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The ligand polyhedral model and its application to the fluxional behaviour of $M_4(CO)_{12-n}$ (M = Co, Rh, Ir; $n = 1, 2, 4$) clusters ☆

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Abstract

A number of mechanisms have been previously proposed to explain the observed fluxional behaviour of related cluster species of the general type $M_4(CO)_{12-n}L_n$ (M = Co, Rh, Ir; $n = 1, 2, 4$). Here, a combination of metal core libration and an icosahedral–anticubeoctahedral–icosahedral ligand polyhedral rearrangement, arising from the ligand polyhedral model, is used to account for this observed behaviour. The ideas proposed are general and may be applied to all systems containing icosahedral, cubeoctahedral or anticubeoctahedral ligand shells.

Keywords: Ligand polyhedral model; Fluxionality; Cobalt complexes; Rhodium complexes; Iridium complexes; Carbonyl complexes; Cluster complexes

1. Introduction

Considerable effort has been put into the establishment and rationalisation of the fluxional processes which the tetranuclear carbonyls $M_4(CO)_{12}$ (M = Co, Rh or Ir) and their substituted derivatives undergo [1]. Early studies led Cotton et al. [2,3] to suggest that the dominant bridge-opening mechanistic pathway involved a $C_{3v} \rightleftarrows T_d$ rearrangement of the molecular structure (see Fig. 1). This corresponds to the change from the ground-state C_{3v} structure established by single crystal X-ray diffraction studies for both $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ to the intermediate T_d structure found for $Ir_4(CO)_{12}$, and has been employed to account for all or part of the fluxional behaviour of a variety of tetranuclear systems, including $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$ [3], $RhCo_3(CO)_{12}$ [4] and $Ir_4(CO)_{11}L$ [5,6] (e.g. L = PEt_3, PPh_3 or $CNBu^t$).

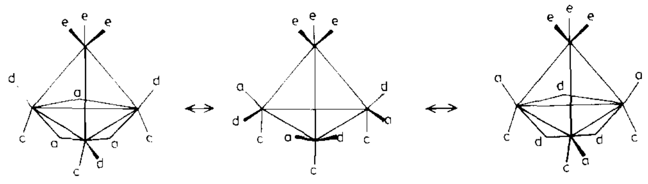

Fig. 1. The Cotton mechanism of rearrangement.

In earlier work [4] we have shown that the Cotton mechanism alone is insufficient to explain the two types of carbonyl scrambling observed in $RhCo_3(CO)_{12}$ and argued that a concerted bridge-cleavage/bridge-formation process is more reasonable. Later work by Mann et al. [7] has followed the same basic pattern and the idea of fundamental bridge-cleavage ⟷ bridge-formation has remained.

In 1978 we offered a more comprehensive view of carbonyl fluxionality in which we recognised that a consideration of both the polyhedral rearrangement of the complete ligand shell, combined with the libration of the metal core within the ligand polyhedron, was of importance, rather than the more conventional view of localised scrambling of CO over the central cluster unit or about individual metal atoms [8]. This view was based on the ligand polyhedral model, which considers that the structures of the cluster carbonyls are based on the relative orientation of the central metal cluster unit M_m within the ligand polyhedral shell L_n. Using this approach, we have come to more fully appreciate the limitations of the original Cotton mechanism of ligand fluxionality. Whenever an all-terminal intermediate is required for a fluxional process within the $M_4(CO)_{12}$ or related system, it has been generally assumed in the past, to be the quasi-T_d form, in which the ligands define the vertices of a cubeoctahedron (see Fig. 2(a)). This assumption is reasonable because

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☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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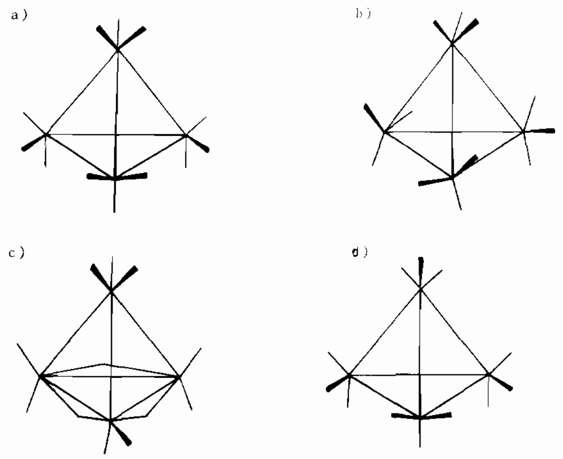


Fig. 2. Ligand arrangements for M_4L_{12}: (a) the T_d cubeoctahedron; (b) the T icosahedron; (c) the C_{3v} icosahedron; (d) the C_{3v} anticubeoctahedron.

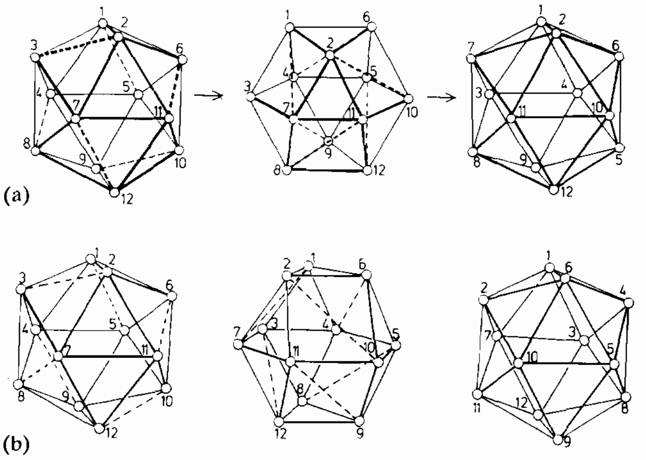


Fig. 3. Icosahedral rearrangement mechanisms: (a) via a cubeoctahedral complementary geometry; (b) via an anticubeoctahedral complementary geometry. – – –, Edges broken/formed.

this arrangement of ligands has been observed in molecular structures of several Ir_4 species. It was also for this reason that we previously supposed that the complementary geometry for the fluxional process adopted in the ligand polyhedral model approach was the cubeoctahedron. However, we must recognise that two other possibilities exist, both of which have been largely ignored. The first is based on an icosahedral envelope with overall quasi-T symmetry (see Fig. 2(b)) and has been shown [8,9] to be the lowest energy geometry for $M_4(CO)_{12}$ species. There is one example of an M_4 species adopting the quasi-T geometry: the X-ray single crystal structure of $Co_4(CO)_8(Me_2AsCC_2F_4CAsMe)_2)_2$ shows an all-terminal species [10], with the As atoms and the CO ligands describing an icosahedral envelope [11]. The T icosahedral form is closely related to the C_{3v} triply bridged, alternative icosahedral geometry (see Fig. 2(c)) observed for many $M_4(CO)_{12-n}L_n$ species, the two being interconverted by a small rotation of the M_4 tetrahedron (relative to the icosahedral ligand envelope) about its pseudo-C_3 axis. This is highly significant to the approach adopted here.

The second possibility is based on an anticubeoctahedral arrangement of ligands, and possesses an overall pseudo-C_{3v} molecular symmetry (see Fig. 2(d)). We have not found any single crystal X-ray structures for $M_4(CO)_{12-n}L_n$ species which adopt this geometry in the solid state [11], although it is relatively common in the trinuclear $M_3(CO)_{12-n}L_n$ species [12] (M = Ru, Os).

Contrary to our previous proposal we have now discovered that problems arise when the cubeoctahedron is adopted as the standard terminal intermediate for $M_4(CO)_{12-n}L_n$ fluxionality. Rearrangements following the icosahedral ⟷ cubeoctahedral ⟷ icosahedral route (see Fig. 3(a)) conserve all antipodal relationships between the ligands. However, it is known that at higher temperatures, total CO exchange is observed, which means that these antipodal relationships must be destroyed. This requires a modification of our original mechanism. However, we have recently demonstrated that in the icosahedron ⟷ anticubeoctahedron ⟷ icosahedron mechanism (see Fig. 3(b)) antipodal ligand relationships are destroyed and conclude that the anticubeoctahedron must be a better complementary geometry than either the cubeoctahedron or the T icosahedron. In this paper we re-examine much of the apparently conflicting information on $M_4(CO)_{12-n}L_n$ fluxionality and aim to show that the anticubeoctahedral complementary geometry provides a reasonable, and most importantly, a general explanation of the data observed for icosahedral $M_4(CO)_{12-n}L_n$ species.

2. Discussion

2.1. The fluxional behaviour of $Ir_4(CO)_{11}(L)$

The vast majority of data on carbonyl fluxionality within these systems has been collected for iridium complexes and falls into two distinct groups. The first retains the all-terminal, cubeoctahedral ligand envelope ground-state structure seen in the parent $Ir_4(CO)_{12}$ species [13]. The second adopts the quasi-C_{3v} icosahedral ligand ground-state arrangement favoured by $Co_4(CO)_{12}$ [14] and $Rh_4(CO)_{12}$ [15]. It has been proposed that fluxionality for $Ir_4(CO)_{11}L$ complexes with an all-terminal structure, e.g. L = PH_2Ph [7], $P(OMe)_3$ [16] or $CNBu^t$ [6], proceeds via a reverse Cotton mechanism, i.e. $T_d \longleftrightarrow C_{3v} \longleftrightarrow T_d$. The basis for this argument is provided by evidence for the existence of a second, bridged isomer for L = PH_2Ph and $P(OMe_3)$, although no evidence exists for a second isomer of $Ir_4(CO)_{11}(CNBu^t)$. The low temperature fluxional processes for the L = PH_2Ph and L = $CNBu^t$ species are very similar, both maintaining the relationship between

L and its antipodal carbonyl (*) (see Fig. 4(a)), which is consistent with the original $T_d \longleftrightarrow C_{3v} \longleftrightarrow T_d$ mechanism. However, at higher temperatures $Ir_4(CO)_{11}(CNBu^t)$ undergoes a second fluxional process which destroys the L/* antipodal relationship. Thus, rearrangement via a cubeoctahedral geometry alone cannot be responsible (see above). Indeed, it may not be safe to assume that the mechanisms employed by $Ir_4(CO)_{11}(PR_3)$ are the same as those used by $Ir_4(CO)_{11}(CNBu^t)$ at low temperature. There is no structural evidence to prove that the ligand shell in $Ir_4(CO)_{11}(PH_2Ph)$ is of cubeoctahedral geometry, only that all carbonyl groups are bonded in the terminal mode. If $Ir_4(CO)_{11}(PH_2Ph)$ adopted the *T* icosahedral geometry, simple libration of the metal core about any one of the four possible C_3 axes (through the Ir_4 tetrahedron) would have precisely the same effect as that described by Mann et al. [7]. These four libration modes are not degenerate because of the presence of a non-carbonyl ligand in the outer polyhedron. Libration would, like the Cotton mechanism, also proceed via C_{3v}-bridged species, accounting for their presence in solution.

In addition to this low-energy libration process, we propose that the second fluxional process in $Ir_4(CO)_{11}(CNBu^t)$ occurs via an anticubeoctahedral complementary geometry, which removes the relationship between L and its antipodal carbonyl. It has been assumed that the $CNBu^t$ complex exists predominantly as the cubeoctahedral isomer, even at elevated temperatures, which would require the fluxional pathway to be of the form cubeoctahedron ⟷ icosahedron ⟷ anticubeoctahedron ⟷ icosahedron ⟷ cubeoctahedron. However, as previously stated, it would appear that even at the lowest temperatures, icosahedral forms (*T* or C_{3v}) co-exist with the cubeoctahedral isomer. Therefore, at higher temperatures it would be reasonable to assume that the icosahedral forms would be at least as accessible as the cubeoctahedral isomer, in which case the fluxional pathway would be icosahedron ⟷ anticubeoctahedron ⟷ icosahedron.

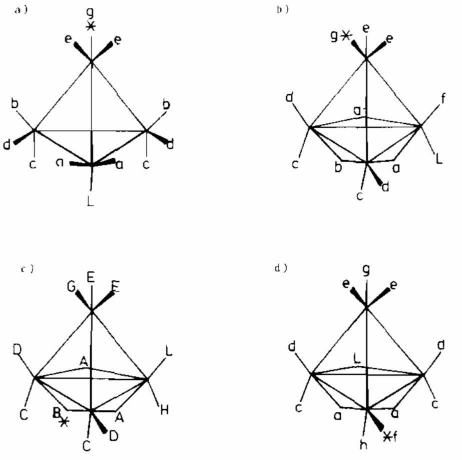


Fig. 4. Observed forms of $M_4(CO)_{11}L$: (a) the cubeoctahedron; (b) P_{axial} substitution of a C_{3v} icosahedron; (c) $P_{equatorial}$ substitution of a C_{3v} icosahedron; (d) bridge substitution of a C_{3v} icosahedron. The carbonyl antipodal to L is marked with an asterisk (*).

The second group of monosubstituted M_4 clusters, M = Ir, L = PEt_3 [7a], PPh_2Me [5], μ-SO_2 [17] (Scheme 2) preferentially adopt the icosahedral pseudo-C_{3v} ligand symmetry (see Fig. 4(b)–(d)). For the phosphine ligands there are two isomers possible, one with L in a basal axial position (Fig. 4(b)) and one with the ligand in a basal equatorial position (Fig. 4(c)). Both isomers are observed for L = PEt_3, the preferred conformation being basal axial. For L = PPh_2Me, this is the only isomer observed. Indeed, the preference for basal axial substitution increases with increasing ligand bulk [5].

The fluxional behaviour of the PEt_3 complex is virtually identical to that of the PPh_2Me complex. Initially, carbonyls b, d, a and f exchange, followed by the inclusion of c and e, and then finally total fluxionality occurs. The strong similarity in the behaviour of the two clusters leads us to believe that fluxionality in the PPh_2Me complex may also be dependent upon interconversion with a minor isomer. Indeed, Stuntz and Shapley [5a] noted that resonance g altered slightly between −88 and 20 °C, which they attributed to a small but increasing amount of P_{eq} isomer.

We believe that the process of P_{ax}/P_{eq} interconversion is a consequence of libration of the Ir_4 core within the icosahedral ligand envelope (see Fig. 5(a)). This motion about a pseudo-C_2 axis converts a → A, b → G, c → E, d → D, e → C, f → H and g → B, (where lower case indicates P_{ax} and upper case P_{eq}) and is in accordance with the atomic displacement thermal parameters (adps) data for the motion of the Co_4 unit in $Co_4(CO)_{12}$ [18]. These suggestions are similar to those of Mann et al. [7b]. An alternative libration mode about C_3 axes is also shown in Fig. 5(b).

If we now consider the effect of ligand polyhedral rearrangement, via an anticubeoctahedral complemen-

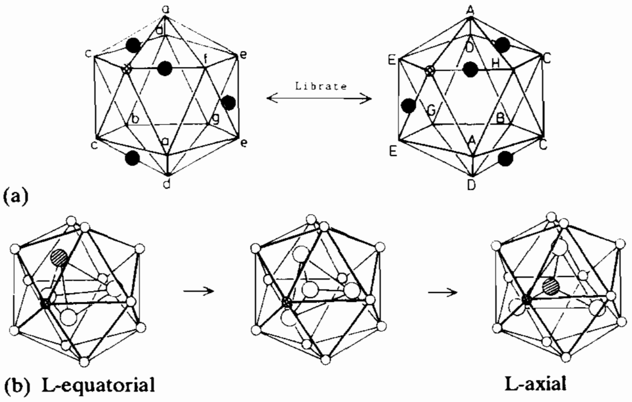
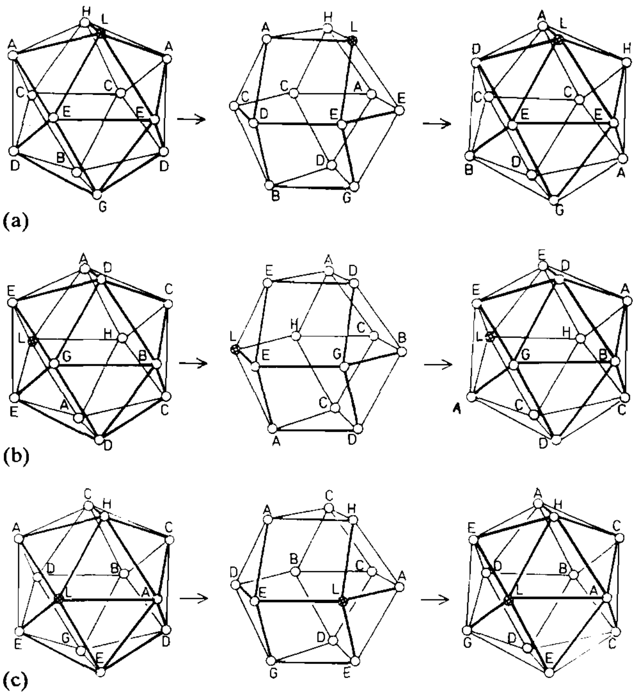
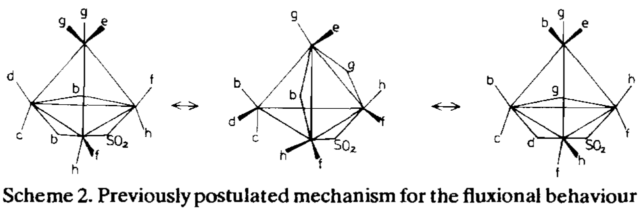


Fig. 5. (a) Proposed metal core libration for $M_4(CO)_{11}L$ about a C_2 axis. (b) Alternative libration mode about C_{3v} axes.

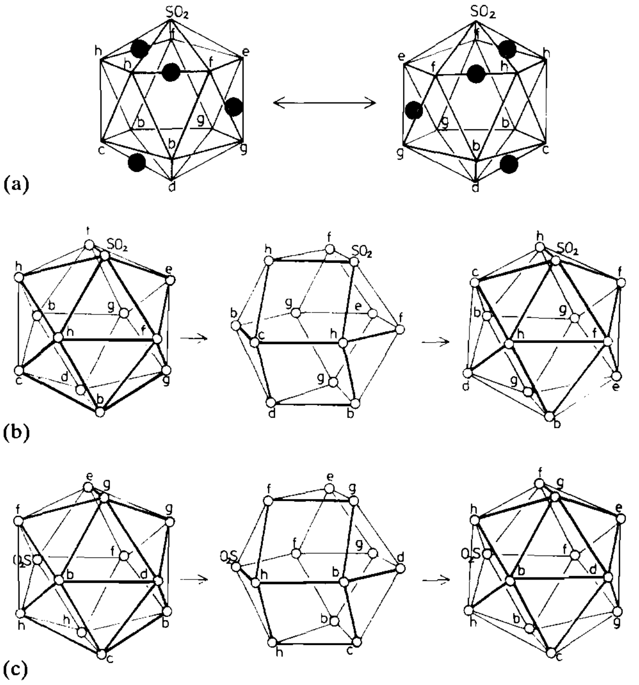
tary geometry, on the P_{eq} isomer we have a number of modes which can operate. One of these modes, mode I (see Scheme 1), brings about the conversion of $A \rightarrow H \rightarrow A \rightarrow D \rightarrow B \rightarrow D$, giving rise to a 6(2A, B, 2D, H) to 2(2E) to 2(2C) to 1(G) ratio of signals. If we then also apply mode II (see Scheme 1), which exchanges $E \rightarrow A \rightarrow C \rightarrow C \rightarrow A \rightarrow E$, the ratio of signals becomes 10(2A, B, 2C, 2D, 2E and H) to 1(G). To achieve total fluxionality, mode III (see Scheme 1) is also invoked, converting $A \rightarrow C \rightarrow C \rightarrow D \rightarrow G \rightarrow E$. Mode III is one of a degenerate pair. We agree that the P_{eq} isomer is kinetically more important in the fluxional process. If the same modes were applied to the P_{ax} isomer, mode II would be unaffected, but mode I would exchange $a \rightarrow f \rightarrow a \rightarrow d \rightarrow g \rightarrow d$ and mode III $a \rightarrow e \rightarrow e \rightarrow d \rightarrow b \rightarrow c$, although at elevated temperatures the overall effect would be the same. The change in mode I might also explain the observed effect on the g resonance, i.e. a very small amount of the P_{ax} isomer might also be exchanging. Our view of exchange in $Ir_4(CO)_9(\mu\text{-}CO)_2(\mu\text{-}SO_2)$ is shown in Scheme 3.



Scheme 1. Proposed fluxional pathways of $Ir(CO)_{11}L$: (a) mode I; (b) mode II; (c) mode III.



Scheme 2. Previously postulated mechanism for the fluxional behaviour of $Ir_4(CO)_9(\mu\text{-}CO)_2(\mu\text{-}SO_2)$.



Scheme 3. Proposed fluxional pathways for $Ir_4(CO)_9(\mu\text{-}CO)_2(\mu\text{-}SO_2)$: (b) mode I; (c) mode II.

2.2. The fluxional behaviour of $Ir_4(CO)_{10}L_2$

Although a number of bis-substituted species have been prepared, it appears that fluxionality studies have been carried out mainly on species with one, bidentate ligand. In such cases, the solid state structures and solution behaviour are dictated by restrictions placed by the ligand on the complex. The possible substitution patterns for two ligands are shown in Fig. 6. In reality, only the diaxial bridging [19,20] and axial-equatorial chelating [21,22] forms have been observed in the solid state.

The ^{31}P NMR spectra of $Ir_4(CO)_{10}$(dmpe) [19a], $Ir_4(CO)_{10}$(dppb) [19b] and $Co_4(CO)_{10}$(dppe) [20] do change from a single resonance to two signals at very low temperature. It has been suggested [19b] that the two P ligands are in slightly different magnetic environments, due to the configuration of the hydroarbon bridge and that the facile flexing of the chain averages the two P signals. Further variable temperature studies on the ^{13}C NMR spectrum of $Ir_4(CO)_{10}$(dppb) [19b] corroborate this view, showing concomitant averaging of b/b′, f/f′ and g/g′ only. The chelated species, $Ir_4(CO)_{10}$(diars) [21], $Ir_4(CO)_{10}$(dppm) [22] and $Ir_4(CO)_{10}$(1,5-COD) [23] also exhibit fluxional behaviour.

The fluxional behaviour of $Ir_4(CO)_{10}$(diars) is similar but not identical, to that of $Ir_4(CO)_{10}$(1,5-COD). In the $Ir_4(CO)_{10}$(diars) species [21], the initial exchange pattern is $b \longleftrightarrow g$, $As_{ax} \longleftrightarrow As_{eq}$ and c, c′, d, d′, e, e′ interchange. At higher temperatures a and a′ become

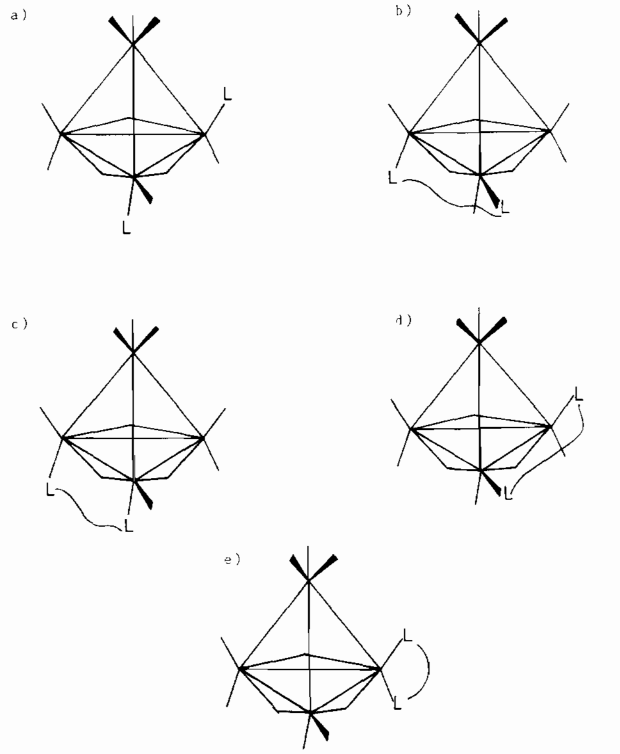
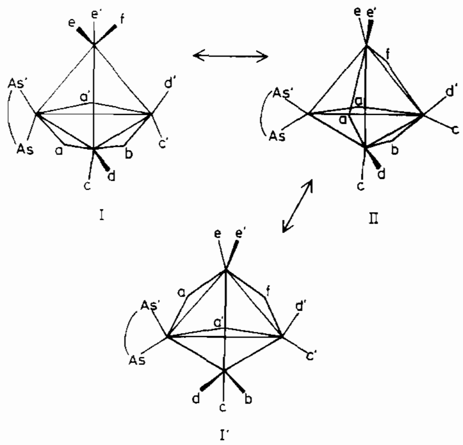


Fig. 6. Possible substitution patterns for $M_4(CO)_{10}L_2$: (a) axial-equatorial monodentate; (b) axial-equatorial bridging; (c) diaxial bridging; (d) diequatorial bridging; (e) axial-equatorial chelating.



Scheme 4. Previously postulated mechanism for the fluxional behaviour of $Ir_4(CO)_{10}$(diars). Ir labels are omitted for clarity.

involved and, finally, total exchange takes place. The mechanism for the process originally proposed by Shapley et al. is given in Scheme 4. However, it was noted, at the time, that the proposed mechanism was not obviously related to the observed distortions in the solid-state structure. Additionally, it had not proved possible to deduce a mechanism for total carbonyl fluxionality, although the possibility of local exchange at an apical Ir atom was considered. Roulet and coworkers [23] reappraised the NMR data and pointed out that the previous mechanism would require intermediates which break the 18-electron rule and would be unprecedented. From the NMR data it was concluded that the axial/equatorial As exchange requires a change of apical Ir atom and that the motion must be concerted if a and a′ are not involved. In the case of $Ir_4(CO)_{10}$(1,5-COD), axial/equatorial C=C exchange is observed but either a or a′ is involved in the initial exchange process, apparently requiring a → (a, c), b → g, c → (a, e), d → (d, e), e → (c, d) and g → b. The authors suggested that the process need not be concerted.

We believe that the fluxional behaviour of both complexes may be explained by a combination of Ir_4 core libration and the icosahedral ⇄ anticubeoctahedral rearrangement and that they are very similar in nature. From an examination of the solid-state structure of $Ir_4(CO)_{10}$(diars), it is possible to identify a pseudo-C_2 axis which passes between the two As atoms and between carbonyls b and g (see Fig. 7). Libration of the Ir_4 core about this axis interchanges A_{ax} with A_{eq} and simultaneously equilibrates b and g. This motion, in conjunction with the operation of mode I (see Scheme 5(a)) which interchanges carbonyls c/c′, d/d′ and e/e′, leads to a predicted 6(c/c′, d/d′, e/e′) to 2(a/a′) to 2(b/g) ratio of signals in a ^{13}C NMR spectrum, in accord with the experimental data. If, in addition to these processes, the operation of mode II is involved (see Scheme 5(a)), then carbonyls a/a′, d/d′ and e/e′ exchange, leading to an 8(a/a′, c/c′, d/d′, e/e′) to 2(b/g) ratio of signals. Finally, operation of the third mode, III (see Scheme 5(b)) leads to total scrambling of all carbonyls.

In the case of $Ir_4(CO)_{10}$(1,5-COD), the libration axis remains the same, causing a → a, b → g, c → e, d → d, e → c and g → b. The further requirements a → c, c → a, d → e and e → d are met by the mode shown in Scheme 6.

2.3. *The fluxional behaviour of $M_4(CO)_8L_4$ (M = Co, Rh, Ir)*

This is the final group of complexes for which variable temperature ^{13}C NMR data are readily available. The complexes fall into two categories: those with four, monodentate ligands, e.g. $Rh_4(CO)_8\{P(OPh)_3\}_4$ [24] and

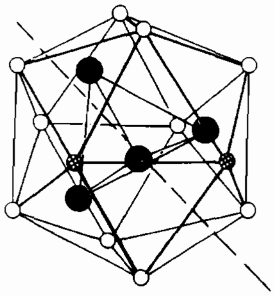
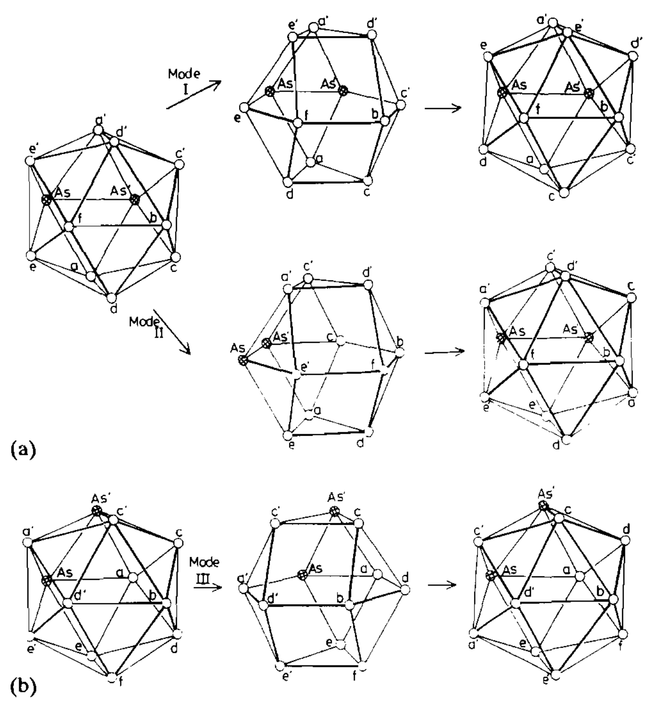
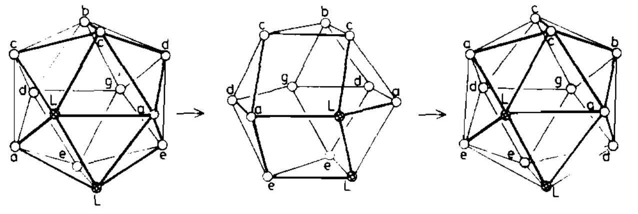


Fig. 7. Proposed libration axis for $Ir_4(CO)_{10}$(diars). ●, Ir; ⊗, As.



Scheme 5. Proposed fluxional pathways for $Ir_4(CO)_{10}(diars)$.



Scheme 6. Proposed fluxional pathways for $Ir_4(CO)_{10}(1,5\text{-}COD)$.

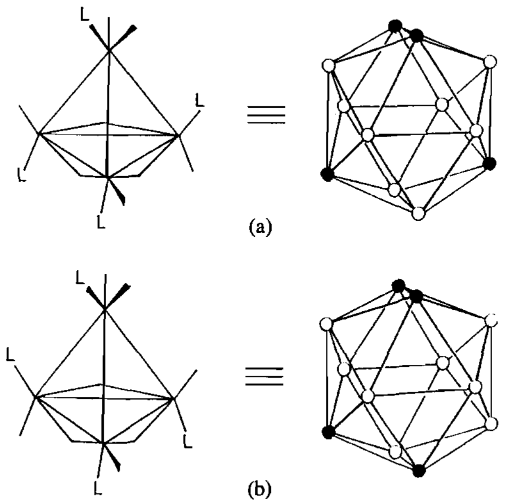
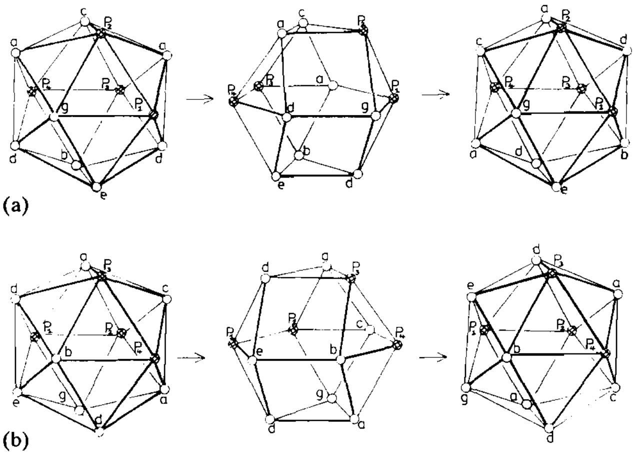


Fig. 8. Substitution patterns for $M_4(CO)_8L_4$: (a) all monodentate ligands; (b) two bidentate ligands.

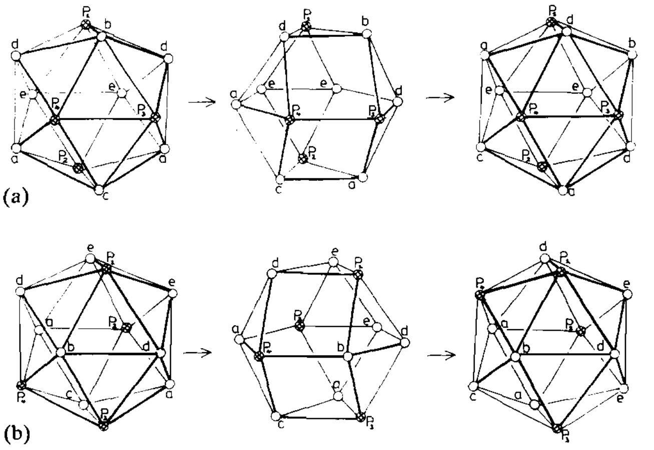


Scheme 7. Proposed fluxional pathways for $Co_4(CO)_8(dmpm)_2$: (a) mode I; (b) mode II.

those with two, bidentate ligands, e.g. $Co_4(CO)_8(dmpm)_2$ [25]. In the case of $Rh_4(CO_8)\{P(OPh_3)_4\}$, the initial fluxional process involves six carbonyls, leaving e/e′ unaffected. At higher temperatures all the carbonyls become fluxional and the four P ligands become equivalent [24]. For $Co_4(CO)_8(dmpm)_2$, all eight carbonyl resonances appear to broaden at the same rate [25].

We believe that, despite subtle differences in the coordination patterns of $Rh_4(CO)_8\{P(OPh)_3\}_4$ and $Co_4(CO)_8(dmpm)_2$, the same lowest energy fluxional process is employed for both clusters. At higher temperatures, the additional constraints on $Co_4(CO)_8(dmpm)_2$ require different modes to be used from those involved by $Rh_4(CO)_8\{P(OPh)_3\}_4$. In order to understand both the similarities and differences, one must consider the fact that four ligands *cannot* be distributed equally about the icosahedral ligand envelope. Therefore, the number of possible substitution patterns is severely restricted, especially as each metal atom may only coordinate to one P atom (see Fig. 8). In turn, the number of available anticubeoctahedral rearrangement modes is further reduced, particularly for $Co_4(CO)_8(dmpm)_2$ where the P atoms are constrained to occupy adjacent sites on the icosahedral ligand shell. Only two ligand polyhedral rearrangement modes remain viable but these are sufficient to scramble all eight carbonyls (see Scheme 7). Thus mode I interchanges a → c → a → d → b → d and mode II exchanges d → a → c → a → g → e.

Despite the different coordination pattern for $Rh_4(CO)_8\{P(OPh)_3\}_4$ [1,2,8,10] compared with [1,2,8,9] for $Co_4(CO)_8(dmpm)_2$, mode I exchanges the same six carbonyls a → c → a → d → b → d (see Scheme 8). However, mode II interchanges P_4 → d → e → e → a → c and causes $P_{ax} + P_{eq}/P$ exchange without altering the 1,2,8,10 tetra-substitution pattern (see Scheme 8). This, in turn, equilibrates the four P atoms and all eight carbonyls when employed in addition to mode I. The same modes might also be employed to explain the fluxionality of $Ir_4(CO)_8(Ph_2AsMe)_4$ [26]. It is interesting to note that, in contrast to lesser substituted species, libration of the metal about a C_2 axis within the icosahedral ligand shell will not cause equilibrium of the four P ligands



Scheme 8. Proposed fluxional pathways for $Rh_4(CO)_8\{P(OPh_3)\}_4$: (a) mode I; (b) mode II.

or the eight CO ligands. Nevertheless, it is expected to occur as a 'hidden' process or, indeed, may even be forbidden. However, in the case of $Co_4(CO)_8(dmpm)_2$ *only*, libration about any one of the Co_4 C_3 axes will equilibrate the four P-donor atoms without altering their relative positions within the ligand polyhedral shell.

3. Conclusions

In conclusion, we believe that combinations of metal core libration and/or the icosahedral ⟷ anticubeoctahedral rearrangement modes may account for the fluxional behaviour observed in a wide variety of $M_4(CO)_{12-n}L_n$ species. The ideas do not discount previous individual mechanisms, such as the Cotton merry-go-round. Indeed, our approach embraces many aspects of this other work. In many cases, the end result is exactly the same, but we feel that the anticubeoctahedral pathway has the advantage of being a wholly general mechanism, applicable to the full range of $M_4(CO)_{12-n}L_n$ systems. Moreover, our approach avoids the necessity for ligands to adopt unusual (and unobserved in the solid-state) bonding modes, remaining in accord with the 18-electron rule.

Acknowledgements

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