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SOLID STATE STRUCTURE OF TWO IRON CARBONYL COMPLEXES DERIVED FROM BARBARALONE AND THE ISOBULLVALENE RING SKELETON.
CHARACTERIZATION OF A POSSIBLE "HOMOBUTADIENE–$Fe(CO)_3$" COMPLEX

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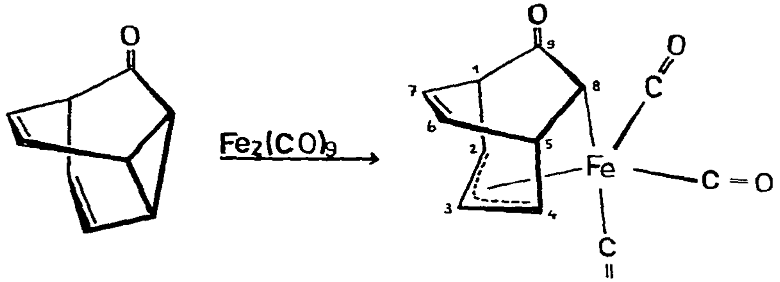
Summary

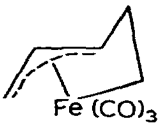
The structures of two iron carbonyl complexes derived from vinylcyclopropane systems have been determined. One of the complexes may be classified as a "homobutadiene" complex.

As in the case of conjugated dienes, vinylcyclopropane systems can be bonded to the dienophilic $Fe(CO)_3$ group [1]. The reaction of tricyclo-[3.3.1.0^{2,8}]nona-3,6-diene-9-one ("barbaralone") (I) [2] with an excess (three equivalents) of $Fe_2(CO)_9$ in absolute ether (25°; 30 h) gives a compound of composition $C_{12}H_8FeO_4$ (II) (m/e 272). The compound (II) can be obtained pure as pale yellow crystals by chromatography on silica with chloroform, followed by recrystallization from chloroform/ether (m.p. 135—136°; yield 56%). On the basis of ^{1}H NMR measurements the structure 2,3,4,8-h^4-bicyclo[3.2.2]-nona-3,6-diene-2,8-yl-9-one·$Fe(CO)_3$ was suggested for (II) [1b].

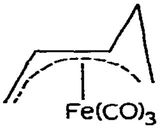


(I) (II)

In (II) the ligand could be bonded to the $Fe(CO)_3$ group either in a π-allyl- and σ-C-fashion (IIa) or as a "homobutadiene"-unit (IIb). An X-ray analysis was carried out to provide proof of the overall structure suggested for (II), and to attempt to distinguish between these valence isomeric forms. This work also represents a continuation of our interest in the structures of iron carbonyl complexes of multicyclic hydrocarbons [3—5].



(IIa)



(IIb)

The very pale yellow transparent crystals of (II) belong to the orthorhombic system with $a = 14.800(8)$, $b = 8.775(4)$, and $c = 8.412(4)$ Å. The space group is $Pna2_1$ and there are four molecules of $C_9H_8OFe(CO)_3$ (mol. wt. 271.9) in the unit cell. The structure (hydrogen atoms included but not refined, all other atoms refined with anisotropic temperature factors) has been refined to an R-factor of 0.061 on 727 non-zero reflections measured on a Picker FACS-1 diffractometer using Mo-K_α radiation (λ 0.7107 Å). A stereoscopic view of the molecular structure is shown in Fig. 1.

In (II) the iron atom complexes to the atoms C(2), C(3), C(4), and C(8) with Fe---C distances of 2.131(19), 2.037(16), 2.104(14), and 2.080(14) Å; the Fe—C(9) distance is much longer, 2.731(15) Å. The C(2)—C(3) and C(3)—C(4) lengths of 1.38(3) and 1.35(2) Å suggest a delocalized structure; and the geometry of this part of the hydrocarbon supports a π-allyl—iron interaction. In such a picture, Fe—C(8) would be considered as a σ-bond (IIa).

An alternative would be to regard the complex as a "homobutadiene" iron complex (IIb), in which one might expect to see some distortion of the normal geometry in the vicinity of C(4), C(5), and C(8). The C(4)---C(8) distance is 2.40(2) Å and the C(4)—C(5)—C(8) angle is 102(1)° *. The C(8)—C(9) bond is quite short [1.41(3) Å] and the four atoms C(2), C(3), C(4), and C(8) comprise a moderately good plane (deviations from −0.05 to 0.09 Å), although these deviations are much greater than those found in normal butadiene—$Fe(CO)_3$ complexes [7]. The orientation of the three carbonyl groups attached to iron, with one CO group almost linearly extended from C(8), is not that found in normal butadiene—$Fe(CO)_3$ complexes [7] and therefore tends to support the π-allyl, σ-bond formulation**.

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* In a corresponding iron carbonyl complex derived from bullvalene [1a] this angle is 104.3° [6].

** It is of interest that Cotton and Troup [8] have recently informed us that they prepared compound (II), along with several others, by treatment of bicyclo[6.2.0]deca-2,4-6-triene with diiron nonacarbonyl. It is further of interest that the material which these authors obtained by crystallization from pentane was triclinic, but had effectively the same molecular structure as that reported here for the orthorhombic form obtained from chloroform/ether. In neither form is there any evidence for incorporation of solvent in the crystal; the calculated densities for the orthorhombic and triclinic forms are 1.66 and 1.65 $g \cdot cm^{-3}$, respectively. We thank Professor Cotton for communicating his results to us prior to publication.

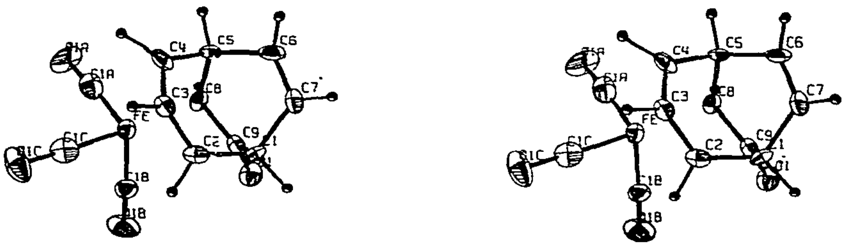
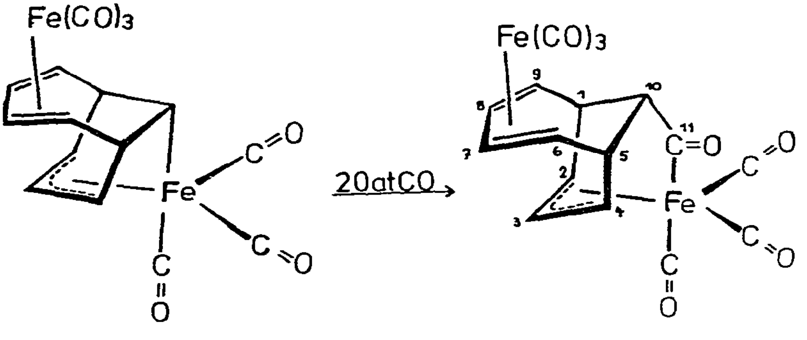


Fig. 1. Stereoscopic drawing of the structure of the $C_9H_8OFe(CO)_3$ complex (II). The hydrogen atoms are located at the most probable positions as determined from the difference map.

In contrast to (II), which does not react with carbon monoxide (100 atm.; 25°; two weeks), the structurally related compound (III) [1a] takes up one equivalent of carbon monoxide even under atmospheric pressure [1b]. A compound, (IV), $C_{17}H_{10}Fe_2O_7$ (m/e 439) precipitates from a saturated solution of (III) in benzene on reaction with carbon monoxide in an autoclave (20 atm.; 40 h) and can be obtained pure by recrystallization from ether (m.p. 134—136°; yield almost quantitative). On the basis of ^1H NMR and IR measurements, the structure 6,7,8,9-h^4: 2,3,4,11-h^4-bicyclo[4.3.1]undeca-2,6,8-triene-4,11-yl-11-one· $[Fe(CO)_3]_2$ was suggested [1] for (IV). The yellow transparent crystals of (IV) are monoclinic with $a = 12.007(6)$, $b = 11.842(7)$, $c = 12.742(7)$ Å, and $\beta = 107°47(2)$. The space group is $P2_1/c$ and there are four molecules of $C_{11}H_{10}OFe_2(CO)_6$ (mol. wt. 438.8) in the unit cell. The structure, including hydrogen atoms with isotropic temperature factors and with all non-hydrogen atoms being given anisotropic temperature factors, has been refined to an R-factor 0.052 on 1632 non-zero reflections collected as before. A stereoscopic view of the structure is shown in Fig. 2.



(III) (IV)

In (IV), one iron atom, Fe(1), complexes to C(6), C(7), C(8), and C(9) in the normal fashion [7] with distances of 2.117(10), 2.018(16), 2.028(15), and 2.138(14) Å, respectively; the four complexed atoms are planar within the accuracy of the analysis. The other iron atom complexes to C(2), C(3), C(4), and C(11) with distances of 2.145(9); 2.038(10), 2.173(10), and 1.991(10) Å, respectively. In this case, the four complexed atoms do not approach coplanarity

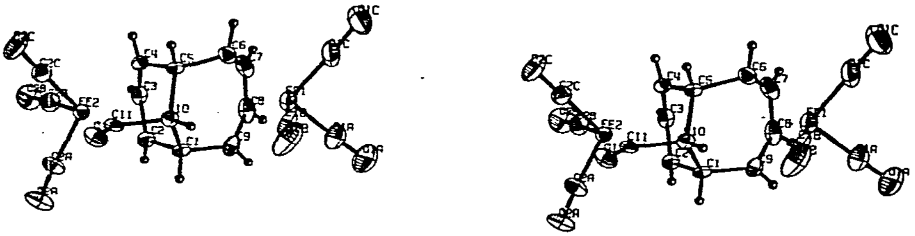


Fig. 2. Stereoscopic drawing of the structure of the $C_{11}H_{10}OFe(CO)_6$ complex (IV).

and the "homobutadiene" formulation is, of course, inappropriate. There are no apparent abnormalities in the geometry of the exocyclic carbonyl group; the C(10)—C(11)—O(12) angle is 121.8(8)°. Certainly the Fe—C σ-bond in this case is shorter than the supposedly corresponding bond in (II). The orientation of the Fe(2)$(CO)_3$ group with respect to the four complexing atoms is similar to that found in (II) with C(11) lying almost linearly along the line joining the C(2B)—O(2B) vector to the iron atom Fe(2).

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