X-Ray Molecular Structure of Allene-trimer Complexes of Hexacarbonyldi-iron

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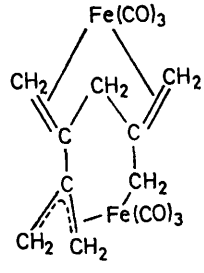
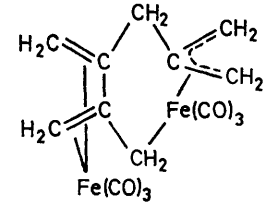
Summary The molecular structures of two of the three isomers of $Fe_2(CO)_6(C_9H_{12})$ have been determined by *X*-ray structure analysis.

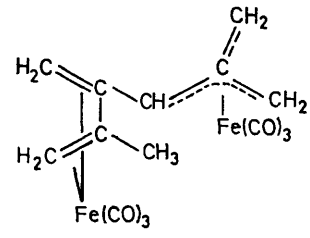
REACTION of allene (1·2—2·0 equiv.) with dodecacarbonyltri-iron (1 equiv.) gives an allene-dimer complex, $Fe_2(CO)_6(C_6H_8)$ and a small amount of an allene-trimer complex, $Fe_2(CO)_6(C_9H_{12})$ (I), m.p. 100—101°.[1] Complex (I) isomerizes to complex (II), m.p. 123—125°, at 100—110° in toluene or in *o*-dichlorobenzene, and the more stable complex (III), m.p. 117—118°, is obtained by thermal isomerization of complex (I) or (II) in *o*-dichlorobenzene or in refluxing toluene. Proposed structures[1] for these isomers are as shown. When excess of allene is added to any of these isomers in n-hexane polymerization of the allene occurs as in the reaction with dodecacarbonyltri-iron.



(I)



(II)



(III)

Single crystals of these isomers have been examined by *X*-ray diffraction, and the molecular structures of (II) and (III) have been determined. *Crystal data*: complex (I): yellow powder, triclinic, $a = 10{\cdot}21$, $b = 12{\cdot}26$, $c = 7{\cdot}07$ Å, $\alpha = 106°$, $\beta = 99{\cdot}7°$, $\gamma = 96{\cdot}2°$, $U = 804$ Å^3, $Z = 2$, $D_c = 1{\cdot}65$ g cm^{-3}; complex (II): orange-yellow crystals, monoclinic, space group $P2_1/a$, $a = 13{\cdot}561(1)$, $b = 17{\cdot}912(5)$

$c = 6{\cdot}826(1)$ Å, $\beta = 104{\cdot}21° \pm 0{\cdot}01°$, $U = 1603$ Å^3, $D_m = 1{\cdot}63$ g cm^{-3}, $Z = 4$, $D_c = 1{\cdot}66$ g cm^{-3}, $\mu = 150{\cdot}8$ cm^{-1} (for Cu-K_α, $\lambda = 1{\cdot}5418$ Å); complex (III): lemon yellow

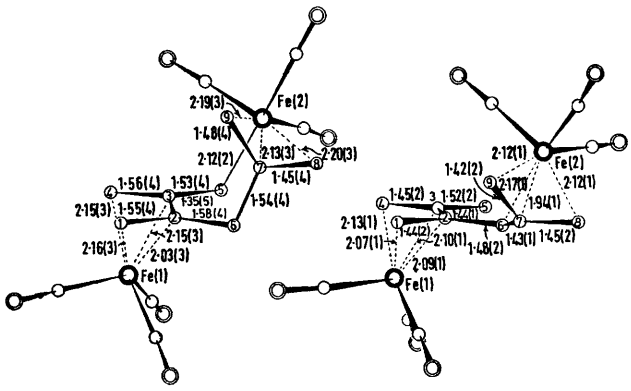


FIGURE. *Molecular geometries of* $Fe_2(CO)_6(C_9H_{12})$ *isomers* (II) *and* (III). *E.s.d.'s in parentheses.*

crystals, triclinic, space group $P\bar{1}$, $a = 13{\cdot}591(5)$, $b = 8{\cdot}766(3)$, $c = 7{\cdot}074(3)$ Å, $\alpha = 104{\cdot}010° \pm 0{\cdot}004°$, $\beta = 79{\cdot}680° \pm 0{\cdot}004°$, $\gamma = 96{\cdot}880° \pm 0{\cdot}004°$, $U = 799$ Å^3, $D_m = 1{\cdot}63$ g cm^{-3}, $Z = 2$, $D_c = 1{\cdot}66$ g cm^{-3}, $\mu = 13{\cdot}2$ cm^{-1} (for Mo-K_α, $\lambda = 0{\cdot}7107$ Å).

Intensity data were collected on a Rigaku on-line, four-circle, single-crystal diffractometer. During the data collection complex (II) decomposed gradually under irradiation. 1341 reflexions for complex (II) and 3708 for complex (III) were collected using Cu-K_α and Mo-K_α radiation, respectively. Both structures have been solved by the heavy-atom method, and refined by block-diagonal least-squares using anisotropic thermal factors for non-hydrogen atoms: $R = 0{\cdot}13$ for complex (II) and 0·08 for complex (III) for 1204 and 3388 non-zero reflexions respectively.

The Figure shows the molecular geometries. In complex (II), the allene-trimer fragment includes a 1,3-diene [C(1)—(4)] and a π-allyl [C(7)—(9)] portion. Each iron atom of two $Fe(CO)_3$ groups co-ordinates to the diene and π-allyl parts, respectively; there is no direct iron–iron bond. C(5) is connected by a σ-bond to Fe(2) of a $Fe(CO)_3$ group. The allene-trimer moiety in complex (III) contains a 1,3-diene [C(1)—(4)] and a trimethylenemethane [C(6)—(9)] portion, which are co-ordinated by $Fe(CO)_3$ groups. Two $Fe(CO)_3$ groups are isolated and again there is no iron–iron bond. Unlike complex (II) there is no direct Fe(2)–C(5) bond. An unusual feature is that three C–C distances in the diene part are equal [1·44(2), 1·44(1), and 1·45(2) Å], and that the carbon atom skeleton of the trimethylenemethane part is non-planar similar to that in (phenyltrimethylene-methane)tricarbonyl-iron.[2]

We thank Professor Sei Otsuka and his co-workers for crystals and for discussions.

(*Received, November 1st, 1971; Com.* 1902.)

[1] S. Otsuka, A. Nakamura, and K. Tani, *J. Chem. Soc.* (*A*), 1971, 154.
[2] M. R. Churchill and K. Gold, *Chem. Comm.*, 1968, 698.