

Tetracarbonyldi- μ -2,2,5,5-tetramethylhex-3-yne-di-iron. A Novel Complex Containing an Iron-Iron Double Bond

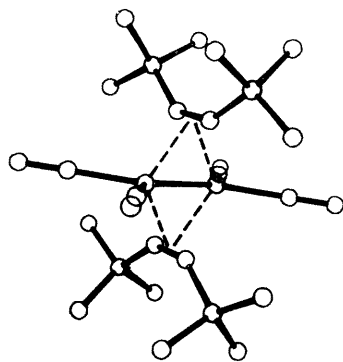
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Summary The reaction of $\text{Fe}_3(\text{CO})_{12}$ with 2,2,5,5-tetramethylhex-3-yne gives a complex which appears to contain an iron-iron double bond.

THE reactions of alkynes with iron carbonyls have been shown to give a variety of products depending on both the nature of the carbonyl and the acetylene.¹ These products frequently possess cyclic structures and in an attempt to prepare a per-*t*-butylated system we have treated 2,2,5,5-tetramethylhex-3-yne [di-*t*-butylacetylene, (I)] with $\text{Fe}_3(\text{CO})_{12}$. Although the reaction failed to produce the desired product it did lead to a novel compound which we believe constitutes the first example of an organo-iron complex containing an iron-iron double bond.

The reaction of (I) with $\text{Fe}_3(\text{CO})_{12}$ in refluxing methylcyclohexane yielded a black-violet crystalline product (42% of composition)† of composition‡ ($\text{C}_{10}\text{H}_{18}$)₂ $\text{Fe}_2(\text{CO})_4$ (II). The air stable compound was purified by sublimation at 100° and 0.1 mm Hg. The complex exhibits unusual thermal stability, subliming without decomposition at 175° in air.



(II)

FIGURE

The complex, slightly soluble in non-polar organic solvents, insoluble in polar solvents, exhibits a single sharp n.m.r. absorption at τ 8.65 (CS_2). The i.r. spectrum (CS_2) displays terminal metal carbonyl bands at 1955 and 1920 cm^{-1} . No bridging or ketonic carbonyl absorptions are observed. The mass spectrum does not show a parent molecular ion peak (M *m/e* 500), but peaks are observed at

m/e 472($M - \text{CO}$), 444($M - 2\text{CO}$), 416($M - 3\text{CO}$), 388($M - 4\text{CO}$), 332($M - \text{Fe}$), and 276($M - 2\text{Fe}$).

The structure of (II) has been determined by a single crystal X-ray diffraction study.‡ Crystals of (II) obtained by sublimation at 100° and 0.1 mm Hg are monoclinic, $P2_1/c$, $a = 9.706$, $b = 14.403$, $c = 8.903$ Å, $\beta = 96.14^\circ$. The unit cell contains only two molecules, so that each molecule lies at an inversion centre. Using 1678 observed reflections out of 2117 measured with $\text{Cu-K}\alpha$ radiation, the structure was solved by the heavy atom method and has been refined, including all hydrogen atoms, to a conventional R value of 0.042 and a weighted R value of 0.032.

The molecular geometry is shown in the Figure. The two iron atoms and four C=O groups lie in the same basal plane. The four acetylene carbons form a plane normal to this basal plane, with Fe-C(acetylene) distance of 2.048, 2.113, 2.049, and 2.116 Å. The acetylene C-C distance is 1.283 Å, while the distances from C(acetylene) to the quaternary C atoms are 1.506 and 1.507 Å. The Bu^t groups are bent away from the $\text{Fe}_2(\text{CO})_4$ plane, so that the angles at the acetylene carbons are 142.6 and 143.0°.

The most interesting distance observed in this structure is the extremely short Fe-Fe distance, 2.215 Å. The Fe-Fe distance of a typical series of organo-di-iron complexes containing metal-metal single bonds varies from 2.37 to 2.77 Å.^{2,3} The presence of an iron-iron double bond in the complex is consistent with the unusually short metal-metal distance observed. The diamagnetic behaviour of the complex is consistent with a structure in which each iron atom accepts two electrons from each of two acetylenes, two electrons from each of two carbonyls, and shares two electron pairs with the other iron, thus obeying the effective atomic number rule.

Attempted chemical additions to the metal-metal double bond were unsuccessful. The complex did react with iodine in benzene but only with extensive decomposition. Treatment of the complex with HCl in benzene or with hydrogen in the presence of 5% palladium on charcoal gave only starting material. These negative results may be a consequence of the steric bulk of the Bu^t groups which could prevent attack at the iron-iron bond.

Although multiple metal-metal bonding has been proposed between elements of the second and third transition series,^{4,5} we believe this to be the first example involving two iron atoms.

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† Calculated for $\text{C}_{24}\text{H}_{36}\text{Fe}_2\text{O}_4$: C = 57.6; H = 7.2. Found: C = 58.1; H = 7.3%.

‡ Details of the structure determination, final atomic parameters and molecular geometry will be reported elsewhere.

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