The Nature of $[Fe_3(CO)_{12}]$ in Solution

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Summary The possible existence of a new isomeric form of $[Fe_3(CO)_{12}]$ in solution is discussed and a new mechanism of CO-migration proposed.

DODECACARBONYLTRI-IRON has the crystal structure (**1**).[1] Essentially it consists of a triangular arrangement of iron atoms with two asymmetric carbonyl bridges along one edge and ten terminally bound carbonyl ligands. Poliakoff and Turner[2] have shown that in an argon matrix at 20 K, $[Fe_3(CO)_{12}]$ has an i.r. spectrum reasonably consistent with this geometry. There is a weak band at 2110 cm^{-1}, weak and medium intensity bands at *ca.* 1870 and 1830 cm^{-1} and six medium to strong bands between 2015 and 2060 cm^{-1}. In solution the structure is thought to change since the i.r. spectrum is not easily reconciled with (**1**). For $[Fe_3(CO)_{12}]$ in n-hexane[3] there is a weak band at 2103 cm^{-1}, four bands of variable intensity in the region 2000—2050 cm^{-1} but only very weak, broad bands at *ca.* 1867 and 1838 cm^{-1}. Cotton and Hunter[4] argue that the weakness of the absorptions in the bridging region indicates that only a very small amount of the molecules present possess the C_{2v} structure (**1**), and since the variation in energy in passing over a continuous range of structures, from a non-bridged form (**2**) [*pseudo*-$Os_3(CO)_{12}$] to one with a pair of symmetrical bridges, is small (estimated to be < 5 kcal mol^{-1}), the broad and unresolved terminal CO absorptions can be regarded as the convolution of many spectra due to a whole range of structures which differ from each other only in the degree of asymmetry associated with the two CO bridges. Interconversion between the two extreme limits (**1**) and (**2**) *via* this continuous range of configurations leads to CO scrambling.

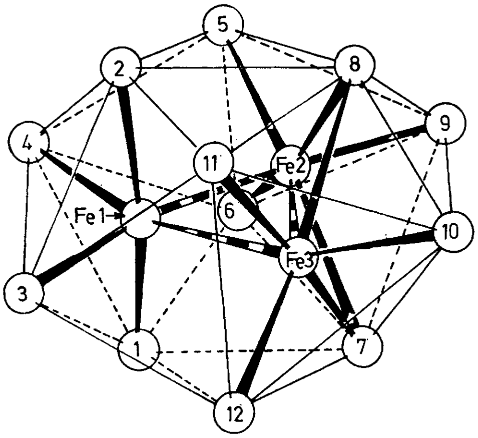


FIGURE 1. Structure of $[Fe_3(CO)_{12}]$ in the solid. Fe(1)(CO^1 $CO^2CO^3CO^4$); Fe(2)($CO^5CO^6CO^7CO^8CO^9$); Fe(3)($CO^7_BCO^8_B$ $CO^{10}CO^{11}CO^{12}$).

Implicit in Cotton's scheme is the view that (**2**) possesses the *pseudo*-$[Os_3(CO)_{12}](D_{3h})$ structure. Since $[Fe_3(CO)_{12}]$ in the crystal is known to have the favourable icosahedral arrangement of twelve CO groups and $[Os_3(CO)_{12}]$ has the less favourable cubo-octahedral arrangement (Figure 4) it may be taken that the interconversion $C_{2v} \rightarrow D_{3h}$ corresponds to a change of the twelve CO groups from an icosahedron to a cubo-octahedron about the metal triangle. This process suffers from two limitations. First it does not equilibrate all the CO groups; this is achieved only after repeated concerted shifts of two CO groups *i.e.* after several interconversions $C_{2v} \rightleftarrows D_{3h}$, and secondly we estimate that for the change $C_{2v} \rightarrow D_{3h}$ a substantial increase in all Fe–Fe distances from *ca.* 2·60 (average) to 2·80 Å is required. As an alternative explanation, we may consider that the icosahedral arrangement of the twelve CO groups is maintained during the fluxional process and that equilibration of these groups is brought about by the reorientation of the Fe_3 triangle within the CO-icosahedron. This process corresponds to a truly concerted process and implies the simultaneous formation and breaking of CO-bridges.[5]

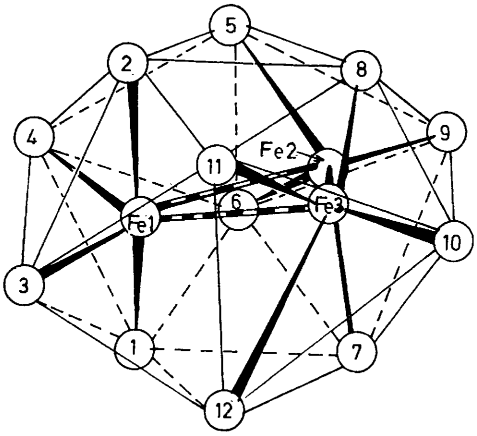


FIGURE 2. Non-bridged isomer (D_3) of $[Fe_2(CO)_{12}]$ Fe(1)(CO^1 $CO^2CO^3CO^4$); Fe(2)($CO^5CO^6CO^7CO^9$); Fe(3)($CO^8CO^{10}CO^{11}CO^{12}$).

Figure 1 shows the orientation of Fe_3 within the CO-icosahedron corresponding to structure (**1**). Rotation of the Fe_3 triangle by 30° about the C_2 axis which passes through the unique Fe atom Fe(1) produces a second isomeric form of $[Fe_3(CO)_{12}]$(**3**). This is also based on the icosahedron of CO groups (Figure 2) but in contrast to forms **1**) and (**2**) all the CO groups are equivalent (and terminal bonded) and all the Fe–Fe distances are equal (*ca.* 2·60 Å).[6] This structure does not correspond to *pseudo*-$[Os_3(CO)_{12}]$ in which there are two kinds of CO ligand (axial and equatorial) and, in contrast to the previously proposed mechanism, the equilibration of the twelve CO groups is brought about in a single step and does not necessitate the repeated concerted shifts of pairs of CO groups. Further rotation about the same axis (or either of the two other equivalent C_2 axes) generates a third form (**4**) which superficially resembles (**1**) in that it contains two $Fe(CO)_3$ units, an $Fe(CO)_4$ unit, and a similar relationship between the Fe–Fe distances: Fe(1)–Fe(2) = Fe(1)–Fe(3) = *ca.* 2·60 Å; Fe(2)–Fe(3) = 2·50 Å. However, in contrast to (**1**), which contains two edge-bridging CO groups, the two remaining CO ligands occupy positions above and below the Fe_3 triangle.

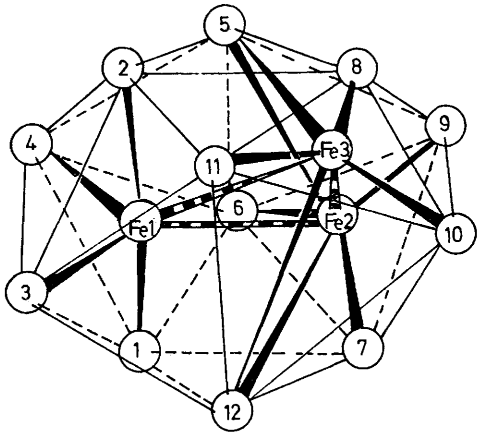


FIGURE 3. Isomer with triple bridger (C_2). Fe(1)(CO^1CO^2 CO^3CO^4); Fe(2)($CO^5_TCO^6CO^7CO^9CO^{12}_T$; Fe(3)$CO^5_TCO^8CO^{10}$ CO^{11} CO^{12}).

Formally these CO groups may be regarded as bridging the iron atoms Fe(2) and Fe(3); however, in fact they are in close proximity to all three iron atoms (Figure 3). According to our model some displacement towards atoms Fe(2) and Fe(3) is expected. Further rotation by 30° regenerates (**3**) and then (**1**) and so on. The fluxional behaviour of $[Fe_3(CO)_{12}]$ may therefore be described as (**1**) $\rightleftharpoons$ (**3**) $\rightleftharpoons$ (**4**) $\rightleftharpoons$ (**3**) $\rightleftharpoons$ (**1**).

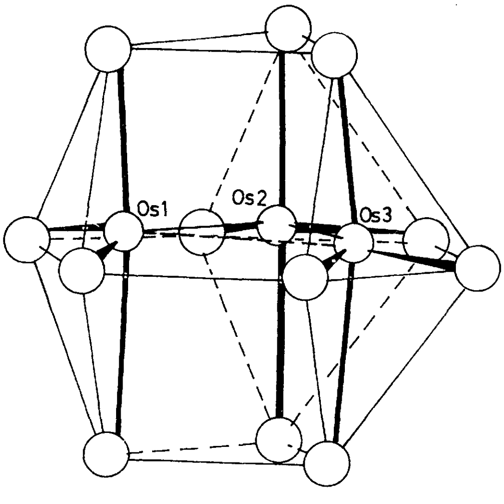
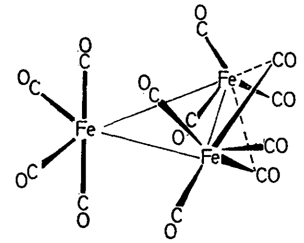


FIGURE 4. Cubo-octahedral structure of $[Os_3(CO)_{12}]$.

Structures (**3**) and (**4**) not only follow naturally from the rotation of the Fe_3 triangle within the CO-icosahedron but also provide a reasonable, alternative explanation of the i.r. spectrum of $[Fe_3(CO)_{12}]$ in solution. For a molecule (**3**) with D_3 symmetry, six terminal carbonyl absorptions are i.r.-active ($2A_2 + 4E$) and of these, four ($4E$) are expected to be broad. The band at 2103 cm^{-1} and the broad, unresolved terminal CO absorptions in the region 2000—2050 cm^{-1} may be attributed mainly to this isomer in solution (*ca.* 95%),[5] and the weak bands at 1867 and 1838 cm^{-1} to small amounts of isomer (**1**) and/or isomer (**4**) also present.

In our view, therefore, it is not necessary to invoke a multitude of isomers to account for the behaviour of $[Fe_3(CO)_{12}]$ in solution.

Carbonyl scrambling in $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ may also occur *via* the same D_3 intermediate. Rearrangement of the CO polyhedron in these molecules from cubo-octahedral to icosahedral, which is equivalent to a change in molecular geometry from D_{3h} to D_3, equilibrates all the carbonyl groups in a single step and does not necessitate the formation of CO bridges (C_{2v}). The generation of the D_3-form is not unreasonable; the predicted equivalent Os–Os distances of 2·65 Å are close to the sum of the metallic radii (2·70 Å). Formation of a bridged intermediate of symmetry C_{2v} is less reasonable; in this case one Os–Os distance must decrease to *ca.* 2·50 Å and the two others to *ca.* 2·65 Å.



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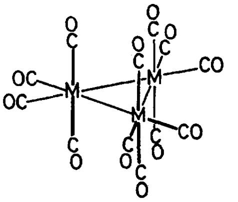

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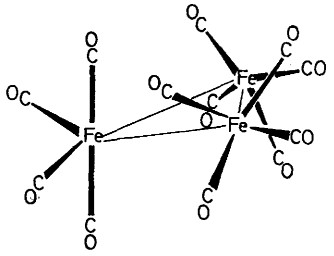

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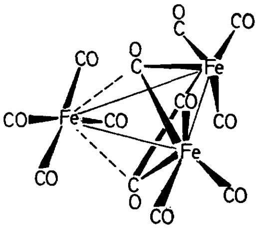

(4)

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