Reactions of Co-ordinated Ligands. Part 21.[1] Reaction of 3,3,3-Trifluoroprop-1-yne with Methyl- and Benzyl-dicarbonyl(η-cyclopentadienyl)iron and of Hexafluorobut-2-yne with Tricarbonyl(1—3-η-2-methylallyl)cobalt. Crystal and Molecular Structure of [1—5-η-*exo*-1-Acetyl-2,4,6-tris(trifluoromethyl)cyclohexadienyl](η-cyclopentadienyl)iron

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The u.v. irradiation of a hexane solution of 3,3,3-trifluoroprop-1-yne and $[\mathrm{FeR(CO)_2(\eta\text{-}C_5H_5)}]$ (R = Me, $\mathrm{CH_2C_6H_5}$, or $\mathrm{C_3H_5}$) affords the vinyl complexes $[\mathrm{Fe\{C(CF_3){=}C(H)R\}(CO)_2(\eta\text{-}C_5H_5)}]$ (R = Me, $\mathrm{CH_2C_6H_5}$, or $\mathrm{C_3H_5}$) arising from *cis* insertion of the acetylene, and η^5-pyranyl complexes $[\mathrm{Fe\{OC(R){-}CH{-}C(CF_3){-}CHC(CF_3)\}(\eta\text{-}C_5H_5)}]$ (R = Me or $\mathrm{CH_2C_6H_5}$). In the case of the methyl and benzyl systems, [1—5-η-*exo*-1-acyl-2,4,6-tris(trifluoromethyl)cyclohexadienyl](η-cyclopentadienyl)iron complexes are also formed. An *X*-ray determination of the molecular structure of the acetyl compound shows that the 3,3,3-trifluoroprop-1-yne molecules have linked head to tail to form a six-membered ring of envelope conformation, with five atoms coplanar and η^5-bonded to the iron atom. The cyclopentadienyl ring is likewise η^5-bonded to the iron and completes a parallel-plane sandwich. The sixth carbon atom of the $\mathrm{C_6}$ ring bends away from the metal, and the acetyl group completes a tetrahedral arrangement around this atom, again bending away (*exo* configuration) in the same sense. The bond lengths in the planar portion of the $\mathrm{C_6}$ ring suggest extensive delocalisation. The crystals are monoclinic, space group $P2_1/n$ (no. 14) with $Z = 4$ in a unit cell of dimensions $a = 13.025(3)$, $b = 10.432(2)$, $c = 12.503(2)$ Å, and $\beta = 101.93(5)°$. The structure has been solved by heavy-atom methods from 3 236 independent intensities measured on a four-circle diffractometer and refined to R 0.056. The possible reaction paths available for the formation of these products are discussed. A reinvestigation of the reaction of hexafluorobut-2-yne with $[\mathrm{Co(CO)_3(\eta^3\text{-}2\text{-}MeC_3H_4)}]$ has afforded only the two compounds $[\mathrm{Co\{C(CF_3){=}C(CF_3)CH_2C[CH_2{-}C(CF_3){=}C(CF_3)H]{=}CH_2\}(CO)_3}]$ and $[\mathrm{Co\{C(CF_3){=}C(CF_3)CH_2C(Me){=}CH_2\}(CO)_3}]$ there being no evidence for the formation of a bis-insertion product.

STUDIES of the reactions of hexafluorobut-2-yne with transition-metal complexes containing carbon to metal σ bonds have led to the isolation of products arising from apparent insertion reactions.[2-8] In seeking to understand more fully the reaction paths which are followed, we have examined the photochemical reaction of the unsymmetrical acetylene 3,3,3-trifluoroprop-1-yne with the iron complexes $[\mathrm{FeR(CO)_2(\eta\text{-}C_5H_5)}]$ (R = Me, $\mathrm{CH_2C_6H_5}$, or $\mathrm{C_3H_5}$). Previously,[5] an acetylide has been implicated in the reaction of $\mathrm{CF_3C_2H}$ with $[\mathrm{RuMe(PPh_3)_2(\eta\text{-}C_5H_5)}]$.

RESULTS AND DISCUSSION

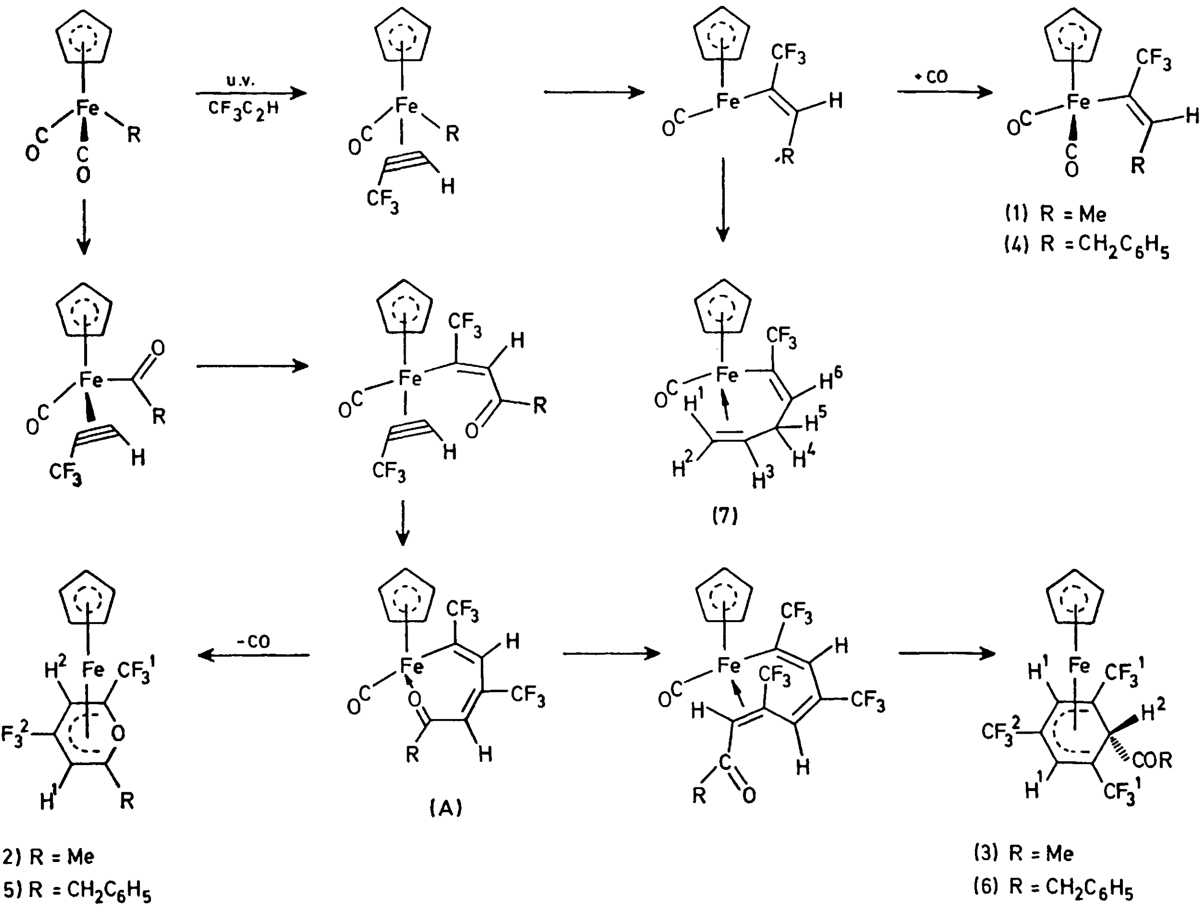
3,3,3-Trifluoroprop-1-yne does not react thermally with either methyl-, benzyl-, or σ-allyl-dicarbonyl(η-cyclopentadienyl)iron; however, u.v. irradiation in hexane solution led to products arising from the insertion into σ-carbon–iron bonds of one, two, and three acetylene molecules. Column chromatography of the reaction mixture obtained from $[\mathrm{FeR(CO)_2(\eta\text{-}C_5H_5)}]$ (R = Me or $\mathrm{CH_2C_6H_5}$) afforded in both cases three complexes (1), (2), (3), and (4), (5), (6) respectively. Repeated attempts to effect a complete separation of (1) from (2) or (4) from (5) were unsuccessful. Structural characterisation was therefore made on the basis of i.r., ^{1}H and ^{19}F n.m.r., and mass spectra obtained with partially separated materials.

Considering first compounds (1) and (2), the i.r. spectrum of the mixture showed only two terminal carbonyl bands at 2 032 and 1 984 cm^{-1} indicating the presence of (1) with the illustrated structure (Scheme 1), this compound arising from the insertion of one $\mathrm{CF_3C_2H}$ molecule into a Fe–Me σ bond. In agreement, the mass spectrum showed a parent ion due to (1), and peaks due to the consecutive loss of two carbon monoxide groups. Examination of the ^{19}F n.m.r. spectrum of the mixture of (1) and (2) showed the presence of a quintet at 56.8 p.p.m., which is assigned to the arrangement $\mathrm{FeC(C}F_3\mathrm{){=}C(H)Me}$ present in (1). The magnitude of the coupling $J(\mathrm{CF_3H}) = 3$ Hz suggests[9] that the $\mathrm{CF_3}$ and H substituents have a relative *cis* configuration, and in support of this assignment $J(\mathrm{CF_3Me})$ was observed to have a value of 3 Hz. A coupling of this magnitude is found in the compound $[\mathrm{Fe\{C(}CF_3\mathrm{){=}C(H)}CH_2\mathrm{CH{=}CH{=}CH_2\}(CO)_3}]$,[9] where the CF_3 and CH_2 groups definitely have a relative *trans* configuration.

The ^{1}H spectrum showed a singlet at τ 5.1 attributable to $\eta\text{-}\mathrm{C_5H_5}$, a doublet at τ 8.1 assigned to a methyl group, and a broad multiplet at τ 3.2 due to a vinylic hydrogen. All these signals are consistent with the presence in the mixture of a compound with the structure illustrated for (1), and the magnitude of the coupling $J(\mathrm{HMe})$ of 7 Hz is in agreement with the methyl group and the vinylic hydrogen having a relative *gem* configuration.

As listed in the Experimental section the spectra of the mixture containing the benzyl compounds (4) and (5) showed all the expected features for (4), a complex isostructural with (1).

The absence of other terminal or ketonic carbonyl bands in the i.r. spectra of the mixture of (1) and (2) or (4) and (5), together with the presence in the mass spectra of parent peaks assignable to species with the molecular formula $[\mathrm{Fe}\{\overline{\mathrm{OC(R)CH{-}C(CF_3)CH{-}C}}(\mathrm{CF_3})\}(\mathrm{C_5H_5})]$ ($R = \mathrm{Me}$ or $\mathrm{CH_2C_6H_5}$) suggested that the other components of the mixtures were pyranyl complexes.



SCHEME 1

η^5-Pyranyl and η^3-pyranyl compounds have been previously observed as products in the reaction of phenylacetylene with $[\mathrm{MnR(CO)_5}]$ ($R = \mathrm{Me}$ or $\mathrm{C_6H_5}$)[10] and 3,3-dimethylbut-1-yne with $[\mathrm{MoMe(CO)_3(\eta^5\text{-}C_9H_7)}]$[11] respectively.

In agreement with the suggestion that (2) and (5) have the illustrated η^5-pyranyl structures, the ^{1}H spectrum of, for example, (2) showed two singlets at τ 5.0 and 5.6, which are assigned to the olefinic protons H^2 and H^1, together with singlets at τ 5.4 and 8.1 attributable to η-C_5H_5 and Me protons. The ^{19}F n.m.r. spectrum confirmed the incorporation of two 3,3,3-trifluoroprop-1-yne molecules showing two singlet CF_3 resonances at 60.1 (CF_3^2) and 69.5 p.p.m. (CF_3^1). The lack of coupling between the trifluoromethyl groups or olefinic hydrogens suggested that the acetylenes have linked together head-to-tail. The spectral data for the benzyl analogue (5) closely parallelled those observed for (2), indicating isostructural compounds.

The more interesting products (3) and (6) incorporating three acetylene molecules were fortunately easily separable by column chromatography from the other components of the reaction mixture. Elemental analysis and mass spectrometry indicated a molecular formula $[\mathrm{Fe}\{(\mathrm{CF_3C_2H})_3\mathrm{COR}\}(\eta\text{-}\mathrm{C_5H_5})]$ ($R = \mathrm{Me}$ or $\mathrm{CH_2C_6H_5}$), and examination of the ^{19}F and ^{1}H spectra (see Experimental section) suggested a head-to-tail linkage of the three 3,3,3-trifluoroprop-1-yne molecules. In order to establish unequivocally the structure of these species a single crystal *X*-ray diffraction study was carried out with compound (3).

The molecular structure of (3) is shown in Figure 1, which also gives the crystallographic numbering system. Table 1 shows the atomic positional parameters, Table 2 the bond lengths and bond angles, while Figure 2 shows the packing of the molecules in the monoclinic unit cell. The iron atom is sandwiched between the cyclopentadienyl ring, to which it is η^5-bonded, and a new C_6 ring system formed by head-to-tail linking of three molecules of 3,3,3-trifluoroprop-1-yne. As might be expected from the 18-electron rule, the C_6 ring is η^5-bonded to the iron atom, and in consequence is of envelope conform-

TABLE 1

Atomic positional parameters with estimated standard deviations

Atom	*x*	*y*	*z*
C(01)	0.043 5(4)	0.088 7(5)	0.164 5(5)
C(02)	0.057 6(5)	0.060 9(5)	0.275 1(5)
C(03)	−0.042 6(6)	0.029 7(4)	0.294 9(6)
C(04)	−0.115 9(5)	0.042 3(4)	0.197 1/6)
C(05)	−0.062 0(5)	0.078 6(5)	0.115 7(5)
H(01)	0.100(6)	0.115(7)	0.128(6)
H(02)	0.129(6)	0.062(7)	0.322(6)
H(03)	−0.049(5)	0.009(6)	0.363(5)
H(04)	−0.194(7)	0.031(8)	0.186(6)
H(05)	−0.083(6)	0.102(7)	0.037(7)
Fe	−0.043 43(3)	0.214 72(4)	0.238 44(4)
C(1)	0.035 9(3)	0.386 6(3)	0.239 3(3)
C(2)	0.021 2(3)	0.353 6(3)	0.344 9(3)
C(3)	−0.082 7(3)	0.327 6(3)	0.357 3(3)
C(4)	−0.164 6(3)	0.325 6(3)	0.263 3(3)
C(5)	−0.139 0(2)	0.359 7(3)	0.163 0(3)
C(6)	−0.052 2(3)	0.455 4(3)	0.162 0(3)
C(11)	0.146 2(3)	0.398 7(5)	0.223 2(4)
F(111)	0.151 8(2)	0.383 9(4)	0.118 5(3)
F(112)	0.186 5(2)	0.515 2(4)	0.249 9(3)
F(113)	0.211 3(2)	0.314 3(4)	0.279 7(3)
C(31)	−0.103 7(4)	0.294 7(5)	0.467 2(3)
F(311)	−0.028 7(4)	0.228 2(6)	0.527 8(3)
F(312)	−0.189 2(3)	0.228 2(4)	0.462 7(3)
F(313)	−0.114 9(5)	0.397 2(4)	0.523 6(3)
C(51)	−0.220 6(3)	0.346 0(4)	0.061 1(3)
F(511)	−0.180 6(2)	0.326 1(3)	−0.026 9(2)
F(512)	−0.287 0(2)	0.251 0(4)	0.064 9(2)
F(513)	−0.278 4(3)	0.452 9(3)	0.037 8(3)
H(2)	0.075(4)	0.335(5)	0.404(4)
H(4)	−0.224(4)	0.289(4)	0.271(3)
H(6)	−0.033(3)	0.459(4)	0.094(3)
C(7)	−0.075 7(3)	0.592 8(4)	0.195 5(3)
C(8)	−0.009 1(5)	0.699 6(5)	0.168 1(6)
O	0.144 9(3)	0.612 8(3)	0.242 7(3)

ation. Atoms C(1)—C(5) are coplanar and equidistant (Table 2) from the iron atom, while C(6) bends away along the C(1) · · · C(5) vector to give a dihedral angle of 122° between the two planar portions of the ring. The bond lengths in the bent-away part of the ring, C(1)–C(6) and C(5)–C(6), correspond to normal single bonds (mean 1.51_4 Å), while those in the part of the ring which is η^5-bonded to the iron atom are effectively equidistant (mean 1.41_4 Å), suggesting extensive delocalisation. The three C–CF_3 bonds (mean 1.49_2 Å) also appear to be significantly shorter than single C–C bonds, due partly to the hybridisation state of the ring atoms and partly to that of the trifluoromethyl-carbon atom where, as often, the mean F–C–F angle (106.1°) is significantly less than the ideal tetrahedral value. The enhanced *p* character of the C–F bonds gives a concomitant enhanced *s* character to the C–CF_3 bond. Significantly the acetyl group is on the opposite side of the C_6 ring to the iron atom.

TABLE 2

Interatomic distances (Å) and bond angles (°)

(*a*) Distances

C(1)–C(2)	1.416(5)	C(3)–C(31)	1.495(6)
C(2)–C(3)	1.419(5)	C(31)–F(311)	1.306(6)
C(3)–C(4)	1.415(4)	C(31)–F(312)	1.302(6)
C(4)–C(5)	1.408(5)	C(31)–F(313)	1.305(6)
C(5)–C(6)	1.510(5)	C(5)–C(51)	1.487(5)
C(6)–C(1)	1.518(4)	C(51)–F(511)	1.328(5)
C(1)–C(11)	1.496(6)	C(51)–F(512)	1.323(6)
C(11)–F(111)	1.335(6)	C(51)–F(513)	1.343(5)
C(11)–F(112)	1.338(6)	C(6)–C(7)	1.542(5)
C(11)–F(113)	1.322(6)	C(7)–C(8)	1.495(7)
		C(7)–O	1.193(6)
Fe–C(1)	2.069(3)		
Fe–C(2)	2.029(4)		
Fe–C(3)	2.042(4)		
Fe–C(4)	2.032(4)		
Fe–C(5)	2.060(3)		
Cyclopentadienyl ring			
Fe–C(01)	2.073(6)	C(01)–C(02)	1.387(9)
Fe–C(02)	2.065(5)	C(02)–C(03)	1.416(10)
Fe–C(03)	2.054(5)	C(03)–C(04)	1.393(9)
Fe–C(04)	2.047(5)	C(04)–C(05)	1.402(10)
Fe–C(05)	2.067(6)	C(05)–C(01)	1.387(8)

(*b*) Angles

C(1)–C(2)–C(3)	117.7(3)	F(312)–C(31)–F(313)	105.6(5)
C(2)–C(3)–C(4)	119.0(3)	C(4)–C(5)–C(51)	118.6(3)
C(3)–C(4)–C(5)	117.4(3)	C(6)–C(5)–C(51)	117.4(3)
C(4)–C(5)–C(6)	119.3(3)	C(5)–C(51)–F(511)	113.0(3)
C(5)–C(6)–C(1)	98.7(3)	C(5)–C(51)–F(512)	113.5(3)
C(6)–C(1)–C(2)	118.6(3)	C(5)–C(51)–F(513)	112.0(3)
C(6)–C(1)–C(11)	119.7(3)	F(511)–C(51)–F(512)	106.5(4)
C(2)–C(1)–C(11)	117.7(3)	F(511)–C(51)–F(513)	104.4(3)
C(1)–C(11)–F(111)	111.8(3)	F(512)–C(51)–F(513)	106.8(3)
C(1)–C(11)–F(112)	112.4(4)	C(5)–C(6)–C(7)	114.9(3)
C(1)–C(11)–F(113)	113.6(4)	C(1)–C(6)–C(7)	115.6(3)
F(111)–C(11)–F(112)	104.6(4)	C(6)–C(7)–O	120.7(4)
F(111)–C(11)–F(113)	106.7(4)	C(6)–C(7)–C(8)	118.3(4)
F(112)–C(11)–F(113)	107.3(3)	O–C(7)–C(8)	121.0(4)
C(2)–C(3)–C(31)	120.3(3)	C(01)–C(02)–C(03)	106.6(5)
C(4)–C(3)–C(31)	120.7(3)	C(02)–C(03)–C(04)	108.2(6)
C(3)–C(31)–F(311)	113.4(4)	C(03)–C(04)–C(05)	107.9(6)
C(3)–C(31)–F(312)	113.6(3)	C(04)–C(05)–C(01)	107.5(5)
C(3)–C(31)–F(313)	111.7(4)	C(05)–C(01)–C(02)	109.7(6)
F(311)–C(31)–F(312)	105.8(5)	Mean C–C–F	112.7
F(311)–C(31)–F(313)	106.0(4)	Mean F–C–F	106.1

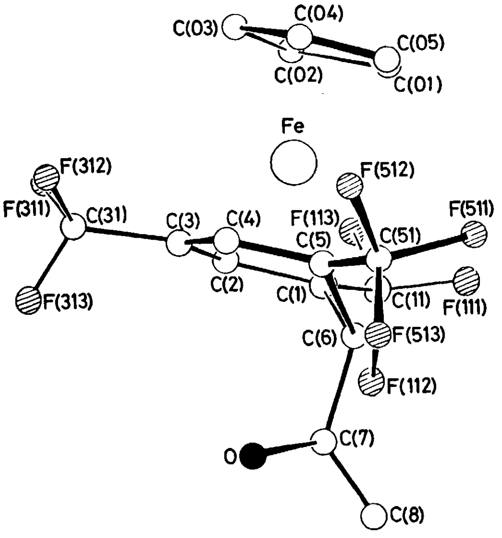


FIGURE 1 The molecular structure of (3)

With the establishment of the structure of (3) in the solid state, interpretation of the ^1H and ^{19}F n.m.r. spectra in solution was straightforward, and it followed that the benzyl complex (6) is isostructural with (3). Of further interest was the absence of coupling between the CF_3 and H substituents on the C_6 ring of both (3) and (6). This serves to confirm the analysis of the n.m.r. spectra of (2) and (4) in terms of the illustrated head-to-tail linked η^5-pyranyl structures.

As previously mentioned, the reaction on u.v. irradiation of σ-allyldicarbonyl(η-cyclopentadienyl)iron with 3,3,3-trifluoroprop-1-yne was also examined. In this case only one product (7) was obtained, and analysed as a 1 : 1 adduct. Examination of the i.r., ^1H and ^{19}F n.m.r. spectra showed that the acetylene had formally inserted into the iron–carbon σ bond of the σ-allyl system, the acetylenic carbon carrying the trifluoromethyl group being bonded to the iron. As in the reactions of [Co(η^3-allyl)(CO)$_3$] with fluoro-olefins,[1] the olefin which was originally part of the allyl system is co-ordinated to the metal atom.

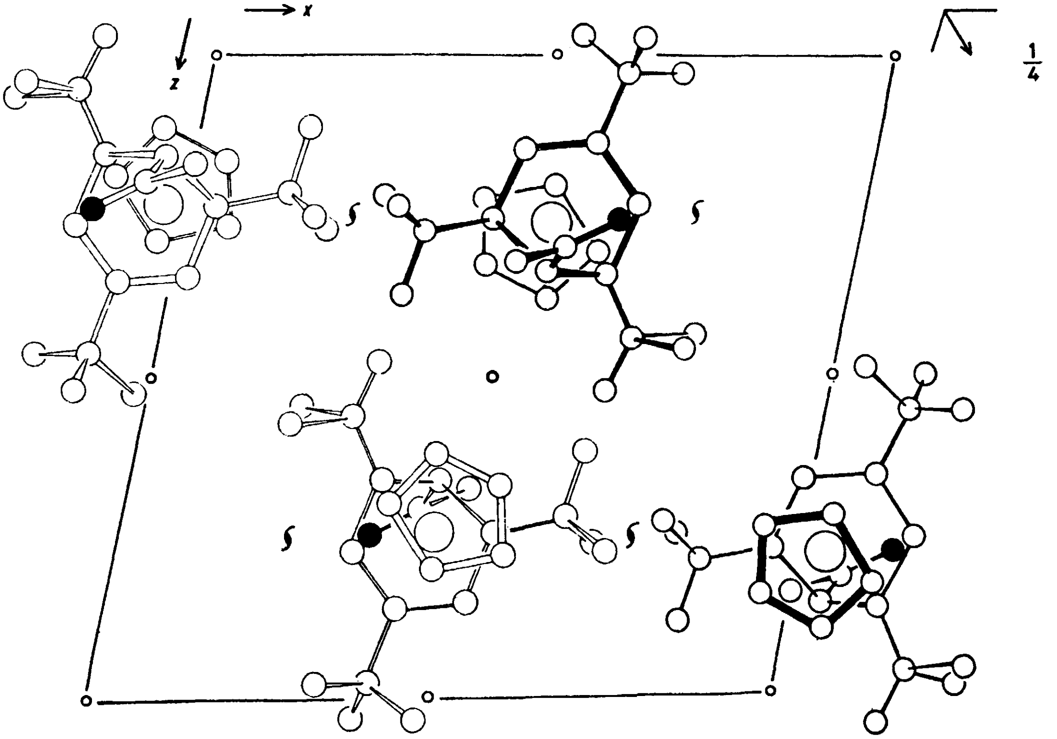


FIGURE 2 Contents of the monoclinic unit cell, viewed in projection down *b* looking towards the origin

As illustrated, the formation of the compounds (1), (4), and (7) can be understood in terms of the capture of the photochemically generated co-ordinatively unsaturated species [FeR(CO)(η-C_5H_5)] (R = Me, $CH_2C_6H_5$, or $CH_2CH{=}CH_2$) by a molecule of 3,3,3-trifluoroprop-1-yne, this being followed by the rapid migration of the R group from iron onto the co-ordinated acetylene thus achieving a formal *cis*-insertion reaction. The regioselectivity of the insertion reaction can be dependent on both steric and electronic effects. In a study of the insertion reactions of the bulky molecule 3,3-dimethylbut-1-yne, steric effects were thought[11] to have a controlling influence; however, it is well established that electronegative substituents have a considerable stabilising effect on carbon-to-transition-metal σ bonds, and we suggest that this electronic effect controls the reactions with 3,3,3-trifluoroprop-1-yne, leading to the observed stereochemistry.

The formation of the η^5-pyranyl compounds (2) and (5) and the η^5-[*exo*-1-acyl-2,4,6-tris(trifluoromethyl)cyclohexadienyl]iron compounds (3) and (6) requires that there is a competing reaction path, which as illustrated (Scheme 1) involves, as a first step, the migration of the R group from iron onto co-ordinated carbon monoxide, a CF_3C_2H molecule occupying the vacated co-ordination site. The migration of the acyl group onto the acetylene affords a σ-bonded vinyl ketone complex. Then the generated vinyl ketone group can migrate onto a further co-ordinated acetylene to give an intermediate of type (A) (Scheme 1). In molybdenum chemistry there is precedent for both of these steps.[11,12] In the case of the reaction of 3,3-dimethylbut-1-yne with [MoMe(CO)$_3$(η^5-C_9H_7)] a η^3-pyranyl complex was isolated; the reaction paths discussed[11] for the formation of a pyranyl system from a σ-oxahexatrienylmolybdenum complex can be extended to include the formation of the iron complexes (2) and (5).

The formation of the C_6-ring systems present in (3) and (6) suggests that the intermediate (A) undergoes a competitive insertion reaction with a further 3,3,3-trifluoroprop-1-yne molecule. As illustrated in Scheme 2, the resulting acyl-substituted ferrahexatrienyl species can adopt two conformations (B) and (C). It is interesting that conformer (B), *via* consecutive intramolecular insertion reactions generating successively ferramethylcyclopentadiene and ferrabicyclo[3.1.0]hexane intermediates,* leads to an *endo*-1-acyl-2,4,6-tris(trifluoro-

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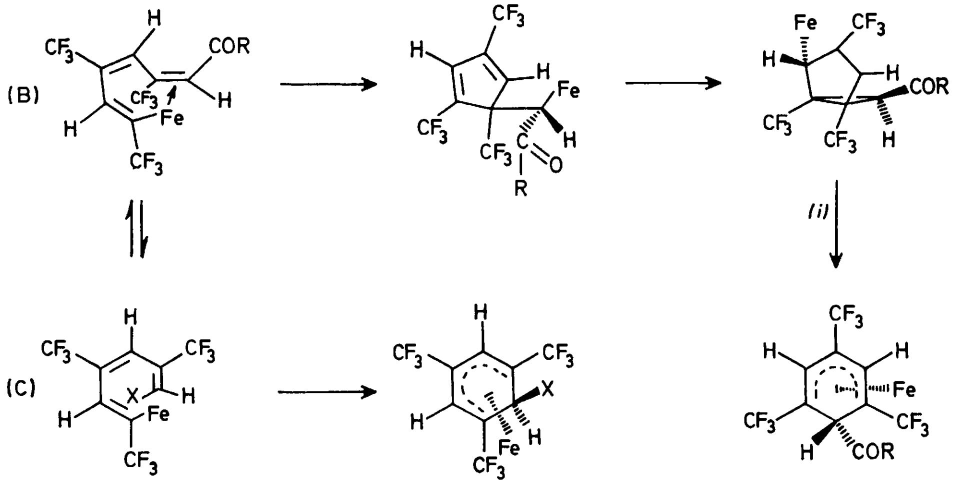
* Intermediates of this type have been implicated in the related insertion reactions of acetylenes and vinylpalladium(II) species (see ref. 13).

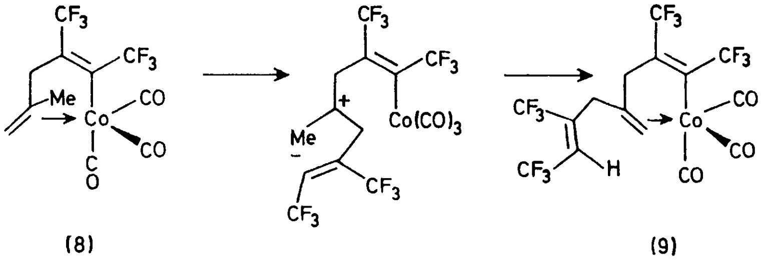
methyl)cyclohexadienyliron complex rather than the observed *exo* isomer. While it is possible that a subsequent thermodynamically controlled step leads to an *endo*- to *exo*-isomer conversion, it is also clear that conformer (C) generates directly the observed stereochemistry * *via* one insertion reaction.



SCHEME 2 X = COR where R = Me or $CH_2C_6H_5$; (*i*) disrotatory ring-opening reaction

In a previous study of the thermal reaction of hexafluorobut-2-yne with tricarbonyl(1—3-η-2-methylallyl)-cobalt evidence was obtained for a product which had apparently arisen *via* consecutive insertion reactions of two acetylene molecules.[14] In view of the results obtained with the cyclopentadienyl iron system it was thought worthwhile to try and reaffirm this observation.

Reaction of an excess of hexafluorobut-2-yne with $[Co(CO)_3(\eta^3\text{-}2\text{-}MeC_3H_4)]$ in tetrahydrofuran as solvent led to polymerisation of the acetylene. Column chromatography of the reaction mixture afforded two complexes (8) and (9). Elemental analysis, mass and i.r. spectroscopy showed that the products were tricarbonyl 1 : 1 and 2 : 1 adducts of $CF_3C_2CF_3$ and $[Co(CO)_3(\eta^3\text{-}2\text{-}MeC_3H_4)]$ respectively.



(8) (9)

The ^1H and ^{19}F n.m.r. spectra of (8) showed resonances consistent with the illustrated structure arising from the formal *cis* insertion of the acetylene into a cobalt σ-allyl bond. Related reactions have been observed with iridium(I) [7] and palladium(II) [2] η^3-allyl compounds.

Examination of the ^1H n.m.r. spectrum of (9) showed that the complex had not been formed by consecutive insertion of two acetylene molecules,† there being no evidence in the spectrum for the presence of the methyl group present in the starting material. Instead the spectrum showed a quartet [J(HF) 11 Hz] at τ 3.8, which can be assigned to the vinylic hydrogen $C(CF_3)=CH(CF_3)$, two equivalent protons appearing as a singlet at τ 6.4, and the remaining hydrogens forming a complex multiplet centred at τ 6.8. These spectral features suggested the illustrated structure for (9), which was also consistent with the appearance in the ^{19}F n.m.r. spectrum of two trifluoromethyl resonances with similar chemical shifts to those in compound (8), and in addition two other CF_3 resonances at 58.5 and 61.8 p.p.m., that at high field showing additional coupling to vinylic hydrogen. It is possible that (9) arises *via* electrophilic attack by $CF_3C_2CF_3$ on the co-ordinated olefin present in (8), the resulting dipolar species collapsing by proton abstraction from the adjacent methyl group followed by rotation about a C–C bond. A related process was observed [15] in the reaction of hexafluoropropene with tricarbonyl(cyclohexa-1,3-diene)iron.

EXPERIMENTAL

Hydrogen-1 and ^{19}F n.m.r. spectra were recorded using Varian Associates HA100 and JEOL PFT-100 spectro-

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* The thermally allowed disrotatory ring closure of an acyl-substituted σ-ferrahexatrienyl intermediate does not generate the observed stereochemistry. We consider it unlikely that a photochemical conrotatory process is occurring.

† Attempts to isolate the previously observed product or to obtain it by reaction of (8) with more $CF_3C_2CF_3$ were unsuccessful. This difficulty could have arisen due to varying rates of acetylene polymerisation affecting the availability of the acetylene for further reactions.

meters, respectively. Fluorine chemical shifts are relative to CCl_3F (0.0 p.p.m., external). Carbon-13 n.m.r. spectra (^1H decoupled) were measured ($CDCl_3$ or CD_2Cl_2 solutions) on a JEOL PFT-100 spectrometer at 25.1 MHz, the shifts are relative to $SiMe_4$. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Mass spectra were measured on an A.E.I. MS902 spectrometer operating at 70 eV.* Reactions were carried out in a dry oxygen-free nitrogen atmosphere.

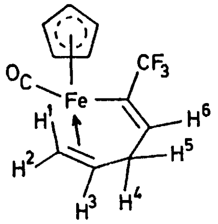
Reactions of 3,3,3-*Trifluoroprop*-1-*yne*.—(a) *With dicarbonyl*(η-*cyclopentadienyl*)*methyliron*. 3,3,3-Trifluoroprop-1-yne (13 mmol) was condensed (−196 °C) into a Carius tube (100 cm^3) containing $[FeMe(CO)_2(\eta\text{-}C_5H_5)]$ (0.9 g, 4.5 mmol) dissolved in hexane (20 cm^3). The tube and contents were irradiated (250 W, Hanovia u.v. lamp) for 15 d. The solvent was removed *in vacuo*, and the residue chromatographed on an alumina-packed column (20 × 2 cm). Elution with hexane gave unchanged iron complex followed by a yellow band, which on crystallisation (−78 °C) from hexane afforded an inseparable mixture (0.15 g) of compounds (1) and (2) (ratio 1 : 7.5). Repeated attempts to separate these materials were unsuccessful; therefore, the following spectroscopic data were collected on the mixture and analysed in terms of the illustrated structures. Compound (1) showed ν(CO)(hexane) at 2 032s and 1 984s cm^{-1}; ^1H n.m.r. resonances ($CDCl_3$) τ 3.1 [m, 1 H, H^1, $J(H^1Me)$ 7, $J(H^1CF_3)$ 2.5 Hz], 5.1 (s, 5 H, C_5H_5), 8.1 [d, 3 H, Me, J(H–Me) 7 Hz]; ^{19}F n.m.r. resonances $[(CD_3)_2CO]$ 56.9 p.p.m. [q, 3 F, CF_3, $J(CF_3Me)$ 2.5, $J(CF_3H^1)$ 2.5 Hz]; the mass spectrum showed peaks at *m/e* 286 (*P*), 258 (*P* − CO), and 230 (*P* − 2CO). Compound (2) showed ^1H n.m.r. resonances ($CDCl_3$) at τ 5.0 (s, 1 H, H^2), 5.4 (s, 5 H, C_5H_5), 5.55 (s, 1 H, H^1), and 8.1 (s, 3 H, Me); ^{19}F n.m.r. resonances $[(CD_3)_2CO]$ at 60.1 (s, 3 F, $CF_3{}^2$), and 69.5 p.p.m. (s, 3 F, $CF_3{}^1$); the mass spectrum showed peaks at *m/e* 352 (*P*), 231 (*P* − FeC_5H_5), and 212 (*P* − $FeFC_5H_5$).

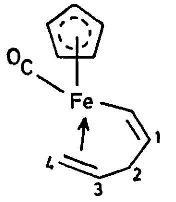
Further elution with hexane–methylene chloride (4 : 1) produced an orange fraction, which on recrystallisation (−78 °C) from hexane afforded orange *crystals* of (3) (0.14 g, 6.5%) (Found: C, 43.4; H, 2.8. $C_{16}H_{11}F_9FeO$ requires C, 43.1; H, 2.5%), ν(Nujol) at 3 080w, 1 720s, 1 530w, 1 320s, 1 290s, 1 280s, 1 230s, 1 190s, 1 175s, 1 160s, 1 136s, 1 120s, 1 109s, 855m, 692m, and 688m cm^{-1}. N.m.r. spectra: ^1H ($CDCl_3$), τ 4.5 (s, 2 H, H^1), 5.3 (s, 5 H, C_5H_5), 6.4 (s, 1 H, H^2), and 8.2 (s, 3 H, Me); ^{19}F $[(CD_3)_2CO]$, 59.9 (s, 3 F, $CF_3{}^2$), and 61.3 p.p.m. (s, 6 F, $CF_3{}^1$). The mass spectrum showed peaks at *m/e* 428 (*P* − 2F), 404 (*P* − MeCO − F), 282 $[C_6H_3(CF_3)_3]$, and 263 $[C_6H_3(CF_3)_3 - F]$.

(b) *With benzyldicarbonyl*(η-*cyclopentadienyl*)*iron*. Similarly, irradiation (14 d) of a solution of benzyldicarbonyl(η-cyclopentadienyl)iron (1.25 g, 4.7 mmol) and 3,3,3-trifluoroprop-1-yne (10 mmol) in hexane (20 cm^3) gave on chromatography (alumina; elution with hexane) an inseparable mixture of (4) and (5) (1 : 8) (0.08 g). Compound (4) showed ν(CO)(hexane) at 2 035s and 1 986s cm^{-1}; ^1H n.m.r. resonances ($CDCl_3$) τ 2.7 (br m, 5 H, C_6H_5), 3.1 [tq, 1 H, H^1, $J(H^1CH_2)$ 7, $J(H^1CF_3)$ 2.5 Hz], 5.1 (s, 5 H, C_5H_5), and 6.4 [m, 2 H, CH_2, J(HF) 2.5, $J(H^1CH_2)$ 7 Hz]; ^{19}F n.m.r. resonance $[(CD_3)_2CO]$ 56.9 p.p.m. [q, 3 F, CF_3, $J(CF_3Me)$ 2.5, $J(CF_3H^1)$ 2.5 Hz]; the mass spectrum showed peaks at *m/e* 362 (*P*), 334 (*P* − CO), and 306 (*P* − 2CO). Compound (5) showed ^1H n.m.r. resonances ($CDCl_3$) at τ 2.7 (br m, 5 H, C_6H_5), 5.0 (s, 1 H, H^2), 5.4 (s, 1 H, H^1), 5.45 (s, 5 H, C_5H_5), and 6.5 (br s, 2 H, CH_2); ^{19}F n.m.r. resonances $[(CD_3)_2CO]$ at 60.0 (s, 3 F, $CF_3{}^2$) and 69.3 p.p.m. (s, 3 F, $CF_3{}^1$); the mass spectrum showed peaks at *m/e* 428 (*P*) and 3.7 (*P* − FeC_5H_5).

Further elution with hexane–methylene chloride (3 : 2) afforded an orange band, which on collection and recrystallisation (−78 °C) from hexane gave orange crystals of (6) (0.05 g, 3%) (Found: C, 50.7; H, 3.0. $C_{22}H_{15}F_9FeO$ requires C, 50.6; H, 2.9%), ν(Nujol) at 3 105w, 1 730s, 1 535w, 1 315w, 1 275s, 1 265s, 1 245m, 1 180s, 1 160s, 1 145s, 1 120s, 1 096w, 852w, 738m, and 688m cm^{-1}. N.m.r. spectra: ^1H ($CDCl_3$), τ 2.7—3.1 (m, 5 H, C_6H_5), 4.6 (s, 2 H, H^1), 5.4 (s, 5 H, C_5H_5), 6.2 (s, 1 H, H^2), and 6.6 (s, 2 H, CH_2); ^{19}F $[(CD_3)_2CO]$, 60.0 (s, 3 F, $CF_3{}^2$) and 61.2 p.p.m. (s, 6 F, $CF_3{}^1$). The mass spectrum showed peaks at *m/e* 523 (*P* − F), 504 (*P* − 2F), and 282 $[C_6H_3(CF_3)_3]$.

(c) *With allyldicarbonyl*(η-*cyclopentadienyl*)*iron*. A solution of allyldicarbonyl(η-cyclopentadienyl)iron (0.85 g, 3.9 mmol) and 3,3,3-trifluoroprop-1-yne (13 mmol) in hexane (20 cm^3) was sealed in a Pyrex tube and irradiated (15 d). The solvent was removed *in vacuo* and the residue chromatographed on alumina. Elution with hexane gave ferrocene and $[Fe(\eta^3\text{-}C_3H_5)(CO)(\eta^5\text{-}C_5H_5)]$. Further elution with hexane–methylene chloride (2 : 1) gave an orange band, which on recrystallisation (−78 °C) from hexane gave orange *crystals* of (7) (0.15 g, 14%) (Found: C, 50.5; H, 3.8. $C_{12}H_{11}F_3FeO$ requires C, 50.7; H, 3.9%), ν(CO)(hexane) at 1 988 cm^{-1}; ν(Nujol) at 1 325m, 1 260m, 1 245s, 1 116s, 1 085s, 927m, 915w, 878w, 852m, 817w, and 725w cm^{-1}. N.m.r. spectra: ^1H ($CDCl_3$), τ 3.8 (br m, 1 H, H^6), 4.7 [m, 1 H, H^3, $J(H^1H^3)$ 12, $J(H^2H^3)$ 9, $J(H^4H^3) = J(H^5H^3)$ 4 Hz], 5.3 (s, 5 H, C_5H_5), 6.75 [d, 1 H, H^2, $J(H^2H^3)$ 9 Hz], 6.9 [dm, 1 H, H^4, $J(H^4H^5)$ 18, $J(H^4CF_3)$ 4 Hz], 7.6 [dm, 1 H, H^5, $J(H^4H^5)$ 18, $J(H^5CF_3)$ 4 Hz], and 7.8 [d, 1 H, H^1 $J(H^1H^3)$ 12 Hz]; ^{19}F $[(CD_3)_2CO]$, 57.6 p.p.m. [dt, 3 F, CF_3, $J(H^6CF_3)$ 2, $J(H^4CF_3)$ 4 Hz]; ^{13}C ($CDCl_3$), −144.3 [q, C^1, $J(C^1CF_3)$ 10 Hz], −83.1 (s, C^5), −76.8 (s, C^3), −48.4 (s, C^4), and −37.0 p.p.m. (s, C^2). The mass spectrum showed peaks at *m/e* 284 (*P*), 256 (*P* − CO), and 121 (FeC_5H_5).





Reaction of Hexafluorobut-2-*yne with Tricarbonyl*(1—3-η-2-*methylallyl*)*cobalt*.—Hexafluorobut-2-yne (13 mmol) was allowed to react (1.5 h, room temperature) with a solution of $[Co(CO)_3(\eta^3\text{-}2\text{-}MeC_3H_4)]$ (1.27 g, 6.4 mmol) in tetrahydrofuran (20 cm^3) contained in a tube fitted with a Westef stopcock. Volatile material was removed *in vacuo* and the residue chromatographed on alumina. Elution with hexane gave a yellow band, which on recrystallisation (−78 °C) from hexane gave yellow *crystals* of (8) (0.4 g, 17%), m.p. <20 °C (Found: C, 36.3; H, 1.8. $C_{11}H_7CoF_6O_3$ requires C, 36.6; H, 3.0%), ν(CO)(hexane) at 2 095s, 2 048s, and 2 034s cm^{-1}. N.m.r. spectra ^1H ($CDCl_3$), τ 6.6 (s, 2 H, H^1 and H^2), 6.7 [q, 2 H, H^4 and H^5, $J(HCF_3{}^1)$ 3 Hz], and 7.95 (s, 3 H, Me^3); ^{19}F $[(CD_3)_2CO]$, 53.3 [qt, 3 F, $CF_3{}^1$, $J(CF_3{}^1CF_3{}^2)$ 14 Hz, $J(CF_3{}^1H^4)$ 3 Hz] and 59.1 p.p.m. [q, 3 F, $CF_3{}^2$, $J(CF_3{}^1CF_3{}^2)$ 14 Hz]. The mass spec-

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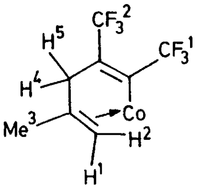
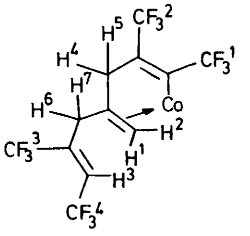
* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

trum showed peaks at *m/e* 360 (P), 332 ($P-$ CO), 304 ($P-$ 2CO), and 276 ($P-$ 3CO).

Further elution with hexane–methylene chloride (1 : 1) afforded a pale yellow band, which on recrystallisation (−78 °C) from hexane–methylene chloride (4 : 1) gave yellow *crystals* of (9) (0.27 g, 18%) (Found: C, 34.4; H, 1.5. $C_{15}H_7CoF_{12}O_3$ requires C, 34.5; H, 1.3%), ν(CO)-(hexane) at 2 102s, 2 055s, and 2 040s cm^{-1}. N.m.r. spectra: ^{1}H ($CDCl_3$) τ 3.8 [q, 1 H, H^3, $J(H^3CF_3{}^4)$ 11 Hz], 6.4 (s, 2 H, H^1 and H^2), 6.7 (br m, 2 H, H^6 and H^7), and 6.9 (br m, 2 H, H^4 and H^5); ^{19}F [$(CD_3)_2CO$], 53.2 p.p.m.





[qt, 3 F, CF$_3{}^1$, $J(CF_3{}^1CF_3{}^2)$ 14, $J(CF_3{}^1H^4)$ 3 Hz], 58.5 [q, 3 F, CF$_3{}^4$, $J(CF_3{}^3CF_3{}^4) = J(CF_3{}^4H^3)$ 11 Hz], 59.2 [q, 3 F, CF$_3{}^2$, $J(CF_3{}^1CF_3{}^2)$ 14 Hz], and 61.8 p.p.m. [q, 3 F, CF$_3{}^3$, $J(CF_3{}^3CF_3{}^4)$ 11 Hz]. The mass spectrum showed peaks at *m/e* 494 ($P-$ CO), 466 ($P-$ 2CO), and 438 ($P-$ 3CO).

Structure Determination of Complex (3) [1—5-η-exo-1-*Acetyl*-2,4,6-*tris(trifluoromethyl)cyclohexadienyl*](η-*cyclopentadienyl)iron, by* X-*Ray Diffraction*.—Crystals of the complex grow as volatile orange prisms. A suitable crystal was sealed into a Lindemann tube; intensities were measured for $2\theta < 50°$ on a Syntex $P2_1$ four-circle diffractometer. Of the total recorded independent intensities, 3 236 had $I > 2.5\sigma(I)$, where $\sigma(I)$ is the standard deviation based on counting statistics, and only these were used in the solution and refinement of the structure. All computations were carried out with the ' *X*-Ray ' system of programs [16] available for the CDC 7600 at the London Computing Centre.

Crystal data. $C_{16}H_{11}F_9FeO$, $M = 445.9$, Monoclinic, $a = 13.025(3)$, $b = 10.432(2)$, $c = 12.503(2)$ Å, $\beta = 101.93(5)°$, $U = 1\,662$ Å^3, D_m not measured, $Z = 4$, $D_c = 1.78$ g cm^{-3}, $F(000) = 888$, space group $P2_1/n$ (no. 14). Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 10.2$ cm^{-1}.

Structure solution and refinement. The iron atom was located from a Patterson synthesis, and all the remaining atoms (including hydrogen for the two ring systems, but not those for the methyl group) by successive electron-density difference syntheses. The structure was refined by blocked-matrix least squares, with anisotropic thermal parameters for all non-hydrogen atoms. Isotropic thermal parameters were used for the located hydrogen atoms; both these and the positional parameters were included in the least-squares refinement. No attempt was made to include the H atoms of the methyl group. No correction for *X*-ray absorption was made [$\mu(\text{Mo-}K_\alpha) = 10.2$ cm^{-1}]. Refinement converged at R 0.056 (R' 0.066) with a mean shift-to-error ratio in the last cycle of 0.004. A weighting scheme of the form $1/w = (xy)$ with $x = b/\sin\theta$ if $\sin\theta < b$, $x = 1$ if $\sin\theta \geqslant b$, and $y = F_o/a$ if $F_o > a$, $y = 1$ if $F_o \leqslant a$, in which $a = 25.0$ and $b = 0.28$, gave a satisfactory analysis. The final electron-density difference synthesis showed no peaks >0.3 or < -0.4 e Å^{-3}. Scattering factors were from ref. 17 for carbon, fluorine, and oxygen, ref. 18 for hydrogen, and ref. 19 for iron, where also corrections for the effects of anomalous dispersion were applied (Fe: $\Delta f' = 0.301$, $\Delta f'' = 0.845$). Atomic positional parameters are in Table 1, interatomic distances and angles in Table 2. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22654 (16 pp.).*

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* For details see Notices to Authors No. 7 in *J.C.S. Dalton*, 1979, Index issue.

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