Addition of Hexafluorobut-2-yne to Co-ordinated 1,3-Dienes; Crystal Structures of the Adducts $[Ru(CO)_2\{P(OCH_2)_3CMe\}(C_6H_8)(C_4F_6)_2]$ and $[Fe(CO)_2\{P(OCH_2)_3CMe\}(C_7H_8)(C_4F_6)_2]$

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Summary Hexafluorobut-2-yne forms 1:1 adducts with tricarbonyl(butadiene or 2,3-dimethylbutadiene)iron and tricarbonyl-(*o*-styryldiphenylphosphine)iron, whereas tricarbonyl(cyclohexa-1,3-diene)-iron and -ruthenium, and tricarbonyl(cycloheptatriene)iron form unusual 1:2 adducts identified by *X*-ray crystallography.

IN a recent study[1] of the reaction of hexafluorobut-2-yne (HFB) with $[Rh(cod)Cl]_2$ and [Ir(cod)acac] both a 1,4-addition of HFB to co-ordinated cyclo-octa-1,5-diene (cod) and the formation of an iridiacyclopentene were observed. We have examined the reaction of HFB with d^8 tricarbonyl (1,3-diene)-iron(0) and -ruthenium(0) species, and have obtained evidence for the apparent insertion of HFB between the metal and both carbon atoms of an olefin.

Whereas, u.v. irradiation of a hexane solution of HFB and tricarbonyl(isoprene)iron and tricarbonyl-(*cis*- or *trans*-pentadiene)iron gives only the known[2] tricarbonyl-[tetrakis(trifluoromethyl)cyclopentadienone]iron complex, the corresponding reactions of tricarbonylbuta-1,3-diene)-iron and tricarbonyl(2,3-dimethylbuta-1,3-diene)iron afforded respectively, in moderate yields, the 1:1 adducts [(I), m.p. 38°, ν_{CO} (hexane) 2068s, 2034s, 2021m, $\nu_{C=C}$ 1631m cm^{-1}] and [(II), m.p. 46°, ν_{CO} (hexane) 2080s, 2025s, 2007s, $\nu_{C=C}$ 1631m cm^{-1}], which are assigned the illustrated structures† on the basis of ^1H and ^{19}F n.m.r. data. That

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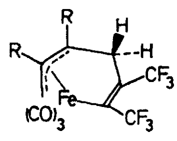
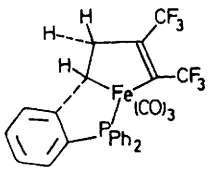
† Satisfactory elemental analyses and mass spectra were obtained for all compounds.

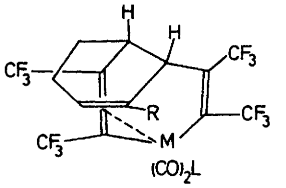
this kind of reaction is not limited to co-ordinated 1,3-dienes is illustrated by the observation that similar irradiation of a hexane solution of tricarbonyl(*o*-styryldiphenylphosphine)iron and HFB gave the crystalline 1 : 1 adduct [(III), m.p. 144°, ν_{CO} (hexane) 2079w, 2016s, $\nu_{C=C}$ 1614m cm^{-1}].



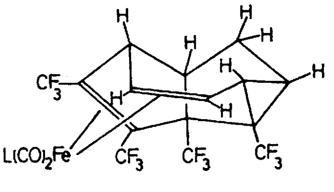
(I; R = H)
(II; R = Me)



(III)



(IV; M = Fe, L = CO, R = H)
(V; M = Ru, L = CO, R = H)
(VI, M = Ru, L = P(OCH$_2$)$_3$CMe, R = H)
(VII; M = Ru, L = CO, R = Me)



(VIII; L = CO)
(IX; L = P(OCH)$_3$CMe)

In contrast, the reaction of HFB with tricarbonyl(cyclohexa-1,3-diene)-iron or -ruthenium gave the crystalline 1 : 2 adducts (IV) and (V), there being no evidence for the intermediacy of species analogous to (I) and (II). Since the n.m.r. spectra of these complexes did not define a unique structure a single crystal *X*-ray diffraction study of (VI) [obtained by a simple displacement reaction of (V)] was undertaken establishing the structure shown in Figure 1.

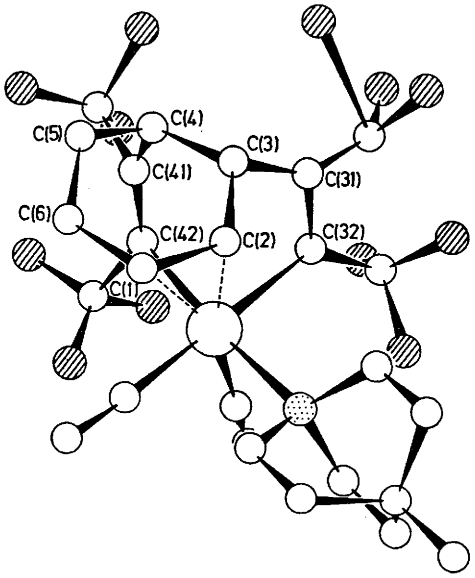


FIGURE 1. Molecular structure of [Ru(C_6H_8)(C_4F_6)$_2$(CO)$_2${P-(OCH$_2$)$_3$CMe}]. Bond distances (e.s.d.s. in parentheses): Ru–C(1) = 2·48(2), Ru–C(2) = 2·34(2), Ru–C(32) = 2·07(2), Ru–C(42) = 2·19(2), C(1)–C(2) = 1·38(2), C(2)–C(3) = 1·49(2), C(3)–C(4) = 1·57(2), C(4)–C(5) = 1·58(2), C(5)–C(6) = 1·50(3), C(6)–C(1) = 1·50(3) Å.

Crystal data: Monoclinic, space group $P2_1/c$, $a = 8{\cdot}875(5)$, $b = 17{\cdot}841(9)$, $c = 16{\cdot}517(5)$ Å, $\beta = 94{\cdot}51(3)°$, $Z = 4$; $R = 0{\cdot}077$ for 2418 independent reflections (Syntex $P2_1$ four-circle diffractometer using Mo-K_α monochromated *X*-radiation).

Thus, in (VI) the 6-membered ring C(1) to C(6) is retained as a nearly planar cyclohexene 1,2η- bonded to the ruthenium *via* the ethylenic link between C(1) and C(2). The two hexafluorobut-2-yne molecules have formally inserted between the ruthenium and both carbon atoms [C(3) and C(4)] of one of the original olefinic bonds of the cyclohexadiene forming the 7-membered rutheniacyclohepta-1,5-diene ring system, in which the co-ordination state of the ruthenium is close to octahedral with the ring system occupying three facial sites.

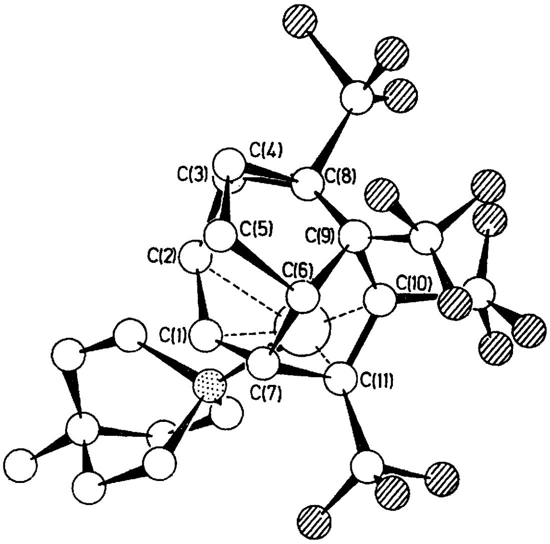


FIGURE 2. Molecular structure of [Fe(C_7H_8)(C_4F_6)$_2$(CO)$_2${P-(OCH$_2$)$_3$CMe}]; the two carbonyl groups have been omitted for clarity. Selected bond lengths (with e.s.d.s in parentheses) are Fe–C(1) = 2·181(6), Fe–C(2) = 2·246(6), Fe–C(10) = 2·153(5), Fe–C(11) = 2·047(5), C(1)–C(2) = 1·395(8), C(2)–C(3) = 1·478(8), C(3)–C(4) = 1·508(8), C(3)–C(8) = 1·529(8), C(4)–C(8) = 1·533(9), C(4)–C(5) = 1·504(9), C(5)–C(6) = 1·519(9), C(6)–C(7) = 1·530(8), C(1)–C(7) = 1·504(8) Å.

A similar reaction of tricarbonyl-(2-methylcyclohexa-1,3-diene)ruthenium with HFB gave (VII), indicating that the acetylenes preferentially attack the unsubstituted double bond.

In attempting to generalise this new reaction a remarkably complex ring-forming process was discovered. Irradiation of a solution of HFB and tricarbonyl(cycloheptatriene)-iron afforded a crystalline 1 : 2 adduct (VIII). A single crystal *X*-ray diffraction study of the phosphite-substitution product (IX)‡ established the structure shown in Figure 2. *Crystal data:* monoclinic, space group $P2_1/n$, $a = 8{\cdot}647(3)$,

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‡ Comparison of the n.m.r. data for (VIII) and (IX) showed that the displacement of carbon monoxide by P(OCH$_2$)$_3$CMe did not lead to molecular rearrangements.

$b = 29{\cdot}650(9)$, $c = 9{\cdot}371(3)$ Å, $\beta = 92{\cdot}87(3)°$, $Z = 4$; $R = 0{\cdot}059$ for 3297 independent reflections. From the crystal structure of the complex (IX) the original cycloheptatriene ring can be identified as atoms C(1)—C(7). Addition of two molecules of HFB has taken place on the *endo*-face of the C_7 ring 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), and also a three-membered ring C(3)–C(4)–C(8). The iron atom is bonded to the quadricyclic ligand by an olefinic bond C(1)–C(2) originating in the C_7 ring, and to the bistrifluoromethyl substituted olefinic bond C(10)–C(11) generated from one of the acetylene molecules. The coordination state of the iron atom is approximately trigonal bipyramidal, with one carbonyl group and the C(1)–C(2) link occupying the axial sites, the other carbonyl, the phosphite, and the C(10)–C(11) double bond occupying the equatorial sites.

There is no precedent for a reaction of this kind, and studies are in progress to examine the interrelationship of the reactions leading to the formation of the complexes (I)–(VIII).

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[2] J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 1962, 3488; R. D. Dickson and D. B. W. Yawney, *Austral. J. Chem.* 1967, **20**, 77.