Synthesis and Molecular Structure of Bis(μ_4-but-1-yne)-undecacarbonyl-*quadro*-tetrairon (4 *Fe–Fe*)

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The title complex has been obtained by treating $[Fe_3(CO)_{12}]$ with but-1-yne in hydrocarbon solvents, and is 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 $a = 8.700(7)$, $b = 9.125(9)$, $c = 17.541(15)$ Å, $\alpha = 112.8(1)$, $\beta = 104.5(1)$, and $\gamma = 106.0(1)$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to *R* 0.043 for 2 204 observed reflections. The molecule is a cluster in which the four metal atoms are in a tetrahedrally distorted square arrangement. Of the 11 carbonyl groups co-ordinated to the metal atoms, eight are terminal, one is symmetrically bridging two iron atoms, and two are very asymmetrically bridging. Each of the two alkyne ligands is σ-bonded to two iron atoms on the opposite vertices of the cluster and π-bonded to the other two. The substituted cluster has an Fe_4C_4 core in which the metal and carbon atoms occupy the vertices of a triangulated dodecahedron. Propyne, but-2-yne, and pent-1-yne complexes of similar stoicheiometry have also been obtained.

WE have previously reported the syntheses and crystal structures of the new trinuclear complexes $[Fe_3(CO)_8(HC_2Me)_3]$,[1] $[Fe_3(CO)_8(HC_2Me)_4]$,[2] and $[Fe_3(CO)_7(HC_2Et)_4]$,[3] obtained, together with other known tri- and binuclear complexes, in the reactions of $[Fe_3(CO)_{12}]$ with substituted alkynes in hydrocarbon solvents.

We now describe the tetranuclear complexes $[Fe_4(CO)_{11}(RC_2R')_2]$ [$R = H$, $R' = Me$, (1); $R = H$, $R' = Et$, (2); $R = H$, $R' = Pr^n$, (3); $R = R' = Me$, (4)], which are obtained in the above reactions in 1% yields; these complexes are, to our knowledge, the first tetranuclear iron carbonyl acetylenes whose structures have been determined. Ruthenium complexes of similar formulae [4] and tetranuclear osmium derivatives have been reported [5] but not structurally characterized.

A number of unsubstituted and variously substituted carbonyl hydrides and carbonyls of the transition metals are known and have been reviewed by Chini; [6] most of these complexes are characterized by a tetrahedral arrangement of the metal atoms, as found for $[Ru_4(CO)_9(Me_3C_{10}H_5)]$,[7] $[Rh_2Fe_2(CO)_8(\pi\text{-}C_5H_5)_2]$,[8] and $[RhFe_3(CO)_{11}(\eta\text{-}C_5H_5)]$.[9] The square-planar tetranuclear cluster is rare and has been found recently in $[Fe_4(CO)_{11}(NEt)(ONEt)]$,[10] while a triangulated planar tetranuclear cluster was reported previously for $[Re_4(CO)_{16}]^{2-}$.[11] A severely distorted tetrahedral arrangement, known as a 'butterfly' disposition, was reported for $[Co_4(CO)_{10}(EtC_2Et)]$,[12] $[Ru_4(CO)_{11}(C_8H_{10})]$,[13] and $[Ru_4(CO)_{10}(C_{12}H_{16})]$,[14] that is for derivatives containing an alkyne or diene.

In the title complex, the four metal atoms are disposed at the vertices of a tetrahedrally distorted square and each of the two alkyne molecules is bonded σ or π to the four metal atoms, similarly to the bonding found for $[Co_4(CO)_{10}(EtC_2Et)]$ [12] and $[Ru_4(CO)_{11}(C_8H_{10})]$; [13] all these clusters are characterized by M_4C_n cores in which the metal and carbon atoms occupy the vertices of an irregular polyhedron. This behaviour has been recently discussed by Wade,[15] in order to describe the bonding in 'structures (which) cannot be adequately rationalized in terms of two-centre electron-pair bonds.'

The isolation of tetranuclear species by reaction of $[Fe_3(CO)_{12}]$ in hydrocarbon solutions is also of interest.

EXPERIMENTAL

Synthesis and Purification of the Complexes.—Complexes (1)—(4) are obtained by treating $[Fe_3(CO)_{12}]$ in refluxing n-heptane under dry nitrogen with an excess of the gaseous or liquid alkynes, as already reported.[1-3,16] Yields are of the order of 1% with respect to the iron carbonyl; the purification of the products was performed on t.l.c. preparative plates, in two separate steps. The reaction mixtures, each containing *ca.* 30 compounds, were fractionated and further purified by t.l.c. Complex (2) is obtained as a microcrystalline powder; crystals suitable for *X*-ray analysis were obtained by slowly evaporating cyclohexane solutions of it. Found: C, 33.55; H, 1.50; Fe, 36.9; O, 28.1. Calc. for $C_{17}H_8Fe_4O_{11}$ (1): C, 33.4; H, 1.30, Fe, 36.4, O, 28.0%; *M* 611.63. Found: C, 35.85; H, 1.90, Fe, 34.7; O, 27.55. Calc. for $C_{19}H_{12}Fe_4O_{11}$ (2): C, 35.75; H, 1.65; Fe, 35.0; O, 27.6%; *M* 639.68. Found: C, 37.9; H, 2.55; Fe, 33.6; O, 25.95. Calc. for $C_{21}H_{16}Fe_4O_{11}$ (3): C, 37.75; H, 2.40; Fe, 33.45; O, 26.4%; *M*

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[1] E. Sappa, L. Milone, and A. Tiripicchio, *J.C.S. Dalton*, 1976, 1843.

[2] S. Aime, L. Milone, E. Sappa, and A. Tiripicchio, *J.C.S. Dalton*, 1977, 227.

[3] E. Sappa, A. Tiripicchio, and A. M. Manotti Lanfredi, *J.C.S. Dalton*, 1978, in the press.

[4] B. F. G. Johnson, J. Lewis, and K. T. Schorpp, *J. Organometallic Chem.*, 1975, **91**, C13.

[5] B. F. G. Johnson, J. W. Kelland, J. Lewis, and S. K. Rehani, *J. Organometallic Chem.*, 1976, **113**, C42.

[6] P. Chini, *Inorg. Chim. Acta Rev.*, 1968, **2**, 31.

[7] M. R. Churchill, K. Gold, and P. H. Bird, *Inorg. Chem.*, 1969, **8**, 1956.

[8] M. R. Churchill and M. V. Veidis, *Chem. Comm.*, 1970, 529.

[9] M. R. Churchill and M. V. Veidis, *J. Chem. Soc.* (*A*), 1971, 2995.

[10] G. Gervasio, R. Rossetti, and P. L. Stanghellini, *J.C.S. Chem. Comm.*, 1977, 387.

[11] R. Bau, B. Fontal, H. D. Kaesz, and M. R. Churchill, *J. Amer. Chem. Soc.*, 1967, **89**, 6374.

[12] L. F. Dahl and D. L. Smith, *J. Amer. Chem. Soc.*, 1962, **84**, 2450.

[13] A. J. Canty, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1973, 2056; R. Mason and K. M. Thomas, *J. Organometallic Chem.*, 1972, **43**, C39.

[14] R. Belford, M. I. Bruce, M. A. Cairns, M. Green, H. P. Taylor, and P. Woodward, *Chem. Comm.*, 1970, 1159.

[15] K. Wade, *Chem. in Britain*, 1975, **11**, 177.

[16] W. Hubel, in 'Organic Syntheses *via* Metal Carbonyls,' vol. I, eds. I. Wender and P. Pino, Interscience, New York, 1968, p. 273.

667.73. Found: C, 36.0; H, 2.00; Fe, 35.15; O, 26.85. Calc. for $C_{19}H_{12}Fe_4O_{11}$ (4): C, 35.75; H, 1.65; Fe, 35.0; O, 27.6%; *M* 639.68.

Crystal Data.—$C_{19}H_{12}Fe_4O_{11}$ (2), $M = 635.65$, Triclinic, $a = 8.700(7)$, $b = 9.125(9)$, $c = 17.541(15)$ Å, $\alpha = 112.8(1)$, $\beta = 104.5(1)$, $\gamma = 106.0(1)°$, $U = 1\,129(2)$ Å^3, $Z = 2$, $D_c = 1.87$ g cm^{-3}, $F(000) = 636$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 25.76 cm^{-1}, space group $P\bar{1}$ from structure determination.

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)	−672(2)	−1 651(2)	1 469(1)
Fe(2)	−1 931(2)	733(2)	1 847(1)
Fe(3)	−1 233(2)	845(2)	3 430(1)
Fe(4)	1 190(2)	−158(2)	3 132(1)
O(1)	−2 613(16)	−5 412(11)	259(6)
O(2)	527(16)	−1 553(13)	78(7)
O(3)	−3 681(15)	−1 377(12)	−115(6)
O(4)	−676(15)	3 981(13)	1 769(7)
O(5)	−5 113(12)	1 098(13)	1 942(6)
O(6)	−1 738(10)	4 049(9)	4 109(6)
O(7)	4 910(12)	2 194(13)	4 175(7)
O(8)	1 386(10)	2 003(10)	5 200(5)
O(9)	−4 057(9)	−906(9)	3 837(5)
O(10)	1 761(10)	−2 083(10)	4 076(5)
O(11)	2 236(14)	−2 615(12)	1 932(7)
C(1)	−1 867(20)	−3 934(16)	751(8)
C(2)	68(19)	−1 571(15)	631(8)
C(3)	−2 897(19)	−636(16)	646(9)
C(4)	−1 154(16)	2 733(16)	1 802(8)
C(5)	−3 856(18)	987(15)	1 908(8)
C(6)	−1 565(11)	2 773(12)	3 838(6)
C(7)	3 489(17)	1 300(15)	3 755(9)
C(8)	440(13)	1 458(12)	4 465(7)
C(9)	−2 979(13)	−251(12)	3 672(6)
C(10)	1 530(13)	−1 338(13)	3 705(7)
C(11)	1 417(15)	−1 849(14)	2 106(7)
C(12)	653(13)	936(11)	2 266(7)
C(13)	560(10)	1 955(10)	3 055(6)
C(14)	1 790(16)	3 870(13)	3 640(9)
C(15)	3 221(21)	4 615(18)	3 364(13)
C(16)	−1 370(13)	−1 639(10)	2 564(6)
C(17)	−2 601(13)	−1 347(11)	2 027(6)
C(18) *	−4 428(19)	−2 714(18)	1 582(11)
C(19) *	−4 815(24)	−4 387(21)	1 667(13)
C(181) *	−2 342(21)	−3 347(20)	2 569(12)
C(191) *	−4 358(25)	−4 455(29)	2 026(16)
H(12)	167(9)	174(9)	213(4)
H(141)	113(11)	455(11)	367(6)
H(142)	238(13)	413(13)	418(7)
H(151)	394(13)	586(14)	379(7)
H(152)	265(14)	461(14)	286(7)
H(153)	399(11)	412(10)	333(5)

* C(18) and C(181) and C(19) and C(191) are distributed in two statistical positions of equivalent occupancy.

Unit-cell dimensions, determined from rotation and Weissenberg photographs, were refined by a least-squares procedure applied to the 20 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 flat prismatic crystal of dimensions *ca.* 0.23 × 0.08 × 0.40 mm was mounted with its *c* axis parallel to the ϕ axis of the diffractometer and all the reflections in the range $2.4 < \theta < 25°$ were measured. Of 3 876 independent reflections, 2 204 having $I > 2\sigma(I)$ were considered observed and used in the analysis. The intensity data were corrected for Lorentz and polarization factors, but no correction for absorption was made because of the low value of μR. The absolute scale and the overall temperature factor were determined by Wilson's method.

Structure Determination and Refinement.—The structure was solved by Patterson and Fourier methods and the refinement was performed by means of the SHEL-X system of computer programs.[17] Four cycles of full-matrix least squares were carried out using anisotropic thermal parameters for all the heavy atoms. At this stage a difference-Fourier map revealed two peaks whose heights were close to those of the carbon atoms. These peaks could be explained only by one but-1-yne molecule having the ethyl group disordered and distributed in two positions of equivalent occupancy. All the six hydrogen atoms of the non-disordered but-1-yne molecule were localized by inspection of the ΔF map. Further least-squares cycles were then computed including these hydrogen atoms and the four statistical carbon atoms of the disordered but-1-yne molecule 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 0.043 (observed reflections only).

Atomic scattering factors for non-hydrogen atoms were taken from ref. 18, and for hydrogen atoms from ref. 19. Final atomic co-ordinates are given in Table 1. A list of observed and calculated structure factors and of thermal parameters is available from the authors or as Supplementary Publication No. SUP 22206 (25 pp.).* All the 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 were recorded on a Beckman IR-12 spectrometer in n-heptane solutions. The following absorptions were observed in the CO stretching region: (1), 2 043vs(sh), 2 030vs, 2 018vs(sh), 1 995s,br, 1 850w; (2), 2 060s, 2 022vs(sh), 2 012vs, 1 994s, 1 987s, 1 973m(sh), 1 855w; (3), 2 058m(sh), 2 048s, 2 029vs, 2 017vs(sh), 1 986s, 1 975m(sh), 1 883w; and (4), 2 060m, 2 048m, 2 029vs, 2 017vs(sh), 1 986vs(sh), 1 979vs(sh), and 1 860w cm^{-1}.

The mass spectra were recorded on a Varian CH-5 instrument, equipped with a direct-inlet system and operating at 70 eV.† For all the complexes, the parent ion and stepwise loss of 11 CO groups was observed. The $[Fe_4(CO)(RC_2R')_2]^+$ ions are very intense. Detailed discussion of the results will be reported elsewhere.[20]

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

The structure is characterized by a tetranuclear cluster of iron atoms co-ordinated by 11 carbonyls and by two σ- and π-bonded but-1-yne molecules. Eight

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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.

[17] G. Sheldrick, SHEL-X, Program for Crystal Structure Determination, University of Cambridge, 1975.

[18] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[19] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[20] E. Sappa and V. Raverdino, unpublished work.

carbonyls (two on each iron atom) are terminal, as shown by the angles Fe–C–O (176.7—179.6°). One carbonyl symmetrically bridges Fe(1) and Fe(4) as confirmed by the Fe(1)–C(11) and Fe(4)–C(11) (1.976 and 1.963 Å) bond distances and by the Fe(1)–C(11)–O(11) and Fe(4)–C(11)–O(11) angles (138.3 and 142.3°). The remaining two carbonyls can be considered as very unsymmetrically bridging the Fe(2)–Fe(1) and Fe(3)–Fe(4) sides of the cluster [Fe(2)–C(3) 1.789, Fe(1)–C(3) 2.705, Fe(3)–C(8) 1.780, and Fe(4)–C(8) 2.586 Å]. The bridging character of these CO groups is confirmed by the angles Fe(2)–C(3)–O(3) (169.3°) and Fe(3)–C(8)–O(8) (169.0°) which are narrower than those formed by the terminal carbonyls. Considering these unsymmetrical CO bridges, it is interesting to note that the carbonyl groups are, on the whole, nearly equally shared by all the four iron atoms. In fact the Fe(1) and Fe(4) atoms, sharing five carbonyls, are also unsymmetrically bridged by a carbonyl 'belonging' to the Fe(2) and Fe(3) atoms, each bound to three carbonyls.

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)	2.633(4)	Fe(2)–C(13)	2.229(9)
Fe(1)–Fe(4)	2.515(5)	Fe(2)–C(17)	1.997(12)
Fe(2)–Fe(3)	2.644(4)	Fe(3)–C(6)	1.760(11)
Fe(3)–Fe(4)	2.608(4)	Fe(3)–C(8)	1.780(11)
Fe(1)–C(1)	1.767(12)	Fe(3)–C(9)	1.817(12)
Fe(1)–C(2)	1.764(17)	Fe(3)–C(13)	2.013(11)
Fe(1)–C(11)	1.976(14)	Fe(3)–C(16)	2.133(10)
Fe(1)–C(12)	1.998(9)	Fe(3)–C(17)	2.209(9)
Fe(1)–C(16)	2.152(12)	Fe(4)–C(7)	1.810(12)
Fe(1)–C(17)	2.173(13)	Fe(4)–C(10)	1.767(14)
Fe(2)–C(3)	1.789(13)	Fe(4)–C(11)	1.963(13)
Fe(2)–C(4)	1.803(16)	Fe(4)–C(12)	2.145(13)
Fe(2)–C(5)	1.776(17)	Fe(4)–C(13)	2.187(11)
Fe(2)–C(12)	2.113(12)	Fe(4)–C(16)	1.991(10)

Fe(2)–Fe(1)–Fe(4)	87.5(1)	C(12)–Fe(2)–C(17)	87.0(5)
Fe(1)–Fe(2)–Fe(3)	84.7(1)	C(13)–Fe(2)–C(17)	87.9(4)
Fe(2)–Fe(3)–Fe(4)	85.4(1)	Fe(2)–Fe(3)–C(6)	88.5(3)
Fe(1)–Fe(4)–Fe(3)	87.9(1)	Fe(2)–Fe(3)–C(8)	145.7(4)
Fe(2)–Fe(1)–C(1)	127.1(6)	Fe(2)–Fe(3)–C(9)	120.2(3)
Fe(2)–Fe(1)–C(2)	104.7(5)	Fe(2)–Fe(3)–C(13)	55.2(3)
Fe(2)–Fe(1)–C(11)	135.0(4)	Fe(2)–Fe(3)–C(16)	76.4(3)
Fe(2)–Fe(1)–C(12)	52.1(3)	Fe(2)–Fe(3)–C(17)	47.6(3)
Fe(2)–Fe(1)–C(16)	76.4(3)	Fe(4)–Fe(3)–C(6)	139.6(4)
Fe(2)–Fe(1)–C(17)	48.0(3)	Fe(4)–Fe(3)–C(8)	69.3(4)
Fe(4)–Fe(1)–C(1)	125.6(5)	Fe(4)–Fe(3)–C(9)	126.0(4)
Fe(4)–Fe(1)–C(2)	125.9(5)	Fe(4)–Fe(3)–C(13)	54.7(3)
Fe(4)–Fe(1)–C(11)	50.1(3)	Fe(4)–Fe(3)–C(16)	48.4(3)
Fe(4)–Fe(1)–C(12)	55.3(3)	Fe(4)–Fe(3)–C(17)	76.6(3)
Fe(4)–Fe(1)–C(16)	50.0(3)	C(6)–Fe(3)–C(8)	95.9(5)
Fe(4)–Fe(1)–C(17)	79.3(3)	C(6)–Fe(3)–C(9)	91.2(5)
C(1)–Fe(1)–C(2)	88.4(7)	C(6)–Fe(3)–C(13)	89.6(5)
C(1)–Fe(1)–C(11)	94.1(7)	C(6)–Fe(3)–C(16)	162.8(4)
C(1)–Fe(1)–C(12)	179.1(6)	C(6)–Fe(3)–C(17)	125.4(4)
C(1)–Fe(1)–C(16)	94.4(6)	C(8)–Fe(3)–C(9)	93.8(5)
C(1)–Fe(1)–C(17)	94.5(6)	C(8)–Fe(3)–C(13)	90.7(5)
C(2)–Fe(1)–C(11)	92.2(6)	C(8)–Fe(3)–C(16)	101.2(5)
C(2)–Fe(1)–C(12)	91.3(6)	C(8)–Fe(3)–C(17)	138.7(5)
C(2)–Fe(1)–C(16)	175.6(6)	C(9)–Fe(3)–C(13)	175.3(4)
C(2)–Fe(1)–C(17)	145.5(6)	C(9)–Fe(3)–C(16)	89.4(5)
C(11)–Fe(1)–C(12)	86.8(5)	C(9)–Fe(3)–C(17)	87.7(4)
C(11)–Fe(1)–C(16)	84.2(5)	C(13)–Fe(3)–C(16)	88.4(4)
C(11)–Fe(1)–C(17)	121.7(4)	C(13)–Fe(3)–C(17)	88.1(4)
C(12)–Fe(1)–C(16)	86.0(4)	C(16)–Fe(3)–C(17)	37.5(4)
C(12)–Fe(1)–C(17)	85.3(4)	Fe(1)–Fe(4)–C(7)	129.7(5)
C(16)–Fe(1)–C(17)	37.7(4)	Fe(1)–Fe(4)–C(10)	122.3(4)
Fe(1)–Fe(2)–C(3)	72.6(5)	Fe(1)–Fe(4)–C(11)	50.6(4)
Fe(1)–Fe(2)–C(4)	125.9(5)	Fe(1)–Fe(4)–C(12)	50.0(3)
Fe(1)–Fe(2)–C(5)	141.2(5)	Fe(1)–Fe(4)–C(13)	79.9(2)
Fe(1)–Fe(2)–C(12)	48.3(3)	Fe(1)–Fe(4)–C(16)	55.6(3)
Fe(1)–Fe(2)–C(13)	76.6(3)	Fe(3)–Fe(4)–C(7)	122.0(5)
Fe(1)–Fe(2)–C(17)	53.9(3)	Fe(3)–Fe(4)–C(10)	108.1(4)
Fe(3)–Fe(2)–C(3)	146.0(5)	Fe(3)–Fe(4)–C(11)	137.0(4)
Fe(3)–Fe(2)–C(4)	119.7(4)	Fe(3)–Fe(4)–C(12)	75.5(3)
Fe(3)–Fe(2)–C(5)	87.5(4)	Fe(3)–Fe(4)–C(13)	48.7(3)
Fe(3)–Fe(2)–C(12)	75.2(3)	Fe(3)–Fe(4)–C(16)	53.3(3)
Fe(3)–Fe(2)–C(13)	47.9(3)	C(7)–Fe(4)–C(10)	88.3(5)
Fe(3)–Fe(2)–C(17)	54.7(3)	C(7)–Fe(4)–C(11)	96.8(6)
C(3)–Fe(2)–C(4)	94.2(7)	C(7)–Fe(4)–C(12)	95.9(6)
C(3)–Fe(2)–C(5)	94.5(7)	C(7)–Fe(4)–C(13)	91.0(6)
C(3)–Fe(2)–C(12)	105.4(6)	C(7)–Fe(4)–C(16)	174.1(5)
C(3)–Fe(2)–C(13)	142.2(6)	C(10)–Fe(4)–C(11)	89.5(5)
C(3)–Fe(2)–C(17)	91.3(6)	C(10)–Fe(4)–C(12)	172.0(5)
C(4)–Fe(2)–C(5)	90.7(7)	C(10)–Fe(4)–C(13)	150.2(5)
C(4)–Fe(2)–C(12)	89.4(6)	C(10)–Fe(4)–C(16)	90.2(5)
C(4)–Fe(2)–C(13)	86.4(5)	C(11)–Fe(4)–C(12)	83.2(5)
C(4)–Fe(2)–C(17)	174.1(5)	C(11)–Fe(4)–C(13)	120.1(5)
C(5)–Fe(2)–C(12)	160.0(5)	C(11)–Fe(4)–C(16)	88.9(5)
C(5)–Fe(2)–C(13)	123.3(5)	C(12)–Fe(4)–C(13)	37.0(4)
C(5)–Fe(2)–C(17)	91.1(6)	C(12)–Fe(4)–C(16)	86.4(4)
C(12)–Fe(2)–C(13)	36.8(4)	C(13)–Fe(4)–C(16)	87.5(4)

TABLE 2 (*Continued*)

(*b*) In the carbonyl groups

O(1)–C(1)	1.149(13)	O(7)–C(7)	1.122(14)
O(2)–C(2)	1.142(22)	O(8)–C(8)	1.155(13)
O(3)–C(3)	1.138(16)	O(9)–C(9)	1.132(15)
O(4)–C(4)	1.129(20)	O(10)–O(10)	1.131(18)
O(5)–C(5)	1.140(20)	O(11)–C(11)	1.144(19)
O(6)–C(6)	1.144(14)		

Fe(1)–C(1)–O(1)	177.1(14)	Fe(3)–C(8)–O(8)	169.0(11)
Fe(1)–C(2)–O(2)	178.7(14)	Fe(3)–C(9)–O(9)	178.7(9)
Fe(2)–C(3)–O(3)	169.3(15)	Fe(4)–C(10)–O(10)	179.4(11)
Fe(2)–C(4)–O(4)	179.6(12)	Fe(1)–C(11)–O(11)	138.3(9)
Fe(2)–C(5)–O(5)	177.9(14)	Fe(4)–C(11)–O(11)	142.3(10)
Fe(3)–C(6)–O(6)	178.3(10)	Fe(1)–C(11)–Fe(4)	79.4(5)
Fe(4)–C(7)–O(7)	176.7(13)		

(*c*) In the organic ligands

C(12)–C(13)	1.374(15)	C(181)–C(191)	1.564(23)
C(13)–C(14)	1.510(12)	C(12)–H(12)	1.12(8)
C(14)–C(15)	1.529(20)	C(14)–H(141)	0.95(11)
C(16)–C(17)	1.397(16)	C(14)–H(142)	0.86(11)
C(16)–C(181)	1.560(22)	C(15)–H(151)	0.98(9)
C(17)–C(18)	1.491(16)	C(15)–H(152)	0.90(13)
C(18)–C(19)	1.544(22)	C(15)–H(153)	0.91(11)

Fe(1)–C(12)–Fe(2)	79.6(4)	Fe(1)–C(17)–Fe(2)	78.2(4)
Fe(1)–C(12)–Fe(4)	74.7(4)	Fe(1)–C(17)–Fe(3)	108.5(5)
Fe(2)–C(12)–Fe(4)	113.6(5)	Fe(2)–C(17)–Fe(3)	77.7(4)
Fe(1)–C(12)–C(13)	127.1(8)	Fe(1)–C(17)–C(16)	70.3(6)
Fe(2)–C(12)–C(13)	76.2(7)	Fe(1)–C(17)–C(18)	122.1(9)
Fe(4)–C(12)–C(13)	73.2(6)	Fe(2)–C(17)–C(16)	121.9(8)
Fe(2)–C(13)–Fe(3)	76.9(3)	Fe(2)–C(17)–C(18)	122.6(9)
Fe(2)–C(13)–Fe(4)	107.5(4)	Fe(3)–C(17)–C(16)	68.3(5)
Fe(3)–C(13)–Fe(4)	76.6(4)	Fe(3)–C(17)–C(18)	127.7(9)
Fe(2)–C(13)–C(12)	67.0(6)	C(16)–C(17)–C(18)	115.4(11)
Fe(2)–C(13)–C(14)	127.9(8)	C(17)–C(18)–C(19)	119.8(15)
Fe(3)–C(13)–C(12)	118.8(8)	C(16)–C(181)–C(191)	122.0(17)
Fe(3)–C(13)–C(14)	120.3(8)	H(12)–C(12)–Fe(1)	122(4)
Fe(4)–C(13)–C(12)	69.8(6)	H(12)–C(12)–Fe(2)	121(4)
Fe(4)–C(13)–C(14)	123.9(8)	H(12)–C(12)–Fe(4)	125(4)
C(12)–C(13)–C(14)	120.9(10)	H(12)–C(12)–C(13)	111(4)
C(13)–C(14)–C(15)	118.2(12)	H(141)–C(14)–H(142)	108(10)
Fe(1)–C(16)–Fe(3)	112.1(5)	H(141)–C(14)–C(13)	109(6)
Fe(1)–C(16)–Fe(4)	74.7(4)	H(141)–C(14)–C(15)	106(6)
Fe(3)–C(16)–Fe(4)	78.3(4)	H(142)–C(14)–C(13)	113(9)
Fe(1)–C(16)–C(17)	72.0(6)	H(142)–C(14)–C(15)	102(8)
Fe(1)–C(16)–C(181)	122.9(9)	H(151)–C(15)–H(152)	103(10)
Fe(3)–C(16)–C(17)	74.2(6)	H(151)–C(15)–H(153)	105(9)
Fe(3)–C(16)–C(181)	123.0(9)	H(151)–C(15)–C(14)	111(7)
Fe(4)–C(16)–C(17)	123.8(8)	H(152)–C(15)–H(153)	116(10)
Fe(4)–C(16)–C(181)	127.9(9)	H(152)–C(15)–C(14)	105(8)
C(17)–C(16)–C(181)	108.3(11)	H(153)–C(15)–C(14)	116(6)

The iron atoms of the cluster are at the vertices of a tetrahedrally distorted square. Fe(1), Fe(2), Fe(3), and Fe(4) are 0.40, -0.27, 0.25, and -0.37 Å out of the mean least-squares plane passing through them.

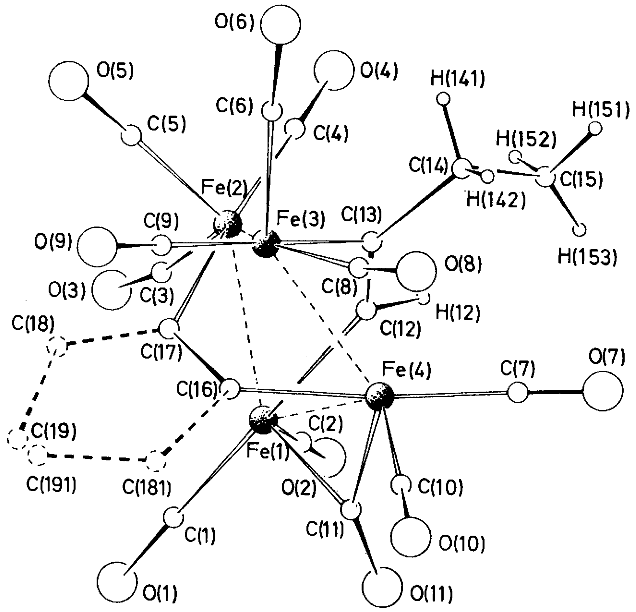

FIGURE 1 Perspective view showing the molecular shape and the atomic numbering

The equation of this plane is: $-0.714\,4X - 0.659\,2Y - 0.234\,8Z = 1.723\,7$.* The irons on the opposite vertices of the square are displaced on the same side with respect to the mean plane in such a way as to show nearly S_4 symmetry. The cluster can be described as being derived from a tetrahedron in which the Fe(1)–Fe(3) and Fe(2)–Fe(4) edges are elongated and approach each other, but are maintained almost perpendicular so that Fe(1)–Fe(3) and Fe(2)–Fe(4) become non-bonding distances (3.555 and 3.562 Å respectively). The Fe–Fe bond distances in the cluster are of the same order as those found in other iron carbonyl acetylenic clusters; the shortest one, Fe(1)–Fe(4), corresponds to the symmetrically CO-bridged metal atoms.

Each of the two but-1-yne molecules is σ or π bonded to all the four atoms of the cluster. Two σ bonds are formed between the acetylenic carbons of each molecule and two iron atoms on opposite vertices of the cluster; two other π bonds are formed between the same carbons and the other two iron atoms. The bonding of the alkyne molecules to the cluster is presented in Figure 2. The Fe–C σ bonds (1.991—2.013 Å) are in good agreement with reported values in complexes showing a comparable alkyne arrangement such as the 'violet isomer' of $[Fe_3(CO)_8(PhC_2Ph)_2]$.[21] The Fe–C π bonds (2.113—2.187 Å) are similar to the usual values for this sort of bonding.

The ethyl group of one alkyne molecule is disordered and statistically bound to C(16) and C(17). The two acetylenic bonds C(16)–C(17) and C(12)–C(13) are almost perpendicular. The acetylenic carbons are in an elongated tetrahedral arrangement with all the non-bonded carbons nearly equidistant (2.83—2.94 Å). The mean planes through Fe(1)–C(12)–C(13)–Fe(3) and Fe(4)–C(16)–C(17)–Fe(2) are perpendicular (dihedral angle, 89°); the equations of these planes are $-0.511\,6X + 0.658\,0Y - 0.552\,5Z = -1.965\,5$ [Fe(1), Fe(3), C(12), and C(13) are displaced from this plane by -0.001, 0.001, 0.035, and -0.034 Å respectively] and $0.469\,8X - 0.305\,1Y - 0.828\,3Z = -3.550\,4$ [Fe(4), Fe(2), C(16), and C(17) are displaced from this plane by 0.001, -0.001, -0.028, and 0.028 Å respectively]. The tetrahedron of the iron atoms and that of the acetylenic carbon atoms interpenetrate in such a way as to form an Fe_4C_4 cage in which the heteroatoms are at the vertices of a rather regular triangulated dodecahedron.

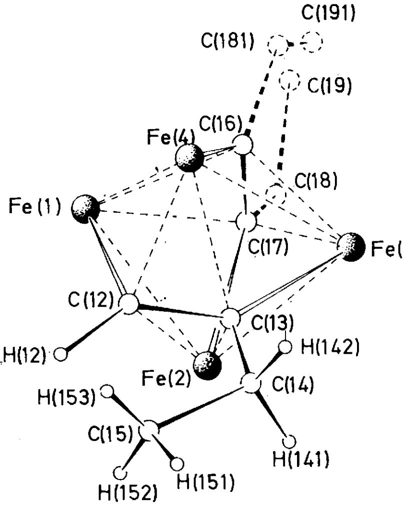

FIGURE 2 Bonding of the acetylene molecules to the metal cluster. The iron atoms and the acetylenic carbon atoms are in a triangulated dodecahedral arrangement

It is noteworthy that, if one considers each alkyne molecule as a four-electron donor (one electron for each σ bond and two electrons for π bonding), two electrons are missing in this cluster with respect to the effective atomic number rule. Very few cases are known of electron-deficient tri- and tetra-nuclear clusters, the most outstanding example being $[Os_3(CO)_{10}H_2]$.[6] On the other hand, a number of clusters containing one or two electrons more than required by the effective atomic number rule is known.[6] Moreover, in some iron and ruthenium complexes such as $[Fe_3(CO)_9(PhC_2Ph)]$ [22] and $[Ru_3(CO)_9(C_2Bu^t)H]$ [23] the alkyne behaves as a formal six- or five-electron donor. We therefore consider that in the title complex the alkyne molecules behave

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* X, Y, Z, are co-ordinates (Å) obtained from the fractional ones by applying the matrix: $\|a\sin\gamma, 0, -c\sin\alpha\cos\beta^*|a\cos\gamma, b, c\cos\alpha|0, 0, c\sin\alpha\sin\beta^*\|$.

[21] R. P. Dodge and V. Shomaker, *J. Organometallic Chem.*, 1965, **3**, 274.

[22] J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hubel, *J. Amer. Chem. Soc.*, 1966, **88**, 292.

[23] M. Catti, G. Gervasio, and S. A. Mason, 3rd European Crystallographic Meeting, Zürich, September 1976.

formally as five-electron donors; in this way the Fe_4C_4 core could be treated as a ‘ *closo*-carbaborane ’ [15] in which nine electron pairs (four from the Fe–Fe bonds and five from the two alkynes) would be disposable for delocalized bonding in a polyhedron having eight vertices.

TABLE 3

Carbon–carbon bond distances for μ_3-η, μ_3-η^2, and μ_4-η^2 (see ref. 24) co-ordinated acetylenes

Complex	Co-ordination mode of the acetylene	C–C Distance (Å)	Ref.
$[Fe_3(CO)_8(PhC_2Ph)_2]$ ‘ violet isomer ’	$\mu_3-\eta$	1.395 1.375	21
$[Ni_4(CNBu^t)_4(PhC_2Ph)_3]$	$\mu_3-\eta^2$	1.344	*a*
$[Ru_3(CO)_9(C_2Bu^t)H]$	$\mu_3-\eta^2$	1.315	23
$[Fe_3(CO)_7(C_2Ph)(\eta\text{-}C_5H_5)]$	$\mu_3-\eta^2$	1.299	*b*
$[Fe_3(CO)_9(PhC_2Ph)]$	$\mu_3-\eta^2$	1.409	16,22
$[Os_3(CO)_7(PhC_2Ph)_3]$	$\mu_3-\eta^3$	1.33	*c*
$[Co_4(CO)_{10}(EtC_2Et)]$	$\mu_4-\eta^2$	1.44	12
$[Ru_4(CO)_{11}(C_8H_{10})]$	$\mu_4-\eta^2$	1.43	13
$[Fe_4(CO)_{11}(HC_2Et)_2]$	$\mu_4-\eta^2$	1.374 1.397	*d*

[a] M. G. Thomas, E. L. Muetterties, R. O. Day, and V. W. Day, *J. Amer. Chem. Soc.*, 1976, **98**, 4645. [b] K. Yasufuku, K. Aoki, and H. Yamazaki, *Bull. Chem. Soc. Japan*, 1975, **48**, 1616. [c] G. Ferraris and G. Gervasio, *J.C.S. Dalton*, 1973, 1933. [d] This work.

Another interesting feature is the C–C acetylenic distance. Values of C–C distances have been related [24] to the ease of reducing the acetylenic triple bond by hydrogen. In Table **3** some values for the C–C distances of triply and quadruply bridging alkynes are compared with those found in complex (2); it can be seen that the values found for (2) are intermediate between those of the triply and quadruply bridging alkynes. However, complex (2) is the first to contain two alkyne molecules which are both quadruply bridging, and therefore the C–C elongation on co-ordination is indicative of some activation of the triple bond of both the alkyne molecules.

The formation of tetranuclear complexes from more simple precursors is not uncommon in cluster chemistry, and could be due either to the condensation of $Fe_n(CO)_m$ fragments (n = 1 or 2) or to the presence in solution of some tetranuclear hydrides such as the recently reported [25] $[Fe_4(CO)_{13}H]^-$ which shows a ‘ butterfly ’ cluster. The formation of tetranuclear hydride species, in the presence of moisture in solution, has previously been reported for $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$.[26]

The nuclearity of complex (2), some aspects of its fragmentation in the mass spectrometer,[20] and the co-ordination of two alkynes which have not interacted, point to the formation of this complex at an early stage in reactions between iron carbonyls and alkynes.

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[24] E. L. Muetterties and S. T. Olin, *Bull. Soc. chim. belges*, 1976, **85**, 451.

[25] M. Manassero, M. Sansoni, and G. Longoni, *J.C.S. Chem. Comm.*, 1976, 919.

[26] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1973, **57**, C84.