

## Crystal and Molecular Structure of Di- $\mu$ -chloro-bis-[[1-(dicarbonyl- $\pi$ -cyclopentadienylferrio)-2-phenylethyne]copper(I)]

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The crystal structure of the title compound has been determined by conventional methods from the intensities of 1578 non-zero reflections measured on a diffractometer and refined to  $R$  0.071. Crystals are monoclinic, with  $a = 12.57(1)$ ,  $b = 18.27(2)$ ,  $c = 7.15(1)$  Å,  $\beta = 115.3(1)^\circ$ , space group  $P2_1/a$ , and have two dimeric molecules per unit cell. The dimer comprises two asymmetric units related by a centre of inversion to give a central planar ring of alternating Cu and Cl atoms. The Cu-Cl distances are equivalent at 2.287(3) Å and the Cu  $\cdots$  Cu distance across the ring is 3.069(2) Å. Each Cu atom is symmetrically  $\pi$ -bonded to the C<sub>2</sub> unit of the phenylethynyl group [Cu-C 2.01(2) Å], and the CuC<sub>2</sub> moieties are coplanar with the Cu<sub>2</sub>Cl<sub>2</sub> ring. The ethynyl link is 1.23(1) Å, with Fe-C-C-Ph angles of ca. 162°.

THE reaction between  $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}]$  and  $\text{CuC}_2\text{Ph}$  affords a yellow-orange crystalline air-stable adduct in 30% yield.<sup>1</sup> The i.r. spectrum (in  $\text{CHCl}_3$ ) shows two  $\nu(\text{CO})$  bands at 2052 and 2002  $\text{cm}^{-1}$ , while the  $^1\text{H}$  n.m.r. spectrum shows a sharp singlet at  $\tau$  4.7 ( $\text{C}_5\text{H}_5$ ) and a broad signal at  $\tau$  2.7 ( $\text{C}_6\text{H}_5$ ). The mass spectrum shows only peaks found in the spectrum of  $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}\text{CPh}]$ . Osmometric molecular-weight determinations indicate that dissociation occurs in solution.

### EXPERIMENTAL

The crystals were characterised by photographic methods. Intensities were measured on a two-circle auto-diffractometer according to methods described previously;<sup>2</sup> crystal axis:  $c$ ; size of crystal:  $0.1 \times 0.1 \times 0.5$  mm; geometry: equi-inclination; mode:  $\omega$ -scan; scan speed,  $1^\circ \text{min}^{-1}$ ; scan interval:  $(2.0 + 0.3/L)^\circ$  where  $L$  is the Lorentz correction for the reflection  $hkl$ ; background count (before and after scan): 0.5 min; check reflection: every 20 reflections; radiation: Mo- $K_\alpha$ , with Zr filter. No. of reflections observed 1578 [according to the criterion  $I > 2.5\sigma(I)$ ].

*Crystal Data.*— $[\text{C}_{15}\text{H}_{10}\text{ClCuFeO}_2]_2$ ,  $M = 753.8$ , Monoclinic,  $a = 12.57(1)$ ,  $b = 18.27(2)$ ,  $c = 7.15(1)$  Å,  $\beta = 115.3(1)^\circ$ ,  $U = 1484$  Å<sup>3</sup>,  $D_m$  (by flotation) 1.67,  $Z = 2$ ,  $D_c = 1.69$ ,  $F(000) = 752$ . Mo- $K_\alpha$  X-radiation,  $\lambda = 0.7107$  Å,  $\mu(\text{Mo-}K_\alpha) = 25.3 \text{ cm}^{-1}$ . Space group  $P2_1/a$ .

*Structure Solution and Refinement.*—The copper and iron atoms were located from a three-dimensional Patterson synthesis, and the remaining atoms from electron-density

difference syntheses. Least-squares refinement of the structure (in which  $\Sigma w\Delta^2$  was the function minimised) made use of anisotropic thermal parameters ( $\beta_{33}$  constant)

TABLE I  
Atomic positional and thermal parameters, with estimated standard deviations in parentheses

| Atom  | $x/a$      | $y/b$      | $z/c$       | $U \times 10^2$<br>Å <sup>2</sup> * |
|-------|------------|------------|-------------|-------------------------------------|
| Cu    | 0.4907(1)  | 0.4452(1)  | 0.3311(2)   | †                                   |
| Cl    | 0.6227(2)  | 0.4566(2)  | 0.6695(4)   | †                                   |
| Fe    | 0.6600(1)  | 0.3010(1)  | 0.2949(2)   | †                                   |
| C(1)  | 0.7576(13) | 0.3366(8)  | 0.1322(21)  | 6.6(4)                              |
| C(2)  | 0.8116(14) | 0.2727(9)  | 0.2634(26)  | 8.3(4)                              |
| C(3)  | 0.8389(13) | 0.2955(9)  | 0.4725(22)  | 7.1(4)                              |
| C(4)  | 0.8051(13) | 0.3646(9)  | 0.4650(22)  | 7.5(4)                              |
| C(5)  | 0.7574(14) | 0.3919(10) | 0.2622(25)  | 8.1(4)                              |
| C(6)  | 0.5760(10) | 0.2325(7)  | 0.1331(18)  | 4.8(3)                              |
| O(6)  | 0.5154(9)  | 0.1843(6)  | 0.0296(15)  | 7.6(3)                              |
| C(7)  | 0.6337(9)  | 0.2766(6)  | 0.5053(16)  | 3.8(2)                              |
| O(7)  | 0.6134(8)  | 0.2617(5)  | 0.6466(14)  | 6.4(2)                              |
| C(8)  | 0.5236(9)  | 0.3616(6)  | 0.1794(15)  | 3.5(2)                              |
| C(9)  | 0.4281(9)  | 0.3890(6)  | 0.0649(14)  | 3.3(2)                              |
| C(91) | 0.3197(8)  | 0.4045(6)  | -0.1155(14) | 3.0(2)                              |
| C(92) | 0.3198(10) | 0.4024(7)  | -0.3079(17) | 4.8(3)                              |
| C(93) | 0.2152(11) | 0.4127(8)  | -0.4890(19) | 5.7(3)                              |
| C(94) | 0.1125(13) | 0.4240(9)  | -0.4721(22) | 7.0(4)                              |
| C(95) | 0.1081(11) | 0.4289(7)  | -0.2759(19) | 5.3(3)                              |
| C(96) | 0.2123(10) | 0.4185(7)  | -0.1029(17) | 4.6(3)                              |

\*  $B = 8\pi^2U$ . † Anisotropic thermal parameters in the form  $\exp\{-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + hka^*b^*U_{12} + hla^*c^*U_{13} + klb^*c^*U_{23})\}$  with parameters ( $\times 10^2$ ):

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$  |
|------|----------|----------|----------|----------|----------|-----------|
| Cu   | 3.71(8)  | 3.56(9)  | 3.35     | 0.29(6)  | 1.16(5)  | -0.38(5)  |
| Cl   | 4.44(16) | 4.36(18) | 4.15     | 1.27(13) | 1.07(12) | -0.37(12) |
| Fe   | 2.90(8)  | 3.07(10) | 2.82     | 0.38(6)  | 0.97(5)  | -0.06(6)  |

for Cu, Cl, and Fe in the final stages, and separate scale factors for each reciprocal layer. The final weighting

<sup>1</sup> M. I. Bruce, R. Clark, Judith Howard, and P. Woodward, *J. Organometallic Chem.*, 1972, **42**, C107.

<sup>2</sup> C. J. Gilmore and P. Woodward, *J.C.S. Dalton*, 1972, 1387.

scheme, chosen to keep the variation of  $\Delta F$  with ranges of  $F$  and of  $(\sin \theta/\lambda)$  to a minimum, was:  $1/w = \sigma_F^2 + 0.0125|F_0|^2$ , in which  $\sigma_F$  is the standard deviation derived from counting statistics.<sup>2</sup> All computational work was carried out with the 'X-Ray System' on an Atlas computer.<sup>3</sup> Final atomic positional and thermal parameters with their standard deviations are in Table 1, bond lengths

TABLE 2  
Bond lengths (Å) and bond angles (°) \*

|                       |             |                   |             |
|-----------------------|-------------|-------------------|-------------|
| (a) Distances         |             |                   |             |
| Cu-Cl                 | 2.283(3)    | Cu-C(9)           | 2.003(10)   |
| Cu-Cl'                | 2.291(3)    | C(8)-C(9)         | 1.234(13)   |
| Cu-Cu'                | 3.069(2)    | Fe-C(8)           | 1.906(10)   |
| Cl-Cl'                | 3.392(4)    | C(9)-C(91)        | 1.447(11)   |
| Cu-C(8)               | 2.016(12)   |                   |             |
| Carbonyl groups       |             |                   |             |
| Fe-C(6)               | 1.725(11)   | Fe-C(7)           | 1.732(13)   |
| C(6)-O(6)             | 1.192(15)   | C(7)-O(7)         | 1.174(17)   |
| Cyclopentadienyl ring |             |                   |             |
| Fe-C(1)               | 2.12(2)     | C(1)-C(2)         | 1.47(2)     |
| Fe-C(2)               | 2.08(2)     | C(2)-C(3)         | 1.44(2)     |
| Fe-C(3)               | 2.06(1)     | C(3)-C(4)         | 1.33(2)     |
| Fe-C(4)               | 2.06(1)     | C(4)-C(5)         | 1.40(2)     |
| Fe-C(5)               | 2.13(2)     | C(5)-C(1)         | 1.37(2)     |
|                       | (Mean 2.09) |                   | (Mean 1.40) |
| Phenyl group          |             |                   |             |
| C(91)-C(92)           | 1.38(2)     | C(94)-C(95)       | 1.43(2)     |
| C(92)-C(93)           | 1.41(1)     | C(95)-C(96)       | 1.38(1)     |
| C(93)-C(94)           | 1.36(2)     | C(96)-C(91)       | 1.41(2)     |
|                       | (Mean 1.38) |                   |             |
| (b) Angles            |             |                   |             |
| Cu-Cl-Cu'             | 84.3(1)     | C(93)-C(94)-C(95) | 122(1)      |
| Cl'-Cu-Cl             | 95.7(1)     | C(94)-C(95)-C(96) | 117(1)      |
| Fe-C(8)-C(9)          | 164.3(9)    | C(95)-C(96)-C(91) | 122(1)      |
| C(6)-Fe-C(7)          | 96.0(6)     | C(96)-C(91)-C(92) | 119(1)      |
| C(7)-Fe-C(8)          | 93.1(5)     | Fe-C(6)-O(6)      | 176(1)      |
| C(6)-Fe-C(8)          | 87.2(5)     | Fe-C(7)-O(7)      | 178(1)      |
| C(8)-C(9)-C(91)       | 161(1)      | C(1)-C(2)-C(3)    | 106(1)      |
| C(9)-C(91)-C(92)      | 119(1)      | C(2)-C(3)-C(4)    | 108(1)      |
| C(9)-C(91)-C(96)      | 123(1)      | C(3)-C(4)-C(5)    | 112(1)      |
| C(91)-C(92)-C(93)     | 121(1)      | C(4)-C(5)-C(1)    | 108(1)      |
| C(92)-C(93)-C(94)     | 119(1)      | C(5)-C(1)-C(2)    | 107(1)      |

\* Estimated standard deviations include cell parameter errors.

TABLE 3

Equations of some least-squares planes in fractional coordinates,  $x$ ,  $y$ ,  $z$ ; distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1): Cyclopentadienyl ring C(1)-(5)

$$11.909x + 5.455y - 2.157z = 10.581$$

[C(1) -0.008, C(2) 0.004, C(3) 0.002, C(4) -0.008, C(5) 0.010]

Plane (2): Phenyl ring C(91)-(96)

$$2.181x + 17.977y - 0.269z = 8.011$$

[C(91) -0.010, C(92) 0.004, C(93) 0.009, C(94) -0.016, C(95) 0.009, C(96) 0.004]

Plane (3): Central planar portion of dimer: Cu, Cl, Fe C(8), C(9), C(91), Cu', Cl', Fe', C(8'), C(9'), C(91')

$$8.911x + 11.380y - 4.308z = 7.991$$

[Cu 0.021, Cl -0.131, Fe 0.045, C(8) 0.016, C(9) -0.030, C(91) -0.042]

and angles in Table 2, and some least-squares planes in Table 3. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21088 (10 pp., 1 microfiche).<sup>\*</sup> Atomic scattering factors are those of ref. 4.

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

## DISCUSSION

The crystal structure of the title compound shows that it is dimeric in the solid state, of molecular formula  $C_{30}H_{20}Cl_2Cu_2Fe_2O_4$  with two asymmetric units related by a centre of inversion (see Figure 1, which also shows the atom numbering sequence). The  $Cu_2Cl_2$  ring is planar, with angles at Cu 95.7(1) and at Cl 84.3(1)°. The Cu-Cl distances are not significantly different, mean 2.287(3) Å. Across the ring the  $Cu \cdots Cu$  distance is 3.069(2) Å. Each copper atom is symmetrically bonded to the  $C_2$  unit of the phenylethynyl group, the  $CuC_2$  moieties being coplanar with the  $Cu_2Cl_2$  ring (Table 3). The  $Cu \cdots Cu'$  vector bisects the two multiple bonds orthogonally: the distances Cu-C(8) and Cu-C(9) are not significantly different [mean 2.01(1) Å]. The multiple bond C(8)-C(9) is of length 1.23(1) Å. Atom C(9) is  $\sigma$ -bonded to a phenyl group

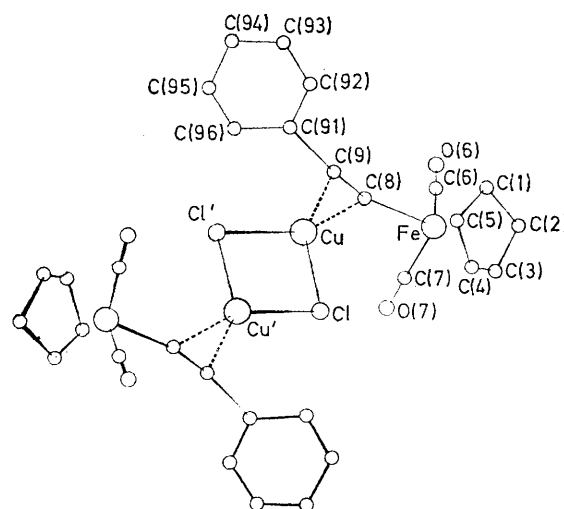


FIGURE 1 View of the dimeric molecule, showing the atom numbering sequence

C(91)-C(96) at a distance of 1.45(1) Å, while C(8) is  $\sigma$ -bonded to the iron atom of a  $(\pi-C_5H_5)Fe(CO)_2$  unit at a distance of 1.91(1) Å; both bonds are coplanar with the whole central portion of the molecule. The C(91)-C(9)-C(8)-Fe sequence is coplanar but non-linear, with angles at C(9) and C(8) of 161(1) and 164(1)°. The geometry of the  $(\pi-C_5H_5)Fe(CO)_2$  group closely resembles that found in many other compounds containing it; the iron atom can be considered to take up an octahedral configuration, with the cyclopentadienyl ring occupying three facial positions. Figure 2 shows the packing of the molecules in the monoclinic unit cell.

The structure of the title compound is generally similar to that of  $Pt(PPh_3)_2(C_2Ph_2)$ ,<sup>5</sup> but differs from

<sup>3</sup> 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.

<sup>4</sup> H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

<sup>5</sup> J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometallic Chem.*, 1967, **7**, P9.

it in having a transition metal  $\sigma$ -bonded to the acetylene. The length of the carbon-carbon multiple bond in  $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{Ph}_2)$  was not very accurately measured ( $1.32 \pm 0.09 \text{ \AA}$ ), so little can be deduced from its magnitude, but the angles between the C-C bond and the C-Ph bonds were *ca.*  $140^\circ$  (no  $\sigma$  given). The C-C stretching frequency is lowered considerably, to the range  $1750\text{--}1770 \text{ cm}^{-1}$ , and the co-ordination around the Pt atom is substantially planar. The diphenylethynyl

configuration and the bond lengths suggest that extensive delocalisation occurs, involving both metal atoms, the acetylenic fragment, and possibly the phenyl group. This feature, which probably involves back-bonding from filled orbitals on the Cu atom into  $\pi^*$  orbitals on the acetylene, must contribute to the enhanced stability of the complex over that of the free acetylide.<sup>6</sup> The Fe-C(8) distance [ $1.906(10) \text{ \AA}$ ] is somewhat shorter than expected for an Fe-C(*sp*) single bond,<sup>7,8</sup> but is

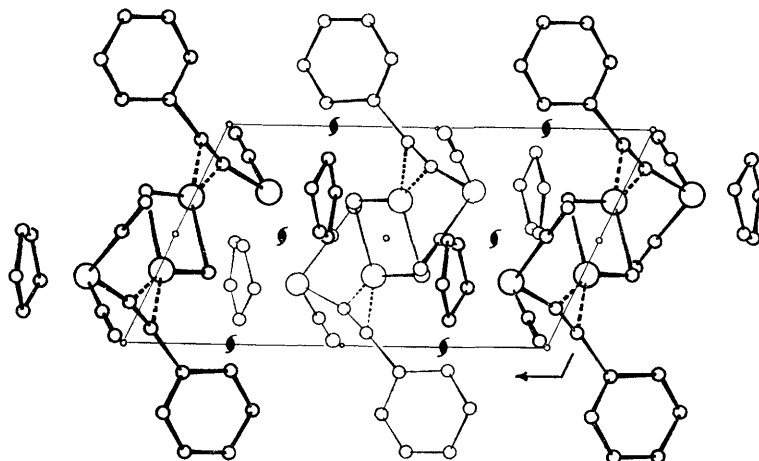


FIGURE 2 Contents of one unit cell, seen in projection down  $b$ , looking towards the origin

ligand in  $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{Ph}_2)$  is thus most simply formulated as divalent and bidentate. On the other hand, the simple acetylide  $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}_2\text{Ph})$ , the structure of which is reported in the preceding paper, shows bond angles at the  $\text{C}_2$  unit which do not differ significantly from  $180^\circ$  and has a C-C bond length of  $1.201(9) \text{ \AA}$ . The title compound is intermediate between these two situations in that the C-C bond is of length  $1.233(13)$  and the angles at the C atoms are *ca.*  $162^\circ$ . Both the

configuration and the bond lengths suggest that extensive delocalisation occurs, involving both metal atoms, the acetylenic fragment, and possibly the phenyl group. This feature, which probably involves back-bonding from filled orbitals on the Cu atom into  $\pi^*$  orbitals on the acetylene, must contribute to the enhanced stability of the complex over that of the free acetylide.<sup>6</sup> The Fe-C(8) distance [ $1.906(10) \text{ \AA}$ ] is somewhat shorter than expected for an Fe-C(*sp*) single bond,<sup>7,8</sup> but is

closely similar to that found for Ni-C in two separate determinations<sup>9,10</sup> of the crystal structure of *trans*- $\text{Ni}(\text{C}_2\text{Ph})_2(\text{PEt}_3)_2$  [ $1.87(1)$  and  $1.847(11) \text{ \AA}$ ]. We thank Miss Sheila Lindsay for some preliminary measurements on the crystal which was provided by Professor M. I. Bruce, 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.

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<sup>6</sup> A. I. Gusev and Yu. T. Struchkov, *J. Struct. Chem.*, 1970, **11**, 340.

<sup>7</sup> M. R. Churchill, *Perspectives in Structural Chem.*, 1970, **3**, 91.

<sup>8</sup> V. G. Adrianov, B. P. Biryukov, and Yu. T. Struchkov, *J. Struct. Chem.*, 1969, **10**, 1014.

<sup>9</sup> G. R. Davies, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. (A)*, 1967, 1750.

<sup>10</sup> W. A. Spofford, P. D. Garfagna, and E. L. Amma, *Inorg. Chem.*, 1967, 1553 and Errata, 2677.