

Carbon–Carbon Formation at Di-iron Centres. Part 2.¹ Reactivity of $[\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})\{\mu\text{-C(R)C(R)H}\}]$ Complexes toward $\text{MeOC(O)C}\equiv\text{CC(O)OMe}$ ($\text{R} = \text{Ph}$) and $\text{CF}_3\text{C}\equiv\text{CCF}_3$ ($\text{R} = \text{Ph}$ or H); X-Ray Crystal Structures of $[\text{Fe}_2(\text{CO})_5\{\mu\text{-C(OEt)C(C(O)OMe)C(C(O)OMe)\}\}\{\mu\text{-C(Ph)C(Ph)H}\}]\cdot\text{H}_2\text{O}$ and $[\text{Fe}_2(\text{CO})_5\{\mu\text{-C(CF}_3\text{)C(CF}_3\text{)CHCHCH(OMe)\}\}]^\dagger$

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The complexes $[\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})\{\mu\text{-C(R)C(R)H}\}]$ ($\text{R} = \text{H}$ or Ph), which result from the reaction of triethyloxonium tetrafluoroborate with $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})\{\mu\text{-C(R)C(R)H}\}]^-$, react at room temperature with $\text{MeOC(O)C}\equiv\text{CC(O)OMe}$ ($\text{R} = \text{Ph}$) and $\text{CF}_3\text{C}\equiv\text{CCF}_3$ ($\text{R} = \text{H}$ or Ph). For $\text{R} = \text{Ph}$, the complexes $[\text{Fe}_2(\text{CO})_5\{\mu\text{-C(OEt)C(R')C(R')}\}\{\mu\text{-C(R)C(R)H}\}]$ [$\text{R}' = \text{CF}_3$ or C(O)OMe] have been isolated. The structure has been established by a single-crystal X-ray diffraction study of the derivative with $\text{R}' = \text{C(O)OMe}$. The complexes result from the loss of one molecule of carbon monoxide and from the insertion of the alkyne into the iron–carbon bond of the carbyne bridge to give a dimetalla-allyl group. When $\text{R} = \text{H}$, the complex formed has the formulation $[\text{Fe}_2(\text{CO})_6\{\mu\text{-C(CF}_3\text{)C(CF}_3\text{)CHCHCH(OMe)\}]$, as established by an X-ray structure determination of the methoxy derivative. This complex results from the insertion of hexafluorobut-2-yne into the iron–carbon σ bond of the vinyl group, the coupling of the vinyl end of this new fragment with the ethoxycarbyne, and the 1,2-hydrogen shift of one hydrogen to the carbyne group. In this compound, the ethoxy group is very labile and can be replaced by a methoxy group by action of methanol. This replacement is reversible. The ethoxy group can also be replaced by a diethylamino-group by the action of diethylamine, but in this case the reaction is not reversible. This lability of the alkoxy group is explained by the unsymmetrical mode of bonding to one iron of the π -bonded $\text{CH}=\text{CH}(\text{OEt})$ end of the organic bridge, which favoured nucleophilic attacks.

The synthesis of the dinuclear anionic complexes² $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})\{\mu\text{-C(R)C(R)H}\}]^-$ has opened up a new area in the extensive field of the study of the reactivity of organic molecules at dinuclear centres.³ We have shown that when $\text{R} = \text{Ph}$, these complexes react easily with activated alkynes to give products resulting either from the double insertion of the alkyne and of the carbon monoxide into the carbon–iron σ bond of the ethenyl group or from the insertion of the alkyne into the carbon–hydrogen bond of the ethenyl group.¹

A further point of interest concerning these anionic complexes is that the bridging carbon monoxide is nucleophilic enough to react with carbo-cations such as C_2H_5^+ to give $[\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})\{\mu\text{-C(R)C(R)H}\}]$, neutral complexes containing two different organic bridges. In the case where $\text{R} = \text{Ph}$, we have shown that an intramolecular coupling of the ethoxycarbyne and the 1,2-diphenylethenyl ligand occurs readily to give hexacarbonyl- μ -[2'-3'- η -3-ethoxy-1,2-diphenylpropane-1,2-diyl-3-ylidene- $\text{C}^{1-3}(\text{Fe}^1), \text{C}^3(\text{Fe}^2), \text{C}^{2'-3}(\text{Fe}^2)$]-di-iron($\text{Fe}-\text{Fe}$).⁴

In this paper, we relate the result of the interaction of $[\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})\{\mu\text{-C(R)C(R)H}\}]$ complexes with hexa-

fluorobut-2-yne ($\text{R} = \text{Ph}$ or H) and dimethyl acetylenedicarboxylate ($\text{R} = \text{Ph}$).

Experimental

All reactions were performed under a nitrogen atmosphere. ¹H N.m.r. spectra were recorded on a Perkin-Elmer R12 or on a Bruker WH90 spectrometer and ¹³C n.m.r. spectra on a Bruker WM250 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer in hexadecane solutions in the $\nu(\text{CO})$ stretching region. The complexes $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})\{\mu\text{-C(R)C(R)H}\}]$ ($\text{R} = \text{Ph}$ or H) were prepared by published procedures.² Elemental analyses were performed in our laboratory.

Preparation of $[\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})\{\mu\text{-C(Ph)C(Ph)H}\}]$, (1a).— $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})\{\mu\text{-C(Ph)C(Ph)H}\}]$ (1 g) in dichloromethane (10 cm³) was added to the suspension of triethyloxonium tetrafluoroborate (300 mg) in dichloromethane (10 cm³). The solution was stirred for 1 h at room temperature and the solvent was then evaporated to dryness. The residue was extracted with pentane (2 × 20 cm³). Concentration of this solution and cooling to -20°C gave 750 mg of $[\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})\{\mu\text{-C(Ph)C(Ph)H}\}]$ as red crystals (70% yield), m.p. 92°C (decomp.). I.r.: $\nu(\text{CO})$ at 2 066m, 2 034vs, 2 000s, 1 996 (sh), 1 985s, and 1 966m cm⁻¹. ¹H N.m.r. [$(\text{CD}_3)_2\text{CO}$]: δ 7.20 (Ph), 5.09 (qt, J 7.3 Hz, OCH_2), 3.48 (CH), 1.65 (t, J 7.3 Hz, CH_3); ¹³C n.m.r. (CD_2Cl_2) (except phenyl resonances): δ 383.8 (COEt), 211.2 (CO), 182.8 [FeC(Ph)-], 87.9 [CH(Ph)], 87.2 (OCH_2CH_3), 15.3 (OCH_2CH_3) [Found for (1a): C, 53.60; H, 3.10. Calc.: C, 53.75; H, 3.10%].

[†] 1,1,1,2,2-Pentacarbonyl- μ -[η -1,2-diphenylethenyl- $\text{C}^1(\text{Fe}^1), \text{C}^{1-2}(\text{Fe}^2)$]- μ -[η -1-ethoxy-2,3-di(methoxycarbonyl)prop-1-en-1-yl-3-ylidene- $\text{C}^{1-3}(\text{Fe}^1), \text{C}^{1-3}(\text{Fe}^2)$]-di-iron($\text{Fe}-\text{Fe}$) hydrate and μ -[2-3:4-5- η -5-methoxy-1,2-bis(trifluoromethyl)penta-2,4-dien-1-ylidene- $\text{C}^{1-3}(\text{Fe}^1), \text{C}^{1,4,5}(\text{Fe}^2)$]-bis(tricarbonyliron)($\text{Fe}-\text{Fe}$) respectively.

Supplementary data available (No. SUP 56195, 10 pp.): thermal parameters, H-atom co-ordinates, full bond distances and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.

Preparation of $[\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})(\mu\text{-CHCH}_2)]$, (**1b**).— $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CHCH}_2)]$ (1 g) dissolved in dichloromethane (10 cm³) was added to a suspension of triethyloxonium tetrafluoroborate (400 mg) in dichloromethane (10 cm³). The solution was stirred for 20 min at room temperature and the solvent was evaporated to dryness. Extraction with two 20-cm³ portions of pentane and evaporation to dryness left a brown-yellow liquid which was not further purified but identified by its i.r. and ¹H n.m.r. spectra. I.r.: $\nu(\text{CO})$ at 2 072m, 2 038s, 2 003s, 1 989ms, and 1 969m cm⁻¹. ¹H n.m.r. (CD_2Cl_2): δ 9.08 (dd, J_1 13.3, J_2 8.7 Hz, 1 H), 4.68 (qt, J 6.9 Hz, 2 H), 3.38 (d, J_2 8.7 Hz, 1 H), 2.15 (d, J_1 13.3 Hz, 1 H), 1.40 (t, J 6.9 Hz, 3 H).

Preparation of $[\text{Fe}_2(\text{CO})_5\{\mu\text{-C}(\text{OEt})\text{C}[\text{C}(\text{O})\text{OMe}]\text{C}[\text{C}(\text{O})\text{OMe}\}\}\{\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{H}\}]$, (**2**).—To (**1a**) (500 mg) dissolved in dichloromethane (10 cm³) was added $\text{MeOC}(\text{O})\text{C}\equiv\text{CC}(\text{O})\text{OMe}$ (120 μl , 1 mol equiv.) and the solution stirred for 3 h. The solution was then evaporated to dryness. The residue was dissolved in a minimum amount of dichloromethane and methanol (15 cm³) was added. Cooling to -20°C gave 380 mg of (**2**) (62.2%) as green crystals, m.p. 84°C (decomp.). I.r.: $\nu(\text{CO})$ at 2 071m, 2 030 (sh), 2 026s, 2 004m, and 1 968m cm⁻¹. ¹H n.m.r. [$(\text{CD}_3)_2\text{CO}$]: δ 7.12 (Ph), 6.12 (CH), 4.64, 4.60 (qt, J 7.1 Hz, OCH_2), 3.80 (OMe), 3.75 (OMe), 1.50 (t, J 7.1 Hz, CH_3); ¹³C n.m.r. (CD_2Cl_2) (except phenyl resonances): δ 221.3 (COEt); 213.7, 213.3, 207.3, 206.2, 202.7, 200.7 [CO + FeC(Ph)]; 173.8, 163.2 [C(O)OMe]; 99.1 [CC(O)OMe]; 78.1 [C(Ph)H]; 73.2 (OCH_2CH_3); 51.2, 51.1 (OMe); 14.9 (OCH_2CH_3) [Found for (**2**): C, 52.95; H, 3.65. Calc.: C, 53.35; H, 3.50%].

Preparation of $[\text{Fe}_2(\text{CO})_5\{\mu\text{-C}(\text{OEt})\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)\}\{\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{H}\}]$, (**3**).—From a vacuum line, a stoichiometric amount of hexafluorobut-2-yne was added to (**1**) (0.5 g) in dichloromethane (20 cm³) in a vessel fitted with a Teflon stopcock. The solution was stirred for 15 h at room temperature. At the end of the reaction the solution was treated as described for (**2**). Cooling at -20°C gave 350 mg of (**3**) as green crystals (55.5%), m.p. 111°C (decomp.). I.r.: $\nu(\text{CO})$ at 2 078m, 2 040 (sh), 2 037s, 2 014m, and 1 982m cm⁻¹. ¹H n.m.r. [$(\text{CD}_3)_2\text{CO}$]: δ 7.12 (Ph), 6.11 (CH); 4.62, 4.43 (qt, J 7.1 Hz, OCH_2), 1.54 (t, J 7.1 Hz, CH_3); ¹⁹F n.m.r. (CD_2Cl_2) [from $\text{CF}_3\text{CO}(\text{OH})$ as external reference]: δ 19.54 (qt, J 7.3 Hz), 6.1 (qt, J 7.3 Hz); ¹³C n.m.r. (CD_2Cl_2): δ 224 (COEt); 212.6, 211.2, 206.3, 205, 202.2, 201.4 [CO + Fe-C(Ph)]; 119.8 (qt, J 278 Hz, CF_3), 98.1 (qt, J 38 Hz, CCF_3), 73.9 [CH(Ph)], 73.3 (OCH_2CH_3), 14.7 (OCH_2CH_3) [Found for (**3**): C, 47.65; H, 2.35. Calc.: C, 48.00; H, 2.45%].

Preparation of $[\text{Fe}_2(\text{CO})_6\{\mu\text{-C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{CHCHCH}(\text{OEt})\}]$, (**4**).—From a vacuum line a stoichiometric amount of hexafluorobut-2-yne was added to brown-yellow (**1b**), obtained from $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CHCH}_2)]$ (1 g), dissolved in dichloromethane, in a vessel fitted with a Teflon stopcock. The solution was stirred overnight at room temperature. At the end of the reaction, the solution was evaporated to dryness and the residue was dissolved in a small amount of ethanol and cooled at -20°C to give 0.450 g of $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{CHCHCH}(\text{OEt})\}]$ as orange crystals {36% yield based on $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CHCH}_2)]$ }, m.p. 88°C . I.r.: $\nu(\text{CO})$ at 2 078m, 2 038s, 2 016m, 2 003m, 1 998m, and 1 984m cm⁻¹. ¹H n.m.r. (CD_2Cl_2): δ 5.3 (d, J 9.7 Hz, 1 H), 4.24 (d, J 3.3 Hz, 1 H), 4.02 (complex multiplet $\text{OCH}_2 + \text{CH}$), 1.22 (t, J 7.1 Hz, CH_3) [Found for (**4**): C, 34.30; H, 1.65. Calc.: C, 34.20; H, 1.50%].

Preparation of $[\text{Fe}_2(\text{CO})_6\{\mu\text{-C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{CHCHCH}(\text{OMe})\}]$, (**5**).—Dissolution of (**4**) in methanol (5 cm³) at room

Table 1. Crystal data and experimental details of the X-ray diffraction studies of complexes (**2**)- H_2O and (**5**)

Formula	(2)- H_2O $\text{C}_{28}\text{H}_{21}\text{Fe}_2\text{O}_{10}\cdot\text{H}_2\text{O}$	(5) $\text{C}_{14}\text{H}_6\text{F}_6\text{Fe}_2\text{O}_7$
<i>M</i>	647.2	511.9
System	Monoclinic	Monoclinic
<i>a</i> /Å	32.138(4)	17.438(3)
<i>b</i> /Å	8.559(1)	13.776(2)
<i>c</i> /Å	22.203(3)	7.703(1)
β /°	107.25(2)	106.68(2)
<i>U</i> /Å ³	5 833(2)	1 773(1)
Space group	<i>C2/c</i>	<i>P2₁/n</i>
<i>D_c</i> /g cm ⁻³	1.47	1.92
<i>Z</i>	8	4
<i>F</i> (000)	2 648	928
$\lambda(\text{Mo-K}\alpha)$ /Å	0.710 69	0.710 69
$\mu(\text{Mo-K}\alpha)$ /cm ⁻¹	10.8	17.8
Measured intensities	1 331 ($\theta < 25^\circ$)	1 701
Observed intensities	1 316	1 625
	[<i>I</i> > 2.5 σ (<i>I</i>)]	[<i>I</i> > 2.5 σ (<i>I</i>)]

temperature and cooling at -20°C gave quantitatively orange crystals of (**5**), m.p. 134°C (decomp.). I.r.: $\nu(\text{CO})$ at 2 079m, 2 038s, 2 019m, 2 003s, 1 998s, and 1 985w cm⁻¹. ¹H n.m.r. (C_6D_6): δ 4.54 (d, J 9.3 Hz, 1 H), 3.57 (d, J 3 Hz, 1 H), 3.34 (dd, J_1 9.3, J_2 3 Hz, 1 H), 2.63 (3 H); ¹³C n.m.r. (CD_2Cl_2): δ 209.1 (CO), 122.9 (CH, J 188 Hz), 61.4 (OMe, J 146.6 Hz), 60.8 (CH, J 164.6 Hz), 48.4 (CH, J 170.2 Hz). Selective proton decoupling⁵ showed that the resonance at 122.9 is associated to the proton doublet at 4.54 p.p.m. [Found for (**5**): C, 32.55; H, 1.05. Calc.: C, 32.85; H, 1.15%].

Reaction of (**5**) with Diethylamine.—To (**5**) (200 mg) in CH_2Cl_2 (10 cm³) was added an excess of diethylamine and the solution stirred for 1 h. After evaporation to dryness and recrystallization in a dichloromethane-ether mixture, pale orange crystals of $[\text{Fe}_2(\text{CO})_6\{\mu\text{-C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{CHCHCH}(\text{NEt}_2)\}]$, (**6**) were obtained in nearly quantitative yield, m.p. 167°C . I.r.: $\nu(\text{CO})$ at 2 065m, 2 023s, 1 996m, 1 984m, and 1 974m cm⁻¹. ¹H n.m.r. (CD_2Cl_2): δ 6.14 (d, J 8.6 Hz, 1 H), 3.78 (d, J 2.9 Hz, 1 H), 3.17 [complex multiplet, $\text{N}(\text{CH}_2)_2$], 2.58 (dd, J_1 2.9, J_2 8.6 Hz, 1 H), 1.29 (t, J 7.1 Hz), 1.22 (t, J 7.4 Hz).

Crystal-structure Determinations.—A. $[\text{Fe}_2(\text{CO})_5\{\mu\text{-C}(\text{OEt})\text{C}[\text{C}(\text{O})\text{OMe}]\text{C}[\text{C}(\text{O})\text{OMe}\}\}\{\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{H}\}]\cdot\text{H}_2\text{O}$, (**2**)- H_2O . A small crystal was selected and mounted on a Philips PW-1100 four-circle diffractometer. The unit cell was measured from centring 25 reflections ($6 < \theta < 12^\circ$) and refined by least squares techniques. Intensities were collected with $\text{Mo-K}\alpha$ radiation, using the ω -scan technique (scan width 1° , scan speed 0.3° s^{-1}). 1 331 Reflections were measured with $\theta < 25^\circ$. No significant intensity variation was observed in three reflections measured over 2 h. Crystallographic data are given in Table 1.

The structure was solved by direct methods using the MULTAN 80 system of computer programs.⁶ An *E*-map from the set with the highest combined figure of merit revealed 40 non-hydrogen atoms. Refinements were carried out by full-matrix least-squares methods using the SHELX 76 computer program.⁷ The function minimized was $w\|F_o - |F_c|\|^2$ where $w = [\sigma^2(F_o) + 0.000 54|F_o|^2]^{-1}$. Isotropic refinements led to $R = 0.15$, and a subsequent difference synthesis showed a double peak, which was assigned to the O atom according to the results of a Fourier synthesis. A difference synthesis performed after the anisotropic refinements led to the localization of 18 H atoms which were refined with an overall isotropic factor while

Table 2. Atomic co-ordinates with estimated standard deviations (e.s.d.s) in parentheses for (2)·H₂O

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Fe(1)	3 811(1)	2 566(3)	-4 139(1)	C(74)	4 225(13)	5 114(29)	-6 161(12)
Fe(2)	3 830(1)	24(3)	-4 645(1)	C(75)	4 496(8)	4 024(30)	-5 784(11)
C(1)	5 389(7)	442(27)	-3 287(11)	C(76)	4 338(7)	2 964(20)	-5 421(9)
C(2)	4 962(6)	1 237(25)	-3 595(9)	C(81)	3 161(7)	633(18)	-6 028(10)
O(3)	4 620(4)	383(12)	-3 442(5)	C(82)	2 735(7)	861(19)	-6 374(11)
C(4)	4 207(7)	595(18)	-3 780(8)	C(83)	2 582(7)	397(23)	-7 006(13)
C(5)	3 864(6)	-297(18)	-3 710(9)	C(84)	2 855(12)	-361(24)	-7 297(10)
C(6)	3 503(6)	592(15)	-4 029(7)	C(85)	3 287(9)	-602(21)	-6 952(14)
C(51)	3 876(6)	-1 719(21)	6 682(11)	C(86)	3 439(6)	-138(21)	-6 330(12)
O(51)	3 991(5)	-3 009(16)	6 545(6)	C(11)	4 202(6)	4 084(20)	-4 206(8)
O(52)	3 747(4)	-1 478(13)	7 163(7)	O(11)	4 442(5)	5 059(15)	-4 208(6)
C(52)	3 699(8)	-2 823(23)	-2 463(11)	C(12)	3 866(7)	3 009(25)	-3 326(12)
C(61)	3 052(6)	234(21)	-4 064(8)	O(12)	3 876(5)	3 200(18)	-2 813(7)
O(61)	2 762(5)	1 121(15)	-4 115(7)	C(13)	3 336(6)	3 873(19)	-4 407(9)
C(62)	2 558(7)	-1 860(24)	-4 035(10)	O(13)	3 024(5)	4 497(14)	-4 550(6)
O(62)	2 983(4)	-1 331(14)	-4 038(6)	C(14)	3 581(6)	-1 771(24)	-4 927(10)
C(7)	3 687(5)	2 043(17)	-5 086(8)	O(14)	3 425(4)	-2 968(15)	-5 096(6)
C(8)	3 302(5)	1 158(17)	-5 351(8)	C(15)	4 275(6)	-505(19)	-4 893(9)
C(71)	3 882(8)	3 096(24)	-5 484(9)	O(15)	4 574(4)	-1 048(15)	-5 027(6)
C(72)	3 611(8)	4 106(21)	-5 903(10)	O(H ₂ O)	4 841(12)	4 601(42)	2 361(24)
C(73)	3 796(10)	5 149(28)	-6 213(11)				

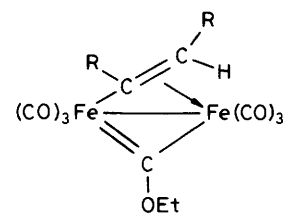
Table 3. Atomic co-ordinates with e.s.d.s in parentheses for (5)*

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Fe(1)	1 685(1)	3 069(2)	5 723(3)	C(71)	1 741(12)	1 725(12)	2 461(22)
Fe(2)	3 103(1)	2 696(2)	5 362(3)	F(72)	962(7)	1 552(7)	1 991(13)
C(1)	4 557(10)	4 135(12)	2 947(22)	F(73)	1 936(7)	1 729(7)	917(13)
O(2)	4 131(7)	4 331(7)	4 302(13)	F(74)	2 065(6)	899(6)	3 288(13)
C(3)	3 362(10)	4 076(10)	3 801(19)	C(11)	2 268(11)	3 424(13)	7 933(23)
C(4)	2 867(11)	4 271(10)	5 001(18)	O(11)	2 647(8)	3 692(10)	9 365(15)
C(5)	1 995(9)	4 270(11)	4 403(19)	C(12)	725(12)	3 607(13)	5 793(21)
C(6)	1 637(10)	3 511(11)	3 168(17)	O(12)	178(8)	3 944(11)	5 913(18)
C(7)	2 008(8)	2 604(10)	3 556(18)	C(13)	1 372(10)	1 895(12)	6 218(19)
C(61)	929(13)	3 778(17)	1 651(33)	O(13)	1 142(8)	1 145(9)	6 553(16)
C(61')	1 308(30)	4 016(31)	1 481(82)	C(21)	3 065(12)	1 571(13)	6 501(23)
F(62')	648(14)	4 637(12)	1 692(28)	O(21)	3 076(8)	863(9)	7 263(18)
F(62)	252(12)	3 446(18)	1 829(21)	C(22)	3 937(11)	3 042(12)	7 290(21)
F(63)	1 104(24)	4 370(38)	476(63)	O(22)	4 455(8)	3 264(10)	8 518(15)
F(63')	857(36)	3 283(35)	247(65)	C(23)	3 621(10)	2 168(11)	3 837(22)
F(64)	929(47)	3 576(55)	-96(71)	O(23)	3 875(8)	1 784(9)	2 838(18)
F(64')	346(47)	3 045(53)	895(93)				

* Occupancy factors: 0.73(4), C(61); 0.25(4), C(61'); 0.76(4), F(62'); 0.81(4), F(62); 0.32(4), F(63); 0.54(4), F(63'); 0.33(4), F(64); 0.20(4), F(64').

the remaining atoms were refined anisotropically. The final *R* factor was 0.055 (*R'* = 0.053). The assignment of the O atom to the double peak was confirmed by a Fourier synthesis at this stage. The final difference synthesis did not allow the determination of the hydrogen atoms of the C(1) methyl group and the disordered water molecules. Final atomic co-ordinates are given in Table 2.

B. [Fe₂(CO)₆{μ-C(CF₃)C(CF₃)CHCHCH(OMe)}], (5). The conditions were the same as for (2) and the main crystallographic data are given in Table 1. The function minimized was $w\|F_o\| - |F_c\|^2$, where $w = [\sigma^2(F_o) + 0.00034|F_o|^2]^{-1}$. Isotropic refinements led to *R* = 0.18, and a subsequent difference synthesis revealed eight peaks sensitive to the localization of non-obtained CF₃ groups. Anisotropic refinements led to a final *R* factor of 0.069 (*R'* = 0.066) when the occupancy factor of disordered atoms was also refined. A final difference synthesis revealed the localization of three hydrogen atoms which have not been refined. The remaining peaks were less than 0.2 e Å⁻³. Final atomic co-ordinates are given in Table 3.



R = Ph (1a) or H (1b)

Figure 1. Proposed structure for complexes (1a) and (1b)

Results and Discussion

The complex [PPh₄][Fe₂(CO)₆(μ-CO){μ-C(Ph)C(Ph)H}] reacts readily at room temperature with triethyloxonium tetrafluoroborate to give a neutral complex (1a) which analyses as Fe₂(CO)₆(COEt)[C(Ph)C(Ph)H]. Proton n.m.r. gives evidence for the presence of OEt and C(Ph)C(Ph)H groups and

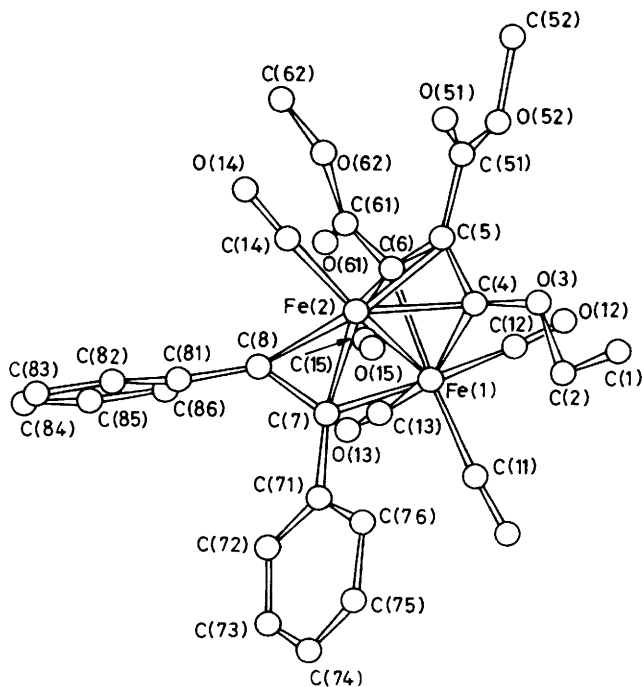
Table 4. Selected interatomic distances (Å) and bond angles (°) with e.s.d.s in parentheses for (2)·H₂O

Fe(1)–Fe(2)	2.457(4)	C(5)–C(6)	1.39(2)	Fe(2)–C(6)	2.01(1)	C(7)–C(8)	1.42(2)
Fe(1)–C(4)	2.12(2)	C(5)–C(51)	1.49(2)	Fe(2)–C(7)	1.97(2)	C(7)–C(71)	1.52(2)
Fe(1)–C(6)	2.01(1)	C(51)–O(51)	1.23(2)	Fe(2)–C(8)	2.17(2)	C(8)–C(81)	1.50(2)
Fe(1)–C(7)	2.07(2)	C(51)–O(52)	1.27(2)	Fe(2)–C(14)	1.76(2)	C(11)–O(11)	1.14(2)
Fe(1)–C(11)	1.84(2)	O(52)–C(52)	1.45(2)	Fe(2)–C(15)	1.74(2)	C(12)–O(12)	1.14(2)
Fe(1)–C(12)	1.80(2)	C(6)–C(61)	1.46(2)	C(1)–C(2)	1.50(2)	C(13)–O(13)	1.14(2)
Fe(1)–C(13)	1.80(2)	C(61)–O(61)	1.18(2)	C(2)–O(3)	1.44(2)	C(14)–O(14)	1.15(2)
Fe(2)–C(4)	2.00(2)	C(61)–O(62)	1.36(2)	O(3)–C(4)	1.33(2)	C(15)–O(15)	1.18(2)
Fe(2)–C(5)	2.06(2)	O(62)–C(62)	1.44(2)	C(4)–C(5)	1.39(2)		
Fe(2)–Fe(1)–C(4)	51.3(5)	C(8)–Fe(2)–C(14)	87.7(7)	Fe(1)–Fe(2)–C(4)	55.7(4)	C(5)–C(51)–O(51)	123(2)
Fe(2)–Fe(1)–C(6)	52.5(4)	C(14)–Fe(2)–C(15)	89.4(8)	Fe(1)–Fe(2)–C(5)	70.1(4)	C(5)–C(51)–O(52)	114(2)
Fe(2)–Fe(1)–C(7)	50.8(4)	O(3)–C(2)–C(1)	109(2)	Fe(1)–Fe(2)–C(6)	52.3(4)	O(51)–C(51)–O(52)	123(2)
Fe(2)–Fe(1)–C(11)	118.5(5)	C(4)–O(3)–C(2)	120(1)	Fe(1)–Fe(2)–C(7)	54.4(5)	C(52)–O(52)–C(51)	118(1)
Fe(2)–Fe(1)–C(12)	129.5(7)	Fe(1)–C(4)–Fe(2)	73.1(6)	Fe(1)–Fe(2)–C(8)	79.3(5)	C(6)–C(61)–O(61)	128(2)
Fe(2)–Fe(1)–C(13)	119.7(5)	C(5)–C(4)–O(3)	124(1)	Fe(1)–Fe(2)–C(14)	150.0(6)	C(6)–C(61)–O(62)	144(1)
C(4)–Fe(1)–C(6)	63.1(7)	O(3)–C(4)–Fe(1)	135(1)	Fe(1)–Fe(2)–C(15)	120.6(6)	O(61)–C(61)–O(62)	120(2)
C(4)–Fe(1)–C(7)	97.1(6)	O(3)–C(4)–Fe(2)	137(1)	C(4)–Fe(2)–C(5)	39.9(6)	C(62)–O(62)–C(61)	118(1)
C(6)–Fe(1)–C(7)	89.4(6)	C(5)–C(4)–Fe(1)	94(1)	C(4)–Fe(2)–C(6)	65.2(7)	C(8)–C(7)–Fe(1)	115(1)
C(4)–Fe(1)–C(11)	104.1(7)	C(5)–C(4)–Fe(2)	72(1)	C(5)–Fe(2)–C(6)	39.9(5)	C(8)–C(7)–Fe(2)	77(1)
C(6)–Fe(1)–C(11)	167.0(7)	C(6)–C(5)–C(4)	102(1)	C(4)–Fe(2)–C(7)	104.4(7)	C(71)–C(7)–C(8)	122(2)
C(7)–Fe(1)–C(11)	90.0(7)	C(4)–C(5)–Fe(2)	78(1)	C(5)–Fe(2)–C(7)	123.5(6)	C(71)–C(7)–Fe(1)	118(1)
C(4)–Fe(1)–C(12)	85.5(8)	C(6)–C(5)–Fe(2)	78(1)	C(6)–Fe(2)–C(7)	92.0(6)	C(71)–C(7)–Fe(2)	137(1)
C(6)–Fe(1)–C(12)	87.7(8)	C(51)–C(5)–Fe(2)	133(1)	C(4)–Fe(2)–C(8)	134.9(6)	C(7)–C(8)–C(81)	123(1)
C(7)–Fe(1)–C(12)	174.8(8)	C(51)–C(5)–C(4)	129(2)	C(5)–Fe(2)–C(8)	125.7(6)	C(7)–C(8)–Fe(2)	62.7(9)
C(11)–Fe(1)–C(12)	93.8(8)	C(51)–C(5)–C(6)	129(1)	C(6)–Fe(2)–C(8)	86.0(6)	C(81)–C(8)–Fe(2)	122(1)
C(4)–Fe(1)–C(13)	160.2(7)	C(61)–C(6)–C(5)	125(1)	C(7)–Fe(2)–C(8)	39.8(5)	O(11)–C(11)–Fe(1)	175(2)
C(6)–Fe(1)–C(13)	97.2(7)	C(5)–C(6)–Fe(1)	99(1)	C(4)–Fe(2)–C(14)	129.5(8)	O(12)–C(12)–Fe(1)	174(2)
C(7)–Fe(1)–C(13)	84.3(7)	C(5)–C(6)–Fe(2)	72(1)	C(5)–Fe(2)–C(14)	97.2(8)	O(13)–C(13)–Fe(1)	175(2)
C(11)–Fe(1)–C(13)	95.6(7)	C(61)–C(6)–Fe(1)	133(1)	C(6)–Fe(2)–C(14)	100.4(8)	O(14)–C(14)–Fe(2)	178(2)
C(12)–Fe(1)–C(13)	91.7(8)	C(61)–C(6)–Fe(2)	128(1)	C(7)–Fe(2)–C(14)	125.0(8)	O(15)–C(15)–Fe(2)	171(2)

the occurrence of a signal at 383.8 p.p.m. in the ¹³C n.m.r. spectrum reveals the bridging nature of the COEt group.⁸ We consequently propose the structure shown in Figure 1 for (1a) in which the two iron atoms are bridged by a 1,2-diphenylethenyl group and an ethoxycarbonyl ligand.

The [Fe₂(CO)₆(μ-CO)(μ-CHCH₂)]⁻ anion also reacts readily with triethyloxonium tetrafluoroborate to give a neutral dinuclear complex, (1b). This compound is isolated as an oil and decomposes slowly at room temperature to give a product which has not been identified so far. This instability prevents the full characterization of (1b), but it has been identified spectroscopically by comparison with (1a). Freshly prepared, its proton n.m.r. spectrum shows the presence of an ethoxy group and a vinyl group. The chemical shifts of the protons of the latter clearly show that the mode of bonding of this group has not been affected: it is σ-bonded to one iron and η²-bonded to the other. Further, the i.r. spectrum is very similar to that of (1a). We consequently propose the formulation [Fe₂(CO)₆(μ-COEt)(μ-CHCH₂)] for (1b).

The organic nature of the two bridging groups strongly impelled us to check the reactivity toward unsaturated organic molecules. In a first approach, we studied the action of the activated alkynes hexafluorobut-2-yne and dimethyl acetylenedicarboxylate. Both react readily at room temperature with (1a), leading to two new complexes, (2) and (3) respectively, having very similar i.r. spectra in the ν(CO) stretching region. The only difference is a shift to higher frequencies in the case of complex (3), probably due to the fact that CF₃ is a stronger electron-withdrawing group than C(O)OMe. The proton and ¹³C n.m.r. spectra are also very similar. Compared to the starting material, (1a), two points have to be noted: (i) the proton of the vinylic group shifts from 3.48 to 6.12 for (2) and to 6.11 for (3); (ii) in the ¹³C n.m.r. spectra the resonance of the carbyne bridge shifts from 383.8 p.p.m. for (1a) to 221.3 for (2) and 224 p.p.m. for (3).

**Figure 2.** Structure of complex (2) showing the atomic numbering scheme

All these results show that the same type of reaction has occurred with both alkynes and, further, that this reaction induces a great change in the bonding mode of the bridging groups of (1a). Nevertheless, the precise nature of the reaction was difficult to ascertain only on the basis of spectroscopic data.

Table 5. Selected interatomic distances (Å) and bond angles (°) with e.s.d.s in parentheses for (5)

Fe(1)–Fe(2)	2.617(3)	C(6)–C(61)	1.48(2)	Fe(2)–C(7)	2.02(1)	C(71)–F(72)	1.32(2)
Fe(1)–C(5)	2.09(1)	C(6)–C(61')	1.44(6)	Fe(2)–C(21)	1.79(1)	C(71)–F(73)	1.33(1)
Fe(1)–C(6)	2.04(1)	C(7)–C(71)	1.47(2)	Fe(2)–C(22)	1.82(1)	C(71)–F(74)	1.35(1)
Fe(1)–C(7)	2.01(1)	C(61)–F(62)	1.31(2)	Fe(2)–C(23)	1.83(1)	C(11)–O(11)	1.17(1)
Fe(1)–C(11)	1.78(2)	C(61)–F(63)	1.32(3)	O(2)–C(1)	1.47(1)	C(12)–O(12)	1.09(2)
Fe(1)–C(12)	1.85(2)	C(61)–F(64)	1.43(5)	C(3)–O(2)	1.33(1)	C(13)–O(13)	1.16(1)
Fe(1)–C(13)	1.78(1)	C(61')–F(62')	1.48(5)	C(3)–C(4)	1.46(2)	C(21)–O(21)	1.14(1)
Fe(2)–C(3)	2.36(1)	C(61')–F(63')	1.45(6)	C(4)–C(5)	1.46(2)	C(22)–O(22)	1.15(2)
Fe(2)–C(4)	2.21(1)	C(61')–F(64')	1.35(7)	C(5)–C(6)	1.43(2)	C(23)–O(23)	1.12(1)
				C(6)–C(7)	1.40(2)		
Fe(2)–Fe(1)–C(5)	73.7(4)	C(22)–Fe(2)–C(21)	87.7(7)	C(13)–Fe(1)–C(7)	93.7(5)	C(7)–C(6)–Fe(1)	68.8(7)
Fe(2)–Fe(1)–C(6)	74.6(4)	C(23)–Fe(2)–C(3)	77.9(5)	C(13)–Fe(1)–C(11)	99.8(6)	C(5)–C(6)–C(61)	117(1)
Fe(2)–Fe(1)–C(7)	49.6(3)	C(23)–Fe(2)–C(4)	114.7(5)	C(13)–Fe(1)–C(12)	91.3(7)	C(5)–C(6)–C(61')	103(1)
Fe(2)–Fe(1)–C(11)	81.9(5)	C(23)–Fe(2)–C(7)	94.4(6)	Fe(1)–Fe(2)–C(3)	102.8(3)	C(7)–C(6)–C(61)	128(1)
Fe(2)–Fe(1)–C(12)	167.0(5)	C(23)–Fe(2)–C(21)	93.7(6)	Fe(1)–Fe(2)–C(4)	71.0(4)	C(7)–C(6)–C(61')	132(2)
Fe(2)–Fe(1)–C(13)	101.6(5)	C(23)–Fe(2)–C(22)	101.7(7)	Fe(1)–Fe(2)–C(7)	49.4(3)	Fe(1)–C(6)–C(61)	129(1)
C(6)–Fe(1)–C(5)	40.5(5)	C(1)–O(2)–C(3)	115(2)	Fe(1)–Fe(2)–C(21)	87.1(5)	Fe(1)–C(6)–C(61')	156(2)
C(7)–Fe(1)–C(5)	71.1(4)	O(2)–C(3)–C(4)	120(1)	Fe(1)–Fe(2)–C(22)	114.8(5)	C(6)–C(7)–C(71)	124(1)
C(7)–Fe(1)–C(6)	40.4(4)	O(2)–C(3)–Fe(2)	112.8(8)	Fe(1)–Fe(2)–C(23)	143.5(5)	C(6)–C(7)–Fe(1)	70.8(7)
C(11)–Fe(1)–C(5)	95.2(6)	C(4)–C(3)–Fe(2)	65.9(6)	C(3)–Fe(2)–C(4)	37.0(4)	C(6)–C(7)–Fe(2)	112.3(9)
C(11)–Fe(1)–C(6)	134.0(6)	C(3)–C(4)–C(5)	124(1)	C(3)–Fe(2)–C(7)	88.9(5)	C(71)–C(7)–Fe(1)	128.2(9)
C(11)–Fe(1)–C(7)	131.4(6)	C(3)–C(4)–Fe(2)	77.1(7)	C(4)–Fe(2)–C(7)	82.5(5)	C(71)–C(7)–Fe(2)	121.8(10)
C(12)–Fe(1)–C(5)	93.4(6)	C(5)–C(4)–Fe(2)	100.3(8)	C(21)–Fe(2)–C(3)	170.1(6)	Fe(1)–C(7)–Fe(2)	81.0(4)
C(12)–Fe(1)–C(6)	97.0(6)	C(4)–C(5)–C(6)	115(1)	C(21)–Fe(2)–C(4)	151.5(6)	O(11)–C(11)–Fe(1)	178(1)
C(12)–Fe(1)–C(7)	128.6(6)	C(4)–C(5)–Fe(1)	103.8(8)	C(21)–Fe(2)–C(7)	97.1(6)	O(12)–C(12)–Fe(1)	177(2)
C(12)–Fe(1)–C(11)	97.7(7)	C(6)–C(5)–Fe(1)	67.7(7)	C(22)–Fe(2)–C(3)	88.8(5)	O(13)–C(13)–Fe(1)	177(1)
C(13)–Fe(1)–C(5)	163.5(5)	C(5)–C(6)–C(7)	115(1)	C(22)–Fe(2)–C(4)	85.5(6)	O(21)–C(21)–Fe(2)	177(2)
C(13)–Fe(1)–C(6)	123.2(6)	C(5)–C(6)–Fe(1)	71.8(7)	C(22)–Fe(2)–C(7)	162.9(6)	O(22)–C(22)–Fe(2)	179(1)
						O(23)–C(23)–Fe(2)	173(1)

For this reason, the structure of (2) was determined by X-ray analysis.

Structure of (2)·H₂O.—Water of crystallization was found in the crystal which certainly originated from the accidental use of wet methanol as the crystallization solvent. A view of the [Fe₂(CO)₅{μ-C(OEt)C[C(O)OMe]C[C(O)OMe}]₂{μ-C(Ph)-C(Ph)H}] molecule with the atom numbering is shown in Figure 2. Bond distances and angles of interest are given in Table 4.

Figure 2 shows that (2) results from the insertion of the alkyne into one iron-carbyne bond with the loss of one molecule of carbon monoxide, while the 1,2-diphenylethenyl group is preserved.

The new organic bridge formed can be described as a dimetalla-allyl group η³-bonded to Fe(2). The C(6) atom is equidistant from Fe(1) and Fe(2) but the C(4) atom is slightly asymmetrically bonded to Fe(1) and Fe(2), while the Fe(1)–C(4) distance is the longer of the iron-carbon distances in this allyl unit. This type of reaction whereby an alkyne couples with a μ- or μ₃-alkyldiyne ligand has already been observed in di-⁹ and tri-nuclear¹⁰ complexes.

The 1,2-diphenylethenyl ligand is σ-bonded to Fe(1) and η²-bonded to Fe(2) in the usual manner to other known complexes of this type.¹¹

As for the Fe₂(CO)₅ unit, the Fe–Fe distance of 2.457(4) Å is quite short for a Fe–Fe single bond.¹² This shortening is probably due to the steric hindrance imposed by the allyl and 1,2-diphenylethenyl bridges. Fe(1) is surrounded by three carbonyl groups and the C(4), C(6), and C(7) atoms, thus defining a distorted octahedron. The Fe(1)(CO)₃ group shows normal iron-carbon distances and iron-carbon oxygen angles.

The geometry around Fe(2) is more difficult to describe. The Fe(2) atom is bonded to C(4), C(5), C(6), C(7), C(8), and to the two carbonyl ligands C(14)O(14) and C(15)O(15). Fe(1)Fe(2) and C(14)C(15) form a plane which separates the two organic frag-

ments. It is noteworthy that the Fe(2)–C(14) and Fe(2)–C(15) distances are substantially shorter than the iron-carbon distances in the Fe(1)(CO)₃ group. This seems normal, due to the fact that Fe(2), which is η²-bonded to the 1,2-diphenylethenyl group and η³-bonded to the allyl group, is bonded to two carbonyl groups only.

Finally, taking into account the metal-metal bond, each iron atom is surrounded by 18 valence electrons.

In summary, both alkynes react with (1a) at room temperature to give a dinuclear complex in which the alkyne couples to the carbyne ligand to form a dimetalla-allyl ligand. In this reaction, the 1,2-diphenylethenyl bridge is preserved and one molecule of carbon monoxide is evolved.

Complex [Fe₂(CO)₆(μ-COEt)(μ-CHCH₂)] (1b) reacts with hexafluorobut-2-yne at room temperature to give a complex, (4), isolated by crystallization in ethanol. This compound shows six i.r.-active bands in the ν(CO) stretching region slightly shifted to higher frequencies compared to (1b). In the proton n.m.r. spectrum, apart from the OEt resonances, two doublets with different coupling constants are observed, each representing one proton. This suggests that a third vinylic signal is obscured by ethoxy resonances. The chemical shifts of these CH resonances clearly show that the mode of bonding of the vinyl group has been modified.

In an attempt to obtain better crystals of (4), methanol was used as solvent. The isolated crystals showed a slightly different i.r. spectrum and proton n.m.r. data evidenced this difference: the ethoxy group had been replaced by a methoxy group while the other resonances were only slightly affected, except for the appearance of a double doublet which had previously been masked by the OCH₂ resonance in (4). Further, proton-coupled ¹³C n.m.r. for this new compound, (5), indicated the presence of three CH groups at 122.9, 60.8, and 48.4 p.p.m.

The occurrence of three CH groups and the unexpected lability of the ethoxy group strongly induced us to determine by

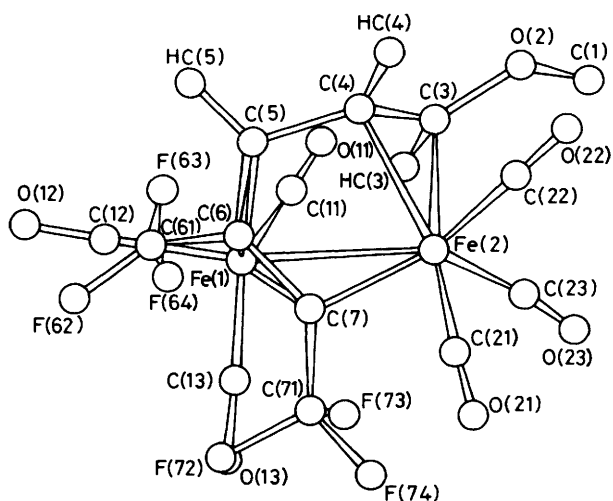


Figure 3. Structure of complex (5) showing the atomic numbering scheme

X-ray analysis the precise nature of the organic fragment formed in the reaction with hexafluorobut-2-yne. This study has been carried out with (5), for which we obtained crystals suitable for X-ray analysis.

Structure of (5).—The molecular structure of (5) with the atom numbering is shown in Figure 3. Bond distances and angles of interest are given in Table 5.

Examination of Figure 3 shows that (5) consists of a $\text{Fe}_2(\text{CO})_6$ unit linked by an organic bridge which results formally from the insertion of hexafluorobut-2-yne into the iron-carbon σ bond of the vinyl bridge, from the coupling of the vinyl group with the carbyne bridge, and from the 1,2-hydrogen shift from the vinyl group to the carbyne carbon. Further, this structure confirms that the methoxy group replaced the ethoxy group of the carbyne bridge.

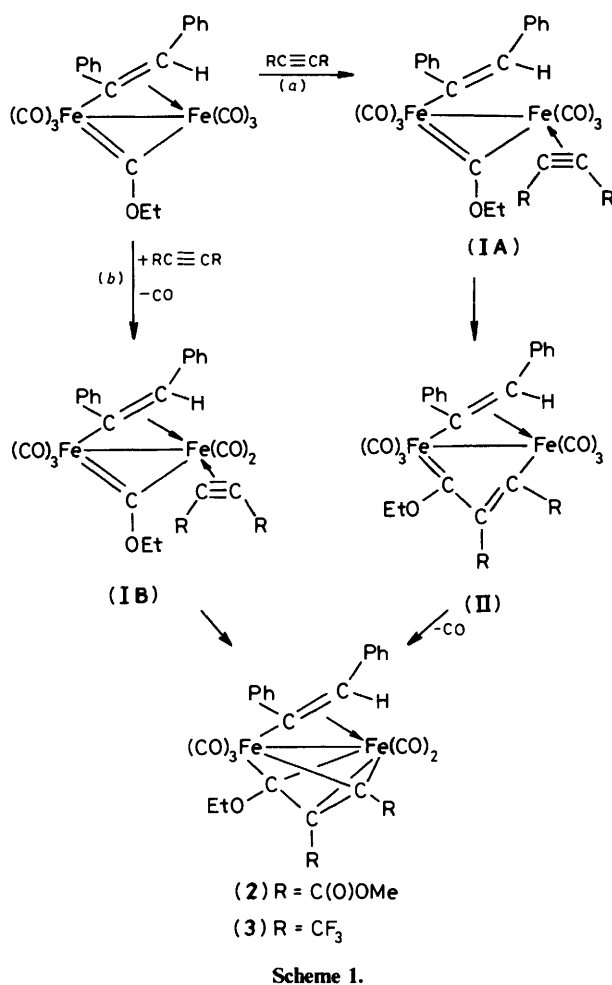
This organic group is η^2 -bonded to Fe(2) by C(3)–C(4) and bonded to Fe(1) by the C(5)C(6)C(7) allylic fragment. This bonding is very similar to that found for one of the products of the reaction of 2,7-dimethyloxepine with $[\text{Fe}(\text{CO})_5]$, namely hexacarbonyl[3-4- η^5 -6- η^1 -(7-oxo-octa-3,5-diene-2,3-diyl)]di-iron.¹³

Examination of the carbon-carbon distances in the C(3)–C(7) chain gives evidence of extensive delocalization, with values ranging from 1.40 to 1.46 Å. For bonding the iron atoms, C(7) is nearly equidistant from Fe(1) and Fe(2), and Fe(1) is nearly equidistant from C(5), C(6), and C(7).

The most important feature of this structure is that Fe(2) is unsymmetrically bonded to the olefin part of the molecule, C(3)C(4), with Fe(2)–C(3) being longer than Fe(2)–C(4) by 0.15 Å. A similar situation has been found for cationic mononuclear complexes of iron bonded to vinyl ethers.¹⁴ Further, these mononuclear complexes provided the first experimental evidence of theoretical predictions¹⁵ that molecular distortion in metal-olefin bonding may play a significant role in determining their reactivity with nucleophiles. So, the unsymmetrical mode of bonding with iron of the vinyl ether part of the organic group of (5) explains the observed lability of the ethoxy group of (4) in methanol solution.

In the $\text{Fe}_2(\text{CO})_6$ unit, the Fe–Fe bond length of 2.617(3) Å is quite long for an iron-iron single bond distance,¹² but it is in the same range as that found for the product resulting from the reaction of 2,7-dimethyloxepine with $[\text{Fe}(\text{CO})_5]$ [2.642(1) Å]¹³ where the organic bridge is very similar. The $\text{Fe}(\text{CO})_3$ units have normal bond distances and bond angles.

Now having exact knowledge of the nature of (4) and (5), a



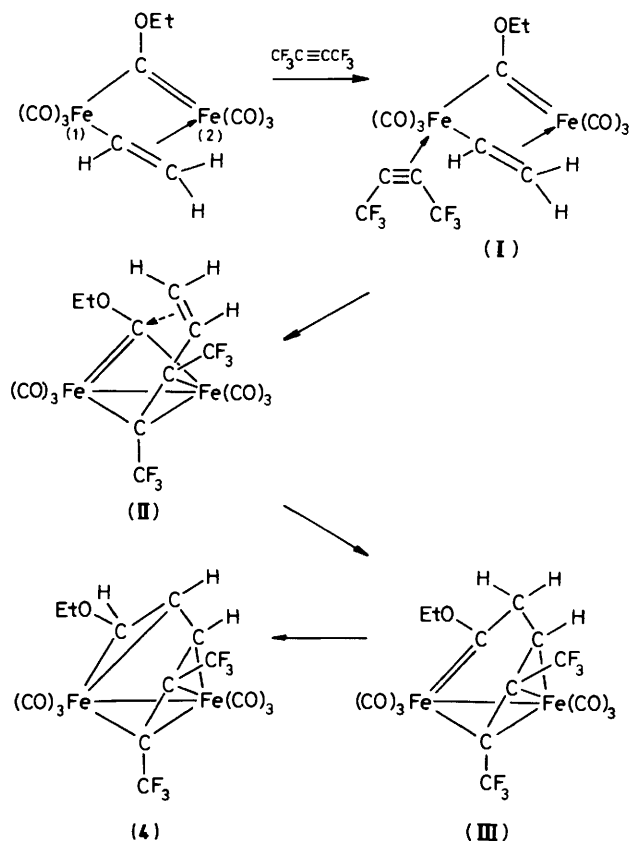
more precise analysis of the n.m.r. data can be carried out. Two doublets and one double doublet have been observed for the CH resonances in the proton n.m.r. spectrum of (5). The most deshielded doublet with a coupling constant of 9.3 Hz is attributed to HC(3) *trans* to HC(4) and the other doublet with a coupling constant of 3 Hz to HC(5). The double doublet is attributed to HC(4). Selective proton-decoupling allowed assignment of the resonance at 122.9 p.p.m. in ¹³C n.m.r. to C(3).

To confirm further our explanation concerning the origin of the lability of the OEt group in (4), we checked that (5) regenerated (4) in solution in ethanol. This is the case and the reaction is rapid.

We extended this reaction to another nucleophile, namely diethylamine. Here again, the substitution of the OR group by NEt₂ occurred readily at room temperature, but in this case the reaction could not be reversed even in boiling ethanol. These observations parallel those made for the mononuclear cationic iron complexes bonded to vinyl ether¹⁴ even though in our case the complexes are neutral and *a priori* less subject to nucleophilic attack.

In summary, hexafluorobut-2-yne reacts readily with (1b) to give a complex in which all the organic fragments are coupled: the hexafluoro-2-butyne has been inserted into the iron-carbon bond of the vinyl group and the vinyl end of this new fragment has been coupled to the carbyne bridge, with subsequent migration of one hydrogen to the carbyne group.

This result has to be contrasted with that observed with $[\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})\{\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{H}\}]$ (1a), which reacts with the alkynes $\text{RC}\equiv\text{CR}$ [R = CF₃ or C(O)OMe] to give products



in which coupling of the alkyne occurs only with the carbyne bridge and with evolution of one molecule of carbon monoxide. So, in the case of (1b), the product of the reaction, (4), is very different and taking into account the quite low stability of (1b), it could be suspected that in fact hexafluorobut-2-yne reacts with the unidentified product of rearrangement. To check this hypothesis, we left (1b) to decompose and then added hexafluorobut-2-yne: no reaction occurred. Consequently, (4) is the result of the reaction of the alkyne with (1b).

So, it appears that, depending on the nature of the ethenyl bridge, hexafluorobut-2-yne interacts either with the carbyne bridge [in the case of (1a)] or with the ethenyl bridge [in the case of (1b)].

In Scheme 1 we present the proposed mechanism for the formation of (2) and (3). Two paths are likely for the first step which is the entering of the alkyne into the co-ordination sphere of the complex. In path (a), a vacant site results from the opening of the 1,2-diphenylethenyl bridge, allowing the alkyne to be co-ordinated. Then, insertion occurs into the iron-carbon bond of the carbide bridge, leading to (II), and, in a further step, departure of carbon monoxide gives the final product.

In path (b), the entering of the alkyne is allowed by the departure of one molecule of carbon monoxide, leading to (IB) which then rearranges the final product.

It can be pointed out that under an atmosphere of carbon monoxide at atmospheric pressure, no reaction occurs between dimethyl acetylenedicarboxylate and (1a). Nevertheless, this cannot allow the prediction of the preferred path, as in path (a) carbon monoxide can compete with the alkyne preventing the bonding of the alkyne to iron.

In the case of the reaction of (1b) with hexafluorobut-2-yne, it is more difficult to propose a mechanism. There is no CO

departure in the reaction and furthermore an intermediate of type (IA) in Scheme 1 would not allow the insertion of the alkyne into the iron-carbon bond of the ethenyl bridge. For these reasons, we propose the mechanism shown in Scheme 2. One way of creating a vacant site on one of the iron atoms is to localize the two-electron bond of the carbyne ligand on Fe(2) with subsequent iron-iron bond breaking. In this case, Fe(1) is electronically unsaturated, which allows the bonding of hexafluorobut-2-yne to iron. The second step could be the insertion of hexafluorobut-2-yne into the iron-carbon σ bond of the vinyl group, leading to intermediate (II). In this intermediate, the vinyl group seems to be in a propitious situation for nucleophilic attack on the carbyne bridge, giving the new intermediate (III) (some examples of nucleophilic attack on bridging carbyne ligands have recently been reported¹⁶).

The structure of intermediate (III) is based on the following arguments: (i) the allylic-type bonding around Fe(2) seems reasonable by comparison with known structures,⁴ and (ii) a bridging position seems to be a very strained situation for the C(OEt) carbon whereas a terminal bonding mode is more realistic. Further, the iron-iron bond is retained in such a situation. The problem of the mechanism of the 1,2-hydrogen shift is less clear to establish, as a metal-assisted migration is not really necessary when taking into account the electron-deficient nature of the carbon bonded to the ethoxy group.

From a comparison of the two proposed mechanisms shown in Schemes 1 and 2, the reason for the difference in behaviour of (1a) and (1b) is not clear. The study has to be extended to other cases of ethenyl bridges to ascertain a possible steric influence.

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