Crystal Structure of the Unusual Product of Reaction between σ-(β-Acetylvinyl)dicarbonyl-(π-cyclopentadienyl)iron and Enneacarbonyldi-iron

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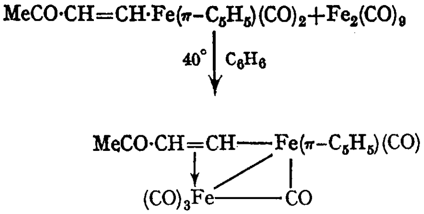
THE reaction between σ-(β-acetylvinyl)dicarbonyl-(π-cyclopentadienyl)iron and enneacarbonyldi-iron gives[1] the unusual π-complex whose structure has been proposed on the basis of its i.r. and ^1H n.m.r. spectra:



To establish the structural formula of this new complex unequivocally and to determine the geometrical characteristics of the molecule we have undertaken an *X*-ray study based on partial three-dimensional data. Crystal data: $C_{14}H_{10}O_6Fe_2$, $M = 386$, monoclinic, space group $P2_1/c$, $a = 12{\cdot}86$, $b = 8{\cdot}70$, $c = 13{\cdot}96$ Å, $\beta = 110{\cdot}5°$, $U = 1463$ Å^3, $D_m = 1{\cdot}72$, $D_c = 1{\cdot}76$, $Z = 4$.

Intensities of *ca.* 650 independent reflections were estimated visually, disregarding absorption corrections, from $h0'$—$3l$ layers taken in the equi-inclination Weissenberg goniometer with unfiltered Cu-K_α radiation. The structure was solved by the standard heavy-atom technique and refined by the isotropic full-matrix least squares method. The discrepancy index is $R = 0{\cdot}096$ with the mean overall temperature factor $B = 4{\cdot}8$ Å^2. The probable errors in interatomic distances are: Fe–Fe, $\pm 0{\cdot}00_7$; Fe–C, $\pm 0{\cdot}01$; C–O, $\pm 0{\cdot}02$; C–C, $\pm 0{\cdot}02$ Å.

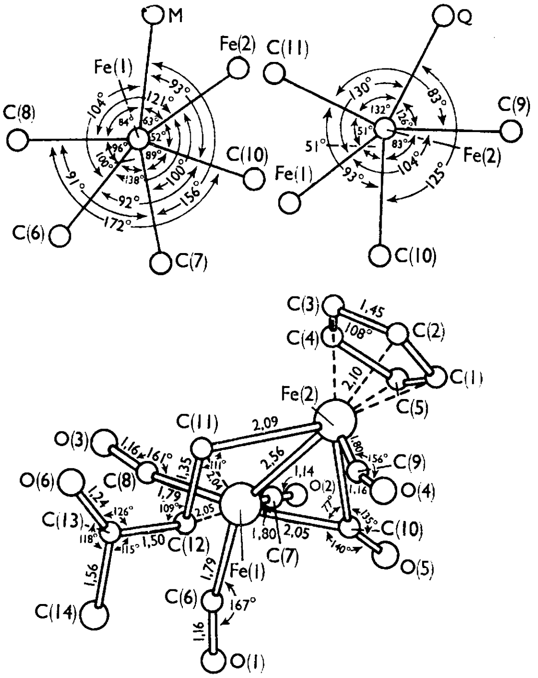
The molecular configuration is represented in the

Figure which also shows bond-lengths and angles. One of the iron atoms, Fe(2), is connected with the acetylvinyl radical by a σ-bond, the other, Fe(1), participates in a π-interaction with the ethylenic bond of this ligand. The Fe(1)–Fe(2) bond length $2{\cdot}55_6$ Å does not differ fundamentally from those found in other binuclear iron π-complexes with bridging ligands {*e.g.* 2·49 Å in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$[2] and 2·527 Å in reddish-orange isomer of $Fe_2(CO)_6C_2H_2)_3$[3]}. As usual this interatomic distance is shorter than the Fe–Fe bond-length in π-complexes without bridging ligands. The interatomic interactions result in the formation of a highly strained four-membered metallocycle containing Fe(1), C(12), C(11), and Fe(2) atoms. The co-ordination around the Fe(1) atom is distorted octahedral with the ethylenic C(11)–C(12) bond to one of the terminal carbonyl groups, C(7)O(2). The M–Fe(1)–C(7) angle is 156° [where M is the midpoint of the C(11)–C(12) bond]. The other iron atom Fe(2) is seven-co-ordinate and Q–Fe–L angles vary in the range 125—132°, which is normal for such configurations [Q is the centre of the cyclopentadienyl ring, L = other ligands]. The Fe(1)–C(11) and Fe(1)–C(12) distances (2·04 and 2·05 Å respectively) are close to those usually found in iron complexes containing ethylenic ligands: 2·04 Å in the racemic complex $Fe(CO)_4$–fumaric acid,[4] 2·09 and 2·10 Å in $(CO)_4Fe(CH_2{=}CHCN)$.[5] The mean Fe(2)–C(π-C_5H_5) distance is 2·10 Å, a typical value for semi-sandwich iron–cyclopentadienyl π-complexes. The π-C_5H_5 is planar (the maximum deviation from planarity is *ca.* 0·01 Å) with an average C–C bond length of 1·45 Å.

The interatomic Fe–C and C–O distances for terminal carbonyl groups are normal (average values 1·79 and 1·16 Å respectively). However, in contrast to most iron–carbonyl complexes studied there are significant divergencies of Fe–C–O fragments from linearity. The maximum divergence amounts to *ca.* 24° for the Fe(2)–C(9)–O(4) group. These deformations are probably due to large steric hindrances resulting from seven-co-ordination around Fe(2) [there are many non-valence intramolecular contacts involving the C(9) atom which are shorter than 2·6—2·8 Å].

The bridging carbonyl group is symmetrically disposed relative to both iron atoms, but the Fe–C(bridge) distance, 2·05 Å, is distinctly longer than those usually found for carbonyl bridges {1·85 Å in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$[2] and 1·91 Å in $(\pi\text{-}C_5H_5)(CO)Fe(CO)(C{=}NPh)Fe(CO)(\pi\text{-}C_5H_5)$[6]}. The O(5) atom projects out of the Fe(1)Fe(2)C(10) plane by as much as 0·4 Å.

Comparison of the Fe–C σ-bond-length found here (2·09 Å) with analogous distances involving carbon atoms of various ligands shows that this bond distance is rather insensitive to the ligand. Thus in the black isomer of $Fe_2(CO)_6(C_2H_2)_3$[7] it is 2·123 Å, in complexes containing aromatic ligands, such as $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$[8] and $(\pi\text{-}C_5H_5)Fe(CO)(\sigma\text{-}C_5H_5)PPh_3$,[9] it is 2·11 and 2·12 Å respectively.



FIGURE

It is of interest that in the complex studied the acetylvinyl ligand acquires the *cis*-conformation as distinct from the energetically more favoured *trans*-form existing in the free ligand molecule. Such a configurational difference is probably steric in origin since a *trans*-conformation for the acetylvinyl ligand would give rise to intolerably short distances (*ca.* 2·8—3·1 Å) between the Me-group and the C(8) and O(3) atoms of the neighbouring carbonyl group. Still more noticeable is the fact that the π-interaction of the ethylenic part of this ligand with Fe(1) does not result in the lengthening of the C(11)–C(12) bond (this distance 1·35 Å compares well with the standard C=C double bond-length 1·337 Å[10]) contrary to what was established for most π-complexes of this type. A 'double bond preservation' is consistent with a planar system comprising the Fe(2), C(11), C(12), C(13), C(14), and O(6) atoms, though the Fe(2)–C(11)–C(12) and C(11)–C(12)–C(13) bond angles are very nearly tetrahedral (111 and 109° respectively). The decrease in these angles may, however, be due to a drawing together action of the Fe(1)–Fe(2) bond by metallocycle closure. The other bond distances and angles in the acetylvinyl ligand have the usual values. The increase in the C(12)–C(13)–O(6) bond angle to 126° and a corresponding decrease in the other two angles at the C(13) atom may be a trivial consequence of mutual repulsion between these atoms and the C(8)O(3) carbonyl group.

We intend to clarify some unusual geometrical features of this molecule by means of an *X*-ray investigation of a series of analogous π-complexes with β-ketovinyl ligands.

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