Acta Cryst. (1981). B**37**, 1532–1537

Benzocyclobutadienes.
6.* Two Tricarbonyliron Complexes from a Stable Benzodicyclobutadiene

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(*Received* 27 *October* 1980; *accepted* 6 *February* 1981)

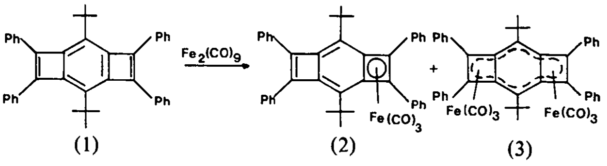
Abstract

The reaction of a stable benzodicyclobutadiene with nonacarbonyldiiron affords a monoiron complex $C_{45}H_{38}FeO_3$ [(2) M_r = 682·64, triclinic, $P\bar{1}$, $Z = 2$, a = 10·267 (4), b = 12·466 (1), c = 14·756 (2) Å, α = 91·62 (1), β = 99·84 (2), γ = 76·05 (2)°, μ(Mo $K\alpha$) = 0·41 mm^{-1}] and a diiron complex $C_{48}H_{38}Fe_2O_6.CH_2Cl_2.\frac{1}{2}C_5H_{12}$ [(3) M_r = 943·47, monoclinic, $C2/c$, $Z = 4$, a = 16·307 (5), b = 17·749 (3), c = 16·95 (1) Å, β = 102·93 (4)°, μ(Mo $K\alpha$) = 0·71 mm^{-1}]. Both structures were solved by the heavy-atom method and refined to R = 0·038 and 0·063 for 5824 and 1559 diffractometer data respectively. In (2), one four-membered ring is strongly tetrahapto coordinated by an $Fe(CO)_3$ group, as in pure cyclobutadiene complexes. This leads to a pronounced double-bond fixation in the fused benzene ring. In (3), both four-membered rings are tetrahapto coordinated but, in contrast to (2), the $Fe(CO)_3$ groups are shifted towards the molecular periphery. (3) can be regarded as an organometallic anthracene. From the structures (2) and (3), the notation benzodicyclobutadiene for (1) seems to be justified.

Introduction

Winter & Butters (1981*b*) described the structure of the tetrahapto tricarbonyliron complex of 1,2-di-*tert*-butyl-3,4,5,6-tetramethylbenzocyclobutadiene. From the structure of the free ligand (Winter & Butters, 1981*a*), we were able to study the changes within the ligand by complexation: the benzocyclobutadiene behaves as a four-electron cyclobutadiene donor or, in other words, the transition metal recognizes the cyclobutadiene character of the benzocyclobutadiene molecule. In contrast to the pure cyclobutadiene complexes, the complexation of the four-membered ring is disturbed by the fused benzene ring. Consequently, the outer double bond of the four-membered ring is much more strongly coordinated to Fe, and the complex represents a compromise between an aromatic benzene and an aromatic cyclobutadiene–$Fe(CO)_3$ unit.

In this connection, we were interested in the question of whether the only benzodicyclobutadiene (1) so far known (Toda & Ohi, 1975) provides cyclobutadiene complexes too, or if (1) behaves more like a benzene derivative and shows dihapto coordination of the fused double bonds. In a preliminary communication (Butters, Toda & Winter, 1980), we reported our first results according to the scheme:



The present study reports full details of the X-ray structure determinations of (2) and (3).

Experimental

Preparation of the complexes

An equimolar mixture of (1) and $Fe_2(CO)_9$ was heated in xylene under reflux for 4 h (N_2 atmosphere). After evaporation of the solvent, the residue was recrystallized from benzene. (2) crystallized out initially (yield 85%) and (3) was obtained from the mother liquor (yield 5%). Further purification by repeated recrystallizations from benzene afforded analytically pure samples: (2) as red prisms (m.p. 495–496 K) and (3) as black-red prisms (m.p. 487–489 K).

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* Part 5: Winter & Butters (1981*b*).

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0567-7408/81/081532-06$01.00

Data collection, solution and refinement of the structures

For (2), preliminary precession photographs showed good crystal quality and triclinic diffraction symmetry. With (3), we had difficulty in obtaining crystals suitable for X-ray diffraction. After many attempts, crystals of acceptable quality were prepared by a vapor diffusion method with dichloromethane/pentane (Brown & Trefonas, 1970). Because these crystals were stable only in the presence of the solvent, they were sealed in a Lindemann capillary with a drop of mother liquor. Precession photographs showed monoclinic diffraction symmetry and systematic extinctions typical for the space groups *Cc* or *C*2/*c*.

Lattice constants were obtained by least squares from the setting angles of 25 reflections measured on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Crystal data and further experimental details are listed in the *Abstract* and Table 1.*

In comparison to (2), the crystals of (3) were of considerably poorer quality, as seen by the low number of reflections with $F_o \geq 2\sigma(F_o)$.

The solution and refinement of (2) was straightforward. After location of the Fe atom from a Patterson map, all further non-H atoms were located by a difference synthesis. Full-matrix least-squares refinement with isotropic temperature factors led to $R = 0{\cdot}107$. H atoms were introduced in agreement with a ΔF synthesis at their calculated positions and, in the following cycles, the CH_3 groups and the CH groups of the benzene rings were treated as rigid groups (C—H = 1·08 Å). The final *R* values in Table 1 relate to anisotropic temperature factors for all non-H atoms and a common isotropic temperature factor for H (which refined to $\bar{U} = 0{\cdot}091$ Å^2). The 525 parameters had to be divided into 3 blocks (observations: parameters 11:1). The anisotropic refinement seemed to us to be justified because refinement with an anisotropic temperature factor for Fe alone (observations:parameters 34:1) led to $R = 0{\cdot}091$ and e.s.d.'s for the atomic coordinates higher by a factor of two. As an independent check, a ΔF map was found to be essentially flat and no unusual systematic variation of $\sum w(F_o - F_c)^2$ *versus* *h*,*k*,*l*, index parity, $|F_o|$ or $(\sin\theta)/\lambda$ was observed.

Table 1. *Data collection and refinement parameters for* (2) *and* (3)

Data collection		
Crystal size (mm)	0·42 × 0·50 × 0·55	0·20 × 0·30 × 0·35
Scan mode	ω/θ	ω/θ
Scan width $\Delta\omega$ (°)	0·9 + 0·35 tan θ	1·0 + 0·35 tan θ
Maximum scan time (s)	50	60
2θ range (°)	6–54	6–50
Radiation	Mo $K\alpha$	Mo $K\alpha$
Number of reflections collected	7700	4371
Number of independent observed reflections with $F_o \geq 2\sigma(F_o)$	5824	1559
Final refinement		
R	0·038	0·063
R_G (unit weights)	0·031	0·076

The solution of (3) was complicated by the fact that the volume of the *C*-centered monoclinic cell indicated $Z = 4$ and we originally thought the structure to be (4). So, we tried to solve the Patterson synthesis and to refine the structure in the space group *Cc*. High correlation coefficients in the refinement and unreasonable geometries between the atoms induced us to shift the molecule to the special position of the twofold axis in *C*2/*c*. The successful refinement of (3) with point group C_2 confirmed the latter space group. After convergence of the refinement with isotropic temperature parameters ($R = 0{\cdot}12$), a difference synthesis showed a number of peaks which could be interpreted as disordered dichloromethane and pentane solvent molecules. To obtain a reasonable ratio of observations:parameters, we refined all non-H atoms anisotropically, except the solvent atoms, which proved to give best results when refined with isotropic temperature factors and an occupancy of 0·5 (disorder around the twofold axis); the CH_3 groups and the CH groups of the benzene rings were treated as rigid bodies (C—H = 0·96 Å) and the H atoms were given a common isotropic temperature factor, which refined to $\bar{U} = 0{\cdot}073$ Å^2. A final difference synthesis showed several peaks within the disordered solvent cluster (electron densities between 0·43 and 0·31 e Å^{-3}), but the quality of the crystal allowed no further sensible interpretation. The flat variance of $\sum w(F_o - F_c)^2$ *versus* *h*,*k*,*l*, index parity, $|F_o|$ and $(\sin\theta)/\lambda$ demonstrated the validity of the weighting scheme. Scattering factors, corrected for anomalous dispersion, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). All calculations were performed on a Telefunken TR 440 computer at the Zentrum für Datenverarbeitung der Universität Tübingen; the major programs used were *SHELX* by G. Sheldrick, *XANADU* by J. Roberts & G. Sheldrick and *PLUTO* by S. Motherwell. Final fractional coordinates, interatomic distances and angles are given in Tables 2–7.

Results and discussion

The molecular structures (and the atom numbering) are shown in Figs. 1 and 2.

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* Lists of H atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35929 (51 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional parameters* ($\times 10^5$ *for* Fe *and* $\times 10^4$ *for* C, O) *and equivalent isotropic thermal parameters* ($\times 10^4$) *for complex* (2) *with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} U_{22} U_{33})^{1/3}$.

	x	y	z	U_{eq} (Å^2)		x	y	z	U_{eq} (Å^2)
Fe(1)	137 (3)	40531 (3)	21875 (2)	364 (2)	C(22)	−2532 (2)	3219 (2)	980 (1)	335 (11)
O(1)	−1621 (2)	6074 (2)	1230 (2)	760 (14)	C(23)	−3533 (2)	2663 (2)	1066 (2)	494 (14)
O(2)	523 (3)	5047 (2)	3993 (1)	910 (17)	C(24)	−4656 (3)	2737 (3)	375 (2)	614 (17)
O(3)	2461 (2)	4132 (2)	1446 (2)	1075 (19)	C(25)	−4782 (3)	3363 (2)	−405 (2)	543 (16)
C(1)	−1353 (2)	3094 (2)	1729 (1)	324 (11)	C(26)	−3794 (3)	3900 (2)	−502 (2)	519 (16)
C(2)	−1158 (2)	3152 (2)	2734 (1)	289 (10)	C(27)	−2669 (3)	3829 (2)	178 (2)	447 (14)
C(3)	−1870 (2)	3371 (2)	3528 (1)	282 (10)	C(28)	−1800 (2)	2592 (2)	5984 (1)	338 (11)
C(4)	−1091 (2)	2778 (2)	4264 (1)	299 (10)	C(29)	−1248 (3)	2712 (2)	6904 (2)	471 (14)
C(5)	−941 (2)	2502 (2)	5272 (1)	326 (11)	C(30)	−2012 (3)	2687 (2)	7591 (2)	546 (17)
C(6)	399 (2)	1967 (2)	5311 (1)	330 (11)	C(31)	−3326 (3)	2548 (2)	7373 (2)	548 (16)
C(7)	358 (2)	2160 (2)	4315 (1)	297 (10)	C(32)	−3885 (2)	2451 (2)	6470 (2)	485 (14)
C(8)	1111 (2)	2022 (2)	3634 (1)	299 (10)	C(33)	−3130 (2)	2471 (2)	5781 (2)	417 (13)
C(9)	250 (2)	2504 (2)	2779 (1)	304 (10)	C(34)	1402 (2)	1361 (2)	6078 (1)	356 (11)
C(10)	43 (2)	2443 (2)	1773 (1)	345 (11)	C(35)	1448 (3)	263 (2)	6244 (2)	595 (17)
C(11)	−3259 (2)	4188 (2)	3500 (1)	337 (11)	C(36)	2360 (4)	−313 (3)	6970 (2)	760 (22)
C(12)	−3279 (3)	4825 (2)	4407 (2)	444 (13)	C(37)	3221 (3)	200 (3)	7529 (2)	630 (19)
C(13)	−4416 (2)	3582 (2)	3335 (2)	509 (15)	C(38)	3183 (3)	1290 (3)	7384 (2)	586 (17)
C(14)	−3518 (3)	5053 (2)	2723 (2)	454 (14)	C(39)	2269 (2)	1880 (2)	6655 (2)	505 (15)
C(15)	2640 (2)	1504 (2)	3751 (2)	368 (12)	C(40)	694 (2)	1719 (2)	1087 (1)	393 (12)
C(16)	3377 (3)	2098 (3)	4509 (2)	668 (20)	C(41)	904 (3)	2128 (2)	271 (2)	581 (16)
C(17)	2907 (3)	287 (2)	4013 (3)	756 (22)	C(42)	1499 (4)	1414 (3)	−361 (2)	770 (22)
C(18)	3248 (3)	1602 (3)	2892 (2)	571 (17)	C(43)	1882 (3)	294 (3)	−190 (2)	769 (21)
C(19)	−994 (3)	5271 (2)	1593 (2)	498 (14)	C(44)	1665 (3)	−126 (2)	610 (2)	656 (19)
C(20)	364 (3)	4681 (2)	3277 (2)	574 (16)	C(45)	1061 (3)	586 (2)	1243 (2)	514 (15)
C(21)	1515 (3)	4087 (2)	1741 (2)	650 (18)					

Table 3. *Positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^3$) *for complex* (3) *with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} U_{22} U_{33})^{1/3}$.

	x	y	z	U_{eq} (Å^2)		x	y	z	U_{eq}/U (Å^2)
Fe(1)	1238 (1)	664 (1)	7015 (1)	36 (1)	C(16)	1464 (10)	2674 (14)	4305 (10)	60 (13)
C(1)	1097 (7)	1704 (8)	6489 (7)	32 (8)	C(17)	1485 (10)	3110 (11)	4981 (11)	73 (13)
C(2)	1621 (7)	1703 (7)	7316 (7)	31 (7)	C(18)	1367 (9)	2769 (10)	5968 (10)	62 (11)
C(3)	873 (7)	1642 (7)	7658 (7)	29 (7)	C(19)	2475 (8)	2058 (8)	7605 (7)	28 (8)
C(4)	350 (7)	1629 (7)	6841 (7)	26 (7)	C(20)	3201 (9)	1634 (9)	7746 (9)	52 (10)
C(5)	550 (7)	1634 (7)	8357 (7)	31 (7)	C(21)	3993 (8)	1990 (13)	8006 (9)	43 (12)
C(6)	1067 (7)	1737 (7)	9233 (7)	31 (8)	C(22)	4042 (11)	2744 (11)	8108 (10)	66 (13)
C(7)	2010 (7)	1678 (10)	9296 (9)	49 (10)	C(23)	3323 (11)	3155 (9)	7962 (9)	60 (12)
C(8)	818 (9)	1105 (9)	9770 (8)	51 (10)	C(24)	2554 (10)	2820 (9)	7718 (8)	52 (10)
C(9)	883 (9)	2489 (9)	9551 (9)	56 (11)	Dichloromethane molecule, s.o.f. = 0·5				
C(10)	1977 (9)	370 (8)	6458 (10)	53 (10)	C(25)	0	3663 (30)	7500	2000*
O(10)	2456 (8)	184 (8)	6101 (8)	102 (10)	Cl(25)	576 (26)	4495 (25)	7394 (27)	2000*
C(11)	425 (9)	−15 (8)	6589 (8)	43 (9)					
O(11)	−73 (7)	−456 (6)	6363 (7)	68 (8)	Pentane molecule, s.o.f. = 0·5				
C(12)	1721 (9)	157 (8)	7918 (10)	50 (11)	C(26)	265 (69)	4756 (55)	8206 (64)	291 (45)
O(12)	2044 (8)	−203 (7)	8446 (8)	84 (10)	C(27)	*380 (61)*	*4705 (53)*	*10353 (61)*	*219 (38)*
C(13)	1244 (7)	2017 (8)	5723 (8)	35 (8)	C(28)	311 (83)	4810 (60)	9332 (82)	300 (48)
C(14)	1242 (8)	1581 (9)	5045 (8)	48 (10)	C(29)	909 (52)	4675 (44)	10161 (53)	193 (34)
C(15)	1362 (11)	1925 (13)	4347 (11)	70 (13)	C(30)	−526 (72)	4849 (63)	8967 (69)	299 (51)

* Fixed.

The most prominent feature in (2) is the coordination of the Fe(CO)$_3$ group to the four-membered ring, which is very similar to the pure cyclobutadiene complexes. As we have shown previously (Straub, Döring & Winter, 1979; Winter & Butters, 1981*b*), the usual central position of the Fe above the four-membered ring in tricarbonyl(cyclobutadiene)iron complexes (Efraty, 1977) is disturbed by fusion of the four-membered ring with a benzene ring. In other words, the benzene ring tries to retain its aromatic sextet and the

Table 4. *Bond lengths* (Å) *between non*-H *atoms in* (2) *with e.s.d.'s in parentheses*

Fe(1)–C(1)	2·072 (2)	C(5)–C(28)	1·469 (3)
Fe(1)–C(2)	2·096 (2)	C(6)–C(7)	1·488 (3)
Fe(1)–C(9)	2·084 (2)	C(6)–C(34)	1·479 (3)
Fe(1)–C(10)	2·076 (2)	C(7)–C(8)	1·353 (3)
Fe(1)–C(19)	1·776 (2)	C(8)–C(9)	1·463 (3)
Fe(1)–C(20)	1·787 (3)	C(8)–C(15)	1·528 (3)
Fe(1)–C(21)	1·787 (3)	C(9)–C(10)	1·465 (3)
C(1)–C(2)	1·464 (3)	C(10)–C(40)	1·475 (3)
C(1)–C(10)	1·458 (3)	C(11)–C(12)	1·537 (3)
C(1)–C(22)	1·475 (3)	C(11)–C(13)	1·537 (4)
C(2)–C(3)	1·469 (3)	C(11)–C(14)	1·540 (3)
C(2)–C(9)	1·468 (3)	C(15)–C(16)	1·518 (4)
C(3)–C(4)	1·354 (2)	C(15)–C(17)	1·524 (4)
C(3)–C(11)	1·534 (3)	C(15)–C(18)	1·525 (4)
C(4)–C(5)	1·509 (3)	C(19)–O(1)	1·143 (3)
C(4)–C(7)	1·491 (3)	C(20)–O(2)	1·141 (3)
C(5)–C(6)	1·369 (3)	C(21)–O(3)	1·143 (4)

Mean distance in the phenyl rings: 1·384 (4).

Table 5. *Bond angles* (°) *between non*-H *atoms in* (2) *with e.s.d.'s in parentheses*

C(19)–Fe(1)–C(20)	96·7 (1)	C(7)–C(8)–C(9)	109·4 (2)
C(19)–Fe(1)–C(21)	94·6 (1)	C(7)–C(8)–C(15)	125·3 (2)
C(20)–Fe(1)–C(21)	99·9 (1)	C(15)–C(8)–C(9)	125·2 (2)
C(10)–C(1)–C(2)	90·6 (1)	C(8)–C(9)–C(10)	144·9 (2)
C(10)–C(1)–C(22)	130·1 (2)	C(8)–C(9)–C(2)	123·1 (2)
C(22)–C(1)–C(2)	135·6 (2)	C(2)–C(9)–C(10)	90·2 (1)
C(1)–C(2)–C(3)	144·0 (2)	C(9)–C(10)–C(1)	89·8 (2)
C(1)–C(2)–C(9)	89·4 (2)	C(9)–C(10)–C(40)	136·0 (2)
C(3)–C(2)–C(9)	124·4 (2)	C(1)–C(10)–C(40)	130·6 (2)
C(2)–C(3)–C(4)	109·4 (2)	C(3)–C(11)–C(12)	109·6 (2)
C(2)–C(3)–C(11)	123·6 (2)	C(3)–C(11)–C(13)	110·9 (2)
C(11)–C(3)–C(4)	127·0 (2)	C(3)–C(11)–C(14)	110·9 (2)
C(3)–C(4)–C(5)	146·8 (2)	C(12)–C(11)–C(13)	110·2 (2)
C(3)–C(4)–C(7)	125·3 (2)	C(12)–C(11)–C(14)	106·9 (2)
C(5)–C(4)–C(7)	87·3 (1)	C(13)–C(11)–C(14)	108·2 (2)
C(4)–C(5)–C(6)	91·8 (2)	C(8)–C(15)–C(16)	109·1 (2)
C(4)–C(5)–C(28)	138·8 (2)	C(8)–C(15)–C(17)	109·1 (2)
C(28)–C(5)–C(6)	129·1 (2)	C(8)–C(15)–C(18)	113·5 (2)
C(5)–C(6)–C(7)	92·8 (2)	C(16)–C(15)–C(17)	109·5 (2)
C(5)–C(6)–C(34)	130·6 (2)	C(16)–C(15)–C(18)	106·4 (2)
C(34)–C(6)–C(7)	136·4 (2)	C(17)–C(15)–C(18)	109·1 (2)
C(6)–C(7)–C(8)	144·4 (2)	Fe(1)–C(19)–O(1)	177·7 (2)
C(6)–C(7)–C(4)	88·0 (2)	Fe(1)–C(20)–O(2)	175·1 (3)
C(4)–C(7)–C(8)	127·4 (2)	Fe(1)–C(21)–O(3)	178·5 (3)

Table 6. *Bond lengths* (Å) *between non*-H *atoms in* (3) *with e.s.d.'s in parentheses*

Fe(1)–C(1)	2·04 (1)	C(2)–C(19)	1·51 (2)
Fe(1)–C(2)	1·98 (1)	C(3)–C(4)	1·46 (1)
Fe(1)–C(3)	2·20 (1)	C(3)–C(5)	1·40 (1)
Fe(1)–C(4)	2·22 (1)	C(4)–C(5)	1·43 (1)
Fe(1)–C(10)	1·77 (1)	C(4)–C(6)	1·55 (1)
Fe(1)–C(11)	1·82 (1)	C(6)–C(7)	1·52 (1)
Fe(1)–C(12)	1·80 (2)	C(6)–C(8)	1·55 (2)
C(1)–C(2)	1·47 (1)	C(6)–C(9)	1·49 (2)
C(1)–C(4)	1·48 (1)	C(10)–O(10)	1·14 (2)
C(1)–C(13)	1·48 (2)	C(11)–O(11)	1·13 (1)
C(2)–C(3)	1·47 (1)	C(12)–O(12)	1·13 (1)

Mean distance in the phenyl rings: 1·37 (2).

Table 7. *Bond angles* (°) *between non*-H *atoms in* (3)

E.s.d.'s 1° for all angles.

C(10)–Fe(1)–C(11)	97	C(5)′–C(4)–C(3)	125
C(10)–Fe(1)–C(12)	95	C(3)–C(5)–C(6)	126
C(11)–Fe(1)–C(12)	99	C(3)–C(5)–C(4)′	111
C(2)–C(1)–C(4)	88	C(4)′–C(5)–C(6)	123
C(2)–C(1)–C(13)	132	C(5)–C(6)–C(7)	113
C(4)–C(1)–C(13)	134	C(5)–C(6)–C(8)	109
C(1)–C(2)–C(3)	91	C(5)–C(6)–C(9)	110
C(1)–C(2)–C(19)	127	C(7)–C(6)–C(8)	107
C(3)–C(2)–C(19)	134	C(7)–C(6)–C(9)	108
C(2)–C(3)–C(4)	89	C(8)–C(6)–C(9)	110
C(2)–C(3)–C(5)	147	Fe(1)–C(10)–O(10)	180
C(4)–C(3)–C(5)	124	Fe(1)–C(11)–O(11)	176
C(1)–C(4)–C(3)	91	Fe(1)–C(12)–O(12)	174
C(1)–C(4)–C(5)′	143		

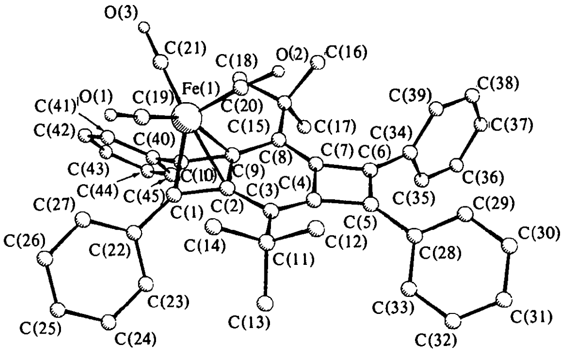


Fig. 1. Perspective view of (2).

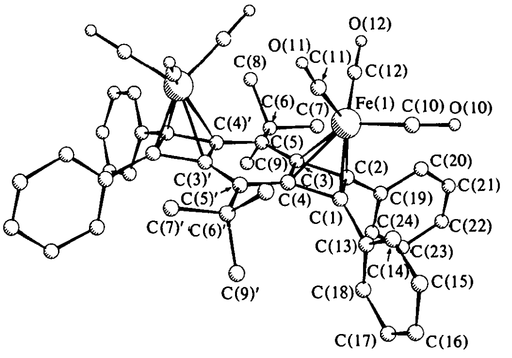


Fig. 2. Perspective view of (3). The twofold crystallographic axis passes through the center of the six-membered ring.

Fe–C distances to the four-membered ring differ by ~0·12 Å. This repulsion effect of the benzene ring is not so distinct in (2). The difference between the Fe(1)–C(1), Fe(1)–C(10) and the Fe(1)–C(2), Fe(1)–C(9) lengths is only about 0·02 Å and their absolute values are typical for pure cyclobutadiene iron complexes. The coordination of the four-membered ring is depicted more clearly in Fig. 3.

Within the error limits, the C(1)–C(2)–C(9)–C(10) ring is planar and square (bond lengths 1·464 ±

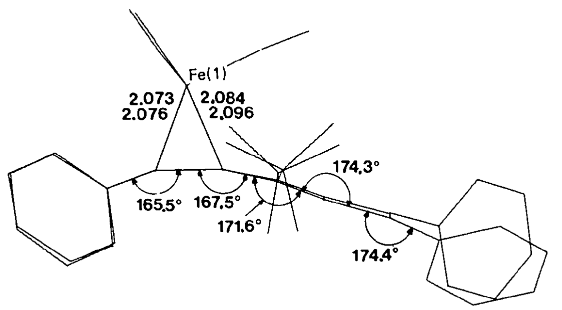


Fig. 3. Side view of (2) along C(1)—C(10) (lengths in Å).

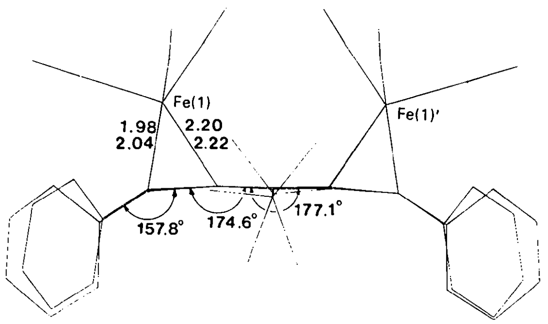


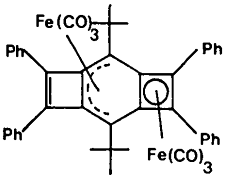
Fig. 4. Side view of (3) along C(1)—C(2) (lengths in Å).

0·006 Å), and the degree of sp^3 hybridization is in the same range at all of these ring atoms. This is also shown in Fig. 3 by the angles at which the substituents are bent out of the cyclobutadiene plane. In comparison, in the (benzocyclobutadiene)tricarbonyliron previously described (Winter & Butters, 1981*b*), the four- and six-membered rings are inclined by only 5° along the corresponding C(2)—C(9) bond.

Of course, the aromatic-type coordination of the $Fe(CO)_3$ group to one of the four-membered rings in (2) has a strong influence on the remaining uncoordinated part of the benzodicyclobutadiene ligand: as shown in Table 4, there is a distinct double-bond fixation in the benzene ring. The differences between long and short bonds are in the range 0·11–0·14 Å, and with respect to the double bonds C(3)—C(4) and C(7)—C(8) [1·354 (2) and 1·353 (3) Å], the six-membered ring behaves more like a 1,3-cyclohexadiene than a benzene ring. Obviously, the ability of the six-membered ring to retain the maximum amount of resonance energy is weakened in (2) by the fusion of a second four-membered ring [C(4) to C(7)].

One could regard the uncoordinated part of the ligand ring system as a benzocyclobutadiene which is fused to a coordinated cyclobutadiene, but this can be done only with some reservations: first the differences between the bond lengths in the six-membered ring are not so pronounced in free benzocyclobutadienes (Tsukada, Shimanouchi & Sasada, 1977, 1978; Winter & Butters, 1981*a*) and, secondly, in all three benzocyclobutadiene structures studied so far, the central ring was more or less planar, whereas the folding of the C(2) to C(9) ring in (2) is somewhat greater (Fig. 3). The electronic state of the monoiron complex (2) is probably best reflected in the usual structural formula (2).

After structure solution of (2), we expected the structure of the diiron complex to be (4), because within the six-membered ring in (2) we had detected a fairly distinct butadiene unit, which is known to coordinate very easily with iron carbonyls (Davis & Pettit, 1970; Krüger, Barnett & Brauer, 1978). As Fig. 4 shows, both tricarbonyliron groups coordinate both four-membered rings. In contrast to (2), the tricarbonyliron groups are not located above the middle of the four-membered rings: they are shifted to the outer double bonds C(1)—C(2) and C(1)'—C(2)'. The side view in Fig. 4 demonstrates how strongly the C(1)—C(2) bonds are coordinated.



(4)

The differences between the Fe(1)—C(1), Fe(1)—C(2) and Fe(1)—C(3), Fe(1)—C(4) lengths are 0·16–0·22 Å and therefore greater by a factor of nearly two in comparison to the tricarbonyl(1,2-di-*tert*-butyl-3,4,5,6-tetramethylbenzocyclobutadiene)iron complex (Winter & Butters, 1981*b*). The coordination mode of the four-membered rings has to be described as intermediate between tetrahapto and dihapto, because the bonds Fe(1)—C(1) and Fe(1)—C(2) [2·04 (1) and 1·98 (1) Å] are much shorter than Fe(1)—C(3) and Fe(1)—C(4) (for a review of Fe—C distances see Krüger *et al.*, 1978) and the phenyl substituents C(13) to C(18) and C(19) to C(24) are bent out of the four-membered ring plane by ~22° (*exo* to Fe). To our knowledge, this latter value is the largest found for cyclobutadiene complexes (for references see Efraty, 1977). In (2), the corresponding angle is 14·5° and in tricarbonyl(1,2-di-*tert*-butyl-3,4,5,6-tetramethylbenzocyclobutadiene)iron (Winter & Butters, 1981*b*), we have found a value of ~16°; in this latter case, the tricarbonyliron group is similarly shifted toward the outer double bond, although not so pronouncedly as in (3). For the only other benzocyclobutadiene complex studied by X-ray diffraction (Davis & Pettit, 1970), data concerning the coordination geometry are not available.

Figs. 3 and 4 show that the central benzodicyclobutadiene ligand remains more planar in (3), because the coordination to the C(3)—C(4) and C(3)′—C(4)′ atoms is weaker.

A further interesting question is to what extent the six-membered ring retains its aromatic resonance energy. Regarding the geometry of the six-membered ring, there are only two bond lengths which are slightly different within the error limits: shorter bonds C(3)—C(5), C(4)—C(5)′, C(5)—C(4)′ and C(3)′—C(5)′ with 1·40–1·43 (1) Å, and longer bonds C(3)—C(4) and C(3)′—C(4)′ with 1·46 (1) Å. This situation is difficult to describe in the usual valence-bond formulae, and we believe that the most suitable description is formula (3): by complexation of both four-membered rings, the benzodicyclobutadiene moiety becomes a fully delocalized system. In analogy to the well-known conversion: anti-aromatic cyclobutadiene → aromatic tricarbonyl(cyclobutadiene)iron, (3) can be regarded as an organometallic anthracene (von Ragué Schleyer, 1980). Furthermore, the geometric principle of the six-membered ring in (3) resembles the bond-length distribution of the central six-membered ring in anthracene (Cruickshank, 1956, 1957; Pauling, 1960, 1980).

In both structures, the geometries of the *tert*-butyl, phenyl and $Fe(CO)_3$ groups are in the usual range and there are no intra- or intermolecular contacts significantly shorter than the van der Waals contacts.

We think that our present study allows the following conclusion: the $Fe(CO)_3$ group has a strong tendency towards tetrahapto cyclobutadiene coordination and, from this point of view, the ligand system (1) can be classified as benzodicyclobutadiene and not as a benzene with two ‘ethylene handles’.

We are grateful to the Deutsche Forschungsgemeinschaft for financial support of this work.

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