Rh derivative bonding takes place through the semibridging carbonyls with little net metal−metal interaction. Electron bookkeeping techniques, in spite of having little in common with the "true" quantomechanical description of bonds, satisfy the fundamental need of the chemist to make the most reasonable predictions using the simplest model of their realm. Chemically, a 34-CVE count is normally associated with stable dimeric

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(46) Since local charges might originate from long-range $d \rightarrow \pi^*$ interactions, we implicitly handle the "asymmetric" part of $d \rightarrow \pi^*$ interactions. However, the concerted bending of a group of CO ligands (a compensating set in Cotton's terminology) does not afford any charge separation (as in $[Cr_2(CO)_{10}]^{2-}$) and is not accounted for by the local charge approach.

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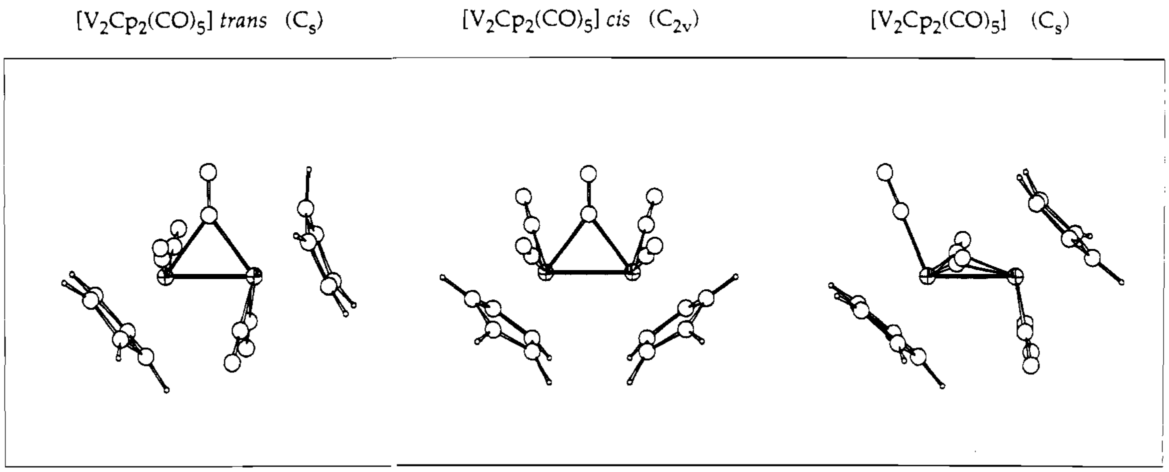

Figure 5. Three different stereoisomers of $V_2(CO)_5(Cp)_2$.

Table 4. Comparison between Calculated and (Observed) Local Geometries of Bridging Carbonyl Ligands

$V_2(CO)_5(Cp)_2$ (Symmetry Idealized to C_s)[a]		
metal	V−C, Å	V−C−O, deg
V1	1.95 (1.94)	163 (169)
V2	2.42 (2.42)	129 (123)
$[Fe_3(CO)_{11}]^{2-}$		
metal	Fe−C, Å	Fe−C−O, deg
Fe1,μ_3C	1.86 (1.85)	143 (143)
Fe2,μ_3C	2.20 (2.21)	127 (129)
Fe1,μ_2C	2.83 (2.72)	137 (135)
Fe2,μ_2C	1.94 (1.96)	136 (138)

[a] Local charges, *e*: V1, +0.18; V2, −0.18; Fe1, −0.76 (−0.092 below Q_{av}); Fe2, −0.62 (+0.046 above Q_{av}).

species, and this is rationalized *a posteriori* by "assuming" the sharing of two electrons through a M−M bond. This is also the only assumption made in the computation of local charges (apart from the normalizing factor *a*) and, *inter alia*, local charges do not rely on the distinction between dative and covalent bonds.

In the light of the computed local charges for the minimized structures, it clearly follows that steric forces favor the most symmetric C_{2h} conformation while the smearing of the local charges favors the maximization of the M−CO connectivity with the most electron-demanding metal. The competition between these two effects results from the fact that in the minimized structures the metal atoms are not formally neutral. According to the agreement between experimental and modeled geometries, the blending between steric and electronic factors in our model appears to be reasonably well parametrized.

$V_2(CO)_5(Cp)_2$. $[V_2(CO)_5(Cp)_2]$ was one of Cotton's key compounds in his dissertation about charge equalization.[7] The minimum-energy conformer has C_s symmetry and an overall stereogeometry fairly close to the experimental one (Figure 5 and Table 4). This confirms both Cotton's original qualitative arguments (the $V(CO)_3(Cp)$ fragment is datively bonded to the $V(CO)_2(Cp)$ one and the two semibridging μ_2-CO's occur in order to dissipate the negative charge accumulated on the latter fragment) and the present, more quantitative, formulation (the two semibridging μ_2-CO's donate *ca.* 3 electrons to the closer V atom and *ca.* 1 electron to the other one). Moreover, because we may minimize the steric energy of different stereoisomers, such as the *trans*-C_s and *cis*-C_{2v} reported in Figure 5, by imposing either a symmetric μ_2-CO and/or a different symmetry, we now understand why these conceivable isomers are avoided. Indeed, even if they offer a perfect solution to the smearing of the local charge, they are intrinsically unstable on steric grounds (Table 2).

$[Fe_3(CO)_{11}]^{2-}$. It was proposed in 1959 that the $[Fe_3(CO)_{11}]^{2-}$ dianion is composed of a triangular array of $Fe(CO)_3$ fragments which are coordinated to one another by two μ_3-CO ligands in addition to the M−M bonds (Figure 6B).[54] However, a successive crystal structure analysis of the $[NEt_4]^+$ salt showed that the cluster possesses a symmetric μ_2-CO, a semibridging μ_3-CO, and (crystallographically imposed) C_s symmetry (Figure 6A).[55] On the other hand, a third isomer can be derived from this latter one by transforming the semibridging μ_3-CO into an axial CO of a C_{2v}-$Fe(CO)_4$ fragment (Figure 6C). The agreement between the minimum-energy isomer (A) and the experimental geometry is fairly good (Table 4). Moreover, the present computations show that the isomer with two μ_3-CO group (B), in spite of the perfect smearing of charges, is destabilized on steric grounds having a steric energy 2.3 kcal mol^{-1} above the global minimum. The third isomer (C), where all the three Fe atoms reach the closed-shell requirements when the two charges are localized on the two Fe atoms carrying the μ_2-CO group, has an unfavorable charge distribution (−0.14, −0.93, −0.93) and accordingly has a steric energy 0.9 kcal mol^{-1} above the global minimum, the local charge contribution being 1.3 kcal mol^{-1}.

Conclusions

It is intrinsic to molecular mechanics to express the total steric energy as a sum of different contributions (*i.e.*, the various force field components); as a consequence, minimum-energy structures are, by definition, those realizing the better compromise between different tendencies. We have modeled carbonyl clusters as if they were under the influence of (mainly) three different forces: (i) valence forces, constraining the CO to float on the EPS surface maintaining the CO vector approximately perpendicular to the surface; (ii) van der Waals interactions, conveying both the (few) strong repulsion responsible for nonpenetrability of bodies and the (many) weakly attractive interactions; (iii) local charge interactions, addressing the fulfillment of the local electron bookkeeping but also favoring the conformations associated with the better spread of the total charge on the cluster.

Local charge effects favor the crowding of ligands around electron-poor centers and are particularly evident in the realm

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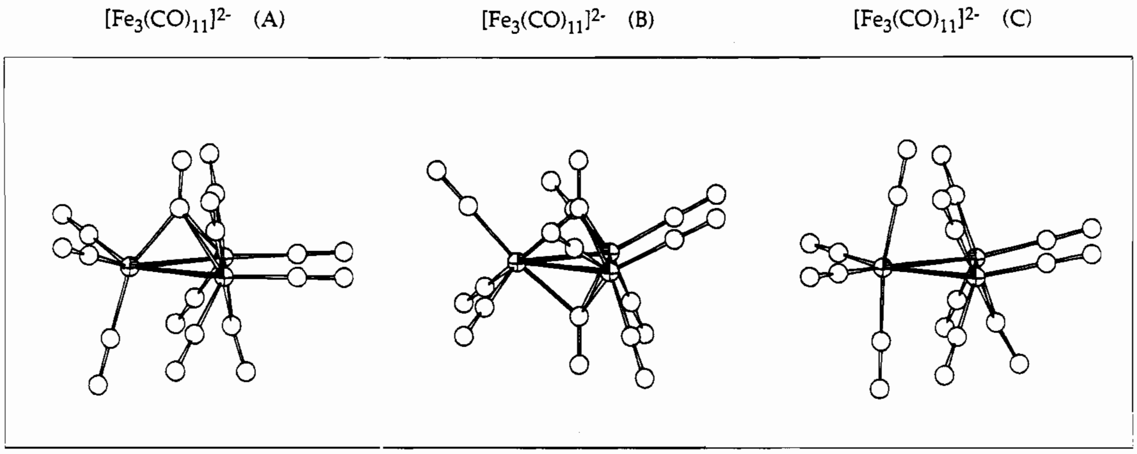
$[Fe_3(CO)_{11}]^{2-}$ (A) $[Fe_3(CO)_{11}]^{2-}$ (B) $[Fe_3(CO)_{11}]^{2-}$ (C)

Figure 6. Three different stereoisomers of $[Fe_3(CO)_{11}]^{2-}$.

of heteronuclear BCMC (such as $[FeCo(CO)_8]^-$) and/or in the presence of ligands "isosteric" with CO but carrying a different charge (CN^-) or donating a different number of electrons (NO).[21] However, even for homonuclear BCMC, there are situations where steric and local charge effects conflict because the best steric conformation of carbonyl ligands does not correspond to a reasonable distribution of local valence electrons and/or charges (as in $Fe_2(CO)_9$ and $[Fe_3(CO)_{11}]^{2-}$).

It has been straightforward to consider ligands with a definite connectivity pattern and locally connected CO's together. In spite of the rough parametrization of the Cp ligand, we have correctly reproduced the experimental $V_2(CO)_5(Cp)_2$ stereochemistry and, remarkably, we have been able to dismiss for steric reasons the alternative *trans*-C_s and *cis*-C_{2v} isomers, even if they offer a perfect solution to the smearing of the local charge, quantifying and extending Cotton's description of this system.

The EPS approach, implying that all the carbonyls feel the same (metal-centered) potential in all the surface points, is the quantitative formulation of the kernel of Johnson's LPM: the freedom of carbonyls about the metal cage or, the other way round, the freedom of the metal cage to librate within the ligand envelope. However, as shown earlier for octahedral BCMC[21] and now for a few dimeric species, the stereochemical variability within a given $[M_mM'_{m'}(CO)_n]^{q-}$ class of derivatives cannot be accounted for by intramolecular steric interactions only. From this point of view, LPM, in spite of being very useful in offering a "different" point of view on fluxionality, is inadequate for dealing with the stereochemistry of BCMC. It is only the interplay among many different factors (inter- and intramolecular steric interactions, charge and local bookkeeping equalization, and more specific electronic effects) that determines the real structure.[21] However, the correct blending of the different effects is difficult to reach because, as suggested by many experimental findings,[1-7] the potential energy surface of metal carbonyl clusters is quite soft.

To counterbalance the CO connectivity freedom (intrinsic to the EPS approach) with the control of local valence electrons is a major advance in the task of building a force field for metal carbonyl clusters. However, since the are some more effects in need of being considered (like the intermolecular vdW interactions) or parametrized (like the tendency of certain metals for a definite local ligand stereogeometry), it is still difficult to use MM computations to foresee the correct ligand stereochemistry of BCMC. Steric energies can be, anyway, safely used to justify small distortions around a given geometry or to exclude a particularly crowded stereoisomer.

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