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THE DIMER OF HEPTAFULVENEIRON TRICARBONYL

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Summary

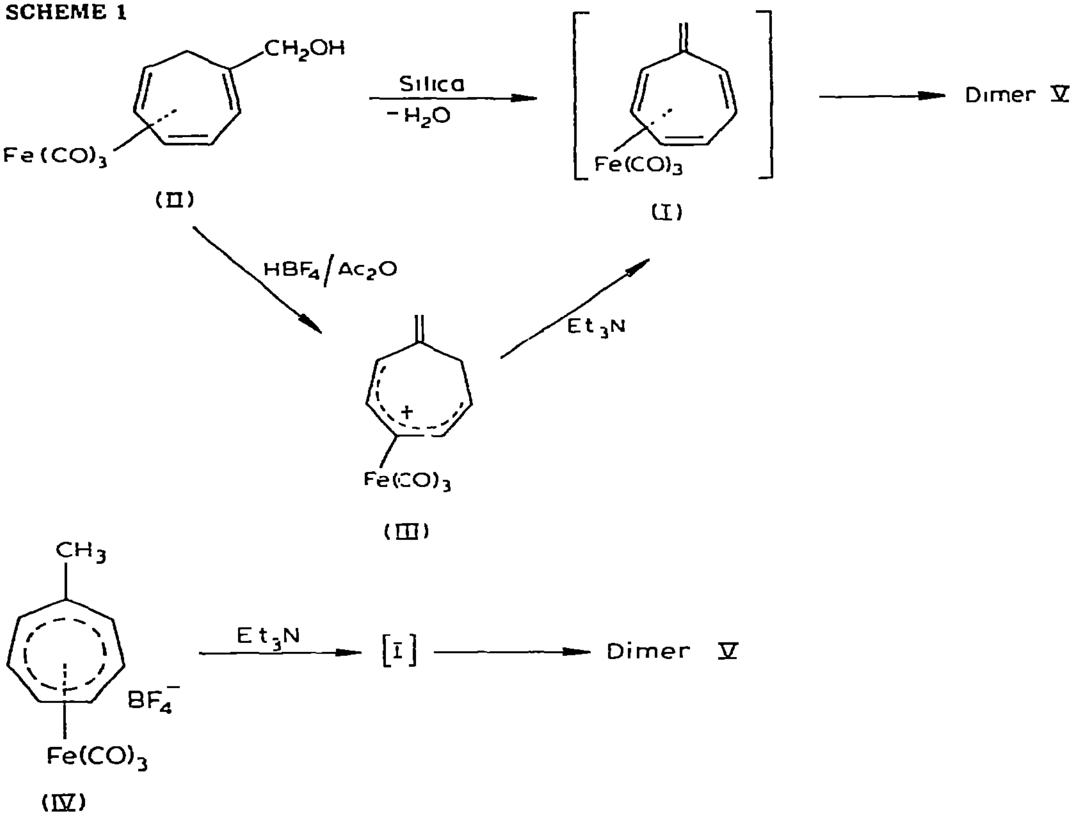
The preparation of the fluxional methyltropyliumiron tricarbonyl from two different precursors is described. Attempts to convert the salt into the parent complex of heptafulvene—$Fe(CO)_3$ provides a dimer, $C_{22}H_{14}Fe_2O_6$, whose structure has been determined by extensive deuterium labelling and NMR spectroscopy, and by X-ray diffraction methods.

The dimer is formed by addition across the exocyclic double bond, the electrocyclic dimerisation [which is the formally non-allowed (8 + 8) π-cycloaddition] being promoted by the metal tricarbonyl fragment. The intramolecular bonding in 3,3'-ethano-1,1'-bis(cyclohepta-2,4,6-trienyl)diiron hexacarbonyl is discussed together with its mechanism of formation.

Introduction

The synthesis and chemistry of iron tricarbonyl complexes of heptafulvene have recently been the subject of a number of reports [1—4]. Attempts to prepare the parent unsymmetrical complex I by dehydration of II gave a dimeric product [1]. Hunt reported that by treating III with triethylamine in ether solution, a dimer, of unidentified structure, was obtained [2]. More recently, Lewis et al. [3] reported their comprehensive studies of heptafulveneiron tricarbonyl chemistry and commented on the structure [5] of the dimer using double-irradiation NMR methods. One of us (A.E.) attempted the use of methyltropylium-iron tricarbonyl as a stable source of complex I, but again treatment of the salt with triethylamine led to the same dimer [3]. A structure determination of the dimer V was achieved by differential deuterium labelling of the various carbon positions and the complete solid state structural analysis described earlier [5] and here agrees with findings based on 100 MHz ^1H NMR spectra in four different labelling experiments coupled with resonance techniques (See Fig. 1 and Table 1).

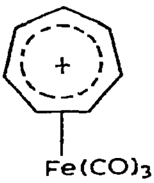
SCHEME 1



Experimental

(i). Synthesis and spectroscopy

Methyltropyliumiron tricarbonyl tetrafluoroborate (IV) was prepared by acid treatment (HBF_4/Ac_2O) of either of the two possible complexed isomeric alcohols VIII and Xa. The secondary alcohol VIII was prepared by $LiAlH_4$ reduction (at −78°) of 4,5,6,7-*tetrahapto*-2-methyltroponetricarbonyliron (VII). The latter was obtained from reaction of 2-methyltropone (VI) [6] with $Fe_2(CO)_9$. The tertiary alcohol Xa was prepared in high yield by addition of methyllithium, at −78°, to troponeiron tricarbonyl (IX) (Scheme 1). The NMR spectrum of IV, at room temperature, was interpreted in terms of a rapid valence tautomerism of the C_7H_7 ring, by analogy to the parent cation tropyliumtricarbonyliron XI [8]*.



(XI)

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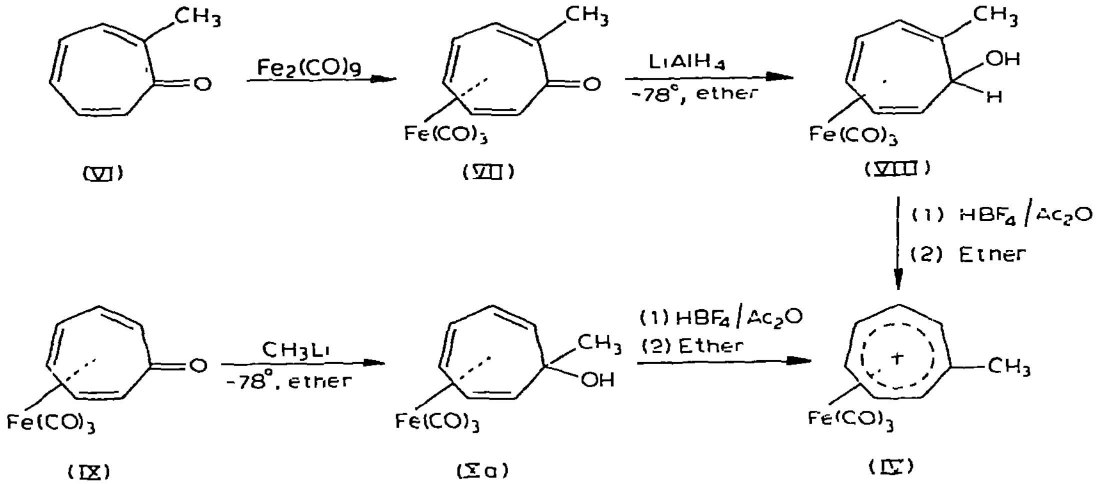
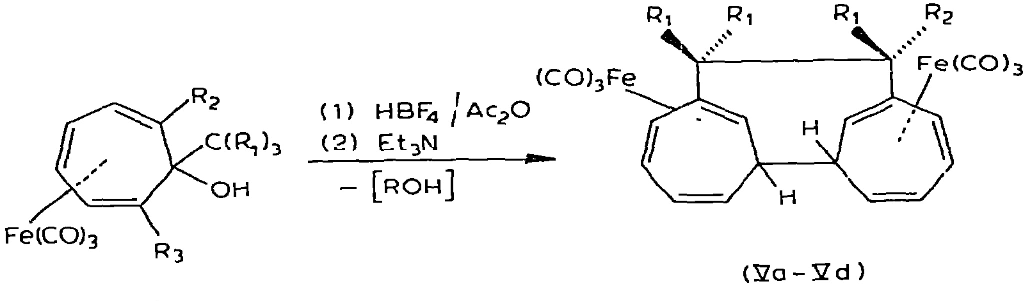
* Full details on the NMR spectra at various temperatures of mono- and di-substituted, tropyliumiron tricarbonyl cations will be published elsewhere.

SCHEME 1



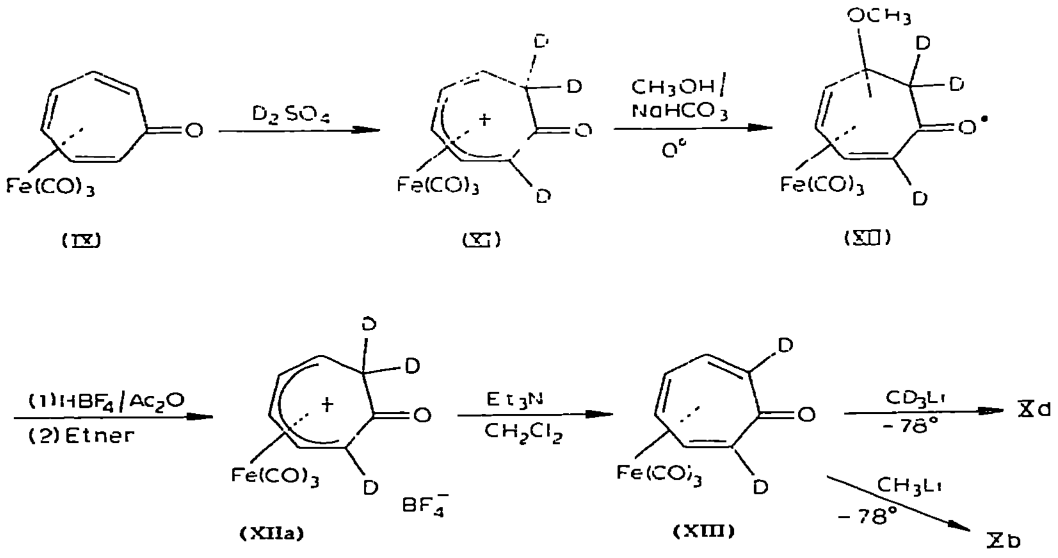
That IV could be prepared from two isomeric alcohols VIII and Xa, strengthens the argument for its fluxional character.

Starting with alcohols Xb—Xd labelled in the shown positions and carrying out the two steps mentioned above, the correspondingly labelled dimers were obtained (dimer Va—Vd could also be prepared in small amounts by passing alcohols Xa—Xd through a silica-gel column which served as a dehydrating agent)



a. $R_1 = R_2 = R_3 = H$
b. $R_2 = R_3 = D$; $R_1 = H$
c. $R_2 = R_3 = H$; $R_1 = D$
d. $R_2 = R_3 = R_1 = D$

Thus Xc is an addition product of CD_3Li to tropenetricarbonyliron at −78°; Xb and Xd were obtained from the reaction of CH_3Li and CD_3Li respectively with 2,7-d_2-troponetricarbonyliron (XIII). To prepare XIII, we made use of the fluxional behaviour of IX in strong acidic media [7a, b]. Thus IX incorporates three deuterium atoms per molecule as cation, when dissolved in D_2SO_4, and then in a simple reaction converts into XIII in good yield (Scheme 2). The structure of alcohols Xa—Xd was established from their mass spectra, elemental analyses and NMR spectra. In the mass spectra of Xa—Xd the most abundant ion is M^+—CO



followed by stepwise losses of two carbon monoxides and by further fragmentation of either HOH or DOH.

^1H NMR spectra were measured on a Varian HA 100 and Jeol-60 Hz instrument. Mass spectra were based on an Atlas CH-4 instrument.

(ii). Synthetic methods

Preparation of methyltropyliumiron tricarbonyl tetrafluoroborate (IV). 790 mg Xa, in 2 ml Ac_2O, were treated with a small excess of HBF_4/Ac_2O prepared from 1.5 ml 40% aq. HBF_4 in 4 ml acetic anhydride) in an ice bath, and the immediate yellow precipitation completed by stirring with 50 ml ether for a few minutes. Filtration, followed by washing with ether, gave 700 mg of a fine yellow salt, m.p. 70°. (Found: C, 40.02; H, 2.64. $C_{11}H_9BF_4FeO_3$ calcd.: C, 39.80; H, 2.71%.) NMR (CD_3NO_2): τ 3.89 (m, 2H), 4.42 m (4H) and 7.9 (s, 3H) ppm.

Dimer V (general method). Excess triethylamine was added to a slurry of IV (250 mg) in methylene chloride (10 ml). Extraction with ether/water and

TABLE 1

NMR PARAMETERS FOR DIMER Va

Chemical shift [a] (τ, ppm)		Coupling constants [b] (Hz)			
H_5	4.23	$J_{4,5}$	11.0	$J_{6,7}$	7.5
H_7	4.75	$J_{4,3}$	4.0	$J_{6,4}$	4.5
H_4	5.04	$J_{4,2}$	2.0	$J_{8a,8b}$	8.0
H_3	7.02	$J_{2,3}$	4.0		
H_6	7.25	$J_{2,7}$	1.5		
H_2	7.47				
H_{8a}	6.92	$J_{5,6}$	8.0		
H_{8b}	7.55	$J_{5,3}$	1.5		
		$J_{5,7}$	1—1.5		

[a] Determined at 100 MHz and relative to TMS. [b] Coupling constants were determined by spin decoupling at 100 MHz of the NMR spectra of the four dimers, Va-Vd.

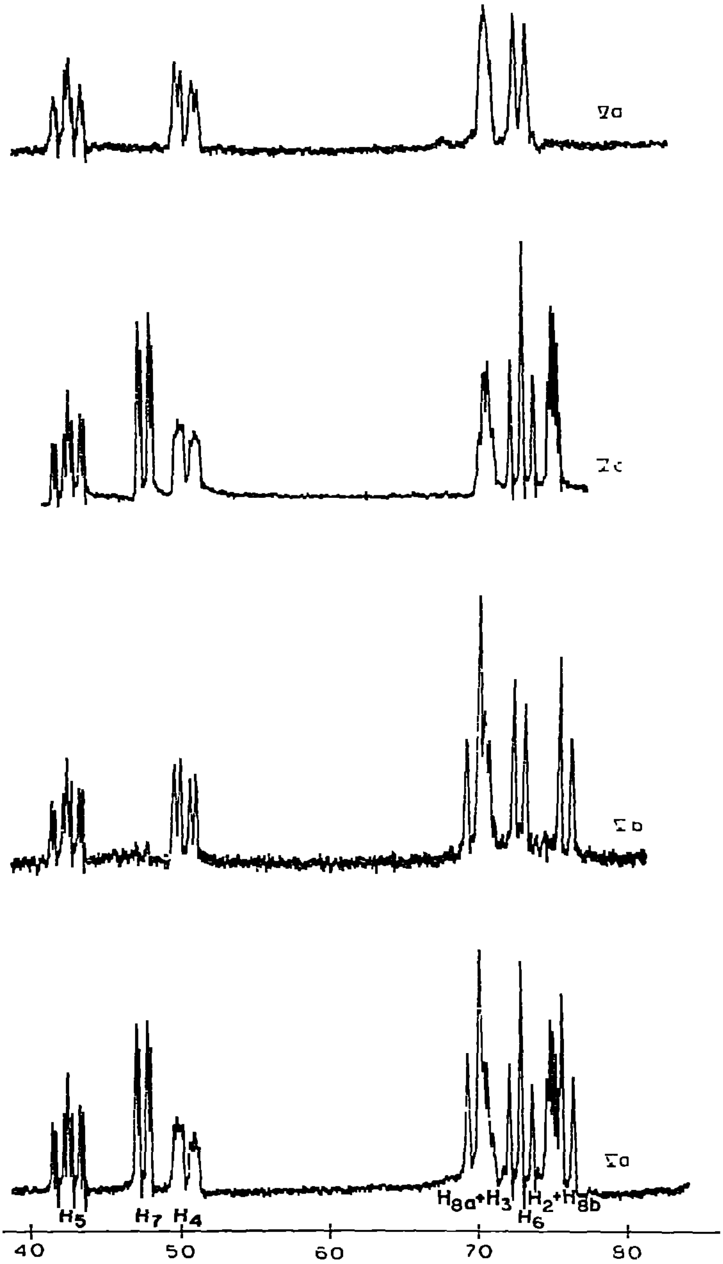
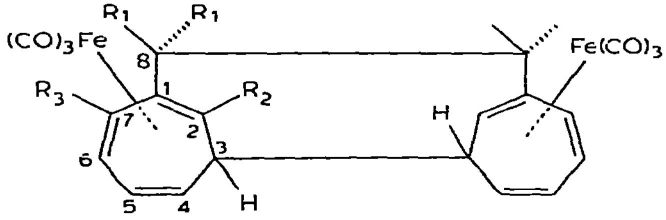


Fig. 1. NMR spectra of the dimers Va—Vd (in $CDCl_3$) at 100 MHz with TMS as internal reference.



(Va : $R_1 = R_2 = R_3 = H$
Vb : $R_2 = R_3 = D$; $R_1 = H$
Vc : $R_2 = R_3 = H$; $R_1 = D$
Vd : $R_2 = R_3 = R_1 = D$)

TABLE 2

DECOUPLING EXPERIMENTS ON THE DIMERS V

Site of irradiation	Chemical shifts (τ, ppm) [a]					
	H$_5$	H$_7$	H$_4$	H$_3$	H$_6$	H$_2$
Dimer Vc	4.23 dt	4.75 dd	5.04 dq	7.02 q (AB)	7.25 t	7.47 pentet
	Fate of the pattern (collapses into):					
H$_5$				t	dd	
H$_7$				m	a	dd
H$_4$				m	t	dd
H$_3$	dd	dd	dd			
H$_6$	dt	narrow ABq	dq			
H$_2$		d	dd			
Dimer Vd	4.23 dt		5.04 dd	7.02 m	7.25 d	
	Collapses into					
H$_5$			d	d	d	
H$_4$	d			d	d	
H$_3$	dd		d			
H$_6$	d		d			

[a] dt = double triplet, q = quartet, m = multiplet, dd = double doublet, t = triplet.

washing with dilute HCl, drying over $MgSO_4$ and evaporation in vacuo, gave a yellow oil (164 mg, 70%) which crystallizes on standing. Recrystallization from hexane (or further purification on AR silica) gave m.p. 162°. (Mass spectrum is th same as reported earlier [3]).

(4,5,6,7-Tetrahapto-2-methyltropone)tricarbonyliron (VI). 2-Methyltropone (2.0 g) and $Fe_2(CO)_9$ (8 g) were stirred in benzene (50 ml) at 55° for 1.5 h. All volatile materials were removed in vacuo to give a red oil, which could either be chromatographed on basic alumina using CH_2Cl_2 as eluent or recrystallized from hexane to afford the product VI as red needles (1.94 g, 45%), m.p. 71–72°. IR (n-hexane): 2062, 2005, 1996 cm^{-1} (M–CO). ($CDCl_3$): 1615 cm^{-1} (C=O). The mass spectrum showed a molecular peak at m/e 260 and successive loss of 4 CO's at m/e 232, 204, 276 and 248. (Found: C, 48.59; H, 3.12; Fe, 22.40. $C_{11}H_8FeO_4$ calcd.: C, 50.83; H, 3.3; Fe, 21.49%.) NMR ($CDCl_3$): τ 3.64 (m, 3H), 6.85 (m, 1H), 8.52 (d, 3H, J = 1.5 Hz).

(4,5,6,7-Tetrahapto-1-methyl-1-hydroxytropylideneiron tricarbonyl (Xa–d). The general method is given for the preparation of Xa: To troponeiron tricarbonyl (1.01 g) in ether (40 ml) at 78° was added a three-fold molar excess of methyllithium in ether (2M). The reaction was stirred at –78° for 0.5 h, hydrolysed with water and dilute HCl (1/4), washed with water, dried over $MgSO_4$ and evaporated in vacuo. The oil obtained was chromatographed on AR silica (cc-7). A small amount of dimer V (92 mg) is eluted first with hexane, and then benzene eluted the next yellow 75% band which was determined to be the alcohol Xa (790 g). Recrystallization from hexane gave m.p. 55–56°. IR (hexane): 2048, 1985 (C=O); ($CDCl_3$): 3590 (OH), 1410, 1264 and 1100 cm^{-1}. (Found: C, 50.52; H, 3.81; Fe, 21.16. $C_{11}H_{10}FeO_4$ calcd.: C, 50.44; H, 3.82; Fe, 21.32%.) NMR of Xa ($CDCl_3$): τ 4.3 (dd, 1H, J = 11 and 8.5 Hz), 4.67 (dt, 1H), 4.97 (ddd, 1H), 6.67 (td, 1H,

J = 7.5 Hz), 7.05 (bt, 1H) and 8.65 (s, 3H); Xb ($CDCl_3$): τ 4.25 (d, 1H, J = 8.5 Hz), 4.4—4.8 (m), 7.04 (dt, 1H, J = 7.5 Hz), 8.1 (s, 1H) and 8.65 (s, 3H) ppm.

(2,7-d_6-Tropone)iron tricarbonyl (XIII). To a solution of IX (1.94 g) in 5 ml dry methylene chloride was added sulphuric acid-d_2, the reaction mixture being stirred for 12 h. The organic layer was removed by decanting and the acid layer poured onto a vigorously stirred slurry of sodium carbonate in CH_3OH at 0°. After 15 min, the methanolic solution was diluted with water, and, after complete evolution of CO_2, the mixture was extracted with CH_2Cl_2 (3 × 15 ml). The combined CH_2Cl_2 extracts were washed with water, saturated NaCl solution, dried over $MgSO_4$ and evaporated. The resulting yellow residue could be purified on basic alumina (eluted with CH_2Cl_2) and recrystallized from hexane to give XI as yellow plates, m.p. 79° [7], mass spectrum m/e 281, 253 ($M^+ - CO$), 225 ($M^+ - 2CO$), ($M^+ - 3CO$), 167 ($M^+ - 3CO + CH_2O$). NMR ($CDCl_3$): τ 4.38 (m, 2H), 6.73 (d, 1H), 6.65 (s, 3H), 6.1 (bs, 1H). Treatment of XII in 3 ml Ac_2O with a little excess of HBF_4/Ac_2O yielded the cation XII (2.12 g) which was worked up by the same procedures as for IV. Triethylamine was added to a suspension of the salt (2.12 g) in 5 ml CH_2Cl_2, the yellow colour of the solution turning deep-red on generation of 2,7-d_2-tropone. The usual work-up afforded 1.4 g (82%) of XIII, the isotope purity of which was found to be > 91% by the NMR spectrum; ($CDCl_3$): τ 3.44 (d, 1H, J = 8.0 Hz), 3.62 (d, 2H), 7.28 (pentet, 1H).

(4,5,6,7-Tetrahapto-2-methyl-1-hydroxytropylidene)iron tricarbonyl (VIII). An excess of lithium aluminium hydride was added slowly to a vigorously stirred solution of VI (500 mg) in 50 ml ethyl ether at −78°. The solution was then allowed to warm and water (2 ml) added cautiously with stirring, followed by 20 ml dilute HCl (1/4). The ether layer was washed with dilute aqueous sodium chloride and dried and evaporated at reduced pressure to give a yellow oil, which was further purified on basic alumina column: 320 mg (64%). NMR ($CDCl_3$): τ 4.35 (dd, 1H, J = 9 Hz), 4.6 (pentet, 2H), 6.45 (m, 2H), 6.9 (d, 1H), 8.32 (d, 3H), 8.68 (s, 1H). Alcohol VIII is very sensitive and oxidizes readily to the corresponding ketone, VI.

(iii). Crystallography

Crystal data: $C_{22}H_{14}Fe_2O_6$, M = 486. Orthorhombic, a = 13.59 (3), b = 15.11 (3), c = 20.32 (4) Å, Z = 8, U = 4173 Å^3; D_m = 1.52 g cm^{-3} (flotation in aqueous zinc chloride), D_c = 1.55 g cm^{-3}. Space group *Pbca* from systematic absences $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$. The unit cell data are based on a least squares analysis of high angle reflexions on Weissenberg photography (Cu-K_α, λ = 1.5418 Å) and precession photographs (Mo-K_α, λ = 0.7107 Å).

The crystals were yellow blocks and intensity data were obtained from one of dimensions 0.035 × 0.010 × 0.009 cm. Integrated reflexion intensities were obtained by ω-scan methods on a Pailred diffractometer, all reflexions within the layers h, 0—9, l being surveyed. Reflexion intensities were accepted as observed if independent background measurements did not differ significantly (3σ) and if $F^2_{obs} \geqslant 2.5\ \sigma(F^2_{obs})$. 771 independent reflections resulted which were corrected for the usual geometrical factors but not for absorption (μ Mo-K_α = 14.3 cm^{-1}).

The structural analysis was completed by a combination of Patterson and repetitive Fourier analyses and refined by full-matrix least squares methods to dis-

TABLE 3

THE DIMER OF HEPTAFULVENEIRON TRICARBONYL: ATOMIC PARAMETERS FROM THE X-RAY ANALYSIS AND THEIR E.S.D.'S (FRACTIONAL COORDINATES × 10^4)

Atom	x/a	y/b	z/c	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe1	4631 (2)	1009 (3)	2172 (3)	3.81	4.53	3.33	0.46	0.81	0.13
Fe2	3191 (2)	3427 (3)	−5 (2)	3.08	3.92	3.72	−0.21	0.70	−0.12
O1	4077 (12)	2719 (20)	2783 (10)	7.5					
O2	3049 (12)	782 (14)	1147 (8)	6.6					
O3	3509 (14)	−306 (18)	2997 (10)	8.4					
O4	9570 (12)	384 (14)	663 (8)	6.5					
O5	3877 (12)	3902 (16)	1316 (9)	7.5					
O6	4245 (12)	3210 (18)	4783 (8)	7.1					
C1	4192 (17)	2034 (24)	2544 (13)	4.8					
C2	3645 (16)	873 (22)	1558 (11)	4.6					
C3	3927 (21)	261 (28)	2677 (14)	7.3					
C4	9025 (16)	828 (22)	390 (10)	4.3					
C5	3605 (18)	3737 (22)	768 (10)	6.2					
C6	3820 (17)	2540 (21)	4873 (11)	4.7					
C7	6098 (13)	2408 (17)	1668 (9)	2.5					
C8	5481 (14)	1617 (20)	1475 (9)	3.5					
C9	5702 (13)	704 (20)	1559 (10)	3.7					
C10	5866 (15)	358 (22)	2209 (12)	4.9					
C11	5886 (15)	960 (23)	2762 (11)	5.1					
C12	6432 (13)	1774 (20)	2803 (10)	3.5					
C13	6596 (13)	2389 (21)	2345 (9)	3.8					
C14	1679 (14)	76 (19)	4027 (10)	4.0					
C15	1943 (13)	1056 (19)	4568 (9)	3.2					
C16	2368 (13)	1709 (19)	4081 (8)	3.0					
C17	1933 (13)	2582 (18)	3901 (9)	3.3					
C18	1489 (15)	3157 (20)	4433 (11)	4.7					
C19	1546 (14)	1989 (20)	73 (12)	4.6					
C20	1922 (15)	2763 (21)	447 (11)	4.3					
C21	1735 (15)	3667 (19)	221 (10)	4.1					
C22	1771 (14)	110 (19)	4355 (10)	4.0					

TABLE 4

THE IRON HEPTAFULVENE DIMER. MOLECULAR PARAMETERS AND THEIR E.S.D.'S

Intramolecular bond lengths (Å)			
(a). Metal—carbon bonds			
Fe1—C1	1.783 (34)	Fe2—C4	1.780 (27)
Fe1—C2	1.746 (22)	Fe2—C5	1.732 (27)
Fe1—C3	1.733 (35)	Fe—C6	1.710 (30)
Fe1—C8	2.125 (22)	Fe2—C16	2.179 (18)
Fe1—C9	2.073 (20)	Fe2—C15	2.059 (20)
Fe1—C10	2.065 (24)	Fe2—C21	2.062 (21)
Fe1—C11	2.199 (22)	Fe2—C20	2.195 (24)
(b). Carbon—carbon bonds			
C8—C9	1.42 (4)	C16—C15	1.51 (3)
C9—C10	1.44 (3)	C15—C21	1.42 (3)
C10—C11	1.45 (4)	C21—C20	1.46 (4)
C11—C12	1.44 (4)	C20—C19	1.49 (4)
C12—C13	1.33 (4)	C19—C18	1.32 (3)
C13—C7	1.53 (3)	C18—C17	1.51 (3)
C7—C8	1.51 (4)	C17—C16	1.49 (4)
C7—C17	1.64 (3)		
C9—C14	1.52 (3)		
C14—C22	1.63 (3)		
C22—C15	1.51 (4)		
(c) Carbon—oxygen bonds			
C1—O1	1.15 (4)	C4—O4	1.14 (3)
C2—O2	1.17 (3)	C5—O5	1.20 (3)
C3—O3	1.22 (4)	C6—O6	1.18 (4)
Bond angles (degrees)			
C1—Fe1—C2	103.2 (1.3)	C4—Fe2—C5	91.1 (1.2)
C1—Fe1—C3	101.1 (1.5)	C4—Fe2—C6	99.1 (1.3)
C2—Fe1—C3	91.1 (1 3)	C5—Fe2—C6	101.5 (1.3)
C1—Fe1—O1	173 (2)	C4—Fe2—O4	176 (3)
C2—Fe1—O2	180 (3)	C5—Fe2—O5	176 (3)
C3—Fe1—O3	176 (3)	C6—Fe2—O6	179 (2)
C8—C9—C10	120 (2)	C16—C15—C21	120 (2)
C9—C10—C11	119 (3)	C15—C21—C20	122 (2)
C10—C11—C12	126 (2)	C21—C20—C19	121 (2)
C11—C12—C13	130 (2)	C20—C19—C18	131 (3)
C12—C13—C7	124 (2)	C19—C18—C17	126 (2)
C13—C7—C8	118 (2)	C18—C17—C16	120 (2)
C7—C8—C9	128 (2)	C17—C16—C15	126 (2)
C8—C7—C17	109 (2)	C7—C17—C16	108 (2)
C13—C7—C17	109 (1)	C7—C17—C18	109 (2)
C10—C9—C14	120 (3)	C16—C15—C21	120 (2)
C8—C9—C14	120 (2)	C21—C15—C22	121 (2)
C9—C14—C22	106 (2)	C15—C22—C14	107 (2)

crepancy indices of $R_1 = 0.070$ and $R_2 = 0.069$. The least squares function minimised was $\Sigma w(|F_o| - |F_c|)^2$, the weights w of observations being, $w = (18.00 - 0.009 F_o + 6.4 \times 10^{-5} F_o^2)^{-\frac{1}{2}}$.

For the final cycle of least squares, $\Sigma w\Delta^2/N-V$, where N is the total number of reflexions and V the least squares variables, is 1.535 and terminal coordinate shifts were all less than 0.7 σ.

Scattering factors used were those for Fe(O), O and C, the iron factor being corrected for the real part of anomalous dispersion; no contribution from hydrogen atoms was included. Atomic parameters are listed in Table 3, bond lengths

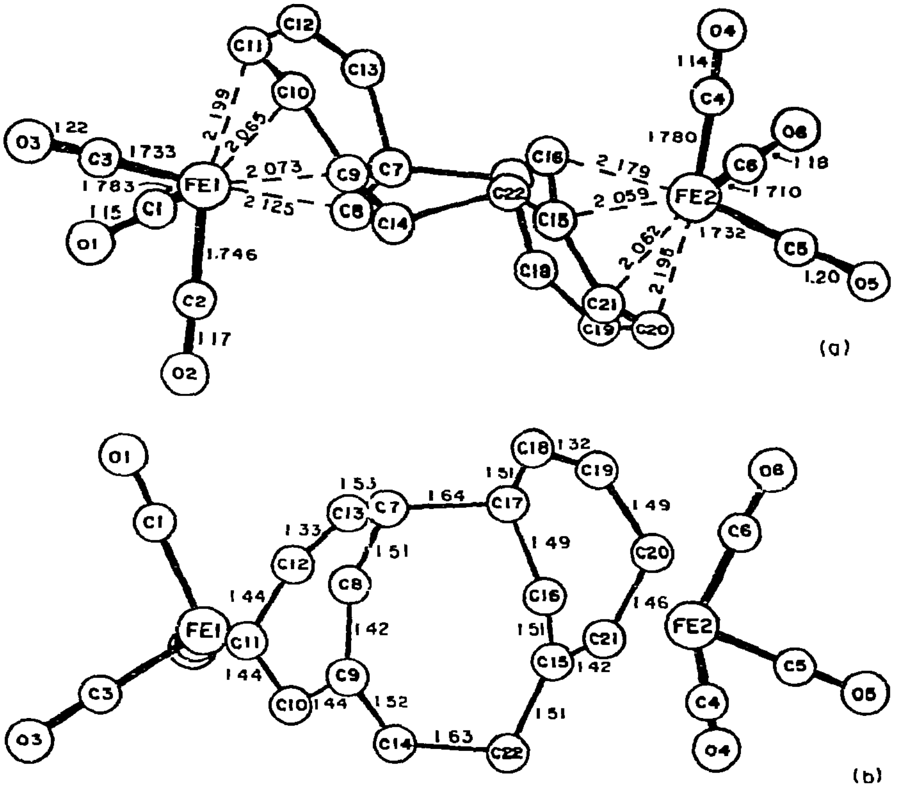


Fig. 2. Dimeric heptafulveneiron tricarbonyl: (*a*) atom labelling and metal—ligand bond lengths, (*b*) bond lengths in the tricyclic ligand.

and angles in Table 4. Atom labelling and important dimensions are shown in Figs. 2a and 2b. A listing of observed and calculated structure factor amplitudes may be obtained from one of the authors (R.M.).

Discussion

The molecular structure

The magnetic resonance and crystallographic data indicate the complex as 3,3′-ethano-1,1′-bis(cyclohepta-2,4,6-trienyl)diiron hexacarbonyl, with diene fragments of the tricyclohexadecahexaene ligand bound to iron tricarbonyl moieties. It is well established, and in accord with the rare gas 'rule' [5, 9], that cyclic polyenes adopt a dihedral conformation on bond formation with, say, the four-electron acceptor iron tricarbonyl fragment and the conformations of the two crystallographically non-equivalent cycloheptatrienyl rings are very similar. The dihedral angle between the planes containing C8, C9, C10 and C11 (direction cosines of the normal 0.9764, 0.1711, —0.1319; r.m.s. deviation of atoms from the mean plane, Δ = 0.02 Å) and C7, C8, C11, C12, C13 (direction cosines 0.8011, —0.4816, —0.3553; r.m.s. Δ = 0.02 Å) is 41.7° while that betweeen C15, C16, C20 and C21 (direction cosines 0.9236, —0.2641, —0.2778;

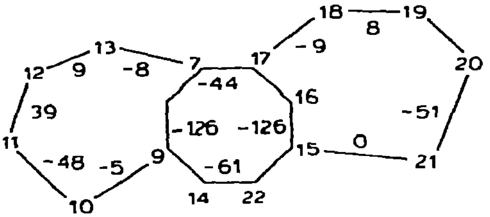


Fig. 3. Torsion angles in the tricyclic ligand (°).

r.m.s. Δ 0.00 Å) and C16, C17, C18, C19 and C20 (direction cosines 0.8889, 0.4529, −0.6787; r.m.s. Δ = 0.02 Å) is 43.9°. The two diene fragments are surprisingly, perhaps, only 26.7° from strict parallelness.

The eight-membered ring can be seen to have a slightly distorted crown conformation, the torsion angles (degrees) in the tricyclic ligand being shown in Fig. 3.

The general stereochemistry of the diene—iron tricarbonyl groups follows the general pattern summarised some time ago [10] and which has been more precisely analysed in a recent publication [11]. The iron—terminal carbon (butadiene) bond length averages 2.18 Å while that to the 'inner' carbon atoms is of length 2.06 Å. While the carbon—carbon bond lengths C11—C10, C10—C9 and C8—C9 are, as expected, identical within experimental error, there seem to be some significant differences in the remaining diene fragment; however, our inclination is to believe that this reflects systematic underestimates in the standard deviations.

The observed head-to-head dimerisation poses some mechanistic problems. It would seem possible to develop a rational mechanistic scheme involving the trimethylenemethaneiron tricarbonyl complex (1,6,7,8,h^4-heptafulveneiron tricarbonyl) as an intermediate but Kerber and Ehntholt [4] have summarized evidence that the 1,6,7,8,h^4-isomer is more stable than 1,2,3,4,h^4-heptafulveneiron tricarbonyl. It seems obvious that dimerisation is via a radical reaction but it is unclear why 1,2,3,4 coordination, with diene fixation, stabilises radical character on the exocyclic carbon. In any event, a knowledge of the dimerisation or polymerisation mechanism of the free hydrocarbon seems indispensable before discussions of the iron—carbonyl promoted reaction can be taken further.

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