Synthesis and Crystal Structure of Heptacarbonyl-μ_3-(pent-1-en-1-yl-3-ylidene)-(η-1,2,3-triethylcyclopentadienyl)-*triangulo*-tri-iron (3 *Fe–Fe*): The Cleavage of an Acetylenic Triple Bond on a Metal-atom Cluster

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The title complex has been synthesized by treating $[Fe_3(CO)_{12}]$ with ethylacetylene, and characterised by i.r. and mass spectra. The crystal structure has been determined by *X*-ray methods. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 7.674(8)$, $b = 10.966(9)$, $c = 17.652(12)$ Å, $\alpha = 97.5(1)$, $\beta = 119.9(1)$, and $\gamma = 101.8(1)°$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by block-diagonal least squares to R 0.042 for 2 953 observed reflections. The molecule is formed by a trimetal atom cluster; oligomerization of the alkyne and cleavage of an acetylenic triple bond afford a 1,2,3-triethylcyclopentadienyl unit η-bonded to one iron atom, and an ethylallyl unit σ- and η-bonded to all the three iron atoms. Of the seven carbonyl groups co-ordinated to the metal atoms, one unsymmetrically bridges two iron atoms and another very unsymmetrically triply bridges all the metal atoms of the cluster. An analogous complex can be obtained from n-propylacetylene. Experiments on co-oligomerization between acetylene and ethyl- or n-propyl-acetylene, and between diethyl-, di-n-propyl-, and dimethyl-acetylene and the corresponding asymmetrical acetylenes, have also been made.

TREATMENT of $[Fe_3(CO)_{12}]$ with acetylenes RC_2R' and HC_2R (R,R' = H, Me, Et, Pr^n, Bu^t, or Ph) yields tri-, bi-, and mono-nuclear carbonyl complexes containing up to four acetylenic units. Cyclization of three acetylenes is observed in complexes $[Fe_2(CO)_6(RC_2R')_3]$;[1] by CO insertion within the acetylenes, $[Fe_2(CO)_5\{(RC_2R')_3(CO)\}]$[2,3] and $[Fe_2(CO)_6\{(RC_2R')_2(CO)\}]$[4] are formed. A ferracyclopentadiene ring is present in $[Fe_3(CO)_8(RC_2R')_2]$[5] and $[Fe_2(CO)_6(RC_2R')_2]$,[6,7] both containing bridging or semi-bridging CO groups.

We recently described two new trinuclear complexes, $[Fe_3(CO)_8(HC_2Me)_3]$[8] (containing a nearly planar ferracyclohexadiene ring) and $[Fe_3(CO)_8(HC_2Me)_4]$[9] (in which three HC_2Me units form a 1,3-dimethyl-2-vinylcyclopentadienyl η-bonded to one iron atom, and the fourth gives a propylidyne group σ-bonded to the three iron atoms). Inter- and intra-molecular hydrogen shifts are required for the formation of such substituents from HC_2Me.

Treatment of $[Fe_3(CO)_{12}]$ with ethyl- and n-propyl-acetylene gave, beside the above complexes, new complexes $[Fe_3(CO)_7(HC_2R)_4]$ [R = Et, (1); R = Pr^n, (2)]. The crystal structure of (1) has now been determined.

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Two independent substituents are bonded to the trinuclear cluster: an ethylallyl unit σ- and η-bonded to the three metal atoms, and a 1,2,3-triethylcyclopentadienyl unit η-bonded to one iron atom. The formation of these substituents from acetylenes can be explained only by the cleavage or ' dichotomy '[10] of the $C\equiv C$ triple bond of a molecule of ethyl- or n-propyl-acetylene. The only other reported example of such behaviour, to our knowledge, is the cleavage of diethylacetylene in the presence of $CrCl_3$.[10] In the present complex one of the carbonyl groups unsymmetrically bridges two iron atoms, and another very unsymmetrically triply bridges the metal atoms of the cluster.

EXPERIMENTAL

Synthesis and Purification of the Complexes.—Complex (1) was obtained in 0.5% yields (with respect to the iron carbonyl) by refluxing $[Fe_3(CO)_{12}]$ under dry nitrogen in n-heptane with an excess of gaseous ethylacetylene for 45 min; the acetylene was purchased from Merck–Schuchardt and contained, as impurities, 2% of diethylacetylene and 2% of acetylene. Complex (2) was obtained in 1% yields (with respect to the iron carbonyl) by treating, under the same conditions, an excess of liquid n-propylacetylene with $[Fe_3(CO)_{12}]$; the acetylene was obtained by Fluka and was 99.3% pure, the major impurity being di-n-propylacetylene.

The reaction mixtures, each containing about 30 compounds, were fractionated and further purified by preparative t.l.c. (Kieselgel P.F.; eluant, diethyl ether–light petroleum). The complexes were crystallized from n-heptane at -4 °C, and the large crystals of (1) were redissolved in n-heptane and allowed to crystallize at -20 °C [Found: C, 47.95; H, 5.10; Fe, 28.0; O, 19.9. Calc. for $C_{23}H_{24}Fe_3O_7$ (1): C, 47.65; H, 4.15; Fe, 28.9; O, 19.3%; *M*, 579.98. Found: C, 51.0; H, 6.20; Fe, 26.0; O, 16.8. Calc. for $C_{27}H_{32}Fe_3O_7$ (2): C, 51.0; H, 6.05; Fe, 26.35; O, 17.6%; *M*, 636.11].

Other Reactions.—Refluxing $[Fe_3(CO)_{12}]$ under a nitrogen atmosphere and in n-heptane solution for 45 min with the pairs C_2H_2–HC_2Et, C_2H_2–HC_2Pr^n, HC_2Et–EtC_2Et, and HC_2Pr^n–$Pr^nC_2Pr^n$ did not increase the yields of complexes (1) and (2). Under similar conditions, $[Fe_3(CO)_{12}]$ and C_2H_2–HC_2Me or HC_2Me–MeC_2Me gave no complexes having comparable stoicheiometry to (1) or (2). In these reactions the usual complexes obtained from each of the RC_2R and HC_2R with $[Fe_3(CO)_{12}]$ were recovered, together with some unidentified derivatives probably due to co-cyclization of the acetylenes.

Crystal Data.—$C_{23}H_{24}Fe_3O_7$, $M = 579.98$, Triclinic, $a = 7.674(8)$, $b = 10.966(9)$, $c = 17.652(12)$ Å, $\alpha = 97.5(1)$, $\beta = 119.9(1)$, $\gamma = 101.8(1)°$, $U = 1\,212(2)$ Å^3, $Z = 2$, $D_c = 1.59$ g cm^{-3}, $F(000) = 592$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) $= 18.10$ cm^{-1}, space group $P\bar{1}$ from structure determination.

Unit-cell dimensions, determined from rotation and Weissenberg photographs, were refined by a least-squares procedure applied to 18 measured reflections.

Intensity Data.—Intensity data were collected on a Siemens AED single-crystal diffractometer by use of zirconium-filtered Mo-K_α radiation and the ω—2θ scan technique. A prismatic crystal of dimensions *ca.* 0.32 × 0.12 × 0.35 mm was mounted with its *c* axis coincident with the ϕ axis of the diffractometer, and all the reflections with $2 < \theta < 25°$ were measured. Of 4 250 independent reflections, 2 953 having $I > 2\sigma(I)$ were considered as observed. The intensity data were corrected for Lorentz and polarization factors, but no correction was made for absorption effects because of the low value of μR. The absolute scale and the overall temperature factor were determined by Wilson's method.

TABLE 1

Fractional atomic co-ordinates (× 10^4 for Fe, O, and C, × 10^3 for H) with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Fe(1)	154(2)	299(1)	2 489(1)
Fe(2)	3 105(2)	2 389(1)	3 680(1)
Fe(3)	1 714(2)	2 199(1)	2 013(1)
O(1)	5 335(10)	846(7)	3 257(5)
O(2)	4 298(13)	1 758(10)	5 388(5)
O(3)	6 738(13)	4 741(8)	4 595(6)
O(4)	5 557(13)	4 080(8)	2 415(7)
O(5)	−1 068(14)	2 923(9)	397(6)
O(6)	2 243(12)	151(7)	978(5)
O(7)	−3 271(11)	935(7)	1 076(5)
C(1)	4 198(15)	1 382(9)	3 301(7)
C(2)	3 823(15)	2 000(10)	4 721(7)
C(3)	5 289(16)	3 809(10)	4 238(7)
C(4)	4 048(16)	3 349(10)	2 260(7)
C(5)	−20(17)	2 642(10)	1 030(7)
C(6)	2 041(15)	929(10)	1 407(7)
C(7)	−1 673(15)	853(9)	1 634(6)
C(8)	−35(13)	1 555(8)	3 262(6)
C(9)	303(14)	2 886(9)	3 259(6)
C(10)	1 274(13)	3 378(8)	2 815(6)
C(11)	1 753(18)	4 829(10)	2 917(8)
C(12)	−81(21)	5 200(11)	2 232(10)
C(13)	1 460(14)	−1 125(8)	3 046(6)
C(14)	909(14)	−1 350(8)	2 150(6)
C(15)	−1 291(14)	−1 572(8)	1 587(6)
C(16)	−2 104(13)	−1 464(8)	2 158(6)
C(17)	−374(14)	−1 203(8)	3 071(6)
C(18)	−483(18)	−1 116(10)	3 901(7)
C(19)	−277(22)	−2 325(13)	4 212(9)
C(20)	−4 385(14)	−1 706(9)	1 850(7)
C(21)	−5 462(17)	−3 096(11)	1 731(9)
C(22)	−2 577(17)	−1 960(10)	563(7)
C(23)	−3 130(24)	−3 383(11)	168(8)
H(8)	−50(11)	119(7)	368(5)
H(9)	30(11)	355(7)	372(5)
H(111)	289(12)	515(8)	278(5)
H(112)	222(12)	536(7)	351(5)
H(121)	9(12)	621(8)	233(5)
H(122)	−79(13)	474(8)	154(6)
H(123)	−97(12)	503(8)	242(5)
H(13)	290(12)	−93(7)	358(5)
H(14)	196(12)	−134(7)	199(5)
H(181)	−183(12)	−100(7)	376(5)
H(182)	65(12)	−35(7)	438(5)
H(191)	−54(12)	−225(7)	466(5)
H(192)	−155(13)	−305(8)	379(5)
H(193)	91(12)	−230(8)	430(5)
H(201)	−442(12)	−118(7)	233(5)
H(202)	−527(12)	−159(7)	125(5)
H(211)	−488(12)	−328(7)	226(5)
H(212)	−693(12)	−335(7)	146(5)
H(213)	−550(12)	−380(7)	119(5)
H(221)	−178(12)	−144(7)	43(5)
H(222)	−366(12)	−167(7)	39(5)
H(231)	−405(12)	−384(7)	38(5)
H(232)	−196(13)	−369(8)	50(6)
H(233)	−389(13)	−388(8)	−37(6)

Structure Determination and Refinement.—The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares, first with isotropic and then with anisotropic thermal parameters. A final ΔF

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map gave the positions of all the hydrogen atoms. Further least-squares cycles were then computed including these hydrogen atoms with isotropic thermal parameters. Unit weights were chosen at each stage of the refinement after analyzing the variation of $|\Delta F|$ with respect to $|F|$. The final R was 0.042. Atomic scattering factors for non-hydrogen atoms were taken from ref. 11 and for hydrogen atoms from ref. 12. Final atomic co-ordinates are given in Table 1. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22208 (23 pp.).* Calculations were carried out on the Cyber 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna.

RESULTS AND DISCUSSION

Spectra.—The i.r. spectra of the complexes were recorded on a Beckman IR-12 spectrometer (KBr optics) in n-heptane solution. The following absorptions were observed in the CO stretching region: (1) 2 056s (sh), 2 052s, 2 010vs, 1 995s, 1 988s, 1 980s, 1 973s, 1 865m, 1 853m; (2) 2 055s (sh), 2 051s, 2 010vs, 1 995s, 1 988s, 1 979s, 1 972s, 1 864m, and 1 852m cm^{-1}.

The mass spectra were recorded on a Varian CH-5 single-focusing instrument operating at 70 eV.† The complexes show the parent ion and stepwise loss of seven CO groups. The most intense peak for both (1) and (2) corresponds to the ion $[Fe_3(CO)_2(HC_2R)_4]^+$. No metallic fragments containing less than four acetylenic units were detected. Detailed discussion of the mass spectral results will be reported elsewhere.

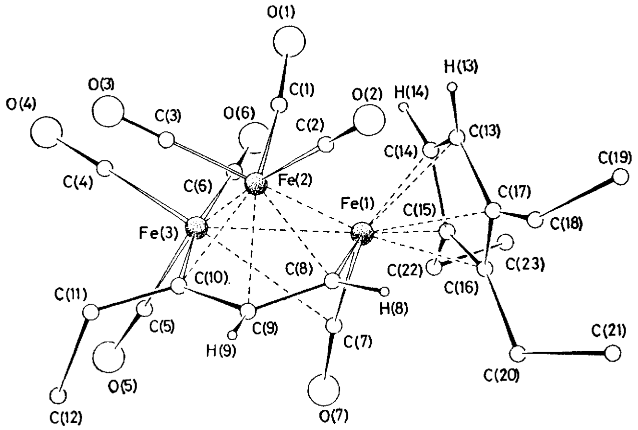

FIGURE 1 View showing the molecular shape and the atomic numbering. The hydrogen atoms, except those of the cyclopentadienyl ring, have been omitted

X-*Ray Structure*.—The structure of complex (1) is presented in Figure 1. Bond distances and angles in the molecule are reported in Table 2.

The structure of complex (1) consists of a trinuclear cluster of iron atoms bound to seven carbonyls, a σ,η-ethylallyl, and an η-triethylcyclopentadienyl group.

TABLE 2

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) In the co-ordination sphere of the iron atoms

Fe(1)–Fe(2)	2.583(5)	Fe(2)–C(2)	1.776(12)
Fe(1)–Fe(3)	2.631(4)	Fe(2)–C(3)	1.758(10)
Fe(2)–Fe(3)	2.542(4)	Fe(2)–C(8)	2.083(10)
Fe(1)–C(1)	2.590(11)	Fe(2)–C(9)	2.113(11)
Fe(1)–C(7)	1.758(10)	Fe(2)–C(10)	2.097(10)
Fe(1)–C(8)	1.889(11)	Fe(3)–C(1)	2.552(11)
Fe(1)–C(13)	2.114(10)	Fe(3)–C(4)	1.773(12)
Fe(1)–C(14)	2.111(11)	Fe(3)–C(5)	1.789(11)
Fe(1)–C(15)	2.105(9)	Fe(3)–C(6)	1.780(13)
Fe(1)–C(16)	2.099(9)	Fe(3)–C(7)	2.413(11)
Fe(1)–C(17)	2.125(11)	Fe(3)–C(10)	1.992(12)
Fe(2)–C(1)	1.765(13)		

Fe(2)–Fe(1)–Fe(3)	58.3(1)	Fe(1)–Fe(2)–C(9)	76.6(3)
Fe(1)–Fe(2)–Fe(3)	61.8(1)	Fe(1)–Fe(2)–C(10)	85.8(3)
Fe(1)–Fe(3)–Fe(2)	59.9(1)	Fe(3)–Fe(2)–C(1)	70.1(3)
Fe(2)–Fe(1)–C(1)	39.9(2)	Fe(3)–Fe(2)–C(2)	162.5(2)
Fe(2)–Fe(1)–C(7)	104.3(3)	Fe(3)–Fe(2)–C(3)	102.8(4)
Fe(2)–Fe(1)–C(8)	52.8(3)	Fe(3)–Fe(2)–C(8)	86.4(3)
Fe(2)–Fe(1)–C(13)	100.7(3)	Fe(3)–Fe(2)–C(9)	78.9(3)
Fe(2)–Fe(1)–C(14)	120.7(3)	Fe(3)–Fe(2)–C(10)	49.7(3)
Fe(2)–Fe(1)–C(15)	159.5(3)	C(1)–Fe(2)–C(2)	98.4(5)
Fe(2)–Fe(1)–C(16)	150.0(3)	C(1)–Fe(2)–C(3)	98.1(6)
Fe(2)–Fe(1)–C(17)	113.3(3)	C(1)–Fe(2)–C(8)	115.6(5)
Fe(3)–Fe(1)–C(1)	58.5(2)	C(1)–Fe(1)–C(9)	142.4(4)
Fe(3)–Fe(1)–C(7)	63.1(4)	C(1)–Fe(2)–C(10)	119.3(4)
Fe(3)–Fe(1)–C(8)	87.9(3)	C(2)–Fe(2)–C(3)	91.6(5)
Fe(3)–Fe(1)–C(13)	129.4(3)	C(2)–Fe(2)–C(8)	87.1(5)
Fe(3)–Fe(1)–C(14)	109.0(3)	C(2)–Fe(2)–C(9)	105.9(5)
Fe(3)–Fe(1)–C(15)	118.0(3)	C(2)–Fe(2)–C(10)	141.8(4)
Fe(3)–Fe(1)–C(16)	151.0(3)	C(3)–Fe(2)–C(8)	146.2(5)
Fe(3)–Fe(1)–C(17)	167.0(3)	C(3)–Fe(2)–C(9)	109.4(5)
C(1)–Fe(1)–C(7)	121.5(5)	C(3)–Fe(2)–C(10)	89.4(5)
C(1)–Fe(1)–C(8)	92.0(4)	C(8)–Fe(2)–C(9)	39.9(4)
C(1)–Fe(1)–C(13)	76.1(4)	C(8)–Fe(2)–C(10)	71.8(4)
C(1)–Fe(1)–C(14)	82.2(4)	C(9)–Fe(2)–C(10)	39.1(4)
C(1)–Fe(1)–C(15)	119.7(4)	Fe(1)–Fe(3)–C(1)	59.9(3)
C(1)–Fe(1)–C(16)	141.7(4)	Fe(1)–Fe(3)–C(4)	145.5(4)
C(1)–Fe(1)–C(17)	108.5(4)	Fe(1)–Fe(3)–C(5)	119.7(4)
C(7)–Fe(1)–C(8)	83.1(4)	Fe(1)–Fe(3)–C(6)	82.8(4)
C(7)–Fe(1)–C(13)	154.5(4)	Fe(1)–Fe(3)–C(7)	40.5(2)
C(7)–Fe(1)–C(14)	120.6(4)	Fe(1)–Fe(3)–C(10)	86.7(3)
C(7)–Fe(1)–C(15)	89.5(4)	Fe(2)–Fe(3)–C(1)	40.6(3)
C(7)–Fe(1)–C(16)	93.9(5)	Fe(2)–Fe(3)–C(4)	93.2(3)
C(7)–Fe(1)–C(17)	129.9(5)	Fe(2)–Fe(3)–C(5)	145.3(4)
C(8)–Fe(1)–C(13)	116.7(4)	Fe(2)–Fe(3)–C(6)	117.8(4)
C(8)–Fe(1)–C(14)	155.1(4)	Fe(2)–Fe(3)–C(7)	88.7(2)
C(8)–Fe(1)–C(15)	146.0(5)	Fe(2)–Fe(3)–C(10)	53.5(3)
C(8)–Fe(1)–C(16)	107.5(4)	C(1)–Fe(3)–C(4)	85.6(5)
C(8)–Fe(1)–C(17)	94.1(4)	C(1)–Fe(3)–C(5)	173.9(5)
C(13)–Fe(1)–C(14)	38.4(4)	C(1)–Fe(3)–C(6)	78.5(4)
C(13)–Fe(1)–C(15)	65.1(4)	C(1)–Fe(3)–C(7)	100.4(4)
C(13)–Fe(1)–C(16)	65.8(4)	C(1)–Fe(3)–C(10)	93.7(4)
C(13)–Fe(1)–C(17)	39.0(5)	C(4)–Fe(3)–C(5)	94.8(6)
C(14)–Fe(1)–C(15)	39.1(4)	C(4)–Fe(3)–C(6)	93.1(6)
C(14)–Fe(1)–C(16)	66.1(4)	C(4)–Fe(3)–C(7)	172.6(5)
C(14)–Fe(1)–C(17)	65.4(4)	C(4)–Fe(3)–C(10)	93.9(5)
C(15)–Fe(1)–C(16)	39.8(4)	C(5)–Fe(3)–C(6)	95.4(5)
C(15)–Fe(1)–C(17)	65.9(4)	C(5)–Fe(3)–C(7)	79.7(5)
C(16)–Fe(1)–C(17)	39.4(4)	C(5)–Fe(3)–C(10)	92.3(5)
Fe(1)–Fe(2)–C(1)	70.3(4)	C(6)–Fe(3)–C(7)	92.3(5)
Fe(1)–Fe(2)–C(2)	102.4(3)	C(6)–Fe(3)–C(10)	169.1(5)
Fe(1)–Fe(2)–C(3)	162.8(4)	C(7)–Fe(3)–C(10)	81.5(4)
Fe(1)–Fe(2)–C(8)	46.2(3)		

(*b*) In the carbonyl groups

O(1)–C(1)	1.174(16)	O(5)–C(5)	1.134(14)
O(2)–C(2)	1.133(15)	O(6)–C(6)	1.152(16)
O(3)–C(3)	1.160(12)	O(7)–C(7)	1.160(12)
O(4)–C(4)	1.143(15)		

Fe(1)–C(1)–Fe(2)	69.8(4)	Fe(2)–C(3)–O(3)	178.8(11)
Fe(1)–C(1)–Fe(3)	61.5(3)	Fe(3)–C(4)–O(4)	179.3(11)
Fe(2)–C(1)–Fe(3)	69.4(4)	Fe(3)–C(5)–O(5)	177.5(13)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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

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TABLE 2 (*Continued*)

Fe(1)–C(1)–O(1)	123.5(8)	Fe(3)–C(6)–O(6)	175.8(10)
Fe(2)–C(1)–O(1)	164.0(9)	Fe(1)–C(7)–O(7)	160.6(10)
Fe(3)–C(1)–O(1)	123.5(8)	Fe(1)–C(7)–Fe(3)	76.4(4)
Fe(2)–C(2)–O(2)	179.4(11)	Fe(3)–C(7)–O(7)	123.0(8)
(*c*) In the organic ligands			
C(8)–C(9)	1.431(14)	C(12)–H(122)	1.05(9)
C(9)–C(10)	1.410(17)	C(12)–H(123)	0.89(9)
C(10)–C(11)	1.523(14)	C(13)–H(13)	0.98(7)
C(11)–C(12)	1.508(18)	C(14)–H(14)	0.98(9)
C(13)–C(14)	1.389(15)	C(18)–H(181)	0.98(9)
C(13)–C(17)	1.416(17)	C(18)–H(182)	0.98(6)
C(14)–C(15)	1.412(13)	C(19)–H(191)	0.91(9)
C(15)–C(16)	1.430(18)	C(19)–H(192)	0.97(7)
C(15)–C(22)	1.507(14)	C(19)–H(193)	0.84(9)
C(16)–C(17)	1.426(11)	C(20)–H(201)	0.98(9)
C(16)–C(20)	1.501(15)	C(20)–H(202)	0.98(8)
C(17)–C(18)	1.501(18)	C(21)–H(211)	0.88(8)
C(18)–C(19)	1.508(18)	C(21)–H(212)	0.94(8)
C(20)–C(21)	1.510(16)	C(21)–H(213)	1.13(9)
C(22)–C(23)	1.501(16)	C(22)–H(221)	0.89(9)
C(8)–H(8)	1.06(9)	C(22)–H(222)	0.87(9)
C(9)–H(9)	1.02(9)	C(23)–H(231)	1.03(9)
C(11)–H(111)	1.02(9)	C(23)–H(232)	0.96(9)
C(11)–H(112)	0.97(8)	C(23)–H(232)	0.85(8)
C(12)–H(121)	1.07(9)		
Fe(1)–C(8)–Fe(2)	81.0(4)	C(19)–C(18)–H(182)	111(5)
Fe(1)–C(8)–C(9)	123.7(8)	H(181)–C(18)–H(182)	108(7)
Fe(2)–C(8)–C(9)	71.2(6)	C(18)–C(19)–H(191)	105(5)
C(8)–C(9)–C(10)	119.3(9)	C(18)–C(19)–H(192)	110(5)
Fe(2)–C(9)–C(10)	69.8(4)	C(18)–C(19)–H(193)	99(6)
Fe(2)–C(10)–Fe(3)	76.8(3)	H(191)–C(19)–H(192)	95.8)
Fe(2)–C(10)–C(11)	128.9(7)	H(191)–C(19)–H(193)	124(8)
Fe(3)–C(10)–C(11)	122.9(8)	H(192)–C(19)–H(193)	123(8)
Fe(2)–C(10)–C(9)	71.0(6)	H(201)–C(20)–H(202)	114(7)
Fe(3)–C(10)–C(9)	121.1(7)	C(16)–C(20)–H(201)	108(6)
C(9)–C(10)–C(11)	115.8(9)	C(16)–C(20)–H(202)	114(6)
C(10)–C(11)–C(12)	113.9(11)	C(21)–C(20)–H(201)	106(5)
Fe(1)–C(13)–C(14)	70.7(5)	C(21)–C(20)–H(202)	102(5)
Fe(1)–C(13)–C(17)	70.9(6)	C(20)–C(21)–H(211)	110(6)
C(14)–C(13)–C(17)	109.3(9)	C(20)–C(21)–H(212)	117(5)
C(13)–C(14)–C(15)	108.3(10)	C(20)–C(21)–H(213)	113(5)
Fe(1)–C(14)–C(13)	70.9(6)	H(211)–C(21)–H(212)	108(8)
Fe(1)–C(14)–C(15)	70.2(6)	H(211)–C(21)–H(213)	113(7)
Fe(1)–C(15)–C(14)	70.7(5)	H(212)–C(21)–H(213)	95.7)
Fe(1)–C(15)–C(16)	69.9(5)	H(221)–C(22)–H(222)	103(8)
Fe(1)–C(15)–C(22)	128.6(7)	C(15)–C(22)–H(221)	103(5)
C(14)–C(15)–C(22)	125.9(10)	C(15)–C(22)–H(222)	107(5)
C(14)–C(15)–C(16)	107.9(8)	C(23)–C(22)–H(221)	116(5)
C(16)–C(15)–C(22)	126.1(10)	C(23)–C(22)–H(222)	115(5)
Fe(1)–C(16)–C(15)	70.3(6)	C(22)–C(23)–H(231)	106(5)
Fe(1)–C(16)–C(20)	128.0(7)	C(22)–C(23)–H(232)	111(6)
Fe(1)–C(16)–C(17)	71.3(6)	C(22)–C(23)–H(233)	134(6)
C(15)–C(16)–C(17)	107.3(9)	H(231)–C(23)–H(232)	96(8)
C(15)–C(16)–C(20)	126.4(8)	H(231)–C(23)–H(233)	95(9)
C(17)–C(16)–C(20)	126.0(9)	H(232)–C(23)–H(233)	107(9)
C(16)–C(17)–C(18)	126.7(11)	Fe(2)–C(8)–H(8)	124(5)
C(13)–C(17)–C(16)	107.3(9)	Fe(1)–C(8)–H(8)	115(4)
C(13)–C(17)–C(18)	125.9(9)	C(9)–C(8)–H(8)	122(4)
Fe(1)–C(17)–C(18)	128.9(7)	C(8)–C(9)–H(9)	121(5)
Fe(1)–C(17)–C(13)	70.1(6)	C(10)–C(9)–H(9)	117(5)
Fe(1)–C(17)–C(16)	69.3(5)	Fe(2)–C(9)–H(9)	118(5)
C(17)–C(18)–C(19)	110.5(10)	C(10)–C(11)–H(111)	110(5)
C(16)–C(20)–C(21)	112.1(9)	C(10)–C(11)–H(112)	115(5)
C(15)–C(22)–C(23)	112.3(9)	H(111)–C(11)–H(112)	108(7)
C(14)–C(13)–H(13)	125(6)	C(12)–C(11)–H(111)	103(5)
C(17)–C(13)–H(13)	125(5)	C(12)–C(11)–H(112)	106(5)
Fe(1)–C(13)–H(13)	124(5)	C(11)–C(12)–H(121)	117(5)
C(13)–C(14)–H(14)	122(5)	C(11)–C(12)–H(122)	118(6)
C(15)–C(14)–H(14)	130(5)	C(11)–C(12)–C(123)	101(5)
Fe(1)–C(14)–H(14)	125(5)	H(121)–C(12)–H(122)	110(6)
C(17)–C(18)–H(181)	109(5)	H(121)–C(12)–H(123)	95(8)
C(17)–C(18)–H(182)	109(5)	H(122)–C(12)–H(123)	113(8)
C(19)–C(18)–H(181)	110(5)		

Five of the carbonyls [two on Fe(2) and three on Fe(3)] are purely 'terminal' as shown by the angles Fe–C–O (175.8—179.4°). One carbonyl group can be considered as very unsymmetrically triply bridging: the angle Fe(2)–C(1)–O(1) (164.0°) and the distances Fe(2)–C(1) (1.765), Fe(1)–C(1) (2.590), and Fe(3)–C(1) (2.552 Å) indicate a possible interaction of this CO group with the three iron atoms, although very weak with two of them. The distances Fe(1)–C(1) and Fe(3)–C(1) are indeed of the order of Fe–C distances found for very unsymmetrical bridging CO. The seventh carbonyl is unsymmetrically disposed between Fe(1) and Fe(3) as shown by the distances Fe(1)–C(7) (1.758 Å) and Fe(3)–C(7) (2.413 Å) and by the Fe(1)–C(7)–O(7) angle (160.6°). Examples of very unsymmetrical CO bridges are found in $[Fe_3(CO)_7(C_2Ph)(\eta\text{-}C_5H_5)]$,[13] $[Ru_3(CO)_6(C_7H_7)(C_7H_9)]$,[14] $[V_2(CO)_5(C_5H_5)_2]$,[15] $[Rh_2Fe_2(CO)_8(\eta\text{-}C_5H_5)_2]$,[16] $[RhFe_3(CO)_{11}(\eta\text{-}C_5H_5)]$,[17] $[Fe_2(CO)_6(C_4H_4)]$,[18] and $[Fe_3(CO)_8(HC_2Me)_3]$.[8]

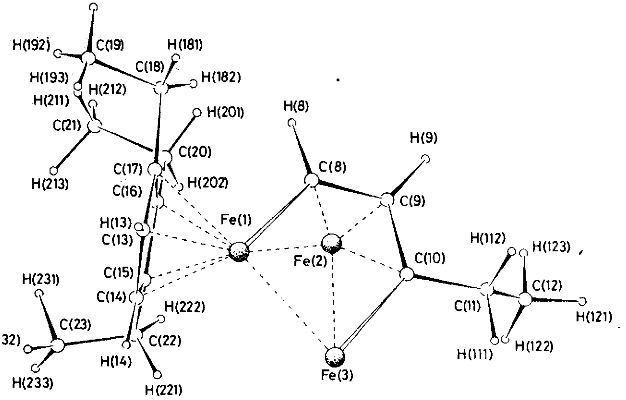

FIGURE 2 The bonding of the organic substituents to the cluster. The carbonyl groups have been omitted for clarity

The Fe–Fe distances are in the range of those found in other acetylenic carbonyl iron clusters, the longest distance corresponding to the two iron atoms with the doubly bridging CO.

The bonding of the two organic substituents to the cluster is presented in Figure 2. The C(8) and C(10) atoms of the allyl group form two σ bonds to Fe(1) and Fe(3) respectively. These bonds (1.889 and 1.992 Å) are at the low end of reported iron–allyl distances, indicating a strong interaction of the allyl group with the cluster. The double bond in this ligand is delocalized on C(8)—C(10) as shown by the nearly equal C–C distances (1.431 and 1.410 Å). The π-electron cloud over C(8)—C(10) interacts with Fe(2) so as to position this atom equidistant from the carbon atoms. In this

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way the allyl group is σ- or η-bonded to all the three iron atoms of the cluster.

The atoms C(8)—C(10) of the allyl group, together with Fe(1) and Fe(3), form a five-membered heterocyclic ring. This is nearly planar, the equation of the best plane through it being: $-0.5983X + 0.2203Y - 0.7704Z = -1.5418$ [where X, Y, Z are co-ordinates (Å) obtained from the fractional ones applying the matrix: $\|a \sin\gamma, 0, -c \sin\alpha \cos\beta^* | a \cos\gamma, b, c \cos\alpha | 0, 0, c \sin\alpha \sin\beta^*\|$]. Deviations from this plane are: Fe(1) 0.002, Fe(3) −0.001, C(8) −0.081, C(9) 0.079, C(10) 0.002, C(11) 0.057, and Fe(2) −1.658 Å.

The cyclopentadienyl group η-bonded to Fe(1) only is quite planar. The best plane through the carbons of the ring C(13) · · · C(17) has the equation $-0.1478X - 0.9854Y - 0.0846Z = 2.0213$. Displacements from this plane are C(13) −0.003, C(14) −0.002, C(15) 0.006, C(16) −0.008, C(17) 0.007, C(18) 0.110, C(20) 0.080, and C(22) 0.121 Å. The dihedral angle formed by this plane with the plane through the iron atoms is 60.4°.

Both the organic ligands in the present complex are worth mentioning since their formation requires cleavage of an ethylacetylene triple bond: the ethylallyl group corresponds to one molecule of ethylacetylene plus a CH group and the 1,2,3-triethylcyclopentadienyl group is formed by two ethylacetylenes plus a CEt group, the CH and CEt groups being the fragments derived from cleavage of a triple bond in one molecule of ethylacetylene. The only other explanation for the formation of a 1,2,3-substituted cyclopentadienyl ring and of the ethylallyl substituent is co-cyclization of ethylacetylene and diethylacetylene with cleavage of a triple bond of acetylene present as impurity in the diethylacetylene employed. The present experiments on co-oligomerization of acetylenes, together with the absence of acetylene in the n-propylacetylene from which complex (2) is obtained, are evidence for the cleavage of ethylacetylene instead of acetylene.

Also noteworthy is the activation of C–C bonds in the formation either of the substituted cyclopentadienyl ligand or of the ethylallyl group. Activation of C–C bonds in the formation of substituted cyclopentadienyls has also been observed for other iron carbonyl derivatives.[19] Complexes (1) and (2) require, for the formation of the ethyl- or n-propyl-allyl group, the activation of a C–C bond and the formation of a new C–C bond; ruthenium hydrides $[Ru_3(CO)_9(C_nH_m)H]$ [20] have been described which contain a substituted allyl unit bonded to metals as in (1) and (2). However, in all these ruthenium derivatives, except $[Ru_3(CO)_9(PhC{\cdot}C_6H_4)H]$,[21] the substituted allyl unit is obtained by C–H activation in ethylenes, dienes, and acetylenes, and not by C–C activation.

The mechanism of formation of complexes (1) and (2) is still unclear; a multistep reaction pattern is probably required according to two possible routes. The first route implies the co-ordination of two acetylenes, dimerized as '*cis*-butadiene,' and of a third one, followed by co-ordination and cleavage of a fourth acetylenic unit. The second route implies an internal rearrangement of the complexes $[Fe_3(CO)_8(HC_2Et)_4]$ or $[Fe_3(CO)_8(HC_2Pr^n)_4]$, obtained in good yields in the same reactions, with release of CO and interaction of the unsaturated substituent of the cyclopentadienyl unit with the bridging CEt or CPr^n group. To date, some chemical and mass-spectral evidence has been obtained [22] which could support the second mechanism.

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