Benzocyclobutadienes.
5.* The Tricarbonyliron Complex of 1,2-Di-*tert*-butyl-3,4,5,6-tetramethylbenzocyclobutadiene

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Abstract

Tricarbonyl(1,2-di-*tert*-butyl-3,4,5,6-tetramethylbenzocyclobutadiene)iron, $C_{23}H_{30}FeO_3$, is monoclinic, $P2_1/c$, $Z = 4$, with $a = 9.279$ (3), $b = 16.400$ (3), $c = 16.070$ (3) Å, $\beta = 120.10$ (2)°. Final $R = 0.048$ for 4656 observed reflections. The tricarbonyliron group coordinates in a tetrahapto mode to the four-membered ring, but the complex may not be regarded as a pure cyclobutadiene complex, because the Fe atom is shifted away from the middle above the four-membered ring, indicating a tendency of the benzene ring to retain some of its resonance energy. The structure of the complexed benzocyclobutadiene moiety is compared with that of the uncomplexed ligand.

Introduction

Since the prediction that cyclobutadiene might be stabilized by transition metals (Longuet-Higgins & Orgel, 1956), many cyclobutadiene metal complexes have been prepared and a considerable amount of structural information has become available on these complexes by X-ray and electron diffraction and by microwave spectroscopy (Efraty, 1977). Surprisingly, there are very few chemical and structural studies on the related benzocyclobutadiene complexes. In a preliminary communication, we described the first synthesis of a benzocyclobutadiene complex (2) with the stable benzocyclobutadiene (1) as starting material, together with some X-ray data of (2) (Straub, Döring & Winter, 1979):

(1)   (2)
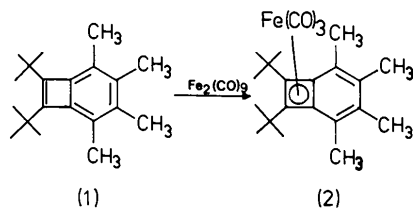
* Part 4: Winter & Butters (1981).

The first benzocyclobutadiene complex characterized by X-ray diffraction (Davis & Pettit, 1970) was prepared by the halobutene route (Efraty, 1977).

In the present paper, we describe the X-ray analysis of the complex (2) and compare it with the structure of the free ligand (1), which we have determined earlier (Winter & Straub, 1978; Winter & Butters, 1981) and which enables us to study the structural changes of a benzocyclobutadiene after complexation.

Experimental

Orange-red crystals (m.p. 477–478 K), suitable for X-ray diffraction, were obtained by recrystallization from hexane. Preliminary Weissenberg and precession photographs showed monoclinic symmetry and systematically extinct reflections typical for the space group $P2_1/c$. A crystal $0.34 \times 0.43 \times 0.50$ mm was mounted on a glass fibre and with an Enraf–Nonius CAD-4 diffractometer (graphite monochromator, Mo $K\alpha$ radiation) cell dimensions were determined by least squares from the measured setting angles of 25 reflections: $a = 9.279$ (3), $b = 16.400$ (3), $c = 16.070$ (3) Å, $\beta = 120.10$ (2)°, $V = 2115.7$ Å^3. Intensities were collected at room temperature in a 2θ range of 6–50° ($\omega/2\theta$ scans). After correction for background, Lorentz and polarization effects, 4658 independent reflections with $I \geq 2\sigma(I)$ were classified as observed and used in further calculations. Absorption corrections were not applied [μ(Mo $K\alpha$) = 0.68 mm^{-1}].

The position of the Fe atom was obtained from a Patterson synthesis and the positions of all non-hydrogen atoms were obtained from a difference map phased on the Fe parameters. The positional and isotropic thermal parameters of these atoms were refined to $R = 0.094$ by full-matrix least squares, minimizing the function $\Delta = \sum w(||F_o| - |F_c||)^2$. After anisotropic refinement, the H atoms were introduced as rigid CH$_3$ groups (C–H = 1.08 Å) and in agreement with a difference synthesis. When refinement converged at $R = 0.059$ (a common isotropic thermal

parameter refined to $\bar{U} = 0.108$ Å^2 for all H atoms), it became obvious that the strong low-angle reflections 230 and 121 were severely affected by secondary extinction. After exclusion of these reflections from further refinement, a final $R = 0.048$ and $R_G = 0.055$ [$R_G = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$] were obtained. The weighting scheme $w = k/[\sigma^2(F_o) + gF_o^2]$ was adopted, in which k and g refined to 0.1101 and 0.0347. The validity of the weighting scheme was demonstrated by the flat variance of $\sum w(F_o - F_c)^2$ versus h,k,l, index parity, F_o and $(\sin \theta)/\lambda$. A final difference synthesis showed no significant peaks.

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 and G. Sheldrick and *PLUTO* by S. Motherwell. Final fractional coordinates, interatomic distances and angles are given in Tables 1–3.*

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* Lists of hydrogen-atom coordinates, thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35965 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^5$ *for* Fe, $\times 10^4$ *for all other non-hydrogen atoms) and U_{eq} values* ($\text{Å}^2 \times 10^4$) *with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}
Fe(1)	40355 (4)	40737 (2)	19927 (2)	312 (2)
O(1)	1444 (2)	2924 (1)	734 (2)	683 (13)
O(2)	3679 (4)	5138 (1)	453 (2)	797 (16)
O(3)	6989 (3)	3248 (2)	2202 (2)	741 (14)
C(1)	2988 (2)	4725 (1)	2622 (1)	349 (9)
C(2)	4795 (3)	4925 (1)	3047 (1)	351 (10)
C(3)	5210 (2)	4130 (1)	3529 (1)	312 (9)
C(4)	3488 (2)	3928 (1)	3131 (1)	324 (9)
C(5)	2989 (3)	3186 (1)	3381 (2)	399 (11)
C(6)	4258 (3)	2711 (1)	4054 (2)	430 (12)
C(7)	5985 (3)	2910 (2)	4449 (2)	417 (12)
C(8)	6506 (3)	3601 (1)	4200 (2)	367 (11)
C(9)	8314 (3)	3790 (2)	4585 (2)	537 (16)
C(10)	7276 (4)	2309 (2)	5151 (2)	645 (18)
C(11)	3829 (4)	1936 (2)	4398 (3)	690 (19)
C(12)	1206 (4)	2915 (3)	2918 (3)	744 (22)
C(13)	1391 (3)	5216 (2)	2232 (2)	499 (13)
C(14)	1034 (5)	5765 (2)	1380 (3)	801 (22)
C(15)	1523 (5)	5737 (3)	3062 (3)	923 (26)
C(16)	−107 (4)	4665 (3)	1891 (4)	782 (24)
C(17)	5882 (3)	5683 (2)	3282 (2)	487 (13)
C(18)	6465 (5)	5911 (2)	4328 (3)	767 (22)
C(19)	7348 (4)	5533 (2)	3126 (3)	731 (20)
C(20)	4945 (5)	6415 (2)	2631 (3)	700 (20)
C(21)	2446 (3)	3369 (1)	1234 (2)	433 (12)
C(22)	3801 (4)	4734 (2)	1063 (2)	506 (13)
C(23)	5837 (3)	3564 (2)	2111 (2)	457 (12)

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

Fe(1)–C(1)	2.023 (3)	C(5)–C(12)	1.501 (4)
Fe(1)–C(2)	2.030 (2)	C(6)–C(7)	1.434 (4)
Fe(1)–C(3)	2.144 (2)	C(6)–C(11)	1.517 (5)
Fe(1)–C(4)	2.144 (3)	C(7)–C(8)	1.369 (4)
Fe(1)–C(21)	1.787 (3)	C(7)–C(10)	1.524 (4)
Fe(1)–C(22)	1.768 (3)	C(8)–C(9)	1.501 (4)
Fe(1)–C(23)	1.792 (3)	C(13)–C(14)	1.530 (5)
C(1)–C(2)	1.495 (3)	C(13)–C(15)	1.536 (6)
C(1)–C(4)	1.489 (3)	C(13)–C(16)	1.512 (5)
C(1)–C(13)	1.518 (3)	C(17)–C(18)	1.532 (5)
C(2)–C(3)	1.466 (3)	C(17)–C(19)	1.523 (6)
C(2)–C(17)	1.525 (3)	C(17)–C(20)	1.542 (4)
C(3)–C(4)	1.431 (3)	C(21)–O(1)	1.137 (3)
C(3)–C(8)	1.435 (3)	C(22)–O(2)	1.141 (4)
C(4)–C(5)	1.429 (3)	C(23)–O(3)	1.129 (4)
C(5)–C(6)	1.373 (3)		

Table 3. *Bond angles* (°) *between non-hydrogen atoms (e.s.d.'s in parentheses)*

C(21)–Fe(1)–C(22)	96.3 (1)	C(6)–C(7)–C(8)	122.6 (2)
C(21)–Fe(1)–C(23)	100.2 (1)	C(6)–C(7)–C(10)	118.0 (2)
C(22)–Fe(1)–C(23)	95.1 (1)	C(10)–C(7)–C(8)	119.3 (2)
C(2)–C(1)–C(4)	88.4 (1)	C(7)–C(8)–C(3)	115.7 (2)
C(2)–C(1)–C(13)	135.3 (2)	C(7)–C(8)–C(9)	122.4 (2)
C(13)–C(1)–C(4)	131.5 (2)	C(9)–C(8)–C(3)	121.8 (2)
C(1)–C(2)–C(3)	89.1 (2)	C(1)–C(13)–C(14)	114.1 (3)
C(1)–C(2)–C(17)	137.9 (2)	C(1)–C(13)–C(15)	107.5 (2)
C(17)–C(2)–C(3)	129.0 (2)	C(1)–C(13)–C(16)	111.2 (2)
C(2)–C(3)–C(4)	91.8 (2)	C(14)–C(13)–C(15)	109.7 (3)
C(2)–C(3)–C(8)	146.4 (2)	C(14)–C(13)–C(16)	106.3 (3)
C(8)–C(3)–C(4)	121.5 (2)	C(15)–C(13)–C(16)	107.8 (4)
C(3)–C(4)–C(1)	90.7 (2)	C(2)–C(17)–C(18)	107.2 (3)
C(3)–C(4)–C(5)	121.2 (2)	C(2)–C(17)–C(19)	111.2 (2)
C(1)–C(4)–C(5)	147.9 (2)	C(2)–C(17)–C(20)	112.9 (2)
C(4)–C(5)–C(6)	115.7 (2)	C(18)–C(17)–C(19)	111.6 (3)
C(4)–C(5)–C(12)	123.0 (2)	C(18)–C(17)–C(20)	108.8 (3)
C(12)–C(5)–C(6)	121.3 (2)	C(19)–C(17)–C(20)	105.1 (3)
C(5)–C(6)–C(7)	123.1 (2)	Fe(1)–C(21)–O(1)	178.4 (3)
C(5)–C(6)–C(11)	119.0 (2)	Fe(1)–C(22)–O(2)	177.3 (3)
C(11)–C(6)–C(7)	117.9 (2)	Fe(1)–C(23)–O(3)	178.8 (2)

Results and discussion

A view of (2) with the atom numbering is given in Fig. 1.

In agreement with (benzocyclobutadiene)tricarbonyliron (Davis & Pettit, 1970), the Fe atom coordinates to the four-membered ring in a tetrahapto mode. The benzo-fusion of this four-membered ring causes some significant alterations in comparison to the usual geometry of pure cyclobutadiene metal complexes. These latter compounds show only small departures from the square ring geometry (mean C—C distance: 1.459 ± 0.012 Å), and in most cases the metal atoms are located equidistant from all four cyclobutadiene C atoms (Efraty, 1977). In (2), short Fe—C(1) and Fe—C(2) bonds of 2.023 (2) and 2.030 (2) Å and long
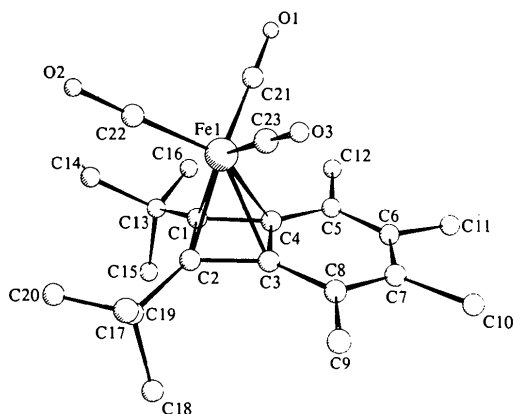
Fig. 1. Perspective view of (2).

Fe—C(3), Fe—C(4) bonds of 2·144 (2) Å are observed. The analogous distances in tricarbonyl(tetraphenyl-cyclobutadiene)iron are all 2·07 (2) Å (Dodge & Schomaker, 1965). This means that the Fe strongly coordinates to the C(1),C(2) atoms, which show, with respect to the C(1)—C(2) distance [1·495 (3) Å] and the valency angles, high sp^3 hybridization. The coordination geometry is depicted more clearly in Fig. 2: the C(3),C(4) bridging atoms retain most of their sp^2 hybridization and the Fe atom is shifted away from the six-membered ring. As a consequence, the four-membered ring (planar within experimental error) is inclined to the six-membered ring (planar within ±0·02 Å) at only 5° (exo with respect to Fe) and the substituent lines C(1)—C(13) and C(2)—C(17) bend out of the cyclobutadiene plane at 16·4 (3) and 15·2 (3)° (Fig. 2).

In the four-membered ring C(1)—C(4) and C(2)—C(3), which are of equal length in the free ligand (Winter & Butters, 1981), are significantly different [1·489 (3) and 1·466 (3) Å]. A possible reason may be sought in the destroyed C_{2v} symmetry, which is shown by the uncomplexed benzocyclobutadiene. The three carbonyl groups of the Fe(CO)₃ unit are rotated by
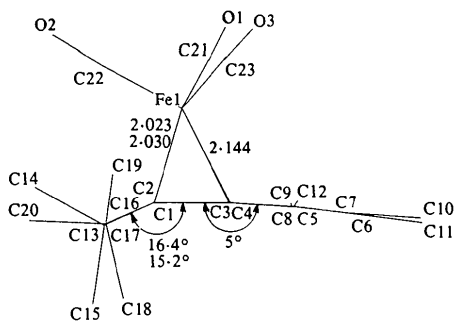
approximately 6° from the C_s symmetry position and the different electronic interactions, connected with this rotation and the shift of the Fe towards C(1)—C(2), may be responsible for these different bond lengths.

The local C_{3v} symmetry of the Fe(CO)₃ group, which has been confirmed by electron diffraction and microwave spectroscopy in tricarbonyl(cyclobutadiene)iron (Oberhammer & Brune, 1969; Lucken, Pozzi & Ramaprasad, 1973) and by X-ray diffraction in tricarbonyl(tetraphenylcyclobutadiene)iron (Dodge & Schomaker, 1965), is no longer retained in the present benzocyclobutadiene complex. The distance from Fe to the carbonyl C(22) is 0·02 Å shorter than the other two Fe—C(carbonyl) distances and the valency angles between the carbonyl groups [95·5 ± 2·5°, ED (Davis & Speed, 1970), 98·1 ± 0·8°, ED (Oberhammer & Brune, 1969) for tricarbonyl(cyclobutadiene)iron; and 96·5 ± 1·7°, X-ray (Dodge & Schomaker, 1965) for tricarbonyl(tetraphenylcyclobutadiene)iron] are 95·1, 96·3 and 100·2° (Table 3). This observation is confirmed by the IR spectrum of (2), which shows a splitting of the E band [2023, 1950 and 1915 (shoulder) cm⁻¹, CCl₄]. In a simple description, the structural differences of the coordination geometry in (2) compared with normal cyclobutadiene complexes reflect the compromise between an aromatic benzene ring and an aromatic cyclobutadiene–Fe(CO)₃ unit.

Irngartinger, Kimling, Krebs & Mäusbacher (1975) have shown that the Fe atom is easily shifted away from the middle above the cyclobutadiene ring by bulky substituents. In our case the Fe(CO)₃ unit shifts towards the bulky tert-butyl groups and this demonstrates clearly the electronic origin of the Fe(CO)₃ shift.

The complexation of the four-membered ring leads to a certain degree of double-bond fixation in the benzene ring. In Fig. 3, the bond lengths in the uncomplexed and complexed ligand are summarized.

The magnitudes of bond localization in the six-membered rings are nearly equal in the two cases, but the sequence of bond orders is reversed in (2). With respect to bond lengths, the six-membered ring must be
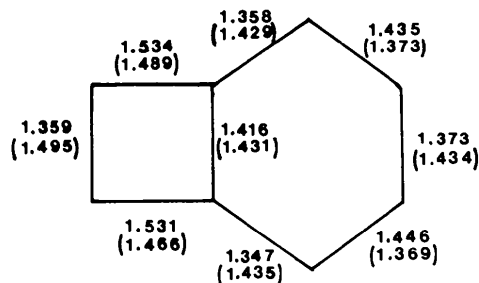

Fig. 2. Schematic view of (2) along C(2)—C(1). (Distances in Å.)

Fig. 3. Schematic representation of bond lengths (Å) in the benzo-cyclobutadiene unit for the uncomplexed (numbers without parentheses, $\bar{\sigma} = 0.003$ Å) and complexed case (numbers in parentheses, $\bar{\sigma} = 0.003$ Å).

regarded as intermediate between a 1,3,5-cyclo-hexatriene and a fully delocalized benzene ring. The corresponding results for the other benzocyclo-butadiene Fe(CO)$_3$ complex studied by X-ray diffraction (Davis & Pettit, 1970) suggest a slightly higher 1,3,5-cyclohexatrienic character, but in this case the benzene ring is substituted by an ester group [$R =$ COOCH$_3$ at the corresponding C(6) or C(7) in (2)]. The electronic influence of this group on the distribution of bond lengths in the six-membered ring remains an open question.

In any case, H—H coupling constants in the ^{1}H NMR spectrum of the parent compound tricarbonyl-(cyclobutadiene)iron have shown that 'the electron demand of the iron tricarbonyl group leads to a reduction of delocalization of π electrons in the benzene ring' (Günther, Wenzl & Klose, 1970; Günther, Shyoukh, Cremer & Frisch, 1978). The retention of some of the delocalization energy in the benzene ring of (2) is supported by the fact that we could not isolate any di- derivative of (2) with a second Fe(CO)$_3$ group at the six-membered ring, although such a reaction was observed with the parent complex under photochemical conditions (Victor & Ben-Shoshan, 1974).

In the free ligand (1), 16 of all 20 C atoms are planar within ±0·04 Å, so that there is considerable repulsion between the alkyl substituents. By complexation of the four-membered ring, this strain is released to some extent, because the *tert*-butyl groups are bent away from Fe and from one another. This is seen by the exocyclic valency angles at C(1) and C(2): in the free ligand, they are 142·4 (2) and 126·9 (2)° at C(1) and 141·8 (2) and 126·7 (2)° at C(2), whereas the corresponding values in (2) are 135·3 (2) and 131·5 (2)° at C(1) and 137·9 (2) and 129·0 (2)° at C(2).

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