

## Stereochemistry of the Iron Atom in $[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\text{Y}]$ Compounds and its Application to the Tautomerism in Bis[dicarbonyl( $\eta$ -cyclopentadienyl)-iron] and Related Compounds

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The stereochemistry of compounds of the type  $[\text{Fe}(\text{CO})_2(\text{cp})\text{Y}]$ , where cp =  $\eta$ -cyclopentadienyl and Y covers a range of univalent groups and includes groups which can form bridges to the iron atom, is shown to be remarkably close to a regular octahedron. The octahedral geometry does not depend on whether there are bridges present or whether Y is a 'simple' radical. Small deviations are discussed. By assuming that the presence of octahedral geometry in a wide range of structures indicates a certain rigidity in this arrangement, it is shown that the tautomer-interconversion mechanism for  $[\{\text{Fe}(\text{CO})_2(\text{cp})\}_2]$  must involve simultaneous making or breaking of two carbonyl-bridge systems. This mechanism has been suggested previously, in order to explain n.m.r. results, but has not previously been explained. A presentation is made of the general interconversion of isomers of  $[\text{M}(\text{cp})\text{M}'(\text{cp})\text{-ABCD}]$  where A, B, C, and D are ligands which may bridge in pairs.

A LARGE amount of X-ray crystal-structure data has accumulated in recent years for compounds containing the  $\text{Fe}(\text{CO})_2(\text{cp})$  unit (cp =  $\eta$ -cyclopentadienyl).<sup>1-28</sup> In this paper it is shown that the stereochemistry of the iron atom in this group is, in general, very nearly regular octahedral, so far as the angles at iron are concerned. To the best of our knowledge none of the structure analyses quoted treat the data in the way reported here.

The angles and some dimensions found in a number of these molecules of the type  $[\text{Fe}(\text{CO})_2(\text{cp})\text{Y}]$ , where Y covers a range of univalent groups and includes those which can form bridges to the iron atom, are shown in the Table. The list is not intended to be comprehensive. The most important feature is the near constancy of the angles cp-Fe-L, where cp represents the centroid of the cyclopentadienyl carbon atoms and L is a ligand atom. These angles are not only limited in the range over which they vary, but are very close to the angle in a regular

octahedron between the normal to the  $(\bar{1}\bar{1}\bar{1})$  face and the  $\{100\}$  directions  $[\cos^{-1}(-1/\sqrt{3}) = 125.3^\circ]$ . It is to be emphasised that this near constancy holds for the carbonyl-bridged species (I)-(XI) even better than for the non-bridged species. In the latter group some of the ligands are bulky which may explain the slightly greater variation. In a similar way the Fe-cp distance varies much more in the non-bridged compounds than in the bridged ones, the respective ranges being 1.70-1.87 and 1.73-1.76 Å. There is no clear-cut dependence of this distance on the type of ligand Y.

For the bridged structures, the metal-metal distance is remarkably constant, with the possible exception of compound (V) in which the two cp rings are linked, thereby drawing the two halves of the molecule together. In  $[(\text{cp})(\text{OC})_2\text{FeMn}(\text{CO})_5]$ ,<sup>12</sup> which is not bridged, the metal-metal distance of 2.84 Å is much longer than in bridged structures and slightly shorter than in  $[\text{Mn}_2(\text{CO})_{10}]$  (2.92 Å).<sup>29</sup> If it is considered that these long distances

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<sup>16</sup> M. R. Churchill and J. Wormald, *Inorg. Chem.*, 1969, **8**, 1936.

<sup>17</sup> M. A. Bush and P. Woodward, *J. Chem. Soc. (A)*, 1967, 1833.

<sup>18</sup> R. F. Bryan, *J. Chem. Soc. (A)*, 1967, 192.

<sup>19</sup> P. T. Greene and R. F. Bryan, *J. Chem. Soc. (A)*, 1970, 2261.

<sup>20</sup> P. T. Greene and R. F. Bryan, *J. Chem. Soc. (A)*, 1970, 1696.

<sup>21</sup> R. F. Bryan, G. A. Melson, and P. F. Stokely, *J. Chem. Soc. (A)*, 1970, 2247.

<sup>22</sup> R. Restivo and R. F. Bryan, *J. Chem. Soc. (A)*, 1971, 3364.

<sup>23</sup> J. E. O'Connor and E. R. Corey, *Inorg. Chem.*, 1967, **6**, 968.

<sup>24</sup> B. P. Biryukov and Yu. T. Struchkov, *Zhur. strukt. Khim.*, 1968, **9**, 488.

<sup>25</sup> B. P. Biryukov and Yu. T. Struchkov, *Zhur. strukt. Khim.*, 1969, **10**, 95.

<sup>26</sup> B. P. Biryukov, Yu. T. Struchkov, and K. N. Anisimov, *Zhur. strukt. Khim.*, 1968, **9**, 922.

<sup>27</sup> T. Toan and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93**, 2654.

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<sup>29</sup> L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, 1957, **26**, 1750; L. F. Dahl and R. E. Rundle, *Acta Cryst.*, 1963, **16**, 419.

are caused by repulsions between carbonyl groups in *cis*- or *cisoid*-positions on different metal atoms, it would be anticipated that a non-bridged isomer of  $\{[\text{Fe}(\text{CO})_2(\text{cp})]_2\}$  would have a long metal-metal distance, of the order of 2.76 Å, obtained by linear extrapolation. In the non-bridged  $[\text{Fe}_2(\text{CO})_8]^{2-}$  ion the metal-metal distance is 2.75 Å.<sup>30</sup>

and indeed in most of the bridged structures, the two metal atoms, the cp ring centroids where present, and the terminal ligand atoms lie in a plane, providing a very useful plane for projection as shown in Figures 1 and 2.

Using the *cis*-structure,<sup>4</sup> a regular octahedron is constructed with (i) Fe-C<sub>T</sub> as the [001] direction, (ii) Fe-cp as the normal to the (111) face, and (iii) the [001]

Relevant dimensions in the  $\text{Fe}(\text{CO})_2(\text{cp})$  units

Compound	Distances/Å		cp-Fe-L Angles */°			Ref.
	M-M	Fe-cp	cp-Fe-X †	cp-Fe-C		
<i>cis-anti</i> -[(cp)(OC)Fe(μ-CNMe) <sub>2</sub> Fe(CO)(cp)] (I)	2.538	1.748	123.8	124.3	125.2	1
<i>cis</i> -[(cp)(OC)Fe(μ-CO) <sub>2</sub> Fe(CNBU <sup>t</sup> )(cp)] (II)	2.522	1.758	125.8	124.3	125.2	2
		1.753	124.8	123.7	124.2	
<i>cis</i> -[(cp)(OC)Fe(μ-CO) <sub>2</sub> Fe(CNBU <sup>t</sup> )(cp)] (III)	2.524	1.741	125.3	122.9	124.3	3
		1.755	123.9	122.3	125.4	
<i>cis</i> -[(cp)(OC)Fe(μ-CO) <sub>2</sub> Fe(CO)(cp)] (IV)	2.531	1.742	122.7	122.7	123.1	4
		1.748	124.2	121.6	124.7	
<i>cis</i> -[(dte)(OC)Fe(μ-CO) <sub>2</sub> Fe(CO)(dte)] (V)	2.510	1.729	123.0	123.0	123.3	5
		1.743	126.3	122.4	122.6	
<i>trans</i> -[(cp)(OC)Fe(μ-CO) <sub>2</sub> Fe(CO)(cp)] (VI)	2.534	1.754	125.6	121.0	125.0	6
<i>cis</i> -[(cp)(OC)Fe(μ-CO) <sub>2</sub> Co(CO) <sub>3</sub> ] (VII)	2.541	1.729	122.0	119.3	120.8	7
<i>cis</i> -[(cp)(OC)Fe(μ-CO) <sub>2</sub> Co(CO) <sub>2</sub> PMePh <sub>2</sub> ] (VIII)	2.552	1.749	127.0	122.5	124.7	8
<i>cis</i> -[(η-H <sub>5</sub> C <sub>5</sub> )(OC)Fe(μ-CO) <sub>2</sub> Co(CO) <sub>3</sub> ] (IX)	2.540	1.762	127.7	123.2	123.9	9
<i>cis</i> -[(cp)(OC)Fe(μ-CO) <sub>2</sub> Co(CO)(η-C <sub>7</sub> H <sub>7</sub> )] (X)	2.529	1.74	126.1	122.7	124.0	10
<i>trans</i> -[(mcp)(OC)Fe(μ-CO) <sub>2</sub> Co(CO)(η-C <sub>6</sub> H <sub>10</sub> )] (XI)	2.546	1.746	125.1	119.5	121.1	11
		1.739	128.5	123.3	126.3	
[(cp)(OC) <sub>2</sub> FeMn(CO) <sub>5</sub> ] (XII)		1.742	130.1	122.6	126.2	12
		1.697	122.7	123.3	124.6	
[Fe(CO) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> )(cp)] (XIII)		1.813	123.1	126.6	129.6	14
[Fe(CO) <sub>2</sub> (CH <sub>3</sub> CO <sub>2</sub> H)(cp)] (XIV)		1.723	121.9	121.5	126.5	15
[Fe(CO) <sub>2</sub> (C <sub>4</sub> H <sub>9</sub> SO <sub>2</sub> )(cp)] (XV)		1.730	121.9	126.0	126.7	16
[(cp)(OC) <sub>2</sub> Fe(μ-C <sub>4</sub> H <sub>4</sub> )Fe(CO) <sub>2</sub> (cp)] (XVI)		1.690	123.4	124.4	126.7	17
[(cp)(OC) <sub>2</sub> Fe(μ-GeCl <sub>2</sub> )Fe(CO) <sub>2</sub> (cp)] (XVII)		1.73	124	126	128	18
[Fe(CO) <sub>2</sub> (SnPh <sub>3</sub> )(cp)] (XVIII)		1.72	120	120	126	
[Fe(CO) <sub>2</sub> (SnCl <sub>2</sub> Ph)(cp)] (XIX)		1.715	119.4	125.0	125.5	19
[Fe(CO) <sub>2</sub> (SnCl <sub>2</sub> )(cp)] (XX)		1.715	123.6	123.3	124.5	20
[Fe(CO) <sub>2</sub> (SnBr <sub>2</sub> )(cp)] (XXI)		1.718	121.9	124.3	124.6	21
[(cp)(OC) <sub>2</sub> FeSn(Ph)(OSOPh)OH] (XXII)		1.713	122.8	124.9	125.5	22
[(cp)(OC) <sub>2</sub> Fe(μ-SnCl <sub>2</sub> )Fe(CO) <sub>2</sub> (cp)] (XXIII)		1.701	120.7	123.5	126.5	23
[(cp)(OC) <sub>2</sub> Fe(μ-Sn(ONO) <sub>2</sub> )Fe(CO) <sub>2</sub> (cp)] (XXIV)		1.742	122.6	119.6	133.8	24
[(cp)(OC) <sub>2</sub> Fe(μ-SnMe <sub>2</sub> )Fe(CO) <sub>2</sub> (cp)] (XXV)		1.734	122.6	128.6	130.5	24
[(cp)(OC) <sub>2</sub> Fe(μ-Sn(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> )Fe(CO) <sub>2</sub> (cp)] (XXVI)		1.726	120.9	127.3	130.7	25
		1.707	118.6	124.3	130.8	
[(cp)(OC) <sub>2</sub> Fe(μ-PbMe <sub>2</sub> )Fe(CO) <sub>2</sub> (cp)] (XXVII)		1.698	119.4	123.6	128.4	26
		1.867	122.6	127.8	137.2	
[FeCl <sub>4</sub> {SbCl[Fe(CO) <sub>2</sub> (cp)] <sub>2</sub> }] <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub> (XXVIII)		1.839	119.5	120.8	122.2	27
		1.720	124.3	124.3	125.7	
		1.708	123.7	122.8	125.4	
[Fe(CO) <sub>2</sub> (SO <sub>2</sub> CH <sub>2</sub> ·CH:CHPh)(pcp)] (XXIX)		1.716	122.7	123.9	124.5	28
		1.731	122.6	118.8	122.9	

dte = dicyclopentadienyl-*NNN'*-tetramethylethane-1,2-diamine, mcp = η-methylcyclopentadienyl, and pcp = η-pentamethylcyclopentadienyl.

\* cp is the centroid of the η-cyclopentadienyl ring and L is a ligand atom. † For bridged structures X is the non-bridging ligand atom and for non-bridged structures X is the non-carbonyl ligand atom.

A survey of orientations of the cp rings in the compounds showed a very wide variation with no apparent trends.

## RESULTS AND DISCUSSION

**Stereochemistry in  $\{[\text{Fe}(\text{CO})_2(\text{cp})]_2\}$ .**—The closeness of the cp-Fe-L angles to those of a regular octahedron led us to attempt to fit a regular octahedron more precisely to these structures. For *cis*- and *trans*- $\{[\text{Fe}(\text{CO})_2(\text{cp})]_2\}$ , (IV) and (VI), this was achieved in the following manner. In these two bridged molecules,

\* C<sub>T</sub> = Terminal carbonyl carbon, C<sub>B</sub> = bridge carbonyl carbon atom.

direction is normal to the FeC<sub>B</sub>C<sub>B</sub> plane and hence the size of the octahedron is determined from the distance between iron and the mid-point of the C<sub>B</sub> atoms. This direction is the normal to the (110) plane.\* This construction is shown in Figure 1. The Fe-C<sub>B</sub> directions only approximate to regular octahedral directions, being displaced in the (001) plane away from the vertices. The coincidence of the two octahedral edges stems from the fact that the two octahedra are of the same size and that the bridge is symmetric.† Clearly the cp rings do not lie in the faces of the octahedra.

† The molecule does not have a crystallographic mirror plane.

<sup>30</sup> O. S. Mills and F. S. Stephens, unpublished work.

The essential point is that they should be parallel, for the argument is based on the angles at iron rather than distances.

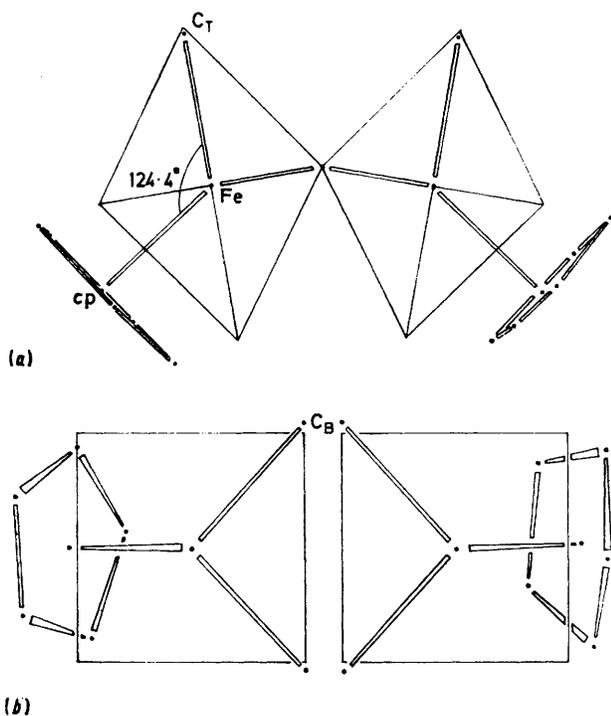


FIGURE 1 Octahedral environments in *cis*- $[\{\text{Fe}(\text{CO})_2(\text{cp})\}_2]$ : (a) projected onto the plane defined by  $[(\text{cp})\text{FeC}_T]_2$ ; (b) projected onto the (001) plane of each octahedron

Figure 1(a) shows the fold in the bridge rather clearly, and strongly suggests that it is due to (i) repulsion between the terminal carbonyl groups, and (ii) possibly a tendency for the iron-iron distance to be shorter than would be possible with a planar bridge without further opening of the  $\text{C}_B\text{-Fe-C}_B$  angles. It is noteworthy that the combination of these two effects does not distort the octahedra by pushing terminal carbonyl groups towards the cp rings, but moves each octahedron as a whole. Possible repulsion between the cp rings is alleviated by the rings being in staggered rotational positions.

The two halves of the *trans*-molecule are related by a crystallographic centre of symmetry.<sup>6</sup> Unlike the *cis*-molecule however the  $\text{Fe-C}_T$  direction is not normal to the  $\text{FeC}_B\text{C}_B$  plane, although the octahedral angle to the  $\text{Fe-cp}$  direction is preserved. Figure 2 shows the effect of superimposing the octahedron constructed for the *cis*-molecule on the *trans*-structure. So far as the terminal carbonyl groups and the cp rings are concerned, the result is virtually identical. However the two octahedra no longer quite manage to share an edge and the bridging carbonyl groups lie in compromise positions between the two octahedral edges. This slight distortion from ideal behaviour could arise from repulsion between terminal carbonyl groups and cp rings on the other metal atom, or repulsion between the terminal and bridging carbonyl groups. Such repulsion could not

bend the bridge because of the symmetry. The observed slip of the octahedral edges represents a slip of the two iron systems which preserves the symmetry, and also has the effect of bringing the iron atoms a little closer. From the point of view of shortening the metal-metal distance, this distortion corresponds to folding of the bridge in the *cis*-structure.

In other structures of bridged  $\text{Fe}(\text{CO})_2(\text{cp})$  units it is possible to draw octahedra in the manner described for the *cis*- and *trans*-dimers. This has been carried out for compounds (IX)—(XI) with very similar results. In the *cis*-molecules (IX) and (X) the carbonyl bridges lie on the octahedral edge, in the *trans*-molecule (XI) they are displaced in a manner almost identical with that found in (VI). In non-bridged structures the carbonyl groups take the places of the bridging groups in bridged structures. They usually lie on the octahedral edge, but are displaced outwards from the corners. In some cases there is displacement off the edge towards the group Y. This is opposite to the displacement in compounds (VI) and (XI).

*Tautomerism in  $[\{\text{Fe}(\text{CO})_2(\text{cp})\}_2]$ .*—The local stereochemistry around the iron atom in  $[\text{Fe}(\text{CO})_2(\text{cp})\text{Y}]$  compounds is, to a good approximation, independent of the group Y and is also independent of whether the carbonyl groups are terminally bonded to the iron atom or whether they take part in bridging to a second

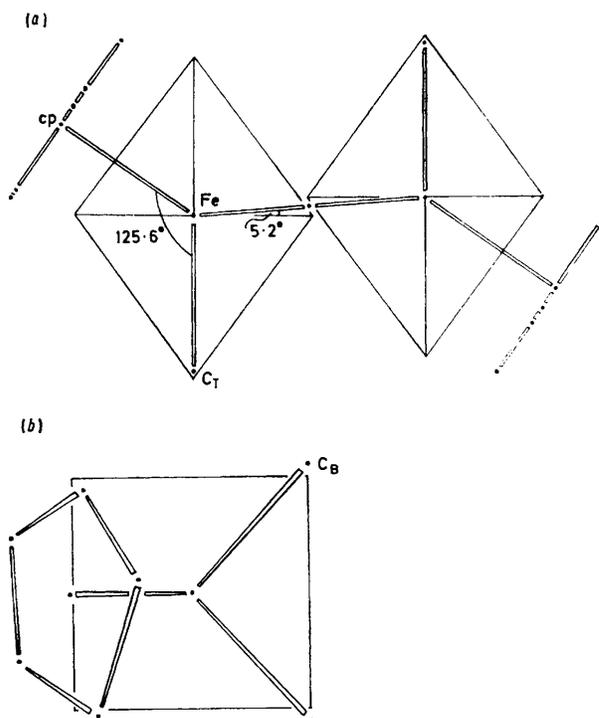


FIGURE 2 Octahedral environments in *trans*- $[\{\text{Fe}(\text{CO})_2(\text{cp})\}_2]$ : (a) projected onto the plane defined by  $(\text{cp})\text{FeC}_T$ ; (b) projected onto the (001) plane of the octahedron

metal atom in the group Y. This observation leads to an explanation of certain features of the tautomerism exhibited by binuclear carbonyl compounds in solution.

It has been demonstrated<sup>31,32</sup> that n.m.r. spectra of solutions of  $[\{\text{Fe}(\text{CO})_2(\text{cp})\}_2]$ <sup>33</sup> and related compounds<sup>34</sup> vary with temperature in a way consistent with the interconversion of *cis*- and *trans*-bridged isomers and

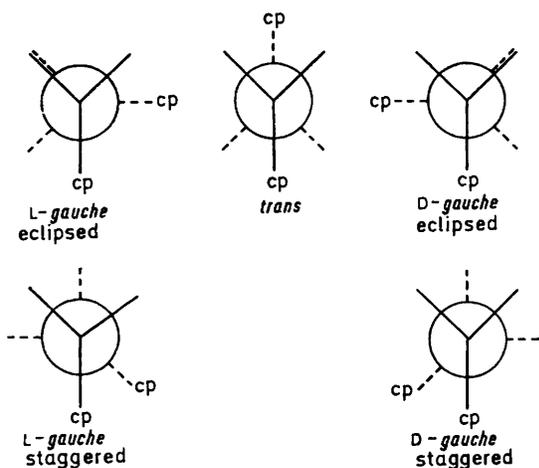


FIGURE 3 Newmann projections of non-bridged configurations

with bridge-terminal carbonyl exchange in the *trans*-isomer. The mechanism involves at its crucial point

bridged isomers, but with longer metal-metal distances. Provided that the 'metal-metal bond' is not included in the iron stereochemistry for bridged species, inter-polarization of this stereochemistry as effectively constant throughout an isomer-interconversion process leads to a simple description of the mechanism for the *cis*-*trans*-interconversion and for bridge-terminal exchange in the *trans*-molecules.

If both octahedra are to remain rigid, the bridge system can be ruptured only such that both bridges are broken simultaneously. Movement of one carbonyl group away from one metal atom towards the other inevitably distorts one or both octahedra. As we show in detail, however, suitable *con*-rotation of the two octahedra leads to simultaneous rupture of two bridges without distorting either octahedron. It is implicit in this statement that the cp rings and the terminal groups also take part in the movement. We believe that the relative rigidity of the octahedra is the underlying explanation of why the carbonyl bridges in these systems are made or ruptured in pairs.

*Tautomerism in  $\text{M}(\text{cp})\text{M}'(\text{cp})\text{ABCD}$ .*—Description of isomeric forms. For a molecule  $\text{M}(\text{cp})\text{M}'(\text{cp})\text{ABCD}$  there are 24 ligand arrangements for each of five configurations described as *trans*-bridged (t.b.), *cis*-bridged

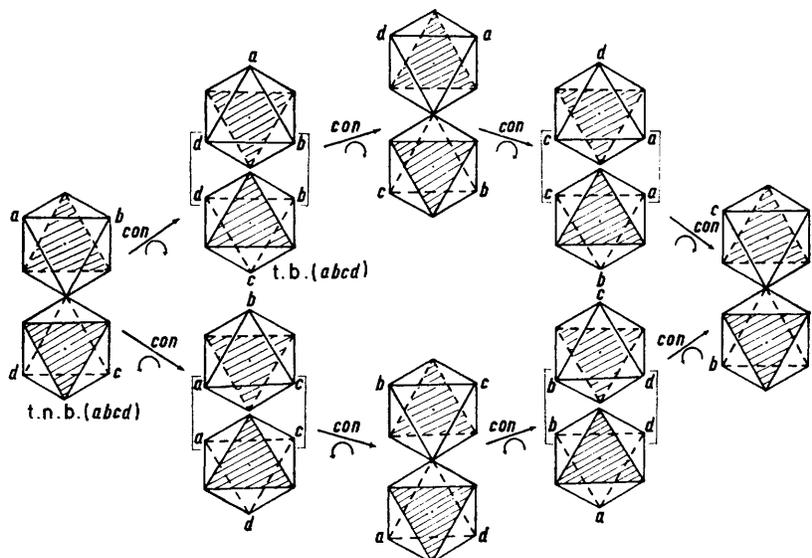


FIGURE 4 Interconversion of a set of *trans*-bridged species by *con*-rotation alone. The angle of rotation at each step is  $60^\circ$ . Shaded faces represent cp rings and M is the in the upper fragments

the concerted rupture (or formation) of two carbonyl bridges, the two original bridged-carbonyl groups going to terminal positions on separate metal atoms and giving a non-bridged intermediate. It is a reasonable conclusion to draw from the above discussion that these non-bridged intermediates would have the same local iron stereochemistry as they have in the *cis*- and *trans*-

(c.b.), *trans*-non-bridged (t.n.b.), *D-gauche*-non-bridged (d.g.), and *L-gauche*-non-bridged (l.g.); D and L refer only to cp ring orientations. The bridged configurations in the case of  $[\{\text{Fe}(\text{CO})_2(\text{cp})\}_2]$  are known stable molecules, but of the non-bridged configurations it is not certain which may be intermediates in the sense of

<sup>31</sup> R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, 1973, **95**, 6589.

<sup>32</sup> R. M. Kirchner, T. J. Marks, J. S. Kristoff, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 6602.

<sup>33</sup> O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Amer. Chem. Soc.*, 1972, **94**, 2550.

<sup>34</sup> R. D. Adams, M. Brice, and F. A. Cotton, *J. Amer. Chem. Soc.*, 1973, **95**, 6594; R. D. Adams and F. A. Cotton, *Inorg. Chem.*, 1974, **13**, 249; R. D. Adams, F. A. Cotton, and J. M. Troup, *ibid.*, p. 257.

lying at potential minima. A qualitative consideration of rotational configurations suggests that *gauche*-forms with dihedral angles of  $45^\circ$  between cp-M bonds would

direction. As this is a *dis*-rotation it may be described as rotation of only half about the M-M' axis with the other half anchored. The individual effects of these two

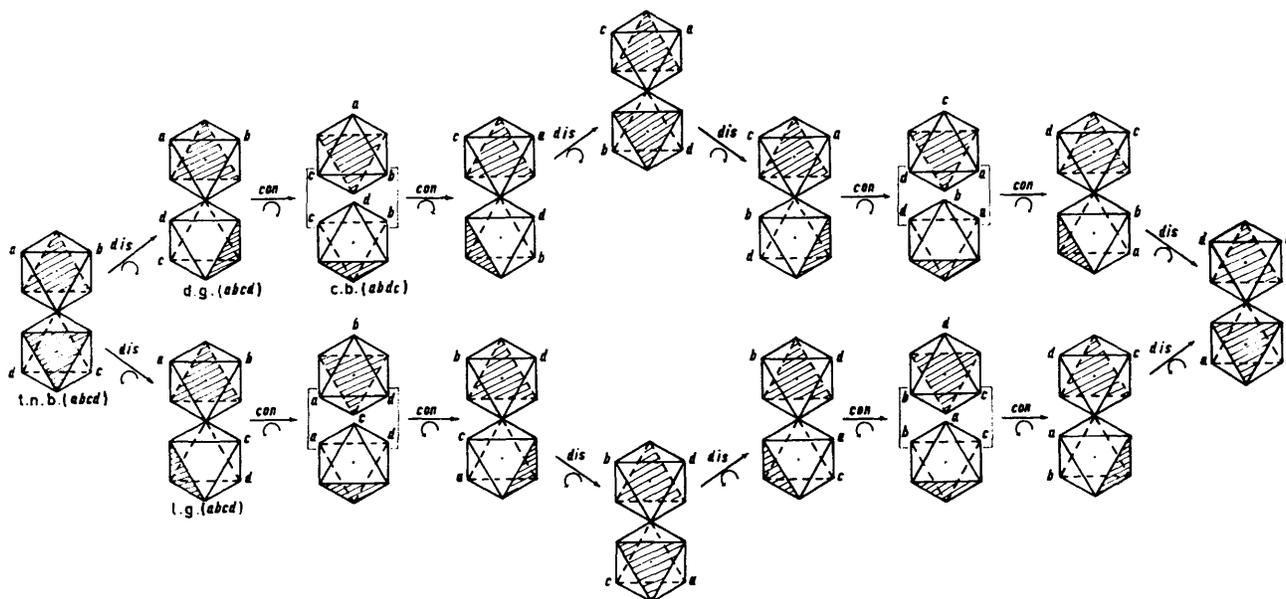


FIGURE 5 Interconversion of a set of *cis*-bridged species. The angle of *con*-rotation at each step is  $60^\circ$  and the *dis*-rotations are  $90^\circ$

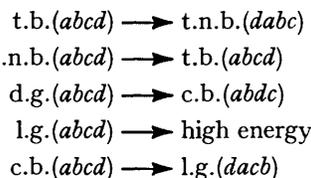
be most stable, as shown in Figure 3, and that *cis*-configurations would be unstable. The *cis*-configurations do not play any part in the reaction scheme and are omitted. *Gauche*-forms are used with a M(cp)-M'(cp) dihedral angle of  $90^\circ$ , as these provide a convenient projection for studying molecular movements.

The molecular configurations may be described in a simple coded manner, assuming that M is in the upper fragment in the Figures, as follows. *trans*-Non-bridged, t.n.b.(abcd), describes the configuration with A and B on metal atom M, C and D on M', with the ligands in clockwise order ABCD as seen in the projection in Figure 4. *trans*-Bridged, t.b.(abcd), describes the molecule with A terminal on atom M, C terminal on M', and B and D in bridge positions. As seen in projection, D is on the left and B on the right (Figure 4). *cis*-Bridged, c.b.(abcd), has A and D in *cis*-terminal positions and C and B in the bridge with clockwise order as seen in projection in Figure 5; A is on atom M, D on M', C is on the left, and B on the right. *gauche*-Non-bridged, d.g.(abcd), has A and D in *cis*-positions, A and B on atom M, and C and D on M'; B and C are *trans* to each other and the cp ring on M' is to the right as seen in projection in Figure 5. Throughout these descriptions the cp rings have the positions shown in Figures 4 and 5.

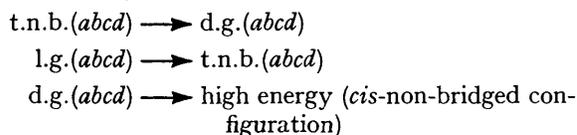
The interconversion between the 120 configurations of this molecule can be described in terms of only two types of molecular movement: (i) a *con*-rotation through  $60^\circ$  of each half of the molecule about axes containing a metal atom and perpendicular to the projections in Figures 4 and 5; (ii) a *dis*-rotation about the M-M'

rotations on members of the basic configurations are summarised below.

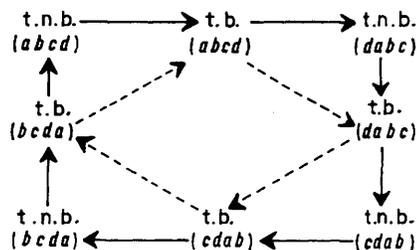
Clockwise *con*-rotation:



*dis*-Rotation, lower half clockwise:



As demonstrated in Figure 4 the *con*-rotations alone are able to interconvert t.n.b. and t.b. forms. These configurations divide into six sets of four bridged and four non-bridged, each set forming a closed loop on *con*-rotation as shown below.



It is possible, even probable in many cases, that the exact t.n.b. configuration is not at an energy minimum and that interconversion of t.b. molecules can occur *directly*, without going through the t.n.b. configuration. The *con*-rotation necessary to achieve this takes the molecule through, or near to, a configuration in which the cp rings are directly opposite each other on the M-M' axis, and the four ligands ABCD are in asymmetric bridging positions. This 'short-cut' route is shown in the diagram as a set of broken lines. Even though exact t.n.b. configurations may not be stable, they form very convenient points from which to reference the interconversion routes. With the *con*-rotations alone, the 24 points divide into six of the closed loops described. The effect of *con*-rotation on a c.b. structure is to convert it into a d.g. or l.g. form. The two are not in general optical isomers (D and L refer here to relative cp ring orientations). Further rotation leads to high energies by bringing the cp rings into strained positions. The *gauche*-forms may be converted into t.n.b. forms by *dis*-rotation about the M-M' axis. A second type of closed loop results containing four t.n.b., four d.g., four l.g., and four c.b. forms as shown in Figure 5.

**Permutation Group.**—The interconversion of t.n.b. configurations alone may proceed by two separate routes. The first goes through t.b. species and may be described in terms of a cyclic permutation  $P$ , such that  $P(abcd) = (dabc)$ . The second route, going through *gauche*-species *via dis*-rotation and c.b. species, may be described in terms of a permutation  $Q$ , such that  $Q(abcd) = (cadb)$ . It can be shown that  $P$  and  $Q$  generate a permutation group of order 24 which is isomorphous with the point groups  $T_d$  and  $O$ . Defining  $\bar{P}P = P\bar{P} = E$  (identity),  $\bar{Q}Q = Q\bar{Q} = E$ ,  $R = PQ\bar{P}$ , and  $\bar{R} = P\bar{Q}\bar{P}$ , the classes of the group, with the corresponding classes of  $O$ , are shown below.

$E$	$(E)$	(i)
$P^2, Q^2, R^2$	$(3C_2)$	(ii)
$PQ, P\bar{Q}, P\bar{Q}, \bar{P}\bar{Q}, \bar{Q}\bar{P}, \bar{Q}P, Q\bar{P}, QP$	$(8C_3)$	(iii)
$P, \bar{P}, Q, \bar{Q}, R, \bar{R}$	$(6C_4)$	(iv)
$PQP, P\bar{Q}P, PRP, P\bar{R}P, QRQ, Q\bar{R}Q$	$(6C_2')$	(v)

Because of the isomorphism with  $O$  and  $T_d$  it is possible to represent the entire network on the surface of a cubo-octahedron, whose vertices represent the t.n.b. configurations as shown in Figure 6. t.b. Species lie on the edges of the square faces, while *gauche*- and c.b. species lie on lines joining corners of separate square faces. Opposite vertices contain enantiomorphic configurations, converted by the permutation  $R^2$ .

The introduction of metal or ligand equivalence into

the system (*e.g.*  $M = M'$  or  $A = B$ , *etc.*) converts certain permutation operations into symmetry operations. For example if  $M = M'$ , then t.n.b.( $abcd$ ) = t.n.b.( $dcba$ ), the operation  $Q^2$  becomes a symmetry operation, and the sub-group  $[E, Q^2]$  a symmetry group of the molecule. All such symmetry groups must be sub-groups of the full permutation group. When the ligands A, B, C, and D are the same the symmetry group reaches the maximum order of 24; the isomorphous point group represents the shape of the

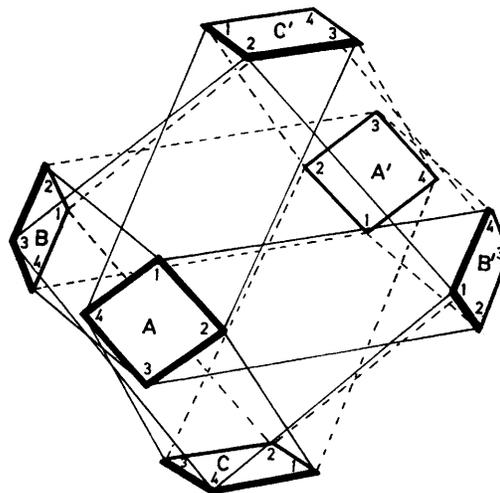


FIGURE 6 Three-dimensional network representation of interconversion paths between *trans*-non-bridged configurations. The lettered squares represent the six sets of the type shown in Figure 4. A and A', *etc.*, are enantiomorphic sets. Other square paths, such as  $A_1-B_2-A_3-B_4-A_1$ , are of the type shown in Figure 5

potential surface. The implications of this high degree of symmetry are beyond the scope of this paper, but would have to be taken into account in a study of the internal oscillations and degeneracies of these systems.

**Conclusion.**—It has been shown that the stereochemistry of iron in compounds  $[\text{Fe}(\text{CO})_2(\text{cp})\text{Y}]$  is nearly regular octahedral regardless of whether Y can bridge to the iron atom. It is almost certain that comparable systems with other metals would behave similarly. A consequence of the relatively rigid local stereochemistry is that binuclear molecules with ligands which can bond either terminally or by bridging two metal atoms can readily interconvert between isomeric forms by the mechanism involving concerted making and breaking of two bridges. It seems likely that this type of mechanism will operate in cluster molecules wherever the local ligand stereochemistry is effectively rigid.

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