Mechanism of the low-energy fluxional process in [Fe$_3$(CO)$_{12-n}$L$_n$] [n = 0–2(3)]: a rebuttal

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We respond to Mann's criticisms of the Ligand Polyhedral Model and its application to the fluxional behaviour of the compounds [Fe$_3$(CO)$_{12-n}$L$_n$]. We reject his proposal that an analysis of a range of compounds by the Dunitz–Bürgi method rules out the possibility of fluxionality by the libration of the Fe$_3$ triangle within the ligand icosahedron, and remind him that the librational mode corresponds to the first concerted bridge-opening bridge-closing mechanism.

We are grateful for the opportunity to respond to some of the criticisms of our work by Mann.[1] It is clear that although he makes a number of complimentary comments about the Ligand Polyhedral Model (LPM) he does not regard it as useful. In making our reply we feel obliged to remind the reader of the background leading to the introduction of the model which we fully accept is different in its approach to all previous methods but nevertheless in many ways follows naturally from current views generally accepted for simple co-ordination compounds. We accept the view that the model does not rely on a localised bonding viewpoint but regards the structures of the binary carbonyls as being driven by steric or packing considerations rather than directed valence bonds. In this connection it is worth noting that the reason such compounds exhibit a high degree of fluxionality, irrespective of the proposed mechanism, is precisely because the metal cluster unit can adjust its bonding orbitals to accommodate a variety of different ligand geometries at a small expense of energy. This is not to say, as Mann implies, that we ignore bonding interactions. As with simpler co-ordination complexes once a ligand geometry has been selected it is a simple matter to draw atom–atom vectors. We recognise that the model, like all other approaches, is probably a long way from reality. However, unlike all other approaches, it offers a coherent approach based on symmetry considerations which recognises the need for a method *to predict* and more fully understand the factors which govern all aspects of *the structures and fluxional behaviour* of the binary metal carbonyls. We would also remind Mann that like all models it offers an *idealised view*.

Mann[1] suggests that the LPM was first developed in 1978 on the basis of the molecular structures of [Fe$_3$(CO)$_{12}$] and [Co$_4$(CO)$_{12}$]. This is incorrect. The model was first proposed in 1976.[2] It was based on ideas derived from a consideration of polyhedral geometries (not in the first instance related to carbonyls) and was applied to a wide range of binary carbonyls in a communication published that year. This was the first time that such an analysis of carbonyl structures had been carried out and our proposal that the structures of these compounds are based on geometric factors (*i.e.* polyhedron or polygon within polyhedron) was entirely new. In the final paragraph of that communication we stated: 'The ideas outlined in this paper may be employed to account for the structures of all binary carbonyl species. They are not restricted to the prediction of CO bridges but may also be used to account for distortions and anomalous bond lengths as *e.g.* [Mn$_2$(CO)$_{10}$]'.

The first full report of much of this work appeared in 1980.[3] The emphasis was on a general approach to all carbonyls and not as Mann suggests to the two dodecacarbonyls above. We would add that nor is the model restricted to the binary carbonyls; it may be applied to a range of other binary systems. In the same communication[2] we also discussed the idea of metal migration within the CO polyhedron with specific reference to [Co$_2$(CO)$_8$] and related dimers and pointed out that this offered an alternative view of the mechanism of fluxional behaviour. To our knowledge, the idea that some aspects of fluxional behaviour could be rationalised on the basis of movement of one polyhedron within another was completely original although libration is a well documented phenomenon. Significantly, we also indicated that the fluxional process was linked to the soft vibrational mode of the Co−Co bond.

The extension of our ideas to the fluxional behaviour of [Fe$_3$(CO)$_{12}$] also first appeared in 1976[4] (see below). In this we record {referring to [Fe$_3$(CO)$_{12}$]}: 'As an alternative explanation, we may consider that the icosahedral arrangement of the twelve CO groups is maintained during the fluxional process and that equilibration of these groups is brought about by the reorientation of the Fe$_3$ triangle within the CO icosahedron. This corresponds to a truly concerted process and implies the simultaneous formation and breaking of CO bridges'.

This predates the report by Mann and co-workers[5] (1989) by a considerable period, and Mann is incorrect when he claims that the idea of a concerted process was first put forward in 1989. Furthermore, contrary to Mann's comments, from the very beginning (1976) we emphasised[2] the need to maintain sensible M−CO contacts and in 1990 warned:[6] 'One constraint that must be imposed on this intermediate ligand polyhedron is that it generates an intermediate ligand structure with reasonable ligand distribution around each metal atom'.

To reject the Model because of its misuse by others is unwarranted. We published a more detailed report of the application of the LPM to fluxional behaviour in 1978[7] (see below). In this report we focused on the polytopal rearrangement of the ligand envelope around the central metal cluster unit. Contrary to Mann's suggestion, this is not the same as the 'merry-go-round process', first developed by Cotton and co-workers[8,9] and considered by him to involve a *quasi*-[Ru$_3$(CO)$_{12}$] intermediate. The Cotton process *may be taken* to correspond to but *one of five possible* modes of icosahedral interconversion; a point we have made repeatedly but one apparently misunderstood or ignored by Mann. Each of the five modes passes through a cube-octahedral complementary geometry and is regarded as a higher energy process than libration. In that report of 1978 we concentrated on the [M$_4$(CO)$_{12}$] (M = Co, Rh or Ir) compounds not [Fe$_3$(CO)$_{12}$]. The iron carbonyl [Fe$_3$(CO)$_{12}$] was not discussed in any significant detail until the concluding section where we said: 'The general mechanism of carbonyl fluxionality, *viz.* that corresponding to polytopal rearrangement of the ligands will not be restricted to [M$_4$(CO)$_{12}$] and related compounds but may be extended to embrace all the binary carbonyls and other similar systems {including $[Fe_3(CO)_{12}]$} (see below). In a previous communication a possible mechanism of fluxional behaviour in $[Fe_3(CO)_{12}]$ was proposed in which the Fe_3 triangle migrated within an essentially undisturbed icosahedron of carbonyl ligands. That proposal is *not* ruled out by the ideas presented here. Clearly, for the most symmetric arrangement of ligands, *e.g.* the icosahedron, this remains the simplest and apparently the lowest-energy process'. We went on further to say: 'In this work we have examined the consequences of the polyhedral interconversion of an icosahedron *via* a cube-octahedral transition state. Although this mode of interconversion *appears* to work well in these and other related systems {*e.g.* $[Fe_3(CO)_{12-n}L_n]$} *it may not be general and other transition states may be involved*. This aspect is under detailed examination and will be reported shortly'.

The implication in Mann's paper that the idea of metal migration was dropped in favour of an icosahedron↔cube-octahedron↔icosahedron is completely wrong and this aspect of our work was addressed in full in later papers.[7,10] We argued[10] that carbonyl fluxionality takes place by a process which involves both the libration of the metal triangle in the carbonyl envelope and the flexing and ultimate polyhedral rearrangement of the carbonyl polyhedron.

Later, we reported work on the fluxional behaviour of $[Fe_3(CO)_{12-n}L_n]$ systems.[11] In his reference to that work Mann states: 'Clearly the theory was inconsistent with the experiment and has to be wrong'. This is completely untrue. In our report we *predicted* that, on the basis of the LPM, operation of the librational motion in the compound $[Fe_3(CO)_{11}(PR_3)]$ would lead to three signals in the high-temperature ^{13}C NMR spectrum in the intensity ratio 5:5:1. Unfortunately, because of the poor quality of the spectra available to us at that time, it appeared that there was disagreement between theory and experiment. Later a spectrum totally in accord with our prediction was obtained.[5] Thus the data not the theory was incorrect. It is a reflection of the *predictive ability* of our approach that we were able to suggest the correct spectrum well before it was published. It follows that Mann is wrong when he claims in his article: 'These intensities (*i.e.* 5:5:1) could not be fitted to any of the existing mechanisms'.

In our paper[11] we also considered the result of a combined interconversion: icosahedron↔cube-octahedron together with a trigonal twist. Naturally, for the reasons discussed above this also proved unsatisfactory. Mann fails to understand that this combined process corresponds to the icosahedron↔anticube-octahedron↔icosahedron interchange, an aspect we developed in more detail in a subsequent report[6] devoted to 'dynamic processes of trinuclear carbonyl clusters $[M_3(CO)_{12}]$ (M = Fe, Ru and Os) and their derivatives'. We did not, as Mann incorrectly concludes, modify 'the LPM from icosahedron↔cube-octahedron↔icosahedron rearrangement to icosahedron↔anti-cube-octahedron↔icosahedron rearrangement'. The former is best applied to the $[M_4(CO)_{12}]$ compounds and the latter to $[Fe_3(CO)_{12}]$. In the same paper[6] we also drew attention to the fact that at higher temperatures, not only is the low-energy librational mechanism required but also a high-energy polyhedral interconversion (icosahedron↔anticube-octahedron↔icosahedron) (see below).

In the past we have tended to believe that Mann's low-energy pathway and our librational pathway were the same and have commented:[12] 'We believe that this librational motion *may* correspond to the *very low-energy process* of fluxional behaviour suggested by Mann and co-workers'. The difference lies in the manner we choose to describe the structures, *e.g.* $[Fe_3(CO)_9L_3]$, involved.

Mann appears to reject the LPM solely on the grounds of its applicability to the fluxional behaviour of $[Fe_3(CO)_{12}]$. The Model is intended to do far more than that. Until 1976, when the basis of the LPM was first proposed,[2] the structures of the simple binary carbonyls $[Co_2(CO)_8]$, $[Fe_2(CO)_9]$, $[Mn_2(CO)_{10}]$, $[Fe_3(CO)_{12}]$, $[Ru_3(CO)_{12}]$, $[Os_3(CO)_{12}]$, $[Co_4(CO)_{12}]$, $[Rh_4(CO)_{12}]$, $[Ir_4(CO)_{12}]$, $[Rh_6(CO)_{16}]$, *etc.* as established by X-ray crystallography were poorly understood. There seemed no apparent reason why, for example, $[Fe_3(CO)_{12}]$ should possess a structure with C_{2v} (strictly C_2) symmetry in which two CO ligands formed bridges along one edge of the Fe_3 triangle, whereas the apparently closely related carbonyls of $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ possess a structure with D_{3h} symmetry and no bridges. Similarly, why should $[Rh_6(CO)_{16}]$ have four three-centre bridges and $[Co_6(CO)_{14}]^{4-}$ eight? This lack of understanding was compounded by the observation that several of the binary carbonyls adopt different isomeric forms (usually in solution). For these isomers it was sometimes difficult, if not impossible, to find an adequate localised bond description. For example, with $[Co_2(CO)_8]$, for which several isomers are thought to exist in solution, two provide no problem and are usually considered to be the dibridged form found in the solid and the non-bridged form with C_{3v} symmetry similar to that found for $[Co_2(CO)_6(OR_3)_2]$ but it is difficult to imagine valence bond representations of those remaining. We concluded that representations involving directed bonds could have an inhibiting effect. In Mann's paper he discusses the fluxional behaviour of $[Fe_3(CO)_{12}]$ and its derivatives and stresses the need to sustain directional valence bonds and argues that such an approach is essential to the understanding of this intriguing phenomenon. We refer the reader to a Scheme taken directly from one of Mann's papers (see Fig. 1). The limitations of the valence bond representation are clear! These limitations were also recognised by Mann who states that: 'As normally drawn, C^1O and C^2O appear to be a long way from C^7O', and then goes on to justify the LPM approach.

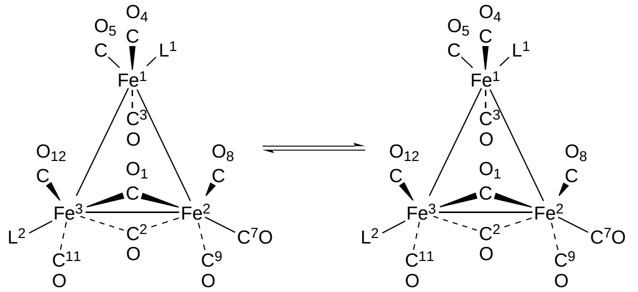


Fig. 1 Scheme 3 taken from ref. 5

Finally, there is the fluxional behaviour which the majority of these carbonyls exhibit. Of all the organometallic species they appear to be the architypical examples of this behaviour, and the advent and ease of access of ^{13}C NMR spectroscopy and of suitably ^{13}CO-enriched samples has permitted a wide and detailed examination of this phenomenon leading to the postulation of many of the *so-called* CO scrambling processes in these carbonyls and their derivatives. At the time, as our initial proposal it appeared that in order to rationalise the available data, a different mechanism or set of mechanisms was proposed for each individual compound and, although some general features such as bridge make–break had emerged, it seemed to us that there must be a method by which *both the number and type* of fluxional processes for a given carbonyl *could be predicted* and related to those of similar systems.

At the onset of our work in 1976, the challenge was to devise a means or model by which the various phenomena (the ground-state structure, the existence of isomers and the fluxional behaviour) could be better understood, and that is what the LPM sets out to do. Its function is not, as Mann implies, solely to provide a mechanism for the fluxional behaviour of $[Fe_3(CO)_{12}]$ and its derivatives.

The essence of the LPM stems from the realisation that the molecular structures of the binary carbonyls are the result of inserting one polyhedron (or polygon) within another. Thus, the molecular structure of $[Fe_3(CO)_{12}]$ is the consequence of inserting a triangle (of Fe atoms) into an icosahedron (of CO ligands) that of $[Ru_3(CO)_{12}]$ of inserting a triangle into an anticube-octahedron, that of $[Co_4(CO)_{12}]$ of inserting a tetrahedron into an icosahedron, that of $[Ir_4(CO)_{12}]$ of inserting a tetrahedron into a cube-octahedron, that of $[Rh_6(CO)_{16}]$ of inserting an octahedron into the 28-faced icosaoctahedron, and that of $[Co_6(CO)_{14}]^{4-}$ of inserting an octahedron into an omnicapped cube, *etc.*, *etc.* The original problem was to discover the optimum CO polyhedron (or cluster co-ordination arrangement) for a given number of CO groups and why this polyhedron could vary according to the metal type. The 'best' co-ordination polyhedra for simple or cluster co-ordination compounds are those which are fully triangulated and whose vertices lie on the surface of a sphere. This restricts them to the three Platonic solids: the tetrahedron, the octahedron (accounting for their wide occurrence in co-ordination chemistry) and the icosahedron. Translating this into chemistry, these polyhedra are best because they offer equivalent metal–ligand bond lengths (strengths!), since all ligands L lie on a sphere with the metal ion at the centre, and equivalent ligand–ligand interactions (since all ligands occupy the corners of equilateral triangles, with all L−L distances the same). Other polyhedra have vertices which lie on the surface of a sphere, *e.g.* the cube and the pentagonal dodecahedron, all prisms, and antiprisms, *etc.*, but none have all triangular faces and hence at equilibrium there are at least two different L−L distances (*e.g.* for the cube, the edge and diagonal). Others have fully triangulated faces but their vertices do not lie on a sphere, examples include the trigonal bipyramid, the pentagonal bipyramid and the triangulated dodecahedron. It follows that not all metal–ligand bond lengths (strengths?) are the same. For these systems there is, if you will, an inherent instability and, if a convenient complementary geometry (see below) is easily accessible by a *soft vibrational mode*, they readily undergo interconversion and, if the energy for the process is right, are fluxional.

In our work we initially took the view[3] that the optimum polyhedra would be those with vertices lying on a sphere (implying of course that the metal unit is spherical) and for the large co-ordination numbers involved adopted the approach originally devised by Stone[13] to ascertain the available polyhedra and their relative energies. This is reasonable since for large co-ordination numbers, despite the restrictions mentioned above, the polyhedra more closely approach a sphere. We immediately recognised the importance of the size of the CO ligand and chose a hard sphere model, assuming the important contact distance as being that based on a sphere around the oxygen, which was derived empirically. Importantly and essential to the success of the model, we found that although the metal–carbon and carbon–oxygen distances varied from carbonyl to carbonyl the metal–oxygen distance remained remarkably constant reflecting the synergic nature of the metal–CO bond. With a radius established, we were then able to calculate the size of the interstitial site within a given polyhedron of CO spheres and, given that, decide on the ability of a metal polyhedron or polygon of known size to fit. Thus, an Fe_3 triangle readily sat in the icosahedron (of radius ratio 0.9), whereas the larger Ru_3 or Os_3 required the larger anti(or twist)cube-octahedron (of radius ratio 1). Hence, the change in geometry from $[Fe_3(CO)_{12}]$ to $[Ru_3(CO)_{12}]$ was easily understood on the basis of this simple hard-sphere model. Put simply, as the size of the metal unit increased the CO polyhedron expanded (by changing shape) to accommodate it. This is an aspect which proved to be important to our consideration of fluxional behaviour {see $[Co_2(CO)_8]$ above}. For the $[M_3(CO)_{12}]$ compounds this means a change from the icosahedron to the anticube-octahedron and for $[M_4(CO)_{12}]$ a change from icosahedron to cube-octahedron. Obviously, the best fit between observation and theory came when both the metal and carbonyl polyhedra had related symmetries. Thus, the octahedron in the omnicapped cube of $[Co_6(CO)_{14}]^{4-}$ gives excellent agreement between experiment and theory (both having O_h symmetry!) and leads naturally to a species with eight triply-bridging and six terminally bonded CO groups. We also adopted the approach of *cascading symmetry*. Simply, this means that we recognised that if the two polyhedra (polygons) were not compatible both would distort to a common symmetry. This is readily seen in $[Fe_3(CO)_{12}]$ where a flattened icosahedron is observed. Strictly the model applies to the binary carbonyls only. However, although care should be exercised in employing the model to other systems, it does seem to work well for substituted derivatives in which tertiary phosphines replace carbonyl groups in the ligand polyhedron. Virtually all phosphines have cone angles larger than CO and as a consequence replacement of CO by R_3P leads to polyhedra with larger interstitial sites. It follows that as CO is replaced by R_3P in $[Ru_3(CO)_{12}]$ the ligand polyhedron shifts from basically an anticube-octahedron towards the icosahedron and the symmetry of the molecule changes from D_{3h} to D_3 or C_{2v}.[10] However, it is important to recognise that the incorporation of R_3P ligands is likely to bring about further, possibly more subtle, changes in the symmetry arising from the three-fold symmetry axis in the phosphine, a point apparently not appreciated by Mann. This is an importtant consideration in any interpretation of X-ray diffraction data. In heterometallic systems, *e.g.* $[RuFe_2(CO)_{12}]$, the larger metal ion will always occupy the larger site within the ligand polyhedron. Thus, within an icosahedron the Ru atom will take up the larger 'butterfly' site and the Fe atoms the smaller triangular sites in the C_{2v} structure and hence bridges will span the two lighter atoms. Similarly, in $[Co_3Rh(CO)_{12}]$ the Rh atom occupies the larger 'butterfly' site, which in this case leads to a bridge between a Co and Rh atom in the C_{3v} structure. In addition to all this we must remember that the ground-state structures are derived for molecules in the crystal and will be subject to the symmetry constraints placed on an individual molecule by its crystallographic environment. This is especially the case for carbonyls with an icosahedral ligand shell which occupy less symmetric environments in the crystal.

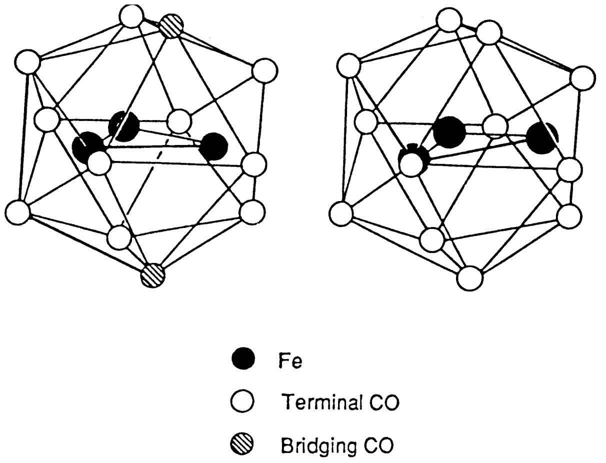


Fig. 2 The C_{2v} and D_3 forms of $[Fe_3(CO)_{12}]$ (taken from ref. 10)

Again, from the onset we also recognised that the insertion of the metal unit into the appropriate CO polyhedron does not always lead to a unique result, simply as a consequence of the geometries of the two polyhedra concerned not of chemistry! Thus, the insertion of the triangle into an icosahedron leads to three different forms (isomers!): the observed C_{2v} (C_2) form, a different but closely related form with the same symmetry but two triply-bridging rather than two edge-bridging CO groups and a third with D_3 symmetry which has no CO bridges (Fig. 2). This latter structure is commonly referred to as the D_3 form and, for convenience, is also used as a label for substituted systems (see below). Each of these three forms may be converted one to another by rotation of the central triangle about

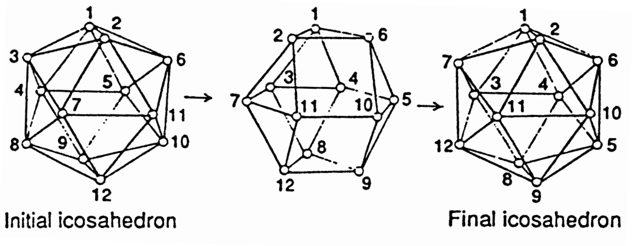


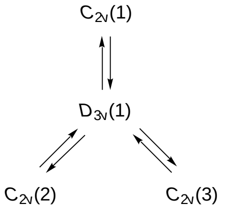
Fig. 3 Interconversion of the ligand polyhedra for the $[M_3(CO)_{12}]$ compounds (taken from ref. 10)

the unique C_2 axis and in our view, since each corresponds to a definite structural type, may be regarded as occupying minima on the energy profile connecting all three. Again we should emphasise that this is solely a function of geometry and applies irrespective of the nature of the ligands or the internal triangle.

At the time we made this discovery there was no evidence for either the second C_2 form or the D_3 form but the change in the IR spectrum of $[Fe_3(CO)_{12}]$ in solution as a function of solvent polarity and temperature was found to be compatible with that predicted for a mixture of the established C_{2v} and proposed D_3 forms, and provided a perfectly reasonable explanation of the previously uninterpretable data. Totally in line with our prediction Grant and Manning[14] reached a similar conclusion concerning the two isomers (C_{2v} and D_3) of $[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$. Since our original suggestion that the second isomer might correspond to the D_3 form there have been recorded countless examples of substituted derivatives of $[M_3(CO)_{12-n}L_n]$ for both Fe and Ru[15] with the predicted D_3 form (although not necessarily of that symmetry). Significantly, this D_3 form of $[Fe_3(CO)_{12}]$ with its icosahedral CO shell is closely related to, but not the same as, the D_{3h} structures observed for $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ with the anti(or twist)cube-octahedral arrangement of CO ligands. This D_3 form may be easily converted to the D_{3h} form by an icosahedron↔anticube-octahedron interconversion of the ligand polyhedron, which corresponds to a polyhedral twist mechanism. Thus, there is a clear, well defined pathway between the various forms [$C_{2v}(1)$, $C_{2v}(2)$, D_3] and between the CO polyhedra (icosahedron, anticube-octahedron) involved (see Fig. 3) and direct evidence for this transition pathway has been obtained from a Dunitz–Bürgi analysis of a range of derivatives.[10]

We may treat other compounds similarly.[16] Thus, for example, the established ground-state structure of $[Co_4(CO)_{12}]$ with three CO bridges and C_{3v} symmetry is formed by the insertion of the Co_4 tetrahedron into an icosahedral CO shell. However, there is a second closely related alternative with no CO bridges and T_d symmetry. These C_{3v} and T_d forms are readily interconverted by rotation of the tetrahedron about the unique C_3 axis. The C_{3v} form is observed crystallographically for both $[Co_4(CO)_{12}]$ {and $[Rh_4(CO)_{12}]$} and, on the basis of detailed NMR and IR spectroscopic analysis, shown to persist in solution. As far as we are aware the T_d form has not been observed directly although we have some evidence of its existence from low-temperature solution IR studies. This T_d form readily converts into the structure found for $[Ir_4(CO)_{12}]$ with T symmetry, no CO bridges and the cube-octahedral CO arrangement emphasising the importance of the process by which the three polyhedra icosahedron, anticube-octahedron and cube-octahedron may interconvert. Similarly, the two isomers of $[Ir_6(CO)_{16}]$, one with four CO-edge bridges and one with four CO-face bridges, are formed by placing the metal octahedron in the 28-faced icosaoctahedron of CO groups, and are connected by rotation of the octahedron by 45° about the appropriate C_4 axis.

As mentioned above, there is a special difficulty with $[Co_2(CO)_8]$ exhibiting as it does several isomeric forms. For eight-co-ordination it is difficult to decide the most favourable polyhedron. There are three immediate contenders;[17] the dodecahedron, the monocapped trigonal prism and the square antiprism. There is a clear and easily understandable relationship between these three. The first converting to the second and that to the third by a series of single edge cleavages with a concomitant small increase in the size of the interstitial site. If we assume that the various isomers have these closely related forms available to them then it is not difficult to appreciate the possible structures they might adopt.



Scheme 1 The proposed pathway for CO-scrambling by the librational mode

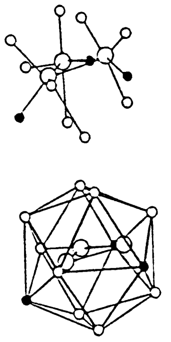


Fig. 4 Predicted structure of the minor isomer of $[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$ (taken from ref. 12)

It was these observations which led us eventually to postulate a low-energy pathway of CO equilibration in $[Fe_3(CO)_{12}]$ and its derivatives which is brought about by the movement of the metal unit within the CO polyhedron. It seemed reasonable to assume that such a low-energy pathway would require minimum energy if it took place by libration between the two extreme forms (D_3 and C_{2v}) rather than complete rotation of the metal unit. Thus, the process would take the form illustrated in Scheme 1. Here the D_3 form is the pivot. At any given moment the Fe_3 triangle may librate about any one of the three equivalent C_2 axes, giving an equal amount of three C_{2v} forms (all equivalent). These in turn generate the same or new D_3 forms. Thus, CO-interchange is achieved instantaneously and does not require a cyclic process.

This is where the fundamental disagreement with Mann lies. (1) First, he does not accept the possibility of the existence of the D_3 isomer either for $[Fe_3(CO)_{12}]$ or its derivatives despite considerable evidence in its favour[15,18] (see below), and despite the results of his own crystal-structure determination of the compound $[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$.[19] The crux of our disagreement with Mann is the method of description of the molecular structure of the compound $[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$ **1** not the structure itself. In 1993[12] we pointed out that the probable structure of **1** was best described as D_3 icosahedral with the 1,7,9 ligand substitution arrangement shown in Fig. 4, emphasising a point made in our earlier paper.[6] This clearly accounted for the ratio of CO signals of 3:3:3[5,19,20] in the ^{13}C NMR spectrum, whereas we consider that Mann's structure (see Fig. 5) does not. We also stated that: 'The relationship between the icosahedral geometry and the anticube-octahedral geometry involves a small rotation of two of the $Fe(CO)_2L$ units'. Aime and co-workers[20] put forward a very similar account in which they fully accepted our view. Mann differs and appears to prefer a description of the structure based on the D_{3h}

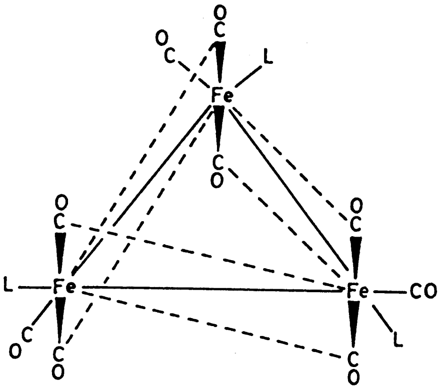


Fig. 5 Structure of the major isomer of $[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$ (taken from ref. 5)

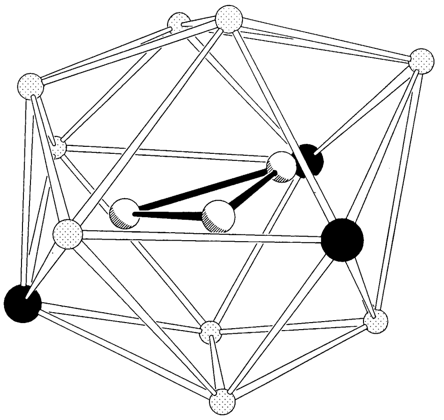


Fig. 6 Polyhedron formed by the 12 ligands in the structure of the major isomer of $[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$

(anticube-octahedron?) ligand arrangement of $[Ru_3(CO)_{12}]$ but with the six axial CO ligands bending to form semi-bridges. From his diagrams and descriptions it appears that the six remaining ligands reside in the equatorial plane (see Fig. 5). This is fundamentally different to our description and this difference, which in our view is extremely important in any consideration of fluxional behaviour, has been emphasised by Mann. He considers the compound to be in a class of its own. However, although apparently questioning our description, in his paper describing the X-ray analysis of **1**,[19] he now states:[1] ‘Examination of the structure shows that each iron has rotated about the pseudo-C_2 axis of the Fe_3 triangle giving what approximates to a D_3 structure’. (By this we take it that he implies from the anticube-octahedron to the icosahedron ligand arrangement.) Clearly in agreement with our description (quoted above). Taking Mann’s crystallographic data, a plot of the O and P atom positions (see Fig. 6) carried out in our laboratories reveals the *quasi*-icosahedral ligand arrangement, totally in accord with our prediction (see Fig. 4).[6,12] Contrary to the statement made by Mann, we did not propose[12] that the axial carbonyls lean towards the nearest non-bonded iron atom to acquire some semi-bridging character since this follows automatically from the icosahedral ligand arrangement. Instead, we stated that: ‘Whether or not one regards the six carbonyls as semi-bridging is subjective’. By this we meant subject to the overall geometry of the ligand polyhedron as we illustrated. Whether or not one sees six semi-bridges, four, two or none is dependent on the chosen viewpoint. In this respect it is similar to $[Mn_2(CO)_{10}]$ in which, as a function of the coordination geometry, the two sets of four equatorial carbonyls bend towards the opposite Mn atom and may be deemed to semi-bridge or bond in a terminal mode.

Earlier, we had suggested[10] that the torsion angle between the two triangles formed by the two sets of axial carbonyl O-atoms above and below the iron triangle as well as the average deviation of the equatorial ligands from the mean plane can be used to determine whether or not a compound has predominantly an anticube-octahedral or icosahedral ligand arrangement. Mann[19] states that ‘When this test is applied to $[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$, the torsion angle is 74.0° and the average deviation of the equatorial phosphorus and oxygen of the mean plane is 0.8 Å’. He goes on to say: ‘The torsion angle is larger than any reported by Johnson *et al.*, while the deviation lies within the range found for icosahedral ligand arrangements on C_{2v} type $[M_3(CO)_{12-n}L_n]$. The cluster does not fit into the analysis, which raises questions as to its validity’. This is incorrect. First, it is geometrically impossible to have a torsion angle of 74.0°. This angle refers to the relative orientation of the two ‘apical’ triangles of the relevant polyhedra, which can only vary from 0° in the anticube-octahedron when they are eclipsed to 60° in the icosahedron (or cube-octahedron) when they are staggered. On checking the crystal-structure data reported by Mann we find that the angle should be corrected to 46° which falls into the band we predict for an icosahedral arrangement. Secondly, the deviation from the plane is strictly dependent on the icosahedral arrangement which is the same irrespective of whether the icosahedron is occupied to yield the D_3 or C_{2v} structure. The suggestion that ‘the cluster does not fit into the analysis’ is thus wrong and our method remains valid as it must, since it is a rigid function of the polyhedral geometry and not a consequence of chemistry.

(2) In his process, Mann proposes that there is no intermediate such as the D_3 form, instead he formulates a continuous process in which the whole CO polyhedron (or Fe_3 triangle) undergoes rotation.[1] This we regard as an unnecessarily high energy process, and prefer the lower-energy libration ($C_{2v} \rightleftharpoons D_3$) pathway. However, it is noteworthy that Mann’s process passes through a structure very close to the D_3 form, and there would appear to be no conflict in the pathway arising from either approach and the Dunitz–Bürgi plot (see below).

(3) Mann argues that his process, which invokes the basic principles of the LPM but envisages rotation about a particular S_{10} axis of the icosahedron, is consistent with his analysis of several structures by the Dunitz–Bürgi method [different to that in (2)] whereas the libration process is not. His argument is flawed for several reasons. (*a*) First, examination of the data given in his Table reveals that with one exception (see below) all the information is concerned with very small angles of rotation (0–6°) about the chosen S_{10} axis. Given that Mann’s proposed rotation is through 36° (we take his value) before a new ground-state geometry is achieved,[1] we should look for displacement or lack of it over a much wider range of rotations than a few degrees. However, we note that in one case the displacement is recorded as *ca.* 5.5° which is *ca.* 30% of the total requirement for libration (18°), for a rotation of 0.59°. In another, the displacement is 4.8° at an angle of 6.3°. These discrepancies are ignored in his discussion, yet if anything they favour the librational process.

The one exception referred to above is the compound $[Fe_3(CO)_{10}\{1,2\text{-}(Me_2As)_2C_6H_4\}]$ (see Fig. 7). Mann[1] argues that this compound provides the strongest evidence in his favour. In his initial paper, he considered[5] its structure to be *quasi*-$[Os_3(CO)_{12}]$ with a clearly drawn *quasi*-anticube-octahedral ligand geometry. However, he goes on to say in the same report: ‘However, the crystal structure of $[Fe_3(CO)_{10}\{1,2\text{-}(Me_2As)_2C_6H_4\}]$ shows that even when the ligand constraints prevent a conventionally bridging structure, the carbonyls become semi-bridging’. In his latest report[1] he now appears to fully accept the LPM and states: ‘Strong evidence for the rotation of the *icosahedron of carbonyls* … comes from the crystal structure of $[Fe_3(CO)_{10}\{1,2\text{-}(Me_2As)_2C_6H_4\}]$ …’. He goes on to say: ‘In comparison with the idealised structure with ligands 5 and 7 (As atoms) (in his diagram they are 7 and 9) coplanar with the iron triangle in $[Fe_3(CO)_{10}\{1,2\text{-}(Me_2As)_2C_6H_4\}]$ the ligands have rotated around the Fe_3 triangle by 18.45° on average. The driving force for this rotation is both arsenic atoms trying to become coplanar with the iron triangle as is normally found.' Not so! The compound is adopting the icosahedral arrangement of ligands as predicted by the LPM; the apparent semi-bridges and the position of the As atoms are a consequence of placing the Fe_3 triangle within the ligand icosahedron to give a D_3 form in complete accord with the predictions of the LPM. The rotation of the two As atoms is required to take the anticube-octahedron to the icosahedron and all structures intermediate between these two extremes.

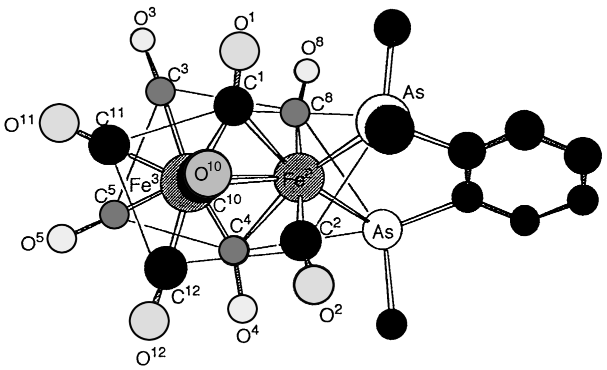


Fig. 7 Structure of $[Fe_3(CO)_{10}\{1,2\text{-}(Me_2As)_2C_6H_4\}]$ (taken from ref. 5)

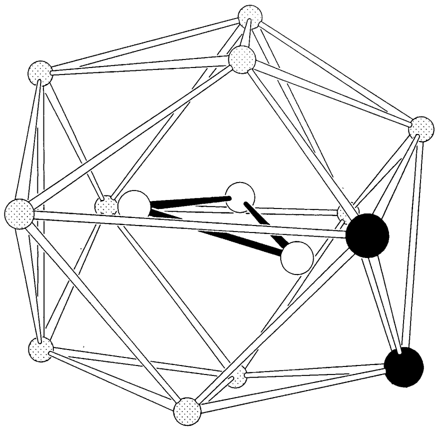


Fig. 8 Alternative view of the molecular structure of $[Fe_3(CO)_{10}\{1,2\text{-}(Me_2As)_2C_6H_4\}]$

According to Mann, this is the compound which most strongly supports his view of fluxionality but this is only because he actually chooses a different rotational axis. To quote: 'P and As ligands are always placed *if possible* in positions 6 and/or 10'. These are the two poles of his chosen S_{10} rotational axis. According to the figure given in his paper,[1] in $[Fe_3(CO)_{10}\{1,2\text{-}(Me_2As)_2C_6H_4\}]$ the two As atoms are placed on Fe_2 and the two different positions 7 and 9. Neither is on the rotational axis. We show an alternative view of the structure (Fig. 8) with As atoms in positions 5 and 6 which clearly demonstrates that it is the perfect example of the result of libration. Referring back to Mann's discussion of the structure (see above) 'in $[Fe_3(CO)_{10}\{1,2\text{-}(Me_2As)_2C_6H_4\}]$ the ligands (As atoms!) have rotated around the Fe_3 triangle by 18.45° on average' and to the comment in his article referring to our work: 'It can therefore be concluded that each C_2 libration produces a rotation of approximately 18°'. It would appear that he agrees with us since an alternative to rotating the As atoms about the Fe triangle by 18.45°, is to rotate the Fe_3 triangle by 18.45° about the two As atoms (libration!).

The real problem with Mann's mechanism is that for chelating ligands it is impossible to position the two donor atoms such that both remain co-ordinated to the same Fe atom during rotation. Whenever a donor atom is not associated with either of the two poles 6 and 10 this will be the case. We suggest that, contrary to Mann's view, this compound provides good evidence in support of the librational mechanism and none for the S_{10} rotation, particularly since that mechanism cannot apply.

(*b*) One of the most telling comments in Mann's paper is: 'There is one relevant compound not included in (*his*) Table 4, $[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$. This compound adopts a structure similar to that found for $[Ru_3(CO)_9\{P(OEt)_3\}_3]$. Due to the stereochemistry of the $P(OPr^i)_3$ ligands, the compound cannot adopt the usual geometry with one Fe–Fe edge bridged by two carbonyls and the axial ligands lean towards semi-bridging positions. The result is a rotation of an average of 24° of the P–Fe–C plane with respect to the Fe_3 triangle. This puts an average angle of 10.5° between the Fe_3 plane and the 6–10 vector'. This evidence clearly favours the librational mechanism yet, as far as we are concerned, for no good grounds is excluded from consideration. It certainly provides evidence *against* Mann's approach.

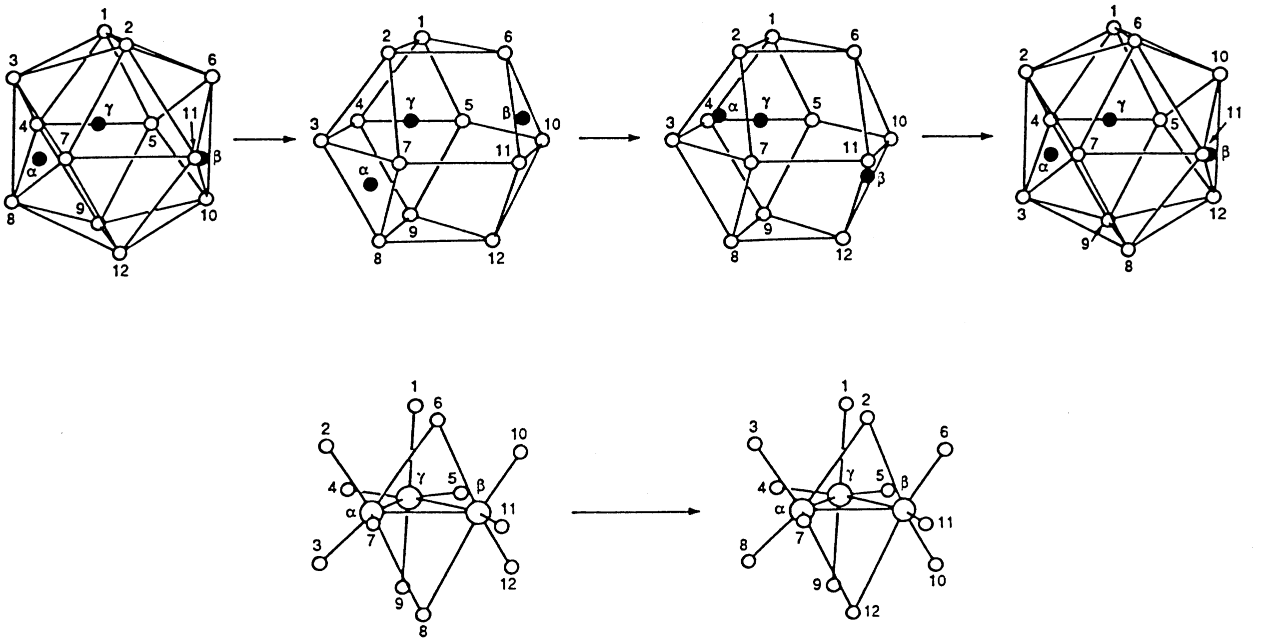


Fig. 9 Effect of one of the five possible modes of polyhedral interconversion for $[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$ (taken from ref. 12)

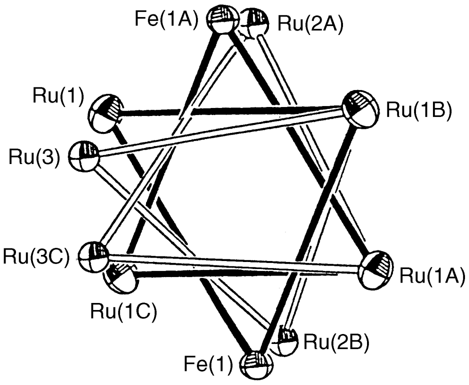


Fig. 10 View of the extended 'Star of David' disorder in the metal atom positions in $[FeRu_2(CO)_{12}]$ at 291 K

Mann also considers that 'Due to the stereochemistry of the $P(OPr^i)_3$ ligands, the compound cannot adopt the usual geometry with one Fe–Fe edge bridged by two carbonyls, with S_{10} rotation being blocked'. Certainly S_{10} rotation will be blocked but if libration were occurring it would be a hidden process since the same ratio of signals *viz.* 3:3:3 would be expected. The activation energy he records is for a higher-energy process which equilibrates both sets of 'axial' carbonyl ligands by one of the modes of the polyhedral interconversion *via* an anticube-octahedral transition state (see Fig. 9). Thus, his argument is invalid.

(4) Direct evidence for the libration pathway of the metal triangle in solid $[M_3(CO)_{12}]$ has been provided from a variable-temperature crystal-structure determination of $[FeRu_2(CO)_{12}]$.[18] Significantly, as the temperature is raised up to 228 K secondary images appear with no apparent change in the space group. These secondary images are shown in Fig. 10; the major component triangle A and triangle B are coplanar and are rotated by 180° relative to each other. But, most importantly, *the remaining triangle lies distinctly out of the plane of the other two.* It is argued that the molecular structure of the 60° and 120° intermediate forms may be deduced as being of C_2 geometry with two edge-bridges (or semi-bridges). This agrees precisely with the pathway predicted for librational motion: $D_3 \Rightarrow C_{2v} \Rightarrow D_3 \Rightarrow C_{2v}$

(5) Finally, one is inclined to ask why, even if one accepts Mann's mechanism, other than it appears to fit some of the available data, is that particular S_{10} axis special? And, what is the driving force for fluxionality? In our approach a complementary geometry (D_3 form) is clearly available and there is good experimental evidence for its existence (the crystal structures of $[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$[20] and $[FeRu_2(CO)_{12}]$[20]). Also where do $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ fit into Mann's scheme? In our approach there is a natural continuity from one structural type to another, we do not have to exclude compounds such as $[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$ (which Mann places in a special class) nor do we have to exclude compounds with chelating ligands such as $[Fe_3(CO)_{10}\{1,2\text{-}(Me_2As)_2C_6H_4\}]$.

In conclusion, we believe that, in the light of the evidence currently available, Mann's attack on the LPM is unjustified. In part, however, we do agree: 'The Ligand Polyhedral Model does present traps for the unwary' (Mann, ref. 1).

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