The Reaction of Hexafluorobut-2-yne and Tetrafluoroethylene with η-Cyclopentadienyl-iron and -ruthenium Complexes; Crystal and Molecular Structures of $[Fe_2(CO)\{C_4(CF_3)_4CO\}(\eta^5\text{-}C_5H_5)_2]$ and $[Fe(COCF_2C_5H_5)(\eta^5\text{-}C_5H_5)]$

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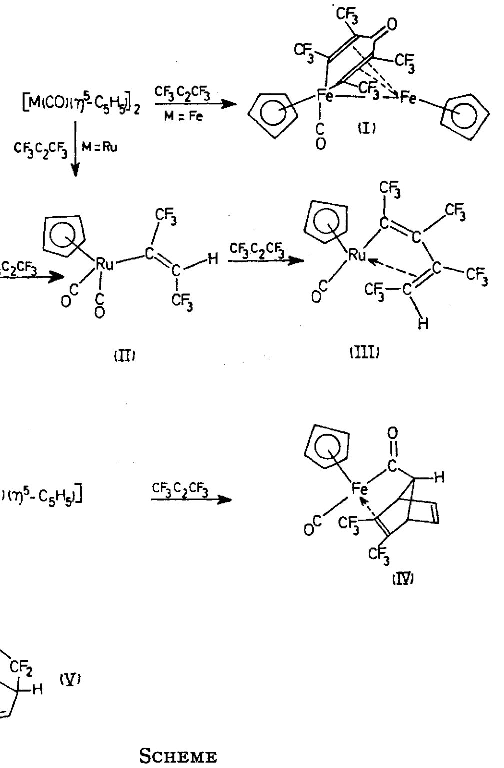
Summary Reaction of $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ with $CF_3C_2CF_3$ affords the ferracyclohexadienone $[Fe_2(CO)\{C_4(CF_3)_4CO\}(\eta^5\text{-}C_5H_5)_2]$, whereas $[Ru(CO)_2(\eta^5\text{-}C_5H_5)]_2$ gives sequentially the *trans*-insertion product $[Ru\{C(CF_3):C(CF_3)H\}(CO)_2(\eta^5\text{-}C_5H_5)]$ and $[RuC(CF_3):C(CF_3)\cdot C(CF_3):C(CF_3)H(CO)(\eta^5C_5H_5)]$; in contrast $[Fe(CO)_2(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)]$ affords $[FeCO\{COC_7H_5(CF_3)_2\}(\eta^5\text{-}C_5H_5)]$ with $CF_3C_2CF_3$ and $[Fe(COCF_2C_5H_5)(\eta^5\text{-}C_5H_5)]$ with C_2F_4, the latter reaction involving cleavage of a C–C bond.

DETAILED understanding of the reactions of olefins and acetylenes with transition-metal complexes has still not been achieved. One approach to this problem is to study the corresponding reactions of the fluorocarbon species and make use of the enhanced stability of the reaction intermediates and products.

U.v. irradiation of a methylene chloride solution of $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ and hexafluorobut-2-yne (HFB) gives the dinuclear complex (I) (20% yield) (Scheme) as black crystals {m.p. 161—162°, $\nu_{CO}(CCl_4)$ 1985s and 1670m cm^{-1}; ^1H n.m.r. ($CDCl_3$) τ 4·85 (s, 5H) and 5·37 (s, 5H); ^{19}F n.m.r. (CH_2Cl_2; rel. CCl_3F) 44·52 [q, 6F, J(FF) 14·0 Hz] and 57·13 p.p.m. [q, 6F, J(FF) 14·0 Hz]}. A single crystal *X*-ray diffraction study established the molecular geometry shown in Figure 1. *Crystal data:* $C_{20}H_{10}Fe_2O_2F_{12}$, $M =$ 613·0, orthorhombic, $P2_12_12_1$, a = 9·446(3), b = 13·708(6), c = 15·748(6) Å, U = 2039(1) Å³, D_c = 2·025, Z = 4, μ-(Mo-K_α) = 16·2 cm^{-1}. The intensity data were recorded on a Syntex $P2_1$ diffractometer (current R factor 0·046).



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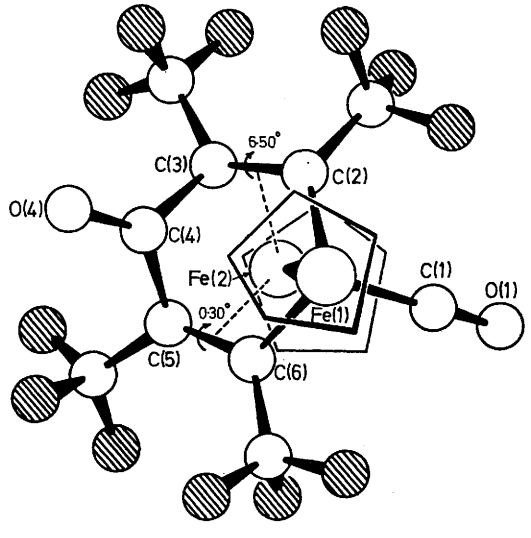

FIGURE 1. The complex $[Fe_2(CO)\{C_4(CF_3)_4CO\}(\eta^5\text{-}C_5H_5)_2]$. Fe–Fe, 2·590(2); Fe(1)–C(1), 1·78(1); Fe(1)–C(2), Fe(1)–C(6), 1·97(1); Fe(2)–C(2), Fe(2)–C(6), 2·00; Fe(2)–C(3), Fe(2)–C(5), 2·00; Fe(2)–C(3), Fe(2)–C(5), 2·12(1) Å; C(2)–C(3), 1·42(1); C(5)–C(6), 143(1) Å. Metal-$\eta^5C_5H_5$ ring distances are 1·71(1) Å for Fe(2) and 1·76(2) Å for Fe(1), with the latter $\eta^5\text{-}C_5H_5$ ring disordered between that shown and its 36° rotamer in the ratio 73 : 27.

Thus (I) is a ferracyclohexa-2,5-diene-one, a type of complex postulated as an intermediate in the formation of both cyclopentadienones and quinones. It has been suggested[1] that this structural feature occurs in the species $[Fe_2(CO)_6\{(R^1C_2R^2)_2CO\}]$, but complex (I) is the first system to be structurally identified. The dinuclear compound has near-mirror symmetry (consistent with ^{19}F n.m.r. studies), the major solid state asymmetry arising from a significant twist about the double bond of one of the alkene C_4 units. The C_5Fe ring is non-planar (and thus of boat conformation) with almost equivalent folding angles of 40·4° and 40·0° across C(2) . . . . C(6) and C(3) . . . . C(5), respectively.

Reaction of $[Ru(CO)_2(\eta^5\text{-}C_5H_5)]_2$ with HFB gave initially the mononuclear complex (II) {m.p. 42°, ν_{CO} (hexane) 2050s, 2000s cm^{-1}, $\nu_{C=C}$ 1615w cm^{-1}; ^1H n.m.r. ($CDCl_3$) τ 4·72 (s, 5H), 3·20 [qq, 1H, J(HF) 2·3, J(HF) 8·2 Hz]; ^{19}F n.m.r. (CH_2Cl_2) 56·67 [dq, 3F, J(FF) 2·3, J(HF) 8·15 Hz] and 60·48 p.p.m, [quintet, 3F, J(FF) 2·3 Hz]}, which was also obtained by direct reaction of $[RuH(CO)_2(\eta^5\text{-}C_5H_5)]$ with HFB. Further reaction led to insertion of a second molecule of HFB with

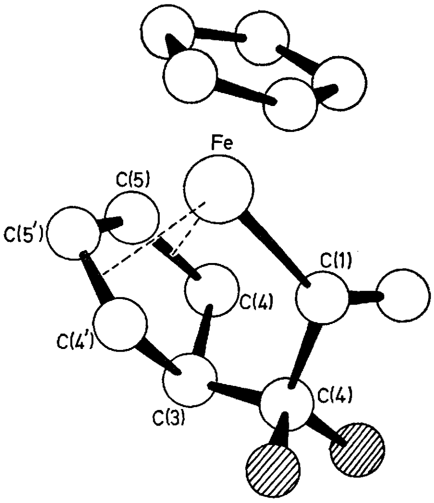

FIGURE 2. The complex $[Fe(COCF_2C_5H_5)(\eta^5\text{-}C_5H_5)]$. Fe–C(1), 1·99(1); Fe–C(4), 2·18(2); Fe–C(5), 2·06(2); and C(3)–C(4), 1·54(2) Å. The $\eta^4\text{-}C_5H_5$ ring has an envelope conformation with an acute folding angle of 25·4°.

retention of configuration to give (III) {m.p. 103—105°, ν_{CO} (CCl_4) 2043s cm^{-1}, $\nu_{C=C}$ 1671w cm^{-1}; ^1H n.m.r. ($CDCl_3$) τ 4·52 (s, 5H) and 5·70 [q, 1H, J(HF) 8·0 Hz]; ^{19}F n.m.r. (CH_2Cl_2) 57·88 [d, 3F, J(HF) 8·0 Hz], 59·02 [q, 3F, J(FF) 8·4 Hz], 61·22 [q, 3F, J(FF) 5·45 Hz] and 64·63 (m, 3F)}. Apart from the comparison with the iron system, formation of the *trans*-insertion product (II) contrasts with the reaction[2] of $[RuH(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ with HFB which gives the *cis*-insertion product $[Ru\{C(CF_3){:}C(CF_3)H\}(PPh_3)_2(\eta^5\text{-}C_5H_5)]$; an illustration of the delicate dependence of stereochemistry (and possibly mechanism) on the nature of the auxilary ligands. Further studies will be required to ascertain whether this is a concerted *trans*-insertion.[3]

Irradiation of a hexane solution of $[Fe(CO)_2(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)]$ and HFB gave (IV) (80—90%) [m.p. 148—151°, ν_{CO} (CCl_4) 1980s, 1668s cm^{-1}], its structure being assigned by comparison of its spectroscopic data with that reported[4] for the 1 : 1 adduct of nickelocene and HFB.

Tetrafluoroethylene (TFE) also reacts with $[Fe(CO)_2(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)]$ to give red crystals of (V) (8%) [m.p. 170° (decomp.), ν_{CO} ($CHCl_3$) 1640s, 1623s cm^{-1}, ^1H n.m.r. ($CDCl_3$) τ 3·35 (m, 2H), 5·38 (s, 5H), 6·90 (m, 2H) and 7·15 (m, 1H); ^{19}F n.m.r. ($CDCl_3$) 149·10 p.p.m. (apparent t)]. The molecular structure (Figure 2) was established by *X*-ray crystallography (current *R* factor 0·060).† *Crystal data:* $C_{12}H_{10}FeOF_2$, $M = 264{\cdot}8$, monoclinic, *Cc*, $a = 12{\cdot}204(3)$, $b = 8{\cdot}386(4)$, $c = 11{\cdot}262(3)$ Å, $\beta = 120{\cdot}11(2)°$, $U = 997(1)$ Å, $D_c = 1{\cdot}763$, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 15{\cdot}5\ cm^{-1}$.

Formation of (V) is especially interesting in that cleavage of the carbon–carbon bond of tetrafluoroethylene has occurred.‡ This is unusual in that such a process has previously been shown to take place only in olefin dismutation reactions.[5]

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† Although the mononuclear species (V) crystallises in a space group lacking a special position, the molecule possesses mirror symmetry within the limits of the experiment. The iron atom, which has a distorted octahedral geometry, is 1·72(2) Å from the centre of the $\eta^5\text{-}C_5H_5$ ring.

‡ The TFE was carefully purified and spectroscopically checked to exclude the possibility that (V) was formed from an impurity.

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