Structures of Binary Carbonyls and Related Compounds. Part 1. A New Approach to Fluxional Behaviour

By **Brian F. G. Johnson** * and **Robert E. Benfield,** The University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The different types of carbonyl scrambling observed in $[M_4(CO)_{12}]$ (M = Co, Rh, or Ir) compounds and substituted derivatives may be explained in terms of a single type of process. The initial icosahedral arrangement of ligands rearranges along a well defined reaction co-ordinate *via* a cubo-octahedral transition state; the existence of different patterns of carbonyl scrambling then arises as a consequence of the geometrical disposition of the metal-atom tetrahedron within the ligand polyhedron. Rather than using a different *ad hoc* mechanism to rationalise each observed fluxional process, this is a single type of carbonyl-scrambling path involving the concerted motion of *all* the atoms in the molecule in ways that are well defined in terms of molecular geometry.

It has been recognised over the last 15 years that intramolecular rearrangement of carbonyl groups in metal carbonyls is a common occurrence. The first proposal of how this might take place was advanced in 1966 in an attempt to reationalise the anomalous solution i.r. spectrum of $[Co_4(CO)_{12}]$.[1] With the advent of ^{13}C n.m.r. spectroscopy as a research technique much information on this fluxional behaviour has been accumulated. Different types of carbonyl scrambling have been observed: (*i*) total carbonyl scrambling over the whole molecule {*e.g.* $[Fe_3(CO)_{12}]$ [2]}; (*ii*) restricted mobility between metal atoms, with some carbonyl groups not participating {*e.g.* $[RhCo_3(CO)_{12}]$ [3]}; (*iii*) localised

---

[1] F. A. Cotton, *Inorg. Chem.*, 1966, **5**, 1083.

[2] F. A. Cotton and D. L. Hunter, *Inorg. Chim. Acta*, 1974, **11**, L9.

[3] B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J.C.S. Chem. Comm.*, 1974, **441**.

carbonyl exchange at individual metal atoms, with no migration occurring between different metal centres {*e.g.* $[Os_6(CO)_{18}]$ [4]}; and (*iv*) complete rigidity of all the carbonyl groups in the molecule {*e.g.*[4] $[Rh_6(CO)_{15}I]^-$}. Depending on the relative magnitude of the activation energies of the different available fluxional processes, a given compound may exhibit different degrees of fluxional behaviour at different temperatures, in which case its ^{13}C n.m.r. spectrum shows temperature dependence. Many such carbonyl cluster compounds have been studied over wide ranges of temperature; some such as $[Fe_3(CO)_{12}]$ exhibit total carbonyl scrambling down to the lowest limit of experimental observation (−150 °C), indicating that the activation energy is <20 kJ mol^{-1}.[2]

The reasons for the existence of different types of fluxional behaviour in metal carbonyl clusters are as yet poorly understood. Restricted exchange of carbonyl groups is often associated with the existence in the molecule of diverse metal-atom environments. This may arise from the presence of a heteroatom, such as in $[RhCo_3(CO)_{12}]$ {but note that $[RuFe_2(CO)_{12}]$ exhibits complete carbonyl scrambling [4]}, or from the possession by the metal-atom polyhedron of unlike types of vertex {*e.g.* $[Os_6(CO)_{18}]$ has three distinct sorts of osmium site in its bicapped tetrahedron of metal atoms [5]}. The occupation of a co-ordination site by a ligand of lower mobility than carbon monoxide may alter the fluxional behaviour of the whole molecule, as instanced by $[Ir_4(CO)_{11}(PMePh_2)]$ [6] and $[Os_3(CO)_{10}(PEt_3)_2]$.[7] A large organic moiety such as 7-isopropyl-1,4-dimethylazulene may occupy several co-ordination sites and severely restrict the possible carbonyl scrambling paths.[8]

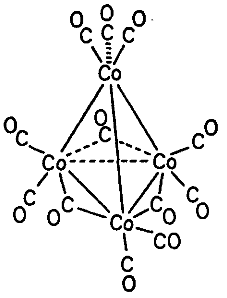
In this paper we present a new proposal for carbonyl-scrambling mechanisms. We believe that this proposal will apply to all the binary carbonyls and related compounds but here we restrict our attention to $[M_4(CO)_{12}]$ compounds and some of their substituted derivatives.

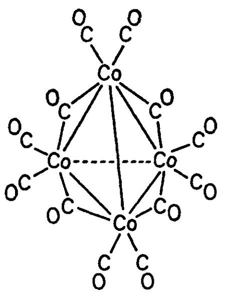
DISCUSSION

(*a*) *Structures and Fluxional Behaviour of* $[M_4(CO)_{12}]$ *Species and Substituted Derivatives* (M = Co, Rh, *or* Ir).—(*i*) $[Co_4(CO)_{12}]$ *and derivatives.* The solid-state structure of $[Co_4(CO)_{12}]$ is difficult to determine accurately because of crystal disorder.[9] It has recently been refined.[10] The molecule has C_{3v} symmetry with both terminal and doubly bridging carbonyl groups; a tetrahedron of cobalt atoms is enveloped by an icosahedron of carbonyl groups. It is of interest from the point of view of the carbonyl-packing theory recently proposed [11] that the nature of the crystal disorder consists of different orientations of the Co_4 tetrahedron within an approximately invariant icosahedral carbonyl arrangement.

In solution, the i.r. spectrum of $[Co_4(CO)_{12}]$ has given rise to much controversy.[12,13] In 1965 Smith [14] pointed out that this spectrum was consistent with D_{2d} symmetry for the molecule in solution. Bor [15] determined the i.r. spectrum of $[Co_4(CO)_{12}]$ in an extremely concentrated n-hexane solution. He found several extra bands of low intensity, including one hidden as a shoulder in an adjacent stronger band. By assigning some very weak absorptions to ^{13}C–O vibrations he was able to arrive at the conclusion that there were indeed six terminal and two bridging carbonyl bands. Noack [16] had obtained similar results using a hexane solution of unspecified concentration, but made slightly different assignments to those of Bor. A recent study involving the calculation of predicted frequencies for the fundamental vibrations, ^{13}C isotopic substitution, and the calculation of difference spectra to isolate the isotopic bands is also said to confirm the C_{3v} structure of $[Co_4(CO)_{12}]$ in solution.

In 1966 Cotton proposed [1] that the $[Co_4(CO)_{12}]$ molecule underwent intramolecular reactions in solution and existed as a tautomeric mixture of C_{3v} and D_{2d} forms which could freely interconvert *via* an unbridged intermediate of T_d symmetry by means of small concerted motions of the carbonyl-group atoms. With the subsequent advent of ^{13}C n.m.r. spectroscopy as a method of investigation of such fluxional behaviour of carbonyl compounds in solution, experiments have been carried out to test this idea. The low-temperature (−100 °C) ^{13}C n.m.r. spectrum of $[Co_4(CO)_{12}]$ in CD_2Cl_2 solution shows three resonances of equal intensity,[17] one in the bridging- and two in the terminal-carbonyl region of the spectrum. This indicates 4 : 4 : 4 carbonyl-group equivalence and is not compatible with the 3 : 3 : 3 : 3 spectrum expected for a molecule of C_{3v} symmetry. It may be that the high quadrupole moment of the ^{59}Co


C_{3v} structure


D_{2d} structure

---

[4] J. Lewis and B. F. G. Johnson, *Pure Appl. Chem.*, 1975, **44**, 43.

[5] R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Amer. Chem. Soc.*, 1973, **95**, 3802.

[6] G. F. Stuntz and J. R. Shapley, *J. Amer. Chem. Soc.*, 1977, **99**, 607.

[7] B. F. G. Johnson, J. Lewis, B. E. Reichert, and K. T. Schorp, *J.C.S. Dalton*, 1976, 1403.

[8] F. A. Cotton, P. Lahuerta, and B. R. Stults, *Inorg. Chem.*, 1976, **15**, 1866.

[9] C. H. Wei, *Inorg. Chem.*, 1969, **11**, 2384.

[10] F. H. Carre, F. A. Cotton, and B. A. Frenz, *Inorg. Chem.*, 1976, **15**, 380.

[11] B. F. G. Johnson, *J.C.S. Chem. Comm.*, 1976, 211.

[12] J. W. Cable and R. K. Sheline, *Chem. Rev.*, 1956, **56**, 1.

[13] F. A. Cotton and R. R. Monchamp, *J. Chem. Soc.*, 1960, 1882.

[14] D. L. Smith, *J. Chem. Phys.*, 1965, **42**, 1460.

[15] G. Bor, *Spectrochim. Acta*, 1963, **19**, 1209.

[16] K. Noack, *Helv. Chim. Acta*, 1962, **45**, 1847.

[17] J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Amer. Chem. Soc.*, 1975, **97**, 1245.

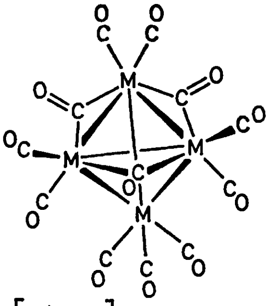
nucleus perturbs the relative intensities of the carbonyl absorptions in this spectrum, obtained in the Fourier-transform mode, even in the presence of $[Cr(pd)_3]$ (pd = pentane-2,4-dionate) as a relaxation agent. However, it should be remembered that the low-temperature ^{13}C n.m.r. of $[Co_4(CO)_{11}\{P(OMe)_3\}]$ [18] and $[RhCo_3(CO)_{12}]$ [3] presented no such difficulty in assigning reasonable relative intensities, and the interpretation of the $[Co_4(CO)_{12}]$ spectrum remains unclear. A ^{59}Co n.m.r. study of $[Co_4(CO)_{12}]$ showed two distinct resonances,[18] with relative intensity 3 : 1. This cleared up earlier confusion over two apparently contradictory sets of results [19,20] and provides further evidence that $[Co_4(CO)_{12}]$ has C_{3v} symmetry in solution.

At higher temperatures the ^{13}C n.m.r. spectrum of $[Co_4(CO)_{12}]$ in CD_2Cl_2 solution shows line broadening (−20 °C), total collapse of the spectrum (10 °C), and the absence of carbonyl resonances (40—70 °C).[17] This is indicative of carbonyl scrambling and is consistent with the mechanism of Cotton, involving an unbridged T_d intermediate. However, no fast-exchange spectrum could be obtained because decomposition occurred at >70 °C. The ^{13}C n.m.r. spectrum of $[Co(CO)_{11}\{P(OMe)_3\}]$ [18] also broadens from its low temperature (−82 °C) limit as the temperature is increased, and collapses by −5 °C. Again, no fast-exchange spectrum could be determined, and in this case it could not be definitely concluded from the line-shape changes that carbonyl scrambling was actually occurring.

The polysubstituted derivatives $[Co_4(CO)_{12-n}\{P(OMe)_3\}_n]$ (n = 1—4) have also been investigated, but by ^1H n.m.r. spectroscopy.[21] Infrared spectra of these compounds are thought to indicate the C_{3v} type structure (three carbonyl bridges per molecule). The ^1H n.m.r. spectra in CH_2Cl_2 were found to be temperature dependent and the existence of an intramolecular process causing this was demonstrated by the observation of two separate sets of ^1H resonances on the addition of extra free ligand at room temperature. At −90 °C the exchange was too fast for a limiting slow spectrum to be observed. It is interesting to note that successive phosphorus-ligand substitution allows fluxional processes to occur at lower temperatures.

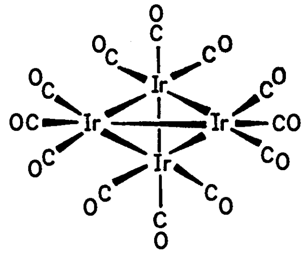
It can thus be seen that, partly arising from quadrupole effects and sample decomposition, no clear evidence of the mechanism of carbonyl exchange in $[Co_4(CO)_{12}]$ and its derivatives has yet been forthcoming.

(*ii*) $[Rh_4(CO)_{12}]$ *and derivatives.* The crystal-structure determination of $[Rh_4(CO)_{12}]$ also presented problems; this time because of crystal twinning. The molecule has (idealised) C_{3v} symmetry, with a tetrahedron of rhodium atoms enveloped by a very distorted isocahedron of carbonyl groups.[9] The reason why the molecule adopts this structure rather than the unbridged T_d structure of $[Ir_4(CO)_{12}]$ is unclear. Intriguingly, a form of $[Ir_4(CO)_{12}]$ with bridging carbonyl groups has been reported in an argon matrix at −58 °C.[22]



$[M_4(CO)_{12}]$ (M = Co or Rh)

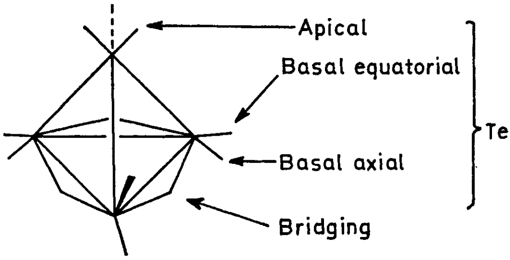
C_{3v}



$[Ir_4(CO)_{12}]$

T_d

In solution the i.r. spectrum of $[Rh_4(CO)_{12}]$ strongly suggests that the molecule has C_{3v} symmetry.[23] The ^{13}C n.m.r. spectrum in CD_2Cl_2 of 70% ^{13}CO-enriched $[Rh_4(CO)_{12}]$, with $[Cr(pd)_3]$ as relaxation agent, at −65 °C showed four resonances of equal intensity, with three in the terminal- and one in the bridging-carbonyl region.[24] This is consistent with the C_{3v} structure which has four different types of co-ordination site. Assignment of the resonances in this spectrum was aided by ^{103}Rh–^{13}C coupling (^{103}Rh, 100% isotopic abundance, $I = \frac{1}{2}$). As the temperature was increased the four signals coalesced at −5 to +5 °C. The collapse of the slow-exchange spectrum was substantially uniform, indicating that no site selectivity was involved, and consistent with the operation of a single carbonyl-scrambling process. At a higher temperature [25] (20 °C) a single broad resonance is observed in the ^{13}C n.m.r. spectrum of $[Rh_4(CO)_{12}]$ (13% ^{13}CO enriched, in $CDCl_3$ solution). At 50 °C the fast exchange limit is reached, a 1 : 4 : 6 : 4 : 1 quintet with ^1J(Rh–C) 17.1 Hz. This unequivocally shows that the carbonyl groups are scrambled rapidly over the four metal atoms by an intramolecular mechanism. Intermolecular exchange would abolish the ^{103}Rh–^{13}C coupling. The proposed mechanism [25] involves uniform breaking of carbonyl



---

[18] M. A. Cohen, D. R. Kidd, and T. L. Brown, *J. Amer. Chem. Soc.*, 1975, **97**, 4408.

[19] E. A. C. Lucken, K. Noack, and D. F. Williams, *J. Chem. Soc.* (*A*), 1967, 148.

[20] H. Haas and R. K. Sheline, *J. Inorg. Nuclear Chem.*, 1967, **29**, 693.

[21] D. Labroue and R. Poilblanc, *Inorg. Chim. Acta*, 1972, **6**, 387.

[22] L. A. Hanlan and G. A. Ozin, *J. Amer. Chem. Soc.*, 1974, **96**, 6324.

[23] W. Beck and K. Lottes, *Chem. Ber.*, 1961, **94**, 2578.

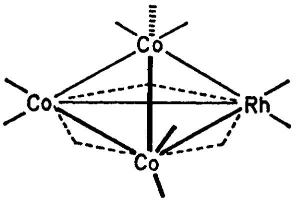
[24] J. Evans, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J.C.S. Chem. Comm.*, 1973, 807.

[25] F. A. Cotton, L. Kruxzynski, B. L. Shapiro, and L. F. Johnson, *J. Amer. Chem. Soc.*, 1972, **94**, 6191.

bridges to form an unbridged intermediate of T_d symmetry (with an implied cubo-octahedral ligand distribution).

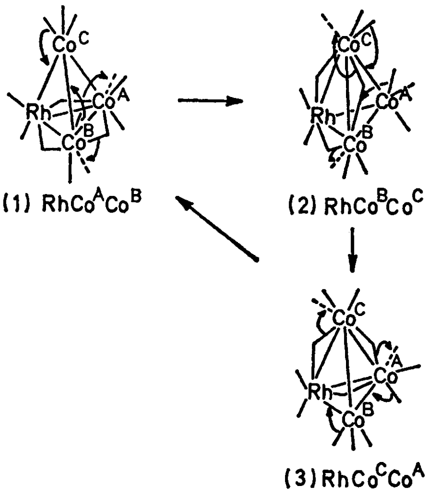
The low-temperature (−55 °C) ^{13}C n.m.r. spectrum of $[Rh_4(CO)_{11}(PPh_3)]$ in CD_2Cl_2 solution indicates that the phosphine is substituted in a basal-axial position.[26] An attempt to record the variable-temperature ^{13}C n.m.r. spectrum of $[Rh_4(CO)_{11}(PMePh_2)]$ was inconclusive, because of sample decomposition.[26]

(*iii*) $[RhCo_3(CO)_{12}]$. The variable-temperature ^{13}C n.m.r. spectrum of this compound has been determined.[3] Owing to the lower symmetry arising from the heterometal atom, which occupies a basal position in the M_3M' tetrahedron (deduced from i.r. spectra[27]), more useful information can be obtained from the ^{13}C n.m.r. spectrum concerning ground-state structure and the precise manner of carbonyl scrambling than for a more symmetrical molecule such as $[Rh_4(CO)_{12}]$. This is in significant contrast to i.r. spectroscopy, where a molecule of low symmetry will give rise to a large number of absorptions so that often little structural information can be deduced.[28]



The low-temperature ^{13}C n.m.r. spectrum of $[RhCo_3(CO)_{12}]$ in CH_2Cl_2 at −85 °C confirms that the rhodium atom is in the basal plane of a carbonyl-bridged structure.[3] There are two sets of carbonyl absorptions in the bridging region, of relative intensity 2 : 1, with the more intense signal split by coupling to the rhodium nucleus. The $^{103}Rh-^{13}C$ coupling was also used to assign the absorptions in the terminal region arising from the two carbonyls bonded to the rhodium atom, which are distinct from one another since they occupy different types of site on the metal cluster. On increasing the temperature to −60 °C, broadening of the resonances occurs, and at −30 °C it was observed that (1) the resonances attributed to the bridging carbonyls and terminal carbonyls bonded to cobalt coalesce, and (2) the two terminal carbonyls bonded to rhodium become equivalent but remain distinct from the other 10 carbonyls; their $^{103}Rh-^{13}C$ coupling is preserved. At a higher temperature (30 °C) a single signal, due to exchange of carbonyls between all the available sites, was observed.

These findings were explained on the basis of a concerted bridge-breaking and -making mechanism which occurred in the intermediate temperature range in such a manner as to maintain the rhodium atom in the basal (bridged) plane of the metal atoms, without allowing it to occupy the apical position. A symmetrical intermediate {such as an unbridged one of T_d symmetry as previously proposed for $[Rh_4(CO)_{12}]$} was



(1) $RhCo^ACo^B$ (2) $RhCo^BCo^C$ (3) $RhCo^CCo^A$

ruled out in this intermediate temperature range, because such a process would not allow the two carbonyl groups bonded terminally to the rhodium atom to preserve their identity from the other 10 carbonyls. At higher temperatures complete carbonyl scrambling does occur in $[RhCo_3(CO)_{12}]$, and it was concluded that the fluxional behaviour of this molecule arises from the operation of two distinct mechanisms, having different activation energies.

(*iv*) $[Ir_4(CO)_{12}]$. No useful information is obtainable from the ^{13}C n.m.r. spectrum of this molecule; it has an unbridged structure of T_d symmetry with all the carbonyls equivalent even in the absence of any fluxional process.

(*v*) $[Ir_4(CO)_{11}(PMePh_2)]$. The substitution into $[Ir_4(CO)_{12}]$ of a phosphine ligand of large cone angle and low π-acid strength causes a rearrangement of the structure to one possessing three bridging carbonyl groups about the basal plane of the Ir_4 tetrahedron. It is known from crystal-structure analysis[29] that in $[Ir_4(CO)_{10}(PPh_3)_2]$ the phosphine ligands occupy one basal-axial and one basal-equatorial site on different metal atoms, and that in $[Ir_4(CO)_9(PPh_3)_3]$ the three phosphines occupy one basal-axial and two basal-equatorial positions, one each on the three iridium atoms in the basal plane. Infrared spectroscopy clearly shows that monosubstituted $[Ir_4(CO)_{11}(PPh_3)]$ adopts a structure with bridging carbonyl groups;[30] comparison of the ^{31}P n.m.r. chemical shifts in $[Ir_4(CO)_{11}(PPh_3)]$ and $[Ir_4(CO)_{11}(PMePh_2)]$ with those of the di- and tri-substituted compounds leads to the conclusion that the single phosphine ligand occupies a basal-axial position.

The variable-temperature ^{13}C n.m.r. spectrum of $[Ir_4(CO)_{11}(PMePh_2)]$ has recently been determined.[6] At

---

[26] J. Evans, unpublished work.

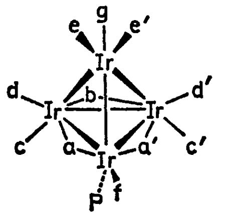
[27] S. Martinengo, P. Chini, V. G. Albano, and F. Cariati, *J. Organometallic Chem.*, 1973, **59**, 379.

[28] P. E. Cattermole, K. G. Orrell, and A. G. Osborne, *J.C.S. Dalton*, 1974, 328.

[29] V. G. Albano, P. Bellon, and V. Scatturin, *Chem. Comm.*, 1967, 730.

[30] K. J. Karel and J. R. Norton, *J. Amer. Chem. Soc.*, 1974, **96**, 6812.

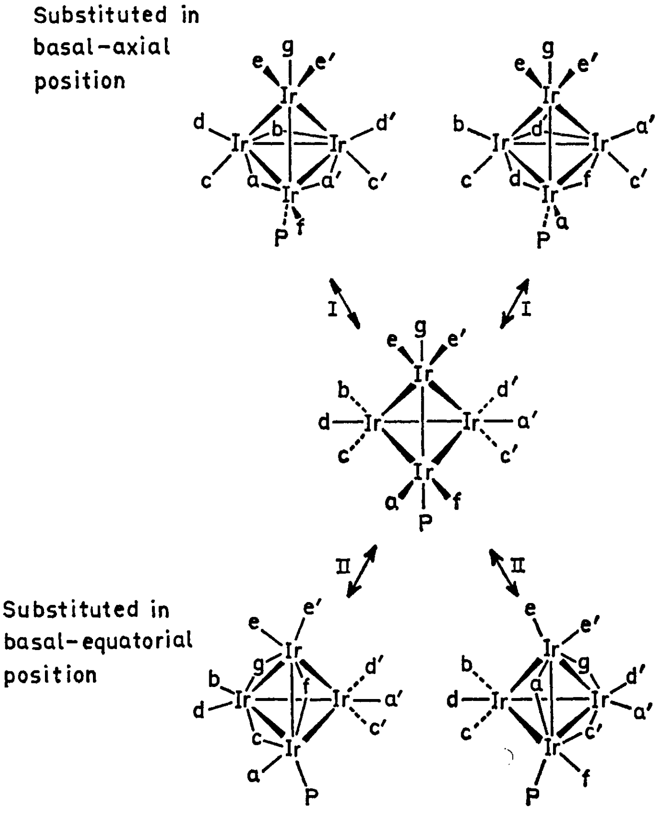
-88 °C the carbonyl region shows a 2 : 2 : 2 : 2 : 1 : 1 : 1 absorption pattern consistent with the proposed structure. With the help of ^{31}P–^{13}C coupling (observed for carbonyls f and g) it was possible to assign all the peaks to their individual carbonyls. The degree of ^{13}CO enrichment was 30—50%. Three distinct stages of carbonyl scrambling were observed at higher temperatures. (1) The signals corresponding to the three bridging and three basal-equatorial carbonyls broaden and coalesce by -33 °C to give a 6 : 2 : 2 : 1 pattern. Carbonyls a, a′, b, d, d′, and f are exchanging at this stage. (2) By -50 °C the signals arising from the two basal axial carbonyls c and c′ and the two apical carbonyls e and e′ begin to broaden; by 2 °C they coalesce with the first set to give a single broad resonance lying at approximately the weighted mean of the individual chemical shifts. There is a 10 : 1 pattern of carbonyl absorptions at this stage, with the apical carbonyl g remaining distinct because it is antipodal to the phosphine within the icosahedron whose vertices are defined by the ligands. This unique carbonyl g is clearly identifiable by its large $^{3}J(^{13}C-^{31}P)$ coupling of 26 Hz. (3) Finally, at 31 °C a third process averages this remaining doublet with the other signal, and a single carbonyl resonance is observed. This is indicative of total site exchange.



The explanation proposed by Stuntz and Shapley[6] for these observations involves an unbridged intermediate analogous to those suggested for $[Co_4(CO)_{12}]$[1] and $[Rh_4(CO)_{12}]$.[25] From the ground-state structure of the molecule, the carbonyl bridges open to produce the unbridged form; reforming the bridges about the same face of the Ir_4 tetrahedron leads to the observed carbonyl-scrambling process at the lowest temperature and reforming the bridges about a different face leads to the intermediate-temperature scrambling, giving 10 : 1 carbonyl equivalence. This latter operation gives a product molecule in which the phosphine ligand is in a basal-equatorial position, and is consequently of higher energy than the ground-state isomer. Thus it can be understood why this process occurs at a higher temperature than the first. Antipodal relationships within the icosahedral arrangement of ligands must be preserved to maintain the unique identity of the carbonyl g, until it is lost at higher temperature (31 °C) when such relationships must be broken up by the operation of a ' non-Cotton ' scrambling process.

The initial step in both the ' Cotton-type ' fluxional processes postulated by Stuntz and Shapley is the concerted opening of the three carbonyl bridges. Thus the two mechanisms have a common intermediate, proceeding along a common path up to the formation of this intermediate. The potential-energy diagram must be of the form shown on page 1559.

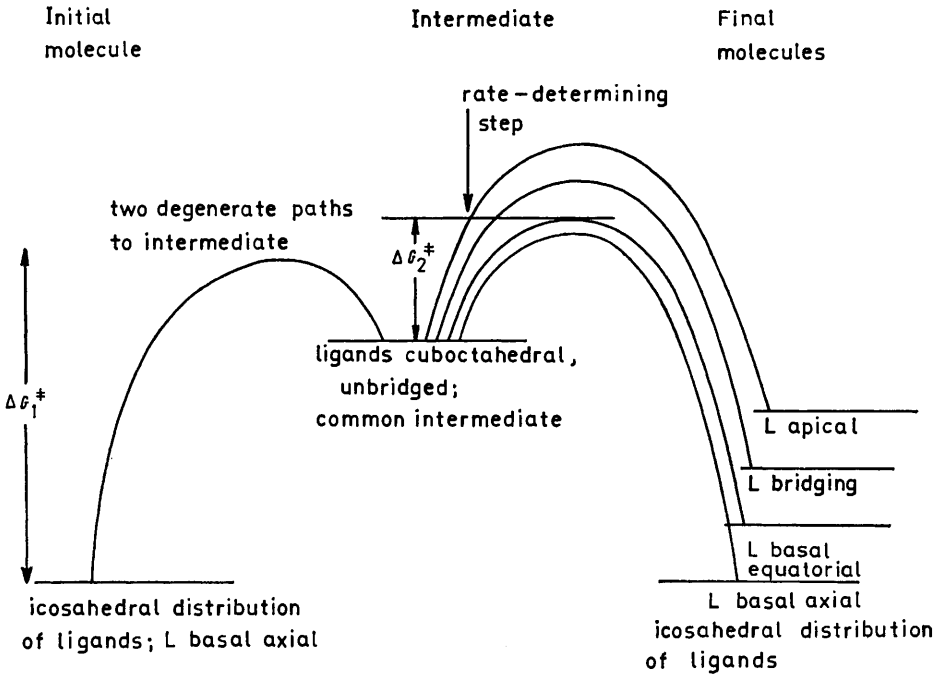
The fact that the different fluxional processes occur over different temperature ranges, and therefore have unequal activation energies, leads to the conclusion that in this reaction scheme the formation of the intermediate is fast, and its collapse to form a product molecule (one of two or more isomers) is the rate-determining step. This seems difficult to justify since one of the fluxional processes (scrambling of the three bridging and three basal-equatorial carbonyls) involves formation of a ground-state bridged structure from the intermediate in precisely the reverse manner to the formation of the intermediate from the initial molecular configuration. The observed kinetic behaviour (collapse of the intermediate being the rate-determining step) is inconvenient to reconcile with the principle of microscopic reversibility, unless $\Delta G_2^{\ddagger} > \Delta G_1^{\ddagger}$ which seems unlikely.



(*vi*) $[Ir_4(CO)_{12-n}L_n]$ ($n = 2$—4). The di-, tri-, and tetra-substituted derivatives with L = $PMePh_2$ show evidence for carbonyl exchange,[6] but no mechanistic evidence has been forthcoming from the variable-temperature ^{13}C n.m.r. spectrum.

A ^{1}H n.m.r. study[28] of the molecules $[Ir_4(CO)_8(EMe_2Ph)_4]$ and $[Ir_4(CO)_8(EMePh_2)_4]$ (E = P or As) showed that the resonances arising from the methyl-group protons broadened and coalesced in a non-uniform manner at high temperatures (>100 °C).

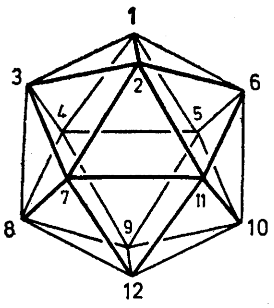
Addition of excess of free $PMePh_2$ to $[Ir_4(CO)_8(PMePh_2)_4]$ led to separate ^1H signals for the complexes and free ligand, indicating that any scrambling process that was taking place was intramolecular. Although i.r. spectroscopy of these compounds had established the presence of bridging carbonyls,[28] ^{13}C n.m.r. did not conclusively establish their ground-state structures, and a variable-temperature ^{13}C n.m.r. investigation was not carried out.

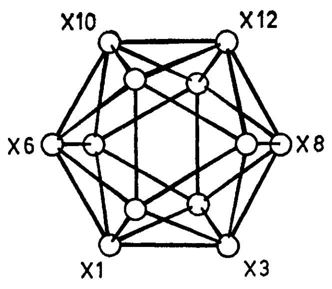


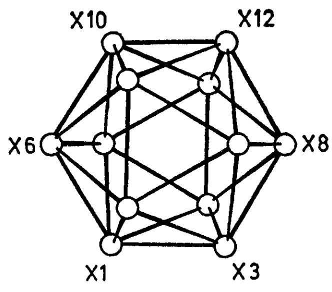
(*b*) *New Proposal for the Carbonyl-scrambling Mechanism in* $[M_4(CO)_{12}]$ *and Related Species* (M = Co, Rh, *or* Ir).—We propose that the different types of carbonyl scrambling observed in $[M_4(CO)_{12}]$ species and the substituted derivatives described above are explicable in terms of a single type of process. The initial isocahedral arrangement of ligands rearranges along a well defined reaction co-ordinate *via* a cubo-octahedral transition state; the existence of different patterns of carbonyl scrambling then arises as a consequence of the geometrical disposition of the metal-atom tetrahedron within the ligand polyhedron. Rather than invoking a different *ad hoc* mechanism to rationalise each observed fluxional process, this is a single type of carbonyl-scrambling path involving concerted motion of all the atoms in the molecule in ways that are well defined in terms of the molecular symmetry.

(*i*) X_{12} *Species* (*icosahedron*). Consider first the regular icosahedron. This is one of the five regular Platonic solids, with 12 vertices, 30 edges, and 20 equilateral triangular faces.[31] In more or less distorted form it is the polyhedron whose vertices are defined by the ligand positions in the tetranuclear dodecacarbonyl derivatives described in the previous section. The regular icosahedron belongs to the point group I_h.

The diagram below shows the icosahedron, together with a stereoscopic view. Successive planes of vertices contain 1, 5, 5, and 1 vertices respectively. This notation can be used to characterise the polyhedron.[32] Alternatively, the icosahedron can be regarded as possessing a 3 : 6′ : 3 arrangement of vertices, where the prime denotes a puckered rather than planar ring of vertices. The vertices of the icosahedron are numbered in a cyclic





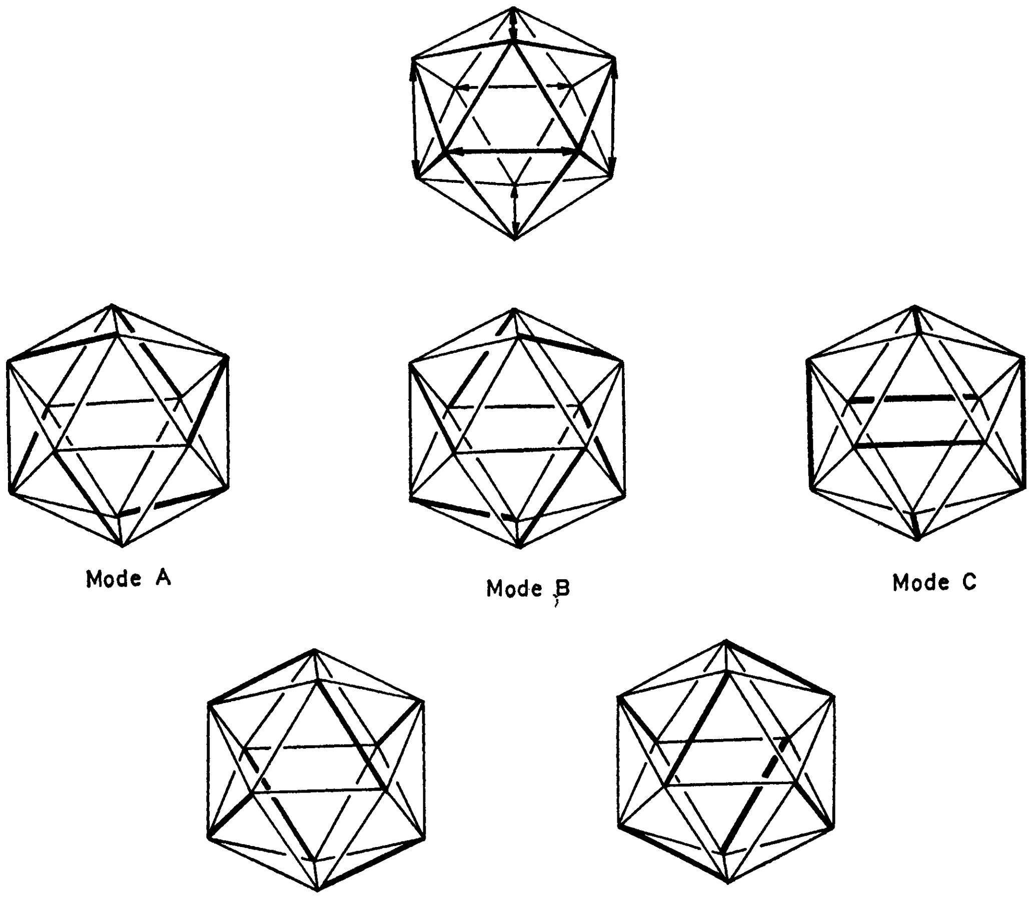


---

[31] D. Hilbert and S. Cohn-Vossen, ' Geometry and the Imagination,' Chelsea Publishing Company, New York, 1952, p. 90.

[32] L. Foppl, *J. Reine Angew. Math.*, 1912, **141**, 251.

order in accordance with the convention suggested by Muetterties and Wright.[33] Vertices in each plane (of 1,5,5, and 1) are numbered consecutively.



Mode A

Mode B

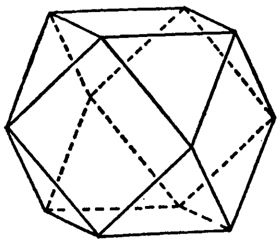
Mode C

Mode D

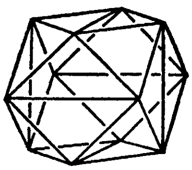
Mode E

The type of distortion of the icosahedron being considered.[34] In these and subsequent diagrams the thick lines denote edges that are being stretched

A concerted operation leading to isomerisation of the icosahedron is the stretching of three orthogonal sets of two coplanar edges.[34] For the isolated icosahedron this mode of distortion has five-fold degeneracy.[35,36] This is most easily seen from the fact that each mode involves the stretching of one edge attached to each vertex, and each vertex has five edges attached to it. As the distortion proceeds the pair of triangular faces enclosing each stretched edge (which in the regular icosahedron[37] have a dihedral angle of 138°12′) became coplanar, forming a single square face. Thus we arrive at the transition state, a cubo-octahedron which is an Archimedean semi-regular solid belonging to the point group O_h. It has 12 vertices, 24 edges (six of the icosahedral edges have been broken to form diagonals of square faces), and 14 faces, of which eight are triangular and six square (six pairs of icosahedral triangular faces have become six single square faces in the cubo-octahedron).



Cubo-octahedron



A cubo-octahedron with six square faces; also depicted are the diagonals of these six square faces. In the icosahedron these correspond to the edges of the polyhedron

---

[33] E. L. Muetterties and C. M. Wright, *Quart. Rev.*, 1967, **21**, 109.

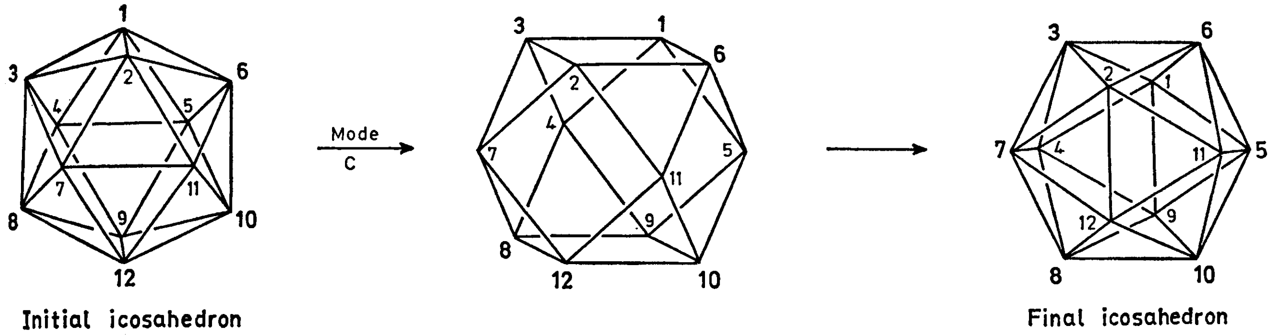
[34] E. L. Muetterties, *J. Amer. Chem. Soc.*, 1969, **91**, 1636.

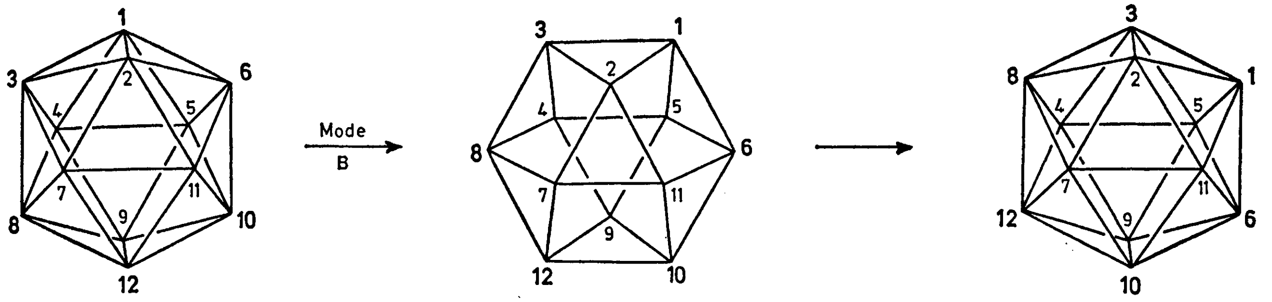
[35] H. D. Kaesz, R. Bau, H. A. Beall, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1967, **89**, 4218.

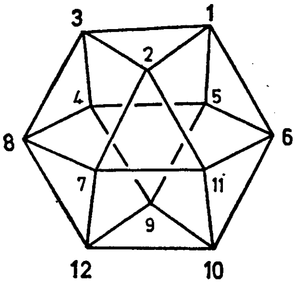
[36] H. S. M. Coxeter, *Mathematische Z.*, 1940, **46**, 380.

[37] A. F. Wells, 'Models in Structural Chemistry,' Clarendon Press, Oxford, 1970, p. 158.

Further distortion along the same reaction co-ordinate, corresponding to collapse of the square faces about their other diagonals, regenerates an icosahedron, in which the relative positions of the vertices have been permuted. It is important to note that antipodal relationships are conserved during this isomerisation process. The cubo-octahedral transition state can collapse to one of only two icosahedra; either it can return to the initial icosahedron or it can continue along its distortion co-ordinate to the final icosahedron.



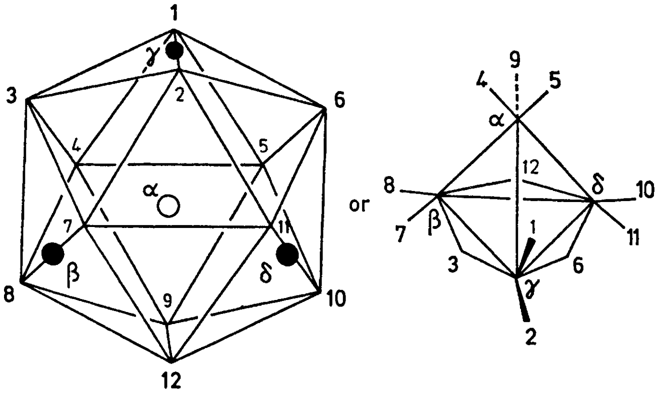




The four planes of six vertices are: (1)(3)(8)(12)(10)(6), (3)(2)(11)(10)(9)(4), (8)(7)(11)(6)(5)(4), and (1)(2)(7)(12)(9)(5)

An alternative way of visualising this distortion mechanism is to view the icosahedron as a $3:6':3$ arrangement, with two staggered equilateral triangles sandwiching a puckered hexagon. The distortion corresponds to the movement of the six vertices of this hexagon into a plane, with concomitant rotation relative to the two triangles, to form the cubo-octahedron. The plane of six vertices then reforms a puckered hexagon while moving round in the same direction as before, to give the product icosahedron. However, this approach can lead to some confusion.

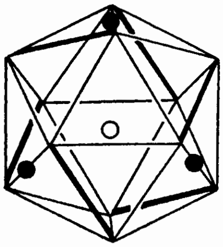
It can be argued that in the cubo-octahedral transition state there are four planes of six vertices (corresponding to the four pairs of staggered triangles that sandwich them) which could *each* undergo motion (in one of two directions) to form a puckered hexagon and so produce an icosahedron. However, it can be shown that for each plane of six vertices in the transition state that are taken to form a puckered hexagon, the two icosahedra that are produced are the initial icosahedron and the same product icosahedron. In other words a given cubo-octahedron can collapse to form one of *only two* icosahedra, which merely have different spatial orientations depending on which plane of six vertices is considered to rotate. The apparent anomaly is resolved because the distortion mode that we are investigating

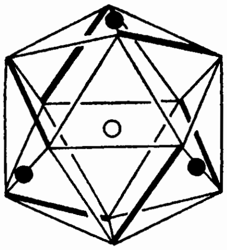


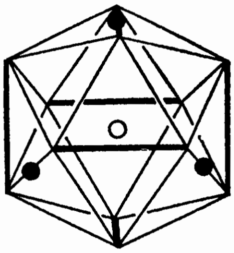
● denotes a metal atom at the front of the polyhedron (as viewed)

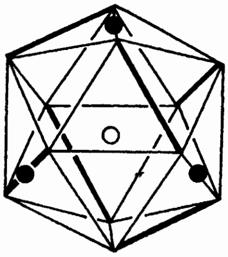
○ denotes a metal atom at the rear

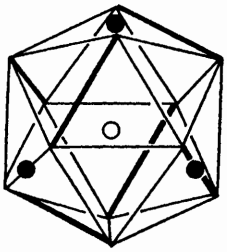
does not correspond to motion of only the six vertices in the central puckered hexagon, but to concerted motion of all the 12 vertices of the polyhedron.

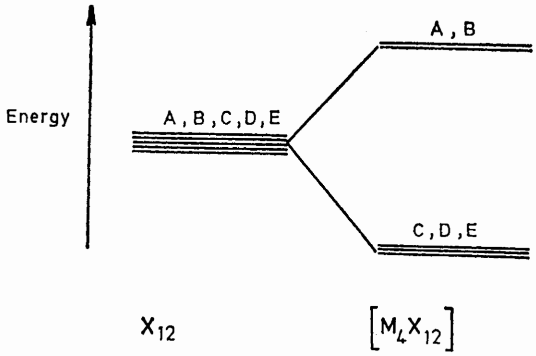

Mode A


Mode B

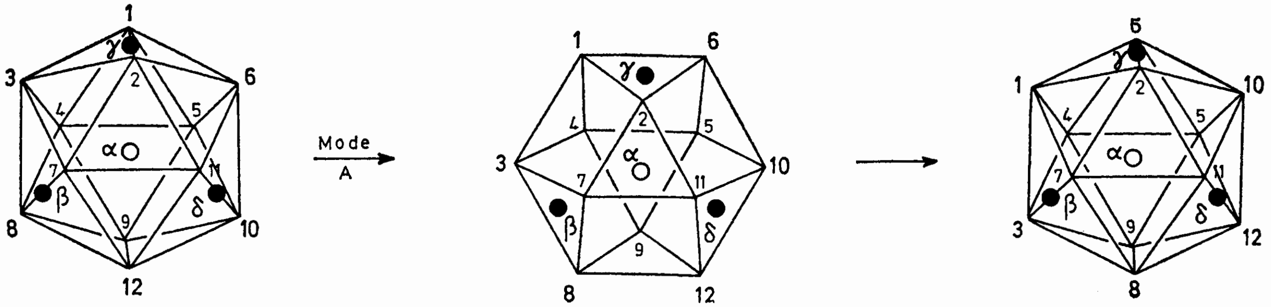

Mode C


Mode D


Mode E

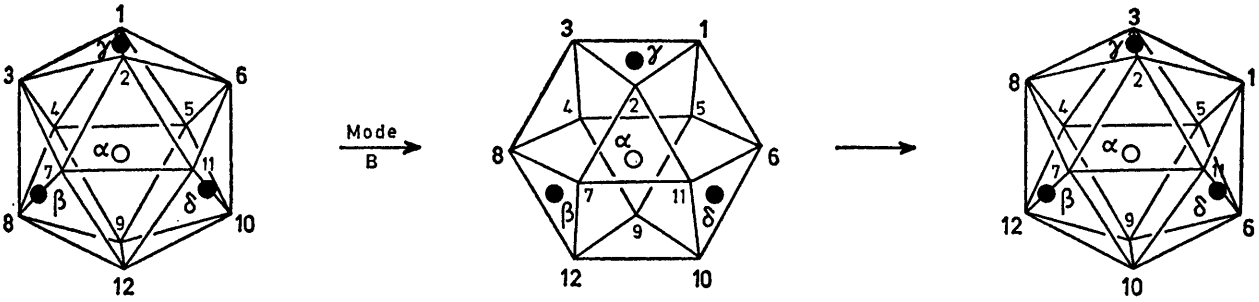


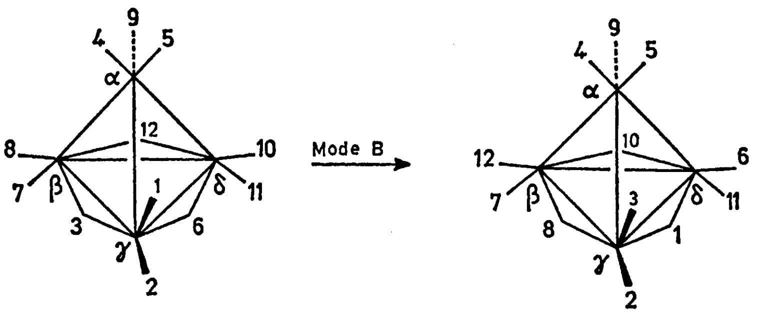
This concerted mechanism of isomerisation of a ground-state icosahedral structure *via* a cubo-octahedral transition state was successfully used by Kaesz *et al.*[35] to explain the observed distribution of products in the thermal rearrangement of the carbaboranes *ortho*-$B_{10}C_2H_{12}$ and 9-bromo-12-carbaborane.



(*ii*) $[M_4X_{12}]$ *Species*. Now we consider a tetrahedron within the icosahedron. This is the idealised geometry to which the $[M_4(CO)_{12}]$ species of C_{3v} symmetry conform. Occupation of preferred co-ordination sites by the metal atoms leads to three metal atoms in a basal plane spanned by bridging carbonyls, and a distinct apical metal atom bonded to terminal ligands only. Because of the geometrical arrangement of the tetrahedron within the icosahedron, the five-fold degeneracy of the distortion to form a cubo-octahedron is lifted. Three of the modes (C—E) involve the stretching of one icosahedral edge whose vertices are the two terminal ligands on a basal atom of the tetrahedron (*e.g.* edge 1—2 in mode C). These form a triply degenerate set. The other two modes (A, B) of deformation of the icosahedron do not involve stretching an edge of this type; they form a doubly degenerate pair.

Now consider the effect of the two types of mode on the molecular isomerisation.





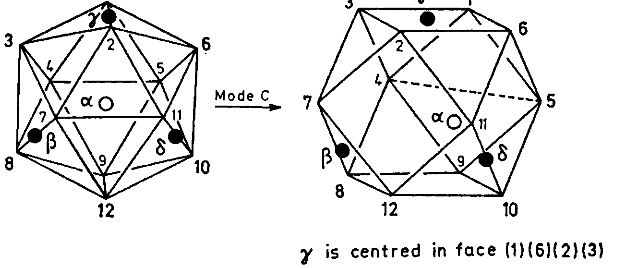
(1) Modes A and B result in a cyclic permutation of the six ligands in the equatorial plane (three bridging and three equatorial basal terminal). Mode A permutes them in one direction, and mode B in the other. Previously proposed scrambling mechanisms involve initial bridge opening to give such an unbridged intermediate, which is then considered to be able to collapse in different ways about the M_4 tetrahedron to give a variety of product molecules (see especially ref. 6).

We know from the X_{12} section (*i*) that the cubo-octahedral transition state can collapse to only one icosahedron (or reverse its initial distortion to re-form the starting icosahedron). So whether or not the final molecular geometry of the $[M_4X_{12}]$ species produced by modes A and B is uniquely defined depends on whether the M_4 tetrahedron can attain one or more orientations within the product icosahedron. If it is assumed that the tetrahedron of metal atoms in the cubo-octahedral transition state does not move with respect to the ligand polyhedron (*i.e.* the cubo-octahedron can collapse about the tetrahedron in one orientation only, as predetermined by the original icosahedral distortion co-ordinate) then in the transition states formed in modes A and B the four metal atoms are *not* equivalent, because the individual ligands are distinguishable by their distinct motions along their own distortion co-ordinates. The geometry shown as produced by each mode is the *unique* product from that isomerisation mode.

The above assumption is not unreasonable, since motion of the M_4 cluster within the cubo-octahedron of ligands would cause the breaking of further metal–ligand bonds, and so be of higher activation energy than rearrangement of the ligand polytope alone.

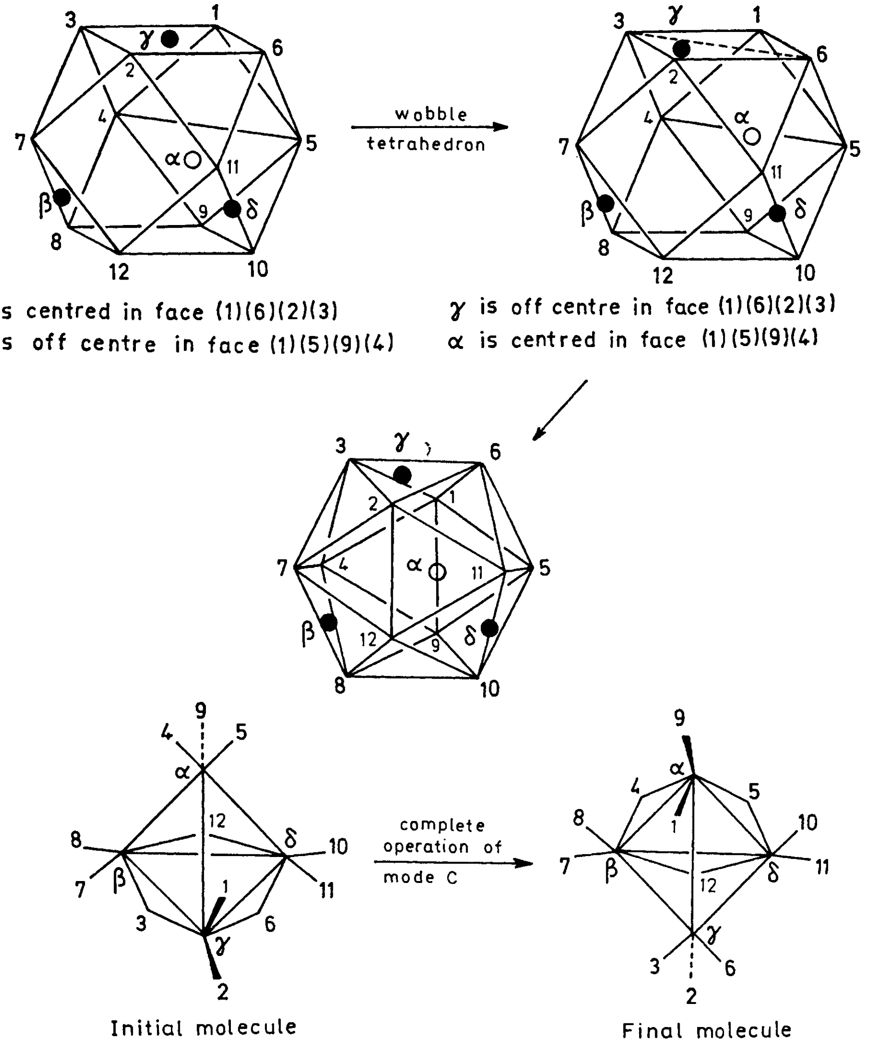
(2) Modes C, D, and E of the $[M_4X_{12}]$ species result in the formation of ligand bridges about a face of the M_4 tetrahedron that was not originally the bridged face. Each of the three non-bridged M_3 faces of the ground-state molecule is converted into the bridged face of the product molecule by one of these triply degenerate modes. The manner of isomerisation caused by these three modes is different from any previously considered mechanism, since it does *not* commence by symmetrical opening of the bridges in the ground-state structure.

On forming the cubo-octahedral transition-state ligand distribution by one of the three modes C—E the four metal atoms occupy reasonably well defined co-ordination positions, but if the cubo-octahedron is allowed to proceed directly to the product icosahedron a molecule of C_{3v} symmetry does not result. Some motion of the M_4 tetrahedron within the ligand polyhedron during the isomerisation process must take place if the stable molecular geometry is to be attained in the product



γ is centred in face (1)(6)(2)(3)
α is off centre in face (1)(5)(9)(4)

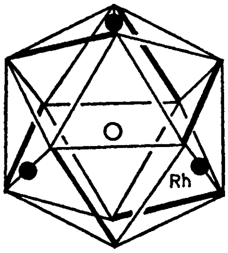
molecule. Examination of the transition state produced by operation of distortion mode C reveals that two of the metal atoms that were originally in the basal plane of the M_4 tetrahedron still occupy positions co-ordinated to their original terminally bound ligands. The third metal atom from the basal plane lies in a position centred in a square face of the cubo-octahedron. The metal atom that was originally situated in the apical position of the M_4 cluster is now located in a position off centre in another square face.



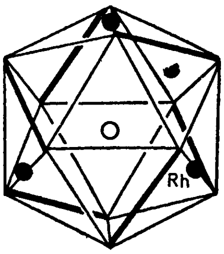
If the M_4 tetrahedron now 'wobbles' by a small amount, to interchange the co-ordination types of the two latter metal atoms without moving the two former metal atoms, then the ligand polyhedron can proceed along its original distortion co-ordinate to produce an icosahedron and form a molecule in the ground-state C_{3v} structure. Such a 'wobbling' motion corresponds in a molecule of the dimensions of $[Rh_4(CO)_{12}]$ to atomic motions of less than 0.5 Å. By comparing the initial and final structures it can be seen that the original apical metal atom has moved into the basal plane of the product molecule. It has been replaced as apical atom by a member of the original basal plane. This latter atom is the one whose two terminally bound ligands defined an icosahedral edge that was stretched in the original deformation of the ligand polytope. It can be seen that this isomerisation mechanism is achieved by concerted motion of all the atoms in the molecule.

Repeated operation of this latter triply degenerate carbonyl-scrambling mode (C, D, and E) results in the exchange of all the ligands over the whole molecule by a single process. This is what is experimentally observed for $[Rh_4(CO)_{12}]$.[24,25] If the other, doubly degenerate, mode (A and B) is operative only at higher temperatures, it would serve only to speed up the rate of total carbonyl scrambling and would not be detected by ^{13}C n.m.r. spectroscopy which at 50 °C already shows the limiting fast-exchange spectrum. The triple and double degeneracy of the isomerisation modes of $[M_4(CO)_{12}]$ may be further lifted by substitution of a carbonyl group by a phosphine ligand, or by introduction of a heterometal atom.

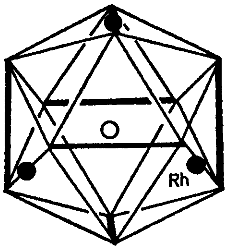
(*iii*) $[M_3M'X_{12}]$ *Species*. The complex $[RhCo_3(CO)_{12}]$ is the only example experimentally studied. Modes A and B again form a degenerate pair, resulting in the scrambling of the three bridging and three equatorial terminal carbonyls. Modes C—E are however no longer degenerate because of the heterometal atom in the basal plane. Modes C and D form a degenerate pair and result in the replacement of the apical cobalt atom by a cobalt atom from the basal plane. The rhodium atom remains in the basal plane and the two carbonyls originally terminally bonded to it remain so, becoming equivalent to one another as they interchange co-ordination type. Mode E is now unique and causes carbonyl bridges to form about the Co_3 face of the metal-atom tetrahedron, sending the rhodium atom into the apical position. Allowing modes C and D to operate alone over the intermediate temperature range gives 10 : 2 equivalence of carbonyl ligands as experimentally observed for $[RhCo_3(CO)_{12}]$. The two Rh–CO terminal carbonyls remain distinct from the others, but equivalent to one another; the other 10 carbonyls are scrambled over the other 10 sites available in the molecule. All the three cobalt atoms become equivalent by the repeated operation of modes C and D, but a ^{59}Co n.m.r. study of this molecule, which could confirm this prediction, has not been carried out.



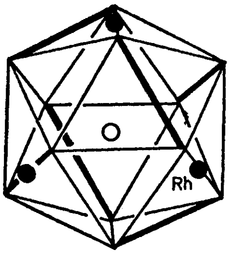
Mode A



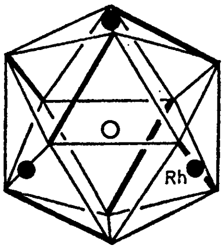
Mode B



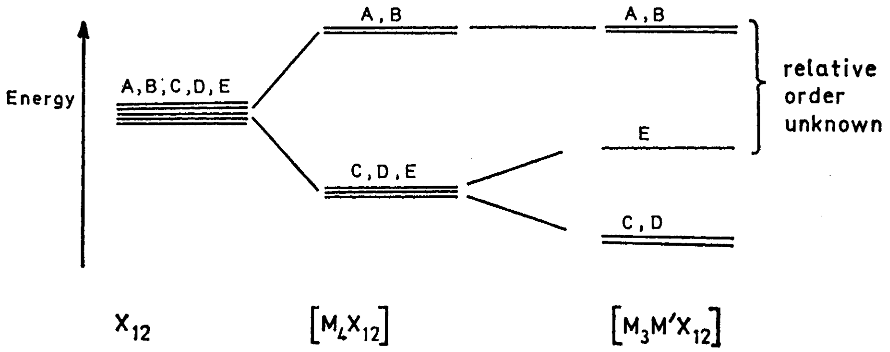
Mode C



Mode D



Mode E



At higher temperatures activation of the other carbonyl-scrambling modes (E alone, or A and B as a degenerate pair) in conjunction with C and D causes total scrambling of all the carbonyls in the molecule, again in accord with experimental observation. It is to be expected that the modes C and D will have lower activation energy than E, because they result in the formation of a product molecule of ground-state structure, with the rhodium atom in the basal plane, instead of a higher-energy isomer with Rh apical, as formed by mode E. Modes A and B are anticipated to have higher activation energies in this particular molecule as they involve breaking of an Rh–CO terminal bond, which is stronger than a Co–CO bond.[38] Modes C and D involve the breaking of terminal bonds to cobalt atoms only, and of Rh–CO(bridging) bonds, but no Rh–CO terminal bonds.

(*iv*) $[M_4(CO)_{11}L]$ *Species*. The only example for which a full ^{13}C n.m.r. study has been completed is $[Ir_4(CO)_{11}(PMePh_2)]$.[6] Substitution of the phosphine

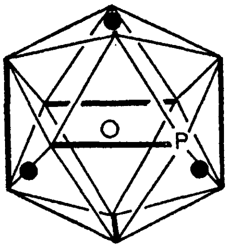
---

[38] J. A. Conner, H. A. Skinner, and Y. Virmani, *Faraday Symp. Chem. Soc.*, 1973, **8**, 18.

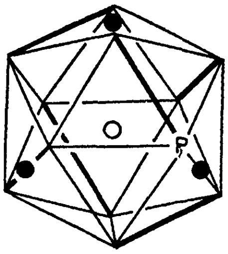
ligand into a basal-axial position again lifts the degeneracy of the scrambling modes (see diagrams). Modes A and B are again degenerate and cause the scrambling of the three bridging and three equatorial basal-terminal carbonyl ligands. In $[Ir_4(CO)_{11}(PMePh_2)]$ this is the lowest-temperature fluxional process to be observed experimentally. The product molecules of modes A and B have the ground-state structure, with the phosphine ligand axially substituted. Modes C and D form a doubly degenerate pair which change the identity of the apical metal atom, and send the phosphine ligand into an equatorial-terminal position. Mode E is unique; it sends the iridium atom to which the phosphine is bonded into the apical position. This is a possibility not previously considered, because of the high energy of the apically substituted isomer.

Mode A Mode B

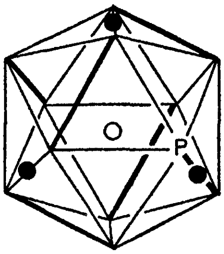
P denotes the position of the phosphorus ligand



Mode C



Mode D

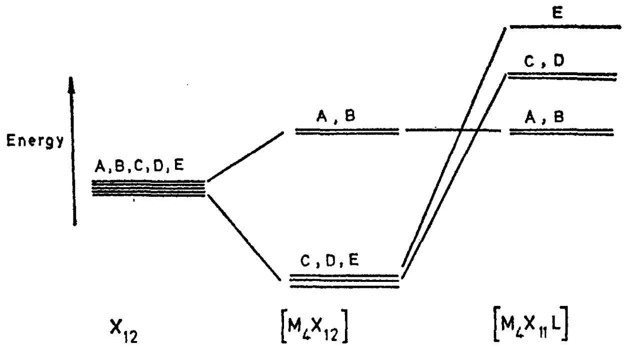


Mode E

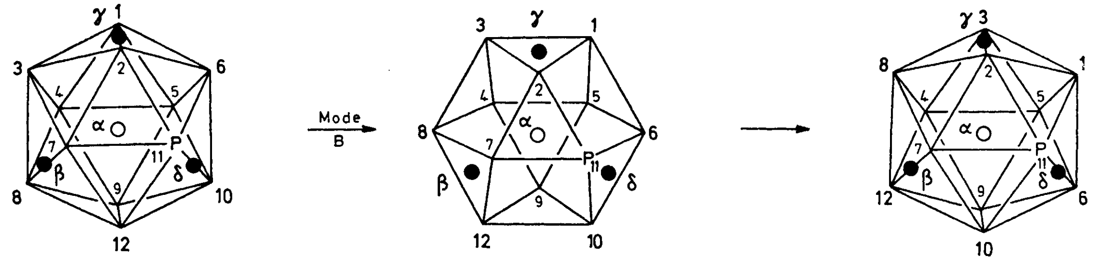
Allowing modes A and B alone to operate at *ca.* −35 °C gives 6 : 2 : 2 : 1 equivalence of the carbonyls, as experimentally observed in $[Ir_4(CO)_{11}(PMePh_2)]$. The three apical carbonyls (one distinguished by its antipodal relationship to the phosphine) and the two basal axial carbonyls do not participate in the scrambling at this temperature. At higher temperatures activation of modes C and D in conjunction with A and B will cause scrambling of all the carbonyls over all the available molecular sites, with the exception of the single carbonyl antipodal to the phosphine. Because of the preservation of antipodal relationships within the ligand polytope during isomerisation, this single carbonyl is uniquely defined, as experimentally observed. Modes C and D are here expected to be of higher activation energy than A and B because they lead to the formation of the equatorially substituted isomer which is of higher energy than the axially substituted isomer (the ground-state structure) formed after operation of modes A or B.

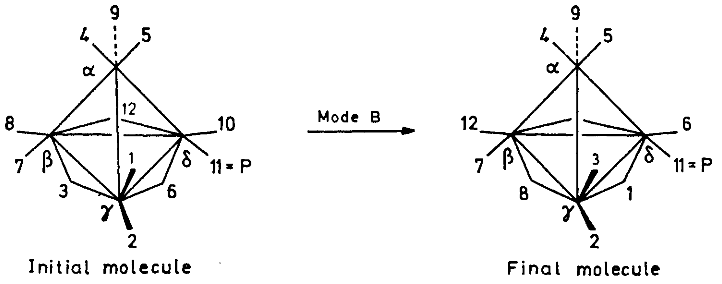
The operation of mode E does not need to be invoked to explain the experimental results of Stuntz and Shapley, but it is not inconsistent with them. It still preserves the unique identity of the single carbonyl antipodal to the phosphine ligand.

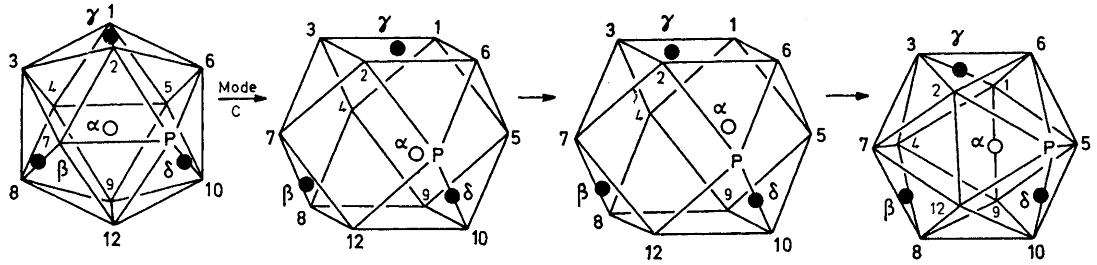
It should be noted here that after the operation of mode C or D, to form a molecule of the equatorially substituted isomer, the six ligands then in the equatorial plane cannot scramble by modes A and B since this would involve phosphine migration into a bridging position. Of the other three modes, two reform the ground-state molecule with the phosphine in an axial position and the third forms a new equatorially substituted molecule in which the phosphine has migrated to a different iridium atom. This is simply a consequence of the formation during carbonyl scrambling of a different isomer of the molecule, for which the effects of the available fluxional operations are different from those for the ground-state structure.

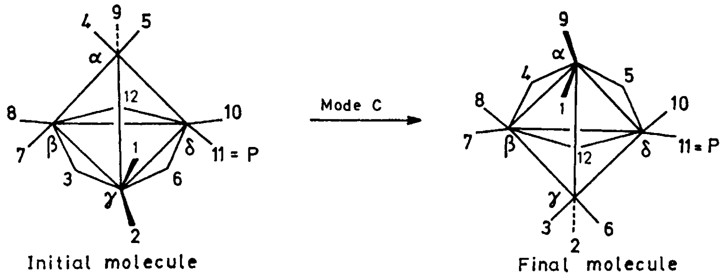


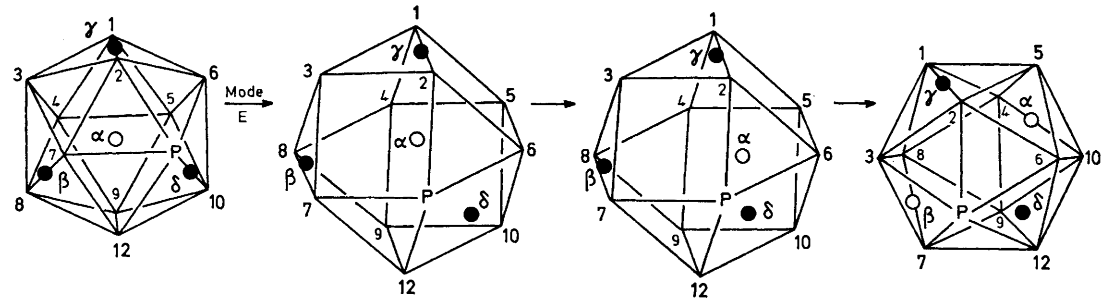
At higher temperature still (31 °C) Stuntz and Shapley[6] observed complete interchange of all the 11 carbonyl groups, indicating that antipodal relationships within

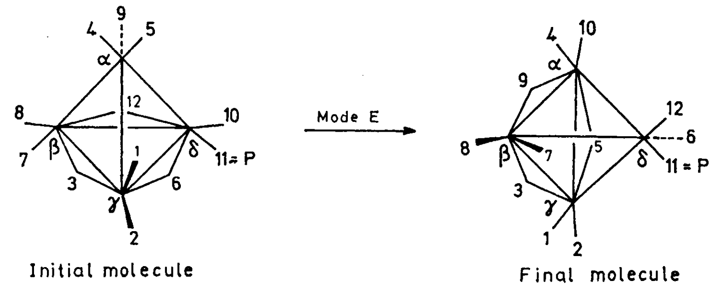

γ 1
3
6
α
P
β
δ
8
10
12
Mode B
3 γ 1
8
6
11
12
10
γ 3
8
1
12
6
10


9
4
5
α
12
8
10
7
β
δ
11 = P
3
6
γ
2
Initial molecule
Mode B
12
6
1
Final molecule


γ 1
3
6
Mode C
α
P
β
δ
8
10
12
7
5

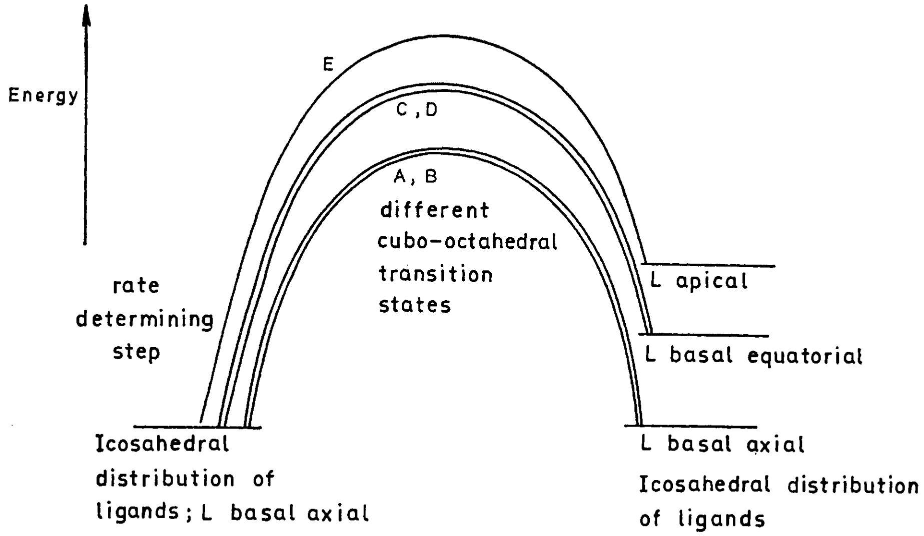

9
4
5
α
12
8
10
7
β
δ
11 = P
3
6
γ
2
Initial molecule
Mode C
Final molecule


γ 1
3
6
Mode E
α
P
β
δ
8
10
12
5
7
1
5
3
10


9
4
5
α
12
8
10
7
β
δ
11 = P
3
6
γ
2
Initial molecule
Mode E
10
12
1
Final molecule

the ligand polytope are no longer conserved. Thus some other fluxional process comes into play; for example, face rotation of a triangle of carbonyls in the cubo-octahedral transition state would lead to total carbonyl scrambling.

The potential-energy diagram for the fluxional process outlined above for $[M_4X_{11}L]$ is of the following form:



The cubo-octahedral form of the ligand arrangement about the M_4 tetrahedron is here considered to be a *transition state* rather than the intermediate implied by Stuntz and Shapley.[6] Because the initial mode of distortion of the molecule uniquely defines the scrambling path and the distribution of ligands in the product molecule, the existence of different scrambling processes that are operative over their own individual temperature ranges can be simply understood in terms of the different modes of distortion having unequal activation energies. The initial distortion of the molecule is the rate-determining step here because as soon as one mode of distortion has commenced it must continue along its own precisely defined reaction co-ordinate (in either the forward or reverse direction), without the opportunity to ' change direction ' after attainment of an intermediate.

Conclusions.—Further study of the fluxional behaviour of tetrametal dodecacarbonyl derivatives will be of great interest. The development of a complete theoretical description of the mechanism of carbonyl scrambling is seriously hindered by the small number of compounds that have been fully investigated. Systems of lower symmetry, such as $[M_4(CO)_{10}L_2]$ (which has already been investigated without success [6]), $[M_4(CO)_8L_4]$ (previously studied by ^{1}H n.m.r.),[28] and molecules containing hetero-metal atoms such as $[M_2M'_2(CO)_{12}]$ and $[M_3M'(CO)_{12-n}L_n]$ are certainly worthy of continued examination so that a more comprehensive picture of the fluxional behaviour of such molecules may be built up.

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 carbonyl 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 arrangements of ligands, *e.g.* the icosahedron, this remains the simplest and apparently the lowest-energy process. A similar mechanism could be considered for $[Rh_4(CO)_{12}]$: the Rh_4 tetrahedron ' wobbling ' within the icosahedron to produce a species with no CO bridges but retaining an icosahedral arrangement of ligands, and therefore different to the $[Ir_4(CO)_{12}]$-type of complex having the cubo-octahedral disposition.

In this work we have examined the consequence of the polyhedral interconversion of an icosahedron *via* a cubo-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.

It is also clear from these studies that for the systems $[RhCo_3(CO)_{12}]$ and $[Ir_4(CO)_{11}L]$ rotation of a triangular face in the cubo-octahedral intermediate occurs. Thus, the simple cubo-octahedral mechanism alone would give a 2 : 8 : 2 relationship, whereas with triangular rotation the 10 : 2 relationship is anticipated. Again this appears to be general and equally applies to $[Fe_3(CO)_{11}L]$ complexes.

[7/1391 *Received*, 1*st August*, 1977]