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THE STRUCTURE OF A TRICARBONYLIRON DERIVATIVE OF BARBARALONE

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Summary

One minor product of the reaction of $Fe_2(CO)_9$ in ether with impure bicyclo[2.6.0]deca-2,4,6-triene, in which the major impurity was cyclooctatetreane, is a derivative of barbaralone, tricyclo [3.3.1.0^{2,8}]nona-3,6-diene-9-one, I, in which the three membered ring has been opened at the 2,8 bond. The systematic name for the compound is (2,3,4,8-η^4-bicyclo[3.2.2]-nona-3,6-diene-2,8-yl-9-one)tricarbonyliron. It is identical to the product which can be obtained by direct reaction of barbaralone with $Fe_2(CO)_9$ in ether. The most likely progenitor of the barbaralone moiety in the present instance is the C_8H_8 impurity, although there is no direct proof of this. Compound I crystallized from pentane at −5° in the triclinic system with unit cell dimensions a 7.476(2), b 11.912(4), c 6.606(2) Å, α 94.55(2)°, β 110.17(2)°, γ 92.38(3)°, V 549.0(3) Å^3 and Z 2. Space group $P\bar{1}$. The structure was solved by Patterson and Fourier methods and refined to R_1 0.021 and R_2 0.031 with all nonhydrogen atoms treated anisotropically and the eight hydrogen atoms treated isotropically, using 1283 reflections having $F_o^2 > 3\sigma(F_o^2)$. The coordination about the iron atom can be described as distorted octahedral if the η^3-allyl is considered to occupy two of the six positions. The three CO ligands are mutually *cis*. The allyl group is *trans* to two of them and the Fe—C σ bond is *trans* to the third. The mean Fe—CO bond length is 1.795(5) Å, the Fe—C(allyl) distances are 2.137(3), 2.069(2) and 2.195(3) Å, and the Fe—C σ bond has a length of 2.110(2) Å. The broad geometrical features of the structure are quite at variance with the concept of a "homobutadiene complex".

Introduction

The reaction of diiron nonacarbonyl with bicyclo[2.6.0]deca-2,4,6-triene has been shown to produce a plethora of products [1–5]. Some of the minor products must, presumably, arise not from the decatriene but from contaminants, one of which is, certainly, cyclooctatetraene and another, probably, cyclooctatriene. We describe here one such minor product, I, which may be represented as a derivative of barbaralone, II [6,7], and can, in fact, be obtained directly from barbaralone as Aumann [8,9] has shown.

Experimental

The reaction of bicyclo[6.2.0]deca-2,4,6-triene with diiron nonacarbonyl in ether at 20° produces several products, as described previously [2]. The products were separated by column chromatography using Woelm activity 2 alumina and eluting with first hexane and then a hexane/ether mixture. On duplicating the above procedure it was found that a light yellow band covering most of the column remained after eluting with the hexane/ether mixture. This remaining band was removed using an ether/acetone (1/1) elutant. The solution was evaporated in vacuo to dryness at 25°. The resulting yellow solid was recrystallized from pentane at −5° to produce crystallographically good crystals, light-yellow in color. A crystal measuring approximately 0.13 × 0.15 × 0.33 mm was selected for data collection and was mounted in a glass capillary to protect it from slow air decomposition.

Preliminary examination of the crystal and data collection were performed on a Syntex $P\bar{1}$ diffractometer equipped with a graphite crystal monochromator using Mo-K_α radiation.

The crystal was found to be triclinic and the space group $P\bar{1}$ was assumed. This choice was later confirmed by the successful solution and refinement of the structure.

The unit cell dimensions at 22° and the orientation matrix for data collection were determined by least-squares refinement of the setting angles for fifteen carefully centered reflections. These dimensions and other crystal data are given in Table 1. A width at half-height of 0.15° was obtained from ω scans of the crystal.

The operation of the diffractometer has been described previously [3]. Intensity measurements were made at 22° using the θ—2θ scan technique and a scan rate that varied from 2.0 to 24.0°/min depending on the intensity of the reflection. Unique data with 2θ(Mo-K_α) values up to 45.0° were collected with a scan range from 0.8° before 2θ(Mo-K_{α_1}) to 0.8° after 2θ(Mo-K_{α_2}). Three standard reflections, collected every 100 reflections, showed no significant change in intensity throughout data collection.

No absorption correction was made in view of the small variation in transmission factors of 79.4 ± 4.0% during data collection. Lorentz and polarization

TABLE 1

CRYSTAL DATA FOR $Fe(CO)_3C_9H_8O$

a	7.476(2) Å	Triclinic
b	11.912(4) Å	Space group $P\bar{1}$
c	6.606(2) Å	Mo-K_α radiation
α	94.55(2)°	μ 14.1 cm^{-1}
β	110.17(2)°	Z 2
γ	92.38(3)°	ρ_{calc} 1.65 g cm^{-3}
V	549.0(3)	

corrections were made; no extinction correction was deemed necessary. Of the 1447 reflections collected, only the 1283 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement of the structure.

*Solution and refinement of the structure**

The iron atom was located using the Patterson method. Two cycles of least-squares refinement of the coordinates of the iron atom gave the following agreement factors: $R_1 = (\Sigma||F_o|-|F_c||)/\Sigma|F_o| = 0.445$ and $R_2 = (\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{1/2} = 0.522$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and w is the weighting factor given as $4|F_o|^2/\sigma^2$. Here σ is the esd of $|F_o|^2$. Scattering factors were taken from the International Tables [10]. Anomalous dispersion effects were included in the calculated structure factors for iron, using $\Delta f'$ and $\Delta f''$ values given by Cromer and Liberman [11].

TABLE 2

ATOMIC POSITIONAL PARAMETERS FOR $Fe(CO)_3C_9H_8$ [a]

Atom	x	y	z
Fe	−0.17535(4)	0.22431(3)	0.20377(5)
O(1)	0.1094(4)	0.0554(2)	0.3103(4)
O(2)	0.0290(3)	0.3820(2)	0.5842(3)
O(3)	−0.4334(3)	0.0879(2)	0.3514(4)
O(4)	0.3209(3)	0.2611(2)	0.0327(4)
C(1)	−0.5103(4)	0.2288(2)	−0.2188(4)
C(2)	−0.3249(4)	0.1695(2)	−0.1413(4)
C(3)	−0.1432(4)	0.2231(2)	−0.0951(4)
C(4)	−0.0989(4)	0.3331(2)	−0.0001(4)
C(5)	−0.2605(4)	0.4080(2)	−0.0148(4)
C(6)	−0.3807(4)	0.4121(3)	−0.2500(4)
C(7)	−0.4983(4)	0.3250(3)	−0.3506(5)
C(8)	−0.3674(4)	0.3517(2)	0.1143(4)
C(9)	−0.5378(4)	0.2815(2)	−0.0157(4)
C(10)	0.0010(4)	0.1216(2)	0.2660(5)
C(11)	−0.0503(4)	0.3196(2)	0.4379(4)
C(12)	−0.3322(4)	0.1415(2)	0.2963(4)
H(1)	−0.606(4)	0.181(2)	−0.289(4)
H(2)	−0.338(4)	0.098(3)	−0.177(4)
H(3)	−0.053(4)	0.177(2)	−0.106(4)
H(4)	0.025(4)	0.362(2)	0.035(4)
H(5)	−0.212(3)	0.478(2)	0.540(4)
H(6)	−0.358(4)	0.477(3)	−0.313(5)
H(7)	−0.570(4)	0.316(3)	−0.502(6)
H(8)	−0.378(4)	0.402(2)	0.235(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits in this and all other tables.

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* The following computer programs written for the IBM360 were used: TRACER, a lattice transformation and cell reduction program by Lawton; DATARED, a data reduction program by Frenz; FOURIER, a Fourier summation program (based on Zalkin's FORDAP) by Dellaca and Robinson and modified by Hodgson; NUCLS, a full-matrix least-squares program (minimizing $\Sigma w(|F_o|-|F_c|)^2$ by Ibers and Doedens, similar to Busing and Levy's ORFLS: SADIAN, a distances and angles program by Baur, rewritten by Frenz and Brice; AGNOST, an absorption correction program by Cahen based on Coppens' DATAP and Tompa analytical subroutines of Cullen's program; PERFACT, a program for analysis of structure factors by Frenz; ORFFE, a function and error program by Busing, Martin, and Levy as modified by Brown, Johnson, and Theissen; ORTEP, a plotting program by Johnson; and LIST, a program for listing the data by Snyder.

TABLE 3

ATOMIC THERMAL PARAMETERS FOR $Fe(CO)_3C_9H_8O$[a]

Atom	β_{11} or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.0116(1)	0.0045(1)	0.0191(1)	0.0008(1)	0.0042(1)	0.0005(1)
O(1)	0.0313(7)	0.0114(2)	0.0505(10)	0.0114(4)	0.0073(6)	0.0042(4)
O(2)	0.0307(6)	0.0091(2)	0.0239(6)	−0.0037(3)	0.0014(5)	−0.0033(3)
O(3)	0.0288(6)	0.0088(2)	0.0369(7)	−0.0048(3)	0.0133(5)	0.0032(3)
O(4)	0.0128(4)	0.0150(3)	0.0429(8)	0.0031(3)	0.0129(5)	0.0065(4)
C(1)	0.0117(5)	0.0073(2)	0.0239(8)	−0.0010(3)	0.0009(5)	−0.0006(4)
C(2)	0.0179(6)	0.0043(2)	0.0210(7)	0.0010(3)	0.0055(5)	−0.0013(3)
C(3)	0.0154(6)	0.0065(2)	0.0214(8)	0.0034(3)	0.0084(6)	0.0013(3)
C(4)	0.0123(6)	0.0066(2)	0.0218(7)	−0.0008(3)	0.0062(5)	0.0018(3)
C(5)	0.0193(6)	0.0044(2)	0.0247(8)	0.0002(3)	0.0078(6)	0.0003(3)
C(6)	0.0212(7)	0.0069(3)	0.0259(8)	0.0043(4)	0.0091(7)	0.0047(4)
C(7)	0.0166(6)	0.0091(3)	0.0212(8)	0.0037(4)	0.0036(6)	0.0026(4)
C(8)	0.0162(6)	0.0055(2)	0.0217(7)	0.0032(3)	0.0074(6)	0.0001(3)
C(9)	0.0127(6)	0.0081(2)	0.0272(8)	0.0041(3)	0.0061(6)	0.0043(4)
C(10)	0.0196(7)	0.0070(2)	0.0289(9)	0.0034(4)	0.0052(6)	0.0018(4)
C(11)	0.0161(6)	0.0067(2)	0.0224(8)	0.0009(3)	0.0055(6)	0.0023(4)
C(12)	0.0175(6)	0.0056(2)	0.0225(8)	0.003(3)	0.0038(6)	0.0003(3)
H(1)	2.9(5)					
H(2)	3.6(6)					
H(3)	3.6(6)					
H(4)	2.9(5)					
H(5)	3.0(5)					
H(6)	4.6(7)					
H(7)	5.2(7)					
H(8)	4.1(6)					

[a] The anisotropic temperature parameters are of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

A difference Fourier map based on the phases determined by the iron atom revealed the positions of all carbon and oxygen atoms. All non-hydrogen atoms were refined isotropically by two full matrix least-squares cycles and then anisotropically by two least-squares cycles to give the agreement indices of R_1 0.040 and R_2 0.060. A difference Fourier map now showed the positions of all eight hydrogen atoms. The non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically in three final least-squares cycles to give final agreement factors of R_1 0.021 and R_2 0.031. In the final cycle of refinement no parameter shift exceeded 0.35 times the standard deviation in the parameter. The esd in an observation of unit weight was 1.019.

No systematic trends were found in the data as a function of $\lambda^{-1}\sin\theta$, $|F_o|$, Miller indices, or reflection number. In the last difference Fourier the eight hydrogen atoms were observed as the highest peaks. The atomic coordinates and thermal parameters with estimated standard deviations are given in Tables 2 and 3, respectively. Root-mean-square amplitudes of thermal vibration are available*.

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* Supplementary material, which includes the r.m.s. amplitudes of thermal vibration and a list of F_o and F_c values has been deposited as NAPS Document No. 02362, with the ASIS/NAPS, c/o Microfiche Publications, 305 E. 46th St., New York, N.Y. 10017. A copy may be secured by citing the document and remitting $1.50 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

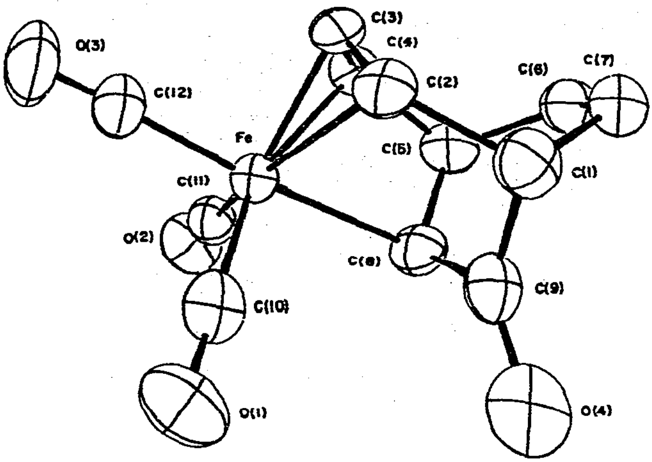

Fig. 1. An ORTEP drawing of the molecular structure, in which the atomic numbering scheme is defined. Each non-hydrogen atom is represented by its ellipsoid of thermal vibration scaled to the 50% probability level. Hydrogen atoms are omitted.

Results

The molecular structure is shown in Fig. 1. The crystallographic numbering scheme is the same as the numbering scheme used in the systematic name of the compound. The important interatomic distances are given in Table 4, and bond angles are given in Table 5. Some mean planes and the dihedral angles between them are recorded in Table 6.

The infrared spectrum of the compound in CS_2 solution has the usual bands, 2065, 2015, 1993 cm^{-1}, for an $Fe(CO)_3$ group. In addition there is a band of medium intensity at 1683 cm^{-1} due to the ketone group.

TABLE 4

BOND LENGTHS (Å)

Fe—C(2)	2.195(3)	C(1)—C(2)	1.526(4)
Fe—C(3)	2.069(2)	C(1)—C(7)	1.511(4)
Fe—C(4)	2.137(3)	C(1)—C(8)	1.518(4)
Fe—C(9)	2.110(2)	C(2)—C(3)	1.399(4)
Fe—C(10)	1.801(3)	C(3)—C(4)	1.382(4)
Fe—C(11)	1.786(3)	C(4)—C(5)	1.513(4)
Fe—C(12)	1.793(3)	C(5)—C(6)	1.509(4)
		C(5)—C(9)	1.528(4)
C(8)—O(4)	1.226(3)	C(6)—C(7)	1.305(4)
C(10)—O(1)	1.137(4)	C(8)—C(9)	1.450(4)
C(11)—O(2)	1.137(3)		
C(12)—O(3)	1.140(3)	C(1)—H(1)	0.86(3)
		C(2)—H(2)	0.86(3)
		C(3)—H(3)	0.91(3)
		C(4)—H(4)	0.92(3)
		C(5)—H(5)	0.91(3)
		C(6)—H(6)	0.94(3)
		C(7)—H(7)	0.95(3)
		C(8)—H(8)	0.98(3)

TABLE 5

SELECTED BOND ANGLES (°)

C(2)—Fe—C(3)	38.2(1)	C(2)—C(1)—C(7)	112.7(2)
C(2)—Fe—C(4)	68.0(1)	C(2)—C(1)—C(9)	106.0(2)
C(2)—Fe—C(8)	79.0(1)	C(7)—C(1)—C(9)	106.2(2)
C(2)—Fe—C(10)	99.3(1)	C(1)—C(2)—C(3)	124.1(2)
C(2)—Fe—C(11)	157.3(1)	C(2)—C(3)—C(4)	121.3(2)
C(2)—Fe—C(12)	95.1(1)	C(3)—C(4)—C(5)	118.6(2)
C(3)—Fe—C(4)	38.3(1)	C(4)—C(5)—C(6)	109.2(2)
C(3)—Fe—C(8)	88.8(1)	C(4)—C(5)—C(8)	103.6(2)
C(3)—Fe—C(10)	86.8(1)	C(6)—C(5)—C(8)	113.2(2)
C(3)—Fe—C(11)	125.9(1)	C(5)—C(6)—C(7)	118.3(3)
C(3)—Fe—C(12)	131.7(1)	C(1)—C(7)—C(6)	117.1(2)
C(4)—Fe—C(8)	68.5(1)	C(5)—C(8)—C(9)	114.9(2)
C(4)—Fe—C(10)	106.1(1)	C(1)—C(9)—C(8)	109.4(2)
C(4)—Fe—C(11)	91.0(1)	O(4)—C(9)—C(1)	124.0(3)
C(4)—Fe—C(12)	156.7(1)	O(4)—C(9)—C(8)	126.5(3)
C(8)—Fe—C(10)	174.6(1)		
C(8)—Fe—C(11)	85.5(1)		
C(8)—Fe—C(12)	93.3(1)		
C(10)—Fe—C(11)	94.6(1)		
C(10)—Fe—C(12)	92.0(1)		
C(11)—Fe—C(12)	102.3(1)		
Fe—C(10)—O(1)	177.5(3)		
Fe—C(11)—O(2)	178.5(2)		
Fe—C(12)—O(3)	178.8(2)		

TABLE 6

Least-squares planes and dihedral angles

Plane	Atoms defining plane	Equation of mean plane[a]
I	C(1),C(2),C(3),C(4),C(5)	$-2.292x - 3.421y + 6.457z = -0.924$
II	C(1),C(5),C(6),C(7)	$6.552x - 5.239y - 3.365z = -3.801$
III	C(1),C(5),C(8),C(9)	$4.273x - 8.823y + 1.598z = -4.646$

Displacement of atoms from mean plane (A)

Plane I		Plane II		Plane III	
C(1)	−0.102	C(1)	−0.006	C(1)	0.097
C(2)	0.176	C(5)	0.006	C(5)	−0.091
C(3)	−0.126	C(6)	−0.012	C(8)	0.155
C(4)	0.010	C(7)	0.012	C(9)	−0.161
C(5)	0.029	C(2)	1.259	C(2)	1.535
Fe	1.874	C(3)	2.013	C(3)	1.913
C(6)	−1.228	C(4)	1.408	C(4)	1.284
C(7)	−1.310	C(8)	−0.835	C(6)	−1.017
C(8)	1.300	C(9)	−1.145	C(7)	−0.911
C(9)	1.092				

Dihedral angles between planes (°)

Planes	
I—II	112.6
I—III	113.6
II—III	133.3

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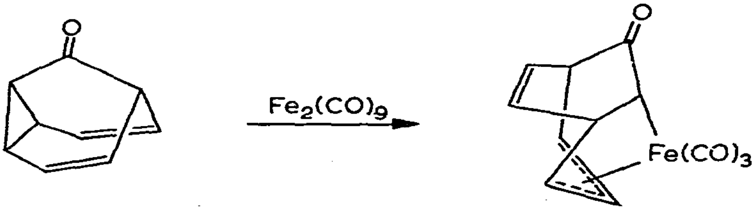
[a] Equations have the form $Ax + By + Cz = D$ where x, y and z are fractional triclinic coordinates.

Discussion

The structure is one of the main types formed by $Fe(CO)_3$ with unsaturated organic molecules, namely the type in which the four electrons needed to complete the conventional 18-electron configuration of the iron atom are obtained from one η^3-allyl group and one Fe—C σ bond. The possibility that this molecule might contain a so-called "homobutadiene" group (in any case, a pure figment of the imagination to date, so far as we know) is certainly not realized. All of the dimensions of the molecule are fully consistent with the η^3-allyl-plus-σ form of bonding.

For various technical reasons, one of which is the fact that we are working with a centric space group, while Paul et al. [9] were working with an acentric one, the present work provides a more accurate structure than that obtained by Paul et al.*, which is the main reason for reporting this work in detail. It appears that the different types of crystals result from the different solvents used: chloroform/ether, *Pna?* [illegible] ne, $P\bar{1}$. This rare, though scarcely unprecedented, dependence upo [illegible] in itself of some interest.

We do not [illegible] ho the title compound was formed under our reaction conditions. It see [illegible] ole that its ultimate antecedent, amongst the starting materials, was the cyclooctatetraene known to be present to the extent of a few percent by weight in the $C_{10}H_{12}$. It is known [12] that $C_8H_8Fe(CO)_3$ rearranges under the influence of $AlCl_3$ to give (barbaralone)$Fe(CO)_3$, although the further observation that no other Lewis acid except $AlCl_3$ was effective makes it uncertain whether this rearrangement could be occurring in our reaction. However, there is no direct evidence for this. It is not impossible that barbaralone itself might have been formed as an intermediate and then reacted with $Fe_2(CO)_9$, just as Aumann has shown it to do:



(I) (II)

The C—H distances lie in the range 0.86 to 0.98 Å; each has an esd of 0.03 Å and the average value is 0.92 ± 0.03 Å. This is typical of the results obtained in the refinement of H atoms in organometallic compounds using relatively high-quality diffractometer data.

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* Among the published dimensions [9] there appears to be a systematic difference between the two determinations, such that *all* bond lengths mentioned by Paul et al. are an average of 1.5 esd's shorter than those we find. While no single discrepancy of this magnitude has any significance, the uniformity strongly suggests that there may be some systematic error. However, Professor Paul informs us that a number of other dimensions not reported by him are greater than ours and, therefore, that no systematic trend exists.

Acknowledgements

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References

1 F.A. Cotton and G. Deganello, J. Amer. Chem. Soc., 94 (1972) 2142.
2 F.A. Cotton and G. Deganello, J. Organometal. Chem., 38 (1972) 147.
3 F.A. Cotton, B.A. Frenz, G. Deganello and A. Shaver, J. Organometal. Chem., 50 (1973) 227.
4 F.A. Cotton and J.M. Troup, J. Amer. Chem. Soc., 95 (1973) 3798.
5 F.A. Cotton, B.A. Frenz, J.M. Troup and G. Deganello, J. Organometal. Chem., 59 (1973) 317.
6 W. von E. Doering, B.M. Ferrier, E.T. Fossel, J.H. Hartenstein, M. Jones, Jr., G. Klumpp, R.M. Rubin and M. Saunders, Tetrahedron, 23 (1967) 3943.
7 L.A. Paquette, R.H. Meisinger and R.E. Wingard, J. Amer. Chem. Soc., 94 (1972) 2155.
8 R. Aumann, Angew. Chem., Int. Ed. Engl., 10 (1972) 188, 189.
9 A.H.-J. Wang, I.C. Paul and R. Aumann, J. Organometal. Chem., 69 (1974) 301.
10 D.T. Cromer, in "International Tables for X-ray Crystallography", Vol. IV, in preparation.
11 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1971) 1891.
12 V. Heil, B.F.G. Johnson, J. Lewis and D.J. Thompson, J. Chem. Soc., Chem. Commun., (1974) 270.