

Application of the Ligand Polyhedral Model to the Fluxionality of $\text{Fe}_3(\text{CO})_{10}(\text{CNCF}_3)(\text{L})$ ($\text{L} = \text{CO}, \text{PMe}_3, \text{PEt}_3, \text{P(OMe)}_3, \text{P(OEt)}_3$)

Brian F. G. Johnson,* Emilio Parisini, and Yvonne V. Roberts

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, U.K.

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Summary: The fluxionality observed for the triiron carbonyl clusters $\text{Fe}_3(\text{CO})_{10}(\text{CNCF}_3)(\text{L})$ ($\text{L} = \text{CO}, \text{PMe}_3, \text{PEt}_3, \text{P(OMe)}_3, \text{P(OEt)}_3$) has been reassessed in the light of the ligand polyhedral model.

In a recent paper, Lentz and Marshall¹ described the synthesis and full characterization of the triiron carbonyl clusters $\text{Fe}_3(\text{CO})_{10}(\text{CNCF}_3)(\text{L})$ ($\text{L} = \text{CO}, \text{PMe}_3, \text{PEt}_3, \text{P(OMe)}_3, \text{P(OEt)}_3$). These clusters were found, by single-crystal X-ray diffraction analysis of the compounds $\text{L} = \text{CO}$ and $\text{L} = \text{P(OMe)}_3$ (two isomeric derivatives), to possess structures entirely analogous to $\text{Fe}_3(\text{CO})_{12}$ and its substituted derivatives with the same basic doubly-bridged C_{2v} geometry. They also observed that, on the basis of detailed ^{13}C NMR spectroscopic studies, the same structures are preserved in solution, but as the temperature is raised, they exhibit fluxional behavior, also clearly related to that of $\text{Fe}_3(\text{CO})_{12}$ and its relatives. To account for this dynamic phenomenon these workers employed the idea of metal skeleton motion within the icosahedral shell of ligands which we first proposed² in 1976 and extended later.²⁻⁴ However, the authors chose to discuss the motion in terms of the rotation of the ligand polyhedron about its 5-fold axis through the CNCF_3 bridge rather than libration of the Fe_3 triangle about a C_2 axis which we prefer for reasons stated earlier.³

Although Lentz and Marshall¹ commented on the complementary features of our proposed dynamic process for $\text{Fe}_3(\text{CO})_{12}$ and related compounds,⁴ they concluded that it could not be directly applied to their systems and implied that the icosahedron \rightleftharpoons anticuboctahedron \rightleftharpoons icosahedral complementary process, which we have recently described in detail,^{3,4} is difficult to apply to their compounds.

In a subsequent paper, Mann,⁵ who had previously conducted a detailed and systematic study of the closely related series of compounds $\text{Fe}_3(\text{CO})_{12-n}[\text{P(OMe)}_3]_n$ ($n = 1-3$),⁶ argued that a concerted bridge opening-closing mechanism would also serve to rationalize the observations of Lentz and Marshall. Although we accept this view, we would wish to offer an alternative explanation based on the ligand polyhedral model.

Recognition of the fact that, in general terms, the cluster carbonyls may be viewed as consisting of one polyhedron

or polygon (the metal cluster unit) within another (the ligand envelope) led us to postulate²⁻⁴ originally that the libration of one polyhedron (the metal unit) within the other (the ligand set) (or vice versa) would provide a low-energy mechanism of fluxionality and *apparent* ligand interchange. The fundamental difference between this type of motion and that described by Cotton⁷ and applied in modified form by Mann^{5,6} is that, in part, this mechanism does not necessitate ligand site reorganization. Thus, the relative positions of the ligands, one to another, within their ligand envelope remain constant throughout the dynamic process, although the type of bond the ligands may have to the central metal unit may change in character, e.g. axial \rightleftharpoons equatorial or terminal \rightleftharpoons bridging. This process can also provide a low-energy route to isomer interconversion in certain circumstances as, for example, in the case of $\text{Fe}_3(\text{CO})_{11}(\text{PPh}_3)$,⁸ although this is not always the case (see below).¹² It seems to us that the effect of this libration corresponds closely to the concerted bridge opening-closing mechanism described by Mann. Certainly, the same two sets of five CO ligands will appear to exchange and one could argue that the D_3 intermediate is related to Mann's proposed intermediate. However, it is *extremely important* to recognize that during this librational motion the ligand envelope will also undergo some perturbation. This perturbation will also be subject to the same symmetry constraints as the librational motion and the two motions (libration and perturbation) will be concerted and synergic, but the contribution of each to the overall dynamic process will be phase-dependent and variable.¹³ The extent of the perturbation of the ligand shell will increase with temperature, and eventually *actual* ligand site exchange will occur and *polyhedral rearrangement* of the ligand envelope will take place. For reasons we have outlined elsewhere,^{4,9} we believe that this polyhedral rearrangement corresponds to the icosahedron \rightleftharpoons anticuboctahedron \rightleftharpoons icosahedral pathway (Figure 1).¹⁴ In this conversion there are ten sets of six polyhedral edges which can be broken, but pairs of these edges are related by mirror symmetry and only five modes need to be considered. Clearly, for the parent icosahedron, these five modes are degenerate. Occupation of this polyhedron by the Fe_3 triangle lifts this 5-fold degeneracy, unless the triangle is undergoing libration. Similarly, substitution

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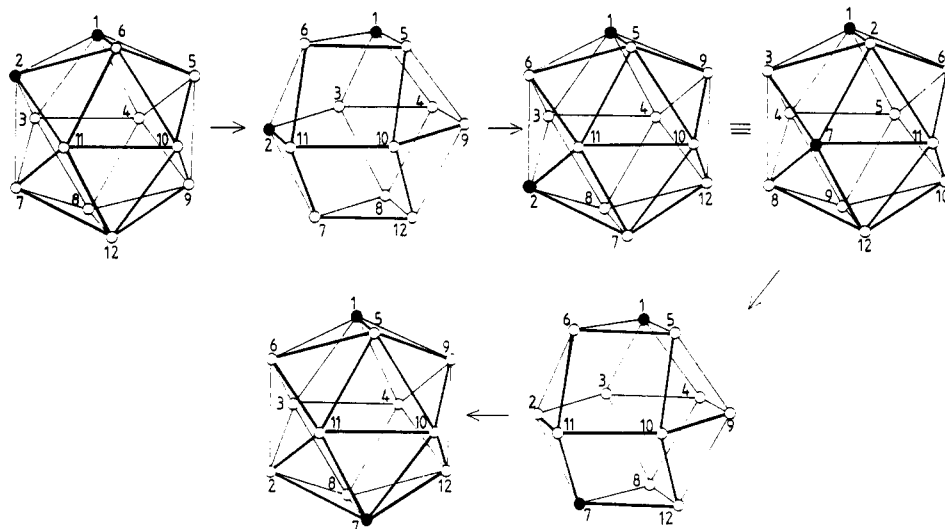
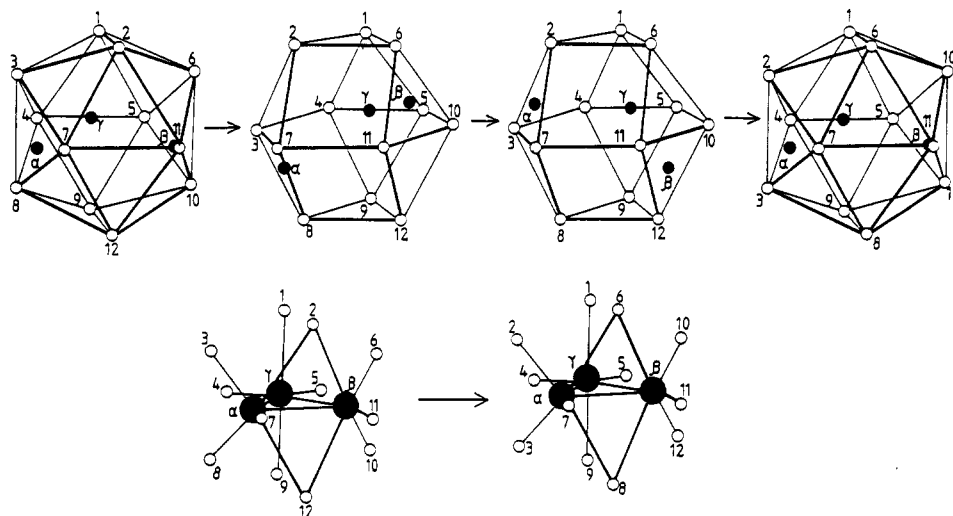


Figure 1. Interconversion of the 1,2-, 1,7-, and 1,12-forms of the disubstituted icosahedron.

Scheme I. Two-Center Exchange about the Bridged Fe-Fe Vector in $\text{Fe}_3(\text{CO})_{12}$ (C_{2v}), According to the LPM and Cotton Approaches



of two CO groups by CNCF_3 and L will further lift the degeneracy of the interconversion process. This loss of degeneracy is important, and it clearly follows that the number of fluxional process relates directly to the loss of symmetry of the ligand envelope.² A feature of this approach is that it embraces the Cotton mechanism.⁷ This is clearly shown by the sequence in Scheme I. Interconversion by one of the *modes* available to the icosahedron \rightleftharpoons anticuboctahedron \rightleftharpoons icosahedron process⁴ has *precisely* the same effect as the Cotton bridge opening-closing mechanism. The effects of the remaining modes are related to, but are not the same, as the cotton mechanism.

We have described this approach in considerable detail elsewhere^{3,4} but would use this opportunity to stress that (1) the librational motion and the polyhedral rearrangement through the anticuboctahedron are *not* independent but are synchronous, (2) the relative contribution each motion makes to the overall dynamic process is dependent upon the phase and, very importantly, the mass of the metal unit involved, and (3) the polyhedral rearrangement process leading to carbonyl site exchange occurs via the anticuboctahedron and, although more wide ranging, embraces the various Cotton approaches⁷ within it.

The structures of the compounds $\text{Fe}_3(\text{CO})_{10}(\text{CNCF}_3)(\text{L})$ have been conveniently described in terms of the ligand

polyhedral model as a triangle of three iron atoms embraced within a *pseudo*icosahedron of 12 ligands.¹ In the cases of $\text{L} = \text{P}(\text{OMe})_3$ and $\text{P}(\text{OEt})_3$, two isomeric forms of the compound have been observed. In all cases, the CNCF_3 ligand adopts a μ_2 -bridging mode and the ligand L coordinates in an equatorial position (Figure 2). According to the LPM the icosahedral shell in these compounds corresponds to the 1,2-disubstituted icosahedral arrangement shown in Figure 2 and, where two isomers exist, the second isomeric form adopts the 1,7-disubstituted icosahedral arrangement (Figure 2b).

For the parent compound ($\text{L} = \text{CO}$; Figure 2), libration about the preferred C_2 axis^{3,4} will lead first to a D_3 isomer and then to a second C_{2v} form and libration about either of the two other C_2 axes (the same) will lead directly to a second C_{2v} form. Continuation of these motions will lead to an "apparently spherical" metal unit. The result of this motion is to leave the *ligand shell unchanged* and thus will generate a 5:5:1 (Figure 3) relationship of peaks¹⁵ in the ^{13}C NMR spectrum, in agreement with the reported data.¹ The unique CO ligand will be that one which is antipodal to the CNCF_3 bridge in the ground-state structure (Figure 2), and the two sets of *apparently* exchanging CO ligands correspond to those described previously.^{1,6}

Throughout this process the ligand cage will flex, and

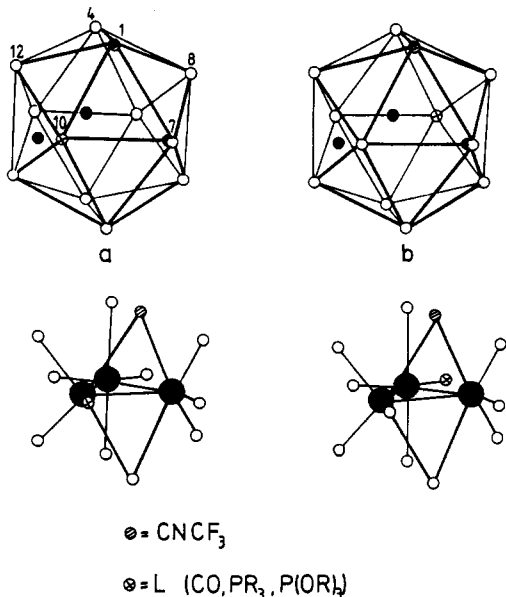


Figure 2. The two isomers of $\text{Fe}_3(\text{CO})_{10}(\text{CNCF}_3)(\text{L})$, according to the ligand polyhedral model.

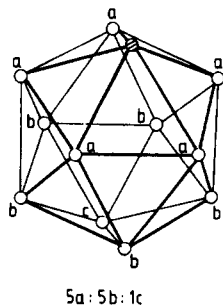


Figure 3. $(\text{CO})_{11}(\text{CNCF}_3)$ icosahedron.

eventually when the temperature is raised sufficiently, the second dynamic motion, viz. icosahedron \rightleftharpoons anticuboctahedron \rightleftharpoons icosahedron, will also emerge. For the parent compound, the monosubstituted icosahedron, $(\text{CO})_{11}(\text{CNCF}_3)$, will now undergo stereochemical rearrangement. Given that for a monosubstituted icosahedron with a rapidly librating metal triangle the five possible modes of interconversion remain degenerate,¹¹ a single dynamic process is predicted, leading to complete ligand scrambling in agreement with observation.¹

For the compounds $\text{Fe}_3(\text{CO})_{10}(\text{CNCF}_3)(\text{L})$, similar dynamic processes are expected. In the compounds for which only one isomer is observed, viz. with L occupying an

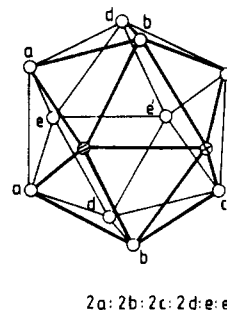


Figure 4. $(\text{CO})_{10}(\text{CNCF}_3)(\text{L})$ icosahedron.

equatorial site adjacent to the CNCF_3 bridge (see Figure 2a), the molecule may be viewed as an Fe_3 triangle inserted into a 1,2-disubstituted icosahedron (see Figure 2a). For the second isomeric form found for $\text{L} = \text{P(OMe)}_3$ or P(OMe)_3 , the Fe_3 triangle resides inside a 1,7-disubstituted icosahedron (Figure 2b). In the first case, libration of the Fe_3 triangle, in a manner related to that given above, will lead to the observed ^{13}C NMR spectrum with signals in the ratio 2:2:2:2:1:1 (see Figure 4). In this instance the two unique CO ligands are those antipodal to CNCF_3 and ligand L. As the temperature is raised, ligand interconversion via the icosahedron \rightleftharpoons anticuboctahedron \rightleftharpoons icosahedron mechanism will also operate. In this case, however, the 5-fold degeneracy of the "naked" icosahedron is lifted by the insertion of CNCF_3 and L to give three modes, viz. a single mode and two doubly degenerate modes. Interconversion of the 1,2-isomer to the 1,7-isomer may be achieved by the mode given in Figure 1.

The operation of the librational motion on the second (1,7-isomer) will lead to ^{13}CO signals in the ratio 2:4:2:2. Unfortunately, this has not yet been confirmed by experiment.¹ Again, the icosahedron \rightleftharpoons anticuboctahedron \rightleftharpoons icosahedron process will occur via three distinct modes, one (singlet), one (doubly degenerate), and a second doubly degenerate mode, and so three further dynamic processes are predicted.¹¹

In conclusion, we offer a coherent explanation of the dynamic behavior of the compounds $\text{Fe}_3(\text{CO})_{10}(\text{CNCF}_3)(\text{L})$ which satisfactorily accounts for the recorded ^{13}C NMR spectroscopic data. Simply, two synchronous processes operate: the libration of the Fe_3 triangle and the polyhedral rearrangement of the ligand envelope. These ideas are based on the ligand polyhedral model and may be universally applied to cluster carbonyls and their derivatives. They offer the advantage of allowing a clear understanding of the ground-state structures, their dynamic properties in both the solid and solution states, the structure of the isomeric forms available, and a clear view of the mechanism of isomer interconversion.

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(12) Mann, B. E. Private communication.

(13) Librational motion is dependent upon the mass of the body and will vary from metal unit to metal unit.

(14) For a fuller description of the process see e.g. refs 3 and 4; a more detailed description for these compounds will be given elsewhere.

(15) These correspond to the two sets suggested by Mann viz., (1) C^{16}O , C^{17}O , C^{18}O , and C^{19}O and (2) C^{14}O , C^{15}O , C^{16}O , C^{17}O , and C^{18}O ; for convenience these are labeled according to Mann's scheme in Figure 2.