Joint Molecular Mechanics and Atom−Atom Pair Potential Computations on the Solid State Dynamics of [Fe₃(CO)₁₂][1]

Angelo Sironi

Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Via Venezian 21, 20133 Milano, Italy

Elucidation of the solid state and solution structures of $Fe_3(CO)_{12}$ (**1**) has been one of the classic problems of cluster chemistry. An excellent account of the early works is available,[2] but the $Fe_3(CO)_{12}$ "saga" is not yet finished. There is still vigorous debate on its solution fluxionality,[3] solvent-dependent isomeric composition,[4] solid state structure,[5] and solid state dynamics.[3a,6]

At room temperature $Fe_3(CO)_{12}$ has ten terminal CO's and two "compensating"[7] asymmetric μ_2-carbonyls bridging the shortest edge of the iron triangle. The molecule has idealized C_2 symmetry (stereoisomer **A** in Figure 1), and it is orientationally disordered about a crystallographic center of symmetry. Variable-temperature magic-angle-spinning ^{13}C NMR shows that $Fe_3(CO)_{12}$ undergoes a dynamic process in the solid state, having an estimated activation energy of *ca.* 10 kcal mol^{-1}, which is frozen out at 180 K.[6c] Two different mechanisms have been proposed for rationalizing this solid state behavior: (i) in-plane 60° jumps of the Fe_3 triangle within the ligand envelope;[6a,c,d] (ii) librational motion of the triangle about the pseudo-2-fold axis.[6e,f] In order to justify the observed "anomalous" chemical shifts (for the bridging CO ligands) in the 180 K solid state NMR spectrum, a further dynamic mechanism, still fast at 180 K, has been proposed: (iii) the concerted bridge opening and closing (about all edges) without CO migration.[3a] The above mechanisms have been formulated either (i, ii) within the ligand polyhedral model (LPM),[8] where only the relative motions of the metal cage and of the ligand envelop matter or (iii) by describing the changes of the carbon atom connectivities in detail. These mechanisms are all "topological" in nature and have not been substantiated by computations of the pertinent activation energies ($E^{\ddagger}$'s).
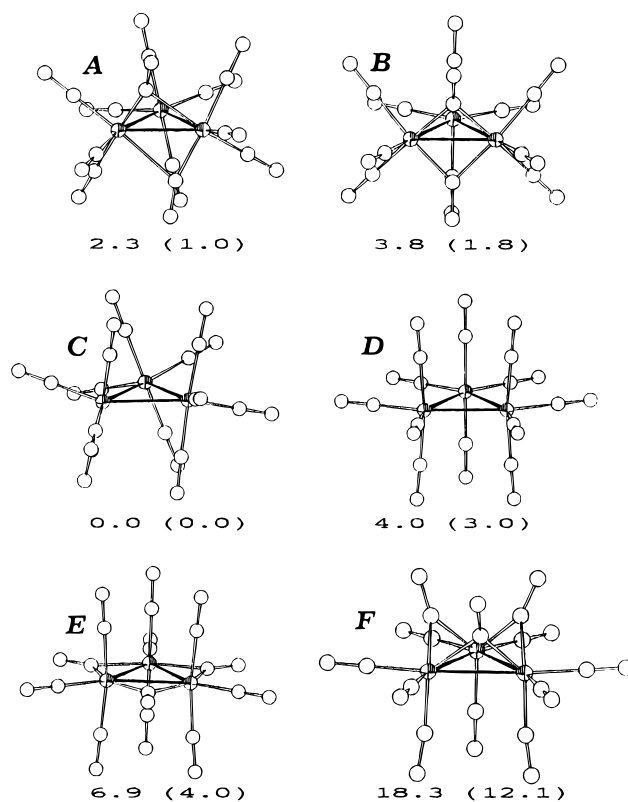

Figure 1. Molecular conformations of the most significant $M_3(CO)_{12}$ (M = Fe, Ru, Os) stereoisomers, minimized with various symmetry constraints: C_2 (**A**), C_{2v} (**B**), D_3 (**C**), D_{3h} (**D**), D_{3h} (**E**), and C_{3v} (**F**). Steric energies (in kcal mol^{-1}), relative to the most stable stereoisomer, are reported for Fe derivatives. The numbers in parentheses refer to Ru derivatives and can also be considered informative for the Os derivatives, given the almost identical sizes of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$.

When steric forces are dominant or all the pertinent electronic interactions are well parametrized in the force field, $E^{\ddagger}$'s can, in principle, be computed with molecular mechanics (MM). Moreover, MM should account for the differences between the solution and solid state dynamics of flexible molecules, even when some "electronic" factors are not well parametrized, since the increased stiffness of molecules in the solid state can be reasonably attributed to the presence of the crystal lattice (*i.e.* to intermolecular steric interactions).

Here we report MM computations on a *flexible* $Fe_3(CO)_{12}$ molecule, surrounded by its pertinent *rigid crystalline environment*, in order to interpret solid state dynamics of the molecule.

Molecular Mechanics of Metal Carbonyl Clusters

Lauher has translated the kernel of LPM into the MM formalism,[8] that is, the freedom of carbonyls to float about the metal cage or, alternatively, the freedom of the metal cage to librate within the ligand envelope.[9]

Lauher's idea of an equal potential surface (EPS) can be easily implemented into a standard MM program, as we have done for the Allinger suite of programs,[10,11] by allowing a variable M−CO connectivity in the so-called local connectivity approach.[12]

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Our computations have clearly led to the conclusion that, **in general**, intramolecular steric interactions are not the leading factor in determining metal carbonyl cluster stereogeometries.[12] This has been further confirmed by showing that the lack of a definite M−CO connectivity, which is intrinsic to the EPS approach, may result in sterically allowed but electronically unreasonable structures.[13] In a conventional MM study, the connectivity of the atoms is exactly defined (and 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, which allows a variable connectivity of the metals, we lose control of the local number of valence electrons on each metal center. As a consequence, the freedom of the carbonyl ligands about the metal cage must be limited with the introduction of a new component of the force field to address the fulfillment of the local electron bookkeeping and favor the conformations associated with the better spread of the total charge.[13]

Osawa has shown how to deal with molecular solids, made of flexible molecules,[14] using a conventional MM program, namely BIGSTRN3.[15] Since MM3 van der Waals parameters are claimed to describe both *intra-* and *inter*molecular interactions correctly,[11c] we have implemented Osawa's approach to Allinger's MM3 program and so are actually able to minimize the conformation of a molecule within a fixed, or periodically updated, crystal lattice.[16]

Computational Details

All the computations were performed with a local version of MM3 upgraded for dealing with carbonyl ligands, in the local connectivity approach,[12] which takes into account formal local charge distribution[13] and, if needed, the crystal lattice.[16] Details on the force field can be found in refs 12 and 13. The actual M−M, M−C_t, and M−C_{μ_2} reference values were 2.680, 1.762, and 1.921 Å, respectively, for M = Fe and 2.850, 1.876, and 2.052, respectively, for M = Ru. The computation made with the Ru parameters can also yield information on the Os derivatives, given the almost identical sizes of $Ru_3(CO)_{12}$[17a] and $Os_3(CO)_{12}$.[18a]

Crystalline $Fe_3(CO)_{12}$ was described in the idealized *ordered $P2_1$* phase with the same lattice parameters of the experimental *disordered $P2_1/n$* phase.[5b] Computations on the related *ordered Pn* phase afforded similar (but not identical) results; for the sake of simplicity, in the following we will limit the discussion to the $P2_1$ phase only. The crystal was simulated by a reference molecule (RM), for which all force field contributions were considered, surrounded by 42 lattice molecules (contained within a sphere of enclosure radius 10 Å), contributing only to the van der Waals packing energy.

Initially, the crystal packing was idealized by (a) starting from the experimental coordinates (for an *ordered* molecule), (b) assigning an arbitrary high force constant to Fe−Fe interactions (in order to force all the Fe−Fe bond lengths as close as possible to 2.68 Å), and (c) reaching the closest steric energy minimum by allowing a correlated deformation of all the molecules in the crystal.

Energy profiles were then computed along three different reaction paths and sampled by stepwise rotation of the Fe_3 triangle of the RM

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Table 1. Stereochemical and Dynamic Data for the $M_3(CO)_{12}$ (M = Fe, Ru, Os) Family

	$Fe_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Os_3(CO)_{12}$
NMR	fluxional down to 123 K[3d] $\Delta G^{\ddagger}_{123}$ < 5.4 kcal mol^{-1}	Solution fluxional down to 173 K[17b] $\Delta G^{\ddagger}_{173}$ < 7.7 kcal mol^{-1}	coalesces at 360 K[17b,18b] $\Delta G^{\ddagger}_{360}$ = 16.5 kcal mol^{-1}
X-ray	stereoisomer **A**[5]	Solid State stereoisomer **E**[17a]	stereoisomer **E**[18a]
NMR	coalesces at 218 K[6c] $\Delta G^{\ddagger}_{218}$ = 10 kcal mol^{-1}	libration of axial carbonyls at 318 K[17c]	rigid at room temperature[18c]

within the ligand envelope. For each point on the energy profiles, the steric energy (molecular plus packing) of the RM was minimized within the limits of a frozen metal frame and a frozen crystal lattice (the starting CO coordinates of the RM being either the experimental ones or those obtained from the minimization of the previous point).

Note that the resulting $E^{\ddagger}$'s are an overestimate of the "true" ones (since neither the molecules surrounding the RM are allowed to relax nor the metal frame allowed to rattle within the ligand cage of the RM) and concern defectual, uncorrelated, processes occurring (randomly) on individual $Fe_3(CO)_{12}$ molecules.

Results and Discussion

MM Computations on Isolated Molecules. The steric energies for many different stereoisomers of the $M_3(CO)_{12}$ (M = Fe, Ru, Os) family have been computed. The results, which parallel those of Lauher,[9] are reported in Figure 1, while Table 1 summarizes a few stereochemical and dynamic features of the family.

Clearly the results presented in Figure 1 do not account for the data in Table 1. In fact, steric energies support the same stereochemistry (**C**) for the whole family, suggest a flatter potential energy hypersurface for the Ru and Os derivatives (rather than for the Fe one), and cannot differentiate between the Ru and Os derivatives (in spite of their different dynamic behavior).[19] However, since the stereochemical variability of $Fe_3(CO)_{12}$ is essentially confined to the limiting structures **A**−**C**, which are very close in energy, and **C** is proposed to be one of the more abundant isomers in many solvents,[3,4] our computations illustrate the nature of $Fe_3(CO)_{12}$ sufficiently well to proceed to the simulations within the crystal lattice.

As suggested by Lauher, simple overlap arguments, not accounted for in his (and our) MM computations, can partially justify the stereochemical choices of the Ru and Os derivatives. In addition, we think that the failure to correctly describe such a simple system is the lack of parametrization of the stereochemical preference of light metals for bridged structures. In fact, as suggested by Evans,[20] the formation of structures containing bridging carbonyls is favored, owing to the greater number of M−L σ-bonds, for the lighter elements because of the more contracted nature of *n*d orbital and the greater (*n*+1)p−*n*d mixing for *n* = 3. This view was recently supported by an extended Hückel fragment molecular orbital analysis showing that bridge formation implies occupation of previously empty,

(19) However, once a particular isomer is assumed to be the correct one, for reasons outside the actual MM parametrization, MM is powerful in foreseeing the principal stereochemical features of the given isomer. In the case of $Ru_3(CO)_{12}$, for instance, MM is able to reproduce the outward bending of the axial MCO angle (174.7° vs 173.0°), the substantial linearity of the equatorial ones (178.8° vs 178.9°), and the actual values of the C_{ax}−M−C_{ax} (173.6° vs 178.3°), C_{eq}−M−C_{eq} (108.6° vs 104.1°), and M−M−C_{eq} (95.7° vs 97.9°) angles.
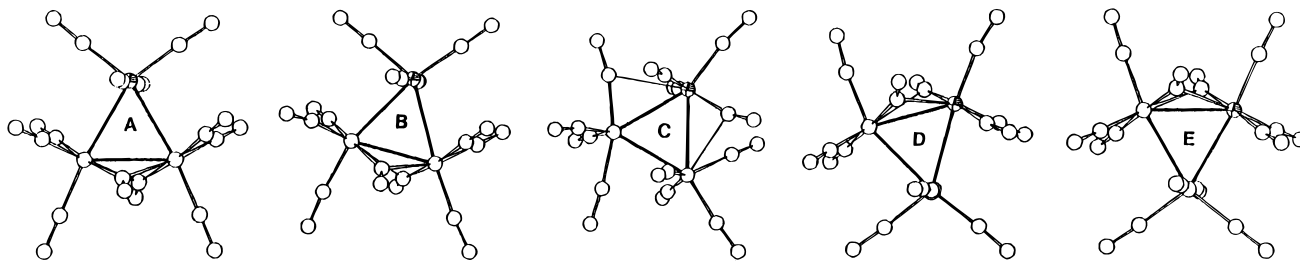(20) Evans, D. G. *J. Chem. Soc., Chem. Commun.* **1993**, 675.

Figure 2. Molecular conformations along reaction path I (rotation of the Fe_3 triangle about its pseudo-3-fold axis) for (A) $\theta = 0°$, (B) $\theta = 15°$, (C) $\theta = 30°$, (D) $\theta = 45°$, and (E) $\theta = 60°$. Fe(1) is highlighted by partial shading.
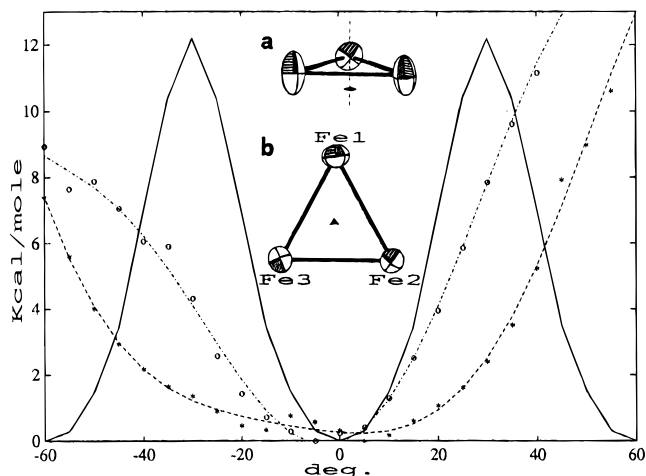

Figure 3. Energy profiles for the selected reaction paths (see text): (I) solid line; (II) stars; and (III) circles. The dashed and dotted lines are polynomial fits to II and III, respectively. Inset: Iron atom atomic displacement parameters (from ref b) in $Fe_3(CO)_{12}$ projected along the pseudo-2-fold axis (a) and the pseudo-3-fold axis (b).

high-energy, orbitals with metal−metal antibonding character which are lowered via interaction with π^* orbitals of the bridging carbonyls.[21] Such a repulsive M−M interaction is more relevant for diffuse d orbitals and eventually favors nonbridged structures for 4d and/or 5d metal clusters. On the contrary, on steric grounds only, we would expect a larger occurrence of bridging carbonyls for second and third row transition metal clusters. Indeed, bridging carbonyls, in spite of the longer M−C interactions, are intrinsically closer to the cluster center;[12] *i.e.* bridged isomers, having normally higher steric energies than the nonbridged ones (for instance, **B** vs **C**, **E** vs **D** and **F** vs **D**), should be favored in less crowded (bigger) systems. However, the presence of a slight steric bias toward non bridged structures does not uniformly affect the potential energy hypersurface of a given system, for instance, **A**, **B** and **C** are much closer in energy than **D**, **E** and **F**.

Differently from what is suggested by the Ligand Polyhedral Model,[8] steric interactions can hardly be considered the key factor for the ligand stereochemistry of metal carbonyl cluster. However, the "different" point of view on fluxionality offered by LPM, *i.e.* the libration of the metal cage within the ligand polyhedron, is appealing and can be particularly useful where solid state dynamics are concerned. Indeed, we will show in the next paragraph that our steric energy computations along the reaction profiles suggested by LPM allow complete rationalization of the solid state dynamics of $Fe_3(CO)_{12}$.

MM Computations within the Crystal Lattice. We have performed computations along three different reaction paths which are somewhat related to mechanisms i−iii. They all consist of (rigid) movements of the Fe_3 triangle about some axis of the original $Fe_3(CO)_{12}$ molecule. These are (I) rotation about the Fe_3 pseudo-3-fold axis, (II) libration about the pseudo-2-fold axis passing through Fe(1) and the midpoint of the bridged edge, and (III) libration about the vector passing through Fe(2), or Fe(3), and the midpoint of the opposite edge. For path I the energy profile is continuous, the molecular conformations on both sides of the maximum are similar, and, in spite of the whole rotation of the metal triangle, the carbon and oxygen atoms only oscillate about their original positions (see Figure 2). Paths II and III were only sampled at the bottom of the potential well since it was impossible to obtain reasonable transition structures (at $\pm 90°$) and to estimate the energy barriers for the complete rotation of the triangle. Slight changes in the starting coordinates for the minimization at $\pm 90°$ lead the procedure to be trapped on different minima associated with very different RM conformations. In particular, using as starting ligand coordinates those obtained from the minimization of the previous point, the clockwise and anticlockwise rotations of the Fe_3 triangle lead to dissimilar structures at $+90$ and $-90°$, respectively, the true transition structure being possibly intermediate between the two and being at much higher energy. However, at the bottom of the potential well the sequence of molecular conformation is continuous and the librations about II and III essentially consist of a concerted bridge opening and closing without carbonyl migration about the edges.

Inspection of Figure 3 clearly shows that (a) the libration motion around the pseudo-2-fold axis (II) is the softer mode about the equilibrium structure, (b) the energy profiles II and III are asymmetric, (c) in-plane 60° jumps of the Fe_3 triangle (I) should be allowed at room temperature (computed $E^\ddagger$ ca. 12 kcal mol^{-1}), and (d) large librations about the equilibrium structure along II and III are still possible at 180 K.

The above observations offer a possible rationale for the solid state dynamics of $Fe_3(CO)_{12}$, as observed by NMR spectroscopy and X-ray diffraction (XRD). Note that NMR and XRD afford complementary information on solid state dynamics, since, roughly speaking, NMR measures the depth while XRD sees the bottom shape of a potential well.[22] Mean-square librational amplitudes (from XRD) can be used, within the appropriate approximations, to evaluate potential barriers,[23] but when more than one pathway is available, it is not necessarily true that the flattest well has the lowest depth. This implies that the analysis of atomic displacement parameters (ADP's) can, at most, trace out the softest reaction coordinate. In the present case, for instance, the particular anisotropy of the ADP's of the three Fe atoms can be used to designate **II** as being the softest libration mode,[5b] in agreement with our computations, but cannot be used to discard I and III as concurrent dynamic processes.

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According to mechanism ii, a libration of $\pm15°$ about the pseudo-2-fold axis (II) is enough to average the local molecular conformation, since it corresponds to a $D_3 \leftrightarrow C_2 \leftrightarrow C_{2v} \leftrightarrow C_2 \leftrightarrow D_3$ isomerization;[6e,f] however, as highlighted by the marked asymmetry of reaction path II, the intermolecular environment cannot be averaged since in the $P2_1$ (or Pn) space group the $Fe_3(CO)_{12}$ molecule is in a general position. The computed $E^{\ddagger}$ for such a libration is less than 1 kcal mol^{-1}, which is consistent with the persistence of large librations at 160 and even at 100 K, as shown by very recent XRD studies of the effect of temperature on the solid state molecular structure of $Fe_3(CO)_{12}$.[5d,e] Therefore, it is obvious that mechanism ii, which is not frozen out even at 100 K, cannot explain the observed coalescence at 220 K and cannot be the dynamic process frozen out at 180 K.[6d]

On the contrary, in-plane 60° jumps of the Fe_3 triangle within the ligand envelope effectively average both molecular and intermolecular environments of the CO ligands by creating the pseudo center of symmetry and allowing all the carbonyls to "see" all the metals within the NMR time scale. Moreover, mechanism i, having a computed $E^{\ddagger}$ close to the experimental one, can effectively explain both the fluxional behavior at room temperature and its freezing out at 180 K.

On top of this, librations along II and III (that is, the concerted bridge opening and closing without carbonyl migration about the edges), which are still active at 180 K, may account for the "anomalous" chemical shifts of the bridging carbonyls (indicating an averaged bridging/terminal character).[3a]

Conclusions

Our estimate of $E^{\ddagger}$ for the in-plane 60° jumps of the Fe_3 triangle, in spite of its closeness to the experimental value, cannot be considered particularly accurate since it is biased by two factors: the assumed rigidity of the crystal lattice and the poor parametrization of "electronic" effects other than charge equalization. In particular, $E^{\ddagger}$ would become smaller if the neighboring molecules were allowed to relax or the metal triangle to rattle within the ligand cage. It is more difficult to evaluate the effects associated with the lack of parametrization of the stereochemical preference of light metals for bridged structures; however, given the high fluxionality of $Fe_3(CO)_{12}$ in solution, the intrinsic molecular contribution to $E^{\ddagger}$, not accounted for by our computations, should be very small.

In spite of the above computational simplifications we believe we have clearly demonstrated that in-plane 60° jumps of the Fe_3 triangle, previously considered forbidden on the base of rigid models,[6e,f] are possible because of the "internal" molecular flexibility of $Fe_3(CO)_{12}$. Moreover, we have shown that the dynamic information offered by atomic displacement parameters must be used with care in interpreting NMR experiments since they offer a picture of the bottom shape rather than that of the depth of the potential well and, if more than one pathway is available, it is not necessarily true that the flattest well has the lowest depth.

Success of the present approach, which can be thought of as the coupling of Kitaigorodsky's atom−atom pairwise potential (AAPP) method to molecular mechanics, in interpreting the solid state dynamics of *flexible* molecules depends on the good parametrization of intra- and intermolecular interactions. As we have seen, a reasonable force field for metal carbonyl clusters has yet to be perfected; however, we are now able to control both the steric and the local electron bookkeeping needs of metal centers, thus ensuring some credibility in the steric energies we compute. Moreover, intermolecular interactions are reasonably well parametrized for low polarity solids, given the great successes of the AAPP method in rationalizing the dynamics of *substantially rigid* molecules.[22,24] On the basis of the above considerations, the present approach could be used quite safely to appreciate differences in the solution and solid state dynamics of flexible molecules and to evaluate the feasibility of proposed dynamic processes.

Finally we would like to comment on the observed crystallographic disorder which, given that the Fe_3 triangle is allowed to rotate about its pseudo-3-fold axis (at room temperature), must have a dynamic rather than static nature. After our computations were completed, we became aware that clear-cut crystallographic evidence for a similar dynamic disorder has been provided by variable-temperature diffraction experiments on a $Fe_2Os(CO)_{12}$ single crystal.[25] $Fe_2Os(CO)_{12}$, besides being isostructural and isoelectronic with $Fe_3(CO)_{12}$, has a closely related crystal structure;[5c,25] accordingly the $Fe_2Os(CO)_{12}$ dynamic behavior in the solid state can be considered strong evidence for the reliability of our computations. The major difference between the two systems arises from the fact that in $Fe_2Os(CO)_{12}$ the disorder is not crystallographically imposed and the average occupancy ratio for the two orientations depends on the temperature (from 12:1 at room temperature to no disorder below 220 K). Obviously, in $Fe_3(CO)_{12}$, the two different orientations are equally populated (at all temperatures)[5d] because the minima at ±60 and at 0°, along path I, are energy degenerate (as required by the site symmetry) while, in $Fe_2Os(CO)_{12}$, the presence of the Os atom (which partially avoids bridging carbonyls) splits the energy degeneration.

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