Crystal Structure of a Hexafluoropropene Adduct of Tricarbonyl(cyclohexa-1,3-diene)iron: 1,1,1,1-Tetracarbonyl-2,3,3-trifluoro-3a,4,5,7a-tetrahydro-5-(1,1,2,3,3,3-hexafluoropropyl)-2-trifluoromethyl-1-ferra-indane

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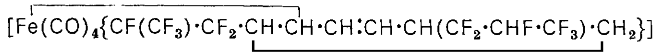
An *X*-ray crystallographic investigation of the structure of



$[Fe(CO)_4\{CF(CF_3){\cdot}CF_2{\cdot}CH{\cdot}CH{\cdot}CH{:}CH{\cdot}CH(CF_2{\cdot}CHF{\cdot}CF_3){\cdot}CH_2\}]$

has shown that the addition of hexafluoropropene to tricarbonyl(cyclohexa-1,3-diene)iron takes place in the molar ratio 2 : 1 and that the hexafluoropropene adds *endo* to the iron atom. It is the CF_2 end of the $CF_2{:}CF(CF_3)$ molecule which becomes attached to the C_6 ring. A possible mechanism is discussed. Crystals are monoclinic, space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions $a = 13.056(7)$, $b = 11.493(6)$, $c = 13.503(7)$ Å, $\beta = 106.92(4)°$. The structure was solved by direct methods from 2 523 independent observed intensities measured on a four-circle diffractometer, and refined to R 0.063.

ULTRAVIOLET irradiation of a hexane solution of hexafluoropropene and tricarbonyl(cyclohexa-1,3-diene)iron leads to the formation of three products.[1] One of these (the subject of this study) can be shown by elemental analysis to be mononuclear and to contain two molecules of hexafluoropropene, but spectroscopic evidence does not lead to a clear stereochemical configuration. As the elucidation of the mechanism of formation of the product required an unambiguous assignment of the orientation and position of the $CF_2{\cdot}CHF(CF_3)$ group relative to the iron atom, this crystallographic study was undertaken.

EXPERIMENTAL

Crystals of the title compound grow as pale yellow plates. The crystal chosen for data collection was 0.35 × 0.32 × 0.20 mm; intensities were measured on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[2] Of the 3 058 independent reflections (to 2θ 50°), 2 523 were considered observed, having $I/\sigma(I) \geqslant 2.5$. No significant crystal decay was observed during data collection, and because of the small value of μ no correction was made for *X*-ray absorption.

RESULTS

Crystal Data.—$C_{16}H_8F_{12}FeO_4$, $M = 548.1$, Monoclinic, $a = 13.056(7)$, $b = 11.493(6)$, $c = 13.503(7)$ Å, $\beta = 106.92(4)°$, $D_c = 1.88$ g cm^{-3}, $Z = 4$, $D_m = 1.86$ g cm^{-3}, $F(000) = 1\,080$. Space group $P2_1/n$. Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 9.48 cm^{-1}. Attempts to solve the structure by vector methods failed, because although the Fe atoms could be easily located (R 0.53) successive electron-density difference syntheses did not reveal positions for the lighter atoms (for Fe, $x \sim \frac{1}{4}$, $z \sim 0$). Direct methods[3] were therefore attempted, and of many possible solutions obtained, all those which did not look chemically plausible were rejected. Of the other, the correctness of the one given is established by its successful refinement. Refinement was by blocked-matrix least squares, with isotropic thermal parameters for all carbon atoms, anisotropic thermal parameters for iron and all fluorine and oxygen atoms, and invariant positional and thermal parameters for the hydrogen atoms (U_H 110% U_C); this led to R 0.063 (R' 0.074). Weights were applied according to $1/w = 1.03 + 0.027\,05|F_o|$, and this scheme gave a satisfactory weight analysis. In the final difference-synthesis the largest peaks were 0.5 eÅ^{-3} in the vicinity of the iron atom, with values much lower than this

TABLE 1

Atomic positional and isotropic thermal parameters ($B = 8\pi^2U$), with estimated standard deviations in parentheses

Atom	x	y	z	$10^2U/Å^2$
Fe	0.246 07(9)	0.212 40(10)	0.988 18(9)	
C(11)	0.356 2(8)	0.108 9(9)	1.023 5(7)	6.1(2)
O(11)	0.426 3(7)	0.045 8(7)	1.049 5(7)	
C(12)	0.310 5(7)	0.295 5(7)	1.105 8(6)	4.9(2)
O(12)	0.353 4(5)	0.345 7(6)	1.177 6(5)	
C(13)	0.309 1(7)	0.300 6(8)	0.906 4(7)	6.1(2)
O(13)	0.351 6(6)	0.350 2(7)	0.858 0(6)	
C(14)	0.172 9(8)	0.116 9(9)	0.882 1(8)	6.3(2)
O(14)	0.130 2(7)	0.052 2(7)	0.821 4(5)	
C(1)	0.168 3(6)	0.110 9(7)	1.081 4(6)	4.8(2)
C(2)	0.239 4(6)	0.078 9(7)	1.185 2(6)	4.8(2)
C(3)	0.223 6(7)	0.102 3(7)	1.274 5(7)	5.3(2)
C(4)	0.124 1(6)	0.169 3(7)	1.282 7(6)	4.6(2)
C(5)	0.085 9(6)	0.250 1(7)	1.188 9(6)	5.0(2)
C(6)	0.065 8(6)	0.178 2(7)	1.089 0(6)	4.8(2)
C(7)	0.026 8(6)	0.251 6(7)	0.992 5(6)	4.8(2)
C(8)	0.114 2(6)	0.319 6(7)	0.963 4(6)	4.4(2)
C(9)	0.073 9(7)	0.381 5(8)	0.857 9(7)	5.7(2)
C(41)	0.146 6(6)	0.238 3(7)	1.381 6(6)	4.7(2)
C(42)	0.186 5(7)	0.165 4(8)	1.481 5(7)	5.6(2)
C(43)	0.183 0(11)	0.224 2(12)	1.580 5(10)	8.8(3)
F(71)	−0.020 3(4)	0.177 4(5)	0.911 0(4)	
F(72)	−0.055 5(4)	0.323 4(5)	1.000 1(4)	
F(8)	0.135 6(4)	0.416 5(4)	1.031 9(3)	
F(91)	0.144 8(5)	0.459 3(5)	0.846 7(4)	
F(92)	0.058 7(5)	0.305 6(6)	0.779 5(4)	
F(93)	−0.017 8(5)	0.438 0(6)	0.844 5(4)	
F(411)	0.224 1(5)	0.319 7(5)	1.388 5(4)	
F(412)	0.056 7(4)	0.297 5(5)	1.382 8(4)	
F(42)	0.119 3(6)	0.067 4(6)	1.471 2(5)	
F(431)	0.226 5(7)	0.160 1(7)	1.660 6(4)	
F(432)	0.081 1(10)	0.241 2(12)	1.579 3(6)	
F(433)	0.229 2(12)	0.321 6(8)	1.589 8(6)	
H(1)	0.146	0.038	1.050	6.4
H(2)	0.301	0.035	1.185	7.1
H(3)	0.276	0.079	1.339	7.5
H(4)	0.073	0.112	1.280	6.7
H(42)	0.256	0.140	1.489	7.8
H(51)	0.021	0.288	1.190	7.1
H(52)	0.139	0.309	1.190	7.1
H(6)	0.014	0.119	1.088	6.7

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[1] M. Green, B. Lewis, J. J. Daly, and F. Sanz, *J.C.S. Dalton*, 1975, 1118.

[2] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

[3] G. M. Sheldrick, SHELX 75, direct methods programme for the solution of centrosymmetric structures.

elsewhere. In the last cycle the mean shift-to-error ratio was 0.05.

Positional and isotropic thermal parameters are in Table 1, interatomic distances and bond angles in Table 2. Atomic scattering factors were the analytic types of ref. 4 for iron (corrected for anomalous dispersion: $\Delta f'$ 0.35, $\Delta f''$ 0.95),[5] fluorine, oxygen, and carbon, and those of ref. 6 for hydrogen. All computational work was carried out (on the CDC 7600 of the University of London) by use of the '*X*-Ray' system of programmes.[7] Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21977 (9 pp., 1 microfiche).*

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances

Fe–C(11)	1.820 (10)	C(7)–C(8)	1.526 (12)
Fe–C(12)	1.834 (8)	C(7)–F(71)	1.386 (9)
Fe–C(13)	1.858 (11)	C(7)–F(72)	1.382 (10)
Fe–C(14)	1.837 (9)	C(8)–F(8)	1.422 (9)
C(11)–O(11)	1.140 (13)	C(9)–F(91)	1.327 (12)
C(12)–O(12)	1.128 (10)	C(9)–F(92)	1.342 (11)
C(13)–O(13)	1.127 (14)	C(9)–F(93)	1.327 (11)
C(14)–O(14)	1.127 (12)	C(4)–C(41)	1.507 (12)
Fe–C(1)	2.172 (9)	C(41)–C(42)	1.544 (12)
Fe–C(8)	2.065 (8)	C(42)–C(43)	1.510 (17)
C(1)–C(2)	1.484 (10)	C(41)–F(411)	1.362(10)
C(1)–C(6)	1.575 (12)	C(41)–F(412)	1.360 (10)
C(2)–C(3)	1.311 (13)	C(42)–F(42)	1.410 (12)
C(3)–C(4)	1.541 (12)	C(43)–F(431)	1.295 (15)
C(4)–C(5)	1.538 (11)	C(43)–F(432)	1.341 (19)
C(5)–C(6)	1.544 (12)	C(43)–F(433)	1.260 (18)
C(6)–C(7)	1.511 (11)		

(*b*) Angles

Fe–C(11)–O(11)	177.3(9)	Fe–C(8)–C(9)	117.9(6)
Fe–C(12)–O(12)	177.6(8)	C(3)–C(4)–C(41)	112.1(6)
Fe–C(13)–O(13)	176.5(9)	C(5)–C(4)–C(41)	109.9(7)
Fe–C(14)–O(14)	175.3(9)	C(4)–C(41)–C(42)	114.7(7)
C(11)–Fe–C(1)	87.9(4)	C(41)–C(42)–C(43)	116.2(8)
C(11)–Fe–C(12)	89.1(4)	C(6)–C(7)–F(71)	107.6(6)
C(11)–Fe–C(13)	93.4(5)	C(6)–C(7)–F(72)	110.1(7)
C(11)–Fe–C(14)	90.3(4)	C(8)–C(7)–F(71)	107.6(7)
C(8)–Fe–C(1)	84.6(3)	C(8)–C(7)–F(72)	111.6(7)
C(8)–Fe–C(12)	88.9(3)	F(71)–C(7)–F(72)	104.6(6)
C(8)–Fe–C(13)	94.1(4)	C(7)–C(8)–F(8)	104.7(7)
C(8)–Fe–C(14)	90.6(4)	Fe–C(8)–F(8)	111.4(4)
C(1)–Fe–C(12)	87.2(4)	C(9)–C(8)–F(8)	101.0(6)
C(12)–Fe–C(13)	93.4(4)	C(8)–C(9)–F(91)	110.8(6)
C(13)–Fe–C(14)	94.7(4)	C(8)–C(9)–F(92)	111.3(7)
C(14)–Fe–C(1)	84.6(4)	C(8)–C(9)–F(93)	113.8(8)
C(11)–Fe–C(8)	172.4(4)	F(91)–C(9)–F(92)	107.2(8)
C(12)–Fe–C(14)	171.8(5)	F(92)–C(9)–F(93)	106.9(7)
C(13)–Fe–C(1)	178.5(3)	F(93)–C(9)–F(91)	106.6(8)
Fe–C(1)–C(2)	114.2(6)	C(4)–C(41)–F(411)	111.8(8)
Fe–C(1)–C(6)	108.9(5)	C(4)–C(41)–F(412)	109.1(6)
C(6)–C(1)–C(2)	111.7(7)	C(42)–C(41)–F(411)	104.9(6)
C(1)–C(2)–C(3)	126.5(8)	C(42)–C(41)–F(412)	109.6(8)
C(2)–C(3)–C(4)	122.1(7)	F(411)–C(41)–F(412)	106.4(6)
C(3)–C(4)–C(5)	108.9(7)	C(41)–C(42)–F(42)	107.8(6)
C(4)–C(5)–C(6)	108.7(7)	C(43)–C(42)–F(42)	105.5(9)
C(5)–C(6)–C(1)	113.1(6)	C(42)–C(43)–F(431)	111.5(11)
C(5)–C(6)–C(7)	112.4(7)	C(42)–C(43)–F(432)	109.8(9)
C(1)–C(6)–C(7)	107.3(7)	C(42)–C(43)–F(433)	110.4(12)
C(6)–C(7)–C(8)	114.7(6)	F(431)–C(43)–F(432)	106.6(12)
C(7)–C(8)–Fe	107.7(5)	F(432)–C(43)–F(433)	108.4(14)
C(7)–C(8)–C(9)	113.2(6)	F(433)–C(43)–F(431)	110.0(10)

DISCUSSION

The molecular structure of the title compound is given in Figure 1,[8] together with the crystallographic numbering of the atoms, and the packing is shown in Figure 2. In diagrammatic form the structure is † (I) and the reason for undertaking this study was to try to shed light on the mechanism of formation of this adduct from tricarbonyl(cyclohexa-1,3-diene)iron and hexafluoropropene.

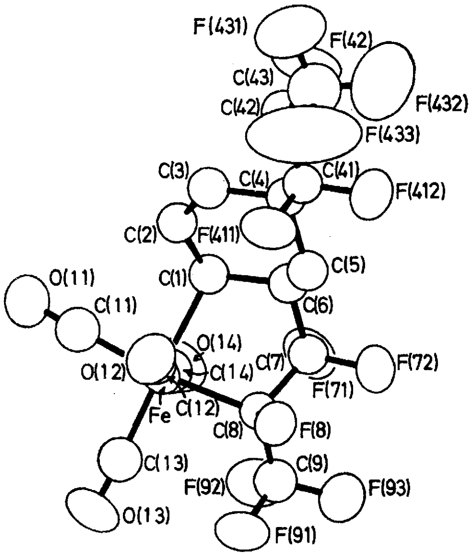
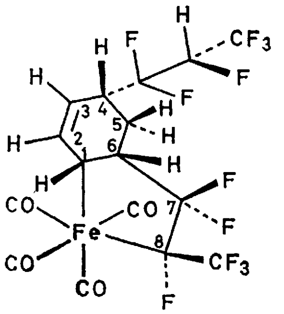


FIGURE 1 View of the molecule looking down an axis perpendicular to the least-squares plane through Fe–C(1)–C(6)–C(7)–C(8), showing 50% probability ellipsoids

The geometry of the molecule itself shows no unexpected features.[9] The C–F bond lengths (which are not corrected for libration, although the F atoms, especially of the CF_3 groups, show high thermal activity) have a mean value of 1.351 Å; the standard value is 1.379 Å. The Fe–C and C–C bonds all have expected



(I)

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

† The diagrammatic structure given here is the enantiomorph of that given in the crystallographic Tables and Figures. This enables immediate comparisons to be made with the various structures given in similar diagrammatic form in ref. 1 and in Scheme 1.

[4] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[5] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[6] R. F. Stewart, E. Davidson, and W. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[7] Technical Report TR 192, Computer Science Center, University of Maryland, June 1972.

[8] Drawn with a modified version of C. K. Johnson's ORTEP, by R. Goddard.

[9] *Chem. Soc. Special Publication*, No. 18, London, 1965.

values, and the stereochemical configuration of the Fe atom is close to ideal octahedral (Table 2).

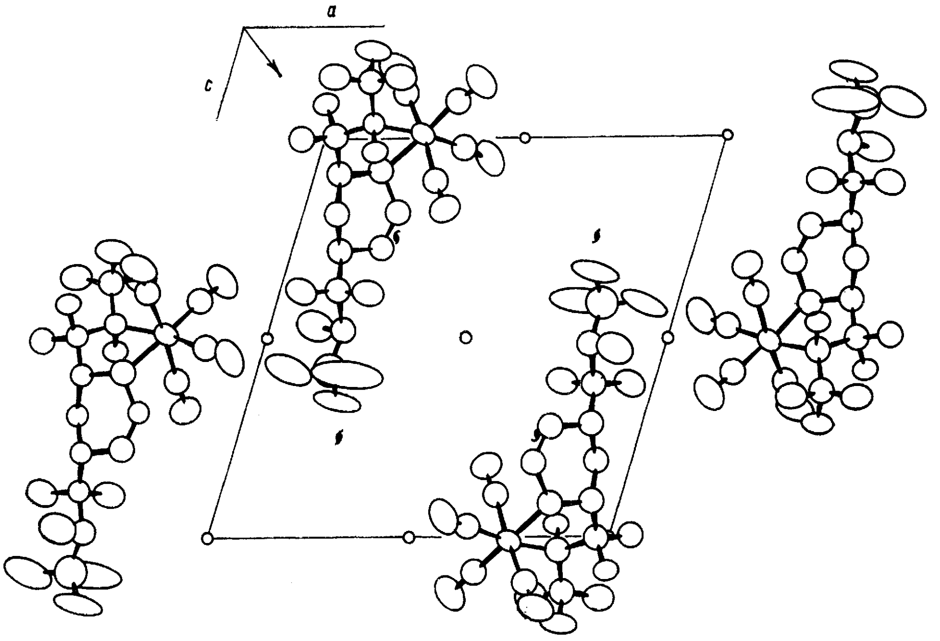


FIGURE 2 Arrangement of molecules relative to the unit cell, viewed down *b*, looking towards the origin. For clarity, molecules which are superimposed in the actual unit cell have been separated and placed in the adjoining cells

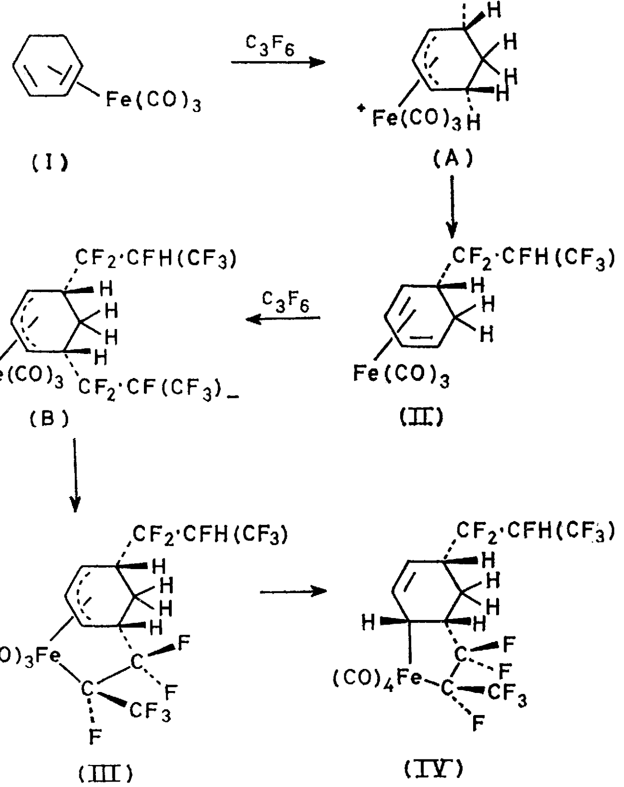
The ferracyclopentane ring shows distortions from planarity characterised by the torsion angles (Table 3), and although the cyclohexene ring is likewise non-planar, the atom sequence C(1)—(4) remains planar because of the double bond between C(2) and C(3) [deviations from the mean plane: C(1) —0.001, C(2) 0.002, C(3) —0.002, C(4) 0.001 Å].

TABLE 3

Some torsion angles (°)

Fe–C(8)–C(7)–C(6)	40.7
F(81)–C(8)–C(7)–C(72)	48.1
F(81)–C(8)–C(7)–C(6)	−102.0
C(9)–C(8)–C(7)–F(71)	53.1
C(9)–C(8)–C(7)–F(72)	−61.0
F(81)–C(8)–C(7)–F(71)	162.2
C(8)–C(7)–C(6)–C(1)	−46.8
F(72)–C(7)–C(6)–C(1)	−173.4
F(71)–C(7)–C(6)–C(1)	72.7
C(7)–C(6)–C(1)–Fe	−28.9

The feature of greatest significance in the structure is that the two hydrogen atoms attached to the carbon atoms of the ring junction, C(1)–C(6), lie in a (—)-*syn*-periplanar [10] conformation with respect to one another. It can therefore be inferred, following the mechanistic patterns discussed by Green *et al.*,[1] that the original addition of hexafluoropropene to the tricarbonyl(cyclohexadiene)iron took place *endo* to the iron atom. Furthermore, it is at the CF_2-end of the hexafluoropropene molecule that addition occurs. A possible mechanism, involving ionic intermediates (A) and (B), is given in the Scheme. The formation of (II) from (I) is clearly facilitated by the stereochemistry of the intermediate (A), as the allyl attachment keeps the five-carbon-atom chain planar and makes a 1,5-interaction especially favourable. Hence the carbanion chain readily abstracts a proton with re-formation of the diene system. A second molecule of hexafluoropropene now adds to the diene system, giving (B), followed by ring closure to yield (III). Finally, by addition of another



SCHEME

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[10] W. Klyne and V. Prelog, *Experientia*, 1950, **16**, 521.

molecule of CO, the π-allyl attachment of the Fe atom becomes a σ-bond, with re-formation of the ethylenic bond of the hexene ring. It may be noted that ring closure occurs only at the stage where hydrogen migration is no longer possible, and that the carbanion carbon atom in (B) becomes a chiral centre, at C(8), in the completed structure (IV). The sign of this chirality will determine whether C(9) lies above or below the plane of the Fe–C(8)–C(7) moiety. The structure as determined had the configuration given in the Scheme.*

An alternative mechanism of formation of (IV), involving simultaneous co-ordination of propene and cyclohexadiene to the iron atom followed by ring condensation, cannot be either preferred or rejected on the basis of the present results.

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* The configuration is opposite to that given in diagram (VI) of ref. 1.