# The Structure of the $C_{16}H_{16}\cdot Fe_3(CO)_9$ Complex Derived from Iron Tricarbonyl Complexes of Dimers of Cyclo-octatetraene

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*Summary* The structure (IV) of the $C_{16}H_{16}\cdot Fe_3(CO)_9$ complex derived from iron tricarbonyl complexes of dimers of cyclo-octatetraene has been shown to contain a vinyl radical to which one of the iron atoms in an $Fe_2(CO)_6$ group forms a $\pi$-bond while the other is $\sigma$-bonded; this result corrects an earlier structural assignment.

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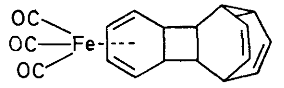
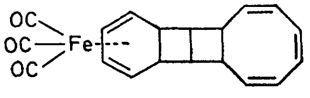
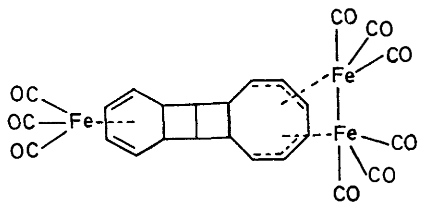
The light-induced reaction of the iron tricarbonyl complexes (I) and (II) of cyclo-octatetraene dimers[1,2,3] with $Fe(CO)_5$ affords a complex of composition $C_{16}H_{16}\cdot Fe_3(CO)_9$ for which structure (III) was suggested on the basis of the n.m.r. spectrum.[1] The $X$-ray analyses of two crystalline modifications of this complex have now been completed to reveal a novel structure (IV), both with respect to the carbon skeleton and to the bonding of an $Fe_2(CO)_6$ group to the hydrocarbon moiety.



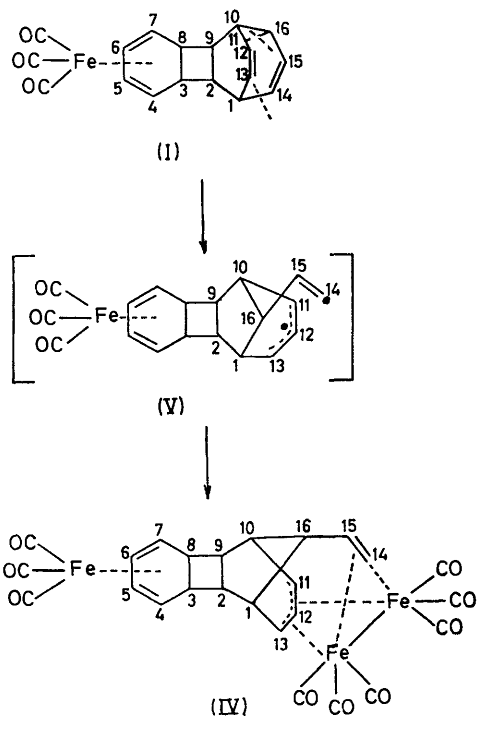
(I)



(II)



(III)



The complex has been obtained in crystalline form both as a benzene solvate and also without solvent being included in the crystal. The $X$-ray analyses of both forms have been carried out. The brownish-red crystals of the complex, obtained by the published procedure,[1] occur as a benzene solvate in the triclinic system with $a = 12{\cdot}742(7)$, $b = 13{\cdot}051(6)$, $c = 9{\cdot}347(5)$ Å, $\alpha = 112°5'(2')$, $\beta = 113°20'(2')$, and $\gamma = 83°40'(2')$. The space group is $P\bar{1}$ and there are two molecules of $C_{16}H_{16}\cdot Fe_3(CO)_9\cdot\frac{1}{2}C_6H_6$ ($M = 666{\cdot}9$) in the unit cell. A total of 1795 independent non-zero structure amplitudes was collected on a Picker FACS-1 computer-controlled diffractometer (Mo-$K_\alpha$ radiation). The structure, incorporating anisotropic temperature factors for the heavy atoms and isotropic temperature factors for the hydrogen atoms, has been refined by full-matrix least-squares methods to an $R$-factor of 0·088 on all observed reflections. A stereoscopic view of the molecule is shown in the Figure.

Recrystallization of the triclinic material from $CDCl_3$ gave solvent-free, brownish yellow crystals which are monoclinic, with $a = 12{\cdot}505(13)$, $b = 12{\cdot}377(9)$, $c = 15{\cdot}639(15)$ Å and $\beta = 97°54'(3')$. The space group is $P2_1/c$ and there are four molecules of $C_{16}H_{16}\cdot Fe_3(CO)_9$ ($M = 627{\cdot}9$) in the unit cell. The structure, incorporating isotropic thermal parameters for the heavy atoms and not including the hydrogen atoms, has been refined to an $R$-factor of 0·133 on 1546 non-zero structure amplitudes collected as described above. The molecular structure and dimensions of the $C_{16}H_{16}\cdot Fe_3(CO)_9$ complex are very similar in the two crystalline forms; in the subsequent discussion the lengths will be given for the more accurately determined triclinic form.

The structure of the complex is seen to be (IV) rather than the previously suggested (III). The unexpected feature of this structure is the simultaneous interaction of the di-iron hexacarbonyl group with the vinyl radical and the allyl function in the bicyclo[3,2,1]octane group. The atom Fe(1) is nearly equidistant from both carbon atoms of the terminal double bond, 2·10(2) and 2·16(2) Å, and is presumably involved in a $\pi$-bond, whereas Fe(2) is very close to the terminal carbon atom, 1·93(2) Å, but much further from the other 2·98(2) Å and can be considered to be $\sigma$-bonded. The length of the exocyclic C–C bond, 1·40(3) Å, is indicative of a double bond. The two iron atoms are almost symmetrically positioned with regard to the allyl group; the Fe(1) - - - C(13) and Fe(1) - - - C(12) distances are 2·16(2) and 2·48(2) Å, whereas Fe(2) - - - C(11) and Fe(2)

---C(12) distances are 2·12(2) and 2·40(2) Å. The Fe(1) ---Fe(2) distance is 2·684(4) Å. No *X*-ray study appears to have been carried out on a complex where there is a similar symmetrical interaction of an $Fe_2(CO)_6$ moiety with an allyl group. The demonstrated nonequivalence of iron atoms 1 and 2 contrasts with the results of Mössbauer measurements,[1] which indicate a similar electronic environment. On the other hand, the net differences in the bonding interactions of Fe(1) and Fe(2) to the organic moiety are indeed slight and are likely to be diminished further by the presence of the Fe–Fe bond. A very similar structure to that for this portion of the complex has been proposed, on the basis of n.m.r. spectra, for a product of the reaction of bullvalene with $Fe_2(CO)_9$.[4] Some of the features of the interaction of the two iron atoms with the exocyclic vinyl radical found herein are exhibited in the complex [$CH_3$·COCH =CH] $Fe_2(CO)_5C_5H_5$[5] and in the iron carbonyl–phenylacetylene complex, $Fe_2(CO)_6(C_6H_5C_2H)_3$.[6] The structure of the cyclohexadiene moiety stabilized by iron tricarbonyl is essentially the same as that observed in (I) and (II),[1–3] with the normal pattern of Fe --- C and C–C lengths.[7]

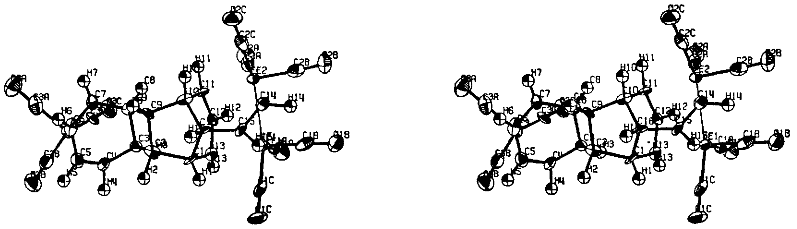


**Figure** *Stereoscopic view of the* $C_{16}H_{16}·Fe_3(CO)_9$ *complex.*

The formation of (IV) from (I) can be rationalized by assuming two bond ruptures between atoms C(1) and C(14) and between C(11) and C(16), followed by the formation of a new C–C bond between atoms C(1) and C(16). This gives rise to the hypothetical biradical (V) which is stabilized by the interactions with the $Fe_2(CO)_6$ group. The bonding of iron atoms Fe(1) and Fe(2) with the vinyl radical moiety represents a novel feature in organo-iron chemistry. The unexpected structure of $C_{16}H_{16}·Fe_3(CO)_9$ demonstrates that unusual rearrangement/fragmentation processes of unsaturated hydrocarbons are promoted in the presence of iron carbonyl fragments. The formation of (IV) from complex (II) furthermore suggests that (II) rearranges first to (I) or to a percursor related to (I) prior to forming (IV). An example of the reverse of the rearrangement (eight-membered ring to a vinyl-substituted six-membered ring) that takes place in the transformation (II) → (IV) has been reported in the case of the formation of cyclo-octa-1,5-diene from 4-vinylcyclohexene by way of a $Pd^{II}$ complex.[8]

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