Addition of Hexafluorobut-2-yne to Tricarbonyl(cycloheptatriene)iron; Crystal Structure of a Phosphite Derivative of the 2 : 1 Adduct, $[Fe(CO)_2\{P(OCH_2)_3CMe\}(C_7H_8)(C_4F_6)_2]$

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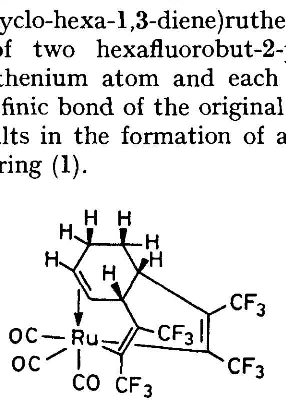
An *X*-ray crystallographic investigation of the structure of $[Fe(CO)_2\{P(OCH_2)_3CMe\}(C_7H_8)(C_4F_6)_2]$ has revealed that the addition of hexafluorobut-2-yne to $[Fe(CO)_3(C_7H_8)]$ takes place in the molar ratio 2 : 1 and that this addition is *endo* to the iron atom. A quadricyclic structure is generated, comprising the original seven-membered ring, two new five-membered rings, and a three-membered bridge ring. A possible mechanism of formation is discussed. Crystals are monoclinic, space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions $a = 8.647(3)$, $b = 29.650(9)$, $c = 9.371(3)$ Å, $\beta = 92.87(3)°$. The structure has been solved by heavy-atom methods from 3 093 independent observed intensities measured on a four-circle diffractometer, and refined to R 0.055 (R' 0.064).

Our earlier investigation[1] into the crystal structure of the adduct formed between hexafluoropropene and tricarbonyl(cyclohexa-1,3-diene)iron has shown that the addition takes place in the molar ratio 2 : 1 and that the hexafluoropropene adds *endo* to the iron atom. We have also shown[2,3] that the addition of hexafluorobut-2-yne to tricarbonyl(cyclo-hexa-1,3-diene)ruthenium leads to the insertion of two hexafluorobut-2-yne molecules between the ruthenium atom and each of the carbon atoms of one olefinic bond of the original cyclohexa-1,3-diene; this results in the formation of a ruthenacyclohepta-2,5-diene ring (1).



(1)

We now present the results of an investigation into the analogous 2 : 1 adduct formed between hexafluorobut-2-yne and tricarbonyl(cycloheptatriene)iron. A remarkably complex quadricyclic structure is generated, but its formation can be understood in terms of a relatively simple mechanism which is discussed. A preliminary report of the structural work has already been given.[2]

EXPERIMENTAL

It was impossible to obtain crystals of $[Fe(CO)_3(C_7H_8)(C_4H_6)_2]$ of sufficient quality for *X*-ray investigation. Accordingly, a simple displacement reaction was utilised with the ligand 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane; this gave good crystals of $[Fe(CO)_2\{P(OCH_2)_3CMe\}(C_7H_8)(C_4F_6)_2]$, and comparison of the n.m.r. spectra[2] for the two species showed that replacement of a terminal CO by $P(OCH_2)_3CMe$ did not cause structural changes.

The dimensions of the yellow prismatic crystal chosen for intensity measurements were 0.43 × 0.30 × 0.33 mm. Intensities were collected to $2\theta = 50°$ on a Syntex $P2_1$ four-circle diffractometer, with Mo-K_α *X*-radiation, at a scan rate which varied from 0.033 to 0.98° s^{-1} as the actual magnitude of a 2-s count varied from 250 to 750. Three check reflections (204, $1\bar{5}5$, $3\bar{9}\bar{1}$) were remeasured every 30 reflections, but no significant decay was observed during 108 h of data collection. Reflections for which $I < 2.5\sigma(I)$ were regarded as unobserved and were not included in either the solution or refinement of the structure. Of the total 4 322 independent reflections, 3 093 were observed.

RESULTS

Crystal Data.—$C_{22}H_{17}F_{12}FeO_5P$, $M = 676.2$, Monoclinic, $a = 8.647(3)$, $b = 29.650(9)$, $c = 9.371(3)$ Å, $\beta = 92.87(3)°$, $U = 2\,399.5(13)$ Å^3, $D_m = 1.86$ g cm^{-3}, $Z = 4$, $D_c = 1.87$ g cm^{-3}, $F(000) = 1\,352$, space group $P2_1/n$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 8.53$ cm^{-1}.

The structure was solved by conventional heavy-atom methods and refined by blocked-matrix least squares, with anisotropic thermal parameters for Fe, F, P, and O only. Hydrogen atoms were located by electron-density difference synthesis and were refined isotropically with $U_H = 1.10\, U_c$ for the C–H bond in question. Weights were applied according to the scheme $1/w = 5.29 - 0.20\,|F_o| + 0.002\,5\,|F_o|^2$, which gave a satisfactory weight analysis. Refinement converged at R 0.055 (R' 0.064), and in the final cycle the mean shift-to-error ratio was 0.000 4. In the final difference synthesis, peaks of ± 0.4 e Å^{-3} appeared in the neighbourhood of the metal atom, with much lower values elsewhere.

Positional parameters are in Table 1, interatomic distances and bond angles in Table 2. No correction for *X*-ray absorption was applied [$\mu(\text{Mo-}K_\alpha) < 10$ cm^{-1}]. 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] carbon, fluorine, oxygen, and phosphorus, and those of ref. 6 for hydrogen. All computational work was carried out on the CDC 7600 computer of the University of London by use of the '*X*-Ray' system of programs.[7] Observed and calculated structure factors, and all thermal parameters, are listed in Supplementary Publication No. SUP 22456 (16 pp.).†

DISCUSSION

The results of the crystal-structure analysis are summarised in Tables 1 and 2. The overall molecular structure, with the crystallographic numbering sequence,

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 1

Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Fe	0.136 49(7)	0.123 55(2)	0.288 59(7)
C(1)	−0.044 1(6)	0.116 9(2)	0.442 0(5)
C(2)	−0.052 3(6)	0.161 0(2)	0.395 2(5)
C(3)	0.000 5(6)	0.203 0(2)	0.468 9(6)
C(4)	−0.004 9(7)	0.209 4(2)	0.628 9(6)
C(5)	−0.019 1(7)	0.166 6(2)	0.714 1(6)
C(6)	0.111 5(6)	0.135 6(2)	0.669 1(6)
C(7)	0.067 5(6)	0.099 4(2)	0.557 9(5)
C(8)	0.150 6(6)	0.209 5(2)	0.559 4(5)
C(9)	0.237 8(6)	0.165 3(2)	0.598 7(5)
C(10)	0.293 1(6)	0.134 4(2)	0.471 7(5)
C(11)	0.211 4(5)	0.091 8(2)	0.473 0(5)
C(61)	0.226 0(7)	0.254 2(2)	0.541 6(7)
F(61)	0.120 7(6)	0.286 6(1)	0.509 6(5)
F(62)	0.302 2(6)	0.268 9(1)	0.659 6(5)
F(63)	0.326 0(6)	0.254 9(2)	0.440 6(5)
C(71)	0.361 1(7)	0.173 6(2)	0.721 9(6)
F(71)	0.481 8(4)	0.198 8(1)	0.687 9(4)
F(72)	0.294 6(4)	0.194 3(1)	0.830 6(3)
F(73)	0.419 2(4)	0.134 6(1)	0.774 5(4)
C(81)	0.461 4(7)	0.139 9(2)	0.433 6(7)
F(81)	0.502 9(4)	0.116 8(2)	0.319 1(4)
F(82)	0.562 0(4)	0.124 9(2)	0.539 8(4)
F(83)	0.495 7(4)	0.182 8(2)	0.411 2(5)
C(91)	0.277 2(7)	0.045 3(2)	0.484 5(6)
F(91)	0.407 2(5)	0.039 1(1)	0.414 7(4)
F(92)	0.314 2(5)	0.034 6(1)	0.621 8(4)
F(93)	0.177 2(5)	0.013 9(1)	0.436 3(5)
Phosphite ligand			
P	−0.036 62(14)	0.093 47(4)	0.142 18(13)
O(11)	0.013 9(4)	0.079 6(2)	−0.014 6(4)
O(12)	−0.181 2(4)	0.125 2(1)	0.106 5(4)
O(13)	−0.116 3(5)	0.047 8(1)	0.190 0(4)
C(111)	−0.105 3(7)	0.058 0(2)	−0.105 3(6)
C(12)	−0.296 3(7)	0.108 3(2)	−0.000 3(6)
C(13)	−0.249 5(7)	0.032 2(2)	0.099 9(6)
C(14)	−0.261 7(6)	0.059 5(2)	−0.037 6(5)
C(15)	−0.387 5(7)	0.041 0(2)	−0.141 6(7)
Carbonyl groups			
C(16)	0.159 3(6)	0.177 1(2)	0.197 3(6)
O(16)	0.180 9(6)	0.210 1(2)	0.140 9(5)
C(17)	0.265 5(6)	0.093 7(2)	0.182 3(6)
O(17)	0.337 5(4)	0.074 2(2)	0.103 5(5)
H(1)	−0.116(6)	0.092(2)	0.411(5)
H(2)	−0.135(6)	0.169(2)	0.326(5)
H(3)	−0.025(6)	0.231(2)	0.411(6)
H(4)	−0.046(6)	0.239(2)	0.665(6)
H(51)	−0.103(6)	0.159(2)	0.701(6)
H(52)	0.005(6)	0.174(2)	0.822(6)
H(6)	0.157(6)	0.121(2)	0.747(6)
H(7)	0.027(6)	0.068(2)	0.596(5)
H(111)	−0.080(6)	0.025(2)	−0.112(6)
H(112)	−0.110(7)	0.073(2)	−0.188(6)
H(121)	−0.294(7)	0.126(2)	−0.078(6)
H(122)	−0.382(7)	0.108(2)	0.047(6)
H(131)	−0.334(7)	0.035(2)	0.154(6)
H(132)	−0.218(7)	0.003(2)	0.072(6)
H(151)	−0.359(7)	0.009(2)	−0.159(6)
H(152)	−0.388(7)	0.058(2)	−0.223(6)
H(153)	−0.466(7)	0.039(2)	−0.104(6)

is in Figure 1, while the molecular packing is shown in relation to the monoclinic unit cell in Figure 2.

As can be seen immediately from Figure 1, addition of two molecules of hexafluorobut-2-yne has taken place on the *endo* face of the cycloheptatriene ring C(1)–C(7), generating two new five-membered rings C(4)–C(5)–C(6)–C(9)–C(8) and C(6)–C(7)–C(11)–C(10)–C(9) together with a three-membered ring $\overline{\text{C(3)–C(4)–C(8)}}$. The iron atom is bonded to this quadricyclic ligand by an olefinic bond C(1)–C(2) originating in the C_7 ring, and to the bis(trifluoromethyl) olefinic bond C(10)–C(11) generated

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances			
Fe–C(1)	2.184(5)	Fe–C(10)	2.156(5)
Fe–C(2)	2.248(5)	Fe–C(11)	2.044(5)
C(1)–C(2)	1.379(7)	C(8)–C(3)	1.526(7)
C(2)–C(3)	1.487(8)	C(8)–C(4)	1.523(8)
C(3)–C(4)	1.514(8)	C(8)–C(9)	1.546(7)
C(4)–C(5)	1.509(9)	C(9)–C(6)	1.572(7)
C(5)–C(6)	1.530(8)	C(9)–C(10)	1.594(7)
C(6)–C(7)	1.532(7)	C(10)–C(11)	1.447(7)
C(7)–C(1)	1.509(7)	C(11)–C(7)	1.526(7)
C(8)–C(61)	1.490(8)	C(10)–C(81)	1.525(8)
C(61)–F(61)	1.348(8)	C(81)–F(81)	1.338(8)
C(61)–F(62)	1.333(8)	C(81)–F(82)	1.363(7)
C(61)–F(63)	1.314(8)	C(81)–F(83)	1.325(8)
C(9)–C(71)	1.551(8)	C(11)–C(91)	1.493(8)
C(71)–F(71)	1.335(7)	C(91)–F(91)	1.341(7)
C(71)–F(72)	1.344(7)	C(91)–F(92)	1.348(7)
C(71)–F(73)	1.345(7)	C(91)–F(93)	1.335(7)
Phosphite ligand			
Fe–P	2.171(1)	O(11)–C(111)	1.453(7)
P–O(11)	1.606(4)	O(12)–C(12)	1.464(7)
P–O(12)	1.588(4)	O(13)–C(13)	1.469(7)
P–O(13)	1.593(4)	C(111)–C(14)	1.523(8)
C(14)–C(15)	1.526(8)	C(12)–C(14)	1.521(8)
		C(13)–C(14)	1.522(8)
Carbonyl groups			
Fe–C(16)	1.820(6)	Fe–C(17)	1.770(6)
C(16)–O(16)	1.132(8)	C(17)–O(17)	1.146(7)
(*b*) Angles			
C(1)–Fe–C(10)	86.0(2)	C(3)–C(8)–C(4)	59.5(3)
C(1)–Fe–C(11)	67.0(2)	C(3)–C(8)–C(9)	114.7(4)
C(2)–Fe–C(10)	90.8(2)	C(4)–C(8)–C(9)	109.2(4)
C(2)–Fe–C(11)	93.3(2)	C(61)–C(8)–C(3)	114.4(5)
C(7)–C(1)–C(2)	125.2(4)	C(61)–C(8)–C(4)	116.7(5)
C(1)–C(2)–C(3)	129.6(5)	C(61)–C(8)–C(9)	124.7(4)
C(2)–C(3)–C(4)	122.8(5)	C(8)–C(9)–C(6)	103.4(4)
C(2)–C(3)–C(8)	126.6(5)	C(8)–C(9)–C(10)	118.0(4)
C(4)–C(3)–C(8)	60.1(3)	C(6)–C(9)–C(10)	103.4(4)
C(3)–C(4)–C(5)	115.2(5)	C(71)–C(9)–C(8)	110.6(4)
C(3)–C(4)–C(8)	60.3(3)	C(71)–C(9)–C(6)	104.0(4)
C(5)–C(4)–C(8)	108.9(5)	C(71)–C(9)–C(10)	115.2(4)
C(4)–C(5)–C(6)	106.2(5)	C(9)–C(10)–C(11)	109.3(4)
C(5)–C(6)–C(7)	116.5(4)	C(81)–C(10)–C(9)	116.0(4)
C(5)–C(6)–C(9)	108.6(4)	C(81)–C(10)–C(11)	124.6(5)
C(7)–C(6)–C(9)	105.2(4)	C(10)–C(11)–C(7)	106.7(4)
C(1)–C(7)–C(6)	112.1(4)	C(91)–C(11)–C(10)	128.4(4)
C(1)–C(7)–C(11)	100.6(4)	C(91)–C(11)–C(7)	114.5(4)
C(6)–C(7)–C(11)	106.0(4)	C(10)–C(81)–F(81)	115.5(5)
C(8)–C(61)–F(61)	111.4(5)	C(10)–C(81)–F(82)	112.0(5)
C(8)–C(61)–F(62)	113.5(5)	C(10)–C(81)–F(83)	111.3(5)
C(8)–C(61)–F(63)	113.8(5)	F(81)–C(81)–F(82)	103.4(5)
F(61)–C(61)–F(62)	104.6(5)	F(81)–C(81)–F(83)	107.2(5)
F(61)–C(61)–F(63)	106.8(5)	F(82)–C(81)–F(83)	106.8(5)
F(62)–C(61)–F(63)	106.1(5)	C(11)–C(91)–F(91)	114.7(5)
C(9)–C(71)–F(71)	115.4(5)	C(11)–C(91)–F(92)	111.0(5)
C(9)–C(71)–F(72)	109.4(5)	C(11)–C(91)–F(93)	112.4(5)
C(9)–C(71)–F(73)	111.5(5)	F(91)–C(91)–F(92)	105.6(5)
F(71)–C(71)–F(72)	107.1(5)	F(91)–C(91)–F(93)	106.5(5)
F(71)–C(71)–F(73)	106.6(5)	F(92)–C(91)–F(93)	106.1(5)
F(72)–C(71)–F(73)	106.4(5)		
Phosphite ligand			
P–Fe–C(1)	83.4(1)	Fe–P–O(11)	118.2(1)
P–Fe–C(2)	89.5(1)	Fe–P–O(12)	113.6(2)
P–Fe–C(10)	161.8(1)	Fe–P–O(13)	117.7(1)
P–Fe–C(11)	121.6(1)	O(11)–P–O(12)	101.9(2)
P–O(11)–C(111)	115.5(3)	O(11)–P–O(13)	100.5(2)
P–O(12)–C(12)	116.2(3)	O(12)–P–O(13)	102.5(2)
P–O(13)–C(13)	116.4(3)	O(12)–C(12)–C(14)	110.4(4)
O(11)–C(111)–C(14)	111.2(4)	O(13)–C(13)–C(14)	109.7(5)
C(111)–C(14)–C(12)	108.3(5)	C(111)–C(14)–C(15)	110.0(4)
C(111)–C(14)–C(13)	108.1(4)	C(12)–C(14)–C(15)	110.3(4)
C(12)–C(14)–C(13)	108.6(4)	C(13)–C(14)–C(15)	111.5(5)

TABLE 2 (*Continued*)

Carbonyl groups

C(16)–Fe–C(17)	95.0(3)	Fe–C(16)–O(16)	176.7(5)
C(16)–Fe–C(1)	119.1(2)	Fe–C(17)–O(17)	173.3(5)
C(16)–Fe–C(2)	82.9(2)	C(17)–Fe–C(1)	144.8(2)
C(16)–Fe–C(10)	99.5(2)	C(17)–Fe–C(2)	171.5(2)
C(16)–Fe–C(11)	139.6(2)	C(17)–Fe–C(10)	97.7(2)
P–Fe–C(16)	98.6(2)	C(17)–Fe–C(11)	93.6(2)
P–Fe–C(17)	82.7(2)		

from one of the acetylene molecules. The four Fe–C bond distances range from 2.04 to 2.25 Å, the longer ones being to the C_7 ring in which the olefinic bond is shorter (Table 2). From the (seemingly significant) variations in bond distances throughout the ring systems some degree of delocalisation in the bonding can be inferred.

Because of the presence of olefinic bonds, the atom sequences C(7)–C(1)–C(2)–C(3) and C(9)–C(10)–C(11)–C(7) are planar. Also, as is often found, the CF_3 ligands show a mean C–F bond length [1.337(8) Å] rather shorter than that found in other compounds (mean for many fluorocarbons 1.379 Å,[8] although the shortening may be apparent rather than real because of the high thermal activity of the fluorine atoms). Moreover, all the F–C–F angles are rather less than the ideal tetrahedral value, suggesting increased *p* character in the C–F bonds and increased *s* character in the C–CF_3 links.

The co-ordination state of the iron atom is approximately trigonal bipyramidal, with one carbonyl group and the C(1)–C(2) link occupying axial sites, the other carbonyl, the phosphite, and the C(10)–C(11) link occupying the equatorial sites. Distances among the carbonyl and phosphite ligands are as expected. There are no unusually short intermolecular contacts in the structure.

Possible mechanisms for the addition of acetylenes to co-ordinated dienes have been discussed previously;[3] the first step is the insertion of one molecule of acetylene between the metal and one atom of an olefinic bond of the diene. If, however, the diene is part of a ring system which contains another olefinic bond, the acetylenic moiety seems to be capable of detaching itself from the metal and joining, again, to one atom of this olefinic bond. If this process occurs twice, as suggested in the Scheme, the resulting molecule for cycloheptatriene will be the quadricyclic moiety found here. In cases where

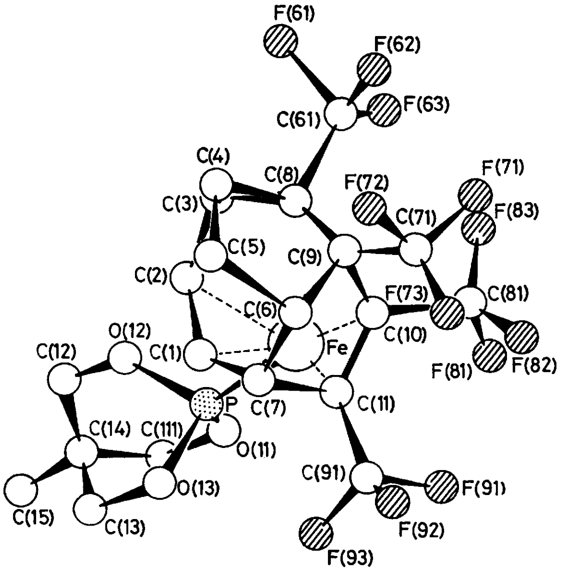


FIGURE 1 Molecular structure of $[Fe(CO)_2\{P(OCH_2)_3CMe\}(C_7H_8)(C_4F_6)_2]$; the two carbonyl groups have been omitted for clarity

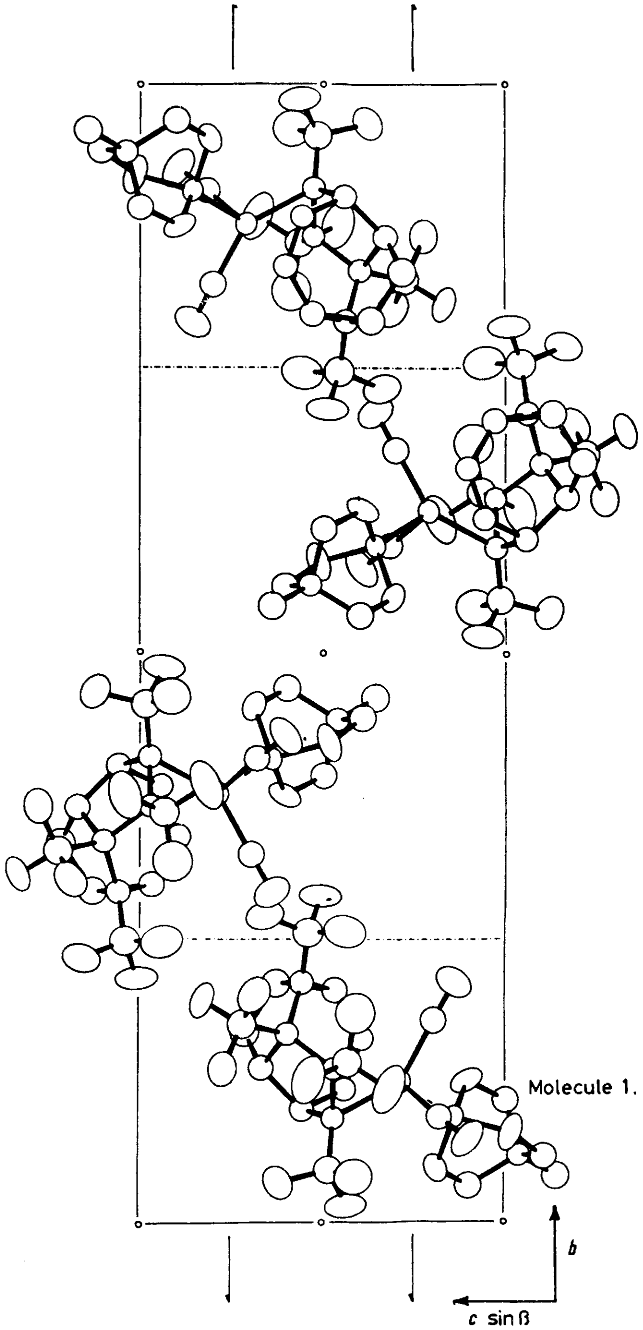
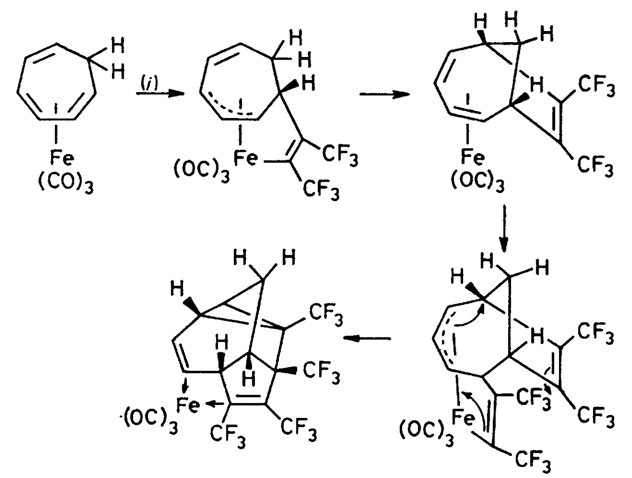


FIGURE 2 Arrangement of molecules in the monoclinic unit cell, viewed down *a* looking towards the origin



SCHEME

an extra olefinic bond is not available {*e.g.* in [Ru(CO)$_3$-(C$_6$H$_8$)]} such detachment of the first molecule of hexafluorobut-2-yne from the metal is not possible; instead, a second molecule of hexafluorobut-2-yne inserts itself between the metal and the other carbon atom of the first olefinic bond.[3] Similar insertions have been reported for cyclo-octa-1,5-diene compounds of rhodium and iridium.[9]

[8/988 *Received*, 26*th May*, 1978]

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