The Structure of a Complex derived from Allene and Di-iron Enneacarbonyl

By Raymond E. Davis

(*Department of Chemistry, The University of Texas at Austin, Austin, Texas* 78712)

The report of a novel type of allene–di-iron complex,[1] $C_3H_4Fe_2(CO)_7$, (I), produced by the reaction of allene with di-iron enneacarbonyl, $Fe_2(CO)_9$, has prompted a single crystal *X*-ray diffraction study of its structure. Compound (I), an oil at room temperature, is not suitable for a crystallographic experiment; so the crystalline triphenylphosphine derivative, $C_3H_4Fe_2(CO)_6PPh_3$, m.p. 99—100, was used.[1]† $C_{27}H_{19}Fe_2O_6P$, monoclinic, $a = 12{\cdot}80$, $b = 9{\cdot}39$, $c = 24{\cdot}60$ Å, $\beta = 119{\cdot}17°$, $Z = 4$; space group $P2_1/c$; Cu-K_α radiation, single-crystal rotation. By use of General Electric XRD-5 diffractometer equipped with single-crystal orienter‡ and a balanced Ni–Co

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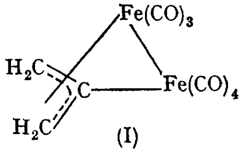
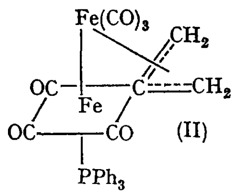
‡ The loan of a single crystal orienter by the General Electric Company is gratefully acknowledged.

filter pair, three dimensional single crystal intensity data were collected by the stationary crystal-stationary counter method, to the limit $2\theta = 130°$ (Cu-K_{α}). Because the background intensity level was rather high, due to iron fluorescence in the crystal, only 2129 of the 3861 possible independent reflections were used.



(I)



(II)

A Fourier E-map including 674 reflections with phases derived by the symbolic addition procedure[2] could not be interpreted in terms of a reasonable chemical structure. The iron and phosphorus positions from this map were taken as the basis for a heavy-atom method structure solution. This structure has been refined to an R value of 0·076 (observed reflections) using the block diagonal approximation to the least-squares method, with individual anisotropic temperature factors.

A stereoscopic drawing[3] of the molecule is shown in the Figure. The allyl ligand is bent, with C–C bond distances of 1·45 and 1·41 Å (both ±0·02 Å) and an internal angle of 116·0 ± 1·3°. One iron atom is π-bonded to this allyl group, at distances 2·18 and 2·19 Å from the terminal carbon atoms and 1·93 Å from the apical carbon atom. This iron atom is bonded to three terminal carbonyl groups. The other iron atom is σ-bonded to the central carbon atom of the allyl ligand, at a distance of 2·03 Å, and carries three terminal carbonyl groups and the triphenylphosphine ligand.

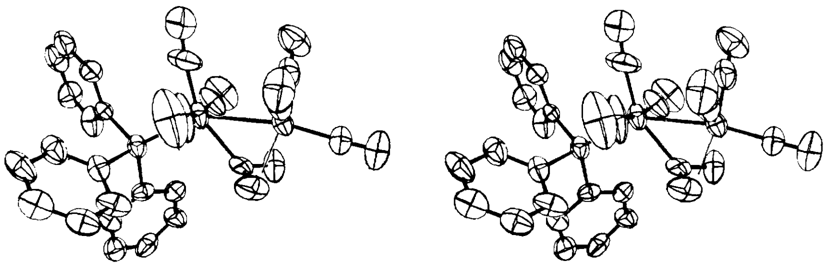


FIGURE. *Stereoscopic diagram. The allyl ligand is in the lower right corner of the diagram. Hydrogen atoms are not shown.*

The two iron atoms are linked by a metal–metal bond of length 2·65 Å. The π-bonded and σ-bonded iron atoms lie on the same side of the plane of the allyl group, 1·84 and 0·93 Å, respectively, from this plane. While the complex is best described by an idealized π-iron–σ-iron formulation, two significant distortions occur: (1) the deviation of the central allylic carbon from a planar, trigonal arrangement, the Fe–C σ-bond lying 27° out of the allyl plane; and (2) the displacement of the π-bonded iron toward the apical carbon. Both distortions may be a result of the Fe–Fe bond.

The complex may be considered in terms of a distorted octahedral co-ordination about the σ-bonded iron, as in (II). It is the carbonyl group *trans* to the other iron which is replaced in the monophosphine derivative. The derivative has approximate C_s symmetry, in addition to having the phosphine ligand rather far removed from the allylic hydrogens, consistent with the observed similarity of the n.m.r. spectra of the C_3H_4 ligand in (I) and (II).[1]

Other bond distances in the molecule are: Fe–P, 2·25 Å; average of three P–C, 1·85 ± 0·02 Å; average of six Fe–C (carbonyl), 1·78 ± 0·03 Å; average of six carbonyl C–O, 1·15 ± 0·02 Å; and average of eighteen phenyl C–C, 1·40 ± 0·03 Å, where these estimated errors are calculated as the standard deviation from the mean value.

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[1] R. Ben-Shoshan and R. Pettit, preceding Communication.

[2] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[3] C. K. Johnson, ORTEP, ORNL-3794 Revised, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.