Dynamic Processes of Trinuclear Carbonyl Clusters $[M_3(CO)_{12}]$ (M = Fe, Ru, or Os) and their Derivatives

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The dynamic motion that the trinuclear carbonyls $[M_3(CO)_{12}]$ (M = Fe, Ru, or Os), and their derivatives $[M_3(CO)_{12-n}L_n]$ undergo in both the solid and solution has been examined. Evidence is presented to suggest that the fluxional behaviour and the isomerisation processes they undergo may be best interpreted in terms of the Ligand Polyhedral Model.

Earlier one of us reported[1] an alternative method of viewing the structures of the binary carbonyls and their derivatives. In the model, which has become known as the Ligand Polyhedral Model (LPM), such carbonyl structures are broken down into two components, 'the outer CO polyhedron' and 'the inner metal cluster polyhedron', the manner in which one is arranged relative to the other governing the number of bridging and terminal carbonyl groups present. This model has proved to be remarkably successful in rationalising a large number of cluster structures and has been applied widely (see *e.g.* ref. 2). Later, the model was applied to fluxional systems.[3] First, it was recognised that some fluxional behaviour may be interpreted in terms of a librational mode of the inner metallic core within the ligand polyhedron. This motion was felt to be particularly relevant to motion in the solid. Secondly, just as with the mononuclear complexes, fluxional behaviour may sometimes be interpreted in terms of ligand polyhedral rearrangements. This is more the case for samples in solution. Clearly with clusters this is a much more complicated process than for monomeric complexes and we have discussed these additional complications in a recent publication.[4] It is important to recognise that these two types of fluxionality are not mutually exclusive and may well occur in concert. In our previous publications we chose as a good example of the latter type of fluxionality the tetranuclear carbonyls $[M_4(CO)_{12}]$ and their derivatives. Unfortunately, however, the generality of the approach does not appear to have been appreciated and mainly for that reason we now report its application to the trinuclear clusters $[M_3(CO)_{12}]$ and their derivatives.

Dynamic Processes of $[M_3(CO)_{12}]$ Derivatives

There continues to be considerable interest in the dynamic behaviour of the trinuclear carbonyls $[M_3(CO)_{12}]$ (M = Fe, Ru, or Os) and their derivatives $[M_3(CO)_{12-n}L_n]$ both in solution and in the solid state.[1–45] The large quantity of reported n.m.r. data makes these systems particularly suitable for analysis in terms of the LPM. In this account we shall first consider the prototypical example, *viz.* $[Fe_3(CO)_{12}]$, then the various substituted derivatives $[Fe_3(CO)_{12-n}L_n]$ (n = 1—3) and the isomers that they exhibit. Following this we shall explore the consequences of the librational modes that might occur and the polyhedral interconversions that account for ligand rearrangements and isomerisations. Finally, we shall consider the carbonyls $[M_3(CO)_{12}]$ (M = Ru or Os) and their substituted derivatives; these provide examples of the trimetallic unit within the alternative anticuboctahedron of twelve ligands.

Elucidation of the solid-state and solution structures of $[Fe_3(CO)_{12}]$ has been one of the classic problems of cluster chemistry. Even after the solid-state molecular structure had been unambiguously established[5] (which was in itself difficult due to the crystallographic disorder problems encountered), there remained considerable doubt concerning the structure in solution. Although the i.r. spectrum[6] of $[Fe_3(CO)_{12}]$ in an argon matrix at 20 K is consistent with the solid-state structure, the solution i.r. spectrum in hexane is not.[7] It was proposed by Cotton and Hunter[8] that $[Fe_3(CO)_{12}]$ could adopt a continuum of structures in solution, ranging from the C_{2v} bridged structure very similar to that observed in the solid to the D_{3h} structure based on that observed for solid $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$. These workers further considered that the C_{2v} structure was favoured in more polar solvents. They also suggested that the low-activation-energy dynamic behaviour of $[Fe_3(CO)_{12}]$ in solution (only one signal observed in the ^{13}C n.m.r. spectrum even at −150 °C) could be rationalised *via* the interconversion of these two extreme structures, which results in cyclic exchange of carbonyls around an edge of the metal triangle (complete equilibration being achieved by this exchange around all edges). The same type of mechanism has also been used to rationalise the fluxional behaviour observed for $[M_3(CO)_{12}]$ (M = Ru or Os)[9–11] and their phosphine- or phosphite-substituted derivative,[12–20] all of which are based on either the parent D_{3h}, anticuboctahedral, structure or the D_3 icosahedral arrangement (see below). However, on the basis of the LPM, it has previously been argued[1] that the Fe_3 triangle is too small to be accommodated within an anticuboctahedron {*i.e.* the D_{3h} structure is not a favourable ground-state structure for $[Fe_3(CO)_{12}]$}, and that it was unlikely to be an intermediate in any fluxional process. Instead it was proposed that the variation in the i.r. spectra could be rationalised by the existence of an alternative isomer of D_3 symmetry which contains all terminally bonded carbonyl ligands but which is also based on an icosahedral distribution of ligands. This structure is considered to be more favourable in non-polar solvents than the bridged C_{2v} structure, although there is still some of the latter structure present. Recent extended *X*-ray absorption fine structure (EXAFS) studies are consistent with this argument, as they are also consistent with the existence of an all-terminal structure in hexane solution, although bridging carbonyls were detected in frozen dichloromethane solutions.[21] This suggests that there is little difference in the relative stabilities of the D_3 and C_{2v} isomers of $[Fe_3(CO)_{12}]$.

Recent ^{13}C magic angle spinning (m.a.s.) n.m.r. studies have shown dynamic behaviour for $[Fe_3(CO)_{12}]$ in the solid state.[32,33] At low temperatures the spectrum was consistent with a C_{2v} ground-state structure; however, six signals were observed in the room-temperature spectrum, none of which had chemical shifts consistent with bridging carbonyls. It was argued[22,23] that this spectrum could be rationalised by invoking rotation of the Fe_3 triangle between the two orientations

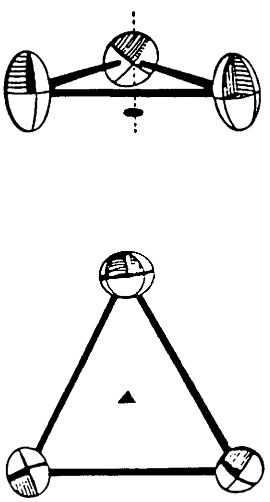

Figure 1. Atomic displacement parameters (adps) of the Fe_3 triangle of $[Fe_3(CO)_{12}]$ showing preferential libration about the unique C_2 axis

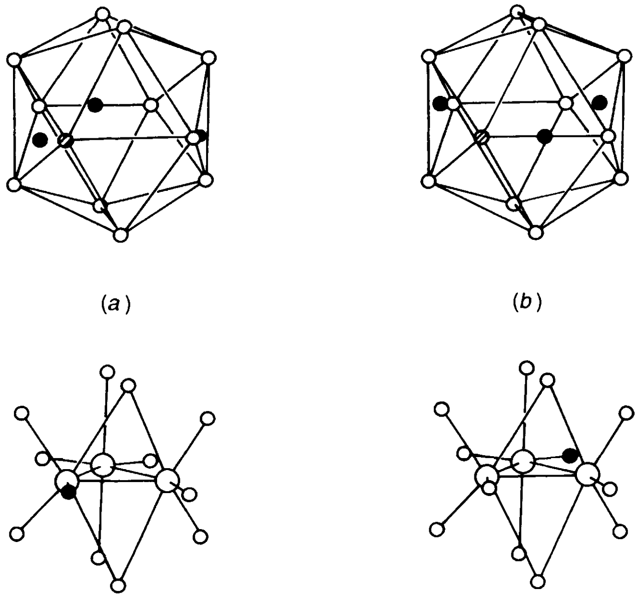

Figure 2. Equatorially substituted isomers of $[Fe_3(CO)_{11}L]$

observed crystallographically (*i.e.* through 60° about the triangular pseudo-C_3 axis). However, we prefer an alternative explanation, which involves the facile interconversion between the energetically similar C_{2v} and D_3 structures.[22] This may occur by the simple libration of the iron triangle about one of its C_2 axes (see Figure 1). At low temperatures only small-amplitude librations of the metal triangle occur but as the temperature increases the amplitude of these librations also increases. In particular, libration about the unique axis of the isosceles Fe_3 triangle (which passes through the unique Fe atom and bisects the bridged Fe–Fe vector) is sufficient to cause the triangle to oscillate between the C_{2v} and D_3 structures. This libration retains a mirror plane of the C_{2v} structure (hence the six signals), and as those carbonyls that are bridging in the C_{2v} structure become terminal in the D_3 structure their chemical shifts move upfield. Analysis of the atomic displacement thermal parameters (adps) of the Fe atoms show preferential motion of the triangle about the proposed axis (Figure 1).[22] Variable-temperature solid-state i.r. studies provide additional evidence for the same libration.[32]

There are three possible C_{2v} orientations that can be generated from a given D_3 orientation *via* rotation about one of the three triangular C_2 axes. However, this change in orientation must be concerted with a slight change in the shape of the ligand polyhedron, *i.e.* it becomes flattened towards the ridged Fe–Fe vector. Thus, for the Fe_3 triangle to move between two C_{2v} orientations *via* a D_3 orientation some slight rearrangement of the ligand icosahedron is required. Such a rearrangement would be expected to be less favourable in the solid state, due to the packing forces present; thus, the motion of the metal triangle is probably limited to libration about one C_{2v} orientation. No such constraints exist in solution, and the interchange between all the possible C_{2v} and D_3 orientations moves the triangle around the whole of the internal volume of the ligand icosahedron, *i.e.* total carbonyl equilibration is achieved. This is slightly different to the mechanism previously proposed originally, which invoked an additional orientation,[3] however the basic idea of carbonyl equilibration *via* motion of the metal polyhedron within the ligand polyhedron is the same. In the above process each carbonyl must adopt a bridging co-ordination mode at some stage.

So far we have only considered the effect of librational motion on the structure of the parent. However as the temperature is raised we must also consider the polyhedral motion that the ligand envelope might also undergo. Earlier we considered the possibility that the icosahedron of carbonyl ligands in $[Co_4(CO)_{12}]$ or $[Rh_4(CO)_{12}]$ could undergo rearrangement *via* a cuboctahedral intermediate. This is also possible for the tri-iron system. In this case, however, the degeneracy of the five modes of interconversion of an isolated icosahedron will be lifted differently. For the parent molecule this aspect is less important than for the various substituted derivatives which are discussed below.

Substitution of one or more carbonyl groups in $[Fe_3(CO)_{12}]$ leads to a wide range of isomeric derivatives. These have been described elsewhere.[4] In this paper we shall be primarily concerned with the fluxional behaviour and isomerisation processes which they undergo. Basically the same rules apply. However, if a carbonyl is substituted by a phosphine or phosphite ligand only limited carbonyl scrambling is possible, since such ligands tend to occupy equatorial, terminal co-ordination sites in trinuclear clusters[24–26] and show little preference for either bridging or axial terminal co-ordination modes. Hence, any dynamic process that involves either of these co-ordination modes for the phosphine or phosphite ligands is considered to be forbidden.

We have previously argued[27] that the simplest way of considering the effect of substitution on the carbonyl-scrambling pattern is to consider the effect of substitution on the symmetry of the ligand polyhedron. An icosahedron can be described in Foppl notation as a 1:5:(5):1 polyhedron; hence, substitution of one carbonyl generates the new $(CO)_{11}L$ quasi-icosahedron in which there are three different sets of carbonyls in the ratio 5:5:1 (Figure 2). Insertion of the iron triangle into this new polyhedral arrangement generates five different isomeric forms; these have been discussed in detail elsewhere.[4] We shall consider only those two isomers which contain L in equatorial, terminal sites (Figure 2). For each of these two isomers equilibration within each of the two sets of five carbonyls will be achieved by libration of the iron triangle about a similar C_2 axis to that described above and shown in Figure 1. This will lead to a 10:1 relationship of carbonyl ligands. Such motion also simultaneously exchanges L between the two possible equatorial co-ordination sites on the metal triangle, *i.e.* interconversion of the two monosubstituted isomers is achieved {it is also interesting that both of these isomers are present in the asymmetric unit of $[Fe_3(CO)_{11}(PPh_3)]$}.[28] A recently recorded low-temperature ^{13}C n.m.r. spectrum of $[Fe_3(CO)_{11}\{P(OMe)_3\}]$ showed three signals in the ratio 5:5:1, with ^{13}C–^{31}P coupling being

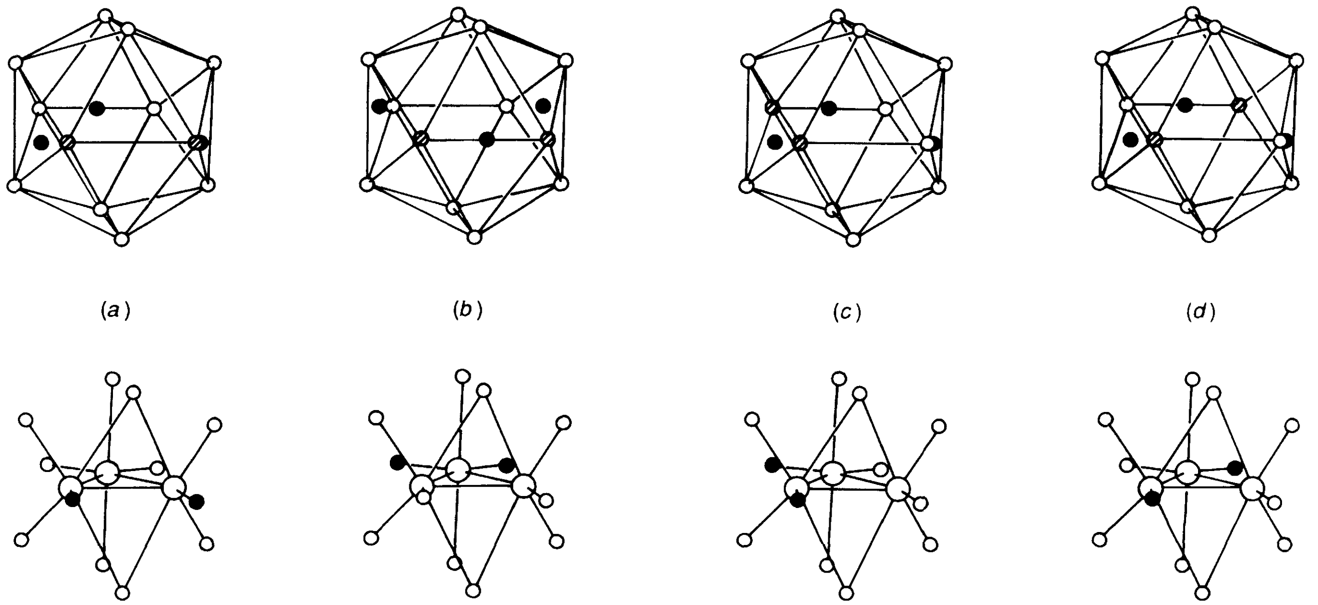

Figure 3. Equatorially substituted isomers of [$Fe_3(CO)_{10}L_2$]

observed for one of the two more intense signals.[29] These observations are completely consistent with the above argument. An earlier ^{13}C n.m.r. study of the same derivative which suggested that the relative intensities were 6:4:1[27] has been discounted.[39] Axial substitution has been observed in [$Fe_3(CO)_{11}(CNBu^t)$][30] and [$Fe_3(CO)_{11}(CNC_6H_4Me)$][31] (substitution occurring at the unique Fe atom); although there have been no ^{13}C n.m.r. studies of this derivative, we would expect that the ground-state structure in CH_2Cl_2 would be observed at low temperatures, since in this case interconversion between the various C_{2v} structures cannot occur by the same librational motion. Similarly with these examples libration about the C_2 axis does not bring about isomer interconversion. It is also important to note that in these quasi-icosahedral geometries the degeneracy of the three C_2 axes is lost.

There are three possible $(CO)_{10}L_2$ icosahedra, *viz.* the 1,2, 1,7, and 1,12 forms. Insertion of the iron triangle into each of the three forms produces a large number of isomeric possibilities. For example, with the 1,2 form six isomers are generated. We have described these forms in detail elsewhere.[4] However, using the constraint that phosphine/phosphite substitution must occur at a terminal equatorial co-ordination site, we shall consider only four of the possible disubstituted isomers of [$Fe_3(CO)_{10}L_2$]. These are illustrated in Figure 3. Again we shall consider the two mechanisms by which carbonyl equilibration or isomerisation might occur. In one of these isomers (*d*), substitution occurs at antipodal vertices of the ligand (1,12) icosahedron. In this case the ten carbonyls in the two pentagonal planes may be equilibrated by the same librational mode (or modes). In the other isomers, the geometry of substitution is such that the interconversion of C_{2v} orientations *via* libration to produce the D_3 orientation is not possible. Hence, the barrier to fluxional behaviour is expected to be higher and it might be possible to freeze out the ground-state structures of these isomers.

There have been two independent variable-temperature ^{13}C n.m.r studies on [$Fe_3(CO)_{10}L_2$] derivatives, each of which reported different observations.[29,33] However, the results of the more recent study are consistent with the predictions of the LPM, and these are now discussed. Thus the ^{13}C and ^{31}P low-temperature n.m.r. spectra are consistent with the presence of two isomers. There is one signal in each spectrum that may be assigned to the 'antipodal' isomer [Figure 3(*d*)], the remaining signals being consistent with asymmetric substitution for the other isomer [Figure 3(*c*)]. [In the two remaining isomers (*a*) and (*b*) which are not observed the phosphites occupy adjacent vertices of the ligand polyhedron, which presumably brings about less favourable steric interactions.]

The isomeric possibilities of the trisubstituted icosahedron, $(CO)_9L_3$, have also been described elsewhere.[4] Given the same constraints as those described above, there are two possible C_{2v} isomers for [$Fe_3(CO)_9L_3$] [Figure 4(*a*) and (*b*)], although two L occupy adjacent vertices of the ligand polyhedron in both, and one D_3 possibility [Figure 4(*c*)]. For L = $P(OR)_3$ (R = Me or Pr^i) two isomers are observed in solution;[29] one of these has been assigned to the C_{2v} isomer (*a*), in which each metal atom is monosubstituted, and the other is the D_3 isomer, in which each metal atom is again monosubstituted. The steric interactions are less in the D_3 isomer (*c*) compared with the C_{2v} isomer (*a*) (since L no longer occupy adjacent vertices): hence, the D_3 isomer would be expected to become more favoured as the cone angle of L increases, and this is observed. It should be noted that there is no need to invoke 'semi-bridging' carbonyls for the all-terminal isomer (as has been suggested),[29] particularly as there is no localised excess of electron density. On the basis of these observations, it was proposed that [$Fe_3(CO)_{12}$] and its derivatives favour the C_{2v} structure in solution, unless there are unfavourable steric interactions.[29] However, we should like to point out that such a conclusion may not be necessarily correct, since it has been clearly shown by i.r. studies that the preferred structure of [$Fe_3(CO)_{12}$] in solution varies with solvent polarity,[8] and the ^{13}C n.m.r. spectra were recorded using only dichloromethane as solvent.

As mentioned above, as the temperature increases the magnitude of the concerted motions of the ligand polyhedron may also increase. It has been argued that these larger motions may be viewed in terms of polyhedral rearrangements[3] (see above), *i.e.* the scrambling of the vertices of an icosahedron can occur *via* rearrangement through an intermediate such as the cuboctahedron (it is important to note that this argument is merely an extension of the mechanism proposed for the interconversion of icosahedral carboranes).[34] One constraint that must be imposed on this intermediate ligand polyhedron is that it generates an intermediate structure with reasonable ligand distributions around each metal atom.

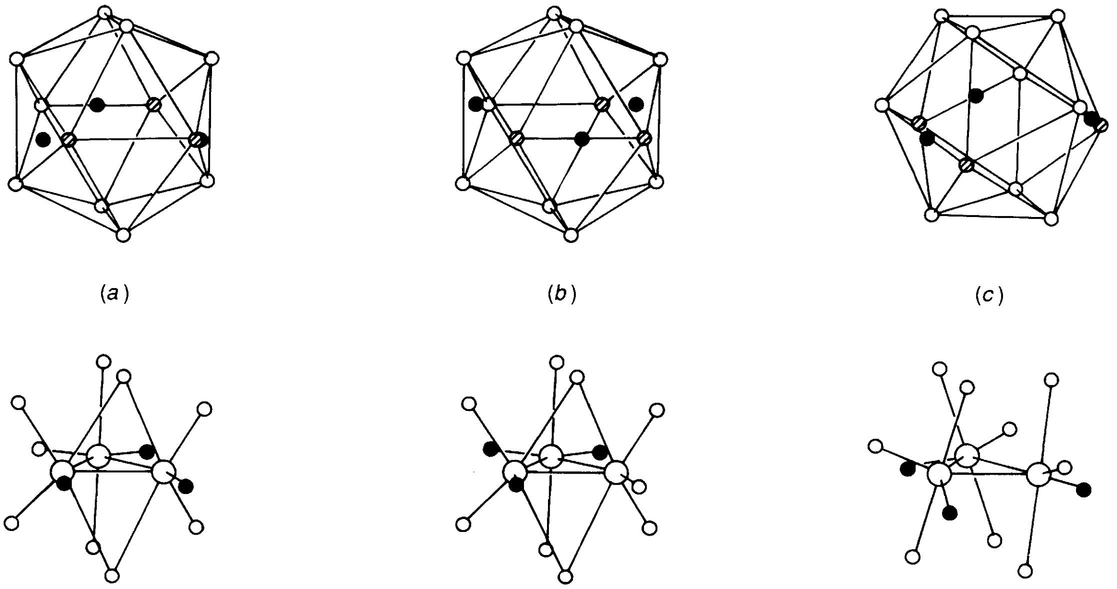

Figure 4. Equatorially substituted isomers of $[Fe_3(CO)_9L_3]$

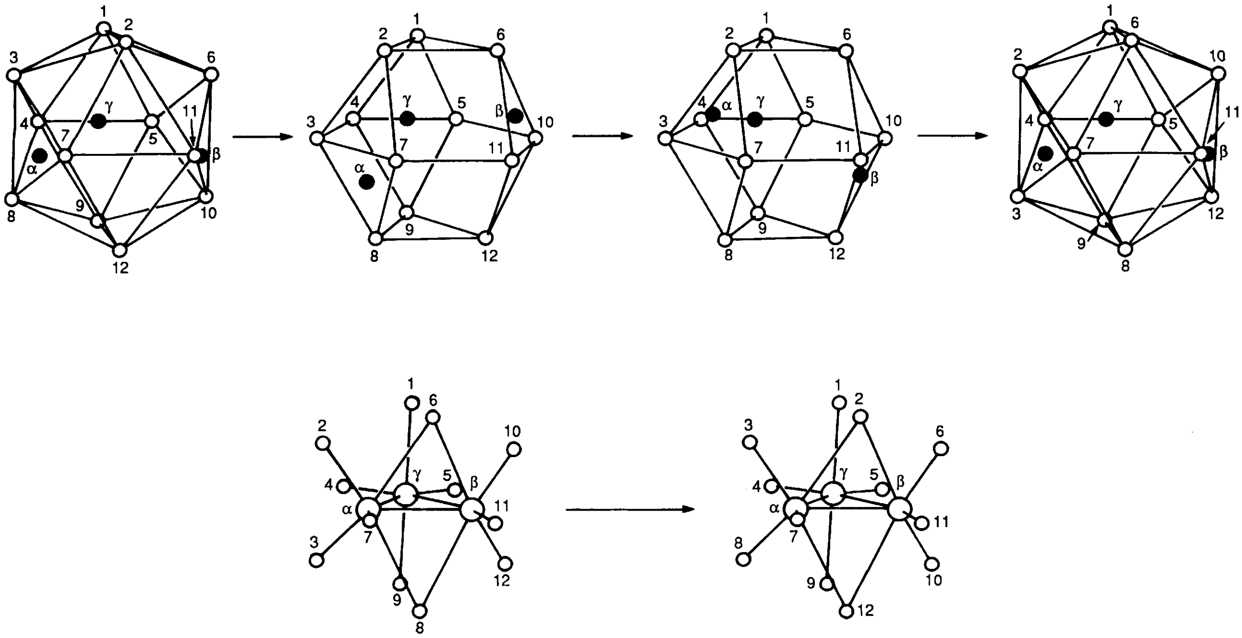

Figure 5. Two-centre exchange about the bridged M–M vector of $[M_3(CO)_{12}](C_{2v})$

It was shown above that the D_3 structure can be readily converted into the D_{3h} structure; hence, the anticuboctahedron is a reasonable polyhedral intermediate. The conversion of an icosahedron into an anticuboctahedron involves the breaking of polyhedral edges to form square faces. There are ten different sets of polyhedral edges which can be broken, although pairs of these sets are related by mirror symmetry, *i.e.* basically only five modes need to be considered. For an isolated icosahedron, these five modes are degenerate: however, as discussed above, if a triangle is placed within the icosahedron this degeneracy is removed. For all the five modes, some concerted motion of the triangle is also required. On the basis of the argument set out earlier, this motion should be the same as that invoked for motion in the solid state and in solution at low temperatures, *i.e.* libration about the unique C_2 axis of the Fe_3 triangle. The effect of this mode on the ligand arrangement corresponds to cyclic permutation of bridging and axial ligands around the bridged Fe–Fe vector (Figure 5). This mechanism is essentially equivalent to that proposed by Cotton and Troup,[5] although it is important to note that in the LPM mechanism this two-centre exchange occurs around only one edge of the C_{2v} structure.

For $[Fe_3(CO)_{11}L]$ this ligand rearrangement causes scrambling of the two pentagonal layers of the ligand polyhedron: this is consistent with the reported coalescence of the two more intense signals in the ^{13}C n.m.r. spectrum as the temperature is increased above -100 °C (*i.e.* there are two signals in the ratio 10:1). Operation of this mode for the axially substituted isomer is also allowed and generates a 6:2:2:1 carbonyl-scrambling pattern. Scrambling of the pentagonal layers of the icosahedron also occurs in the 'antipodal' disubstituted isomer, for which a

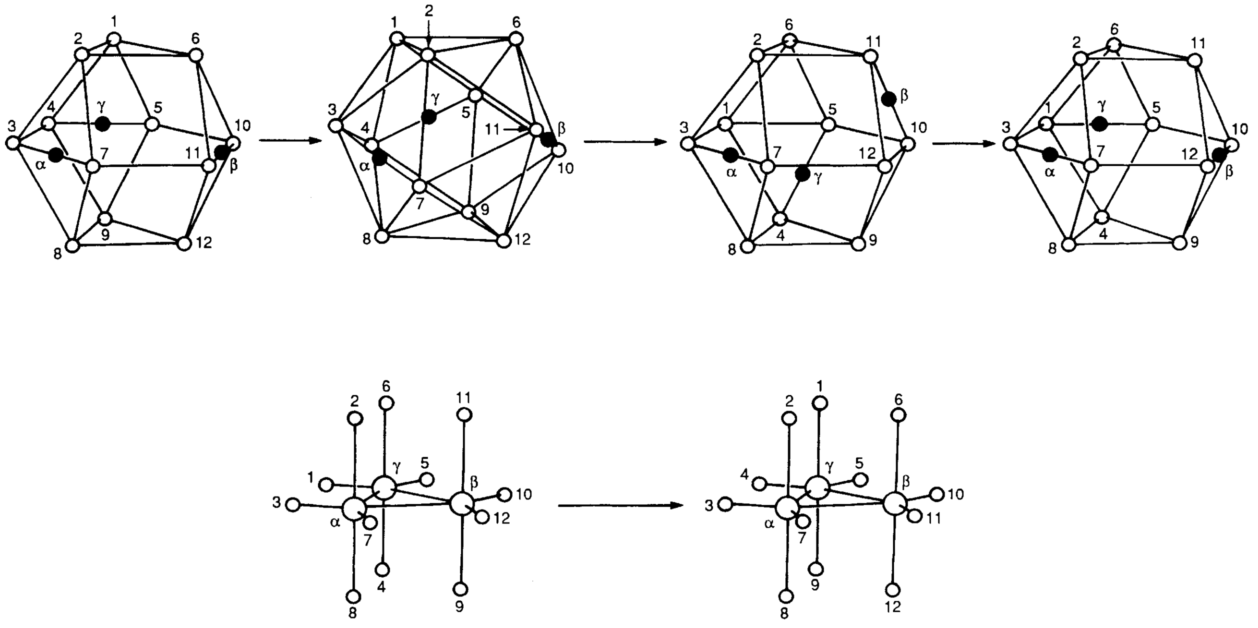

Figure 6. Two-centre exchange about the β–γ vector of $[M_3(CO)_{12}](D_{3h})$

triplet is observed in the ^{13}C n.m.r. spectrum at these higher temperatures, *i.e.* all carbonyls interact with two equivalent P nuclei. This two-centre exchange can also occur in the other disubstituted isomer as well as the C_{2v} isomer of $[Fe_3(CO)_9L_3]$, although it cannot occur in the D_3 isomer (this is discussed in more detail below). It should also be noted that increasing phosphine or phosphite substitution causes an increase in the activation energy for two-centre exchange,[29] which may in part be due to the destabilisation of the D_{3h} intermediate.

A similar mechanism can also be applied to the D_{3h} structure found for the carbonyls $[M_3(CO)_{12}]$ (M = Ru or Os) in the solid. In this structure there are three C_2 axes about which libration, similar to that discussed above, can occur; these are equivalent in the unsubstituted $[M_3(CO)_{12}]$ cluster. However, the effect of these librations on the ligand co-ordination modes are considerably less than that for $[Fe_3(CO)_{12}]$, as (*a*) there is only one reasonable orientation of a triangle within an anticuboctahedron and (*b*) the amplitude of libration decreases with increasing mass of the metal atom. Thus, the ^{13}C m.a.s. n.m.r. spectra of these clusters at room temperature are consistent with their molecular and crystallographic structures,[35,36] although the small changes with temperature observed for $[Ru_3(CO)_{12}]$ suggest that some dynamic process is occurring.[36] At higher temperatures the possibility of ligand polyhedral rearrangement increases. In this case the mechanism is similar to that outlined above for iron except that the sequence is reversed going from anticuboctahedral (D_{3h}) to icosahedral (D_3). Again this motion will be concerted with the librational mode of the metal triangle.

The presence of three librational C_2 axes means that two-centre exchange can occur around all three triangular edges and of the ten possible anticuboctahedron ⟷ icosahedron interconversion modes there are four that generate the two-centre exchange; two of these involving exchange in different directions about the same edge. Operation of these degenerate modes causes total ligand equilibration. Two of these modes are shown in Figures 6 and 7.

The results of ^{13}C n.m.r. studies on $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ are consistent with this mechanism.[9–11] It has been reported that the activation energy for carbonyl equilibration is considerably lower for ruthenium than for osmium,[10,11] *i.e.* the difference between the energies of the ground-state structure (D_{3h}) and intermediate structure (D_3) is less for ruthenium. The intermediate in the above mechanism is always considered to be the non-bridged D_3 structure and not the bridged C_{2v} structure. We believe that there is less difference between the D_3 and D_{3h} structures for ruthenium because of the weaker M–M bond strength compared with osmium.[4] An additional influence may be the relatively smaller amplitude of the librations of the Os_3 triangle.

The degeneracy of these librational or interconversion modes can be removed by substitution of either a metal atom or a carbonyl ligand. For example, the ^{13}C n.m.r. spectrum of $[RuOs_2(CO)_{12}]$ at 30 °C consists of two signals in the ratio 5:1;[9] this is consistent with two-centre exchange around the two Ru–Os edges of the metal triangle (the higher activation energy of two-centre exchange around the Os–Os edge is also consistent with the above arguments). In $[M_3(CO)_{11}L]$, two-centre exchange can only occur around two edges (operation around the other edge would place L in an unfavourable axial co-ordination site). However, whereas for $[Os_3(CO)_{12}]$ the coalescence of the signals due to axial and equatorial carbonyls commences at approximately 70 °C,[9–11] in $[Os_3(CO)_{11}L]$ [L = $P(OMe)_3$][19] it commences at *ca.* −20 and at *ca.* 0 °C for each of the two possible modes respectively, *i.e.* phosphine or phosphite substitution lowers the activation energy for two-centre exchange. On the basis of this simple mechanism the activation energies of the two modes would be expected to be the same, however, the activation energy of the mode that involves two-centre exchange about the Os–Os vector to which L is co-ordinated is found to be lower. A possible rationalisation for this difference is as follows. It was pointed out above that the build-up of electron density on a metal atom due to the substitution of CO by a poorer π-acceptor ligand can be delocalised *via* 'semi-bridging' carbonyls.[37] Since the second stage of the two-centre exchange mechanism must involve transfer of carbonyls between adjacent metal atoms, the presence of L on a metal atom may lower the activation energy for this process by promoting weak 'semi-bridging' interactions. Variable-temperature ^{13}C n.m.r. studies have also been reported for L = PEt_3. Due to the different steric and electronic properties of PEt_3 and $P(OMe)_3$, the activation energy for two-

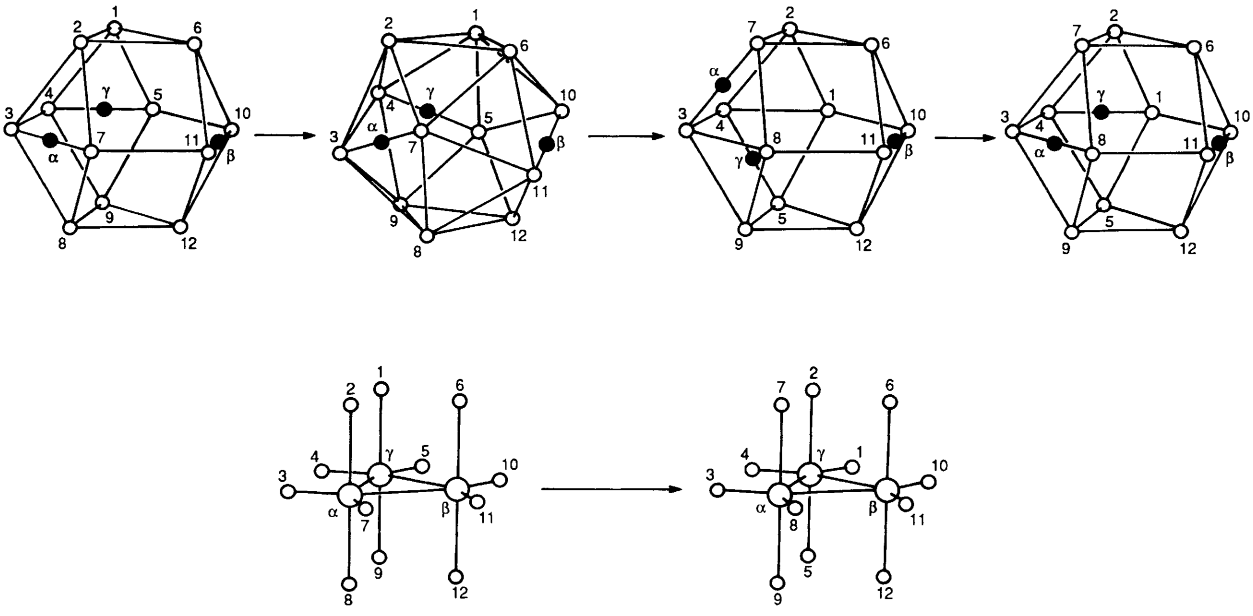

Figure 7. Two-centre exchange about the α–γ vector of $[M_3(CO)_{12}](D_{3h})$

centre exchange in the two derivatives may be different: however, there are insufficient reported data to be able to test this hypothesis, although the higher-activation-energy, two-centre exchange was apparently not observed for L = PEt_3.[14] Increased substitution lowers the activation energy for two-centre exchange still further. It also affects the number of modes that are allowed, *e.g.* none is allowed for the 1,2,3 form of $[Os_3(CO)_9L_3]$. Since the same cyclic processes can also occur in the $D_3 \longrightarrow D_{3h} \longrightarrow D_3$ interconversion, the same argument can be applied to $[Fe_3(CO)_9L_3]$. However, for this interconversion, an increase in steric interactions would be expected to increase the activation energy of two-centre exchange, as an increase in such interactions destabilises the D_{3h} intermediate {as was discussed for the derivatives of $[Fe_3(CO)_{12}]$ (see above)}. Since the derivatives of $[Ru_3(CO)_{12}]$ appear more readily to adopt the D_3 structure, such derivatives might show this opposite trend in activation energies. However, the activation energies for dynamic processes in these clusters are so low that a low-temperature-limiting structure cannot generally be obtained.[20]

It has been noted above that the D_3 structure is generally adopted by clusters containing bidentate ligands co-ordinated by two metal atoms, *e.g.* $[M_3(CO)_{10}\{\mu\text{-}(L\text{-}L)\}]$ [M = Ru, L-L = $Ph_2PCH_2PPh_2$ (dppm);[15] M = Os, L-L = $Ph_2PCH_2CH_2PPh_2$ (dppe);[13,18] L-L = dppm, $Ph_2PCH_2CH_2CH_2Ph_2$ (dppp), $Ph_2PCH_2CH_2CH_2CH_2PPh_2$ (dppb[18])]. For these systems there exist two D_3 enantiomers (Figure 8). In these cases the $D_3 \longrightarrow D_{3h} \longrightarrow D_3$ interconversion interconverts the two D_3 enantiomers (Figure 8). Such a process has been reported as the lowest-energy dynamic process for $[M_3(CO)_{10}\{\mu\text{-}(L\text{-}L)\}]$ (M = Ru, L-L = dppm;[15] M = Os, L-L = dppe;[13,18] L-L = dppm, dppp, or dppb[18]). For such clusters, operation of this mode generates a mirror plane perpendicular to the M-M vector bridged by the bidentate ligand. Two-centre exchange is also observed for these clusters, the activation energy being dependent on both the metal and the chain length of L-L. For L-L = dppm, coalescence occurs at −80 °C for M = Ru,[15] whereas for M = Os the temperature required is considerably greater than 50 °C;[18] for M = Os, L-L = dppb,[18] the coalescence temperature is −60 °C (*i.e.* the more flexible the bidentate ligand, the smaller is the energy difference between the D_3 and D_{3h} structures).

In all the above mechanisms libration of the metal triangle about the C_2 triangular axes is involved. However, another important motion for the anticuboctahedral clusters $[M_3(CO)_{12}]$ is the libration of the metal triangle within its own plane, *i.e.* about the C_3 axis perpendicular to the metal triangle. The effect of such a libration can best be described by considering a model of a metal triangle librating within a ligand hexagon (Figure 9). There are two possible orientations of the triangle. In one the ligands are all terminally co-ordinated, whereas in the other, three are terminally co-ordinated and three are edge-bridging. These two orientations are related by a rotation of 30° about the perpendicular C_3 axis of the triangle. If the ligand hexagon is also considered to be a rigid body librating in its own plane, then only small motions of each polygon in different directions are required to move the metal triangle between the two orientations. If the whole structure then moves as one rigid body so that the triangle returns to its original position the overall process is equivalent to the ligand hexagon rotating through 30° about a fixed triangle, *i.e.* repetition of this process causes complete rotation of the ligand hexagon relative to the metal triangle (this corresponds to the process previously referred to as the 'merry-go-round' process).[38] This motion has been invoked as the lowest-energy dynamic process for $[M_3(CO)_{10}(\text{diazine})]$ (M = Ru[39] or Os[40]), the activation energy for the ruthenium derivative being lower than for the osmium derivative (the coalescence temperatures being −86 and −30 °C respectively). The existence of the two different orientations as ground-state structures (see above) provides further evidence for this mechanism. Similar behaviour has been reported for $[M_3(CO)_{10}(O{=}CNMe_2)]^-$ (M = Ru[41,42] or Os[42]), and it was observed that the activation energy for carbonyl scrambling in the osmium derivative was lower than in the ruthenium derivative. This suggests that the dynamic processes of these clusters may be more complicated than those of the diazine derivatives. The 'merry-go-round' has recently been reported[43] as the lowest-energy dynamic process for $[Os_3(CO)_{11}X]^-$ (X = Cl, Br, I or NCO), the activation energies for this process decreasing in the order NCO > Cl > Br > I. There is no apparent rationalisation for this order on the basis of the LPM.

In $[M_3(CO)_{12}]$ (M = Ru or Os) all equatorial carbonyls are equivalent, so the 'merry-go-round' cannot be detected by ^{13}C n.m.r. spectroscopy (such a process is often referred to as a

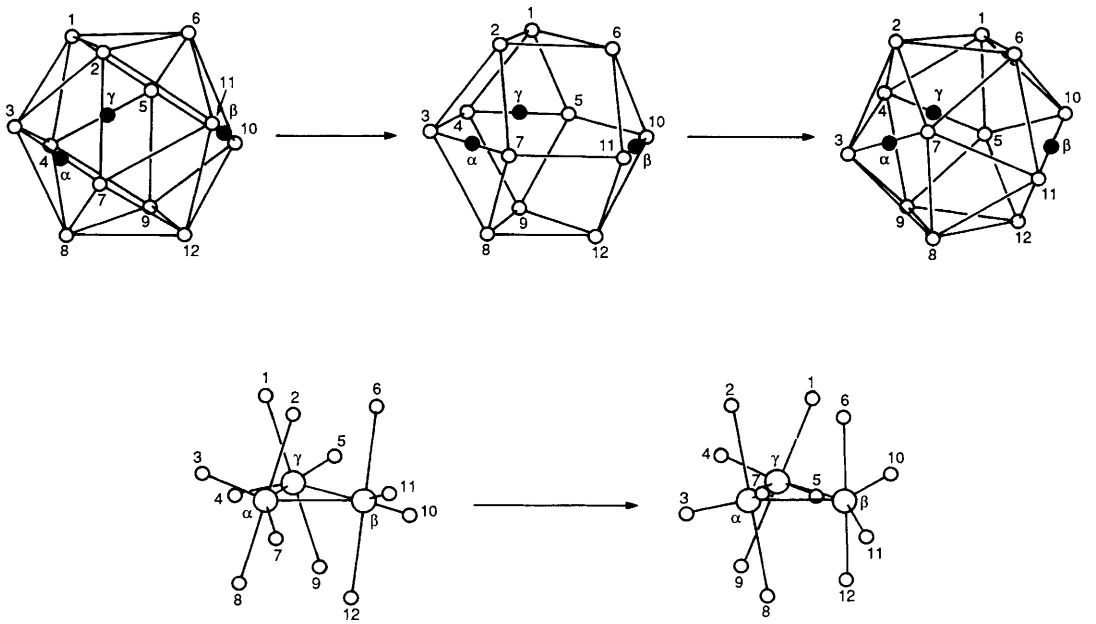

Figure 8. Interconversion of D_3 enantiomers

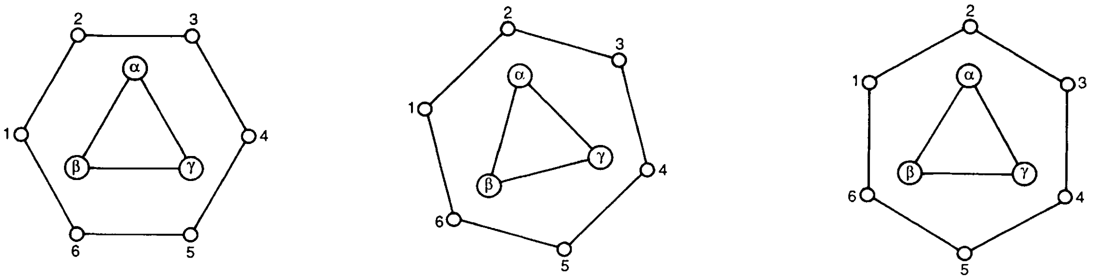

Figure 9. Interconversion of the two orientations of a triangle within a hexagon

'hidden process').[39] Although such motion is considerably more limited in equatorially substituted derivatives, it can exchange phosphines or phosphites between equatorial sites on the same M atom. There is another, more localised dynamic process which can produce the same effect; this is axial–equatorial ligand exchange on a single M atom, which is usually referred to as the 'turnstile' motion or the 'trigonal twist'.[12,17,19,20,44,45] However, we have previously noted that this simply corresponds to rotation of a triangular face of the ligand polyhedron,[27] a mechanism that has been previously discussed by Muetterties[46] for the icosahedron. As the steric interactions in the rather more complex intermediate are considerably greater than in the 'ground-state' polyhedra, the activation energy for this process is generally relatively high.

With $[Os_3(CO)_{11}L]$, for example, the operation of two-centre exchange about two edges equilibrates only ten carbonyls; however, complete carbonyl equilibration is observed at high tempratures. This can be achieved by operation of either the 'merry-go-round' process or triangular rotation which transfers L between the two different equatorial co-ordination sites on the same osmium atom, hence allowing two-centre exchange to occur over the third edge. Both processes also interconvert the inequivalent L of the asymmetrically substituted isomers of $[M_3(CO)_{10}L_2]$ (M = Fe or Os), although the limited 'merry-go-round' process is favoured for M = Fe[3] (the process occurring in the anticuboctahedral transition state), whereas simultaneous triangular rotation about the substituted M atoms has been suggested for M = Os.[45] For both M = Fe and Os it has been proposed that the interconversion of the two observed disubstituted isomers occurs *via* triangular rotation.[17,19,20,45,46]

The solution structures of isocyanide derivatives of $[M_3(CO)_{12}]$ (M = Ru or Os) are complicated by the ability of such ligands to co-ordinate both equatorially and axially[16] (although only axial co-ordination has been observed in the solid state[2]). However, there is evidence for all the above dynamic processes occurring for such derivatives:[16] in particular, two centre exchange allows interconversion of axial and equatorial isomers.

Conclusion

We would emphasise that all the above dynamic processes have previously been rationalised by invoking only localised carbonyl motion.[38] Although this method undoubtedly does have its merits, the approach based on the LPM, discussed above, has the advantage that it shows that there can be a single, coherent, rational basis for the observed carbonyl-scrambling patterns in a whole range of carbonyl compounds. This approach is based on the observation that the metal polyhedron undergoes librational motion within the carbonyl ligand envelope, and that this envelope can also undergo polyhedral rearrangement of the type commonly recorded for simpler monomeric co-ordination compounds. Furthermore it should be recognised that these two motions are concerted and will occur to different extents in the solid and solution.

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