Crystal and Molecular Structure of 1-(Dicarbonyl-π-cyclopentadienylferrio)-2-(phenyl)-ethyne

By **Richard Goddard, Judith Howard,** and **Peter Woodward,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Crystals of the title compound are monoclinic, *a* = 9·473(2), *b* = 9·796(2), *c* = 13·887(3) Å, β = 109·70(2)°, space group $P2_1/n$, *Z* = 4. The structure was solved by conventional methods from 1696 intensity data collected on a diffractometer and has been refined to *R* 0·060. The $(\pi\text{-}C_5H_5)Fe(CO)_2$ fragment has the same geometry as in many other compounds, and the acetylenic linkage is essentially linear. There are no significant intermolecular interactions. The bond lengths of the metal ethynyl group (Fe–C 1·91, –C≡C– 1·21, and C–Ph 1·44 Å) provide a useful comparison with those in other acetylenes.

CRYSTALS of 1-(dicarbonyl-π-cyclopentadienylferrio)-2-(phenyl)-ethyne, $[(\pi\text{-}C_5H_5)Fe(CO)_2(C{:}CPh)]$, are formed in high yield when [PhC:CMgBr] reacts with $[(\pi\text{-}C_5H_5)\text{-}Fe(CO)_2Cl]$ in tetrahydrofuran.[1,2] Although several stable σ-bonded acetylene derivatives of the nickel group have now been prepared,[3-5] the presence of ligands capable of accepting charge from the metal (usually by d_π–d_{π^*} interaction) is always necessary. Details of the stereochemistry of the title compound are of special interest in relation to those compounds where the acetylenic moiety is further π-bonded to some other atom (*e.g.* Cu, see following paper).

EXPERIMENTAL

The crystals were characterised, and intensities collected, on a Syntex $P2_1$ four-circle diffractometer. Size of crystal: 0·13 × 0·30 × 0·60 mm; geometry: equatorial bisecting; mode: θ—2θ scan; scan speed: 1·0—0·03° s⁻¹, according to sampled intensity; scan interval: 1° below θ for $K_{\alpha 1}$ to 1° above θ for $K_{\alpha 2}$; background count (before and after each scan): to give total background time = scan time; check reflections: every 20 measurements; radiation: Mo-K_α with graphite monochromator. No. of reflections measured: 2070; no. observed: 1696 [according to the criterion $I > 2{\cdot}5\sigma(I)$].

Crystal Data.—$C_{15}H_{10}FeO_2$, *M* = 278·1, Monoclinic, *a* = 9·473(2), *b* = 9·796(2), *c* = 13·887(3) Å, β = 109·70(2)°, *U* = 1213 Å³; D_m (flotation) = 1·51, *Z* = 4, D_c = 1·53, *F*(000) = 568. Space group $P2_1/n$. Mo-K_α *X*-radiation, λ = 0·7107 Å; μ(Mo-K_α) = 12·1 cm⁻¹.

The structure was solved by conventional heavy-atom methods and has been refined to *R* 0·060 (including hydrogen atoms). Individual weights were applied according to the scheme: $1/w = \sigma_F{}^2$ in which σ_F is the standard deviation derived from counting statistics; this gave a satisfactory weight analysis. All computational work was carried out with the '*X*-Ray System.'[6] No correction for *X*-ray absorption was applied. Final parameters, and calculated molecular characteristics, are in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21087 (10 pp., 1 microfiche).† Atomic scattering factors are those of ref. 7.

DISCUSSION

The title compound consists of discrete monomeric molecules in which a phenylethynyl group is linearly σ-bonded to a $Fe(CO)_2(\pi\text{-}C_5H_5)$ group (Figures 1 and 2). The $Fe(CO)_2(\pi\text{-}C_5H_5)$ moiety has its usual geometry;

TABLE 1

Atomic positional and thermal parameters, with standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U* × 10²/Å²*
Fe	0·77303(8)	0·90993(7)	0·15461(5)	†
Cyclopentadienyl ring				
C(1)	0·8575(9)	1·1011(7)	0·1349(5)	6·0(2)
C(2)	0·7252(8)	1·0749(7)	0·0511(6)	6·4(2)
C(3)	0·7452(7)	0·9592(7)	0·0012(5)	5·6(2)
C(4)	0·8930(7)	0·9082(6)	0·0528(5)	5·2(1)
C(5)	0·9623(7)	0·9971(6)	0·1341(5)	5·4(1)
H(1)	0·881(8)	1·168(8)	0·193(5)	5(2)
H(2)	0·633(9)	1·132(8)	0·038(6)	6(3)
H(3)	0·687(8)	0·900(7)	−0·054(6)	5(2)
H(4)	0·924(8)	0·828(8)	0·033(5)	6(2)
H(5)	1·056(9)	0·989(8)	0·190(6)	6(2)
Phenylethynyl group				
C(6)	0·6170(6)	0·9636(5)	0·2061(4)	3·9(1)
C(7)	0·5261(6)	0·9914(5)	0·2459(4)	4·2(1)
C(71)	0·4232(6)	1·0233(5)	0·2993(4)	3·8(1)
C(72)	0·3983(8)	0·9292(7)	0·3673(5)	5·7(2)
C(73)	0·3019(8)	0·9610(8)	0·4221(5)	6·5(2)
C(74)	0·2344(8)	1·0856(7)	0·4109(5)	6·0(2)
C(75)	0·2554(7)	1·1784(7)	0·3437(5)	5·5(2)
C(76)	0·3493(7)	1·1488(6)	0·2865(5)	4·9(1)
H(72)	0·446(9)	0·832(8)	0·375(5)	6(2)
H(73)	0·296(8)	0·887(7)	0·484(6)	5(2)
H(74)	0·177(10)	1·110(9)	0·470(6)	8(3)
H(75)	0·201(8)	1·262(8)	0·321(5)	5(2)
H(76)	0·355(7)	1·207(6)	0·235(4)	3(2)
Carbonyl groups				
C(8)	0·6860(6)	0·7498(5)	0·1219(4)	4·1(1)
O(8)	0·6276(5)	0·6472(5)	0·0981(3)	6·3(1)
C(9)	0·8759(6)	0·8639(5)	0·2804(4)	4·1(1)
O(9)	0·9413(5)	0·8334(5)	0·3636(3)	6·3(1)

* $B = 8\pi^2U$. † Anisotropic thermal parameters in the form:

$$\exp.\ -2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]$$

for Fe values

U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
2·94(4)	3·86(4)	3·41(5)	− 0·08(3)	1·61(3)	0·14(3)

---

† For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[1] M. L. H. Green and T. Mole, *J. Organometallic Chem.*, 1968, **12**, 404.

[2] P. W. Jolly and R. Pettit, *J. Organometallic Chem.*, 1968, **12**, 491.

[3] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020; 1960, 1718.

[4] G. Calvin and G. E. Coates, *J. Chem. Soc.*, 1969, 2008.

[5] G. W. Parshall, *J. Amer. Chem. Soc.*, 1966, **88**, 705.

[6] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, *X*-Ray System of Crystallographic Programs for any Computer, Computer Science Centre, University of Maryland Report TR 67 58, revised 1970.

[7] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

the two carbonyl groups are mutually orthogonal, and the Fe atom attains approximately octahedral geometry if the cyclopentadienyl ring is assumed to occupy three co-ordination sites. Interest focusses on the detailed structure of the metal–ethynyl sequence.

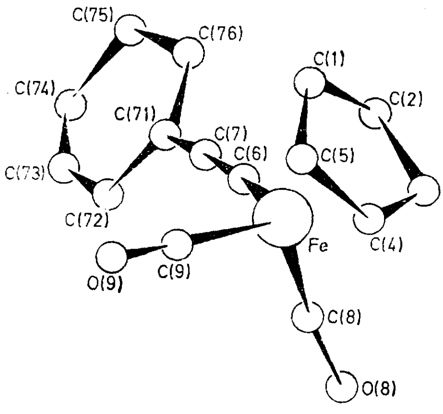

FIGURE 1 The molecular structure in projection along *a* looking towards the origin of the monoclinic unit cell. The atom numbering sequence is also shown

Atoms Fe, C(6), C(7), and C(71)—(76) are substantially coplanar. The $-C\equiv C-$ bond length is not significantly different from that expected for a normal triple bond but, as is well known,[8,9] the lengths of bonds of order 2 to 3 are not very sensitive to small changes of bond order. There is substantial evidence, however, that the real bond order is close to 3; the bond angles at the two carbon atoms of the ethynyl group are close to 180°, and the stretching frequency of the $-C\equiv C-$ bond (2117 cm^{-1}) lies close to the observed range of frequencies for disubstituted acetylenes (2190—2260 cm^{-1})[10] and within the range observed for σ-bonded Au^I alkynyls (2107—2135 cm^{-1}).[11]

TABLE 2

Molecular geometry

(*a*) Distances (Å)			
(i) Cyclopentadienyl ring			
Fe–C(1)	2·091(7)	C(1)–C(2)	1·417(9)
Fe–C(2)	2·108(7)	C(2)–C(3)	1·375(10)
Fe–C(3)	2·113(7)	C(3)–C(4)	1·431(9)
Fe–C(4)	2·092(8)	C(4)–C(5)	1·402(9)
Fe–C(5)	2·090(7)	C(5)–C(1)	1·425(10)
(ii) Phenylethynyl group			
Fe–C(6)	1·920(6)	C(73)–C(74)	1·363(10)
C(6)–C(7)	1·201(9)	C(74)–C(75)	1·364(10)
C(7)–C(71)	1·444(9)	C(75)–C(76)	1·409(11)
C(71)–C(72)	1·396(9)	C(76)–C(71)	1·396(8)
C(72)–C(73)	1·407(12)		
(iii) Carbonyl groups			
Fe–C(8)	1·759(5)	Fe–C(9)	1·749(5)
C(8)–O(8)	1·142(7)	C(9)–O(9)	1·151(7)
(*b*) Angles (°)			
C(1)–C(2)–C(3)	109·3(6)	Fe–C(6)–C(7)	174·4(4)
C(2)–C(3)–C(4)	108·2(6)	C(6)–C(7)–C(71)	176·8(5)
C(3)–C(4)–C(5)	107·5(6)	C(7)–C(71)–C(72)	120·1(5)
C(4)–C(5)–C(1)	108·2(5)	C(71)–C(72)–C(73)	120·6(6)
C(5)–C(1)–C(2)	106·8(6)	C(72)–C(73)–C(74)	120·1(7)
Fe–C(8)–O(8)	178·2(5)	C(73)–C(74)–C(75)	120·3(8)
Fe–C(9)–O(9)	178·8(6)	C(74)–C(75)–C(76)	120·9(6)
C(9)–Fe–C(8)	94·8(2)	C(75)–C(71)–C(71)	119·6(6)
C(9)–Fe–C(6)	86·4(3)	C(76)–C(76)–C(72)	118·4(6)
C(8)–Fe–C(6)	89·3(3)	C(76)–C(71)–C(7)	121·5(5)

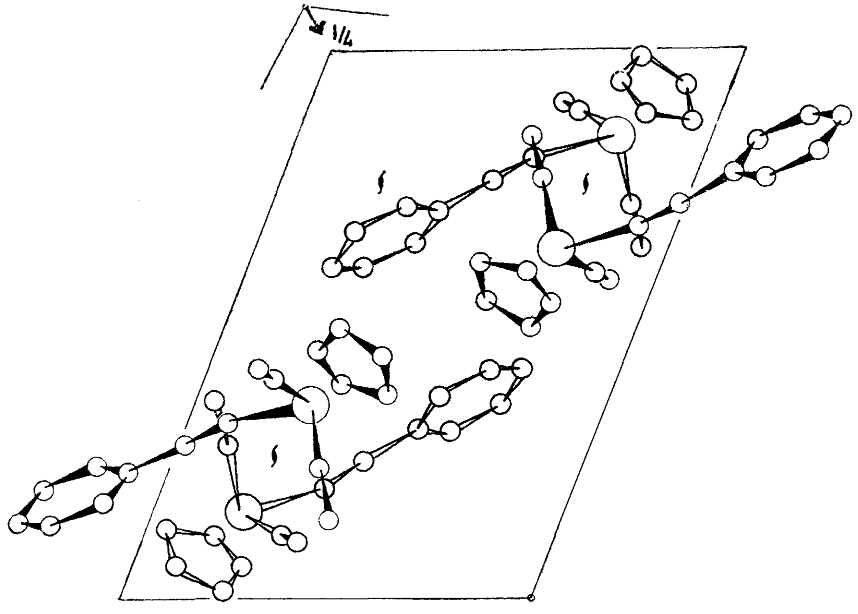

FIGURE 2 The contents of one unit cell, viewed down *b*, looking towards the origin

The Fe–C(6) bond length to the C_2 unit of the phenyl-

---

[8] F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **1964**, **3**, 1495.

[9] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 314.

[10] J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, 1967, **89**, 844.

[11] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1962, 3220.

ethynyl moiety [1·920(6) Å] is, as expected, notably longer than the Fe–(CO) distance [mean 1·754(6) Å] because of the partial double-bond character of all metal–carbonyl bonds. Just how close the Fe–C(6) distance is to that of a true single bond is, however, much more difficult to assess. The sum of the covalent radii for Fe^{II} and C(*sp*) could reasonably be assessed within the range 1·98—2·03 Å,[12] and to this extent the $Fe-C_2$ bond can be asserted to possess some double-bond character.

The length of the bond between the ethynyl group and the phenyl ring [1·438(10) Å] is in close agreement with the sum of the radii for C(sp^2) in aromatic rings (0·75 Å) and C(*sp*) (0·65—0·70 Å).[13]

We thank Professor M. I. Bruce and Dr. O. M. Abu Salah for crystals, and the S.R.C. for financial support and for facilities at the Atlas Computer Laboratory, Chilton, Berkshire, where help was given by Mrs. Carol Hirst.

[4/515 *Received, 15th March*, 1974]

---

[12] M. R. Churchill, *Perspectives in Structural Chem.*, 1970, **3**, 91.

[13] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Wiley, London, 1972, p. 117.