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Preliminary communication

Reactions of copper acetylides. Crystal structure of $[(\pi\text{-}C_5H_5)Fe(CO)_2(C{\equiv}CPh)CuCl]_2$

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Reactions between substituted copper acetylides and suitable transition metal complexes are a fruitful source of unusual types of polynuclear hetero-atom complexes. A recent example is $[IrCu_2(PPh_3)(C_2Ph)_4]_2$ [1], and many other related clusters have been found.

The reaction between $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ and CuC_2Ph affords a yellow-orange, beautifully crystalline air-stable 1/1 adduct (I), m.p. 160–162° (dec.), in 30% yield. The IR spectrum (in $CHCl_3$) shows two ν(CO) bands at 2052 and 2002 cm^{-1}. The proton NMR spectrum consists of a sharp singlet at τ 4.7 (C_5H_5) and a broad signal at τ 2.7 (C_6H_5). The mass spectrum shows only peaks found in the spectrum of $(\pi\text{-}C_5H_5)Fe(CO)_2C{\equiv}CPh$, although heating *in vacuo* results only in decomposition to ferrocene and 1,4-diphenylbutadiyne. The complex is soluble in polar solvents, and osmometric molecular weight determinations indicate that dissociation, probably of a dimeric molecule (see below), occurs.

Crystals of $C_{15}H_{10}ClCuFeO_2$ are monoclinic, $a = 12.57$, $b = 18.27$, $c = 7.15$ Å, $\beta = 115.3°$; space group $P2_1/a$ with $Z = 4$. The intensities of 1838 non-zero reflections were measured on a Supper-Pace 0.01° incrementing auto-diffractometer, using equi-inclination geometry, ω-scan, and Mo-K_α radiation. The structure was solved by conventional heavy-atom methods and has been refined to $R = 0.095$.

Complex (I) is dimeric, with molecular formula $C_{30}H_{20}Cl_2Cu_2Fe_2O_4$, and comprises two asymmetric units related by a centre of inversion (see Fig. 1). The Cu_2Cl_2 ring is planar, with angles at Cu and at Cl 94.6(2) and 85.4(2)°, respectively. The CuCl distances are all 2.267(5) Å, and the Cu–Cu distance is 3.075(4) Å. Each copper is symmetrically bonded to the C_2 unit of the phenylethynyl group, the CuC_2 moieties being coplanar with the Cu_2Cl_2 ring. The Cu–Cu′ vector bisects the two multiple bonds; the distances Cu–C(8) and Cu–C(9) are equal, at 1.99(2) Å. The C(8)–C(9) bond length is 1.27(2) Å. Atom C(9) is σ-bonded to a phenyl group C(91)–C(96) [1.39(2) Å], and C(8) is σ-bonded to the iron atom of a $(\pi\text{-}C_5H_5)Fe(CO)_2$ unit [1.89(2) Å]; both bonds are

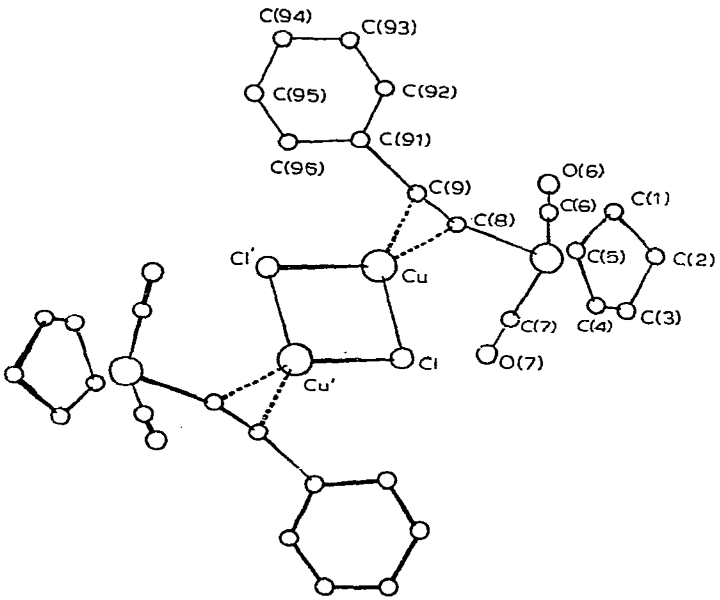

Fig. 1. Molecular structure of $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2Ph)CuCl]_2$ (I).

coplanar with the whole central portion of the molecule. The C(91)—C(9)—C(8)—Fe sequence is non-linear, with angles at C(9) and C(8) both 162(2)°. The geometry of the $(\pi\text{-}C_5H_5)Fe(CO)_2$ group closely resembles that found in many other compounds containing this group.

The structure of complex (I) is related to that of the long-known polymeric $[CuC_2Ph]_n$ [2], and more closely to that of $Pt(PPh_3)_2(C_2Ph_2)$ [3]. In the latter case, the carbon—carbon multiple bond is much closer to π-ethylenic (C—C, 1.32; Pt—C, 2.03 Å). Our complex is isoelectronic with the platinum derivative, but the acetylene is unusual in bearing a σ-bonded transition metal. The Fe—C(8) bond, while shorter than expected for an Fe—C(*sp*) single bond[4], is nevertheless almost identical with that found in *trans*-$Ni(C_2Ph)_2(PEt_3)_2$ [1.87(1) [5] or 1.847(11) Å [6]]. In *cis*-$Pt(CN)(C_2CN)(PPh_3)_2$ [7], deviations from expected bond lengths have been explained in terms of extensive delocalisation, approaching the extreme Pt=C=C=C=N situation. The bond between C(9) and the phenyl ring is virtually equal in length to that found in diphenylacetylene[8], although the phenyl group is rotated some 45° out of the plane of the Cu—C(8)—C(9) fragment.

Formal electron counts give the copper a 16- and the iron an 18-electron configuration. Although there is no direct interaction between the copper and iron atoms (separation 3.47 Å), the bond lengths suggest that extensive delocalisation involving both metal atoms, the acetylenic moiety, and possibly the phenyl group, has occurred. This feature, which probably involves back-bonding from filled copper orbitals into $C{\equiv}C\ \pi^*$ orbitals [analogous to that proposed for $Pt(PPh_3)_2(C_2Ph_2)$ and many similar complexes], must contribute towards the enhanced stability of this complex over that of the free acetylide, for example in photolytic and oxidative reactions.

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Erratum

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Line 5 should read:

-π-cyclopentadienyldicarbonylmangan[5] und -pentacarbonyl-chrom, -molybdän und -wolfram[6], während