On the Mechanisms of Fluxionality and Isomerisation of $[Fe_3(CO)_{12-n}\{P(OMe)_3\}_n]$ (n = 1–3)

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Possible alternative mechanisms based on the ligand polyhedral model have been examined to account for the dynamic behaviour and isomerisation of the triiron derivatives $[Fe_3(CO)_{12-n}\{P(OMe)_3\}_n]$ (n = 1–3). Carbonyl scrambling is considered to occur *via* two fundamental processes. First, a low-energy libration of the metal cluster unit within the ligand polyhedron and secondly, a higher-energy ligand polyhedral interconversion involving an anticubeoctahedral ligand array as the complementary geometry. Isomerisation is also believed to occur *via* related ligand polyhedral rearrangements.

In 1978[1] we put forward an alternative view of the carbonyl-scrambling mechanisms observed for many of the binary carbonyl clusters $M_m(CO)_n$ and their derivatives. We argued that rather than use a different *ad hoc* mechanism to rationalise each observed fluxional process, it would be preferable to seek a carbonyl-scrambling path (or sequence of such paths) which involves the *concerted* motion of all CO groups within the molecule in ways that are well defined by the molecular symmetry of the cluster. In this respect the phenomenon would be similar to that envisaged for the fluxionality of simple mononuclear co-ordination compounds ML_n, where the process is considered to involve the interconversion of the 'ground-state' geometry to the 'final-state' geometry through a 'complementary' (closely related) ligand geometry, *e.g.* the square-based-pyramidal complementary geometry for the fluxionality observed for trigonal-bipyramidal systems ML_5 (see below).

trigonal bipyramid	⇄	square-based pyramid	⇄	trigonal bipyramid
ground state		complementary geometry		final state
(*TBPY*)		(*SPY*)		(*TBPY*)

In many instances, information regarding the nature of such rearrangements may be derived from solid-state structures. If a range of crystal structures of a series of similar (and related) molecules is examined, a variation in structural parameters will be found which should lie along the reaction coordinate between the two (or more) distinct geometries. Furthermore, these rearrangements or polyhedral interconversions are expected to correspond to movement along a soft vibrational mode of the molecule. In the past such arguments have been reserved for simple, monometal complexes ML_n, for which a body of information is available, but we see no reason why the same principles should not be extended to include cluster systems where both the central metal unit M_m and the ligands L_n adopt a well defined polyhedral geometry.

Clearly for systems $M_m(CO)_n$ the problem *appears* more complex since, with few exceptions, the symmetry of the metal polyhedron is usually different from that of the ligand polyhedron.[1,2] In reality this proves to be an advantage and examination of the fluxional behaviour of the cluster carbonyls $M_m(CO)_n$ not only enables the mechanism of carbonyl mobility to be elucidated, but may also provide a suitable way of establishing the complementary geometries of larger polyhedra (n > 10), about which comparatively little is known.[3]

Of special note in this regard is the icosahedron. Following the classic work carried out in the 1960s on the interconversion of 1,2- to 1,7- to 1,12-$C_2B_{10}H_{12}$[4] there has been much speculation on the mechanism by which the icosahedron undergoes rearrangement. An icosahedral ligand polyhedron is frequently observed for the cluster carbonyls[1,5–7] and in particular for $[Fe_3(CO)_{12}]$ and its various substituted derivatives, $[Fe_3(CO)_{12-n}L_n]$[5,6] [L = donor ligand such as $P(OMe)_3$, n = 1–3]. At the time of our original publication we recognised[1] that 'the development of a complete theoretical description of the mechanisms of carbonyl scrambling is seriously hindered by the small number of compounds that have been fully investigated'. We were aware of this limitation but, nevertheless, examined the consequences of the polyhedral interconversion of an icosahedron through a *cubeoctahedral* complementary geometry. In doing so it was pointed out that 'although this mode of interconversion appears to work well in these and other related systems it may not be general, and other transition states may be involved'. Indeed, the cubeoctahedral transition state is not entirely satisfactory. Interconversion *via* the cubeoctahedral complementary geometry maintains the antipodal relationships of all the ligands (see Fig. 1). This has important consequences and, in $[Fe_3(CO)_{11}L]$ for example, it is not possible to equilibrate all eleven carbonyls by this process alone.[4b] One CO ligand, *viz.* that antipodal to L, would remain unique throughout the icosahedron ⇄ cubeoctahedron ⇄ icosahedron process. This longstanding and well examined problem was first encountered in attempts to understand the isomerisation of 1,7- to 1,12-$C_2B_{10}H_{12}$[4b] (see above), and in order to bring about full interconversion of all vertices, it was noted that, amongst other possibilities, rotation of a triangular face in the cubeoctahedral transition state is also required.

More recently, we have established that the *anticubeoctahedron* is a better complementary geometry[6] for fluxionality in $[Fe_3(CO)_{12}]$ and its derivatives. Use of this complementary polyhedron in the interconversion process permits the *eventual* total scrambling of all carbonyls (vertices) since the antipodal relationships are not necessarily retained (Fig. 2). The cubeoctahedron and anticubeoctahedron are closely related (Fig. 3). The conversion of an icosahedron into an anticubeoctahedron involves the breaking of six polyhedral edges to form six square faces just as with the cubeoctahedron, the difference being in the relationship of these six square faces. There are ten different sets of polyhedral edges which can be broken, although pairs of these edges are related by mirror symmetry (see Fig. 4). For an isolated ligand icosahedron $(CO)_{12}$ these modes are degenerate; however, as discussed previously,[6] if a triangle is placed within the icosahedron as in $[Fe_3(CO)_{12}]$, or CO is replaced by a

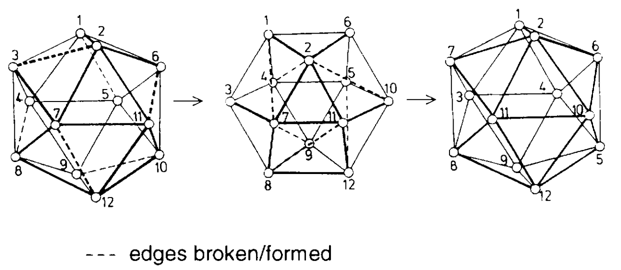


Fig. 1 Interconversion of the icosahedron *via* a cubeoctahedral transition state

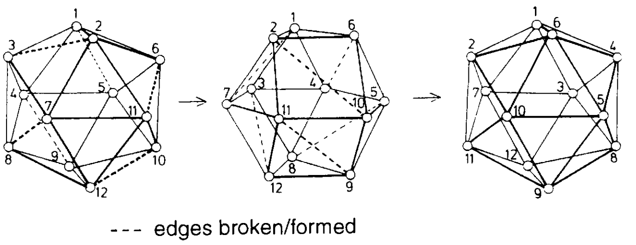


Fig. 2 Interconversion of the icosahedron *via* an anticubeoctahedral transition state

ligand L, this degeneracy is removed (see below). For all modes some concerted motion or libration of the metal triangle is required. This type of motion has been discussed earlier.[1,5,6] It should be the same in the solid state as in solution and it would appear that the preferred librational motion of the M_3 triangle is about its pseudo-two-fold axes,[7] although other possibilities should not be neglected. Following our original suggestion, this idea of libration of the metal polyhedron within the ligand polyhedron has been further employed by Heaton *et al.*[8] to account for the fluxional process in the tetranuclear cluster $[Co_4(CO)_{12}]$.

The main objective of this paper is a reconsideration of the probable structures of the cluster compounds $[Fe_3(CO)_{12-n}\{P(OMe)_3\}_n]$ (n = 1–3) in solution and the dynamic processes they undergo. In part, it serves as a response to an earlier paper by Mann and co-workers[9] in which, on the basis of a series of elegant ^{31}P and ^{13}C NMR studies, the structures these isomeric forms adopt and the dynamic motion they undergo were described. In addition, it also provides an extended and more detailed discussion of our own views of this problem which we considered previously.[6,10] In an earlier communication[10] we pointed out that the number of possible isomeric forms of these derivatives is far more extensive than Mann and co-workers[9] apparently realised and we have also suggested that there is possibly a better description of the dynamic motion they undergo based on the ligand polyhedral model (LPM).[6,11]

Results and Discussion

The overall consequence of librational motion of the Fe_3 triangle within the icosahedral ligand is easy to visualise. Simply, we may regard the librating cluster unit as equivalent to a sphere and, consequently, as the temperature is raised it is only necessary to examine the modes of interconversion of the icosahedral ligand shell. The different modes of interconversion of the icosahedron through an anticubeoctahedral complementary geometry are shown in Scheme 1. Bearing these comments in mind and referring to the modes given in Scheme 1, we shall now examine the fluxional behaviour and isomerisation processes that the derivatives $[Fe_3(CO)_{12-n}\{P(OMe)_3\}_n]$ undergo.

The Molecular Structures of $[Fe_3(CO)_{12-n}L_n]$ *and the LPM.*—We may view the substituted compounds $[Fe_3(CO)_{12-n}L_n]$ in the same way as the binary carbonyls and may sub-divide the cluster into the ligand shell and the central metal unit. In these cases, however, it is necessary to consider in fuller detail the geometry that the ligand shell may adopt.[12] Earlier we gathered evidence to show that in all cases the ligand polyhedron $(CO)_{12-n}L_n$ adopted a quasi-icosahedral geometry.[13] Thus, for $(CO)_{11}L$ there is only one possibility (Fig. 5). For $(CO)_{10}L_2$ there are three possibilities. These are shown in Fig. 6 and correspond to the 1,2-, 1,7- and 1,12-disubstituted icosahedra respectively. Finally, as far as the current work is concerned, we have $(CO)_9L_3$. For this system a greater range of possibilities exists, *viz.* the 1,2,3, 1,2,4, 1,7,8, 1,7,9 and 1,x,12 (x = 2–11) forms (Fig. 7). If we assume that the most stable forms of these polyhedra correspond only to those in which the L · · · L contact is minimised, then it might be concluded that for the disubstituted icosahedron the order of stabilities falls across the series 1,12 > 1,7 > 1,2 and for the trisubstituted icosahedron, across the series 1,7,9 > 1,x,12 > 1,7,8 > 1,2,4 > 1,2,3.

Insertion of the Fe_3 triangle into each of these possibilities generates three classes of isomer. The first is related to the parent compound with two μ-CO bridges [Fig. 8(*a*)]. The second [Fig. 8(*b*)], with no carbonyl bridges, is related to the D_3 structure postulated for $[Fe_3(CO)_{12}]$ in solution.[14] We shall refer to this as the icosahedral all-terminal isomer. Finally, there is third class, which contains two μ_3-CO bridges [Fig. 8(*c*)]. Since no examples of this class have been observed in any derivative studied[13] we shall not consider it further but it should not be forgotten. For brevity, and in line with arguments previously presented, we shall also ignore all possibilities which involve either equatorial substitution or L in a bridging mode.

All these isomers are based on the icosahedral (or quasi-icosahedral) arrangement of ligands. However, there exist additional possibilities which are based on either of the two less-favourable ligand polyhedra, *viz.* the cubeoctahedron or anticubeoctahedron. As far as we are aware, there are no established examples of the cubeoctahedral shell for Fe_3 derivatives; consequently, we shall not consider this possibility further. The anticubeoctahedron, however, has been observed for both $[Ru_3(CO)_{12}]$[15] and $[Os_3(CO)_{12}]$,[16] although in the ruthenium derivative a very slight distortion away from the anticubeocta-

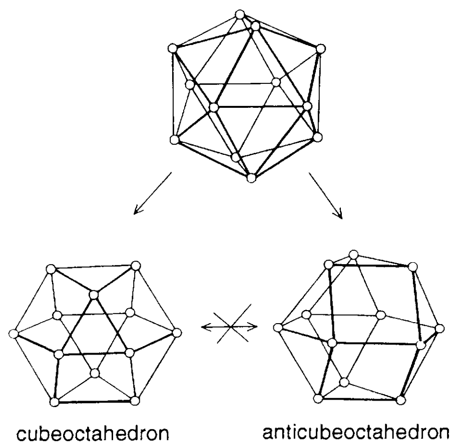


Fig. 3 Relationship between the cubeoctahedron, the icosahedron and the anticubeoctahedron

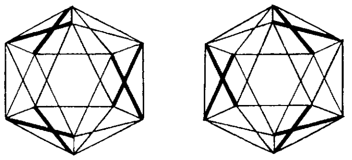
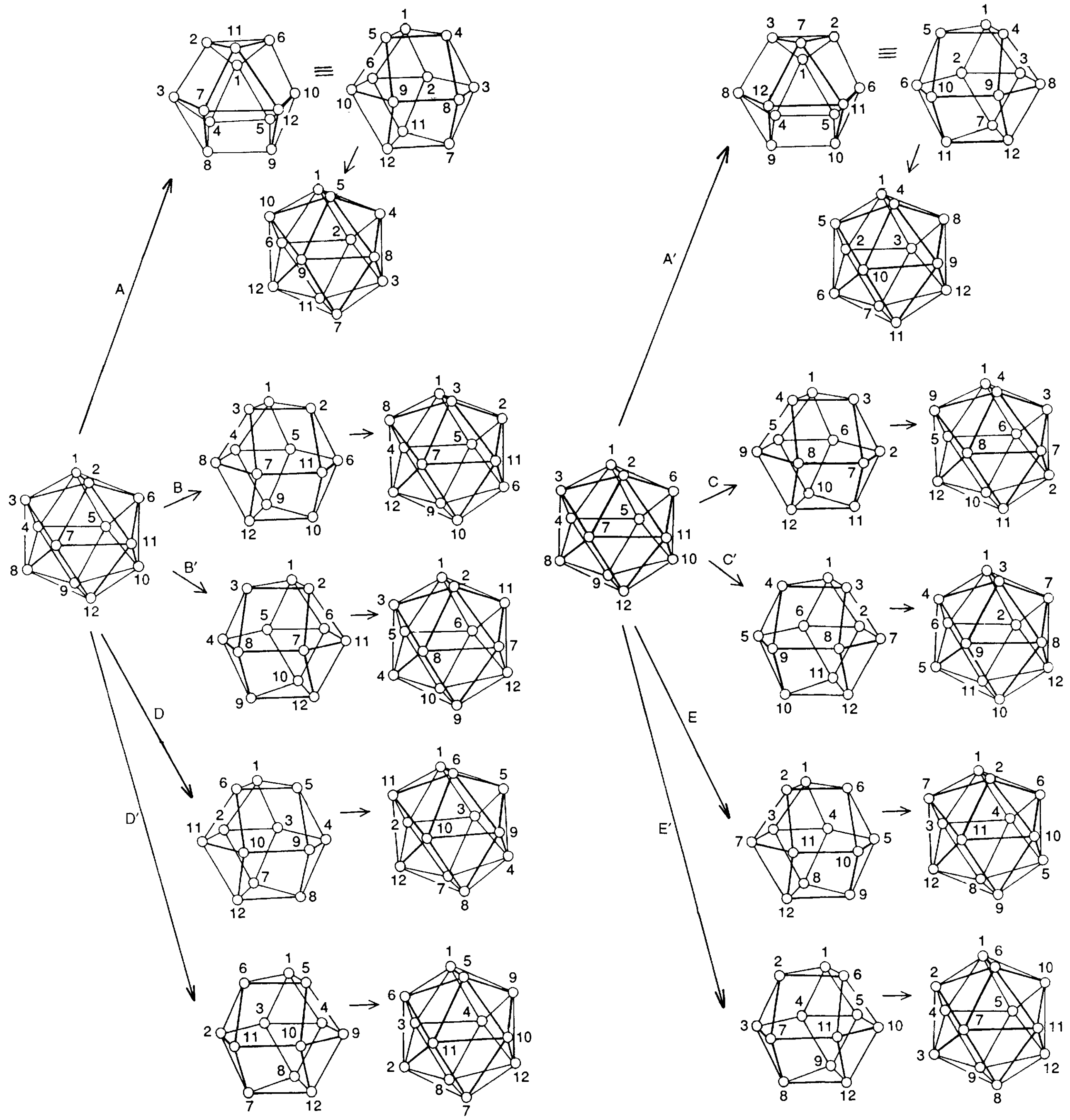


Fig. 4 Mirror-symmetry relationship of bonds for the transition from an icosahedron to an anticubeoctahedron



Scheme 1 Modes of interconversion of the icosahedron through an anticubeoctahedral complementary geometry

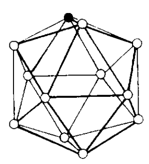


Fig. 5 The icosahedral $(CO)_{11}L$ ligand shell

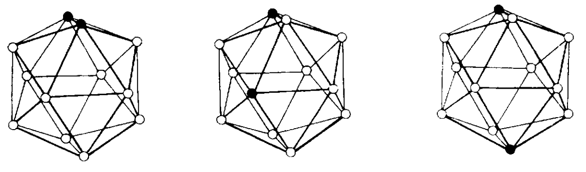


Fig. 6 The 1,2-, 1,7- and 1,12-disubstituted icosahedra

hedron towards the icosahedral distribution is observed. For the various substituted derivatives $[M_3(CO)_{12-n}L_n]$ (M = Ru or Os, n = 1–3), the whole spectrum of geometries, ranging from the anticubeoctahedron to the icosahedron, has been recorded.[13] Again, Mann and co-workers[9] considered some, but not all, of these possibilities.

However, an examination[13] of a large number of the crystallographic structures of a series of $[Fe_3(CO)_{12-n}L_n]$ derivatives has revealed *no evidence* for the existence of an anticubeoctahedral ligand shell. This is in agreement with the prediction of the LPM which states that as the carbonyl ligand is replaced by bulky ligands there will be a tendency of the ligand shell to move away from the 'less-favourable' anticubeoctahedron towards the more-favourable icosahedron. Mann and co-workers[9] concluded that one of the isomers of the compound $[Fe_3(CO)_9\{P(OMe)_3\}_3]$ adopts a quasi-anticubeoctahedral arrangement in which the six axial ligands form semi-bridges. We tend to disagree and believe that this is

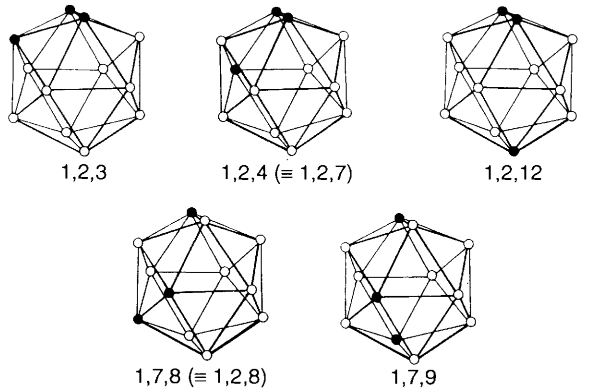


Fig. 7 The 1,2,3-, 1,2,4-, 1,2,12-, 1,7,8- and 1,7,9-trisubstituted icosahedra

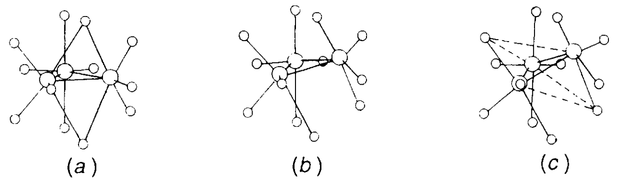


Fig. 8 Possible structures of $[Fe_3(CO)_{12}]$: (*a*) two μ-CO bridges (C_{2v}), (*b*) all-terminal (D_3), and (*c*) two μ_3-CO bridges (C_2)

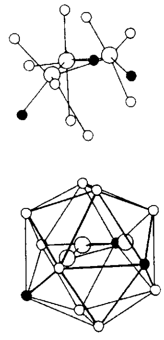


Fig. 9 Schematic diagram of $[Fe_3(CO)_9\{P(OMe)_3\}_3]$ in isomeric form **g**

the D_3-icosahedral structure given in Fig. 9. Whether or not one regards the six carbonyls as semi-bridging is subjective. The relationship between the icosahedral geometry and the anticubeoctahedral geometry involves a small rotation of two of the three $Fe(CO)_3L$ units as shown in Fig. 10.

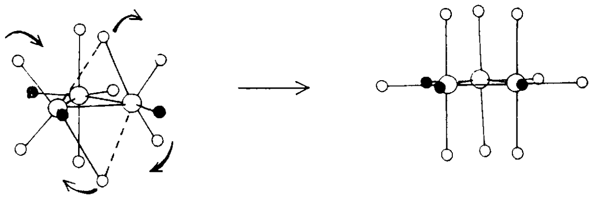


Fig. 10 Interconversion of icosahedral to anticubeoctahedral geometry in $[Fe_3(CO)_9L_3]$ by rotation of $Fe(CO)_3L$ units

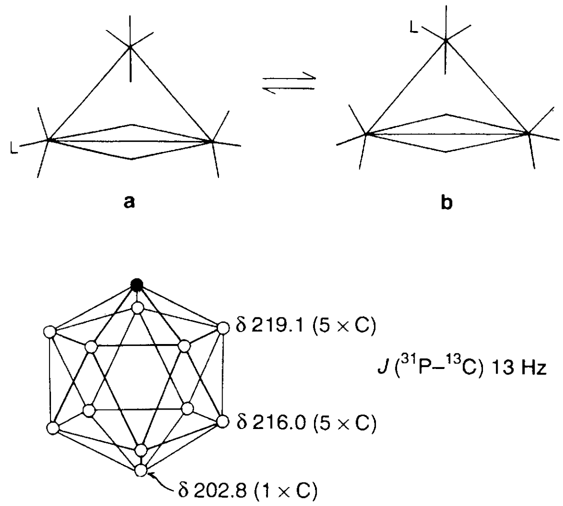


Fig. 11 Interconversion of the two isomeric forms of $[Fe_3(CO)_{11}L]$. Isomers **a** and **b** readily undergo interconversion on libration of the Fe_3 triangle, but the relationship of the vertices within the icosahedral ligand shell is maintained. Further carbonyl exchange is only brought about by polyhedral rearrangement

The Fluxional Behaviour of $M_m(CO)_n$.—According to the LPM[1,2] the structures of the carbonyl clusters $M_m(CO)_n$ may be separated into two components: (*i*) the ligand polyhedral shell $(CO)_n$ and (*ii*) the polyhedral metal unit M_m. The structure adopted by the parent cluster thus depends on the arrangement of the metal cluster unit (*ii*) within the ligand polyhedron (*i*). On this simple basis the structures of most, if not all, cluster carbonyls may be rationalised. It follows that in some cases the dynamic behaviour of these clusters may be viewed in part as occurring when one polyhedron moves *en masse* relative to the other. In our original communication[2] we pointed out that it is immaterial whether the process is viewed as the $(CO)_n$ polyhedron moving around the central M_m polyhedron or as the central M_m unit librating within the outer ligand shell. This is a point frequently overlooked. We did, however, prefer the latter view, *viz.* the libration of the M_m unit within the $(CO)_n$ unit, because we felt that in the solid, given the constraints placed on the movement of the carbonyl ligands by the lattice, it would be the more likely.[7] It must be stressed, however, as we have done previously, that the nature of the libration will be dependent on (*a*) the relative masses of the two units, M_m and $(CO)_n$, (*b*) the phase and temperature of the system under observation, and (*c*) the overall symmetry of the cluster molecule $M_m(CO)_n$.

We believe that this librational motion *may* correspond to the *very low-energy process* of fluxional behaviour suggested by Mann and co-workers.[9] We further suggested that, in addition to this librational motion, a second *type* of dynamic motion will also occur. This, referred to extensively in the introduction, corresponds to the permutation of the vertices of the carbonyl polyhedron *via* a polyhedral rearrangement and is of the type commonly accepted for mononuclear systems, *e.g.* the Berry pseudo-rotation for ML_5 systems. Thus, in summary, we suggest that the dynamic processes observed for carbonyl clusters and in particular those found for $[Fe_3(CO)_{12-n}L_n]$ are of two types, *viz.*, (*i*) the libration of one polyhedron relative to another, and (*ii*) the polyhedral rearrangement of the carbonyl ligands through some suitable complementary geometry; in this case *probably* the anticubeoctahedron. Again, we should emphasise that these two types of motion are not independent, but are closely interlinked. The extent or dominance of one or the other will be dependent on the criteria (*a*)–(*c*) outlined above.

$[Fe_3(CO)_{11}\{P(OMe)_3\}]$.—According to Mann and co-workers[9] this compound exists in the two isomeric forms **a** and **b** shown in Fig. 11, although others are possible.[10] Libration of the Fe_3 unit within the icosahedral ligand shell interconverts these two isomeric forms without causing carbonyl exchange within the ligand polyhedron. Hence, a doublet and two singlets of related intensity 5:5:1 are expected in the low-temperature ^{13}C NMR spectrum (Fig. 11). As the temperature is raised, polyhedral interconversion will also occur.

Examination of modes A, A′, D, D′, E and E′ reveals that, in

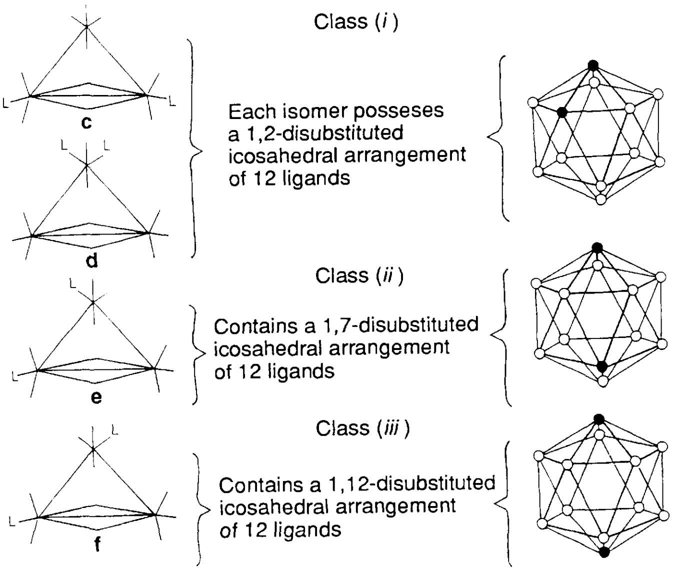


Fig. 12 The expected isomers of $[Fe_3(CO)_{10}L_2]$ based on the icosahedral ligand shell

the course of rearrangement through the anticubeoctahedron, vertices 3 and 10 retain their antipodal relationship. If the ligand $P(OMe)_3$ is placed at vertex 3, then it follows that operations of the degenerate modes A/A′ and D/D′ (or E/E′) will permute the carbonyl ligands occupying vertices 1, 2, 4–9, 11 and 12, but the carbonyl occupying vertex 10 will not be involved. Consequently, a 10:1 ratio of carbonyl signals is expected. Operation of the additional mode B, which removes the antipodal relationship 3 and 10, will bring about the total equilibration of all carbonyls 1, 2 and 4–12.

Hence libration of the Fe_3 triangle, followed first by the operation of modes A/A′ and D/D′ and then A,A′, D/D′ and B, conveniently explains the observed variation of the ^{13}C NMR spectrum with temperature. The low barrier to isomerisation is also readily understood (see also below) since only libration is involved at that stage.

$[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$.—This compound apparently exists in the two isomeric forms **e** and **f** shown in Fig. 12, although there are other possibilities, **c** and **d** (see also Fig. 13).[10] In **e** the ligand polyhedron corresponds to the 1,7-disubstituted icosahedron, and in **f** to the 1,12-disubstituted icosahedron. If we assume, for convenience, that the two $P(OMe)_3$ ligands occupy vertices 3 and 10, then for isomer **f** librational motion of the Fe_3 triangle equilibrates the two different $P(OMe)_3$ ligands but does not modify the relationship of the ligands within the ligand polyhedron. Consequently, the five carbonyls in each of the icosahedral pentagonal layers couple to one ^{31}P nucleus (vertex 3) or the other (vertex 10) respectively (see below) and, because the two sets of five CO ligands are symmetry related, the signal appears as a doublet. At higher temperatures, interconversion of the icosahedral shell through an anticubeoctahedral complementary geometry takes place (see Scheme 1). Operation of modes A/A′ and D/D′ will equilibrate the ten carbonyls 1, 2, 4–9, 11 and 12 (see above), but will retain the *antipodal* relationship of the two $P(OMe)_3$ ligands. Thus, isomer **f** undergoes *carbonyl fluxionality without isomerisation*, giving rise to a triplet in the ^{13}C NMR spectrum. Isomerisation will occur, however, by the operation of, for example, mode B. Use of this mode leads to the formation of the second isomer **e**. In this case, in contrast to $[Fe_3(CO)_{11}\{P(OMe)_3\}]$, isomerisation is *not* brought about by low-energy libration, but by polyhedral interconversion; hence, a higher barrier is expected and observed. These predictions are totally in accord with experiment.[9]

For isomer **e**, libration of the Fe_3 triangle will cause a change in the observed signals to the ratio 4:2:2:1:1. Here, for convenience, we shall assume that the two ligands occupy positions 4 and 7 (it could have been 5 and 11, *etc.*). Operation of mode B permutes carbonyls 8, 3, 2, 6, 10 and 12 and leads to carbonyl fluxionality with a ratio of signals 6:2:2 without isomerisation. Since in this case, according to the LPM, vertices 2 and 12 may be taken to correspond to the two μ-CO bridges in the ground-state molecular structure of **e** and vertices 3, 6, 8 and 10 correspond to axial carbonyls, it follows that mode B equilibrates 2, 3, 8, 12, 10 and 6. Thus, mode B corresponds precisely to the merry-go-round process,[17] emphasising the point made previously[6] that this approach is not an alternative to Cotton's viewpoint,[17] but embraces that viewpoint within it. Other modes, *e.g.* A′, bring about conversion into isomer **f**, as is observed or, with mode C, conversion to the (as yet unobserved) isomeric form **c** or **d**. The modes A, B′, C′, D′ and E/E′ also maintain the 4 to 7 relationship. Combination of these modes would therefore lead to additional scrambling without isomerisation.

$[Fe_3(CO)_9\{P(OMe)_3\}_3]$.—If the twelve ligands are assumed to adopt the icosahedral arrangement for reasons outlined above, then we should consider three of the isomers shown in Fig. 13. In **g** and **h** the structures are based on the C_{2v}-bridged structure adopted by $[Fe_3(CO)_{12}]$ in the solid. In each of the two cases the ligand shell corresponds to the 1,2,12-trisubstituted icosahedron. The third possibility **i**, is based on the all-terminal carbonyl arrangement corresponding to the D_3 form suggested for $[Fe_3(CO)_{12}]$ in solution. Here the ligand shell adopts the highly stable 1,7,9-trisubstituted icosahedral arrangement. Other possibilities based on the anticubeoctahedral arrangement of ligands **j**–**l** are also shown. We shall restrict our attention to forms **g**–**i**. According to Mann and co-workers, isomer **g** is dominant in solution. However, we would emphasise that possibility **h** cannot be excluded on the basis of the NMR data. Libration of the Fe_3 triangle within the 1,2,12-trisubstituted icosahedron, isomer **g**, will not change the ratio of signals observed for the ground-state geometry, *viz.* 2:2:2:2:1. In order for the molecular structure **g** to be realised, we shall assume, for convenience, that the three phosphite ligands will occupy the vertices 4, 7 and 11 (or their symmetry equivalents, *e.g.* 1, 2 and 12). Operation of mode B leads to the permutation of the six vertices 2, 3, 8, 12, 10 and 6, but retains the relationship 4, 7 and 11. Hence, fluxionality without isomerisation takes place. If we were to assume that the Fe_3 triangle remains static during this operation, then this interchange would correspond (as above) to the Cotton merry-go-round mechanism, exchanging the two bridges and four axial carbonyl ligands. At higher temperatures additional modes will operate, *e.g.* C′, which partially destroys the 4, 7, 11 relationship and converts the ligand polyhedron in isomer **g** into that of **i**.

The second isomer **i**, which is favoured for more sterically demanding ligands such as $P(OPr^i)_3$,[18] contains three, chemically distinct, carbonyl environments; hence, it exhibits three signals in the ratio 3:3:3 in the ^{13}C NMR spectrum. The three phosphorus ligands are symmetrically equivalent and libration of the Fe_3 triangle will not alter this distribution. If we assume the three ligands occupy vertices 3, 6 and 12, then modes B, C′, D or E′, which are degenerate, will all bring about carbonyl equilibration without isomerisation, *i.e.* vertices 3, 6 and 12 retain their relationship within the icosahedral shell. Other modes, for example B′, will cause isomerisation to either **g** or **h**.

Conclusion

In this work we have attempted to show that the fluxional and isomerisation processes that $[Fe_3(CO)_{12}]$ and its substituted derivatives are considered to undergo may be understood in terms of the ligand polyhedral model. In contrast to the work we

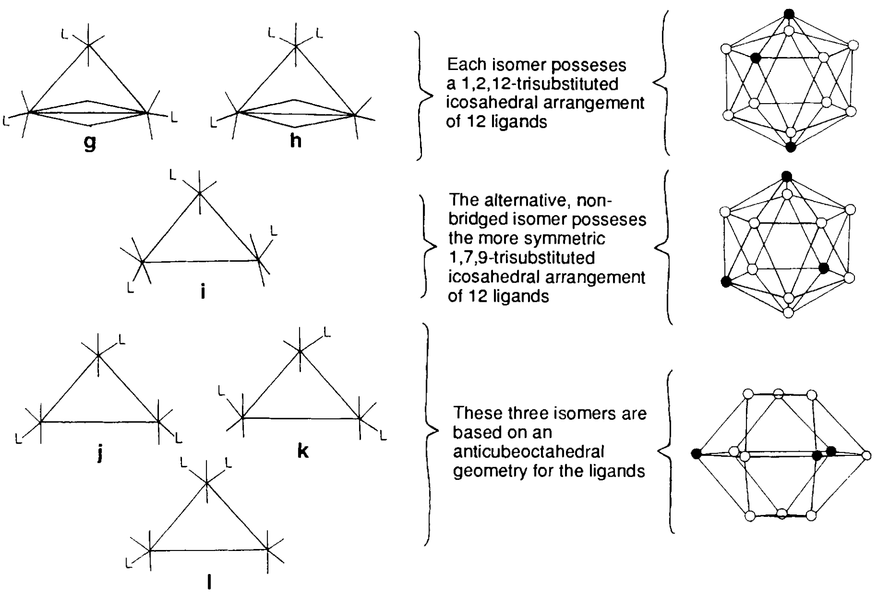


Fig. 13 The expected isomers of [$Fe_3(CO)_9L_3$] based on the icosahedral ligand shell

reported earlier,[5] we now believe that the *anticubeoctahedron*, rather than its close relative the *cubeoctahedron*, is the preferred complementary geometry. This view is supported by the molecular structures reported for a wide range of crystalline samples.[13] The LPM approach clearly illustrates how fluxionality *with* and *without* isomerisation is possible and why the barriers to isomer interconversion vary. We would emphasise that this approach encompasses the mechanisms of Cotton[17] and Mann[9] and their co-workers and does not, as is frequently suggested, offer a counter view. We would also emphasise that the same approach, using the modes illustrated in Scheme 1, may be applied equally successfully to other icosahedral ligand-based clusters such as [$Co_4(CO)_{12}$], [$Rh_4(CO)_{12}$], [$RhCo_3(CO)_{12}$], [$Ir_4(CO)_{12-n}L_n$] and related derivatives.

Acknowledgements

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