The Structures and Fluxional Behaviour of the Binary Carbonyls; A New Approach. Part 3.[1] The Fluxional Behaviour of $[Fe_3(CO)_{11}L]$, L = PR_3 or $P(OR)_3$

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The stereodynamic behaviour of the complexes $[Fe_3(CO)_{11}L]$ [L = PR_3 or $P(OR)_3$], as determined by ^{13}C n.m.r. spectroscopy over a wide temperature range, has been interpreted in terms of an icosahedral $\rightleftharpoons$ cube-octahedral interchange of ligands of the type previously postulated for $[M_4(CO)_{12}]$ (M = Co, Rh, or Ir) and their derivatives.

UNTIL recently, the commonly accepted view of carbonyl scrambling in $[Fe_3(CO)_{12}]$ was that proposed by Cotton and Troup.[2] Their mechanism, which involves the pairwise opening of the two CO bridges, produces an intermediate which possesses a *quasi*-$[Os_3(CO)_{12}]$ structure of D_{3h} symmetry. The closure of bridge pairs around successive Fe–Fe edges leads, ultimately, to the scrambling of all CO ligands. There are two points of note. First, the equilibration of all CO groups is achieved only after numerous inverconversions $C_{2v} \rightleftharpoons D_{3h}$ and secondly, since the bridged Fe–Fe distance is ' short ', there is a ' hidden process ' involving bridge formation selectively along this edge and the Fe triangle undergoes a scissoring mode which makes all Fe–Fe distances equivalent at the same rate as CO interconversion. This scissoring motion, which has not been touched on previously, provides an example of a ' hidden ' metal polytopal rearrangement.

Support for this scissoring motion comes from the recent observation[3] that at room temperature the ^{57}Fe satellite sub-spectrum observed in the ^{13}C n.m.r. spectrum of $[Fe_3(CO)_{12}]$ shows only a doublet [J(Fe–C) = 8.3 Hz]. In principle, two doublets, in the ratio 2 : 1, are expected because two non-equivalent types of iron atoms are in the molecule. We have observed that the iron satellite sub-spectrum still shows a doublet at −80 °C.

We have recently put forward an alternative view[4] of carbonyl scrambling in $[Fe_3(CO)_{12}]$ that is based on the simple idea that the structure of $[Fe_3(CO)_{12}]$ is merely a consequence of the packing of an Fe_3 triangle within an icosahedron of twelve CO groups.[1b,5] According to this proposition three structural forms may be considered, (A), (B), and (C). It would appear that the C_{2v} form (A) is favoured in the solid, but in solution, on the basis of the i.r. data, the D_3 form (B) predominates. It follows that interconversion between the three isomeric forms A $\rightleftharpoons$ B $\rightleftharpoons$ C, which are generated by the simple rotation of the CO polytope about the Fe_3 triangle (or *vice versa*), would lead to the equilibration of the twelve carbonyl groups.

C_{2v}	D_3	C_{2v}
(two edge bridges)	(no bridges)	(two triple bridges)
(A)	(B)	(C)

There is no method at present available by which these two mechanisms may be differentiated. This is not the case, however, with the mono-substituted derivatives $[Fe_3(CO)_{11}L]$ [L = PR_3 or $P(OR)_3$]. A range of these derivatives has been recently synthesized.[6] The complex $[Fe_3(CO)_{11}(PPh_3)]$,[7] which has been the subject of a single-crystal *X*-ray analysis, is known to exist in the crystal as a mixture of two equatorially substituted isomers, which correspond to forms (I) and (II) (Figure 1).

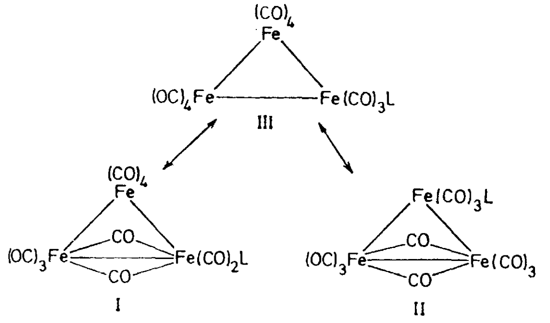


FIGURE 1 Isomer interconversion to two forms of $[Fe_3(CO)_{11}L]$ species

According to either the proposal of Cotton and Troup[2] or that by Johnson,[4] any fluxional process in either (I) or (II) leading to the equilibration of all CO groups will occur through a common intermediate (III) (Figure 1). The structure of this intermediate is different in the two proposals, possessing a *quasi*-$[Os_3(CO)_{12}]$ structure (in which the twelve ligands adopt approximately an anti-cube-octahedral arrangement) according to Cotton and Troup and a *quasi*-$[Fe_3(CO)_{12}]$ structure (B) (in which the twelve ligands adopt approximately an icosahedral arrangement) according to Johnson. In either case all CO groups are terminally bound.

It follows from either proposal that the fluxional process will lead to isomer interconversion (I) $\rightleftharpoons$ (III) $\rightleftharpoons$ (II). It also follows from the proposal of Johnson in which the Fe_3 triangle may be envisaged as rotating rapidly within the ligand icosahedron, that a 5 : 5 : 1 ratio of ^{13}CO resonances will be expected in the high-temperature limiting spectrum of either isomer.

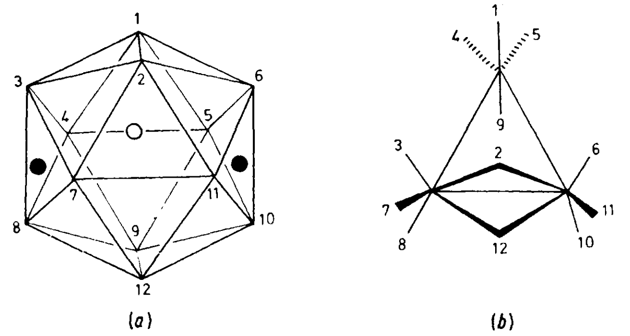
In this work the ^{13}C n.m.r. spectra of $[Fe_3(CO)_{11}L]$

Carbon-13 n.m.r. data for $[Fe_3(CO)_{11}L]$ complexes (at low temperatures)

L	Chemical shift/p.p.m.*			Solvent	θ_c/°C
$PPhMe_2$	224.0 (8.0)	212.3	204.1	CD_2Cl_2	−90
$P(OEt)_3$	221.9 (13.0)	219.0	204.6	$CD_2Cl_2–CF_2Cl_2$	−123
$P(OPr^i)_3$	219.2 (12.2)	221.1	203.1	$CD_2Cl_2–CF_2Cl_2$	−123
$P(OPh)_3$	220.7 (10.6)	213.9	202.4	$CD_2Cl_2–CF_2Cl_2$	−129

* J(CP)/Hz given in parentheses.

[L = PR_3 or $P(OR)_3$] have been recorded over a wide temperature range. These results, which are recorded in the Table, may be taken to indicate that fluxional behaviour occurs. The phosphine and phosphite complexes exhibit a similar set of spectra. For example, in the spectrum of $[Fe_3(CO)_{11}(PPhMe_2)]$ at 35 °C two lines at δ 204.4 (singlet) and δ 217.9 [doublet, $J(^{31}P–^{13}C)$ = 2 Hz] of relative intensity 1 : 10 are observed. On cooling, the resonance at δ 217.9 broadens, collapses, and at −90 °C separates out into two lines at δ 224.0 [doublet, $J(^{31}P–^{13}C)$ = 8 Hz] and 212.3 (singlet). The original line at δ 204.4 is virtually unchanged and at −90 °C is observed at δ 204.1. Thus at −90 °C three signals at δ 224.0, 212.3, and 204.1 of relative intensity 6 : 4 : 1 are observed. On warming the solution above 35 °C, the line at δ 217.9 broadens but some decomposition to $[Fe(CO)_4(PPhMe_2)]$ and $[Fe(CO)_5]$ occurs before a high-temperature limiting spectrum is obtained. It would appear that at 35 °C partial CO scrambling is occurring and that at low temperature a more restricted fluxional process is being observed. The evidence for this more restricted fluxional process is that the ^{13}C n.m.r. spectrum is simpler than that expected for either (I) or (II) and shows no evidence of the bridging CO ligands which are observed in the i.r. spectrum of this complex.



(*a*) (*b*)

FIGURE 2 The structure of $[Fe_3(CO)_{12}]$. (*a*) Polyhedral representation as a triangle of iron atoms within an icosahedron of carbonyls; ● denotes a metal atom at the front of the polyhedron (as viewed), ○ denotes a metal atom at the rear. (*b*) Conventional representation

In the ^{31}P n.m.r. spectra of $[Fe_3(CO)_{11}L]$ a single line is observed in the temperature range −90 °C to 35 °C for L = $PPhMe_2$ and −120 °C to 26 °C for L = $P(OR)_3$, indicating that only one isomer is present.

On the basis of these observations the Johnson mechanism and the Cotton and Troup mechanism may be ruled out. Neither would satisfactorily explain the pattern of spectra observed and an alternative explanation was therefore sought.

We have recently shown that for the tetranuclear

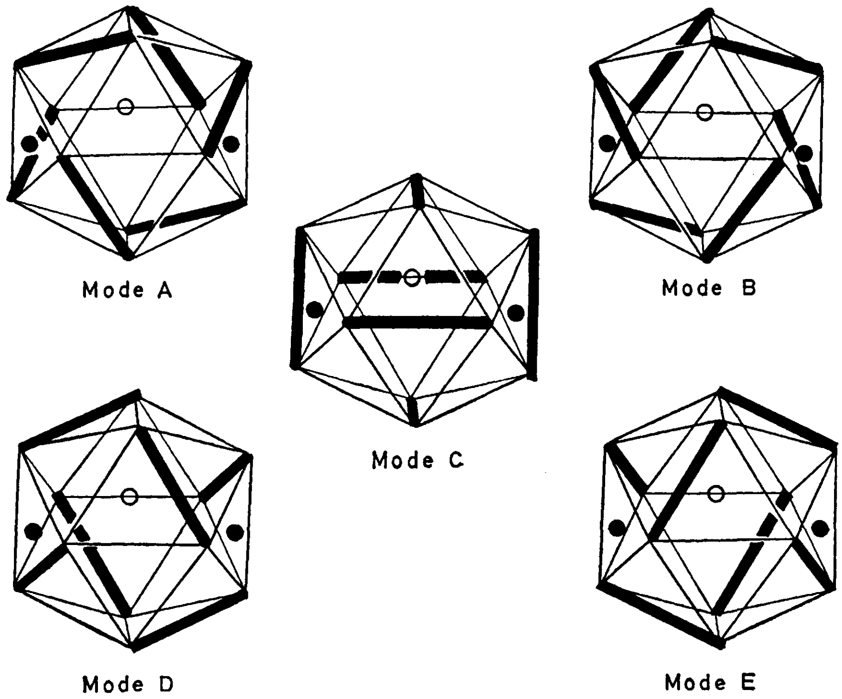


FIGURE 3 The five modes of rearrangement of the icosahedron of ligands in $[Fe_3(CO)_{12}]$. Heavy lines indicate the edges which undergo elongation to produce the appropriate cube-octahedral transition state

carbonyls $[M_4(CO)_{12}]$ (M = Co, Rh, or Ir) and related derivatives, *e.g.* $[Co_3Rh(CO)_{12}]$ and $[M_4(CO)_{12-n}L_n]$, a general mechanistic approach may be applied.[1a] Basically, the polytopal rearrangement of the CO icosahedron *via* a cube-octahedral transition state is considered.

Here we extend this approach to the trinuclear carbonyl $[Fe_3(CO)_{12}]$ and the substituted derivatives $[Fe_3(CO)_{11}(PR_3)]$ and $[Fe_3(CO)_{11}\{P(OR)_3\}]$. We postulate that: (*i*) the twelve carbonyl ligands, which define an icosahedron in the ground-state structure (solid state) of $[Fe_3(CO)_{12}]$ (Figure 2), undergo polytopal rearrangement *via* a cube-octahedral transition state as previously postulated for the tetranuclear dodecacarbonyls. In addition, and again as postulated for the $[M_4(CO)_{12}]$ systems, some rotation of certain polyhedral triangular faces occurs; this corresponds to carbonyl interchange in an unsubstituted $Fe(CO)_3$ unit.

(*ii*) Any motion of the Fe_3 triangle relative to the ligand sphere will be restricted to rotational motion within its own plane. This is not unreasonable since the icosahedral envelope of ligands is somewhat flattened as a consequence of the anisotropic nature of the metal polyhedron.

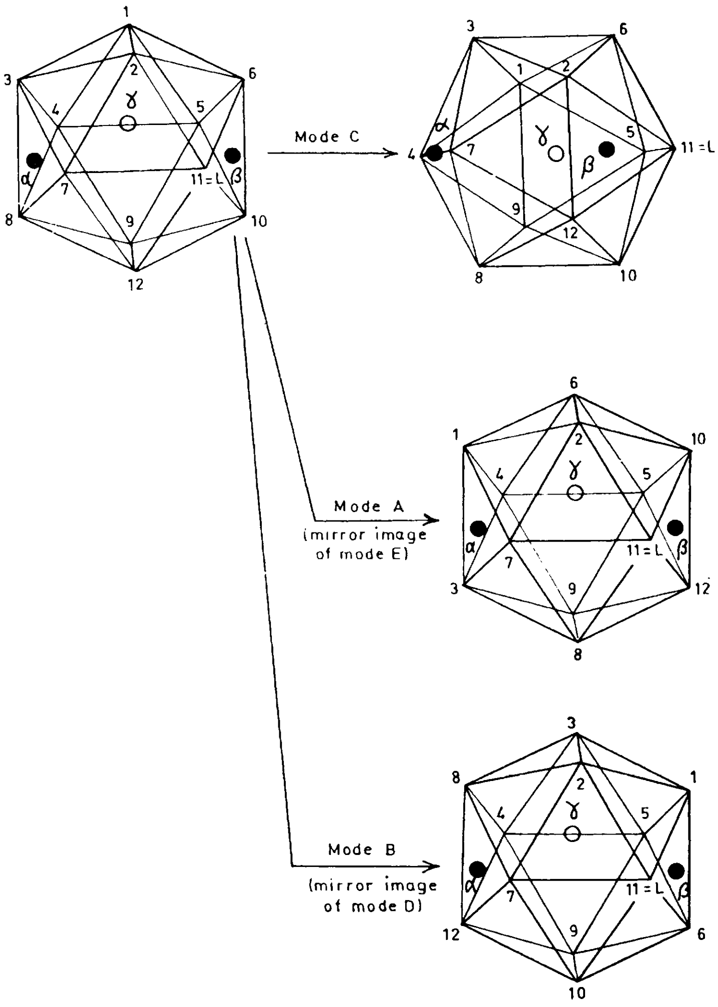


FIGURE 4 Effect of the five modes of ligand rearrangement in $[Fe_3(CO)_{11}L]$ (frontally substituted isomer). The phosphine or phosphite (ligand 11) remains bonded to metal atom β throughout. In mode C, the metal atom triangle is constrained to move only within its own plane. In the other modes, which also involve concerted motion of all 12 (not just six) ligands, motion of the metal atom triangle out of its own plane is necessary; this is kept to the minimum possible

(*iii*) The complexes $[Fe_3(CO)_{11}(PR_3)]$ and $[Fe_3(CO)_{11}\{P(OR)_3\}]$, which do not isomerise as a result of any fluxional process, exist in solution solely as the 'frontally substituted' isomer (I) in agreement with their i.r. spectra.[6]

At the onset of our discussions it is important to remember that in no case (see Table) is a low-temperature limiting spectrum corresponding to the ground-state structure obtained. Even at the lowest temperatures some fluxional behaviour was apparent.

$[Fe_3(CO)_{12}]$.—We have previously considered the concerted rearrangement undergone by an icosahedron enveloping an M_4 tetrahedron.[1a] We now deal with the effect of placing an M_3 triangle within the icosahedron. The rearrangement of the icosahedron *via* the cube-octahedral transition state has five-fold degeneracy. This is lifted by the insertion of the triangle into two sets, one unique and one four-fold degenerate (Figure 3), mode C is unique. With the metal triangle constrained to move only within its own plane, the pattern of carbonyl scrambling is as shown (Figures 4 and 5, L = CO).

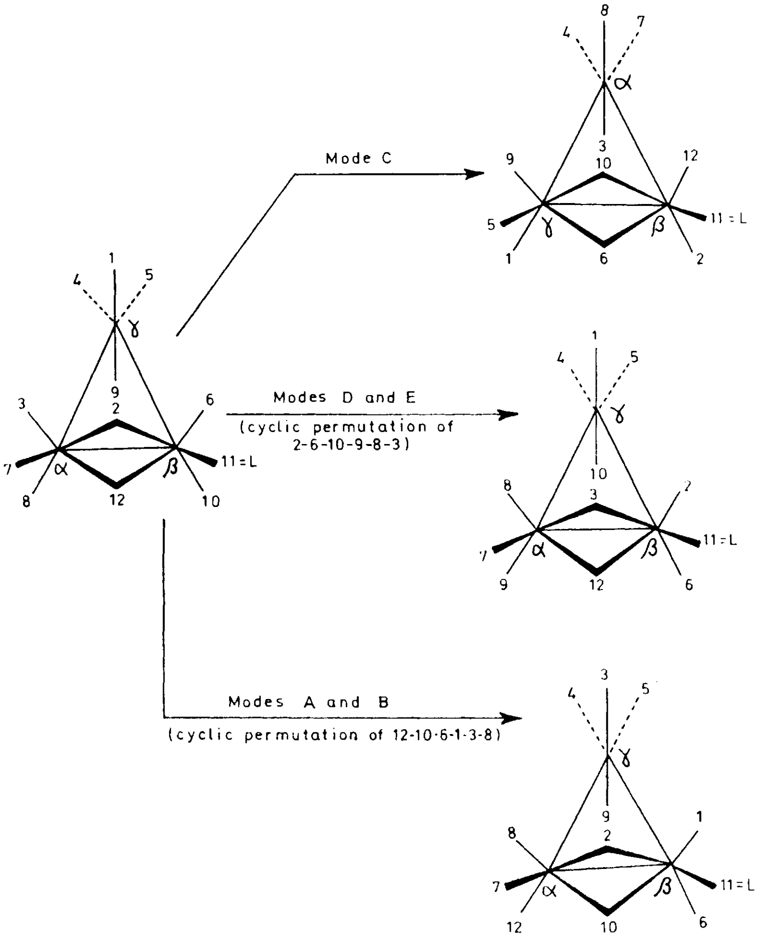
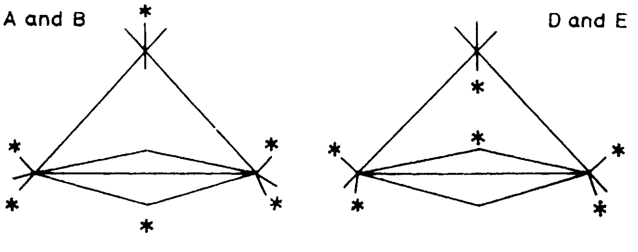


FIGURE 5 Permutation of ligands produced by five scrambling modes of [$Fe_3(CO)_{11}L$] (frontally substituted isomer). The phosphine or phosphite ligand occupies position 11 and is constrained to remain bonded to the same metal atom throughout

This is complicated somewhat by the possibility of two ' product ' molecules, in which the Fe_3 rotation has taken place in opposite directions; however, the conclusions remained unaffected. Operation of mode C produces an 8 : 4 pattern of carbonyl equivalence. If the $Fe(CO)_3$ (frontal) groups are allowed free rotation, then complete equivalence of all twelve carbonyls is obtained. This is the experimental observation although, of course, a variety of alternative mechanisms have satisfactorily rationalised this n.m.r. spectrum.

In preparation for the next section, we now consider the effects of modes A, B, D, and E. Again with the proviso of minimum motion of the M_3 triangle, these modes result in the exchanging of the indicated (asterisked) ligands. This is a surprising pattern of carbonyl scrambling which has not previously been considered.

[$Fe_3(CO)_{11}(PR_3)$] *and* [$Fe_3(CO)_{11}\{P(OR)_3\}$].—We postulate that these molecules exist in solution solely in the frontally substituted form (I). This substitution further lifts the degeneracy of the five modes, see Figure 6. If we follow through the operations of the modes as above, with the restriction that the frontally substituted isomer is always formed, and that the phosphine or phosphite must always remain bonded to the same Fe atom, we conclude that the following scrambling patterns exist [Figures 4 and 5; L = PR_3 or $P(OR)_3$]: mode C alone, 4 : 4 : 2 : 1; modes (B + D) and/or (A + E) alone, 8 : 1 : 1 : 1; all five modes, 8 : 2 : 1 [*i.e.* C plus (B + D) or C plus (A + E) or C plus all four].



If we now allow the unsubstituted frontal $Fe(CO)_3$

group to undergo triangular face rotation to scramble the three carbonyls forming it we conclude: mode C alone, 6 : 4 : 1 (low-temperature exptl. result); all five modes, 10 : 1 (high-temperature exptl. result). Hence these experimental results are explained for the first time. Note particularly that the $C_{2v} \rightleftharpoons D_{3h} \rightleftharpoons C_{2v}$ mechanism of Cotton cannot rationalise the 6 : 4 : 1 pattern of carbonyl equivalence.

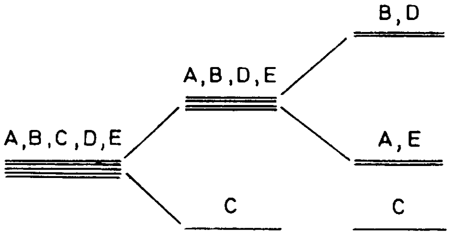


FIGURE 6 Number of modes of rearrangement for X_{12}, M_3X_{12}, and $M_3X_{11}L$ (relative order unknown; however, A produces the same permutational effect as B, E the same as D)

In conclusion we would emphasise that the interconversion process previously considered for $[M_4(CO)_{12}]$ and their substituted derivatives may be extended to $[Fe_3(CO)_{12}]$ and its substituted derivatives. Furthermore, in the case of $[Fe_3(CO)_{11}L]$ the interconversion process involving a polyhedral rearrangement of the twelve ligands (icosahedron $\rightleftharpoons$ cube-octahedron) is, at present, the only one capable of rationalising the ^{13}C n.m.r. data. Studies of other systems which will be published in a subsequent paper also emphasise the general applicability of this approach.

EXPERIMENTAL

The complex $[Fe_3(CO)_{12}]$ was enriched by stirring for some days in a sealed ampoule at 40 °C in the presence of 1 atm * of 90% enriched ^{13}CO (Monsanto Research Corporation). Phosphine and phosphite derivatives were prepared from $[Fe_3(CO)_{12}]$ (*ca.* 30% ^{13}CO enriched) by published procedures.[6]

Carbon-13 n.m.r. spectra were recorded on a JEOL-PFT-100 and on a Varian-XL-100, operating at 25.15 MHz in the Fourier-transform mode. The chemical shifts are downfield positive with respect to internal tetramethylsilane. Accumulations of 500—2 000 transients were made at a spectral width of 1 250 or 5 000 Hz. Phosphorus-31 n.m.r. spectra were recorded on a Varian CFX-20. Solutions were sealed *in vacuo* in 10-mm tubes together with $SiMe_4$ as an internal standard and $[Cr(acac)_3]$ (acac = acetylacetonate) as a relaxing agent. The solvents were $CDCl_3$–CD_2Cl_2 and CD_2Cl_2–CF_2Cl_2. Deuteriated solvents were purchased from C.E.A. and used immediately after drying over molecular sieves.

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* Throughout this paper: 1 atm = 101 325 Pa.

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