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PROPELLANES. XII. IRONTRICARBONYL DERIVATIVES OF 12-OXA[4.4.3]PROPELLA-2,4,7,9-TETRAENE

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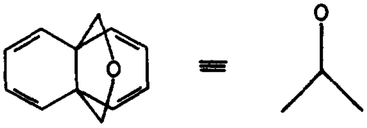
Refluxing the tetraenic ether 1 with diironnonacarbonyl in benzene solution for 24 hr in a nitrogen atmosphere afforded five organometallic derivatives.[1] The nmr spectrum of one of these, m.p. 200-204°C, suggested that this was a symmetrical bis-irontricarbonyl derivative of 1, of structure 2 or 3. An X-ray analysis has been carried out proving that the compound, m.p. 200-204° is 2.



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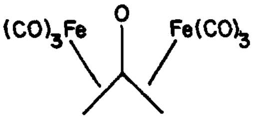

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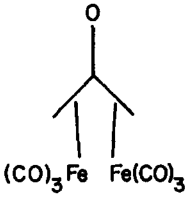

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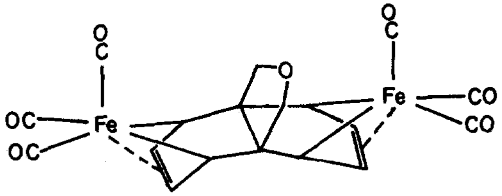

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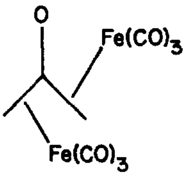

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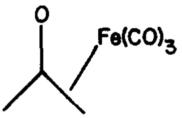

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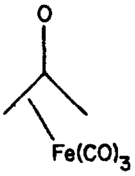

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Its crystals belong either to space group Cc or to C2/c and the structure was solved in the latter. This requires a crystallographic two-fold axis to pass through the molecule and the unit cell to contain 8 half-molecules. The cell dimensions are a = 20.791; b = 7.173; c = 12.625 Å; β = 111.42°. The data were collected on a Picker automatic diffractometer with MoKα radiation ($2\theta \leq 55°$) and 1325 reflections were observed.

The structure was solved by the heavy atom method. The position of the iron atom was determined from a sharpened Patterson map and the rest of the molecule was located from the first Fourier synthesis. The positional and thermal parameters have been refined by least squares and the reliability index (R) is at present 8%. The refinement is being continued.

The iron atoms were found to be on the same side of the cyclohexadiene rings as the oxygen-containing ring. Hence the structure is 2. It may perhaps be represented by 4 in more detail and by the Figure to show the conformation. (The solid and broken lines in 4 do not denote types of bonding).

The five-membered ether ring is planar and the six-membered rings are bent about the $C_1 \cdots C_4$ line by 43°, thus being boat-shaped. The distance between the two double bonds shown in 4 is 3.18 Å. Each iron atom is coordinated to 4 coplanar atoms of the six-membered ring (C_1-C_4). The Fe-C_1 and Fe-C_4 bond distances are 2.11 Å, the Fe-C_2 and Fe-C_3 bond distances are 2.05 Å and the Fe distance to the center of the C_2-C_3 bond is 1.92 Å. The bond lengths in the C_1-C_4 part of the ligand are 1.42 Å for C_1-C_2 and C_3-C_4 and 1.40 Å for C_2-C_3.

The conformation of the cyclohexadiene rings is different from that of free cyclohexadiene[2] but very similar to that found by Churchill and Mason for octafluorocyclohexa-1,3-diene irontricarbonyl.[3] These authors have interpreted the Fe-ligand bonding in their compound to be Fe σ-bonded to C_1 and C_4 and π-bonded to C_2=C_3. In their case the distances from Fe to C_2 and C_3 (2.060 Å) and to the center of the C_2-C_3 bond (1.932 Å) are very similar to ours while their Fe-C_1 and Fe-C_4 distances (1.993 Å) are shorter than ours. Other authors have observed Fe-C σ-bonds up to 2.12 Å in length.[4]

The $Fe(CO)_3$ groups in 2 have approximate C_{3v} symmetry with the Fe-C-O vectors being very close to linear and forming angles of 93-98° with one another. The Fe-C (1.79 Å) and C-O (1.14 Å) distances are normal. The e.s.d.'s in bond lengths range from 0.008 to 0.011 Å. Defining each iron atom as coordinated to C_1, C_4, the middle of the C_2-C_3 bond and to 3 CO groups, the iron is coordinated in a distorted octahedral manner. Complete results of the X-ray analysis will be published (K.B.B.) elsewhere.

The X-ray analysis requires us to correct the structural assignments made for the two symmetrical bis-irontricarbonyl derivatives.[1] The symmetrical bis-derivative, m.p. 200-204°, as proved above, is 2. Its isomer, m.p. 186-187° is 3 (structures 36 and 35 in Ref. 1 must therefore be interchanged).

By using ceric ammonium nitrate, each of the bis-derivatives and the mono-irontricarbonyl derivatives may be decomposed and CO evolution may be measured quantitatively.

Compound 38 in Ref. 1, m.p. 135-138° affords 6 moles of CO, despite the fact that the highest line in its mass spectrum corresponded to $[M-CO]^+$ based on the molecular weight of an isomeric bis-derivative. The structure of this isomer, having an unsymmetrical nmr spectrum, is therefore 5. The structures of the two mono-irontricarbonyl derivatives of 1 reported[1] are now also clear. Removal of only one $Fe(CO)_3$ ligand from 2 by means of ceric ammonium nitrate in methanolic solution (evolution of 3 moles of CO) afforded the mono-irontricarbonyl derivative of m.p. 105-107°. This must therefore be 6. Alternatively, it is interesting to note that although 5, through partial removal of only one $Fe(CO)_3$ ligand, could in principle give both 6 and 7, it gives, selectively, only the mono-irontricarbonyl derivative, m.p. 115-130°, different from 6, and this must therefore be 7.

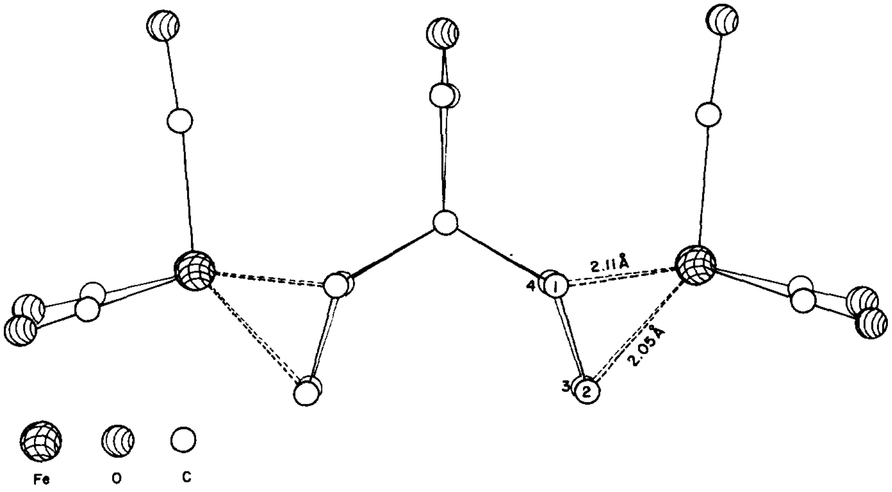

Figure. View of the molecule along the c^*-axis

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